Supercycle Atomic Layer Deposition for the Fabrication of One-, Two-, and Three-Dimensional Structures for Photonic Applications

Dissertation

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Abstract

Atomic layer deposition (ALD) is a thin film deposition technique known for the unique precision of film thickness control combined with the ability to completely conformal functionalize various substrate shapes. Further, ALD processes of at least two different materials can be combined in so-called supercycles to deposit multilayers or to prepare composite structures such as ternary and doped materials. In combination with photonic structures, ALD enables wide tailoring of the functional properties. For example, ALD allows for fine-tuning the optical properties of photonic crystals (PhCs). PhCs are structures consisting of periodically arranged materials with different dielectric constants. Thus, PhCs exhibit wavelength ranges in which light propagation in the PhCs is forbidden, which are denoted as photonic stopbands (PSBs). Moreover, ALD enables coating of different dimensional PhCs (1D, 2D, and 3D) with functional materials, e.g., photocatalysts, which can further expand the properties of PhC structures.

In this thesis, PhCs of different dimensionalities are prepared with ALD-based methods. Compositions and thicknesses of materials deposited with (supercycle) ALD processes are systematically varied to study their influence on the properties of the PhCs. Specifically, the composition-dependent crystallization behavior of 1D PhCs is investigated with a combination of *in situ* and *ex situ* X-ray diffraction, transmission electron microscopy, X-ray reflectometry, and spectroscopic ellipsometry. Porous 2D and 3D PhC templates, namely anodic aluminum oxide (AAO) and inverse opals (IOs), are functionalized with photocatalytically active materials by ALD. Their photocatalytic performance is assessed by degrading organic dyes as model pollutants of water. Post-anodization surface modifications of AAO templates result in stable photocatalysis properties over time, which are crucial for studying functional materials. Precise optimization of the ALDgrown materials' film thickness and composition customizes the composites' functionalities and enhances and stabilizes their photocatalytic performance. Further improvement is obtained when ultra-thin protection layers are deposited to prevent photocorrosion of the photocatalyst. Moreover, semiconductor heterostructures can facilitate charge carrier separation to enhance the photocatalytic performance. Additionally, multilayer IOs consisting of semiconductor heterostructures can provoke photo-induced crystallization, which further tailors the photocatalytic properties. The combination of ALD and PhCs offers the potential to further expand the utilization of tailor-made structures for photonic applications in the future.

Kurzfassung

Die Atomlagenabscheidung (engl. atomic layer deposition, ALD) ist ein Verfahren zur Abscheidung dünner Schichten, das für seine einzigartige Präzision bei der Kontrolle der Schichtdicke in Verbindung mit der Fähigkeit, verschiedene Substratformen vollständig konform zu funktionalisieren, bekannt ist. Außerdem können ALD-Prozesse von mindestens zwei verschiedenen Materialien in sogenannten Superzyklen kombiniert werden, um Multilagen abzuscheiden oder Kompositstrukturen wie beispielsweise ternäre und dotierte Materialien herzustellen. In Kombination mit photonischen Strukturen ermöglicht ALD eine breite Anpassung der funktionellen Eigenschaften. Mit ALD lassen sich beispielsweise die optischen Eigenschaften von photonischen Kristallen (engl. photonic crystals, PhCs) fein abstimmen. PhCs sind Strukturen, die aus periodisch angeordneten Materialien mit unterschiedlichen Dielektrizitätskonstanten bestehen. Daher weisen PhCs Wellenlängenbereiche auf, in denen die Lichtausbreitung im PhC verboten ist, was als photonische Stoppbänder (PSBs) bezeichnet wird. Darüber hinaus ermöglicht ALD die Beschichtung von PhCs verschiedener Dimensionen (1D, 2D und 3D) mit funktionellen Materialien, z. B. Photokatalysatoren, wodurch die Eigenschaften von PhC Strukturen erweitert werden können.

In dieser Arbeit werden PhCs verschiedener Dimensionen mit ALD-basierten Methoden hergestellt. Die Zusammensetzungen und Dicken der mit (Superzyklen) ALD-Prozessen abgeschiedenen Materialien werden systematisch variiert, um ihren Einfluss auf die Eigenschaften der PhCs zu untersuchen. Insbesondere wird das von der Zusammensetzung abhängige Kristallisationsverhalten von 1D PhCs mit einer Kombination aus in situ und ex situ Röntgenbeugung, Transmissions-Elektronenmikroskopie, Röntgenreflektometrie und spektroskopischer Ellipsometrie untersucht. Poröse 2D- und 3D-PhC Template, nämlich anodisches Aluminiumoxid (AAO) und inverse Opale (IOs), werden durch ALD mit photokatalytisch aktiven Materialien funktionalisiert, und ihre photokatalytische Leistung wird durch den Abbau von organischen Farbstoffen als Modellverunreinigungen in Wasser analysiert. Nach der Anodisation vorgenommene Oberflächenmodifikationen der AAO Template führen zu langfristig stabilen photokatalytischen Eigenschaften, die für die Untersuchung funktioneller Materialien essenziell sind. Durch die genaue Optimierung der Schichtdicke und der Zusammensetzung der ALD-gewachsenen Materialien werden die Funktionalitäten der Kompositmaterialien individuell angepasst und ihre photokatalytische Aktivität verbessert. Die Abscheidung von ultradünnen Schutzschichten zur Verhinderung der Photokorrosion des Photokatalysators kann eine weitere Verbesserung bewirken. Darüber hinaus können Halbleiter-Heterostrukturen die Ladungsträgertrennung erleichtern und so die photokatalytische Leistung verbessern. Des Weiteren können mehrschichtige IOs, die aus Halbleiter-Heterostrukturen bestehen, eine photoinduzierte Kristallisation hervorrufen, die die photokatalytischen Eigenschaften weiter anpasst. Die Kombination von ALD und PhCs bietet das Potenzial, die Nutzung von maßgeschneiderten Strukturen für photonische Anwendungen in Zukunft zu erweitern.

Preface

This cumulative thesis consists of five first-authored and shared-first-authored manuscripts and one co-authored publication. The key results of these studies are summarized and explained in the main part of this thesis. Experimental procedures and detailed result analysis can be found in the original manuscripts which are integrated at the end of the thesis. Further co-authored publications are referenced in the Background and the Summary and Future Perspective chapters but their original manuscripts are not included herein.

First-authored and shared-first-authored manuscripts:

- I C. Hedrich, D. Deduytsche, R. R. Petit, T. Krekeler, J.Peng, M. Ritter, J. Dendooven, C. Detavernier, R. H. Blick, and R. Zierold. Tuning the Crystallization Temperature of Titanium Dioxide Thin Films by Incorporating Silicon Dioxide via Supercycle Atomic Layer Deposition. *Surfaces and Interfaces*, 57, 105696, 2025.^[1]
- **II C. Hedrich**, R. R. Petit, M. M. Minjauw, A. R. Burson, C. Detavernier, J. Dendooven, R. H. Blick, and R. Zierold. How Surface Treatments of Anodic Aluminum Oxide Alter the Photocatalytic Performance. *in preparation*.^[2]
- III S. Y. Lim, C. Hedrich, L. Jiang, C. S. Law, M. Chirumamilla, A. D. Abell, R. H. Blick, R. Zierold, and A. Santos. Harnessing Slow Light in Optoelectronically Engineered Nanoporous Photonic Crystals for Visible Light-Enhanced Photocatalysis. ACS Catalysis, 11:12947-12962, 2021. ^[3]
- IV C. Hedrich, A. R. Burson, S. González-García, V. Vega, V. M. Prida, A. Santos, R. H. Blick, and R. Zierold. Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide. *Advanced Materials Interfaces*, 2300615, 2023. ^[4]
- V C. Hedrich, N. T. James, L. G. Maragno, V. de Lima, S. Y. Gómez González, R. H. Blick, R. Zierold, and K. P. Furlan. Enhanced photocatalytic properties and photo-induced crystallization of TiO₂-Fe₂O₃ inverse opals fabricated by atomic layer deposition. ACS Applied Materials & Interfaces, 16, 46964-46974, 2024. ^[5]

Co-authored manuscripts:

VI S. Y. Lim, C. Hedrich, C. S. Law, A. D. Abell, R. H. Blick, K. P. Furlan, R. Zierold, and A. Santos. Nanoporous Anodic Alumina Photonic Crystals for Sunlight Harvesting Applications: A Perspective. *Solar RRL*, 2200480, 2022. ^[6] Further referenced co-authored publications whose original manuscripts are not included:

- VII F. Caddeo, S. Medicus, C. Hedrich, M. Krüger, S. Y. Harouna-Mayer, R. H. Blick, R. Zierold, and D. Koziej. Enhancing Charge Transport in CuBi₂O₄ Films: The Role of a Protective TiO₂ ALD Coating Probed by Impedance Spectroscopy. *Advanced Materials Interfaces*, 2400263, 2024. ^[7]
- VIII S. Haugg, C. Hedrich, R. H. Blick, and R. Zierold. Subtractive Low-Temperature Preparation Route for Porous SiO₂ Used for the Catalyst-Assisted Growth of ZnO Field Emitters. *Nanomaterials*, 11(12):3357, 2021. ^[8]
 - **IX** S. Haugg, **C. Hedrich**, R. H. Blick, and R. Zierold. Field emission characteristics of ZnO nanowires grown by catalyst-assisted MOCVD on free-standing inorganic nanomembranes. *Journal of Physics D: Applied Physics*, 55:255104, 2022. ^[9]
 - X S. Haugg, C. Hedrich, L.-F. Mochalski, I. González Díaz-Palacio, R. Zierold, and R. H. Blick. Enhancement of Field Emission Properties of Carbon Nanotube Forests by Direct Growth of Titanium Nitride-Coated Substrates. *2023 IEEE 36th International Vacuum Nanoelectronics Conference (IVNC)*, 122-124, 2023. ^[10]
 - XI S. Haugg, L.-F. Mochalski, C. Hedrich, I. González Díaz-Palacio, K. Deneke, R. Zierold, and R. H. Blick. Field Emission from Carbon Nanotubes on Titanium Nitride-Coated Planar and 3D-Printed Substrates. *Nanomaterials*, 14:781, 2024.^[11]

First-authored and shared-first-authored manuscripts:

- I C.H. fabricated the structures and conducted the spectroscopic ellipsometry measurements. C.H. and D.D. conducted the XRD measurements. C.H. and R.R.P. conducted the XRR measurements, T.K. conducted the TEM measurements. J.P. conducted the AFM measurements. C.H., D.D., R.R.P., T.K., R.Z. performed the data analysis. C.H. wrote the manuscript. C.H., J.D., C.D., R.H.B., R.Z. conceived the project. M.R., J.D., C.D., R.H.B., R.Z. supervised the project and acquired funding. All authors conducted proofreading and approved the manuscript.
- II C.H. and A.R.B. prepared the AAO structures and conducted the photocatalytic characterization. M.M.M. conducted the XPS measurements. C.H. and R.Z. analyzed the photocatalysis measurements results. C.H., R.R.P., M.M.M., J.D., R.Z. analyzed the XPS data. C.H. wrote the manuscript. C.H., R.R.P., C.D., J.D., R.Z. revised the manuscript. C.H. and R.Z. conceptualized the study. C.D., J.D., R.H.B., R.Z. supervised the study and acquired funding. All authors conducted proofreading and approved the manuscript.
- III S.Y.L. and C.H. contributed equally. C.H. fabricated the ALD-functionalized NAA-PCs and conducted the AFM measurements. S.Y.L., L.J, C.S.L. conducted optical characterization, photocatalysis measurements, and SEM imaging. M.C. conducted the spectroscopic ellipsometry. S.Y.L., C.H., C.S.L., M.C., R.Z., A.S. performed the data analysis. R.Z. and A.S. conceived the project. A.D.A., R.H.B., R.Z., A.S. supervised the project and acquired funding. All authors conducted proofreading and approved the manuscript.
- IV C.H., A.R.B., S.G.-G. prepared the ALD-functionalized AAO-PhCs. C.H., A.R.B., V.V., A.S., R.Z. performed the data analysis. C.H. wrote the manuscript. C.H., A.R.B., V.V., A.S., R.Z. revised the manuscript. C.H. and R.Z. conceptualized the study. V.V., V.M.P., A.S., R.H.B., R.Z. acquired funding. V.V., R.H.B., R.Z. supervised the study. All authors conducted proofreading and approved the manuscript.
- V C.H. and N.T.J. contributed equally. C.H. and N.T.J. fabricated the bilayer and multilayer IOs. N.T.J. and L.G.M. conducted the optical characterization, acquired SEM images, and conducted the XRD measurements. C.H. and N.T.J. conducted the photocatalytic characterization. C.H., N.T.J., L.G.M., V.d.L., S.Y.G.G., R.Z., K.P.F. performed the data analysis. C.H. wrote the manuscript. C.H., N.T.J., L.G.M., V.d.L, S.Y.G.G., R.Z., K.P.F. revised the manuscript. R.Z. and K.P.F. conceptualized the project. S.Y.G.G., R.H.B., R.Z., K.P.F. acquired funding and supervised the project. All authors conducted proofreading and approved the manuscript.

Co-authored manuscripts:

VI All authors wrote, proofread, and approved the manuscript.

Further referenced co-authored publications whose original manuscripts are not included:

- VII F.C. and D.K. conceived the project. F.C., S.M., and M.K. synthesized the CuBi₂O₄ films. C.H. and R.Z. carried out the TiO₂ depositions via ALD. F.C., S.M., and M.K. performed the morphological and photoelectrochemical characterization of the samples. S.Y.H.-M. carried out data processing. F.C. executed the fitting of the EIS data, D.K. supervised the work. F.C. wrote the manuscript with contributions from all co-authors. All authors revised the manuscript.
- VIII S.H. prepared the porous SiO₂ layers. S.H. and C.H. synthesized the NWs. S.H. conducted the spectroscpic ellipsometry measurements, SEM imaging, and the FE measurements. S.H, C.H., and R.Z. preformed the data analysis. S.H. wrote the manuscript. S.H., C.H., and R.Z. revised the manuscript. R.H.B. and R.Z. conceptualized the project, acquired funding, and supervised the project. All authors have read and agreed to the published version of the manuscript.
 - IX S.H. fabricated the SiNx NWs. S.H. and C.H. prepared the NWs. S.H. conducted SEM imaging, FIB milling, and the FE measurements. S.H, C.H., R.Z. performed the data analysis. S.H. wrote the manuscript. S.H., C.H., and R.Z. revised the manuscript. R.H.B. and R.Z. acquired funding, conceived the study, and supervised the study. All authors conducted proofreading and approved the manuscript.
 - X S.H., L.-F.M., C.H. prepared the substrates and the CNTs. S.H., L.-F.M. conducted the FE measurements. S.H., L.-F.M., C.H. conducted SEM imaging and performed the data analysis. S.H. wrote the manuscript. S.H., C.H., I.G.D.-P., R.Z. revised the manuscript. S.H., C.H., R.Z., R.H.B. conceptualized the project. R.H.B. and R.Z. acquired funding and supervised the project. All authors conducted proofreading and approved the manuscript.
 - XI S.H., I.G.D.-P., K.D. prepared the substrates. S.H., L.-F.M., C.H. synthesized the CNTs. S.H., L.-F.M. conducted the FE measurements. S.H., L.-F.M., C.H. conducted SEM imaging and performed the data analysis. S.H. wrote the manuscript. S.H., C.H., I.G.D.-P., K.D., R.Z. revised the manuscript. S.H., C.H., R.Z., R.H.B. conceived the study. R.H.B. and R.Z. acquired funding and supervised the study. All authors have read and agreed to the published version of the manuscript.

Abbreviations

0D	zero-dimensional
1D	one-dimensional
2D	two-dimensional
2.5D	two-and-a-half-dimensional
3D	three-dimensional
AAO	anodic aluminum oxide
AFM	atomic force miscroscopy
ALD	atomic layer deposition
СВ	conduction band
CVD	chemical vapor deposition
GPC	growth per cycle
LSPR	localized surface plasmon resonance
PEC	photoelectrochemistry
PhC	photonic crystal
PSB	photonic stopband
PVD	physical vapor deposition
SC	semiconductor
SEM	scanning electron microscopy
TEM	transmission electron microscopy
UV	ultraviolet
VB	valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectometry

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Motivation and Scope of the Work

The development of renewable energy sources is nowadays essential for reducing the dependence on fossil fuels. ^[12–15] In this context, photonics has become pivotal by enabling the utilization of solar light for energy generation and conversion. ^[16–18] Manipulating light at the nanoscale has the potential to significantly enhance light-matter interactions. Consequently, nanotechnology, which focuses on fabricating custom-designed structures with nanometer-sized dimensions, is of fundamental interest. ^[15] Precise control over the properties and dimensions of these nanostructures is crucial for developing advanced photonic structures with tailored functionalities in the fields of nanotechnology and photonics.

For fabricating nanostructures, atomic layer deposition (ALD) stands out as a thin film deposition technique based on the unique and precise control over material thickness, composition, and uniformity during the process. ^[19–22] The ability of ALD to conformally deposit layers onto complex-shaped substrates combined with a plethora of possible materials highlights the versatility of this method. Preparing nanostructured materials with ALD for photonic applications aims to customize materials' properties and to develop novel materials. Photonic crystals (PhCs) are examples of nanostructures that feature unique optical properties and functionalities which depend on their dimensionality, i.e., one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D).^[23-27] PhCs consist of periodically arranged materials with different refractive indices. Hence, they exhibit wavelength ranges in which light cannot propagate in the PhC. This wavelength range is denoted as photonic stopband (PSB) and the group velocity of light at the PSB edges approaches zero. Accordingly, the lifetime of the respective wavelengths in the PhC structure is prolonged whereby the interaction probability of light with the PhC material significantly increases. This phenomenon, known as slow photon effect, enhances lightmatter interactions.^[28-30] ALD enables fine-tuning of the optical and functional characteristics of PhCs based on tailoring the materials. Specifically, both, the material type and composition as well as the material thickness can be independently optimized for the desired application. As a consequence, ALD can enhance the performance of PhCs across a wide range of applications, for instance, thermal barrier coatings, photovoltaics, and photocatalysis. ^[31–39] The latter example facilitates pollution abatement in water, enabling water purification driven by solar light. Thus, photocatalysis presents a promising technique to realize the access to drinking water for the entire society which is defined as Sustainable Development Goal number 6 by the United Nations.^[40] Herein, photocatalysis is used as exemplary photonic application of porous PhCs prepared with ALD-based methods to demonstrate the structures' potential for sunlight-driven water purification.

In this thesis, PhCs of different dimensionalities are fabricated with ALD-based approaches. In detail, supercycle ALD processes are applied to either directly generate 1D PhCs or are used to coat porous 2D and 3D PhC templates with functional materials. Supercycle ALD denotes the combination of two or more individual ALD processes within

one process – the so-called supercycle. Thus, supercycle ALD allows for *in situ* preparation of multilayered structures, ternary materials, and doped materials. The properties of all these materials can be widely tailored by adjusting the material type, composition, sequence, and thickness within the ALD process. Chapter 2 explains the basic concepts for the ALD-based preparation of tailored photonic structures and their application. A short overview of bottom-up methods for fabricating functional materials emphasizes the flexibility of ALD regarding precise thickness control, substrate geometry, and available materials. Hence, ALD is introduced in more detail. Further, the basics of PhCs are elucidated and ALD-based methods for fabricating PhCs are discussed. Additionally, examples for photonic applications of ALD-grown materials are presented. In Chapter 3, silicon dioxide-incorporated titanium dioxide (TiO₂) structures are fabricated by supercycle ALD process as doped materials and nanolaminates, i.e., 1D PhCs. The influence of the materials' composition and individual layer thickness on the crystallization behavior is systematically studied. Note, the crystallographic phase of materials determines their properties indicating the importance of accurate knowledge of phase transitions to customize materials for the desired application. Anodic aluminum oxide (AAO) structures are applied as templates for fabricating 2D and two-and-a-half dimensional (2.5D) PhCs in Chapter 4. The AAO templates are functionalized with TiO₂ and iron (III) oxide (Fe₂O₃) as photocatalysts by ALD to enhance photocatalytic performances by combining photocatalysts with the unique optical properties of PhCs. Note, photocatalysis is used in this thesis as example for a photonic application of PhCs fabricated with ALD-based techniques. The influence of post-anodization modifications of AAO on the photocatalytic properties is assessed to provide stable templates for further processing. Moreover, the photocatalytic performance of TiO2-functionalized AAO-PhCs with varying TiO2 thickness and optical properties of the PhC templates is studied. In detail, the PhCs' PSB edge is tailored to the absorption of a model pollutant of water for enhanced photocatalytic properties by utilizing the slow photon effect. In the next section, Fe_2O_3 as visible light active photocatalyst is coated onto AAO-PhCs to improve photocatalytic performances. Here, the structures' PSB edge is aligned to Fe₂O₃ which resembles a more general approach for photocatalytic activity enhancement based on the slow photon effect. Further, ultra-thin ALD-deposited protection layers are applied to effectively stabilize the photocatalytic performance of Fe₂O₃. Afterwards, semiconductor heterostructures are coated onto AAO templates by ALD to elucidate their effect on the photocatalytic properties by modifying charge carrier generation and separation according to the heterostructure composition. Chapter 5 combines semiconductor heterostructures of TiO₂ and Fe₂O₃ with the slow photon effect leading to increased photocatalytic performance of inverse opals (IOs) as 3D PhCs. In addition, photo-induced crystallization tailors the photocatalytic properties of multilayer IOs. Finally, an outlook for future work to further improve the functional properties of PhCs prepared with ALD-based methods is given in Chapter 6.

In summary, this thesis reveals the potential of combining PhCs with supercycle ALD for photonic applications. Customization of the structures' functional properties enables tailor-made fabrication and might pave the way for solar light-based energy generation and conversion in the future.

Background

Atomic layer deposition (ALD) is a vapor phase deposition technique based on selflimiting reactions between the substrate surface and gaseous precursors.^[19] Thus, ALD allows for conformally coating even complex-shaped substrates, three-dimensional templates, and high aspect ratio structures without shadowing effects and with precise thickness control – a combination that is difficult to achieve with other physical or chemical gas phase deposition techniques.^[19,41–44] For instance, different types of photonic structures can be prepared with ALD either by directly fabricating them or by coating template structures with functional materials. Photonic crystals (PhCs) are composite materials characterized by their periodically varying refractive indices resulting in specific optical properties, namely the formation of a photonic stopband (PSB) that prevents certain wavelengths of light from propagating through the structure. ^[23–27, 30] Hence, PhCs are used to control light-matter interactions and they are applied in several fields such as optics, sensing, and photocatalysis based on the wide tunability of their optical properties. ^[23–30,45] Photocatalysis is of particular interest as green technology for environmental pollutant removal processes. To increase the efficiency of photocatalytic processes, PhCs are used as templates for photocatalyst materials and can be combined with other approaches, e.g., modification of the photocatalysts' band gap and formation of semiconductor heterostructure, to further boost the photocatalytic performance. In this chapter, bottom-up methods to fabricate tailored materials are summarized and the concept of ALD is explained in more detail. Moreover, the general structure, the optical properties, and the different types of PhCs are described. In addition, a short overview of methods for the production of PhCs is given and ALD-based fabrication processes are explained in more detail. Finally, different photonic applications of ALD-grown materials are presented. In detail, the utilization of ALD and PhCs to tune PSB characteristics, to prepare thermal barrier coatings, and to fabricate light-harvesting structures are summarized and strategies to further improve the performance of photocatalysts are presented. Note, photocatalysis is chosen as an exemplary photonic application which could be improved by tailored fabrication of photonic structures and materials with ALD-based approaches.

2.1. Fabrication of Photonic Structures by Atomic Layer Deposition

The following section explains the principle of ALD and the special requirements when porous substrates or high aspect ratio structures are coated. Moreover, supercycle processes are introduced and the fabrication of delta-doped materials, nanolaminates and ternary materials by applying such processes is discussed. Afterwards, the characteristics of PhCs are elucidated, followed by an overview about the PhC fabrication with ALD-derived approaches. In detail, the preparation of nanolaminates as one-dimensional PhCs

by ALD is explained. Further, ALD functionalization of anodic aluminum oxide (AAO) template structures and two- and two-and-a-half-dimensional PhCs is discussed including the fabrication of AAO by anodization. Finally, the preparation of three-dimensional PhCs by infiltrating self-assembled opal templates is presented.

2.1.1. Bottom-up Methods for Tailored Material Fabrication

Fabricating materials with tailored properties is essential for the progress of photonic applications such as thermal barrier coatings, solar cells, sensors, photocatalysis, photoelectrochemistry, and photothermal conversion. Bottom-up preparation methods play a major role in synthesizing these materials. Each fabrication technique provides unique advantages and is suited for different types of substrates, material deposition, and specific applications. This section shortly explains the principles of common bottom-up techniques including sol-gel, electrodeposition, electroless deposition, physical vapor deposition (PVD), chemical vapor deposition (CVD), and ALD. An overview of these fabrication methods is also included in a perspective article from a collaboration of Prof. Abel Santos', Prof. Kaline Furlans', and our group.^[6] A schematic drawing of a structure functionalized with an additional material layer by the different techniques is depicted in Figure 2.1.

The sol-gel method consists of two steps: First, a precursor solution is hydrolyzed and condensed to form a sol. Second, the sol is transformed to a gel which is an interconnected network of solid particles. ^[46–48] Further modifications such as drying and calcination can result in the formation of dense films. The sol-gel technique is mostly used for producing metal oxides and hybrid organic-inorganic materials. Moreover, various material compositions can be realized by altering the precursor solution. ^[46,49] Sol-gel processes can be conducted at low processing temperatures and different structures such as dense films, aerogels, and xerogels can be deposited with this technique. The method is also suitable for coating inner surfaces of porous structures but the thickness homogeneity control is rather low in the range of several tens to hundreds of nanometers. ^[46,50]

Electrodeposition is an electrochemical process in which metal ions in a solution are reduced to form a film of a conducting or a semiconducting material on a substrate. ^[51–53] To perform electrodepostion, a conductive substrate is required as cathode and is immersed into an electrolyte containing dissolved species of the material which should be deposited. A noble metal is typically used as anode and the application of an electrochemical potential or current between both electrodes results in the material reduction at the cathode and oxidation at the anode. ^[51–53] Thus, the cathode, i.e., the substrate, is coated with the desired material by electrodeposition. This methods provides good control over the deposited thickness as the consumed charge density determines the thickness. ^[54] Electrodeposition is used to deposit metals, metal alloys, and semiconductors with high purity and at fast deposition rates in the range of tens of micrometers per hour. ^[51–54] Functionalization of porous structures is also possible and such templates can either be filled completely to produce nanowires or the process can be tuned to only coat the pore walls to generate nanotubes. However, the latter ones require a very precise setting of



Figure 2.1. Scheme of a complex-shaped porous substrate functionalized by different material deposition techniques. (a) Pristine AAO substrate after fabrication. (b) Application of the sol-gel process deposits a film on the entire substrate surface at low homogeneity control. (c) Electrodeposition requires a back contact. Thus, the backside of the substrate is removed and a conductive layer is applied as back contact before functionalization. Electrodeposition results either in the formation of nanowires by filling the porous structure completely (left) or in the growth of nanotubes based on very precise process control (right). (d) Electroless deposition is utilized after surface modification with catalytic seeds and leads to the growth of a thin film. (e) Sputter deposition as example for physical vapor deposition (PVD) processes coats mainly the top surface of the substrate. (f) Chemical vapor deposition (CVD) results in the deposition of a thin film whose thickness depends on the position in the porous structure. (g) Atomic layer deposition (ALD) coats the substrate homogeneously and highly conformal with a thin film. Freely adapted from publication VI.

the parameters and are very difficult to realize. Since the substrate must be conductive for electrodeposition, porous templates often need to be modified to provide a conductive contact. Depending on the structure of the porous material, uniform deposition inside the entire template can be challenging and demands excellent process control.

Electroless deposition is a method to deposit metals onto a substrate without the need for an external energy such as current, heat, and light. It can be conducted by two different deposition mechanisms: First, a galvanic displacement could be performed which is characterized by redox reactions between more noble metal ions in an electrolyte solution and less noble metal atoms on a substrate. The more noble metal ions from the electrolyte are reduced at the substrate and thus, form a continuous metal film while the less noble metal is dissolved. This process occurs via electron transfer between the dissolved metal ions and the metal atoms at the substrate.^[55] Second, non-conductive substrates can be functionalized with metals by utilizing a reducing agent. The reducing agent is oxidized at the substrate surface and electrons are provided for the reduction of metal ions from the electrolyte. Hence, a metal film forms at the substrate surface. ^[55] In general, electroless deposition can be applied to various substrate materials and shapes, but it often requires a pre-treatment to generate a catalytic seed material for initiating the electroless material deposition on the substrate. Additionally, this method necessitates very precise control of the electrolyte composition and the deposition conditions, such as temperature and pH-value.

PVD bases on the vaporization of a material from a target in vacuum environment and the subsequent (re-)condensation of the vaporized material on a substrate. [56-60] PVD techniques include various methods such as evaporation, sputter deposition, and pulsed laser deposition, all of which differ mainly in the vaporization approach. Deposited materials either feature the same composition as the target or are compound materials formed by the reaction of the vaporized material with a gas or by co-deposition of at least two vaporized materials.^[56-60] All PVD techniques provide high purity and good control over the deposited film thickness and its composition. PVD allows for fabricating a broad material range such as metals, oxides, and nitrides.^[56–59] In detail, PVD is a line-of-sight technique meaning that the material deposition always occurs from one direction, i.e., the target. Consequently, shadowing-effects are present at complex substrate shapes. ^[60] More advanced processes can produce complex structures by adjusting the substrate position, e.g., by oblique angle PVD where the substrate position is changed within the process.^[61,62] Nevertheless, adjusting the substrate position during a PVD process requires high effort and the ability to conformally coat complex shapes or high-aspect ratio structures is limited due to poor step coverage.

CVD relies on the reaction or dissociation of gaseous precursors and material deposition on a heated substrate. CVD is conducted in a continuous flow and the material growth starts with the adsorption of the precursors or intermediate reactants on the substrate. The adsorbed molecules can diffuse on the surface and react with other molecules at the gassolid interface. The material nucleates and grows into the respective structure. ^[63–65] The reactions to deposit materials with CVD processes are induced by temperature, light, plasma, and catalytic compounds at the substrate. Hence, multiple variants of CVD pro-

cesses exist such as thermal, metalorganic, plasma-enhanced, catalyst-assisted, low pressure, light-activated, and hot-filament CVD. ^[63] The multi-directional material deposition, which is only limited by precursor diffusion within the process, enables the direct fabrication of various material shapes such as thin films, two-dimensional (2D) materials, onedimensional (1D) nanowires, and zero-dimensional (0D) nanoparticles. Nevertheless, the diffusion as crucial part of the CVD process limits the capability to homogeneously coat complex substrates and high aspect ratio structures. ^[64] A variety of materials can be fabricated by CVD including semiconductors, metals, and dielectrics. For example, we used CVD to directly grow zinc oxide nanowires or carbon nanotubes on functional substrates as demonstrated in publications VIII-XI. ^[8–11]

ALD is a special form of CVD that allows for highly conformal material deposition independent of the substrate shape in combination with very precise thickness control at the sub-nanometer level. ^[19–22] ALD relies on sequential, self-limiting reactions of precursors in the gas phase with solid surfaces and will be introduced in detail in the next section.

As part of this thesis, it is necessary to deposit semiconducting materials onto substrates in order to utilize the composites for photonic applications. In conclusion, each of the discussed bottom-up fabrication methods has its own advantages and limitations. Nevertheless, ALD is characterized by its unique ability to achieve conformal coatings on complex substrates with high thickness precision. In combination with the wide variety of materials that can be deposited with ALD, this versatile technique is essential for the fabrication of advanced functional materials by tailoring the material properties and adapting substrate shapes to enhance the functional performance. Therefore, photonic structures of different dimensionalities are produced with ALD-based methods in this thesis.

2.1.2. Basics of Atomic Layer Deposition

An ALD cycle consists of two half-cycles in which the two different precursors react with the substrate's surface as shown in (Figure 2.2.). ^[19–21,41–44] First, precursor A is introduced into the reaction chamber and reacts with the substrate in a self-limiting process resulting in a modified surface chemistry. Self-limiting surface reactions stop when all available functional groups at the surface have reacted with precursor molecules. Second, the by-products and unreacted precursor molecules of the previous reaction are removed from the chamber by purging. Third, the second half-cycle is initiated by exposing the substrate to precursor B, which reacts with the modified substrate again in a self-limiting fashion. This reaction results in another change of the surface chemistry providing the same functional groups that were present before starting the first half-cycle. Fourth, left over precursor B molecules and by-products are removed by purging the reaction chamber and afterwards, the next ALD cycle can start. Owing to its inherent self-limitation, each ALD cycle results in the deposition of a constant material thickness in the Ångström range. This deposited thickness rate is also denoted as growth per cycle (GPC) and is characteristic for the combination of precursors, growth temperature, substrate type, and further process conditions.^[19–21] As a consequence, the desired film thickness can be

deposited by adjusting the number of ALD cycles. Although ALD features a relatively slow deposition rate of 0.1 Å to 3 Å compared to other methods, it outperforms all other thin film deposition techniques with its exceptional conformality for coating complex three-dimensional (3D) substrates without shadowing effects and the high precision of film thickness and composition control. ^[22] Thus, ALD is a very versatile method and is applied to functionalize various substrates. A plethora of materials have been grown by ALD since its' discovery in the second half of the 20th century, ^[20,66] for example, oxides, nitrides, sulfides, selenides, tellurides, fluorides, and metals. ^[20] Further, different ALD processes can also be combined in so-called supercycles to deposit composites such as doped materials, nanolaminates, and ternary materials. ^[67,68]

Thermal ALD is the most common used process which applies thermal energy to induce the surface reactions.^[19] Besides this approach, there are also other types such as plasma-enhanced ALD (PEALD) and radical-enhanced ALD, which utilize a plasma and radicals, respectively to generate reactive species for the reactions.^[19] PEALD and radical-enhanced ALD allow for material growth at lower temperatures than required for thermal ALD processes and also enable the deposition of materials which are not accessible by thermal ALD. Photo-ALD utilizes light to induce the surface reactions and can enable the deposition of metals on oxide substrates which is challenging for other ALD processes.^[69] In this work, thermal ALD processes of different metal oxides are applied to modify porous materials because this process type can be operated in stop-flow mode, which will be explained below, to ensure precursor accessibility of high aspect ratio structures.

Coating of Porous Templates and High Aspect Ratio Structures

Porous structures feature higher surface areas compared to bulk parts of the same material volume. Hence, the porous materials also possess more surface sites for reactions with ALD precursors and thereby, more precursor material is required compared to planar substrates. Additionally, diffusion of the precursors inside the porous structure has to be considered. ^[22, 42, 44] Self-limiting surface reactions as characteristics for ALD only result in a continuous film thickness when each surface site is reached by a precursor molecule. Practically, the exposure time of ALD precursors has to be prolonged for porous templates to ensure diffusion into the complete structure. Prolonged exposure times are often realized by utilizing the so-called stop-flow mode. The stop-flow mode disconnects the vacuum pump from the reaction chamber during the pulse and exposure sequences of the ALD half-reactions. In this way, diffusion of molecules into the structures is facilitated due to increased precursor partial pressures in the reaction chamber.^[70] The same principles also apply for high aspect ratio structures, e.g. anodic aluminum oxide. Such high aspect ratio materials feature small pore openings in relation to their pore depth. This faces the bottleneck of enough precursor molecules diffusing into the pores and additionally reaching the pore bottom to allow for conformal coating of the complete substrate. As for porous systems, it can be overcome by increasing the precursor exposure time.^[22] When the exposure is prolonged, also the purge duration has to be increased to remove all



Figure 2.2. Schematic drawing of an ALD cycle. First, precursor A is exposed to the substrate and reacts self-limiting with the functional groups at the surface. Second, by-products and unreacted precursor molecules are removed by purging. Third, precursor B is pulsed into the reaction chamber and reacts self-limiting with the modified substrate surface. Fourth, purging removes by-products and precursor molecules. Ideally, a monolayer of material is deposited after one ALD cycle. The applied cycle number defines the thickness of deposited material.



Figure 2.3. A supercycle ALD process consists of alternating ALD growth of at least two materials. The individual layer thicknesses of material 1 and material 2 are controlled by adjusting the ALD cycle numbers *a* and *b*, respectively. The total material thickness is defined by the number of supercycles *n*.

by-products and unreacted precursor molecules from the reaction chamber. The elongation results in longer ALD process times which often limit the applicability for thicknesses larger than a few nanometers. For instance, thin film deposition onto planar substrates in an optimized reactor last a few seconds per cycle while. Our processes used herein to functionalize porous substrates take around 5 minutes per cycle.

Supercycle Processes

Supercycle ALD processes are combinations of ALD processes for different materials which are joined in one big loop – the so-called supercycle. ^[67, 68] They utilize three or more precursors to deposit at least two different materials. As schematically shown in Figure 2.3., a supercycle consists of *a* ALD cycles for material 1 and *b* cycles to deposit material 2. Accordingly, the repetition of the individual cycles can be varied to reach a desired thickness. Also the number of supercycles *n* can be adjusted to implement a periodic repetition. In this way, supercycle processes allow for easy-to-realize combinations of different materials within the same coating process. Such approaches are often applied to fabricate delta-doped materials, nanolaminates, and ternary materials by ALD. ^[20,67,68,71]

Delta-doping describes the insertion of monolayers of a foreign material (dopant) into a host material. Delta-doping results in distinct dopant concentration profiles in the layered materials, with sharp peaks along the materials' cross-section that resemble delta functions. ^[20,41,42,44,67,72] This method is in contrast to homogeneous doping of a material where the dopant atoms are evenly distributed across the whole volume. Heat treatments could be applied to homogenize the dopant distribution in the material after the deposition. Supercycle ALD enables delta-doping when the host material is deposited for a certain cycle number followed by one cycle, or maximum a few cycles, of the dopant material. The supercycle is repeated until the desired material thickness is obtained. This ALD-based approach renders very simple tuning of the doping ratio, i.e., ratio of host material ALD cycles to dopant ALD cycles.

Nanolaminates are structures composed of thin films with nanometer-sized thicknesses from different materials. Application of supercycle ALD allows for complete tailoring of the individual layer thicknesses and the material ratios by adapting the process parameters.^[19] Specifically, only the number of the respective cycles needs to be modified while all other parameters such as precursor type, pulse times, exposure times, and pump times remain the same.

Ternary materials are composed of three or more elements and can also be fabricated in supercycle ALD processes by using at least three different precursors. ^[20,71] Alternatively, supercycle ALD can be utilized to deposit nanolaminates followed by thermal annealing to produce ternary materials. Ternary material formation has been demonstrated for various materials such as magnesium aluminum oxide or lithium-containing oxides and some more examples of these compounds are given in a review article by Miikkulainen *et al.* ^[20]

In conclusion, ALD is characterized by its unique ability to achieve conformal coatings on complex substrates with high thickness precision. In combination with the wide variety of materials that can be deposited with ALD, this versatile technique is essential for the fabrication of advanced functional materials by tailoring the material properties and adapting substrate shapes to enhance the functional performance. Therefore, photonic structures of different dimensionalities are produced with ALD-based methods in this thesis.

2.1.3. Basic Concepts of Photonic Crystals

PhCs gain increasing interest since their first description in the 1987s due to the ability to control light propagation.^[73] Both, the theoretical description and simulation as well as the experimental realization of the first PhCs were significantly promoted by the contributions from Yablonovitch, Johnson, Joannopoulos, and John. [23, 24, 27, 73-77] In general, PhCs consist of a periodic structure of at least two different dielectric materials. Thus, the refractive index within the structure is periodically modulated resulting in the formation of a wavelength range in which propagation of electromagnetic waves (i.e., light) through the structure is forbidden.^[23–27] Emergence of this forbidden propagation is based on constructive and destructive interference of light within the structure. Due to the forbidden light propagation in PhCs, incoming light of the respective wavelengths is reflected by the structure. In 1993, Yablonovitch published a report about photonic crystals where the similarities and differences of photonic and electronic band structures are discussed. Referring to the similarity to the electronic band gap in semiconductors, the wavelength range of forbidden light propagation can be described as a photonic stopband (PSB).^[27,30] Note, light propagation within the PSB is strongly attenuated but not necessarily completely suppressed.

The PhC's optical properties, namely PSB position, shape, and depth, are determined by the choice of the PhC materials and their periodicity.^[30,78] For example, the PSB position of an inverse opal PhC can be calculated by the following equation based on Bragg's and Snell's laws: ^[28]

$$m\,\lambda_{\rm PSB} = 2\,n_{\rm eff}\,d\tag{2.1}$$

Here, λ_{PSB} is the PSB central wavelength, m is the PSB order, d is the periodicity, and n_{eff} is the effective refractive index of the structure which is typical obtained from effective medium approximation (EMA) models. The EMA approach assumes the PhC as a homogeneous structure composed of a material that features effective properties determined by the individual building blocks and weighted by their percentage volume in the structure. These effective properties define the macroscopic optical properties of the structure. Hence, a refractive index of the whole PhC structure is described as effective refractive index which can be derived from various EMA models such as Maxwell Garnett model, Drude model, and Bruggeman model.^[79-82] According to Equation 2.1, the optical properties of a PhC can be tailored by adapting its' geometrical structure or modifying the utilized dielectric materials. This ability of tuning enables custom-made fabrication of PhCs which is interesting for various application fields, e.g., optoelectronic devices, photocatalysis, photovoltaics, sensors, and energy storage. ^[23-30,45] PhCs can be fabricated as 1D, 2D, and 3D PhCs whereby the number of periodic directions dictates the dimensionality (Figure 2.4.). ^[27, 30, 75] 1D PhCs consist of a compact structure of stacked layers. ^[30] The individual layer thickness can range from a few nanometers up to several micrometers. Especially nanolaminates gain increasing attention for their optical applications.^[83] As their name suggests, the individual layers are only a few nanometers thick rendering them very attractive functional coatings, which are utilized in various industrial processes.^[28] The design of 2D and 3D PhCs is more complex because the periodicity expands over more dimensions. Such PhCs are often produced as porous structures or arrangements where one material is represented by the pore filling medium such as air or a liquid. Typical examples for 2D PhCs are cylindrical pores inside a matrix or nanowire arrays, while direct or inverse opals represent 3D PhCs. ^[24,28,30] PhCs offer a plethora of applications ranging from Fabry-Perót-interferometers and mirror coatings (1D) over catalysis (2D and 3D) or waveguides to sensors. ^[23-30,45] Fabricating PhCs of the different dimensionalities (1D, 2D, or 3D) requires specific methods tailored to the desired structure. Some typical fabrication techniques include wet-chemistry, CVD, ALD, sputtering, lithography, self-assembly of particles, or direct laser writing, to name a few. ^[28, 30, 45] The approaches utilizing ALD are discussed in detail in the next section (2.1.4.).

As a consequence from the formation of forbidden optical modes inside a PhC structure, other optical phenomena are observed at the PSB edges of a PhC. As shown by the optical dispersion of a PhC (Figure 2.5.), the group velocity of light in the structure $\frac{dE}{dk}$ approaches zero at the PSB edge wavelengths. This vanishing group velocity in a PhC is denoted as slow photon effect or slow light and corresponds to the formation of standings waves in the PhC structure. Hence, the presence of photons in the PhC structure is significantly prolonged giving rise to additional interactions with the PhC material. Such an increase of light-matter interaction probability is of great interest for processes in which materials need to absorb light such as the photo-excitation of semiconductors.

Note, an increment of the interaction probability corresponds to improved light absorp-



Figure 2.4. Scheme of PhCs with different dimensionalities. (a) 1D PhCs are periodic structures in one direction (here x-direction) which is characterized by a periodic modulation of the refractive index n in this direction. The other two directions feature constant refractive indices whose value depends on the position in the PhC, i.e., high or low refractive index material. (b) 2D PhCs are periodic in two directions – here x- and y-direction – and the refractive index in the remaining direction is constant. (c) 3D PhCs possess a three-dimensional periodicity which is accompanied by periodic modulations of the refractive index in all three directions.



Figure 2.5. Schematic representation of the photonic dispersion in PhCs resulting in the slow photon effect. At energies close to the PSB, the groups velocity of light $\frac{dE}{dk}$ in the structure, i.e., the slope of the dispersion curve, approaches zero. Standing waves of light with wavelengths of the PSB edges form in the PhC which increase the probability for light-matter interactions in the PhC structure.

tion. ^[28–30] However, certain conditions have to be fulfilled to profit from the slow photon effect. The improved light-matter interactions by the slow photon effect is specific for the wavelengths at the PSB edges. Hence, the light absorption wavelength required for the excitation process, i.e., the semiconductors' band gap, has to overlap with a PSB edge. The absorption wavelength in the semiconductor process can only slightly be changed, if possible at all. However, the PSB position of a PhC can be adjusted by the fabrication as described above and thus, PhCs can be tailored for applications necessitating semiconductor tor excitation to make use of the slow photon effect.

2.1.4. Fabrication of Photonic Crystals with ALD-based Methods

PhCs can be fabricated by different chemical and physical synthesis methods covering both bottom-up and top-down production. Depending on the PhC type, i.e., 1D, 2D, or 3D, and porous or non-porous, various fabrication methods have been reported in literature. [24, 26, 28, 84-86] The compact structure of 1D PhCs requires layer-by-layer deposition of the alternating materials. Sequential layer depositions can for example be realized by sol-gel chemistry, spin-coating, sputtering, PVD, CVD, and ALD.^[25,26,85] 2D PhCs are often composed of regularly arranged pillars of one material surrounded by another medium or of a solid matrix which contains cylindrical pores perpendicular to its surface. Common examples for the first case are ordered nano- or microwire arrays. These are typically fabricated by CVD or lithographic processes. ^[42,45] The production of highly-ordered cylindrical pores can be realized by electrochemical anodization of various metals resulting in self-organization of cylindrical pores.^[86–88] Alternatively, top-down approaches based on selective material removal of lithographically defined areas can also be applied to produce such porous 2D PhCs. ^[25,27,45] Further examples for 3D PhCs are opals and inverse opals (IOs) as well as wood-pile structures. Opals can be fabricated by self-assembly of sub-micron sized particles resulting in hexagonal closed packing of these spheres. ^[26, 28, 84, 85] For IOs, the voids of such assemblies are infiltrated with other materials, for example by sol-gel chemistry or ALD, followed by the removal of the opal template. ^[28, 84, 85] Literature reports the fabrication of wood-pile structures and other 3D PhCs by direct laser writing or lithographic techniques. ^[24–26, 28, 45] The production of 2D and 3D PhCs often requires several individual processing steps. Porous PhCs can be utilized as template structures which are then coated with functional materials. ^[28, 42, 85, 89] ALD allows for the direct production or template functionalization of PhCs of all three dimensionalities.^[42] Examples for these different structures created by ALD-derived approaches are presented in the following which is divided into nanolaminates as 1D PhCs, functionalization of 2D and 2.5D PhC templates produced by anodization of aluminum, and ALD-infiltration of self-assembled particles for 3D PhCs.

1D: Nanolaminates

Nanolaminates can be easily realized with ALD by applying supercycle processes to deposit different materials.^[19,42] The alternating material deposition results in the formation

of 1D PhCs whereby the individual layer thicknesses are precisely controlled according to the self-limiting nature of ALD cycles. Hence, it allows for coating nanolaminates not only onto planar substrates but also onto curved surfaces.

2D and 2.5D: Modification of Anodic Aluminum Oxide

ALD-based synthesis of 2D and 2.5D PhCs is conducted by functionalizing template structures with ALD. Herein, the utilization of anodic aluminum oxide as template is discussed as this offers fast and easy fabrication and especially modifications of the template geometry compared to other structures, i.e., nanowires, and preparation procedures. The term anodization describes the fabrication of metal oxides by electrochemical oxidation of the metal immersed into an electrolyte and under application of a voltage or current. ^[86–88] For some metals such as aluminum or titanium, parameter sets of electrolyte type and concentration, temperature, and applied voltage have been discovered, which result in the formation of regularly ordered, cylindrical pores perpendicular to the materials surface by self-organization. ^[88] Especially the ordered pore formation by anodization of aluminum leading to so-called anodic aluminum oxide (AAO) is extensively studied since its discovery by Masuda and Fukuda in 1995. ^[90]

AAO consists of ordered cylindrical pores with diameters between 10 and 400 nm and lengths up to several hundred micrometers in an aluminum oxide (alumina, Al₂O₃) matrix. The general structure is schematically depicted in Figure 2.6.(a) and the geometrical dimensions such as pore diameter d_p , interpore distance d_{int} , pore length L_p , and barrier layer thickness t_{bl} depend on the specific anodization conditions. ^[86–88,91–94]

Aluminum anodization is performed by utilizing an ultra-pure aluminum part as anode of an electrochemical cell. The most common electrolytes for AAO production are sulfuric acid (H_2SO_4), oxalic acid ($H_2C_2O_4$), and phosphoric acid (H_3PO_4).^[86,87] The electrochemical reactions at the anode during the anodization process include the oxidation of aluminum (Al) atoms to aluminum Al³⁺ ions at the Al surface.

$$Al_{(s)} \longrightarrow Al_{(s)}^{3+} + 3e^{-} \longrightarrow Al_{(aq)}^{3+} + 3e^{-}$$
(2.2)

Dissociation of water molecules at the oxide/electrolyte interface leads, among others, to the formation of oxygen anions (O^{2-}). Based on the applied electric field, these O^{2-} ions migrate towards the anode while Al^{3+} ions move to the cathode.

$$5 H_2 O_{(l)} \longrightarrow O_{(aq)}^{2-} + OH_{(aq)}^{-} + H_3 O_{(aq)}^{+}$$
 (2.3)

Thus, both ion types react to Al_2O_3 at the metal/oxide interface. Accordingly, growth of new Al_2O_3 occurs at the bottom of the structure.

$$2\operatorname{Al}_{(s)}^{3+} + 3\operatorname{O}_{(aq)}^{2-} \longrightarrow \operatorname{Al}_2\operatorname{O}_{3(s)}$$
(2.4)

Note, the aluminum and oxygen ions can move through the solid Al_2O_3 film.^[86] The formation of Al_2O_3 from Al results in volume expansion of the material and thus, imperfections and defects arise in the Al_2O_3 film. These defects provide spots where the



Figure 2.6. Scheme of the geometric structure and the fabrication of AAO. (a) AAO consists of hexagonal-ordered cylindrical pores perpendicular to the surface. The AAO structure is characterized by the pore diameter d_p , the interpore distance d_{int} , the pore length L_p , and the barrier layer thickness t_{bl} which are all determined by the anodization conditions. (b) Anodization is conducted in an electrochemical cell consisting of a hat with integrated stirrer and noble metal wire grid as cathode. The anode is formed by an aluminum sample placed on a copper plate. The cell is filled with an electrolyte and Al₂O₃ growth occurs by oxidation under applied potential or current. In the initial growth stage, an Al₂O₃ thin film forms at the metal/oxide interface while field-assisted dissolution removes Al₂O₃ at the spots of high electric field strength in the film. During steady-state growth, the process is dominated by Al₂O₃ formation at the metal/oxide interface and the electric field distribution results in self-organized pores with well-defined pore diameters and interpore distance.

applied electric fields concentrates which gives rise to electric field-assisted dissolution of the Al₂O₃ layer.

$$Al_2O_{3(s)} + 6H_3O^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 9H_2O_{(l)}$$

$$(2.5)$$

Hence, the defects deepen during ongoing anodization. As this process competes with the Al_2O_3 formation at the metal/oxide interface, steady pore growth is obtained for equilibrium conditions (Figure 2.6.(b)). Furthermore, mechanical stress between neighboring pores leads to their rearrangement during the Al_2O_3 formation. Since the Al_2O_3 growth occurs at the metal/oxide interface, the pore positions are adapted during the formation of new material resulting in a hexagonal closed-packing which minimizes the internal stress in the porous alumina film. Hence, the degree of ordering increases with the anodization time. Further possible reactions at the anode include the release of aluminum ions into the surrounding electrolyte and the oxidation of oxygen ions to elemental oxygen.

$$Al_{(s)}^{3+} \longrightarrow Al_{(aq)}^{3+}$$
(2.6)

$$O_{(aq)}^{2-} \longrightarrow O_{2(g)} + 4e^{-}$$
(2.7)

At the cathode, hydrogen ions H^+ are reduced to hydrogen.

$$2H_3O^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} + 2H_2O_{(l)}$$

$$(2.8)$$

After initial pore formation, the AAO growth rate is constant meaning that the pore length depends linearly on the anodization time. ^[86,87] In general, the growth rate is in the order of micrometers per hour but the exact value depends on the anodization conditions, e.g., electrolyte type and concentration, temperature, and voltage. The self-ordering regimes for the three most common electrolytes define the geometrical characteristics of the resulting AAO structures and are well reported in literature and summarized in review articles. ^[86–88,91–94]

Two-step anodization with intermediate removal of the oxide layer by etching in a H_3PO_4 /chromic acid (H_2CrO_4) mixture leads to a very high ordering degree of the cylindrical pores. ^[86, 87] This approach is based on the microstructure of the Al substrate after anodization: A thin barrier oxide layer forms at the bottom of the cylindrical pores and this features a hemispherical shape. Thus, the Al substrate is patterned by hemispherical concaves which define the top surface after the Al_2O_3 layer removal and serve as starting points for the second anodization step. Accordingly, the applied electric field already focuses to the centers of these concaves and the porous layer growth starts directly from the beginning of the second anodization resulting in a highly-ordered AAO structure. Since the pores are arranged perpendicular to the Al_2O_3 surface, the AAO structure acts as a 2D PhC. The periodicity of such 2D PhC is dictated by the used electrolyte, but the pore diameter can be further tuned either during or after the anodization. For the latter case, the pore diameter can be enlarged by selective wet-chemical etching of Al_2O_3 by aqueous H_3PO_4 solutions. This approach benefits from the onion-like distribution of impurities



Figure 2.7. 2.5D AAO-PhCs feature in-depth diameter modulations. The individual pores are still separated by Al₂O₃ and hence, the periodic refractive index variation does not completely cover all three dimensions. Freely adapted with permission. ^[88] Copyright 2019, *MDPI*.

around the pores which tailors the etching rates depending on the position. [86,91,95,96] Coating the AAO structure with Al₂O₃ by ALD is an opportunity to decrease the pore diameter after the anodization. Due to its precise thickness control and self-limiting reaction steps, ALD is well-suited for conformally coating high-aspect ratio structures such as AAO which is difficult to achieve with other physical or chemical deposition techniques. Pore-diameter tuning during anodization is possible by adjusting the applied voltage as the diameter depends linearly on the voltage.^[86] In addition, the application of periodically pulse-like anodization profiles in voltage (or current) result in the formation of periodic in-depth diameter modulations. ^[88,91,94,97] The individual pulse shape during anodization is transferred to the pore diameter variation. However, it should be noted that the exact pore diameter modulation often appears different compared to the applied voltage or current profile due to the recovery effect of the barrier layer. [98-101] Caused by the thicker barrier layer of AAO fabricated in $H_2C_2O_4$ compared to H_2SO_4 , this recovery effect becomes more pronounced resulting in distorted pulse shapes and distinct time delays. The diameter variation represents a periodic modification of the dielectric constants in the third direction not covered by a 2D PhCs. Nevertheless, the periodicity does not reach the whole third direction because there are regions which are not affected by it (as seen in Figure 2.7.). Thus, we consider this type of AAO as a 2.5D PhC showing mixed characteristics of 2D and 3D PhCs. Since the thickness of the porous layer depends on the anodization time, the diameter modulation periodicity can be tuned by modifying the pulse periodicity which shifts the PSB position of such 2.5D PhC. [3,94,97,102-107] Accordingly, the PSB position is widely tunable across the whole ultraviolet to infrared range of the electromagnetic spectrum. [3,6,86-88,91,94,95,97,106-120]

2D and 2.5D AAO-PhCs can be further modified by ALD coating after anodization. Apart from the above mentioned approach to narrow the pore diameter, ALD can be used to conformally deposit functional materials onto the AAO surface. For example, AAO-PhCs were utilized as template structures for photocatalysts or electrocatalysts deposited by ALD in the past. ^[3, 121–132]

3D: Infiltration of Self-Assembled Particles

A well-established approach for fabricating 3D PhCs is the infiltration of self-assembled particles followed by removal of the template structure to achieve IOs. ^[30–32,42,84,85,133–135] Methods to self-assemble monodisperse particles into hexagonal-closed packed structures are frequently reported in literature. They span, for example, from sedimentation over Langmuir-Blodgett technique and evaporation induced self-assembly to vertical deposition.^[84,85] Such assembled direct opal structures feature voids in-between the individual particles due to the maximum volume filling fraction of 74 % based on the hexagonal-close packing of spherical particles.^[30] These voids can be infiltrated by another material using wet-chemistry, physical, and chemical deposition methods. ^[30, 84, 85] To achieve highly conformal coatings in combination with precise control of the deposited thickness, ALD is the best suited technique to realize such infiltration. [31, 32, 42, 84, 133] Additionally, material accumulation on top of the opal can be circumvented with ALD based on the precise layer thickness adjustment. Polymer particles are typically applied for the template structure, because they can easily be removed after the ALD process by burnout or wet-chemical treatments dissolving the polymer. ^[85] However, silica particles have the advantage of stability against, e.g., temperature or solvents, but are much harder to remove, i.e., delicate fluorine-based chemistry is required. When the particle template is removed, a porous IO is obtained as 3D PhC. Its' PSB position can be independently tuned by the utilized particle size, the coating material, and the coating thickness. ^[31, 32, 133–135] Infiltration of the assembled templates is in principle possible with all existing ALD processes offering a variety of coating materials. However, there are limitations regarding the ALD process types and the compatibility with the template material. For polymer particles the ALD process temperature has to stay below the polymer's glass transition temperature.^[42] Moreover, many polymers are not stable to plasma exposures which limits the use of plasma-enhanced ALD. Furthermore, the thermal or chemical treatment of the ALD-coated structure to remove the template material should not affect the ALDgrown material. The maximum thickness of the ALD-derived film is defined by the minimum volume of the voids in-between the assembled spheres, i.e., the tetrahedral gaps. Hence, maximum coating thicknesses of 7.7% of the template sphere diameter are reported by Míguez et al. from an experimental study.^[136] Taken all these aspects into account, thermal ALD processes operated at low temperatures are most suitable for the fabrication of 3D PhCs by ALD infiltration of self-assembled particles.

The desired application and the compatibility of the ALD process with a potential template structure determines the material selection for preparing ALD-based PhCs. Due to the highly porous nature of the 2D, 2.5D, and 3D templates utilized in this thesis, we apply stop-flow mode for the ALD processes. Metal oxides, namely TiO₂, Fe₂O₃, Al₂O₃, and SiO₂ are deposited as they offer interesting functional properties. Especially the photocatalytic properties of TiO₂ and Fe₂O₃ thin films are utilized herein to characterize and optimize the photocatalytic performance of functionalized PhCs. Moreover, these materials are combined with other materials by ALD to investigate the effect of integrating photocatalytic property enhancement concepts for ALD-based photonic structures.

2.2. Photonic Applications of ALD-grown Materials

In this section, photonic applications of PhCs, that can be prepared with ALD-based methods, are introduced. First, PSB tuning of PhCs by ALD is explained. Second, the concept of thermal barrier coatings is presented and the possibility of utilizing ALD to improve the structures are shown. Third, different light-harvesting applications using PhCs are presented and finally, photocatalysis as exemplary application in this thesis is discussed in more detail.

2.2.1. Photonic Stop Band Tuning

Based on the inherently precise thickness control and the layered material deposition, ALD is well-suited for modifying PhC PSBs. As explained in Section 2.1.3., the PSB position is determined by the PhC's structural periodicity and the effective refractive index. The ALD fabrication of nanolaminates as 1D PhCs has been reported in literature for structures composed of various material combinations such as hafnium oxide (HfO₂)/yttrium oxide (Y₂O₃), ^[137] Al₂O₃/Y₂O₃, ^[138, 139] Al₂O₃/TiO₂, ^[140–143] Al₂O₃/tantalum pentoxide (Ta₂O₅), ^[144] Al₂O₃/zinc oxide (ZnO), ^[145, 146] TiO₂/ZnO), ^[147] TiO₂/SiO₂, ^[142] to name a few. Adjusting the individual layer thicknesses within the nanolaminates tailors the periodicity of the layers and hence, tunes the PSB position. Moreover, varying the ratio of the different materials inside a nanolaminate or changing the type of utilized materials modifies the effective refractive index of the structure and correspondingly also affects the PSB position. These tunable parameters allow for finely adjusting the nanolaminate properties to achieve judiciously designed PSB characteristics of 1D PhCs by ALD. Such nanolaminates are frequently applied as optical coatings. ^[137–139, 143, 144, 147] Examples for optical applications of ALD-grown nanolaminates are Bragg mirrors, narrow bandpass filters, and antireflective coatings, to name a few. [137, 139, 140, 142, 143]

Similar to tailoring 1D PhCs, ALD can also be utilized to expand the properties of 2D and 3D PhCs. ^[148–154] Since these structures are often prepared with porous templates, ALD renders conformal coating of the PhC structures. Besides widening the PhC properties by modifying them with functional materials, such additional material layers can also tune the PSB characteristics by adjusting the PhC's effective refractive index. For instance, Yang *et al.* reported on very precise tailoring of 2D PhC waveguides by ALD with a resonance wavelength variation of 122 pm per ALD cycle for coating thicknesses around 17 nm. ^[151] Furthermore, spectral tuning of the PSB in the visible light range depending on the ALD coating thickness was demonstrated by Sechrist *et al.* for SiO₂ opals functionalized with Al₂O₃ as depicted in Figure 2.8. ^[155]

2.2.2. Thermal Barrier Coatings

Thermal barrier coatings (TBC) are structures added to the surfaces of parts that operate at high temperatures such as turbines. These material systems should protect the turbine parts from material damage due to the high temperature. Hence, TBCs have to withstand these temperatures and serve as thermal insulation layers. ^[156, 157] They typically consist



Figure 2.8. Spectral tuning of the PSB characteristics of an inverse opal coated with different Al₂O₃ thicknesses by ALD. Increasing the coating thickness alters the structures' effective refractive index and thus, redshifts the PSB central wavelength. Adapted with permission. ^[155] Copyright 2006, *American Chemical Society*.

of ceramic materials, for example SiO₂, Al₂O₃, zirconium oxide (ZrO₂), or composites of these materials with further oxides. Many of these materials can be deposited by ALD rendering them very attractive for functionalizing curved parts with TBCs. Moreover, ternary materials provide additional functionalities, i.e., higher temperature stability, and can be fabricated by ALD. Not only the material composition but also the geometrical structure of TBCs can be tuned to improve the thermal insulation properties. Hence, porous structured TBCs are often applied and PhCs enable further tailoring by selectively reflecting infrared radiation at the TBC surface and thus, preventing the radiative heating of underlying parts. As described above ALD-based fabrication of IOs renders precise tuning of the PhC's PSB properties in combination with a wide range of possible material depositions. Furthermore, Furlan *et al.* have shown that IOs composed of mullite can be fabricated by supercycle ALD and subsequent thermal annealing. ^[31,32] The structures feature improve thermal annealing them well-suited as TBCs. ^[31-33]

2.2.3. Light Harvesting Applications

Over the past decades, there has been growing interest in the ability to harness light for sustainable energy production, environmental remediation, and material synthesis. Hence, photonic processes are utilized for various applications ranging from photocatalysis and photoelectrochemistry to photothermal processes and photovoltaics, to name a few. ^[28, 35, 158–166] In this section, the basic concepts of different photonic applications utilizing PhCs will be shortly discussed. Further, the progress in this field is presented with a focus on the material and structural advancements achieved by applying ALD as fabrication technique. Especially tailored material properties allow for enhanced performances and efficiencies of photonic devices.

Photocatalytic processes use light to drive chemical reactions. Since sunlight can induce these reactions, photocatalysis holds great potential for environmental remediation



Figure 2.9. Scheme of photonic applications for sustainable energy production and environmental remediation that could be driven by solar light. This drawing focuses on the application of AAO-PhCs (here denoted as nanoporous anodic alumina photonic crystals, NAA-PCs) as exemplary structures which could be coated with various materials by ALD to provide functional materials. Adapted from publication VI.

and energy conversion. Photocatalysts are typically semiconductors that generate electronhole pairs under illumination with light of energy larger than their band gap. The free charge carriers can then migrate to the photocatalysts surface and induce chemical reactions in compounds which are present in the photocatalysts' environment. ^[35, 158, 159, 167, 168] Nevertheless, photocatalysis faces some limitations for practical applications because the charge carrier generation and separation is often inefficient or the materials decompose under the application. ^[169–171] Thus, various strategies have been developed to improve photocatalytic performances. In general, they aim at improving light-matter interactions by geometrical modifications of the photocatalyst or at enhancing light absorption, charge carrier transport, and separation by tailoring the material.

Photoelectrochemistry (PEC) integrates semiconductors in external electrical circuits to make use of free charge carriers generated by light-excitation of the material. In detail, PEC systems consist of two separated electrodes, i.e., anode and cathode, which are exposed to an electrolyte. Application of a potential or current between the electrodes spatially separates the photo-generated charge carriers. ^[160–162] Both electrons and holes can induce redox reactions in compounds adsorbed at the electrode surfaces, namely oxidation reactions induced by holes at the anode, and reduction reactions at the cathode which are induced by the electrons. As reported for photocatalysis, charge carrier generation and transport through the material are crucial steps during PEC processes. Therefore, optimization of the electrode materials and their structure are important aspects for advancing the functional properties of PEC. ^[160–162]

Photothermal applications utilize the photothermal effect of materials to generate heat from solar light. In detail, light illumination of materials excites electrons which can relax *via* non-radiative pathways and generate heat in this process. ^[163,164] The produced heat can be applied in different processes such as water purification, photothermal manipulators, photothermal catalysis, and photothermal therapy. ^[37,163,172] Despite the fact that metals present good intrinsic light-to-energy conversion properties, their functionality can be further enhanced by nanostructuring. Additionally, other materials such as semiconductors strongly benefit from nanostructuring which renders them applicable for photothermal applications. The size, geometry, and materials of nanostructures determine their photothermal properties. ^[163,164,172,173]

Photovoltaics (PV) denotes the conversion of light into electrical energy. It relies on the photovoltaic effect. ^[165, 166] Briefly, the PV effect describes light-induced generation of free charge carrier in a material. The electronic structure of a semiconductor is characterized by a valence band and a conduction band that are separated by a material specific energy, the so-called band gap. ^[168] If the semiconductor is illuminated with light, it can be excited by light energies larger than its band gap. The semiconductor excitation occurs by absorbing photons resulting in the elevation of electrons from the VB to the CB and simultaneously leaves a positively charged hole in the VB. ^[167] Both, the electron in the CB and the hole in the VB, are free charge carriers and their separation produces a voltage. PV systems typically consist of p-n junction semiconductors that are excited to form electron-hole pairs under light irradiation with energies larger than their band gap energy. The free electrons and holes then move towards the n-type and p-type region of the semiconductor,

respectively, according to their charges. Hence, the spatial separation creates a voltage in the material which can be utilized to drive electrons through a coupled external circuit to generate electrical energy. ^[165, 166] Although solar cells are well-established as sustainable energy source and are based on PV from sunlight, they face limitations with respect to their efficiency. Inefficient utilization of sunlight and non-radiative charge carrier recombination in the semiconductor are the main causes that limit the performance. Various approaches have been developed to improve the light absorption, for instance, combining different materials to widen the absorption spectrum or utilizing advanced geometries to enhance light-matter interactions. ^[6, 166]

In conclusion, photonic light-harvesting applications require customized materials and structures to further enhance their functional properties. ALD-based fabrication approaches offer the ability to precisely engineer the composition, thickness, and surface properties of materials in combination with the possibility to conformally coat complex geometries. Hence, they are often used for fabricating photonic materials and structures as summarized in several review articles. ^[34–39, 164, 173, 174] Photocatalysis is chosen as exemplary photonic application in this thesis and thus, the basic principles and approaches to improve material performance for photocatalysis are discussed in more detail in the next section.

2.2.4. Strategies for Performance Enhancement of Photocatalysts

The term photocatalysis describes light-induced chemical reactions. ^[167] This process type was first reported by Fujishima *et al.* in 1972. ^[175] Since then, different definitions of the term have been given referring to the ability of photons to induce reactions. Since the photons themselves are "consumed" during the reaction, they cannot be considered as a classical catalyst. Instead, they help to start the photocatalytic reactions which can occur within one phase (homogeneous) or at the border of two or more phases (heterogeneous). ^[158, 159, 167, 168] For example, reactions induced in a liquid medium by a solid catalyst are classified as heterogeneous reactions. Moreover, there are different photocatalytic pathways, namely catalyzed or sensitized photoreactions and both are typically referred to as heterogeneous photocatalysis which will be further discussed in this chapter. ^[168] Specifically, a short overview of the steps in a photocatalytic reaction is given, followed by the explanation of several strategies for enhancing photocatalytic activities.

Irradiating a phototocatalytic active material – also called photocatalyt – with light is a crucial step for prompting photocatalytic reactions. Photocatalysts are typically semiconductors featuring electronic band gaps in the UV to visible spectral range. ^[167, 168] Both types of photo-generated free charge carriers, i.e., electrons and holes, possess the ability to induce chemical reactions due to their reductive (electrons) or oxidative (holes) properties. Free charge carriers generated in a solid photocatalyst can move within the material. In heterogeneous photocatalysis, the photocatalyst is in contact with the surrounding medium, i.e., a liquid or a gas. When a free charge carrier reaches the interface


electrolyte photocatalyst

Figure 2.10. Illustration of light-induced excitation and possible subsequent processes in a semiconductor photocatalyst. (i) Irradiating a semiconductor with light of energies larger than the semiconductors' band gap. (II) Absorbing the light excites an electron (e⁻) and a hole (h⁺) to the conduction band (CB) and valence band (VB) of the semiconductor, respectively. (III) The free charge carriers can migrate towards the photocatalyst/electrolyte interface. (IV) Alternatively, electrons and holes could recombine. (V) Free charge carriers at the photocatalysts' surface can induce redox reactions in compounds adsorbed at the photocatalyst surface. Electrons reduce adsorbed species while holes oxides species adsorbed at the interface.

between the photocatalyst and its surrounding, it can induce chemical reactions. For instance, they can facilitate the decomposition of organic compounds to carbon dioxide and water, the conversion of biomass to hydrogen, or the photoreduction of toxic heavy metal ions. ^[168, 176] However, there are alternative processes which can occur to the charge carriers before they reach the surface. Recombination of photo-generated electrons and holes is a common drawback in photocatalysis as these recombined charge carriers cannot contribute to the photocatalytic reaction. A high recombination probability of charge carriers in a material is also reflected as short carrier diffusion length. Different strategies have been developed to prevent such recombination events, for example spatial separation of the charge carriers, and will further be discussed in the following. According to the utilization of light to induce chemical reactions, photocatalysis is considered a green technology with the ability to realize sustainable pathways for chemical production, decomposition, and recycling. ^[177–179] A plethora of ALD-grown materials are reported for application in photocatalysis such as TiO₂, ZnO, Fe₂O₃, or platinum, to name a few. ^[180–182]

Most heterogeneous photocatalysis reactions occur via the Langmuir-Hinshelwood mechanism. The kinetics are briefly explained here and a more detailed description is given in the Appendix.

For photocatalytic degradation of organic molecules in an aqueous environment, water

is typically the second reactant. Since it is present in large amounts in aqueous solutions, its concentration decline due to the photocatalytic reaction is negligible and a constant concentration is assumed. Since the molecule degradation is based on the excitation of the organic compound, the process only depends on the compounds' concentration *c* and thus, is a first order process. ^[183, 184] Langmuir-Hinshelwood kinetics assume a mono-layer adsorption of the analyte molecules and an adsorption-desorption equilibrium of these molecules at the photocatalyst surface before starting the photocatalytic reaction. Since diluted solutions with concentrations much smaller than 10^{-3} mol 1^{-1} are typically analyzed for organic compound decomposition, the rate equation simplifies to a pseudo first-order kinetics as shown in Equation 2.9. ^[183–186]

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \kappa \cdot K \cdot c = k \cdot c \tag{2.9}$$

Here, *c* denotes the dye concentration, *t* is the time, *k* represents the apparent rate constant, which is the product of the reaction rate constant κ and the adsorption coefficient *K*.

Although photocatalysis offers great potential for different areas such as water purification, energy production, and synthetic chemistry, it also faces major challenges which limit the practical applicability up to now. ^[169] For example, TiO₂ as the benchmark photocatalyst features a band gap in the UV range and thus, can only utilize less than 10 %of the solar spectrum. [169, 187] Visible light active photocatalysts often suffer from inefficient charge carrier generation or separation. ^[170, 171] Nevertheless, several approaches have been developed that aim to improve the performance of photocatalysts. [171, 177, 188] The concepts and benefits of these techniques are presented in the next section. Herein, only methods which could potentially be combined with PhC photocatalysts and ALD are introduced, namely nanostructuring, utilization of the slow photon effect, semiconductor band gap modifications, formation of semiconductor heterostructures, combination with co-catalysts, and application of plasmonic materials. The basic concepts of these approaches are briefly explained in the following but the reader is referred to review articles for a detailed description. ^[28, 29, 158, 169, 171, 176–179, 188–191] Possibilities for utilizing ALD to apply the different approaches are shortly presented. Note, the mentioned ALD-grown materials serve as examples for the respective strategy and they do not resemble a complete overview of literature.

Nanostructuring

Reducing the size of photocatalysts to the nanoscale enables new functionalities. First, the size reduction corresponds to an increase of the structures' surface-to-volume ratio. ^[159,192] A surface-to-volume ratio increase is especially interesting for photocatalysis as the reactions occur at the surface of the material. Correspondingly, more surface sites are available for photocatalytic reactions of nanostructured photocatalysts compared to their bulk counterparts of the same material volume rendering the photocatalytic process more efficient with respect to the utilized material amount. Second, nanostructuring offers a variety of possible geometries and dimensions of the nanostructures such as 0D nanoparticles, 1D nanotubes, nanowires, and nanorods, 2D nanosheets and thin films, and

3D nanostructures composed of nanometer-sized building blocks. [171, 177, 193, 194] Since each of these geometries is related to certain properties, the nanostructure can be tailored for the specific application. For photocatalysis, typical nanostructures include nanoparticles, nanowires, and porous 3D nanostructures such as assembled particles. In that sense, PhCs are a specific example of nanostructures with their periodically alternating materials. Third, nanostructuring of materials is often accompanied by the appearance of new functionalities or modifications of their properties. For instance, quantum confinement effects alter the electronic properties of materials and arise when the structure size is reduced to a few nanometers, i.e., the size becomes in the order of the electrons' de Broglie wavelength.^[192–194] One of the most famous examples is the size quantization effect in nanoparticles leading to the formation of an electronic band gap in particles composed of materials that feature metallic properties in bulk such as gold.^[192, 195–197] For both, bulk metallic materials and semiconductors, the band gap widens for nanoparticles with decreasing particle size due to the increasing confinement. Hence, the light absorption wavelength is determined by the nanoparticle size. Fourth, nanostructuring can improve light trapping inside the structure because of increased light scattering which is beneficial for photocatalysis to make efficient use of the solar light.^[177] In total, nanostructuring presents a method to tailor the material's properties for the desired application and hence, can improve the performance of photocatalysts. ALD is well-suited to functionalize the high surface area nanostructures based on the conformal material deposition. For instance, ALD has been applied to modify nanoparticles, nanowires, nanorods, or nanotubes which could be applied photocatalytic applications. ^[180–182] Further, 2D nanostructure photocatalysts can be directly prepared by ALD on planar substrates and also ALD-modified 3D nanostructure photocatalysts are reported in literature. [180, 181]

Slow photon effect

Based on the increased interaction probability between light with wavelengths of the PSB edges and the PhC material, the slow photon effect can be used for photocatalytic processes. Note, both PSB edges, i.e., the blue and the red edge, can be utilized to benefit from the slow photon effect-based enhancement of the photocatalytic properties. For this, two different approaches are reported in literature. On the one hand, a PSB edge is either matched to the absorption of the chemical which should be decomposed by photocatalytic reactions. On the other hand, a PSB edge is aligned with the band gap of a semiconductor photocatalyst as schematically depicted in Figure 2.11.^[28–30] The former approach is often reported for AAO-PhCs which are used to degrade dye molecules as model pollutants of water. ^[3, 104, 116, 198] Dye molecules adsorbed at the photocatalysts' surface get excited by the incoming light. The probability of this process can be enhanced by the slow photon effect. The generated charge carriers are then transferred to the photocatalyst where they can induce further reactions. Efficient photocatalytic activity enhancement is reported for degrading specific components. Nevertheless, the activity is not improved when the same PhC structure is applied for decomposing other chemicals because the PSB edge is no longer aligned with the absorption of the chemical. Hence, the slow photon effect could not be used to improve the photocatalytic performance at other than the



Figure 2.11. Scheme of aligning the PSB position of a PhC to a semiconductor photocatalyst band edge or a dye as example chemical to be degraded in a photocatalytic process. Light-matter interactions in the PhC structure are increased at the blue and red edge of the PSB based on the slow photon effect. Overlapping a PSB edge with the absorption maximum of a dye which should be photocatalytically decomposed increases excitation of the dye (upper right) and thus, is only specific for this compound. Matching a PSB edge to the semiconductor band edge facilitates the excitation of the semiconductor (lower right) and consequently, is independent of the compound that should be degraded. For the sake of clarity, the blue and red edges were schematically aligned to the SC and the dye, respectively, to illustrate both approaches in one figure. Adapted from publication VI.

targeted compound. ^[3, 104, 116, 198] Contrary, aligning a PSB edge to the band gap of a semiconductor photocatalyst allows for a general performance enhancement unspecific of the chemicals decomposed in the photocatalytic reaction. ^[28–30, 199] In this case, the slow photon effect improves the charge carrier generation directly inside the semiconductor. This alignment to the PhC's material has been demonstrated several times for IO PhCs consisting of various photocatalyst materials such as TiO₂, ZnO, Fe₂O₃, or tungsten oxide but not for AAO-PhCs before this thesis. ^[30, 78, 89, 170, 200, 201] Moreover, ALD was applied to conformally coat thin film photocatalysts onto IO templates for utilization of the slow photon effect. ^[78, 202–207]

Semiconductor band gap modification

Modifying the band gap of semiconductor photocatalysts can boost their photocatalytic performance by expanding the utilized light range as summarized in several review articles. [89, 158, 169, 171, 176, 178, 179, 183, 189, 191, 192] Since the band gap defines the light absorption by the materials, it can also limit the applicability of certain materials for photocatalysis when the band gap does not match well to the solar light spectrum. The most prominent example is TiO₂ which features very good photocatalytic properties but suffers from its wide band gap between 3.0 and 3.3 eV that makes use of only 5-10% of the

sunlight spectrum. ^[187] Nevertheless, the band gap of semiconductors can be altered by targeted modifications, i.e., doping to enable more efficient utilization of the solar light. Doping the structures with foreign elements creates local defects in the material, which serve as trap states for the charge carriers. Thus, it narrows the materials' band gap due to localized energy states within the band gap which tunes the light absorption by the structure. ^[171,178] The fabrication method of doped semiconductors determines whether the dopant atoms are homogeneously distributed in the material or the material resembles a delta-doped structure. As explained above, ALD is well-suited for fabricating delta-doped thin films and thus, doped photocatalysts prepared by ALD are frequently reported in literature. ^[181] For example, utilization of aluminum as dopant for TiO₂ or ZnO is a common strategies to tune the materials' band gaps towards the visible light region. ^[181]

Semiconductor heterostructures

Semiconductor heterostructures composed of at least two different semiconductors can facilitate the separation of photo-generated charge carriers inside the structure. Based on the CB and VB edge positions of the semiconductors in contact, different types of heterojunctions are distinguished, which determine the migration of charge carriers (Figure 2.12.).^[89,169,171,177] Type I heterojunctions localize both charge carrier types, i.e., electrons in the CB and holes in the VB, in one component. In type II heterojunctions, electrons migrate towards one semiconductor and holes move to the other one. Thus, this type is very efficient for spatially separating photo-generated charge carriers, which is a crucial prerequisite in photocatalysis to prevent their recombination. Type III heterojunctions are also known as broken gap junctions because the band gaps of the individual components do not overlap. Charge carriers at the material interface are usually not transferred to the other material but could potentially recombine at the interface. Hence, oxidation and reduction reactions occur at the semiconductor with the remaining holes and electrons, respectively.^[178,188,191] Based on the material variety and the cyclic nature of ALD, semiconductor heterostructures can be easily prepared by ALD. [181] With regard to photocatalytic applications, heterostructures reported in literature consist, for example of tin dioxide/titanium dioxide or zinc oxide/titanium dioxide. [208, 209]

Co-catalysts

Co-catalysts are additional materials which are combined with the semiconductor photocatalyst and can aid in the light absorption required for the photocatalytic reactions. ^[177, 188] Further, they could improve the charge carrier separation when they act as electron or hole acceptors and thus, limit the recombination. ^[177, 188] Co-catalysts can also directly take part in the photocatalytic reactions by providing additional reaction sites for certain compounds. ^[188] Deposition of co-catalysts by ALD has also been demonstrated. ^[180, 182]

Plasmonic nanostructures

Plasmonic nanostructures can contribute to photocatalytic performance enhancements based on their unique light harvesting properties. ^[177,210,211] They feature localized surface plasmon resonances (LSPRs) which are defined as collective oscillations of the struc-



Figure 2.12. Different types of semiconductor heterojunctions depending on the CB and VB alignment. (a) Type I heterojunctions facilitate the charge transfer to semiconductor (SC) 1, (b) type II structures promote the charge separation by directing the holes to SC1 and the electrons to SC2, and (c) type III heterojunctions could separate electrons and holes but also render charge carrier recombination at the material interface.

ture's conduction electrons. These oscillations can be excited by irradiating the structures with wavelengths of the LSPR. The LSPRs cause high electric fields at the nanostructure surface and can be utilized to increase light absorption when a plasmonic material is attached to a photocatalyst or serves as photocatalyst itself. The charge carriers included in a LSPR possess high energies. Thus, they are often referred to as hot electrons or hot holes. These hot charge carriers can be injected into the CB (electrons) or VB (holes) of the photocatalyst and can then initiate reactions at the surface. In this way, they provide an additional pathway to generate charge carriers in the photocatalyst which are required for the photocatalytic reactions. ^[177, 178, 210] On the one hand, ALD was applied in previous publications to directly fabricate plasmonic materials for photocatalytic application such as platinum or palladium. ^[19, 20, 180, 182, 212] On the other hand, ALD has often been used to overcoat previously prepared plasmonic nanoparticles with thin layers of TiO₂ or aluminum oxide as photocatalyst or protection layer, respectively. ^[180, 182, 204]

1D Photonic Structures: Nanolaminates

Multilayers of different materials resemble 1D PhCs. They can tune light-matter interactions rendering them very attractive for optics, thermal barrier coatings, and photocatalytic applications. Doping a semiconductor with another element modifies its band gap which can extend the utilized light spectrum. Multilayering and doping of materials are effective strategies to modify the crystallization behavior of certain materials, for example, to shift phase transitions which occur during thermal treatments at higher temperatures. ^[142,213–221] Since the photonic properties of anatase TiO₂ and amorphous TiO₂ differ, it is important to gain precise knowledge of the phase transition conditions. Silicon dioxide (SiO₂) is an interesting candidate for combining it with TiO₂ because of the high refractive index difference of both materials, and the high chemical as well as mechanical stability similar to TiO₂. In publication I, different SiO₂-incorporated TiO₂ thin films are fabricated by supercycle ALD processes and their structural evolution upon thermal annealing is systematically studied with a combination of *in situ* and *ex situ* characterization techniques.

Prior to investigating the crystallization behavior of SiO₂-incorporated TiO₂ thin films, we conducted quartz crystal microbalance (QCM) measurements of the supercycle ALD processes. Mass uptake by physisorption or chemisorption alters the resonance frequency of the quartz crystal used in the QCM measurements. Hence, the frequency change over time can be related to the individual steps in an ALD cycle (precursor pulse, exposure, purge) and how subsequent processes affect each other. The QCM study was performed to ensure compatibility of the TiO₂ and SiO₂ ALD processes applied in this work, because initial growth inhibition during supercycle ALD approaches can occur as previously reported for different material combinations, e.g., TiO2 with Al2O3 and Al2O3 with ZnO. ^[222, 223] Specifically, we combined SiO₂ deposition from tris(dimethylamino)silane (TDMAS) and ozone (O_3) with TiO₂ deposition from titanium tetraisopropoxide (TTIP) and either O₃ or H₂O as oxygen precursor for the TiO₂ growth. Details about the ALD process parameters are given in the Appendix. TiO₂-SiO₂ multilayers are prepared by applying three supercycles each consisting of 10 cycles TiO₂ deposition and 10 cycles SiO₂ deposition. H₂O and O₃ as precursors for TiO₂ growth were tested in two separate supercycle processes. The QCM measurements demonstrate that the oxygen precursor for TiO₂ deposition determines the initial material growth of SiO₂ when changing from TiO_2 to SiO_2 as depicted in Figure 3.1.

Utilization of H_2O results in a high TTIP uptake in the first cycle as indicated by the high frequency change. Afterwards, QCM frequency change per cycle decreases successively until constant values are obtained from the seventh cycle onward (Figure 3.1.(a)). The high initial frequency per cycle change compared to the steady-state is caused by growth inhibition in the following cycles due to isopropyl alcohol (IPA) as by-product. The surface of the quartz crystal is typically terminated with hydroxy-groups (OH-groups).

TTIP molecules physisorb at these groups and react with them resulting in the formation of Ti-O bonds with release of an IPA molecule per reacted isopropyl chain. IPA molecules as by-products should be removed during the purge step of the ALD half-reaction. However, it was shown by Reinke et al. that some isopropyl groups do not react with water molecules.^[224] These unreacted groups adsorbed at the substrates' surface block surface sites for further reactions. Hence, adsorbed IPA groups partially inhibit the growth of TiO₂ resulting in a lower frequency per cycle variation than in the first cycle. ^[222, 224, 225] Saturation of the frequency change per cycle after a certain cycle number (Figure 3.1. upper right) represents stable growth conditions under consideration of the intrinsic inhibition by isopropyl groups. Application of the first TDMAS half-reaction results in a negative frequency per cycle change which resembles removal of previously bound species from the surface. ^[223] This could be caused by the reaction of isopropyl groups as residues from the last TiO₂ cycles with TDMAS molecules. Such loss of atoms causes a mass decrease measured by the QCM and hence, a negative frequency per cycle change. Moreover, the O₃ half-reaction might also contribute to the removal or decomposition of isopropyl species at the surface based on the oxidizing properties of O_3 . In the second SiO₂ ALD cycle, the frequency per cycle change is positive indicating that material is deposited at the QCM surface in this cycle. To be able to draw a more precise conclusion for the reaction mechanism, the individual half-reactions would need to be analyzed in detail which was below the detection limit with the QCM parameters utilized herein. The following TiO₂ and SiO₂ deposition sequences show in general the same structure as described for the first supercycle: TiO₂ growth starts with a high initial frequency per cycle change which is then decreasing and followed by saturation to reach stable values after three cycles. SiO₂ deposition is characterized by a negative frequency per cycle change in the first cycle, then the frequency change increases, and afterwards, stable growth rates are observed.

In contrast to H₂O-based TiO₂ deposition, TiO₂-SiO₂ supercycle processes using O₃ as oxygen precursor for TiO₂ always show positive frequency per cycle changes (Figure 3.1.(b)) – even (if small) for the first SiO₂ ALD cycle after TiO₂ deposition. The reaction of TTIP with O₃ results in direct removal of the isopropoxide chains and formation of Ti-O bonds based on the oxidizing properties of O₃. Hence, no IPA molecules are formed that could block surface sites for further reactions. ^[225] Correspondingly, the TiO₂ surface is terminated by oxygen atoms after an ALD half-cycle and TDMAS molecules pulsed in the first SiO2 cycle of a supercycle immediately react with oxygen atoms chemically bound to the substrate. The positive frequency per cycle change indicates that material growth occurs within all cycles of a TiO₂-SiO₂ supercycle. The different lower initial frequency per cycle change for depositing SiO₂ on TiO₂ compared to the following SiO₂ cycles is probably caused by different deposition characteristics on the underlying surfaces as similarly reported by Wiegand et al. for Al₂O₃ deposition on TiO₂. ^[222] Note, the growth rate of TiO₂ from O₃ is lower (0.30 Å) than for TiO₂ deposition with H₂O (0.38 Å) but the frequency per cycle change is in a similar range. Based on the results from the QCM study, O₃ was chosen as oxygen precursor for TiO₂ ALD process for supercycle ALD process utilized in the following part of this section to ensure constant



Figure 3.1. QCM study of TiO₂-SiO₂ multilayer deposition processes utilizing different oxygen precursors for the TiO₂ growth. A supercycle consists of 10 cycles TiO₂ deposition and 10 cycles SiO₂ deposition and is repeated three times. The frequency change during the whole deposition process is depicted on the upper left for each precursor combination. Close-ups on the data of the frequency change are displayed for the first and second TiO₂-SiO₂ supercycles on the lower left and lower right, respectively. The frequency per cycle change is shown on the upper right and indicates whether material is added or removed in a single cycle, i.e., a positive or a negative value. (a) Application of H₂O as oxygen precursor for TiO₂ results in etching of the material in the respective first SiO₂ cycle within of a supercycle which is characterized by a negative frequency change Δf per cycle. (b) Continuous material growth is observed when O₃ is used as precursor for the TiO₂ layers.

material deposition. Besides TiO_2 -SiO₂ multilayers, a positive initial frequency per cycle is especially important for the fabrication of SiO₂ delta-doped TiO₂ thin films by ALD because this approach introduces only a single SiO₂ ALD cycle in between TiO₂ cycles.

Modifying the Crystallization Properties of Titanium Dioxide by Incorporating Silicon Dioxide (Publication I)

Assessment of the crystallization behavior and the structural properties of SiO₂-incorporated TiO₂ thin films, i.e., multilayers and delta-doped structures produced by supercycle ALD (Figure 3.2.), reveals a dependence of the crystallization temperature (T_{cr}) on the TiO₂ layer thickness and the incorporated SiO₂ content.

ALD-grown TiO₂ layers are amorphous after the fabrication. Crystallization into anatase can be induced by thermal treatments. Herein, *in situ* X-ray diffraction (XRD) measurements demonstrate an increase of T_{cr} with decreasing TiO₂ thickness in TiO₂-SiO₂ multilayers (Figure 3.3.). The *in situ* XRD patterns (left column in Figure 3.3.(a)) depict the appearance of the anatase (101) peak at 25.7° while less intense anatase peaks are also visible in the *ex situ* XRD patterns (right column). Reducing the TiO₂ thickness from 50 nm to 4 nm raises the crystallization temperature non-linearly from 405 °C to 475 °C (Figure 3.4.(a)). A reduction of the TiO₂ thickness in the TiO₂-SiO₂ multilayers increases the interface area-to-volume ratio of these layers. Thus, the interfaces progressively dominate the properties of the TiO₂ layers. ^[218,221] The *ex situ* XRD patterns reveal crystallite sizes in the same order as the TiO₂ film thicknesses for layers thinner than 25 nm caused by the confinement in the multilayers. Increase of the number of TiO₂-SiO₂ interfaces by raised supercycle numbers further strengthens the effect of material interfaces onto the multilayers' properties. All samples crystallize only to anatase phase and no further phase transition to rutile or brookite is observed.

Thermal annealing does not significantly change the structure of TiO_2 -SiO₂ multilayers. X-ray reflectometry (XRR) patterns demonstrate slight thickness reduction caused by the atom rearrangement due to the phase transition. Note, the XRR patterns are not displayed in this section but can be found in the original manuscript I. Moreover, the data indicates a slight roughening of the material interfaces and the surface, which also appears in cross-section transmission electron microscopy (TEM) images as depicted in Figure 3.4.(b). The TEM micrographs also confirm the crystallization of the TiO₂ layers into polycrystalline films while the SiO₂ layers remain amorphous after annealing.

Doping TiO₂ with SiO₂ by supercycle ALD processes presents another possibility to tailor the crystallization temperature of TiO₂ thin films. For a constant total film thickness, T_{cr} from amorphous TiO₂ to anatase increases with increasing SiO₂ content. The sub-monolayers of SiO₂ introduced by single ALD cycles in the supercycle process form material defects in the TiO₂ films. These defects hinder the crystallization due to additional interface energies. Thus, increment of the SiO₂ content shifts the crystallization onset to higher temperatures. For example, pure TiO₂ thin films feature a T_{cr} of 420 °C which raises to 485°C for 10% SiO₂ content (Figure 3.5.(a)). As observed for the multi-

Modifying the Crystallization Properties of Titanium Dioxide by Incorporating Silicon Dioxide



Figure 3.2. Fabrication of SiO₂-incorporated TiO₂ thin films by supercycle ALD. (a) The supercycles combine *a* cycles of TiO₂ deposition from TTIP and O₃ as precursors with *b* cycles of SiO₂ utilizing TDMAS and O₃. Supercycles are repeated *n* times to achieve the desired material thickness. (b) TiO₂-SiO₂ multilayers are fabricated directly onto a p-doped Si wafer covered with a native SiO₂ layer by applying the individual cycle numbers and supercycle number given in the table. The total thickness of the multilayer structure is fixed at 100 nm. (c) SiO₂-doped TiO₂ thin films of 30 nm thickness are deposited by alternating TiO₂ cycles with a single cycle of SiO₂. The TiO₂ and supercycle numbers are adjusted according to the desired SiO₂ content. Note that 100 nm Al₂O₃ and 20 cycles of TiO₂ are applied before starting the supercycle to eliminate influences from the Si substrate. Adapted from publication I.

layers, crystallization results only in anatase TiO₂. SiO₂ doping also tunes the materials' refractive index due to the different refractive indices of both individual materials. ^[213, 226] Specifically, the refractive index of a SiO₂ delta-doped TiO₂ thin film decreases with increasing SiO₂ content. Furthermore, thermal annealing leads to a refractive index increase based on the different crystallographic phase of TiO₂. ^[213, 226] XRR patterns reveal that the film thickness remains almost constant upon annealing and suggest a roughening of the films' surface which is confirmed by atomic force microscopy (AFM) images.

Not only the SiO₂ incorporation into TiO₂ thin films affects the crystallization behavior but also the underlying substrate. Utilization of a silicon wafer with the native silicon dioxide layer as substrate results in a lower T_{cr} of 405 °C and 380 °C for the ALD-grown TiO₂-SiO₂ bilayer and a 45 nm TiO₂ thin film, respectively, than a wafer coated with 100 nm Al₂O₃ before the TiO₂ deposition (420 °C). This difference of T_{cr} for pure TiO₂ films is caused by the different interface energies between the titania layer and SiO₂ or Al₂O₃ as substrate material. ^[221]

To sum up, incorporation of SiO₂ into TiO₂ thin films by supercycle ALD processes allows for increasing the crystallization temperature depending on the material composition. Such behavior is already reported by existing publications utilizing TiO₂-SiO₂ multilayers or homogeneously SiO₂-doped TiO₂. ^[214–216,218,219,221,227–233] However, the crystallization behavior is only analyzed with *ex situ* characterization techniques in these reports. Note, *in situ* characterization as presented herein is required to precisely determine the crystallization temperature. The composition-dependent crystallization behavior enables customized adjustment of the material system and the applied annealing conditions for



Figure 3.3. The TiO₂ crystallization behavior in TiO₂-SiO₂ multilayers depends on the TiO₂ layer thickness and the supercycle number for a constant total thickness. *In situ* (left) and *ex situ* (right) XRD patterns demonstrate the crystallization to anatase phase A and the crystallization temperature is marked by the grey line in the *in situ* patterns. TiO₂-SiO₂ ratios of 1:1 (a-c) and 1:4 (d-f) are utilized and TiO₂ layer thicknesses of (a) 50 nm, (b) 10 nm, (c) 5 nm, (d) 20 nm, (e) 4 nm, and (f) 2 nm are studied. Freely adapted from publication I.



Figure 3.4. (a) The crystallization temperature T_{cr} decreases non-linearly with increasing TiO₂ thickness in TiO₂-SiO₂ multilayers. (b-d) cross-section TEM images of different multilayers before and after thermal annealing. The higher magnified high resolution TEM images in (c) reveal the amorphous TiO₂ phase before annealing and crystal lattices after annealing. Freely adapted from publication I.



Figure 3.5. (a) Increasing the SiO₂ content in SiO₂-doped TiO₂ thin films raises the crystallization temperature $T_{\rm cr}$. (b) The refractive index of the doped TiO₂ film $n_{\rm TiO_2}$ decreases with increasing SiO₂ content based on the lower refractive index of SiO₂ than TiO₂. The refractive index for all film compositions is increased after thermal annealing. Freely adapted from publication I.

the desired application, since crystallization can be induced or prevented by tuning these parameters. Induction of the crystallization could, for example, be important for photocatalytic applications because anatase typically features a higher phototcatalytic activity than amorphous TiO₂. ^[234] Since low concentration SiO₂-doping of TiO₂ tailors the materials' band gap to lower energies, it could allow for more efficient charge carrier generation under solar light irradiation.^[235–237] Nevertheless, to obtain anatase phase in such doped TiO₂ films, it is crucial to know about the influences on T_{cr} . In contrast to initiating the crystallization, some application require amorphous films as those as-prepared by ALD. Necessity of amorphous films is often reported for optical mirrors consisting of different multilayered metal oxides with ultra-smooth interfaces to reduce the losses within the structure. ^[227,238,239] As these devices are typically exposed to thermal treatments during their fabrication, a raised crystallization temperature in delta-doped or multilayer thin films presents a strategy to keep the TiO₂ layers in amorphous state while optical properties remain almost constant. Previous reports of TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂ thin films utilized sol-gel chemistry, ^[214, 216, 230–232] wet-chemical synthesis, ^[233] sputtering, ^[219,228] CVD, ^[215,229] and PVD ^[218,221,227] to grow the structures. These techniques work well for planar substrates but the applicability to other templates is limited due to non-conformal coating of complex substrates and/or less control of the deposited film thickness. In contrast, ALD offers the unique advantage of conformal material growth on all substrate geometries based on the self-limiting reactions. Hence, the supercycle ALD processes presented herein to fabricate SiO₂-incorporated TiO₂ thin films could be easily transferred to complex substrate shapes. For the samples studied in this work, structural properties remain intact during thermal annealing and only slight variations in film thickness, interface roughness, and surface roughness of SiO₂-incorporated TiO_2 are provoked by the TiO_2 crystallization.

2D and 2.5D Photonic Structures: Functionalized Anodic Aluminum Oxide

Depositing photocatalyst materials onto nanostructured templates requires chemical stability of the templates during both the functionalization process and the photocatalytic measurements. Otherwise, degradation of the template material over time could overlay with the evolution of the photocataylsts' functional properties. Consequently, the photocatalytic properties of the functional material cannot be unambiguously identified. In the first section of this chapter, the results from publication II are summarized. We investigate the influence of different post-anodization modifications of the AAO and ALD coating on the photocatalytic performances. These properties are studied by photocatalytic dye degradation and X-ray photoelectron spectroscopy of the AAO surfaces. The second section illustrates how ALD-grown TiO₂ thin films improve the photocatalytic activity of AAO-PhCs whose PSB edge is aligned to the dye being degraded (publication III). This study utilized the slow photon effect to boost the photocatalytic performance of the TiO₂-coated AAO-PhCs. Further, an influence of the TiO₂ thickness on the performance is shown and the degradation mechanism of the dye (methylene blue) is discussed. A more general approach for enhancing the photocatalytic activity of AAO-PhCs is presented in Section 4.3 with the key findings of publication IV. Here, a PSB edge of the PhC structure is tailored to the band gap of Fe₂O₃ which is used as an example photocatalyst in this work. The photocatalytic performance is significantly increased for degrading various dyes when the PSB blue edge overlaps with the Fe₂O₃ band gap due to the slow photon effect. Furthermore, optimization of the Fe₂O₃ film thickness is essential to allow for the maximum photocatalytic activity which is affected by charge carrier dynamics inside the film and mass transport of molecules within the pores of the AAO template. Additionally, we show that an ultra-thin Al₂O₃ protection layer deposited by ALD can effectively avoid photocorrosion of Fe₂O₃. Thus, the performance of Fe₂O₃-AAO-PhCs is stabilized over multiple measurements. The fourth section presents another approach to enhance photocatalysis efficiencies by improving the separation of charge carriers within the photocatalyst. This can be realized, for example, by creating Fe₂O₃-based heterostructures of materials leading to electronic band gap alignment at the interface. Such semiconductor heterojunction at their interface affects the migration of photo-generated charge carriers. The photocatalytic performance of Fe₂O₃-based heterostructures with different ALD-grown metal oxides is assessed. Not only the influence of the type of the second material, but also their sequence (Fe_2O_3 at the top or at the bottom) is investigated to optimize the charge carrier transport within the heterostructures. For this study, the materials are deposited onto AAO structures consisting of straight pores as nanoporous templates to increase the

available surface area compared to planar substrates.

4.1. Post-anodization Modification of Anodic Aluminum Oxide to Generate Chemically Stable Templates (Publication II)

AAO structures are frequently used as templates for coating them with functional materials for application in sensing, energy storage, electronics, (photo)catalysis, and optics. [86, 87, 92, 94, 240] Due to the high surface area of AAO and the wide tunability of the nanostructure's geometrical dimensions, these templates are very attractive for studying material properties. In general, AAO samples consist of Al₂O₃ produced by electrochemical anodization of aluminum and feature hydroxy-groups (OH-groups) at the surface. [87] However, electrolyte ions from the acid utilized for the anodization get incorporated into the structure during the fabrication process. Oxygen vacancies in the AAO are also reported to origin from the fabrication. ^[96, 241–244] Hence, when AAO structures are applied as templates in photocatalysis, these defects could potentially cause overlapping with the properties of the functional materials in photocatalysis performance tests. Furthermore, the electrolyte species could take part in reactions occurring either during functionalization of AAO templates with a photocatalyst or during the photocatalysis measurements themselves because they are incorporated into the structure without necessarily being strongly bound. To identify and in the best case to avoid such uncontrollable, competing effects in the later characterization of semiconductor photocatalysts deposited onto AAO templates, we studied the influence of post-anodization modifications of AAO on their photocatalytic properties. In detail, two different treatments - namely immersion in hydrogen peroxide (H_2O_2) and phosphoric acid (H_3PO_4) – are compared to an asprepared template structure. These modifications are applied to AAO structures prior to functionalization with TiO₂ or Fe₂O₃ as photocatalysts by ALD. Note, two different photocatalysts are chosen for two reasons: First, to establish reference measurements for AAO structures coated with these materials, which is important for further investigation and possible performance optimization of these materials in later experiments. Second, TiO_2 is chosen as a chemically very stable material which is not expected to be significantly influenced by alterations of the substrate's surface chemistry and the repetition of photocatalytic activity measurement. ^[245] Contrary, Fe₂O₃ is known to be less stable and can easily react with various functional groups which could affect its photocatalytic properties. Photocatalytic dye degradation measurements of these post-anodization modified and ALD-functionalized AAO structures reveal stable performances over three consecutive measurements for TiO₂ coated samples independent of the surface treatment while the performance stability for Fe₂O₃ coated structures is determined by the surface modification (Figure 4.1.). Based on the high chemical stability of TiO_2 and the constant degradation rate revealed in consecutive measurements, ^[245] we conclude that the photocatalyst is not affected by the post-anodization modification. However, Fe₂O₃ as less stable photocatalyst is sensitive to the surface modification. AAO structures functionalized with Fe₂O₃ exhibit stable photocatalytic activities over three measurements only when the templates were immersed into H_2O_2 or H_3PO_4 prior to the the ALD coating.



Figure 4.1. Influence of post-anodization modifications on the photocatalytic activity of ALD functionalized AAO structures. (a) TiO₂-coated AAO structures exhibit stable photocatalytic activities over three measurements which corresponds to small standard deviations of the mean activity. (b) The photocatalytic performance of AAO samples functionalized with Fe₂O₃ as chemically less stable photocatalyst depends on the post-anodization treatment. The untreated AAO template, i.e., as-prepared structure, coated with Fe₂O₃ reveals an activity decrease over consecutive photocatalysis measurements while treatments in hydrogen peroxide or phosphoric acid result in stable performances. Figure adapted and modified from publication II.

Contrary, the as-prepared AAO structure functionalized with Fe_2O_3 shows decreasing photocatalytic activities with subsequent measurements. In addition, the prior H_3PO_4 treated Fe_2O_3 sample features a significantly higher activity than the one immersed in H_2O_2 being in contrast to the corresponding TiO₂-functionalized counterparts. The electrolyte ions incorporated into the AAO matrix might cause surface reactions during the photocatalytic measurements after activation by free charge carriers. Such process could alter the surface chemistry of the AAO and hence, also involve the deposited photocatalyst which could influence the photocatalytic performance. Since chemically stable templates are required for screening functional materials, we systematically studied the influence of different post-anodization treatments on the photocatalytic activity of AAO templates.

Specifically, as-prepared AAO structures were compared to AAO samples treated by thermal annealing, exposure to trimethylaluminum (TMA) pulses in an ALD reactor, immersion in H₂O, immersion in H₂O₂, and immersion in H₃PO₄. All of these treatments are typical cases in the processing of AAO templates in this thesis. Figure 4.2. demonstrates that the type of post-anodization treatment determines the stability of the samples' photocatalytic performance over multiple measurements. The photocatalytic activity of an as-prepared AAO samples decreases in consecutive measurements. This decline is probably caused by alterations of the surface chemistry over time which could originate from decomposition or removal of incorporated electrolyte residues. ^[177, 246, 247] AAO structures annealed and exposed to TMA also show significantly different activities in the three measurements. Also H₂O-treated samples still feature varying activities although exposure to aqueous media could potentially dissolve the electrolyte ions from the Al₂O₃ matrix. ^[248] Immersing AAO templates in aqueous solutions containing oxidizing agents stabilizes their performance which is probably caused by dissolution of the electrolyte



Figure 4.2. Photocatalytic performances of post-anodization modified AAO samples demonstrate a dependence of the photocatalytic performance stability on the previously applied treatment. Figure adapted and modified from publication II.

ions and further decomposition of them. In detail, immersion into H₂O reduces the activity decline in subsequent measurements but could not completely avoid it. However, AAO samples treated by H₂O₂ or H₃PO₄ exhibit stable performances. This stabilization could be caused by degradation of the electrolyte ions into stable compounds that do not affect the photocatalytic performance anymore. Since the observed differences in photocatalytic stability are presumably provoked by alterations of the surface chemistry of AAO templates due to the post-anodization treatments as similarly reported for TiO₂ based structures by Monteiro *et al.* and Trochowski *et al.*, ^[248,249] we conducted X-ray photoelectron spectroscopy (XPS) measurements to gain a deeper understanding how these treatments modify the surface chemistry.

As depicted in Figure 4.3., XPS measurements reveal significant changes of the surface chemistry for the different treatments. XPS spectra of the as-prepared AAO sample (Figure 4.3.(a)) reveal Al–OH groups and O–Al–O bonds at the Al_{2p} peak caused by the Al₂O₃ matrix and hydroxy-groups at the surface. The XPS spectra show also different carbon-oxygen as well as carbon-carbon and carbon-hydrogen bonds at the C_{1s} peak. The identified O-C=O, C-C, and C-H bonds origin probably from electrolyte ions – here oxalate – incorporated into the structure during anodization. The O_{1s} peak depicts subpeaks that can be attributed to HO-Al, O-C, Al-O-Al and O=C bonds at the surface. Thermal annealing results in the incomplete removal of -OH-groups and oxalate ions from the surface (Figure 4.3.(b)). Figure 4.3.(c) shows that exposing an AAO structure to TMA strongly reduces the Al-OH content due to the reaction of the TMA molecules with surface -OH-groups to Al₂O₃. Also oxalate ions present at the AAO surface might react with TMA to form aluminum oxalate complexes. The reaction of oxalate species with TMA molecules could cause the decline of the O-C=O peak intensity. However, electrolyte residues inside the alumina matrix cannot be reached by the TMA molecules and the corresponding carbon-containing bonds are still present in the XPS spectra. Fur-

ther, TMA molecules contain methyl groups as ligands which could also react with the surface resulting in carbon-containing bonds. Post-anodization treatments utilizing aqueous media could dissolve oxalate species from the AAO matrix.^[248] Immersion of an AAO sample into H₂O leads to reduced Al-OH, O-C=O, and C-O contents in the XPS data (Figure 4.3.(d)). Oxalic acid species might have been dissolved from the Al_2O_3 matrix and could have partially reacted with the surface forming Al-oxalate or could be physisorbed at the surface. Addition of an oxidizing species such as H₂O₂ to an aqueous solution can not only remove electrolyte residues from the AAO matrix but also further decompose them. It is reported in literature that the use of H₂O₂ leads to the complete oxidation of oxalate ions into carbon dioxide. ^[250] The XPS measurements (Figure 4.3.(e)) indicate a saturation of Al–OH groups and an increasing Al–O–Al group content which could originate from the formation of stable Al-oxalate complexes by the reaction of dissolved oxalate ions with Al–OH groups at the surface. Since H_2O_2 acts as an electron acceptor, it accelerates the Al-oxalate formation. Hence, the proposed Al-oxalate formation ensures template stability unaffected by the surrounding solution or reactions in the photocatalytic measurements. Immersing an AAO structure into H₃PO₄ is frequently reported to enlarge the pore diameter after anodization. $^{[96,241]}$ The etching of Al₂O₃ by H₃PO₄ also results in the removal of incorporated electrolyte ions from the matrix. These ions are then present in the etching solution and can potentially react with the aluminum ions released by the etching. Thus, aluminum-oxalate might form which could be explained by decreasing O-C=O, C-O, and C-C/C-H peak intensities (Figure 4.3.(f)) in combination with increasing contents of Al-O-Al and O=C groups as indicated by the peak at 531.6 eV. However, this energy also represents O=P, O-P, and AI-O-P groups and hence, the peak cannot definitely be correlated to one of these compounds. Further, it suggests the formation of Al-phosphate which is supported by the similar sub-peak ratio for the Al_{2p} peak and the additional P_{2p} peak. These phosphate compounds seem to contribute to the stabilization of the AAO photocatalytic activity.

Based on the XPS study, the photocatalysis performances of the AAO templates functionalized with a photocatalyst (Figure 4.1.) can be related to the stability of either the photocatalyst material or the AAO templates' surface chemistry as following: TiO₂ coating stabilizes the photocatalytic activity independent of the post-anodization treatment. The overall activity is improved with TiO_2 functionalization compared to the uncoated pendants and the activity ratio between the different treatments remains constant. For Fe₂O₃-functionalized AAO templates, the stability is determined by the post-anodization treatment due to the low chemical stability of Fe₂O₃. The as-prepared AAO structure featuring many unsaturated surface groups reveals a decrease in photocatalytic activity, which is probably caused by reactions of electrolyte ions with the Fe₂O₃ induced by photogenerated charge carriers. Such reactions could alter the Fe₂O₃ film and thus, result in an activity decline over consecutive measurements. In contrast, H₂O₂- and H₃PO₄-modified AAO structures as chemically stable templates lead to stable photocatalytic performances after functionalization with Fe₂O₃. Moreover, the photocatalytic activity of the H₃PO₄treated AAO structure is significantly enhanced for coating with Fe₂O₃ (mean activity $1.30 \pm 0.04 \text{ h}^{-1}$) compared to TiO₂ (mean activity $1.04 \pm 0.02 \text{ h}^{-1}$). We assume that this



Figure 4.3. XPS measurements demonstrate the influence of AAO post-anodization modifications on their surface chemistry. The AAO structures are (a) as-prepared, treated by (b) thermal annealing at 450 °C, (c) 15 TMA pulses, or immersed into (d) H₂O, (e) H₂O₂, and (f) H₃PO₄. Figure adapted from publication II. enhancement is caused by local formation of iron phosphate or iron hydroxy phosphate at the AAO/Fe₂O₃ interface by reactions between ferrocene as the ALD iron precursor and phosphate groups at the AAO surface. ^[251–253] Both of these phosphate-containing iron compounds are reported in literature to show good photocatalytic activities and thus, might cause the boost of the photocatalytic performance. ^[251–256]

To conclude, this study emphasizes the importance of chemically stable templates for investigating the properties of functional materials. While chemically stable materials such as TiO_2 are not significantly affected by the surface chemistry, less stable materials are sensitive to minor changes of the surface chemistry as demonstrated for Fe₂O₃. The XPS measurements reveal modifications of the surface chemistry of AAO structures induced by the post-anodization treatments. These results are not only interesting for our photocatalysis studies but could also be relevant to the application of AAO structures as templates in general.

4.2. Component Specific Enhancement: Aligning the Photonic Stop Band Edge with a Dye as Model Pollutant (Publication III)

Precise spectral alignment of a PhC's PSB edge is crucial to make use of the slow photon effect. For most reported AAO-PhCs the PSB edge was tailored to the absorption of a chemical that was degraded. ^[104, 116, 198, 199, 257] The AAO-PhCs in these reports were functionalized with TiO₂ by sol-gel methods and such configuration showed clear photocatalytic activity enhancement for the respective compound. In this section, the PSB red edge of a TiO₂-functionalized AAO-PhC was placed in the proximity to the absorption maximum of methylene blue (MB) as model pollutant being degraded. Modifications of the pore morphology by tuning the pulse duration and functionalization with TiO₂ by ALD (schematically shown in Figure 4.4.) strongly affect the photocatalytic performance. The pulse duration t_{pulse} of stepwise pulses determines the diameter modulation periodicity. The PSB central wavelength λ_{PSB} depends linearly on t_{pulse} with a rate of 0.41 ± 0.04 nm \cdot s⁻¹ in air. Hence, the PSB position of the AAO-PhCs can be tailored across the entire visible region of the electromagnetic spectrum. This PSB position adjustment is in good agreement with existing literature utilizing similar pulse-like anodization profiles. ^[102, 104, 199] Functionalization with TiO₂ by ALD alters the PSB position slightly as the effective refractive index of the composite material increases with increasing TiO₂ thickness. Furthermore, assessment of the PSB characteristics in an aqueous environment demonstrates red-shifting of λ_{PSB} with respect to structures characterized in air due to the higher refractive index of water. [115,258,259] Adjustment of the PSB edge to the desired wavelength in aqueous environment is necessary as the photocatalytic measurements conducted herein are also performed in an aqueous solution.

Photocatalytic performance tests of the ALD-functionalized AAO-PhCs reveal a strong dependence of the photocatalytic activity on the spectral position of the PSB red edge $\lambda_{PSB,red}$ in relation to the absorption spectrum of MB as expected for activity enhancement



Figure 4.4. Scheme of TiO₂-functionalized AAO-PhCs (left). The pore length L_{TP} and the TiO₂ thickness t_{TiO_2} are independently modified to study the influence of the PSB position and the photocatalyst thickness, respectively, as depicted for individual pores on the upper right and lower right. Figure freely adapted from publication III.

by the slow photon effect. In detail, the highest photocatalytic activity of 3.95 ± 0.68 h⁻¹ is observed for a sample anodized with $t_{pulse} = 1200$ s and a TiO₂ thickness of 0.5 nm. This sample features a $\lambda_{PSB,red}$ of 688 ± 17 nm, i.e., close to the red edge of the MB absorption profile. Comparison of the other AAO-PhCs coated with 0.5 nm TiO₂ demonstrates a decrease of the activity when the PSB red edge is no longer aligned with the MB absorption band. Moreover, a strong activity decrease is observed for structures with $\lambda_{PSB,red}$ overlapping with the MB absorption. Although this should theoretically be the ideal configuration to make use of the slow photon effect, we could show that light screening by the MB molecules prevents higher photocatalytic decomposition rates.

AAO-PhCs functionalized with TiO₂ thicknesses of 1 nm or 2 nm show the highest photocatalytic activity for samples fabricated with $t_{pulse} = 900$ s which correspond to a PSB red edge location at the blue edge of the MB absorption band. However, the maximum activity is lower than for the 0.5 nm TiO₂ sample. The reduced maximum activity is probably caused by the higher surface roughness of 0.5 nm ALD deposited TiO₂ compared to thicker films as extracted from AFM measurements. Although thicker TiO₂ films can generate more free charge carriers upon light excitation, the increased surface area of the 0.5 nm coating prevails. For both coating thicknesses (1 nm and 2 nm) a significant reduction of the activity is observed when $\lambda_{PSB,red}$ is positioned within the MB absorption. Similar to TiO₂-AAO-PhCs coated with 0.5 nm TiO₂, the activity recovers for samples with $\lambda_{PSB,red}$ at higher wavelengths. Crystallization of the TiO₂ thin films from



Figure 4.5. Photocatalytic MB degradation activities of TiO₂-AAO-PhCs are determined by the overlap of the PSB red edge (red data points) with the absorption spectrum of MB (blue graph). Additionally, the TiO₂ thickness of (a) 0.5 nm, (b) 1 nm, or (c) 2 nm influences the photocatalytic performance. Freely adapted from publication III.

the as-deposited amorphous phase to anatase further increases the photocatalytic activity of a sample produced with $t_{pulse} = 1200$ s and 2 nm TiO₂ thickness. This observation is in good agreement to many previous reports utilizing TiO₂ for photocatalytic applications and is attributed to a more efficient charge carrier transport towards the catalysts surface. ^[260]

In addition to tailoring the PSB position and TiO₂ thickness of TiO₂-AAO-PhCs, the degradation mechanism of the organic pollutant was studied by varying the H₂O₂ concentration, analyzing the dye absorbance spectra during the photocatalytic measurements, and characterizing the photocatalytic decomposition of 4-chlorophenol (4-CP) as another water pollutant. As shown in Figure 4.6.(a), the measured photocatalytic activity is reduced without H_2O_2 for the reaction. Light-induced free electrons at the TiO₂ surface react with H₂O₂ molecules to OH[•] radicals and OH⁻ ions. OH[•] radicals can induce the decomposition of organic molecules such as MB to CO₂ and H₂O. The generated OH⁻ ions can further react with holes in the VB of TiO₂ resulting in additional OH[•] radicals. However, MB degradation is reduced but still occurs when no H₂O₂ is added to the solution indicating that another dye decomposition pathway is also present at the same time. Spectroscopic ellipsometry measurements of ALD-deposited TiO₂ thin films revealed band gaps of 3.700 eV and 3.675 eV for 0.5 nm and 2 nm coating thickness, respectively. Since the UV content in the emission spectrum of the utilized light source is 0.1 %, the TiO₂ layers can directly be excited by incoming light only to a very small extent. Nevertheless, it was shown in a previous publication by Liu et al., that PSB red edges slightly higher than the band gap of TiO2 can lead to an increase of TiO2-AAO-PhCs.^[257] Dye sensitization of the TiO₂-functionalized AAO-PhCs is another process that can enhance the photocatalytic performance of the structures. In this case, the dye is primarily excited by the incoming light and generated electrons are then transferred to the semiconductor CB, where they can induce further reactions of molecules adsorbed at the surface. [199,261] Furthermore, we could show that N-demethylation of MB occurs during



Figure 4.6. Analysis of the photocatalytic dye degradation mechanism by utilizing TiO₂-AAO-PhCs. (a) The activity depends on the H₂O₂ concentration in the reaction solution. (b) The blue-shift of the MB absorbance maxima over reaction time indicate a degradation of MB by *N*-demethylation. (c) TiO₂-AAO-PhCs are also suitable for decomposing 4-CP as colorless organic compound. Figure freely adapted from publication III.

the photocatalytic decomposition studied herein (Figure 4.6.(b)). [262, 263] The photocatalytic decomposition of 4-CP by TiO₂-AAO-PhCs was studied to test the structures ability to degrade colorless organic compounds. The photocatalytic activity for 4-CP degradation is significantly lower $(0.24 \pm 0.02 \text{ h}^{-1})$ compared to MB decomposition by the same sample $(3.95 \pm 0.68 \text{ h}^{-1})$ which can be explained by three effects. First, 4-CP is known to be a very stable organic molecule which is much harder to decompose than MB.^[264] Second, TiO₂ surface is negatively charged under the conditions of the photocatalysis measurements applied herein. Since 4-CP molecules are also negatively charged, their adsorption at the TiO₂ surface is less likely than that of the positively charged MB molecules. Consequently, repeated interaction reduces dye adsorption at the surface. Third, the absorption maximum of 4-CP is located at 225 nm and hence, the AAO-PhCs PSB edge is not aligned to the absorption band of 4-CP.^[264] Accordingly, photocatalytic performance enhancement by the slow photon effect cannot occur. Despite these limitations, the investigated TiO₂-AAO-PhC structure is still able to photocatalytically decompose the 4-CP solution. This is supposed to occur via charge transfer from the TiO₂ to 4-CP molecules which formed complexes at the TiO₂ surface. ^[264]

Directly comparing the results of photocatalytic dye degradation to earlier publications is in general difficult because the measured photocatalytic activity depends on setupspecific parameters such as the light power and surface area of the photocatalyst. ^[169,265] Since similar samples to the ones prepared in this work have previously been studied in the same photocatalysis setup in the group of Prof. Abel Santos, the photocatalytic performances of these samples can be quantitatively compared. The herein prepared TiO₂-AAO-PhCs show the highest photocatalytic activity of $3.95 \pm 0.68 \text{ h}^{-1}$ for the optimized PSB position and TiO₂ thickness, i.e., 0.5 nm TiO₂. Thus, they outperform different types of sol-gel TiO₂ coated AAO-PhCs, namely distributed Bragg reflectors, ^[104,116] gradient index filters, ^[198] broadband distributed Bragg reflectors, ^[199] and microcavities ^[257] which feature performances between 1.12 h^{-1} and 3.55 h^{-1} . This high performance can be attributed to the precise TiO₂ thickness control and conformality of the ALD-grown TiO₂ thin films in contrast to the other AAO-PhCs functionalized with TiO₂ by sol-gel approaches.

To sum up, this work illustrates the importance of the PSB positioning in relation to the chemical to be decomposed when the slow photon effect should be utilized to improve photocatalytic performances. We could show that the TiO_2 thickness defines the activity which was maximum for the thinnest TiO_2 layers of 0.5 nm. The increased surface roughness of this TiO_2 thickness leads to additional surface sites for the photocatalytic reactions, which result in a photocatalytic performance enhancement. Moreover, this study shed light on the degradation mechanism of MB by TiO_2 -functionalized AAO-PhCs. Since the herein presented structures outperform previous TiO_2 -coated AAO-PhCs, the combination of tailor-made AAO-PhCs and ALD functionalization presents a promising approach towards custom-designed photocatalysts and light-harvesting platforms.

4.3. General Activity Increase: Matching a Photonic Stop Band Edge to the Semiconductor Photocatalyst (Publication IV)

Overlapping a PhC's PSB edge with the band gap of a semiconductor photocatalyst results in a general enhancement of the photocatalytic performance. The enhancement is based on higher interaction probabilities between incoming photons and the photocatalyst due to the slow photon effect. This effect occurs at the photocatalyts band gap energy in this configuration. Charge carrier generation in the photocatalyst by absorption of photons with energies equal to or larger than the band gap is essential for photocatalytic reactions. Since the slow photon effect contributes to a more effective charge carrier generation by photoexcitation, the photocatalytic activity increase is independent of the chemical to be degraded. Hence, it is generally improved for PhCs when a PSB edge is matched to the band gap of the photocatalyst. Such an improvement has been demonstrated several times for IOs built of different semiconductor photocatalysts, namely TiO₂, ^[78, 266–275] Fe_2O_3 , ^[200, 201] ZnO, ^[276, 277] $Fe_2O_3 - SiO_2$, ^[278] and graphitic carbon nitride (g-C₃N₄). Nevertheless, AAO-PhCs were mostly reported to be specifically tuned for alignment of a PSB edge with the absorption of the chemical that should photocatalytically be decomposed as also shown in our results presented in Section 4.2. [3, 104, 116, 198] In 2020, Liu et al. showed for the first time for AAO-PhCs that the photocatalytic performance can also be improved by positioning a PSB edge close to the band gap of TiO₂ as semiconductor photocatalyst.^[199] Despite the activity enhancement by the slow photon effect, TiO₂ is only capable of absorbing UV light which accounts for less than 10% of solar light.

In publication IV, AAO-PhCs were fabricated by pulse-like anodization in oxalic acid $(H_2C_2O_4)$ to prepare diameter-modulated 2.5D PhCs whose PSB position is tailored in such a way that the blue edge is aligned with the band gap of Fe₂O₃ at approximately 564 nm (Figure 4.7.). Fe₂O₃ as a semiconductor with a band gap in the visible light range



Figure 4.7. Schematic drawing of the Fe₂O₃-AAO-PhC fabrication. The AAO-PhC structures are produced by pulse-like anodization and are functionalized with Fe₂O₃ by ALD. Figure freely adapted from publication IV.

is used as exemplary photocatalyst in this study. ^[279] In addition to its visible light activity, Fe₂O₃ offers several advantages for photocatalytic applications such as non-toxicity and abundance on Earth. ^[279, 280] Nonetheless, utilization of Fe₂O₃ is often limited by inefficient charge carrier generation or fast recombination of charge carriers preventing the induction of photocatalytic reactions. ^[281–283] We could show that improving light-matter interactions, for example by the slow photon effect, boosts the photocatalytic performance of Fe₂O₃ as a photocatalyst. The photocatalytic activity increases for Fe₂O₃-AAO-PhCs when the PSB blue edge overlaps with the Fe₂O₃ band gap at around 564 nm.

AAO structures anodized with two different pulse durations t_{pulse} , i.e., 270 s and 275 s, were studied to account for changes of the PSB position. For AAO-PhCs with both investigated anodization pulse durations, the photocatalytic activity increases when the structures are functionalized with Fe₂O₃. However, not only the PSB position alignment but also the applied Fe₂O₃ ALD cycle number – corresponding to the film thickness – and the surface roughness determine the photocatyltic performance. The semiconductor film thickness is known to dictate the charge carrier dynamics in the material. ^[177, 279, 281] Limited charge carrier generation and fast charge carrier recombination are common challenges for Fe₂O₃.^[281–283] Besides the charge carrier dynamics, the film thickness also influences the mass transfer within the pores as increasing the Fe₂O₃ film thickness simultaneously reduces the pore diameter. Hence, diffusion of reactant into the pores and of degradation products out of the pores gets increasingly difficult with rising film thickness. Based on this diffusion limitation, the photocatalytic activity decreases after reaching a certain thickness. The surface roughness of ALD grown Fe₂O₃ thin films depends on the applied cycle number because the nucleation and growth follow the Volmer-Weber mechanism. ^[19,284,285] Here, individual islands of the deposited materials nucleate, which then coalesce into a continuous film. The island formation leads to an increase of the surface roughness for very thin coatings. A high surface roughness of 3.83 nm is herein observed for 77 ALD cycles, which continuously reduces to <1.55 nm after applying 308 Fe₂O₃ ALD cycles. Increased surface roughness correspond to larger surface areas which provide more active surface sites for photocatalytic reactions. Hence, the photocatalytic performance increases. The combination of the aforementioned effects, i.e., PSB alignment, charge carrier dynamics, diffusion limitation, and surface roughness, can explain the photocatalytic performance of the different Fe₂O₃-AAO-PhC samples studied herein.

In summary, AAO-PhCs anodized with pulse durations of 270 s and 275 s both exhibit the highest photocatalytic activity for functionalization with 385 Fe₂O₃ ALD cycles which corresponds to a film thickness of 5 nm. This thickness is optimal for charge carrier generation, separation, and diffusion of molecules within the pores of the AAO-PhCs studied herein.

Ultra-thin ALD-grown Al₂O₃ protection layers can prevent photocorrosion of Fe₂O₃functionalized AAO-PhCs. Photocorrosion denotes the destruction of a photocatalyst material during the reactions, which is accompanied by decreasing photocatalytic activities over consecutive measurements. ^[177, 246, 247] This phenomenon is a common issue for reproducible use of Fe₂O₃ as photocatalyst. ^[247, 286–288] Figure 4.8.(a) shows decreasing activities of 27% within three measurements for Fe₂O₃-AAO-PhCs functionalized with 231 and 308 cycles of Fe₂O₃. Moreover, a structural change of the material at the top surface is also observed in SEM images (Figure 4.8.b). Ultra-thin Al₂O₃ protection layers avoid such photocatalyst material decomposition as depicted in Figure 4.8.(c) and (d). Two ALD cycles significantly reduce the photocorrosion. However, the initial activity is decreased for Al₂O₃-protected Fe₂O₃-AAO-PhCs and this decrease gets stronger for higher ALD cycle numbers of Al₂O₃. Initial activity reduction with increasing Al₂O₃ ALD cycle numbers might be caused by suppression of photo-Fenton reactions by the ultrathin Al₂O₃ layers as less iron ions are exposed to the surrounding solution at the sample surface.^[289] Photo-Fenton reactions utilize iron ions and hydrogen peroxide molecules to generate hydroxal radicals under light illumination.^[289] These highly reactive hydroxyl radicals can degrade organic pollutants in water. Hence, photo-Fenton reactions resemble another pathway for MB degradation by the Fe₂O₃-AAO-PhCs, which can be prevented when the structures are over-coated with protection layers. Nevertheless, application of protection layers stabilizes the photocatalytic performance over consecutive measurements. Since the Fe₂O₃-AAO-PhC protected with 2 cycles Al₂O₃ exhibits the highest initial photocatalytic activity of the protected samples, its stability is further investigated. The photocatalytic activity of the unprotected structure declines by 44% within six measurements while the sample protected with 2 cycles Al_2O_3 shows only a slight activity loss of 4%. Hence, the latter outperforms the unprotected Fe₂O₃-AAO-PhC from the fourth measurements onward. Based on the significantly increased stability within six measurements, it is expected that ultra-thin Al_2O_3 protection layers will also be efficient to stabilize the photocatalytic performance over further measurements.

Tailoring a PSB edge to the semiconductor band gap increases the performance of Fe_2O_3 -AAO-PhCs for degrading three different organic dyes. In contrast, aligning a PSB edge specifically to one of the dyes – here MB – could only partially improve the photocatalytic properties (Figure 4.9.). AAO-PhCs of both PSB positions (at Fe_2O_3 and MB) were investigated with and without photocatalyst functionalization. Photocatalyst functionalization consists of 385 cycles Fe_2O_3 protected by 2 cycles Al_2O_3 . When a PSB edge is matched to the band gap of the semiconductor photocatalyst, a general enhancement occurs because the slow photon effect is solely based on the structure and materials of the Fe_2O_3 -AAO-PhCs. Thus, the photocatalytic activity for degrading all model dyes with Fe_2O_3 -coated AAO-PhCs can be improved by factors of 1.11 for MB, 1.49 for



Figure 4.8. Ultra-thin ALD-grown protection layers stabilize the photocatalytic performance of Fe₂O₃-AAO-PhCs by preventing photocorrosion. (a) Structures with different number of Fe₂O₃ ALD cycles show decreasing photocatalytic activities over three consecutive measurements which is caused by photocorrosion of the material. (b) Top-view SEM images depict structural changes of the Fe₂O₃-AAO-PhC top surface after photocatalysis measurements. (c) Application of ultra-thin Al₂O₃ protection layers significantly stabilize the photocatalytic performance for multiple experiments. (d) SEM images of the top surface confirm an intact surface after photocatalysis measurements for a sample protected with 2 ALD cycles Al₂O₃. Figure adapted from publication IV.



Figure 4.9. The photocatalytic activity of Fe₂O₃-AAO-PhCs is generally enhanced when the PSB edge is aligned to the band gap of Fe₂O₃ independent of the chemical to be degraded. (a) Fe₂O₃ coated AAO-PhCs show higher activities than their uncoated counterparts. Overlapping of the PSB with the Fe₂O₃ band gap increases the performance for all investigated dyes, while matching the PSB to the absorption of MB mainly increases the performance for MB degradation but not for the other two dyes. The maximum activities per dye are defined by the performance of the Fe₂O₃-AAO-PhC with a PSB edge aligned with the Fe₂O₃ band gap. (b) Absorbance spectra of the dyes depict the spectral overlap with the PSB edges of the different AAO-PhCs, i.e. PSB position at Fe₂O₃ band gap or MB and coated (c.) or uncoated (unc.) with the photocatalyst. Figure adapted from publication IV.

rhodamine B (RhB), and 1.35 for methyl orange (MO) compared to their uncoated counterparts. Note, the activities are normalized for each dye to the photocatalytic activity of the coated Fe_2O_3 -AAO-PhC with the PSB edge at the Fe_2O_3 band gap. Matching a PSB edge to MB results in an enhancement for degrading this chemical by a factor of 1.07, but no significant improvement is observed for the other dyes as expected. The latter configuration is specific for MB as model pollutant whereby enhancement by the slow photon effect is not expected for degradation of other chemicals. Note, the slight increase for MO decomposition is within the measurement uncertainty originating from the UV/Vis measurements of the dye concentration.

Improving the photocatalytic performance of Fe₂O₃ by the slow photon effect is in good agreement to literature reports that use a different type of PhC structure – namely IOs – composed of Fe₂O₃. ^[200, 201] Note, since the quantitative degradation rate depends strongly on the utilized setup and reaction conditions such as light source, light intensity, type of organic molecules, and scavenger concentration, the influence of the PSB edge alignment on the photocatalytic performance is only qualitatively compared. ^[3, 169, 265] The publications report about enhanced photo-(electro-)catalytic degradation of chemicals when one PSB edge is aligned with the band gap of Fe₂O₃. Zhu *et al.* observed further improvement for crack-free IO structures compared to samples featuring cracks. ^[200] The formation of cracks within the IO material is a common phenomenon in the production of these structures. ^[32, 290] Such cracks influence the photo-(electro-)catalytic properties due to changes in the charge carrier diffusion within the semiconductor material. Since AAO structures are used as PhC template in this study, cracks do not occur and therefore a homogeneous, Fe₂O₃-coated PhC structure is present in the entire

sample. Besides Fe₂O₃-based IOs, there are various publications on improved photocatalytic activities of photocatalytically active semiconductors by the slow photon effect in inverse opal structures. ^[28, 29, 78, 177, 200, 201, 266–278] The photocatalytic dye degradation results presented herein show similar trends as titania-functionalized broadband AAO-PhCs reported by Liu *et al.* in 2020. ^[199] The PSB edge of their TiO₂-based structures was in the range of the electronic band gap of TiO₂ and they observed the highest photocatalytic activities in their setup for degrading different organic dyes due to the slow photon effect.

In conclusion, we prepared tailor-made Fe₂O₃-AAO-PhCs and systematically studied their optical and photocatalytic properties in this work. By tuning the anodization pulse period and ALD cycle numbers, we optimized structures to match a PSB edge with the semiconductor band gap, leading to enhanced photocatalytic activity. Unlike previous studies that aligned the PSB edge to the absorption maxima of specific chemicals to be degraded, our work demonstrates general photocatalytic performance enhancement for different organic pollutants. The optimized thickness of the ALD-deposited Fe₂O₃ thin films results in maximum photocatalytic performance by balancing the effects of PSB edge positioning, charge carrier dynamics, and mass transport. Additional ultra-thin Al₂O₃ coatings effectively stabilize the photocatalytic performance and prevented Fe₂O₃ photocorrosion.

4.4. Semiconductor Heterostructures in Nanoporous Templates

AAO structures consisting of straight pores can be utilized to systematically study the effect of different materials and sequences of such heterostructures while simultaneously increasing the available surface area. Herein, the photocatalytic performance of Fe_2O_3 -based heterostructures was investigated by coating heterostructures on AAO templates *via* subsequent ALD processes (Figure 4.10.(a)).¹ Fe₂O₃ as visible-light-active photocatalyst was combined with the following materials: Al₂O₃ as insulator which is not expected to significantly affect the photocatalytic performance, SiO₂ as insulating material which is reported to potentially increase photocatalyst. Each of the individual layers was 3 nm in thickness and both possible material deposition sequences, i.e., Fe₂O₃ as first or second layer, were studied. For detailed information about the sample fabrication, please refer to the Bachelor's thesis of Ana Katharina Steffens (Universität Hamburg, 2023). ^[292] Photocatalytic characterization was conducted by monitoring the degradation of MB as model pollutant of water.

Not only the type of the second material but also the sequence in which both layers are deposited by ALD determines the photocatalytic properties of the samples. The structures presented herein consist of AAO templates with 31 ± 14 nm pore diameter, approximately 35 µm pore length, and are functionalized with the different bilayers by

¹The fabrication and characterization of the AAO templates functionalized with heterostructures was mostly conducted by Ana Katharina Steffens as part of her Bachelor's thesis entitled *Semiconductor Heterostructures to Tune Tailor-made Nanoporous Photocatalysts* (2023).



Figure 4.10. Semiconductor heterostructures can tune the photocatalytic activities by modifying the charge carrier separation. (a) Straight AAO templates are functionalized by ALD with one semiconductor deposited first (SC1) and a second semiconductor (SC2) which is deposited afterwards. (b-c) Fe₂O₃ as visible light active photocatalyst is combined with other materials to investigate the effect of the heterostructures on the photocatalytic performance by utilizing Fe₂O₃ either as first (b) or as second layer (c).

ALD. As shown in Figure 4.10.(b), heterostructures consisting of Fe₂O₃ deposited as first (i.e., inner) layer in combination with Al₂O₃ or TiO₂ as second (i.e., outer) layer feature similar photocatalytic activities of 1.02 ± 0.01 h⁻¹ and 0.93 ± 0.02 h⁻¹ in the first measurement, respectively. Based on its wide band gap, ^[293,294] Al₂O₃ is not expected to significantly improve the photocatalytic performance of Fe₂O₃ because it should not affect charge carrier separation. However, formation of local defects at the interface between the two layers could result in trapping of charge carriers. Such trapping could improve the charge carrier separation and thus, increase the photocatalytic activity. Although TiO₂ is a well-known photocatalyst, the coating as second layer onto Fe_2O_3 does not enhance the photocatalytic activity. Since literature suggest that ALD-grown Fe₂O₃- TiO_2 heterostructures form a type II heterojunction, the configuration with the TiO_2 film as top layer might not be optimal for efficient degradation of MB as model pollutant of water.^[295] In this case, electrons migrate towards the TiO₂ layer and holes move to the Fe₂O₃ layer. Overcoating Fe₂O₃ with SiO₂ results in a slight enhancement of the activity (average $1.26 \pm 0.17 \text{ h}^{-1}$). As recently reported by Zhai *et al.*, the formation of Fe-O-Si bonds could explain this behavior. ^[291]

Inversion of the bilayer sequence results in a strong increase of the initial activity for all samples (Figure 4.10.(c)) due to more efficient transfer of photo-generated charge carriers that induce degradation reactions at the structures surface. Additionally, the presence of Fe₂O₃ as top layer for all samples provokes photo-Fenton reactions which contribute to the dye degradation by producing radical species. ^[289]. Further, the photocatalytic activity of all samples decreases during consecutive measurements due to Fe₂O₃ photocorrosion. Depositing Al₂O₃ as first layer simply reduces the pore diameter without affecting the photocatalytic performance. Therefore, the sample composed of 3 nm Al₂O and 3 nm Fe₂O₃ can serve as a reference for the other two bilayer samples with the same Fe₂O₃ thickness as top layer. Utilization of SiO₂ or TiO₂ as first layer significantly enhances the photocatalytic performance to 2.73 ± 0.09 h⁻¹ and 2.78 ± 0.05 h⁻¹, respectively, compared to the Al₂O₃ reference and more pronounced to their inverted counterparts. For

TiO₂ as first layer, the changed direction of the heterojunction could contribute to the enhanced performance. The holes directed to the Fe_2O_3 layer could be more efficient for MB degradation than the electrons which migrate towards the TiO₂ layer. Nevertheless, all heterostructures show a performance decline with increasing measurement number which is probably caused by photocorrosion of Fe_2O_3 at the surface of the structure. For future use of such heterostructures with Fe_2O_3 as second (top) layer, ultra-thin coatings as used in the previous section and publication IV, can be utilized to avoid photocorrosion. The Fe_2O_3 -based heterostructures deposited onto AAO templates in this chapter indicate the potential of semiconductor heterostructures for improving photocatalytic performances by optimizing the charge carrier transport. Moreover, these results emphasize the importance of the heterojunctions direction, i.e., layer sequence, to make efficient use of the separated charge carriers.

3D Photonic Structures: Inverse Opals

In this section, the results of publication V are presented. Inverse opals composed of TiO_2 -Fe₂O₃ as semiconductor heterostructures are fabricated to combine semiconductor heterostructures with a performance enhancement by the slow photon effect. Not only TiO_2 -Fe₂O₃ bilayer IOs, but also TiO_2 -Fe₂O₃-TiO₂ multilayer IOs are investigated. The latter ones show decreased photocatalytic performances due to a non-optimal heterojunction configuration, but give rise to photo-induced crystallization of the TiO_2 layers from the amorphous as-deposited phase to anatase.

Combining Photonic Crystals with Semiconductor Heterostructures (Publication V)

Fabricating PhCs tailored to semiconductor heterostructures can further enhance photocatalytic efficiencies by combining the advantages of both approaches. First, customized PhC structures whose PSB edges overlap with the band gap of a semiconductor enhance the charge carrier generation by utilizing the slow photon effect. Second, the heterostructures drive the charge separation. IOs made of TiO₂-Fe₂O₃ multilayers are herein used as 3D PhCs and reveal a strong dependence on the individual layer thicknesses and on the multilayer sequence.¹ The sample synthesis is schematically depicted in Figure 5.1. Briefly, pure TiO₂ IOs are initially produced by self-assembly of PS spheres into direct opal structures, infiltration of these templates with TiO₂ by ALD, and removal of the PS spheres by burn-out resulting in TiO₂ IOs. Afterwards, these IOs are functionalized with Fe₂O₃ by ALD to produce TiO₂-Fe₂O₃ bilayer IOs. Moreover, TiO₂-Fe₂O₃-TiO₂ multilayer structures are also fabricated by depositing another TiO₂ layer onto the bilayer IOs. For each type, two different IOs with varying sphere sizes, namely 150 nm and 252 nm, are produced to create different PSB positions close to TiO₂ and Fe₂O₃ band gaps.

The photocatalytic performance of pure TiO₂ IOs and TiO₂-Fe₂O₃ bilayer IOs is determined by the size of the PS spheres used as template for the ALD coating (Figure 5.3.(a)). The PS sphere diameter defines the spacing of the IO structure and consequently the PSB position which is crucial to make use of the slow photon effect. In detail, pure TiO₂ IOs show a higher average activity of $0.98 \pm 0.01 \text{ h}^{-1}$ for 150 nm template size than for 252 nm template ($0.86 \pm 0.02 \text{ h}^{-1}$) because the PSB edge of the smaller diameter is aligned to the TiO₂ band gap at around 376 nm. ^[234, 296] In contrast, TiO₂-Fe₂O₃ bilayer IOs with 252 nm template size and 10 ALD pulses Fe₂O₃ coating feature a higher activity ($1.06 \pm 0.09 \text{ h}^{-1}$) than their smaller template counterparts ($0.82 \pm 0.04 \text{ h}^{-1}$) since the PSB edge of the 252 nm template IO is matched to the Fe₂O₃ band gap at around

¹Sample fabrication and characterization were mainly performed by Nithin Thonakkara James from the TUHH as part of his Master's thesis entitled *Hybrid TiO*₂-*Fe*₂*O*₃ *Photonic Structures for Photocatalysis* (2024) in a collaborative project with the group of Prof. Kaline Furlan.



Figure 5.1. (a) Schematic of the inverse opal (IO) fabrication. The schemes represent (i) self-assembly of PS spheres as template, (ii) an assembled template, and (iii) an inverse opal after TiO₂ ALD coating and burn-out of the template. In (iii) the hollow inside of the IOs and the gaps which connect neighboring pores are visible. (b) Cross-section of the hollow sphere shells produced by ALD. A TiO₂ IO (i-ii) is modified with further ALD deposition to fabricate (iii) TiO₂-Fe₂O₃ bilayer IOs and (iv) TiO₂-Fe₂O₃-TiO₂ multilayer IOs. Figure adapted from publication V.

564 nm.^[282,283] Moreover, the TiO₂-Fe₂O₃ bilayer structure facilitates charge carrier separation by the formation of a type II heterojunction as illustrated in Figure 5.3.(b) and mentioned in the previous chapter.^[295] Specifically, recombination is reduced because photo-generated electrons are guided to the TiO₂ layer while the holes migrate towards the Fe₂O₃ layers. For IOs composed of 16 nm TiO₂, an increase of the Fe₂O₃ thickness from only 10 ALD pulses to 2 nm increases the photocatalytic performance of these structures from 1.06 ± 0.09 h⁻¹ to 1.38 ± 0.09 h⁻¹ due to the elevated light absorption by the thicker Fe₂O₃ coating. ^[4, 281] However, further Fe₂O₃ thickness increase to 4 nm corresponds to a decline of the activity. Such a behavior could be caused by higher recombination rates due to the rise in thickness. ^[281] More important, the activity decrease is probably primarily induced by closing of the tetrahedral gaps of the IO structure when the Fe₂O₃ thickness is increased. Tetrahedral gaps and the bigger octahedral gaps are air pockets in between individual assembled spheres as depicted in Figure 5.2. These air pockets appear in closed-packed structures such as IOs. Assuming a maximum coating thickness of 7.7% of the PS sphere diameter results in a closure of the tetrahedral gaps at 19.4 nm for the bigger template size. ^[136] A higher thickness can only be obtained by mass transport through the larger octahedral gaps or at the outer surface of the IOs. Hence, diffusion of molecules within the structure becomes more difficult and thus, the photocatalytic performance decreases. In addition, TiO₂-Fe₂O₃ bilayer IOs consisting of 20 nm TiO₂ and 2 nm Fe₂O₃ on each side exhibit a slightly decreases photocatalytic activity compared the 16 nm TiO₂-4 nm Fe₂O₃ structures. The outer coating thicknesses



Figure 5.2. Description of the structural characteristics of IOs. The left SEM image shows the FCC (111) plane and three neighboring shells are cut in half to be able to see inside them. The air pockets in between the spheres form during closed-packing of the spheres and they are tetrahedral or octahedral gaps as depicted on the right. Adapted with permission. ^[32] Copyright 2018, *Elsevier*.

of both IOs, i.e., 22 nm for the previous one and 20 nm for the latter one, correspond to closed tetrahedral gaps between neighboring pores for 252 nm template structures which underlines the influence of limited diffusion. Note, this thickness is calculated by starting from the surface of the template spheres. Only the TiO_2 layer is deposited onto the direct opals in the first ALD process and is followed by burn-out. Only the outer Fe_2O_3 layer deposited onto the TiO_2 IOs increases the effective thickness, which is relevant for the tetrahedral gap size reduction. The inner Fe_2O_3 layer that grows in the same ALD process based on the self-limiting gas-solid surface reactions reduces the macropore size, because it is deposited at the interior side of the TiO_2 shells. Thus, the total ALD deposited layer thicknesses sum up to 24 nm for both structures, only the shell thickness added to the PS template size (i.e., 22 nm and 20 nm) affects the available size of the interstitial sites.

The observed Fe₂O₃ thickness optimum to obtain the maximum photocatalytic performance of TiO₂-Fe₂O₃ bilayer IOs agrees well to previous reports, which utilized Fe₂O₃ nanocluster-decorated TiO₂ IOs and ALD Fe₂O₃-functionalized TiO₂ powder for dye degradation.^[275,295] Cao et al. reported an optimum Fe₂O₃ thickness of about 2.6 nm for an ALD-grown layer and Pylarinou et al. also measured the maximum performance increase for low Fe₂O₃ loadings of their FeO_x modified TiO₂ IOs. Furthermore, Liu could show that decorating TiO₂ IOs with Fe₂O₃ nanoparticles by hydrotheret al. mal method increases the performance by up to 50%.^[78] Further publications about Fe₂O₃-functionalized TiO₂ nanostructures also reported improved photocatalytic activities compared to the pure TiO₂ counterparts of the structures based on the increased light absorption. [297-299] However, most of the discussed reports either used non-PhC structures or tailored the PSB of the utilized IOs only to the TiO₂ band gap. Thus, these studies did not investigate the effect of aligning a PhC's PSB edge to Fe₂O₃ as semiconductor photocatalyst. In this work, we could show that not only functionalizing TiO₂ IOs with Fe₂O₃ increases the photocatalytic activity of TiO₂-Fe₂O₃ bilayer IOs, but overlap-



Figure 5.3. Photocatalytic performance of bilayer IOs. (a) The template size, TiO₂ thickness, and Fe₂O₃ thickness determine the PSB position and charge carrier transport. The photocatalytic activity increases by making use of the slow photon effect, when a PSB edge overlaps with the band gap of a semiconductor, i.e., 150 nm template for TiO₂ and 252 nm template for Fe₂O₃. (b) Schematic drawing of a type II heterojunction formed between TiO₂ and Fe₂O₃ that facilitates charge separation. Figure adapted from publication V.

ping the PSB edge with the band gap of Fe_2O_3 can further boost the performance based on the slow photon effect in the Fe_2O_3 layer.

Fabrication of TiO₂-Fe₂O₃-TiO₂ multilayer IOs, i.e., TiO₂-Fe₂O₃ bilayer IOs overcoated with an additional TiO₂ layer by ALD, leads to photo-induced crystallization of the inner TiO₂ layers. Our XRD analysis is only sensitive to the inner TiO₂ layer because the outer layers are below the detection limit of the device of a few nanometers. This crystallization is accompanied by progressive changes of the photocatalytic performance over consecutive measurements. Although the initial photocatalytic activity is strongly reduced compared to the bilayer samples, it increases within the first four measurements, then slightly decreases, and stabilizes for all studied multilayer structures (Figure 5.4.(a) and (b)). Note, the multilayer structure is not optimal for the charge transport inside the material because holes get trapped in the Fe₂O₃ layers as schematically depicted in Figure 5.4.(c). Consequently, they are not available to induce photocatalytic reactions at the photocatalyst/electrolyte interface. Hence, the mean activity over three measurements is decreased. In detail, 150 nm template size IOs exhibit activities of 0.83 ± 0.12 h⁻¹ and $1.00\pm0.14~h^{-1}$ for coating thickness of 16 nm TiO_2–2 nm Fe_2O_3–2 nm TiO_2 and 16 nm TiO₂-4 nm Fe₂O₃-2 nm TiO₂. IOs with 252 nm template size result in mean activities of 0.93 ± 0.20 h⁻¹ (16 nm TiO₂-2 nm Fe₂O₃-2 nm TiO₂ and 0.81 ± 0.21 h⁻¹ (16 nm TiO₂-4 nm Fe₂O₃-2 nm TiO₂). Moreover, photo-Fenton reactions cannot contribute to the dye degradation since the Fe₂O₃ layers are no longer present at the surface. Nevertheless, the incorporation of Fe₂O₃ within TiO₂ by the multilayer design facilitates photo-induced crystallization of TiO₂ from amorphous phase into anatase during the photocatalytic reaction. Crystallization of the inner TiO₂ layer after three photocatalysis measurements is confirmed by XRD as depicted in Figure 5.4.(d). The outer TiO_2 layer is too thin to detect crystallographic phases with the XRD device. Since anatase often exhibits a higher photocatalytic activity than amorphous TiO₂, the crystallization results in an ac-
tivity increase within the first four photocatalysis measurements.^[234] The Fe₂O₃ layers provoke this crystallization based on the formation of oxygen vacancies when Fe ions are present within the TiO₂ lattice. ^[300, 301] Such configuration is, for example, obtained at the material interfaces and these defects act as nucleation spots for the crystallization. In addition, the semiconductor heterojunction of TiO₂-Fe₂O₃-TiO₂ multilayers can also enhance the crystallization due to additional material interfaces and localization of charge carries in specific regions of the material. Since oxygen vacancies cannot only provoke crystallization but are also known to raise the photocatalytic activity of TiO₂, their concentration is crucial for the photocatalytic performance of the structures.^[300–304] While the oxygen vacancy amount increases during the initial stage of crystallization, it is reduced in the latter part, and decreases to zero after complete crystallization. Accordingly, the photocatalytic activity of the TiO₂-Fe₂O₃-TiO₂ multilayer IOs first increases due to the anatase formation and increased oxygen vacancy content. Subsequently less vacancies are present resulting in a slight decrease of the photocatalytic activity. Finally, the activity is stable because neither the oxygen vacancy content nor the crystalline phase undergo significant changes anymore. Hence, the anatase phase of the TiO₂ layer dominates the photocatalytic performance of the TiO₂-Fe₂O₃-TiO₂ multilayer IOs. Note, the XRD pattern cannot resolve the phase of the outer TiO₂ layer, which contributes to the dye degradation because the reactions occur at the surface. Although the inner TiO_2 layer is not directly in contact with the dye solution, it could contribute to the degradation by improving the charge carrier generation and transport. Possible photo-induced formation of pseudobrookite (Fe₂TiO₅) as visible-light active photocatalystat the multilayers' surface could also improve the photocatalytic activity. ^[305–309] Note, Fe₂TiO₅ was not observed in the XRD patterns, but the low thicknesses of the Fe₂O₃ layer and the outer TiO₂ layer are below the detection limit of the utilized XRD device. Fe₂TiO₅ formation after thermal annealing of iron oxide structures modified with TiO₂ thin films by ALD was previously hypothesized to improve the photocatalytic performance of such structures.^[298,310,311] This enhancement is based on increased charge carrier generation and improved charge carrier separation by the formation of type II heterojunctions at the interfaces to TiO₂ and Fe₂O₃. Some of the aforementioned publications could detect Fe₂TiO₅ with XPS measurements while others could not clearly confirm a pseudobrookite formation because laboratory XRD devices were used which cannot detect crystallization of thin layers similar to our results. ^[298, 310, 311]

The occurrence of photo-induced crystallization in TiO_2 -Fe₂O₃ multilayer films underlines the sensitivity of photocatalytic properties and structural stability of the semiconductor heterostructure to the type and arrangement. Although the heterojunction formed herein for multilayer IOs is not optimal for efficient photocatalysis, it provokes photo-induced crystallization of the TiO_2 layer. Such photo-induced crystallization has not yet been published for TiO_2 -Fe₂O₃ multilayers in literature. In combination with ALD as fabrication technique, photo-induced crystallization could allow for synthesizing crystalline materials at template structures which cannot withstand annealing treatments that are commonly applied to modify crystallographic phases.



Figure 5.4. Photocatalytic performance and photo-induced crystallization of bilayer IOs. (a) The mean photocatalytic activity is determined by the individual layer thicknesses of TiO_2 -Fe₂O₃-TiO₂ multilayer IOs and template size but features high standard deviations for all samples. (b) The individual activities for seven consecutive measurements reveal an increase in the first four measurements, a slight decrease in the following two measurements, and a stable performance afterwards. (c) Proposed band alignment in the semiconductor heterostructure. Electrons migrate towards the TiO₂ layers and the surface while holes are trapped in the Fe₂O₃ layers. (d) XRD patterns demonstrate anatase TiO₂ after the photocatalysis measurements. Higher peak intensities are observed for multilayer IOs which is caused by photo-induced crystallization of the layer. Figure adapted from publication V.

Summary and Future Perspective

The tailor-made production of ALD-prepared structures of different dimensionalities for photonic applications was demonstrated in this thesis. While nanolaminates were prepared as 1D photonic structures, self-organized AAO structures and self-assembled PS particle direct opals were utilized as templates to generate 2D, 2.5D, and 3D photonic structures as summarized in Figure 6.1. Precise control of the deposited film thickness – as inherently established in an ALD process – was crucial for determining the PhCs' photocatalytic properties by balancing opposing effects such as light absorption, charge carrier migration, diffusion of molecules in the porous structure, and structural characteristics. Multilayering, delta-doping of thin films, and semiconductor heterostructure formation were realized by supercycle ALD processes that allow for combining two materials within the same deposition process. These approaches enabled further customization of the materials' properties for the desired application.



Figure 6.1. Summarizing figure of the ALD-based PhC fabrication and characterization. With increasing dimensionality from 1D to 3D the sample design, the fabrication procedure (blue font), and the characterization (grey font) got more complex.

The key findings of the different manuscripts are summarized below in the order in which they are numbered:

- I As part of this work, material combinations were applied to tailor the properties of ALD-grown materials. Specifically, SiO₂-incorporated TiO₂ thin films were fabricated by supercycle ALD processes to tailor their crystallization behavior, structural stability, and refractive index depending on the material composition. In detail, the TiO₂ film thickness as well as number of interfaces in multilayers and SiO₂ doping concentration determined the crystallization temperature and could result in stabilization of the structural features during thermal annealing.
- **II** The importance of the template's surface chemistry for reliable characterization of functional materials was emphasized by the results of photocatalysis measurements after various post-anodization modifications. Specifically, the influence of the different modifications on the photocatalytic properties of AAO structures with and without photocatalyst functionalization by ALD was assessed. While a chemically stable ALD-deposited photocatalyst exhibits stable photocatalytic activities independent of the template surface chemistry, the properties of a less stable ALD-grown photocatalyst are altered by the underlying template. The study presented herein evaluated the photocatalytic properties of modified AAO templates but we expect that the results can also be transferred to further applications utilizing AAO templates for the preparation of functional materials, such as sensors and energy storage.
- III Tailoring the PSB position of AAO-PhCs in combination with ALD of photocatalysts to make use of the slow photon effect significantly improved the photocatalytic activity of such templates functionalized with ALD-grown TiO₂ as photocatalyst. A PSB edge was aligned to the absorption of MB as chemical to be degraded resulting in an efficient enhancement when the PSB edge was close to but not directly overlapping with the dye's absorption maximum. ALD allowed for very precise TiO₂ thickness control rendering only 0.5 nm TiO₂ most efficient for degrading the organic model pollutants.
- IV While the previous approach only works for photocatalytic decomposition of the specific chemical to which the PSB position is aligned, the matching the PSB position of Fe₂O₃-AAO-PhCs to the band gap of Fe₂O₃ as photocatalyst presents a general photocatalytic performance enhancement. Fe₂O₃-AAO-PhCs can be used to decompose a variety of substances with the same PhC structure as the performance improvement is solely based on the photocatalyst-AAO-PhC structure itself. Variation of the Fe₂O₃ thickness deposited on AAO-PhCs by adapting the ALD parameters revealed the influence of different processes involved in photocatalytic degradation reactions. It was found that a 5 nm Fe₂O₃ thin film is optimal for balancing light absorption, charge carrier migration, and diffusion of molecules within the porous structure. Ultra-thin Al₂O₃ protection layers were successfully deposited

with ALD to prevent photocorrosion of Fe_2O_3 and could therefore stabilize the performance over multiple measurements.

V Besides nanostructuring of photocatalysts and utilization of the slow photon effect, modifying the photocatalyst thin films' properties presents another technique to improve the photocatalytic performance. Formation of semiconductor heterostructures was shown to effectively enhance the performance of ALD-grown photocatalysts both deposited on straight AAO pores and fabricated as inverse opals. TiO₂- Fe_2O_3 bilayer IOs exhibited the highest activity when a 2 nm Fe_2O_3 coating was applied and the PSB red edge of the IO was matched to the band gap of Fe_2O_3 . This optimized Fe₂O₃ thickness was lower than reported for the Fe₂O₃-AAO-PhCs because different PhC structures were applied that influence the charge carrier migration and diffusion of molecules in the porous structures. Here, the slow photon effect was combined with an improved charge carrier separation based on the type II heterojunction of TiO_2 and Fe_2O_3 enabled by the highly conformal material deposition onto the template structures with ALD. Furthermore, the non-optimal heterojunction configuration in TiO₂-Fe₂O₃-TiO₂ multilayer IOs provoked photoinduced crystallization of the TiO_2 layer to anatase. The anatase formation causes a successive increase of the photocatalytic activity until a stable level is obtained based on the superior performance of anatase compared to amorphous TiO₂.

To sum up, the fabrication of PhCs with ALD-derived methods allows for widely tuning the materials properties to fit the desired application. Due to the very precise film thickness control and the exceptionally high film conformality of ALD processes, this technique is ideally suited to functionalize 3D and complex-shaped porous substrates such as AAO-PhCs or IOs and to simultaneously alter material compositions within the same synthesis procedure. This flexibility facilitates the preparation of tailor-made structures by supercycle ALD with accurate optimization of the films' properties for photonic applications. Furthermore, the approach could be easily expanded to other functional materials, for example magnetic materials or phase-change materials, based on the variety of available ALD processes.^[19,20] Possible future strategies and preliminary results to further improve and investigate the performance of ALD-derived photonic structures in photocatalytic applications are outlined in the following part.

Characterization of charge carrier transport and phase transformation mechanisms Scavenger molecules for different charge carriers and radicals could be applied to further investigate the charge transport across semiconductor heterostructures. ^[297, 312–314] As recently reported by Trenczek-Zajac *et al.*, different types of scavengers are an effective tool to identify charge carriers involved in the photocatalytic degradation of organic dyes. ^[297] For example, we studied the effect of different isopropyl alcohol (C₃H₈O, IPA) concentrations on the photocatalytic activity of a straight pore AAO sample coated with 3 nm Fe₂O₃ and 3 nm SiO₂ (Figure 6.2.(a)). IPA can trap holes from the photocatalyst and thus, prevents the induction of dye degradation by these holes. ^[315, 316] We observed an activity decline with increasing IPA concentration which indicates that holes contribute to the dye



Figure 6.2. Scavenger dependent activities of a heterostructure consisting of 3 nm Fe₂O₃ and 3 nm SiO₂ deposited on a straight pore AAO template. (a) The photocatalytic activity of the structure decreases until saturation with increasing IPA concentration. This decline indicates that holes in the photocatalyst contribute to the dye degradation. (b) Also the H₂O₂ concentration affects the observed photocatalytic performance but the influence cannot be unambiguously identified. H₂O₂ molecules can scavenge electrons but they can also take part in other steps and possible pathways of the MB degradation and hence, further studies are required to study the charge carrier migration in the heterostructure and the influence of electrons in the dye degradation.

degradation. However, the photocatalytic activity saturates for concentrations higher than 100 mM suggesting that other species can also induce degradation reactions. For example, different H₂O₂ concentrations were tested because a linear dependence of the measured photocatalytic rate with the concentration is reported in literature for TiO₂-AAO structures. ^[104] Specifically, the concentration of H_2O_2 which is added to the solution is crucial as H₂O₂ contributes to the dye degradation as electron scavenger and in photo-Fenton reactions. ^[3,281,297] Our results showed concentration-dependent activities, but the trend is not consistent for the bilayer sample (Figure 6.2.(b)). H₂O₂ acts as electron scavenger meaning that a concentration increase leads to lower activity when electrons induce the degradation of dye molecules. Specifically, trapped electrons are no longer available at the photocatalysts' surface to induce decomposition reaction. Nevertheless, transfer of electrons to H₂O₂ can also result in the generation of radicals by dissociation of the H₂O₂ molecule. ^[3, 104, 297] Such radicals can the take part in the dye degradation based on their oxidizing character. Since the radicals can induce the dye decomposition, a higher H₂O₂ concentration should result in a faster degradation which is herein characterized by a higher photocatalytic activity k. Moreover, the dissociation of H_2O_2 and thereby the radical generation can also be provoked by illumination. Based on the two competing effects for the influence of the H₂O₂ concentration on the photocatalytic activity, no accurate conclusion regarding the importance of electrons for the degradation reaction in the bilayer heterostructure can be made. Further experiments utilizing more specific electron scavenger such as silver nitrate would be needed to study the charge transfer in the heterostructure in more detail.^[297]

Photoelectrochemical characterization methods could be applied to further investigate the effects of charge carrier transport in PhC photocatalysts and semiconductor heterostructures. Techniques such as photocurrent measurements, impedance spectroscopy, and Mott-Schottky analyses provide information about the material's efficiency in converting light into charge carriers, the charge carrier dynamics, the reaction kinetics, and the electronic properties. Such characterization tools can aid to explain the processes occurring in photocatalysts.^[317–320] For instance, a collaboration of our group with the group of Prof. Dorota Koziej (CHyN, Universität Hamburg) proved that the film thickness of an ALD-grown TiO₂ over-layer on top of copper bismuth oxide (CuBi₂O₄, CBO) determines the structures' PEC properties (publication VII).^[7] In detail, a TiO₂ layer with 15 nm thickness increases the stability of the CBO and simultaneously allows for efficient charge transfer to the electrolyte. Further increase of the TiO₂ thickness to 20 nm results in a significant photocurrent decline by 74 % due to a band mismatch at the TiO₂-CBO interface which promotes charge accumulation and recombination. Hence, accurate engineering of the band alignment of thin films by adapting the ALD-deposited film thickness enables the optimization of PEC devices. To establish a good electrical contact at the back of the photocatalyst, the composition of both AAO-PhC- and IO-based structures must be adapted. For straight AAO templates, this was realized in the past by opening the pore bottoms and applying metal contacts by sputtering and/or electrodeposition. ^[122, 123, 130, 132, 321] In contrast, IOs could for example be prepared on conductive substrates such as indium tin oxide, but the contact area between the IO material and the conductive substrate remains small. To improve the electrical contacts, a conductive opal material, e.g., aluminum-doped zinc oxide, could be deposited as first layer onto the templates by supercycle ALD. This layer can then be used as back contact for electrochemical characterization and it would allow for the same fabrication route as previously utilized for the ALD-derived PhCs. Moreover, such conductive layer could also be beneficial for photocatalysis measurements because it assists the transport of charge carriers.

To apply the PhC photocatalysts investigated in this thesis for real-world processes, the structures' ability to degrade multiple components at the same time should be investigated. Simultaneously decomposing multiple species could, for example, be realized by utilizing a multicomponent mixture which contains different dyes as model pollutants. Moreover, the decomposition of colorless organic compounds, for instance 4-CP, should be studied, as such compounds do not absorb visible light which may affect the photocatalytic degradation mechanism. ^[264, 322] For real-world cleaning of contaminated water, the structures could be applied for filtration combined with *in situ* photocleaning. In such process, the contaminated water passes through a porous filtration system which consist of the PhC structure. ^[323] For AAO-PhCs, the aluminum backside and the Al₂O₃ barrier oxide layer have to be removed to obtain a free-standing flow-through membrane. During filtration, smaller organic contaminants could directly be removed by photocatalytic degradation at the photocatalyst-coated PhC structure. The contaminant degradation by photocatalysts does not require electrical energy because sunlight is utilized to induce the contaminant degradation.

The photo-induced crystallization observed for the TiO_2 -Fe₂O₃-TiO₂ multilayer IOs could be studied in more detail to reveal the phase transformation mechanism. Thus, *in situ* characterization with synchrotron-based X-ray techniques could be utilized to iden-

tify atom rearrangements in the photocatalyst during the photocatalysis reaction. ^[324–326] These results would aid in understanding the origin of the photo-induced crystallization. Hence, inducing crystallization with light irradiation could be applied for materials or template structures which are not suited for the often used thermal crystallization by heat treatments, because the materials experience structural shrinkage and interface blurring as reported for porous IO structures. ^[327]

Applying further strategies to enhance photocatalysis

Optimization of the heterostructure design could further increase the charge separation efficiency in the photocatalyst materials and thus, improve the photocatalytic performance. For example, Barr *et al.* reported ALD-grown thin films on AAO templates, which facilitate charge carrier separation based on their heterojunction configuration. ^[122, 123] Hence, these structure provide good electrochemical properties. Such heterostructure design could also be realized with other ALD-based materials depending on their band edge configuration. Moreover, it would expand the applicability of ALD-fabricated photonic structures.

The combination of photocatalysts with plasmonic nanoparticles (NPs) boosts the photocatalytic performance as explained in Chapter 2. Aligning the nanoparticles' LSPR wavelength with a PSB edge of a PhC template structure can further increase the activity because of the slow photon effect, as recently shown by Collins *et al.* for IOs. ^[328] This approach can also be applied for enhancing the properties of AAO-PhC photocatalysts. Note that the fabrication process of AAO-PhCs is simpler compared to IOs. Specifically, the PSB position of AAO-PhCs can be modified by simply adjusting the anodization parameters rather than changing the PS template particle size. However, deposition of plasmonic NPs into the small diameter pores of AAO is more challenging than depositing them onto IOs. So far, Lim et al. investigated the effect of gold (Au) and silver as plasmonic materials on the photocatalytic properties of TiO₂-functionalized AAO-PhCs.^[116] They observed a decline of the activity in the presence of the plasmonic materials but related it to their fabrication as the plasmonic materials were sputter deposited only on the top-surface of the TiO₂-AAO-PhCs. Thus, the plasmonic material absorbed the respective wavelengths before they could reach the PhC structure. We could overcome this limitation by functionalizing TiO₂-AAO-PhCs with AuNPs by a deposition-precipitation approach modified from the publication by Zanella et al. [329] The SEM images shown in Figure 6.3. represent the deposition of very small AuNPs into AAO structures. The AuNP's LSPR is located at around 540 nm as characterized by UV/Vis measurements. Preliminary photocatalysis measurements show an improvement of the structures activity when TiO₂-AAO-PhCs are functionalized with AuNPs and the PSB edge is aligned with the AuNP LSPR. Indeed, further characterization needs to be conducted to investigate the interplay of the PSB position, AuNP size, and distribution on the photocatalytic performance. Alternative to deposition of NPs by wet-chemical methods, NP synthesis could also be realized by ALD. There are several established ALD processes for depositing plasmonic materials as NPs or thin films, for example gold, silver, platinum, palladium, copper, or titanium nitride.^[19,20] The ALD-based fabrication offers the advantage of the



Figure 6.3. AuNPs as plasmonic material can enhance the photocatalytic performance of AAO-PhCs. (a) SEM images of AAO-PhCs functionalized with small AuNPs (average diameter smaller than 6 nm). The AuNPs are the bright particles at the AAO structure. (b) The UV/Vis transmission measurement shows the LSPR of AuNPs deposited on a straight pore AAO template at around 540 nm. The photograph of the structure on the lower right shows the purple color of the AuNP coated AAO which is caused by the LSPR of the nanoparticles. (c) Preliminary photocatalysis measurements with AuNP decorated AAO-PhCs indicate an increased activity when the PSB edge is designed to match the AuNP LSPR.

inherent high conformality and precise film thickness or particle size control rendering homogeneous functionalization of AAO-PhCs with plasmonic materials feasible. Moreover, application of ALD-grown materials for photocatalysis, e.g., platinum or palladium, has already been demonstrated and hence, presents a promising approach to combine it with PhCs. ^[212, 330, 331]

The performance of PhC photocatalysts could also be further improved by altering the material properties. Since doping can modify the band gap of semiconductors, the optical and photocatalytical properties of the delta-doped TiO_2 thin films could be studied and optimized to utilize visible light for TiO_2 photocatalysis.

Besides multilayering or doping of thin films by ALD, modifications of material properties could also be achieved by fabricating ternary materials that offer new functionalities.^[20,71,332] A prominent example for such ALD-produced ternary material is mullite which features high temperature stability. Thus, mullite is of great interest for application as thermal barrier coating.^[31] In this context, the mullite fabrication by supercycle ALD of Al₂O₃ and SiO₂ on IO templates followed by thermal annealing has been demonstrated.^[31,33] With respect to photocatalytic applications, pseudobrookite is a material that is considered as highly efficient, visible-light active photocatalyst. ^[305–309] However, the fabrication of Fe_2TiO_5 is challenging as the phase separation of Fe_2O_3 and TiO₂ is often thermodynamically favored or long thermal annealing processes are required. ^[307, 309, 333] Some studies report about the Fe₂TiO₅ formation, but the materials often also contain hematite, anatase, and/or rutile.^[307,334] Under thermal annealing of Fe₂O₃-TiO₂ multilayer samples deposited on silicon substrates, we observed the formation of a ternary phase by *in situ* XRD whose peaks origin from Fe₂TiO₅ and no parasitic crystalline phases of Fe_2O_3 or TiO_2 are present (Figure 6.4.). Interestingly, the ternary phase does only form when Fe₂O₃ is utilized as bottom layer for the investigated multilayers - or inversely speaking TiO₂ is the top layer. First photocatalytic tests revealed an enhanced photocatalytic performance of the annealed, i.e., Fe_2TiO_5 , sample compared to the as-prepared multilayer for the first measurements. Furthermore, the photocatalytic activities were stable over three measurements for the annealed multilayer while the activity of the as-prepared structure continuously increased. This surprising observation might be related to photo-induced crystallization either of the TiO₂ layer into anatase as observed for the multilayer IOs in Chapter 5 or of the complete structure into Fe_2TiO_5 . Hence, further consecutive photocatalysis measurements of the as-prepared multilayer thin film would be necessary. Formation of Fe_2TiO_5 at the surface might also contribute to the activity increase of the TiO₂-Fe₂O₃-TiO₂ multilayer IOs. Further investigations would be required to gain a deeper understanding of the phase formation process during thermal annealing, the influence of the layer sequence and individual layer thicknesses, and the evolution of the photocatalytic activity. For all presented samples, i.e., mulitlayers on planar substrates and multilayer IOs, *in situ* X-ray diffraction studies with synchrotron radiation would be needed as they can prove the atom rearrangements during phase transitions. [^{324–326]}

PhC templates could also be tailored to exhibit multiple PSBs in order to support each of the utilized materials by the slow photon effect. Such multi-PSB PhCs have already been reported in literature for both PhC types utilized herein, i.e., AAO-PhCs and IOs as depicted in Figure 6.5. ^[112, 335] The structures could be applied to boost, for instance, the charge carrier generation in both photocatalysts utilized in a semiconductor heterostructure or the light absorption in a semiconductor and a plasmonic material. Apart from using multi-PSB PhC consisting of an IO structure on top of a AAO-PhC as proposed in our perspective article from 2022 (publication VI). Moreover, AAO-PhC or IO templates could also be coated with nanolaminates to provide an additional PhC component.

To conclude, this thesis has demonstrated the versatility of ALD for fabricating photonic structures of varying dimensionalities. Systematic structural characterization of the materials with respect to their composition allowed for tailoring the properties to the desired application. As exemplified by photocatalytic dye degradation, judicious development of the PhC template structure in combination with precise control over the film thickness of ALD-grown materials leads to significant improvement of the photocatalytic properties. Additionally, supercycle ALD approaches allow for further optimization of functional properties by modifying material compositions and sequences. The inherent flexibility of ALD together with the wide range of materials available for ALD growth and the unique ability of conformally coat complex substrates holds great promise for increased customization of functional materials and structures in the future.



Figure 6.4. Pseudobrookite formation from an ALD-grown Fe₂O₃-TiO₂ bilayer under thermal annealing in ambient atmosphere. (a) *In situ* XRD patterns depict the crystallization of the materials. With increasing temperature, the amorphous TiO₂ layer first crystallizes to anatase TiO₂, then a transition to the rutile TiO₂ phase occurs, and finally Fe₂TiO₅ forms and remains stable during the cooling process. (b) The *ex situ* XRD pattern taken after the thermal annealing of the structure proves the existence of Fe₂TiO₅ without the presence of anatase, rutile, or hematite phases. (c) Photocatalysis measurements of the Fe₂O₃-TiO₂ bilayer thin films as-prepared and after annealing show that the performance of the annealed structure is stable over three measurements and higher than the as-prepared sample increases over the three measurements which could arise from photo-induced crystallization and needs to be further investigated.



Figure 6.5. Multi-PSB photonic crystals could further tailor the properties of ALD-grown functional materials. The fabrication of (a) multi-PSB IOs and (b) multi-PSB AAO-PhCs has already been demonstrated in literature and the combination of both PhC types was proposed as another strategy. ^[6,112,335] The figures are freely adapted with permission. ^[6,112,335] Copyright (a) 2016, *American Chemical Society*, (b) 2019, *American Chemical Society*, and (c) 2022, *Wiley-VCH*.

Original Manuscripts

This chapter contains the original manuscripts of the publications I to VI and the respective supporting information. Note that the document sizes were compressed and the figures were reduced to 150 DPI to maintain the whole thesis within the University's size limitation.

7.1. Publication I

Tuning the Crystallization Temperature of Titanium Dioxide Thin Films by Incorporating Silicon Dioxide via Supercycle Atomic Layer Deposition

Carina Hedrich, Davy Deduytsche, Robin R. Petit, Tobias Krekeler, Jun Peng, Martin Ritter, Jolien Dendooven, Christophe Detavernier, Robert H. Blick, and Robert Zierold

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Author contributions: C.H. fabricated the structures and conducted the spectroscopic ellipsometry measurements. C.H. and D.D. conducted the XRD measurements. C.H. and R.R.P. conducted the XRR measurements, T.K. conducted the TEM measurements. J.P. conducted the AFM measurements. C.H., D.D., R.R.P., T.K., R.Z. performed the data analysis. C.H. wrote the manuscript. C.H., J.D., C.D., R.H.B., R.Z. conceived the project. M.R., J.D., C.D., R.H.B., R.Z. supervised the project and acquired funding. All authors conducted proofreading and approved the manuscript. Surfaces and Interfaces 57 (2025) 105696

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Tuning the crystallization temperature of titanium dioxide thin films by incorporating silicon dioxide *via* supercycle atomic layer deposition

Check for updates

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ABSTRACT

Titanium oxide-based nanomaterials are nowadays of great interest in various application fields such as optics, sensing, photocatalysis, and solar cells. Tuning their physical properties by tailoring the geometry or combining them with different materials further expands their applicability and even allows for the generation of new functionalities. The materials' crystalline phase also determines its properties and the crystallization behavior can be modified by doping or multilayering thin films with various materials. For instance, the combination of TiO₂ with silicon dioxide (SiO₂) renders these composites ideal candidates for coatings applied in harsh environments based on the high chemical and mechanical stability of both materials. Applying such coatings in optics, sensing, or photocatalysis require accurate prediction of the evolution of their properties and crystalline phase during heat treatments within the fabrication and application. Herein, we present the fabrication of SiO₂incorporated TiO₂ thin films by supercycle atomic layer deposition (ALD). Specifically, TiO₂-SiO₂ multilayers with varying material ratios, TiO2 thicknesses, and individual layer numbers as well as SiO2-doped TiO2 thin films are prepared. Their crystallization behavior is studied by in situ X-ray diffraction during thermal annealing. The structural properties of the composite materials are assessed by X-ray reflectivity, spectroscopic ellipsometry, and transmission electron microscopy before and after annealing. TiO₂-SiO₂ multilayers show increasing crystallization temperatures from amorphous TiO_2 to anatase with decreasing TiO_2 layer thickness from 50 nm to 4 nm and with increasing number of TiO_2 layers. Their layered structure is retained during annealing while the interfaces roughen slightly. SiO₂-doped TiO₂ thin films demonstrate increasing crystallization temperatures with increasing SiO_2 contents up to 10 %. The refractive index of these doped structures is tailored by the SiO_2 content. Detailed characterization of ALD deposited SiO₂-containing TiO₂ thin films could further expand their application in the future by precisely adjusting the fabrication process for the desired material properties and target application.

1. Introduction

Nanomaterials have gained significant attention over the past decades due to their unique and tunable properties, which find application in various technological fields [1,2]. Among these materials, titanium dioxide (titania, TiO₂) is a very versatile and promising semiconductor based on its optical, electronic, and photocatalytic properties [2–4]. TiO₂ thin films with layer thicknesses on the nanometer scale feature increased surface area-to-volume ratios whereby quantum effects occur and the film's electronic structure, band gap, and crystallographic phase transition behavior change depending on the thickness [2,4–7]. The crystallographic phase of TiO_2 – predominantly amorphous, anatase, rutile, or brookite – determines the materials' structural and functional properties, such as mechanical strength, optical properties, and thermal stability [8,9]. Hence, precise control over the crystallinity is crucial to tailor the properties of TiO_2 thin films for the desired application. Depending on the synthesis method, as-prepared TiO_2 thin films are crystalline or amorphous. The latter ones can be transformed into

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crystalline films by post-processing such as thermal annealing. Structural stabilization of TiO2 thin films upon heat treatments and thus, modification of the crystallization behavior can be achieved by doping or multilayering the films with various materials. The incorporation of foreign atoms locally changes the structure of the TiO₂ thin films and therefore alters the crystallization process. For instance, doping of TiO2 is reported to shift the crystallization temperature to higher temperatures [10–20]. Moreover, such approach influences the phase transition dynamics and can, e.g., suppress the phase transition from anatase to rutile depending on the dopant material and concentration [15–17,20]. Furthermore, the deposition of multilayered structures, where TiO₂ is alternated with layers of other metal oxides creates interfaces influencing nucleation and growth dynamics [8,11,12,19,21-29]. These multilayers can control phase transformation processes, promote the formation of specific crystalline phases such as anatase or rutile, and tailor microstructural characteristics [8,11,19,22,24,27].

This combinatorial approach of doping and multilayering offers a versatile platform to further extend and customize the properties of TiO₂ thin films to suit the intended application [3]. For example, SiO₂ is an interesting material featuring a low refractive index at similar high chemical and mechanical stability as TiO₂ [14]. Thus, multilayers of TiO₂ and SiO₂ can be utilized in different fields such as optics, sensing, thermal barrier coatings, or photocatalysis, to name a few [8,19,21,22, 24,25,30–32]. Previous reports about TiO₂-SiO₂ multilayers observed a thickness dependence of the crystallization temperature on the TiO₂ film thickness ranging from 4 nm to several hundred nanometers [19,21–26]. This correlation arises from the increasing influence of the surface and interface energies onto the crystallographic phase transition with increasing surface area-to-volume ratio of the TiO2 films, i.e., with decreasing film thickness [19,22]. These studies utilized ex situ characterization techniques after annealing the structures at varying temperatures to investigate the crystallization behavior. To precisely determine the crystallization onset, in situ characterization during the thermal annealing would be required but was not reported so far for TiO₂-SiO₂ multilayer thin films. Apart from TiO₂-SiO₂ multilayers, doping of TiO2 with SiO2 presents another possibility to tune the temperature-dependent structural properties. Homogeneously doped films containing TiO₂ and SiO₂ showed composition-dependent crystallization behavior [13-18]. The increase of the TiO₂ crystallization temperature with increasing SiO₂ content can be explained by raised activation energies for the crystallization because additional Si atoms interact strongly with the TiO₂ lattice [14,16,18]. However, both types of SiO₂-incorporated TiO₂ films, i.e., TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂, were prepared by sputtering, sol-gel chemistry, chemical vapor deposition, physical vapor deposition, or wet-chemical synthesis. These deposition techniques face limitations regarding coating conformality on complex-shaped substrates and/or precision of the film thickness control.

To overcome these limitations, atomic layer deposition (ALD) is utilized in this work to produce TiO2-SiO2 multilayers and SiO2-doped TiO₂ thin films. ALD is a gas phase deposition technique that allows for precise thickness control of deposited films on the Ångström scale through sequential self-limiting reactions between gaseous precursors and solid surfaces [33,34]. Thus, three-dimensional or complex-shaped substrates can also be conformally coated by ALD. Furthermore, the combination of different materials in one ALD deposition process can be easily realized by supercycles [34,35]. These supercycles consist of pre-defined numbers of ALD cycles for the different materials carried out consecutively as schematically shown in Fig. 1(a). The desired film thickness per material is obtained by tuning the ALD cycle numbers within the supercycle. In this way, tailored multilayers can be produced by alternating the deposition processes for the different materials. On the other hand, doping of materials is possible by periodically introducing single ALD cycles of the dopant material into the ALD process of the host material [36]. Hence, the properties of the deposited material can be precisely tailored by applying supercycle ALD processes.

Herein, we report on the fabrication of TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂ thin films *via* supercycle ALD. The crystallization behavior of the nanometer thin TiO₂ films is investigated by *in situ* and *ex situ* X-ray diffraction (XRD) during thermal annealing of the structures. Specifically, shifting of the TiO₂ crystallization to higher temperatures with decreasing layer thickness and increasing number of material interfaces is studied in TiO₂-SiO₂ multilayers. Composition-dependent crystallization properties are also observed in SiO₂-doped TiO₂ thin films. In addition, the structural appearance of the composite materials is characterized by X-ray reflectivity (XRR) measurements before and after the annealing. Furthermore, cross-section transmission electron microscopy (TEM) images of TiO₂-SiO₂ multilayers reveal that the layered structure is retained but roughened after thermal annealing. Spectroscopic ellipsometry of SiO₂-doped TiO₂ thin films was used to investigate the change of the refractive index upon annealing.

2. Experimental section

2.1. Materials

P-doped silicon wafers with native SiO_2 layers (thickness 1.4–1.7 nm) were supplied by Siegert Wafer (Germany). Titanium tetraisopropoxide (TTIP, CAS 546–68–9), tris(dimethlamino)silane (TDMAS, CAS 15,112–89–7), acetone (CAS 67–4–1), and isopropyl alcohol (IPA,



Fig. 1. (a) Schematic structure of a supercycle ALD process. The first material (TiO_2) forms by reactions of TTIP and O_3 . The cycles are repeated *a* times until the desired thickness is reached. The second material (SiO_2) is deposited in *b* cycles of TDMAS and O_3 . Both cycles are repeated *n* times as a supercycle. (b) Composition of alternating TiO_2 -SiO_2 multilayers and the respective cycle numbers *a*, *b*, and the supercycle numbers *n* applied for the samples presented in this publication. (c) SiO_2-doped TiO_2 thin films are prepared by introducing single SiO_2 deposition cycles between varying amounts of TiO_2 cycles to achieve different doping ratios. The process parameters are presented, and the structure of the films on top of a Al_2O_3 -coated substrate is depicted.

CAS 67–63–0) were purchased from Sigma Aldrich (Germany). Trimethylaluminum (TMA, CAS 75–24–1) was supplied by Strem Chemicals (France). Milli-Q water (> 16 M Ω cm, H₂O) was used as deionized water (DI-H₂O). Oxygen (5.0) and nitrogen (6.0) were received from Westfalen Gas and SOL, respectively.

2.2. Fabrication

TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂ films were prepared by supercycle ALD processes (Fig. 1a). Silicon wafer pieces were cleaned in acetone and IPA followed by drying under N2 steam for both sample sets. TiO_2 and SiO_2 ALD processes were conducted in a GEMStar XT^{TM} system (Arradiance, USA) under stop-flow conditions. Both materials were deposited at 150 °C in a constant N2 flow of 30 sccm. Ozone (O3) generated by an R-Lab 112 ozone generator (Pacific Ozone, USA) was utilized as oxygen precursor for both processes. TTIP heated to 80 °C and TDMAS at 40 °C were used as titanium and silicon precursor, respectively. The pulse, exposure, and purge times of the individual ALD halfcycle during the TiO₂ process were as following: 0.1 s, 10 s, and 30 s for TTIP and 2 s, 10 s, and 30 s for O₃. SiO₂ deposition was conducted with pulse, exposure, and purge times of 0.05 s, 15 s, and 30 s for TDMAS and 2 s, 40 s, and 30 s for O_3 . The growth per cycle (GPC) was 0.3 Å for Ti O_2 and 0.84 Å for SiO₂ deposition in agreement with existing literature [37-40]. TiO₂-SiO₂ multilayers were deposited on cleaned Si wafers. The TiO₂:SiO₂ ratio and individual layer thicknesses were tuned by varying the TiO_2 and SiO_2 deposition cycles (a and b) as well as the supercycle number (n). All supercycle processes were designed to receive a total coating thickness of 100 nm. Note, the individual cycle and supercycle numbers of the samples investigated are summarized in Fig. 1b. Two different TiO₂:SiO₂ ratios are deposited to test their effect on the crystallization behavior based on the different surface area-to-volume ratio in the layers. A 45 nm pure TiO₂ thin film was prepared on a clean Si wafer by applying 1500 TiO₂ ALD cycles.

SiO₂-doped TiO₂ thin films are fabricated on Si wafer pieces which were previously coated with 100 nm Al₂O₃ by ALD as diffusion barrier to prevent unintended Si-doping of the TiO₂ film by the substrate [41,42]. The alumina ALD process was performed in a home-built ALD system under stop-flow conditions at 150 °C. TMA and DI-H₂O were used as precursors with pulse, exposure, and purge times for both of 0.05 s, 5 s, and 45, respectively. 625 cycles were applied to obtain a film thickness of 100 nm. Deposition of SiO₂-doped TiO₂ was conducted in the Arradiance GEMStar system under the same process conditions as described above for the multilayer structures. One SiO₂ cycle was applied within one supercycle to fabricate SiO₂-doped TiO₂. To ensure a constant base layer, 20 cycles of TiO₂ were applied before starting the supercycle process. The TiO₂:SiO₂ ratio and number of supercycles were varied to tailor the SiO₂ percentage while keeping the total film thickness constant at 30 nm. The process parameters are shown in Fig. 1c.

2.3. Characterization

TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂ films were structurally characterized by *in situ* X-ray diffraction (XRD) during thermal annealing. A Bruker (USA) D8 discover X-ray diffractometer equipped with a home-built annealing chamber (Ghent University) was utilized. Copper Kα radiation was applied, and the samples were annealed in ambient air at a heating rate of 10 °C/min up to 900 °C. *In situ* XRD scans in the range of 20° to 40° were taken with an integration time of 15 s. Data processing of the *in situ* data emphasizes signals with low intensities in order to be able to distinguish them from the background in the color maps. Occasionally, this processing causes signals at the measuring range's edge to be overly amplified. Note, artefacts do not appear in the *ex situ* measurements, which serve as control. Before and after the annealing, a full angle *ex situ* scan from 15° to 65° with a resolution of 0.05°, an offset of 5°, and 4 s integration time was taken for each sample. X-ray reflectivity (XRR) patterns of TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂

films were measured before and after annealing in a Bruker D8 discover system employing Cu K α radiation. XRR measurements were recorded from 0.2° to 4.0° with a step size of 0.01° and an integration time of 1 s per step. Transmission electron microscopy (TEM) images of TiO₂-SiO₂ multilayer cross-sections were acquired with a Thermo Fisher (Germany) Talos F200X in BF and HAADF-Mode. Sample preparation was done with a Thermo Fisher Helios G3UC Focused Ion Beam (FIB) using a standard *in situ* lift-out technique of the FIB lamellae. Spectroscopic ellipsometry characterization for the SiO₂-doped TiO₂ thin films are carried out with a SENpro ellipsometer by SENTECH (Germany). Specifically, Cauchy models have been used to analyze Al₂O₃ as substrate coating material and SiO₂-doped TiO₂ films. Atomic force microscopy (AFM) measurements of SiO₂-doped TiO₂ films were conducted with a Dimension 3100 Atomic Force Microscope (Bruker, USA).

3. Results and discussion

3.1. TiO₂-SiO₂ multilayers

The crystallization temperature of ALD-deposited TiO₂ thin films can be tailored by incorporating SiO₂ either as TiO₂-SiO₂ multilayer structures or by SiO₂-doping. All films are amorphous after deposition and annealing is necessary to induce crystallization. Crystallization from the amorphous TiO₂ phase into polycrystalline anatase films is observed by in situ XRD measurements for layer thicknesses between 4 nm and 50 nm (Fig. 2, left column). Note, silica remains amorphous for all heat treatments performed in this study in agreement with the literature [21, 43]. For the multilayers, the crystallization temperature T_{cr} of TiO₂ increases with decreasing thickness of the individual TiO2 layers within the stack. Note, TiO₂ layers in both investigated TiO₂:SiO₂ thickness ratios of 1:1 and 1:4 with varying individual layer thicknesses transform into anatase. While a crystallization temperature of 405 °C is observed for the 50 nm TiO₂ film, it increases up to 475 $^\circ$ C for a TiO₂-SiO₂ multilayer with 4 nm individual TiO2 layer thickness as summarized in Fig. 3. The anatase (101) peak at 25.7° is visible in the *in situ* XRD plots at temperatures above the crystallization temperature. The $T_{\rm cr}$ is denoted above each plot and marked by a grey line for each sample's plot. Increasing the supercycle number n with a fixed total film thicknesses result in two aspects that affect the crystallization temperature:

First, the individual TiO₂ thickness per layer is decreasing. Consequently, the interface area-to-volume ratio in these thin films is increasing whereby the influence of the interfaces becomes more prominent for the layer's properties [19,22]. Such a reduction in film thickness also restricts the crystallite sizes. Hence, it leads to a broadening of the peaks which is particularly visible in the *ex situ* XRD measurements [7]. By utilizing the peaks' full width at half maximum (FWHM), crystallite sizes were estimated from the anatase (101) peak by the Scherrer equation using a shape factor of 0.9 [44]. The results are summarized in Table 1 and reveal that crystallite sizes are in the range of the film thicknesses for layers thinner than 20 nm. The 50 nm thick TiO₂ film consists of crystallites with an average size of 25.2 nm. This observation indicates that for thicker layers (> 25 nm) the crystallite size upon annealing in our experimental setup is not influenced anymore by the confinement.

Second, the number of TiO₂-SiO₂ interfaces raises which further enhances the influence of the interfaces onto the properties of the overall structure [22]. Based on the different interface energies of amorphous TiO₂ and crystalline TiO₂ with amorphous SiO₂, Durante *et al.* calculated that the crystalline TiO₂ interface is energetically less favorable [22]. Note, T_{cr} for the 2 nm thick TiO₂ layers could not be clearly determined from the *in situ* data and is thus not included in Fig. 3. However, the *ex situ* data after the thermal annealing (Fig. 2g) shows a broad peak with low intensity at 25.8° indicating the anatase (101) peak. Note that the *in situ* measured intensity for this peak is below the detection limit of the XRD setup for such, only a few nanometers thin, film. Follow-up experiments can utilize synchrotron radiation to further quantify the



Fig. 2. In situ (left) and ex situ (right) XRD patterns of TiO₂-SiO₂ multilayers. In (a) the XRD patterns of a pure 45 nm TiO₂ film as reference are shown. The TiO₂:SiO₂ ratio is varied between 1:1 (b-d) and 1:4 (e-g) while the total film thickness is kept constant. The TiO₂ layers crystallize in anatase phase and the crystallization temperature (marked by the grey line in the *in situ* patterns) increases with decreasing TiO₂ film thickness. Peak positions for anatase 'A' (COD 1,010,942) are shown in the ex situ patterns in the right column. TiO₂ layer thicknesses of (b) 50 nm, (c) 10 nm, (d) 5 nm, (e) 20 nm, (f) 4 nm, and (g) 2 nm are investigated.



Fig. 3. The crystallization temperature T_{cr} of TiO₂ layers in TiO₂-SiO₂ multilayers increases with decreasing TiO₂ layer thickness.

Table 1 Crystallite sizes in the TiO_2 layers are calculated from the anatase (101) peak

utilizing the Scherrer equation

utilizing the scherrer equation.						
$\rm TiO_2$ layer thickness /nm	FWHM /°	2 heta /°	Crystallite size /nm			
4	1.90	25.39	4.7			
5	1.52	25.39	5.9			
10	0.84	25.50	10.6			
20	0.46	25.50	19.3			
50	0.35	25.54	25.2			

presence of anatase phase in TiO₂ layers below 4 nm.

As a control, the pure TiO₂ layer (Fig. 2a) shows a crystallization onset at 380 °C. This temperature is even below the measured value for a 50 nm TiO₂ thin film in a bilayer structure (405 °C). We conclude that any overcoating of TiO₂ by SiO₂ affects the crystallization behavior of TiO₂. As explained above, the additional interface energy effectively hinders the crystallization of the TiO₂ layer. Hence, the phase transition in such TiO₂-SiO₂ bilayers needs more energy than in an uncovered TiO₂ resulting in a higher $T_{\rm cr}$.

In general, the TiO_2 -SiO₂ multilayers are structurally stable upon thermal annealing. The film thicknesses, surface roughnesses, and interface roughnesses change only slightly after annealing the TiO_2 -SiO₂ stack structures as revealed by the XRR patterns (Fig. 4). The observed minor modifications are caused by the TiO_2 phase transition and the corresponding rearrangement of atoms [17]. For better comparison, XRR patterns before and after annealing for each sample are shown in Fig. S1. The individual XRR plots were not fitted quantitatively due to the large number of individual layers, which led to a huge dimensionality of fit parameters, but the data is compared qualitatively. Oscillation periodicities increase slightly corresponding to decreasing film thicknesses caused by the densification and crystallization of the TiO_2 layers into the anatase phase [17]. Minor reductions of the oscillation amplitude after annealing suggest that the interfaces roughen slightly [45]. These results are corroborated by TEM analyses before and after thermal annealing (Fig. 5) revealing also the thickness decrease and indicating an increase in the surface roughness.

Specifically, the cross-section TEM images (Fig. 5) demonstrate that the TiO₂-SiO₂ multilayers retain their layered structure upon annealing. Analysis of the individual layer thicknesses was performed by using the software Fiji[46] and the results are summarized in Table 2. Individual layer thicknesses decrease by below 1 nm after the annealing up to 900 °C and the total film thicknesses reduce between 1.5 nm and 9.7 nm depending on the TiO₂:SiO₂ thickness ratio and the supercycle numbers. Furthermore, the TEM analysis supports the *ex situ* XRD measurements showing that TiO₂ and SiO₂ layers are amorphous before annealing. In contrast, after the thermal annealing, TiO₂ layers consist of crystalline grains with different orientation of the crystal lattices (Fig. 5b). This again is in good agreement with the multiple anatase peaks observed by *ex situ* XRD measurements (Fig. 2).

3.2. SiO₂-doped TiO₂ thin films

It was previously reported that utilization of aluminum-doped TiO_2 layers stabilizes the 1D and 3D photonic structures while simultaneously maintaining the high refractive index of the TiO_2 layers [10,11]. This prework motivated us to study the crystallization properties of supercyclic deposited SiO_2 -doped TiO_2 thin films. Silica doping of TiO_2 films is obtained by applying single SiO_2 ALD cycles after a certain number of TiO_2 cycles in supercycle processes. Based on the cyclic nature of the ALD process, the dopant material SiO_2 is introduced as sub-monolayers in between TiO_2 layers. Hence, the structure resembles a delta-doped material characterized by the layered arrangment of host and dopant material with multiple regions of high dopant concentration within narrow profiles along the cross-section [47]. When the total film thickness is kept constant for the ALD process, the SiO_2 content raises with the total number of SiO_2 cycles within the ALD process. Each SiO_2



Fig. 4. XRR patterns of TiO_2 -SiO_2 multilayers before and after annealing demonstrate that the film thicknesses, surface roughnesses, and interface roughnesses change only slightly. Multilayers fabricated with different ALD supercycle numbers are depicted for TiO_2 :SiO₂ ratios of 1:1 (a) and 1:4 (b). Direct qualitative comparison of the same multilayer before and after annealing is presented in Fig. S1.

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Fig. 5. Cross-sectional TEM images of different TiO_2 -SiO₂ multilayers before and after thermal annealing. TEM micrographs before and after annealing (large images of a,b and c) were taken with an HAADF detector in STEM-mode. Here, TiO_2 is displayed in light grey while the SiO₂ layers are dark grey. The TEM images in higher magnification in (b) are HRTEM-images revealing an amorphous TiO_2 layer before annealing and showing lattice planes in the TiO_2 layer after annealing. The TiO_2 and SiO₂ layers are marked in green and blue on the right side of each image, respectively. Note, the thin bottom SiO₂ layers are native silicon dioxide layers of the substrate.

Table 2	
Film thicknesses of the individual layers in TiO2-SiO2 multilayers analyzed by cross-section TEM	images.

Sample	TiO ₂ layer thickness /nm		SiO ₂ layer thickness /nm		Total film thickness /nm	
	before annealing	after annealing	before annealing	after annealing	before annealing	after annealing
TiO ₂ :SiO ₂ 1:1, 1 supercycle TiO ₂ :SiO ₂ 1:4, 5 supercycles TiO ₂ :SiO ₂ 1:1, 10 supercycles	$\begin{array}{l} 51.4 \pm 0.5 \\ 4.9 \pm 0.5 \\ 5.5 \pm 0.2 \end{array}$	$\begin{array}{c} 50.5 \pm 0.5 \\ 4.3 \pm 0.4 \\ 5.3 \pm 0.42 \end{array}$	$\begin{array}{c} 43.8 \pm 0.5 \\ 14.6 \pm 0.3 \\ 4.8 \pm 0.2 \end{array}$	$\begin{array}{c} 43.2 \pm 0.5 \\ 14.5 \pm 0.4 \\ 4.0 \pm 0.4 \end{array}$	$\begin{array}{c} 95.2 \pm 0.5 \\ 96.0 \pm 0.5 \\ 102.6 \pm 0.5 \end{array}$	$\begin{array}{c} 93.7 \pm 0.5 \\ 94.1 \pm 0.5 \\ 92.9 \pm 0.5 \end{array}$

cycle alters the local bonding environment of titanium and oxygen in the TiO₂ film by creating material defects. As discussed above, the introduction of such additional material defects hinders the crystallization of the TiO₂ film during the thermal annealing. Note, an ALD-grown Al₂O₃ layer was deposited as diffusion barrier between the Si substrate and the SiO₂-doped TiO₂ thin film to prevent unintended Si-doping from the substrate [41,42]. Increasing the SiO₂ content in SiO₂-doped TiO₂ thin films leads to a rise of the crystallization temperature as shown in Fig. 6. $T_{\rm cr}$ to the anatase phase increases with the SiO₂ content from 420 °C for 0 % doping until 485 °C for a SiO₂ content of 10 %. *Ex situ* XRD analysis, exemplarily displayed for 7.5 % SiO₂ (Fig. 6g) proves that only the anatase phase is detected and no traces for rutile or brookite can be identified. The ex situ XRD data of the other samples are depicted in Fig. S2. The observed linear trend between 1 % and 10 % SiO $_2$ content (Fig. 6h) is in good agreement with a previous study by Waleczek et al. on the influence of Al₂O₃ doping by supercycle ALD on T_{cr} of TiO₂ films [10].

The high refractive index of TiO_2 is a key feature, which is mitigated by excessive doping with a lower refractive index material. We used spectroscopic ellipsometry data (Fig. 7a) to determine the refractive index as a function of SiO_2 content as-prepared and upon annealing. Note, by employing the supercycle approach, the refractive index can be precisely tailored because the amount of SiO_2 can be finely adjusted. Refractive indices presented in Fig. 7a are measured at SiO_2 -doped TiO_2 samples featuring the same SiO_2 contents but prepared directly on silicon wafers without the Al_2O_3 diffusion barrier to reduce the number of fitting parameters for the analysis. Upon annealing at temperatures above the crystallization, an increase of the refractive index of the SiO_2 - doped TiO₂ films is observed. Such an increase in refractive index is expected due to the TiO₂ film crystallization into the anatase phase [8, 9]. Spectroscopic ellipsometry results of the samples with Al₂O₃ barrier layer are depicted in Fig. S3 and reveal a similar behavior. The XRR measurements of the samples are very similar before and after thermal annealing (Fig. 7b-d and Fig. S4). We therefore conclude, that the film thicknesses of SiO₂-doped TiO₂ films remain almost constant after annealing. However, the reflected intensity decays faster after the annealing. Such behavior could be related to an increase of the surface roughness of the SiO₂-doped TiO₂ films as confirmed by atomic force microscopy measurements (Table 3 and Fig. S5) [8,45]. Note, a significant difference in crystallization temperature is identified when comparing the reference sample containing 0 % doping with the results of the pure TiO₂ sample (shown in Fig. 2a). We attribute this mismatch to the different substrates.

3.3. Influence of the substrate surface

The annealing results of the reference substrates for both types of samples, *i.e.*, multilayers and doped TiO₂ thin films differ. This observation obviously demonstrates that also the utilized substrate affects the crystallization behavior besides multilayering or doping of TiO₂. For the mutiliayer samples, cleaned silicon wafer pieces with 1.7 nm native SiO₂ were directly used as substrates; whereas the SiO₂-doped TiO₂ structures were fabricated on silicon wafer pieces previously coated with 100 nm aluminum oxide (Al₂O₃) by ALD. Although the pure TiO₂ film prepared on the Al₂O₃-coated substrates, *i.e.*, 0 % SiO₂ content in TiO₂, has a thickness of 30 nm, its crystallization temperature of 420 °C (Fig. 6a)



Fig. 6. XRD studies of SiO₂-doped TiO₂ thin films with varied SiO₂ content. (a-f) *In situ* XRD patterns of SiO₂ contents 0 %, 1 %, 2.5 %, 5 %, 7.5 %, and 10 %. The crystallization temperature of anatase formation is inidcated by the grey line. (g) *Ex situ* XRD measurement of the TiO₂ film containing 7.5 % SiO₂ before and after annealing showing the crystallization into anatase phase ('A', COD 1,010,942). (h) The crystallization temperature increases with increasing SiO₂ content.

exceeding the values from the thickness dependence observed for the TiO_2 -SiO₂ multilayers (405 °C, Fig. 3) and for 45 nm pure TiO_2 (380 °C, Fig. 2a). Since different materials are utilized as substrate layers in direct contact with the TiO_2 thin film, the interface energies differ. Durante *et al.* reported on a higher interface energy for TiO_2 in contact with Al_2O_3 than with SiO₂ [22]. As a consequence, more energy is required for the phase transition from amorphous TiO_2 to anatase when an Al_2O_3 -functionalized substrate is used resulting in a higher T_{cr} as observed in our experiments.

4. Conclusion

The crystallization temperature of ALD-deposited TiO₂ from the amorphous to the anatase phase depends on the incorporation of SiO₂ in the form of a multilayer structure or as delta-doping. Specifically, $T_{\rm cr}$ increases with decreasing thickness of individual TiO₂ layers embedded in SiO₂ layers. In both cases, the influence of material interfaces between TiO₂ and SiO₂ layers becomes more dominant for the phase transition. In accordance with this, $T_{\rm cr}$ increases when the SiO₂ content is raised in SiO₂-doped TiO₂ films. Both, TiO₂-SiO₂ multilayers and SiO₂-doped TiO₂ films retain their structural properties after thermal annealing. Minor changes of thicknesses, surface roughnesses, and interface

roughnesses can be attributed to the rearrangement of atoms caused by the TiO₂ phase transition.

The systematic study of the crystallization temperature in SiO₂ containing TiO2 films allows for precise adjustment of annealing temperatures to obtain or to prevent the crystallization of nanometer thin TiO₂ films. By controlling the delta-doping of SiO₂, the refractive index in SiO₂-doped TiO₂ thin films can be tailored. Speaking in terms of generality, fabricating such multilayered or doped structures by ALD enables their application to a wide range of templates not accessible with other deposition techniques such as highly porous structures or three-dimensional complex-shaped templates. On the one hand, the very precise thickness control of ALD processes might pave the way for further reduction of the individual layer thicknesses and hence, for a further increase of the TiO₂ crystallization temperature. On the other hand, such doped materials can, for example, be utilized in photocatalysis because they decrease the optical bandgap of TiO₂ and ease the charge carrier generation [15,16]. In this context, precise knowledge of the increased crystallization temperature is essential as the crystalline anatase phase has a higher photocatalytic activity than amorphous TiO₂ and hence, anatase is desired to be obtained by thermal annealing [48-50].



Fig. 7. (a) TiO₂ refractive index *n* of the SiO₂-doped TiO₂ films determined by spectroscopic ellipsometry at 632.8 nm wavelength. The SiO₂ content tailors the refractive index of the TiO₂ films. The refractive indices increase for all samples after annealing. (b-d) XRR patterns of SiO₂-doped TiO₂ thin films before and after annealing. The patterns are exemplary shown for SiO₂ contents of (b) 0 %, (c) 2.5 %, and (d) 10 %. The XRR data of 1 %, 5 %, and 7.5 % SiO₂ content are displayed in Fig. S4.

Table 3 Surface roughness of SiO₂-doped TiO₂ thin films measured by atomic force microscopy.

SiO ₂ content	Surface roughness /nm		
	Before anneling	After annealing	
0	0.41	0.91	
1	0.19	1.15	
2.5	0.36	2.43	
5	0.42	2.18	
7.5	0.44	2.35	
10	0.26	3.27	

CRediT authorship contribution statement

Carina Hedrich: Writing - original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Davy Deduytsche: Writing - review & editing, Visualization, Methodology, Investigation, Formal analysis, Data curation. Robin R. Petit: Writing - review & editing, Methodology, Investigation, Formal analysis, Data curation. Tobias Krekeler: Writing - review & editing, Methodology, Investigation, Data curation. Jun Peng: Writing - review & editing, Methodology, Investigation, Formal analysis, Data curation. Martin Ritter: Writing - review & editing, Supervision, Funding acquisition. Jolien Dendooven: Writing - review & editing, Supervision, Resources, Project administration, Funding acquisition. Christophe Detavernier: Writing - review & editing, Supervision, Resources, Project administration, Funding acquisition. Robert H. Blick: Writing review & editing, Supervision, Resources, Project administration, Funding acquisition. Robert Zierold: Writing - review & editing, Writing - original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Carina Hedrich, Tobias Krekeler, Jun Peng, Martin Ritter, Robert H. Blick, and Robert Zierold report financial support was provided by German Reserach Foundation. Davy Deduytsche, Robin R. Petit, Jolien Dendooven, and Christophe Detavernier report financial support was provided by Ghent University. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.surfin.2024.105696.

Data availability

Data will be made available on request.

References

 M. Benelmekki, Nanomaterials The Original Product of Nanotechnology, Morgan & Claypool Publishers, San Rafael, California, 2019. C. Hedrich et al.

- [2] N. Kumar, S. Kumbhat, Essentials in Nanoscience and Nanotechnology, John Wiley & Sons Inc., Hoboke, New Jersey, 2016.
- [3] M. Dahl, Y. Liu, Y. Yin, Composite titanium dioxide nanomaterials, Chem. Rev. 114 (19) (2014) 9853–9889, https://doi.org/10.1021/cr400634p.
 [4] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties,
- [4] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, Chem. Rev. 107 (7) (2007) 2891–2959, https:// doi.org/10.1021/cr0500535.
- [5] T. Guang-Lei, H. Hong-Bo, S. Jian-Da, Effect of microstructure of TiO₂ thin films on optical band gap energy, Chin. Phys. Lett. 22 (7) (2005) 1787–1789, https://doi. org/10.1088/0256-307X/22/7/062.
- [6] M. Tallarida, C. Das, D. Schmeisser, Quantum size effects in TiO 2 thin films grown by atomic layer deposition, Beilstein J. Nanotechnol. 5 (2014) 77–82, https://doi. org/10.3762/bjnano.5.7.
- [7] O. Durante, C. Di Giorgio, V. Granata, J. Neilson, R. Fittipaldi, A. Vecchione, G. Carapella, F. Chiadini, R. DeSalvo, F. Dinelli, V. Fiumara, V. Pierro, I.M. Pinto, M. Principe, F. Bobba, Emergence and evolution of crystallization in TiO₂ thin films: a structural and morphological study, Nanomaterials 11 (6) (2021) 1409, https://doi.org/10.3390/nano11061409.
- [8] D.F. Zambrano, R. Villarroel, R. Espinoza-González, N. Carvajal, A. Rosenkranz, A. G. Montaño-Figueroa, M.J. Arellano-Jiménez, M. Quevedo-Lopez, P. Valenzuela, W. Gacitúa, Mechanical and microstructural properties of broadband anti-reflective TiO₂/SiO₂ coatings for photovoltaic applications fabricated by magnetron sputtering, Sol. Energy Mater. Sol. Cells 220 (2021) 110841, https://doi.org/10.1016/j.solmat.2020.110841.
- [9] X. Min Du, R.M. Almeida, Effects of thermal treatment on the structure and properties of SiO₂-TiO₂ gel films on silicon substrates, J. Sol-Gel Sci. Technol. 8 (1–3) (1997) 377–380, https://doi.org/10.1007/BF02436868.
- [10] M. Waleczek, J. Dendooven, P. Dyachenko, A.Y. Petrov, M. Eich, R.H. Blick, C. Detavernier, K. Nielsch, K.P. Furlan, R. Zierold, Influence of alumina addition on the optical properties and the thermal stability of titania thin films and inverse opals produced by atomic layer deposition, Nanomaterials 11 (4) (2021), https:// doi.org/10.3390/nano11041053.
- [11] L. Ghazaryan, S. Handa, P. Schmitt, V. Beladiya, V. Roddatis, A. Tünnermann, A. Szeghalmi, Structural, optical, and mechanical properties of TiO₂ nanolaminates, Nanotechnology 32 (9) (2021) 095709, https://doi.org/10.1088/ 1361-6528/abcbc1.
- [12] G.E. Testoni, W. Chiappim, R.S. Pessoa, M.A. Fraga, W. Miyakawa, K.K. Sakane, N. K.A.M. Galvão, L. Vieira, H.S. Maciel, Influence of the Al₂O₃ partial-monolayer number on the crystallization mechanism of TiO₂ in ALD TiO₂ /Al₂O₃ nanolaminates and its impact on the material properties, J. Phys. Appl. Phys. 49 (37) (2016), https://doi.org/10.1088/0022-372/49/37/375301.
- [13] R.M. Almeida, E.E. Christensen, Crystallization behavior of SiO₂-TiO₂ sol-gel thin films, J. Sol-Gel Sci. Technol. 8 (1–3) (1997) 409–413, https://doi.org/10.1007/ BF02436874.
- [14] G. Calleja, D.P. Serrano, R. Sanz, P. Pizarro, Mesostructured SiO₂-doped TiO₂ with enhanced thermal stability prepared by a soft-templating sol-gel route, Microporous Mesoporous Mater 111 (1–3) (2008) 429–440, https://doi.org/ 10.1016/j.micromeso.2007.08.021.
- [15] C. He, B. Tian, J. Zhang, Thermally stable SiO₂-doped mesoporous anatase TiO₂ with large surface area and excellent photocatalytic activity, J. Colloid Interface Sci. 344 (2) (2010) 382–389, https://doi.org/10.1016/j.jcis.2010.01.002.
- [16] Y. Su, J. Wu, X. Quan, S. Chen, Electrochemically assisted photocatalytic degradation of phenol using silicon-doped TiO2 nanofilm electrode, Desalination 252 (1–3) (2010) 143–148, https://doi.org/10.1016/j.desal.2009.10.011.
- [17] Y.-H. Zhang, A. Reller, Phase transformation and grain growth of doped nanosized titania, Mater. Sci. Eng. C 19 (1–2) (2002) 323–326, https://doi.org/10.1016/ S0928-4931(01)00409-X.
- [18] Z. Zhu, S. Wu, Y. Long, L. Zhang, X. Xue, Y. Yin, B. Xu, Phase-transition kinetics of silicon-doped titanium dioxide based on high-temperature X-Ray-diffraction measurements, J. Solid State Chem. 303 (2021) 122544, https://doi.org/10.1016/ j.jssc.2021.122544.
- [19] H. Sankur, W. Gunning, Crystallization and diffusion in composite TiO₂-SiO₂ thin films, J. Appl. Phys. 66 (10) (1989) 4747–4751, https://doi.org/10.1063/ 1.343784.
- [20] S. Schipporeit, M. Jerman, D. Mergel, Crystallization and conductivity of large-domain Nb-doped TiO₂ films prepared by electron beam evaporation, Thin Solid Films 754 (2022) 139299, https://doi.org/10.1016/j.tsf.2022.139299.
 [21] G. Christidis, O.B. Fabrichnaya, S.M. Koepfli, E. Poloni, J. Winiger, Y.
- [21] G. Chilstuns, O.D. Fabrichiaya, S.M. Koepin, E. Poloni, J. Winger, T. M. Fedoryshyn, A.V. Gusarov, M. Ilatovskaia, I. Saenko, G. Savinykh, V. Shklover, J. Leuthold, Photonic response and temperature evolution of SiO₂/TiO₂ multilayers, J. Mater. Sci. 56 (33) (2021) 18440–18452, https://doi.org/10.1007/ s10853-021-06557-y.
- [22] O. Durante, V. Granata, J. Neilson, G. Carapella, F. Chiadini, R. DeSalvo, R. De Simone, V. Fiumara, V. Pierro, I.M. Pinto, A. Vecchione, R. Fittipaldi, F. Bobba, C. Di Giorgio, Investigation of crystallization in nanolayered TiO₂-based superlattices, Surf. Interfaces 41 (2023) 103309, https://doi.org/10.1016/j. surfin.2023.103309.
- [23] T. Nakayama, Structure of TiO2₂/SiO₂ multilayer films, J. Electrochem. Soc. 141 (1) (1994) 237–241, https://doi.org/10.1149/1.2054690.
 [24] H.-W. Pan, S.-J. Wang, L.-C. Kuo, S. Chao, M. Principe, I.M. Pinto, R. DeSalvo,
- [24] H.-W. Pan, S.-J. Wang, L.-C. Kuo, S. Chao, M. Principe, I.M. Pinto, R. DeSalvo, Thickness-dependent crystallization on thermal anneal for titania/silica nm-layer composites deposited by ion beam sputter method, Opt. Express 22 (24) (2014) 29847, https://doi.org/10.1364/OE.22.029847.

- [25] R.D.Y. Away, C. Takai-Yamashita, T. Ban, Y. Ohya, Photocatalytic properties of TiO₂-Si₂2 sandwich multilayer films prepared by sol-gel dip-coating, Thin Solid Films 720 (2021) 138522, https://doi.org/10.1016/j.tsf.2021.138522.
- [26] A. Hodroj, O. Chaix-Pluchery, M. Audier, U. Gottlieb, J.-L. Deschanvres, Thermal annealing of amorphous Ti–Si–O thin films, J. Mater. Res. 23 (3) (2008) 755–759, https://doi.org/10.1557/JMR.2008.0088.
- [27] D.R.G. Mitchell, G. Triani, D.J. Attard, K.S. Finnie, P.J. Evans, C.J. Barbé, J. R. Bartlett, Atomic layer deposition of TiO₂ and Al₂O₃ thin films and nanolaminates, Smart Mater. Struct. 15 (1) (2006) S57–S64, https://doi.org/10.1088/0964-1726/15/1/010.
- [28] L. Yang, M. Fazio, G. Vajente, A. Ananyeva, G. Billingsley, A. Markosyan, R. Bassiri, M.M. Fejer, C.S. Menoni, Structural evolution that affects the room-temperature internal friction of binary oxide nanolaminates: implications for ultrastable optical cavities, ACS Appl. Nano Mater. 3 (12) (2020) 12308–12313, https://doi.org/ 10.1021/acsanm.0c02798.
- [29] M.C. Cisneros-Morales, C.R. Aita, Crystallization, metastable phases, and demixing in a hafnia-titania nanolaminate annealed at high temperature, J. Vac. Sci. Technol. Vac. Surf. Films 28 (5) (2010) 1161–1168, https://doi.org/10.1116/ 1.3474973.
- [30] N.S. Gluck, H. Sankur, J. Heuer, J. DeNatale, W.J. Gunning, Microstructure and composition of composite SiO₂/TiO₂ thin films, J. Appl. Phys. 69 (5) (1991) 3037–3045, https://doi.org/10.1063/1.348591.
- [31] M. Magnozzi, S. Terreni, L. Anghinolfi, S. Uttiya, M.M. Carnasciali, G. Gemme, M. Neri, M. Principe, I. Pinto, L.-C. Kuo, S. Chao, M. Canepa, Optical properties of amorphous SiO₂-TiO₂ multi-nanolayered coatings for 1064-Nm mirror technology, Opt. Mater. 75 (2018) 94–101, https://doi.org/10.1016/j.optmat.2017.09.043.
- [32] J. Wang, J. Ge, H. Hou, M. Wang, G. Liu, G. Qiao, Y. Wang, Design and sol-gel preparation of SiO2/TiO2 and SiO2/SnO2/SiO2-SnO2 multilayer antireflective coatings, Appl. Surf. Sci. 422 (2017) 970–974, https://doi.org/10.1016/j. apsusc.2017.06.133.
- [33] S.M. George, Atomic layer deposition: an overview, Chem. Rev. 110 (1) (2010) 111–131, https://doi.org/10.1021/cr900056b.
- [34] V. Miikkulainen, M. Leskelä, M. Ritala, R.L. Puurunen, Crystallinity of inorganic films grown by atomic layer deposition: overview and general trends, J. Appl. Phys. 113 (2) (2013), https://doi.org/10.1063/1.4757907.
- [35] M. Weber, A. Julbe, A. Ayral, P. Miele, M. Bechelany, Atomic layer deposition for membranes: basics, challenges, and opportunities, Chem. Mater. 30 (21) (2018) 7368–7390, https://doi.org/10.1021/acs.chemmater.8b02687.
- [36] J. Peng, R. Zierold, Atomic Layer Deposition of Materials. Encyclopedia of Condensed Matter Physics, Elsevier, 2024, pp. 716–728, https://doi.org/10.1016/ B978-0-323-90800-9.00206-7.
- [37] S.K. Kim, G.J. Choi, J.H. Kim, C.S. Hwang, Growth behavior of Al-doped TiO2 thin films by atomic layer deposition, Chem. Mater. 20 (11) (2008) 3723–3727, https:// doi.org/10.1021/cm800280t.
- [38] S.K. Kim, G.J. Choi, C.S. Hwang, Controlling the composition of doped materials by ALD: a case study for Al-doped TiO2 films, Electrochem. Solid-State Lett. 11 (7) (2008) 27–30, https://doi.org/10.1149/1.2909768.
- [39] L. Han, Z. Chen, High-quality thin SiO 2 films grown by atomic layer deposition using tris(Dimethylamino)Silane (TDMAS) and ozone, ECS J. Solid State Sci. Technol. 2 (11) (2013) N228–N236, https://doi.org/10.1149/2.001312jss.
- [40] V.Yu Vasilyev, Review—atomic layer deposition of silicon dioxide thin films, ECS J. Solid State Sci. Technol. 10 (5) (2021) 053004, https://doi.org/10.1149/2162-8777/abffab.
- [41] M. Leskelä, E. Salmi, M. Ritala, Atomic layer deposited protective layers, Mater. Sci. Forum 879 (2017) 1086–1092, https://doi.org/10.4028/www.scientific.net/ MSF.879.1086.
- [42] D. Bae, S. Kwon, J. Oh, W.K. Kim, H. Park, Investigation of Al2O3 diffusion barrier layer fabricated by atomic layer deposition for flexible Cu(In,Ga)Se2 solar cells, Renew. Energy 55 (2013) 62–68, https://doi.org/10.1016/j.renene.2012.12.024.
- [43] T. Tokuda, Crystallization of quartz at high temperatures, Bull. Chem. Soc. Jpn. 30 (7) (1957) 692–693, https://doi.org/10.1246/bcsj.30.692.
 [44] U. Holzwarth, N. Gibson, The Scherrer equation *versus* the "Debye-Scherrer"
- [44] U. Holzwarth, N. Gibson, The Scherrer equation versus the "Debye-Scherrer Equation, Nat. Nanotechnol. 6 (9) (2011) 534, https://doi.org/10.1038/ nnano.2011.145. –534.
- [45] Yasaka, M. X-Ray thin-film measurement techniques. 2010.
- [46] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D.J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, Fiji: an open-source platform for biological-image analysis, Nat. Methods 9 (7) (2012) 676–682, https://doi.org/ 10.1038/nmeth.2019.
- [47] H.-J. Gossmann, E.F. Schubert, Delta doping in silicon, Crit. Rev. Solid State Mater. Sci. 18 (1) (1993) 1–67, https://doi.org/10.1080/10408439308243415.
 [48] J. Zhang, P. Zhou, J. Liu, J. Yu, New understanding of the difference of
- [48] J. Zhang, P. Zhou, J. Liu, J. Yu, New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂, Phys. Chem. Chem. Phys. 16 (38) (2014) 20382–20386, https://doi.org/10.1039/c4cp02201g.
- [49] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Prog. Solid State Chem. 32 (1–2) (2004) 33–177, https://doi.org/10.1016/j. progsolidstchem.2004.08.001.
- [50] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, Understanding TiO2photocatalysis: mechanisms and Materials, Chem. Rev. 114 (19) (2014) 9919–9986, https://doi.org/10.1021/cr5001892.

Tuning the Crystallization Temperature of Titanium Dioxide Thin Films by Incorporating Silicon Dioxide *via* Supercycle Atomic Layer Deposition

Supporting Information

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Figure S1. XRR patterns before and after annealing plotted individually for each nanolaminate sample. The $TiO_2:SiO_2$ ratio was varied from 1:1 (a, c, e) to 1:4 (b, d, f) while supercycle numbers of 1 (a, b), 5 (c, d), and 10 (e, f) were applied.



Figure S2. *Ex situ* XRD measurements of SiO₂-doped TiO₂ thin films with varied SiO₂ content. Peak position of anatase phase ('A', COD 1010942) are marked by the grey dashed lines. Patterns are shown for SiO₂ contents of (a) 0 %, (b) 1 %, (c) 2.5 %, (d) 5 %, and (e) 10 %. Other peaks are caused by the substrate materials, i.e., Si, SiO₂, and Al₂O₃.



Figure S3. Spectroscopic ellipsometry of SiO₂-doped TiO₂ films deposited on Al₂O₃-functionalized substrates demonstrate an increase of the refractive index n at 632.8 nm after thermal annealing.



Figure S4. XRR patterns of SiO₂-doped TiO₂ thin films containing (a) 1 %, (b) 5 %, and (c) 7.5 % SiO₂. The data was measured before and after annealing.



Figure S5. Atomic force microscope images of SiO_2 -doped TiO_2 films before and after thermal annealing revealing a surface roughening after annealing.

7.2. Publication II

How Surface Treatments of Anodic Aluminum Oxide Alter the Photocatalytic Performance

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in preparation

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How Surface Treatments of Anodic Aluminum Oxide Alter the Photocatalytic Performance

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ABSTRACT

Nanostructuring is nowadays of great interest based on unique materials properties, increased surface areas and thus, superior performance while simultaneously reducing the utilized material amount. However, directly nanostructuring functional materials themselves is often technologically challenging. Hence, nanostructured substrates such as anodic aluminum oxide (AAO) can serve as templates for depositing the desired active material onto them. Chemically stable templates are crucial to accurately assess the performance of the functional materials. Since AAO structures contain electrolyte ions incorporated into the aluminum oxide matrix during the

anodization process, their chemical stability is influenced by the processing of the templates. Herein, functionalization of post-anodization modified AAO templates with photocatalyst materials by atomic layer deposition (ALD) is studied to assess the influence of the templates' chemical stability on the photocatalytic properties. Specifically, titanium dioxide as a chemically stable photocatalyst is not affected by the post-anodization treatment of the AAO structure. In contrast, the photocatalytic performance of AAO structures functionalized with iron (III) oxide as an example for an inherent chemically instable photocatalyst depends on the chemical stability of the template. Furthermore, the effect of different post-anodization modifications of AAO structures on their photocatalytic performance and surface chemistry is investigated. Treatments with hydrogen peroxide or phosphoric acid can stabilize the photocatalytic performance of the AAO templates over consecutive measurements. X-ray photoelectron spectroscopy measurements indicate that such stabilization is caused by alterations of the AAO surface chemistry. This work highlights the importance of chemically stable materials as templates for exploring the properties of new functional materials such as photocatalysts.

INTRODUCTION

Achieving high functionality while minimizing material usage is a pivotal aim in materials science.^{1,2} Nanostructuring has emerged as a key strategy to meet this goal, enabling the tailoring of materials at the nanoscale to expand their functionalities.^{2,3} Moreover, nanostructuring leads to significantly enlarged surface areas while the material consumption is simultaneously reduced.^{2–5} Accordingly, nanostructured materials are often utilized either directly or as templates for electronics, photonics, (photo-)catalysis, biomedicine, energy storage and conversion, environmental applications, and magnetic devices.^{2,3,6–8} To identify the properties of functional

materials deposited onto nanostructured templates, it is crucial to use a chemically stable structure as template.^{9,10} Specifically, the template should not decompose or undergo any other chemical changes during the applications as it will be functionalized with an active material.

One prominent example of such nanostructured templates is anodic aluminum oxide (AAO) which has been used for many different applications such as optics, sensing, catalysis, energy storage, or electronics over the past years.^{6,11–14} AAO consists of cylindrical pores inside an aluminum oxide (alumina, Al₂O₃) matrix produced by an electrochemical oxidation also known as anodization.¹³ The pores are aligned perpendicular to the surface and are highly ordered in a hexagonal pattern due to a self-assembly process. AAO provides a large flexibility as template structure, because the pore size, pore morphology, layer thickness, and surface functionalization can be widely tailored within or after the anodization.^{6,13,14} Furthermore, due to the porous nature, AAO templates feature high surface areas which are beneficial for many applications. Anodization is accompanied by contamination of the alumina matrix through the incorporation of electrolyte ions and by formation of oxygen vacancies in the alumina.^{15–19} The contamination percentage is increasing from the inner side of the pores towards the outer part, i.e., the one in contact with the electrolyte during anodization. These contaminations cannot be avoided, but they can cause undesired properties of the alumina such as high photoluminescence intensity.¹⁸⁻²² Moreover, the contaminations could be dissolved by and react with aqueous solutions which are applied, for example, to functionalize the AAO surface. Such dissolution process alters the intrinsic properties of AAO as a template material. Oxygen vacancies present in the alumina matrix are also known to cause photoluminescence of the structure.^{18–20,22,23} Since AAO is often applied as a template structure and thus coated with functional materials, it is essential that the alumina surface is stable against these treatments.^{8,24,25} On the one hand, the surface chemistry has to be modified by depositing a

material of choice onto the AAO template. On the other hand, the surface chemistry should not be altered in a way that affects the properties of the AAO template structure. Chemically stable templates allow for investigating functional materials – even those which are prone to decompose during their application. The influence of AAO's surface chemistry onto its applicability as template structure can for example be studied for photocatalytic applications. Photocatalysis is based on the induction of chemical reactions by irradiation with solar light and it offers a plethora of possible applications such as water or air purification, hydrogen production, self-cleaning surfaces, or energy conversion.^{4,26–30} Since photocatalytic reactions occur at the surface of materials, an increment of the surface area corresponds to an increase of the reactions per time period leading to a more efficient process.^{2–5} Thus, AAO structures provide great potential as template structure for photocatalysts based on their high surface area, comparable inexpensive fabrication, and versatile functionalization possibilities.

This study focuses on the influence of different post-anodization treatments of AAO templates on their photocatalytic properties in order to identify modifications that result in stable AAO templates for this example application. Post-anodization treatments – namely immersion in hydrogen peroxide (H₂O₂) and immersion in phosphoric acid (H₃PO₄) – are applied for testing templates coated with titanium dioxide (TiO₂) or iron (III) oxide (Fe₂O₃) as a photocatalyst and are compared to as-prepared AAO templates functionalized with the respective photocatalysts. The photocatalyst materials are coated onto the AAO structures by atomic layer deposition (ALD). Due to sequential, self-limiting reactions between precursors in the gas phase, and solid substrate surfaces, ALD allows for complete conformal coating of the substrate – here AAO – while simultaneously controlling the deposited film thickness in the sub-nanometer range.^{31–34} TiO₂ coated structures show stable photocatalytic performances over three measurements for all investigated post-anodization modifications. In contrast, the photocatalytic activity of Fe₂O₃functionalized samples is stable for AAO templates immersed in H₂O₂ or H₃PO₄ before the ALD coating but decreases within the subsequent measurements for the as-prepared AAO template. This behavior is probably caused by modifications of the AAO surface chemistry depending on the respective post-anodization treatment. To gain a deeper understanding of the evolution of AAO's surface chemistry during photocatalysis measurements, the photocatalytic performances of postanodization modified AAO structures without additional ALD coating were investigated and further surface modifications were tested. In detail, immersion of AAO samples into water (H₂O), H₂O₂, or H₃PO₄, as well as thermal annealing, or exposure to trimethylaluminum (TMA) are applied as post-anodization treatments and compared to an as-prepared AAO structure. The effect of the different modifications on the AAO is determined by photocatalytic degradation of an organic dye as model pollutant of water and by X-ray photoelectron spectroscopy. This characterization sheds light on changing surface chemistry of AAO samples by post-anodization modifications which is essential to apply such structures as templates for functional materials.

EXPERIMENTAL SECTION

2.1. Materials. Aluminum (Al) chips (99.9997 %, 0.5 cm thickness, 2 cm diameter) were received from Goodfellow GmbH (Germany). Perchloric acid (HClO₄, CAS 7601-90-3), ethanol (C₂H₅OH, EtOH, CAS 64-17-5), isopropyl alcohol (C₃H₈O, IPA, CAS 67-63-0), oxalic acid (H₂C₂O₄, CAS 144-62-7), chromium (VI) oxide (CrO₃, CAS 1333-82-0), phosphoric acid (H₃PO₄, CAS 7664-38-2), methylene blue (C₁₆H₁₈ClN₃S, MB, CAS 122965-43-9), hydrogen peroxide (H₂O₂, CAS 7722-84-1), and titanium tetraisopropoxide (TTIP, CAS 546-68-9) were purchased from Sigma Aldrich (Germany) and used as received. Milli-Q water (> 16 M Ω cm, H₂O) was utilized as deionized water (H₂O) as ALD precursor and to prepare aqueous solutions. Ferrocene (C₁₀H₁₀Fe, Cp₂Fe, CAS 102-54-5) was supplied by Alfa Aesar (Germany) and trimethylaluminum (C₃H₉Al, TMA, CAS 75-24-1) was purchased from Strem Chemicals (France). Nitrogen (6.0) and oxygen (5.0) were supplied by SOL (Germany) and Westfalen (Germany), respectively.

2.2. Fabrication of AAO. AAO templates were produced by two-step anodization of aluminum. Prior to anodization, the Al chips were cleaned by immersion in IPA and H₂O for 30 min, respectively, and were dried under nitrogen stream. The cleaned chips were electropolished in a HClO₄/EtOH solution (1:4, v:v) at 20 V and 5 °C for 3 min. The first anodization step was conducted in aqueous H₂C₂O₄ (0.3 M) at 40 V and 6 °C for 20 h. Afterwards, the formed nanoporous Al₂O₃ film was removed by etching in aqueous H₂CrO₄/H₃PO₄ solution (1.8 wt%/ 6 wt%) at 45 °C for 24 h. The second anodization step was conducted under the same conditions as the first one except the duration which was set to 10 h.

2.3. Surface Modification of AAO. Subsequent to the anodization, AAO samples were treated by different surface modification approaches. One sample was kept as-prepared without further treatment and one was annealed at 450 °C for 1 h on a hotplate. Another AAO sample was exposed to 15 TMA pulses at 150 °C in an ALD system. The pulses consisted of 0.05 s pulse, 60 s exposure, and 90 s purge duration and were operated in stop-flow mode. One sample was immersed into H₂O and afterwards dried with N₂ stream. Another sample was immersed into H₂O₂ (30 wt%) for 24 h and H₂O for another 24 h before it was dried under N₂ stream and one sample was immersed into H₃PO₄ (5 wt%) at 45 °C for 1 min.

For functionalizing AAO samples with a photocatalyst, one as-prepared sample, one sample immersed in H₂O₂ (30 wt%) for 24 h and H₂O for 24 h, and one sample exposed to H₃PO₄ for 1 min were coated with TiO₂ or Fe₂O₃ and an ultra-thin Al₂O₃ protection layer by ALD, respectively. TiO₂ coating was conducted in a GEMStar XTTM (Arradiance, USA) ALD reactor under stop-flow conditions at 150 °C and a N_2 carrier gas flow of 30 sccm. TTIP heated to 80 °C and H₂O at room temperature were pulsed for 0.1 s and 0.05 s, respectively. Exposure and purge times of 60 s and 120 s were applied for both half reactions. 96 cycles were applied to obtain a TiO₂ thickness of 5 nm. Cp₂Fe at 100 °C and O₃ at room temperature were used as precursors in the Fe₂O₃ process which was operated in stop-flow mode at 200 °C in a home-built ALD system. Each Cp₂Fe half-cycle consisted of 2 s precursor pulse, 60 s exposure, and 90 s pumping of the system. The O₃ half-cycle was repeated twice within one complete ALD cycle and 0.08 s precursor pulse, 30 s exposure, and 90 s pump time were applied. Each sample was exposed to 179 cycles for Fe₂O₃ deposition resulting in a coating thickness of 5 nm. Subsequently, the samples were coated with an ultra-thin film of Al₂O₃ as protection layer to prevent photocorrosion of the Fe₂O₃ film.35 Al₂O₃ deposition was conducted in stop-flow mode at 150 °C using TMA and H₂O (both at room temperature) as precursors. Both half-cycles consisted of 0.05 s precursor pulse, 60 s exposure, and 90 s pumping. The samples were coated by 2 cycles Al₂O₃.

2.4. Composition Analysis of Modified AAO.

XPS measurements were conducted in a Theta Probe XPS instrument (Thermo Fisher Scientific Inc., USA) and the XPS data analysis was performed using the CasaXPS software package. A pass energy of 50 eV and 200 eV and a step size of 0.1 eV and 0.5 eV were applied for core level scans and survey spectra, respectively. XPS spectra calibration was based on the C-C component in the

C1s XPS spectrum at 284.8 eV. The XPS spectra were deconvoluted by fitting a Shirley background and asymmetric LA line shapes, LA(50).

2.5. Photocatalytic Characterization.

Photocatalytic characterization was carried out by analyzing the photocatalytic degradation of methylene blue (MB) as a model pollutant of water. A sample was mounted into a home-built photocatalysis cell composed of polyether ether ketone (PEEK) and a soda-lime glass window. The sample was exposed to a MB solution (2.5 mg/l, 8 ml) which also contained H_2O_2 (200 mM) and kept in darkness for one hour to establish the adsorption-desorption equilibrium of the molecules at the samples surface. Subsequently, the system was irradiated with UV-visible light generated by an Euromex LE.5211 halogen lamp. The absorbance of the dye solution was analyzed every five minutes by UV/Vis spectroscopy. For this, 1 ml of the MB solution was pipetted from the photocatalysis cell into a cuvette, analyzed in the spectrometer, and pipetted back. During that time, illumination of the photocatalysis cell was blocked to prevent degradation within this analysis period. Lambert-Beer's law was applied to calculate the MB concentration based on the measured absorbance at every point in time. The photocatalytic reaction is assumed to occur *via* the Langmuir-Hinshelwood mechanism. Since the MB concentration is lower than 10^{-3} mol L⁻¹, the reaction rate can be simplified to a pseudo-first-order kinetics law:

$$\ln\left(\frac{c}{c_0}\right) = -k \cdot t$$

Here, c denotes the concentration of the MB solution at a given time t, c_0 describes the concentration at the beginning of the measurement (t=0 h), and k is the apparent photocatalytic rate constant which is a measure for the photocatalytic activity of a sample. The photocatalytic
MB degradation measurement was repeated three times per sample to monitor changes of the activity over consecutive measurements.

RESULTS AND DISCUSSION

3.1. Fabrication and Photocatalytic Characterization of ALD-coated AAO.

Highly ordered AAO structures featuring a pore length of about 35 μ m and a pore diameter of 25 nm are fabricated by anodization. Herein, the photocatalytic performance of post-anodization treated AAO structures is assessed by the degradation of MB as a model pollutant of water. ALD-coating of photocatalyst materials onto AAO structures exposed to hydrogen peroxide (H₂O₂) or phosphoric acid (H₃PO₄) after the anodization reveals the importance of the post-anodization treatment for the photocatalytic performance and stability of the photocatalyst. On the one hand, a chemically stable photocatalyst – here TiO₂ – is not significantly affected by the post-anodization treatment. On the other hand, an inherent chemically instable photocatalyst – here Fe₂O₃ – is known to get degraded through redox reactions and photocorrosive processes and shows decreasing performance over subsequent measurements.

TiO₂-functionalization of AAO structures by ALD demonstrates stabilization of the photocatalytical properties as depicted in **Figures 1a and 1b**. The 5 nm thick TiO₂ coatings deposited onto the AAO samples are chemically very stable and thus, it is expected that they are not strongly influenced by the underlying template.³⁶ Figures 1a and 1b show stable photocatalytic activities of TiO₂ functionalized AAO structures during three consecutive measurements for all three investigated templates, namely as-prepared AAO, H₂O₂-treated AAO, and H₃PO₄-treated

AAO. The mean activities of as-prepared and H_2O_2 treated samples are very similar (1.18 ± 0.05 h⁻¹ and 1.17 ± 0.04 h⁻¹). However, the structure immersed in H_3PO_4 solution features a lower photocatalytic activity of 1.04 ± 0.02 h⁻¹.

When Fe₂O₃ is utilized as photocatalyst material on different AAO templates, the photocatalytic performance depends on the post-anodization treatment as shown in Figures 1c and 1d. To prevent photocorrosion of the Fe₂O₃ layer at the surface in contact with the dye solution, an ultra-thin Al₂O₃ coating of 2 ALD cycles was deposited onto the structures.³⁵ By analyzing and comparing the data from Fe₂O₃ to TiO₂, three findings have been revealed: First, the photocatalytic performance of Fe₂O₃-functionalized AAO is very stable over three measurements for structures treated with H₂O₂ or H₃PO₄ featuring mean activities of 1.16 ± 0.02 h⁻¹ and 1.30 ± 0.04 h⁻¹, respectively. In contrast, a strong decrease of the activity after the first measurement is observed for an as-prepared AAO template. This performance loss resembles in a high standard deviation (1.23 ± 0.14 h⁻¹). Second, and at the same time, the mean activity for H₃PO₄-treated AAO functionalized with Fe₂O₃ is significantly higher than for a treatment with H₂O₂. Third, this observation is in contrast to the TiO₂-coated AAOs, where the H₃PO₄-treatment reveals the lowest activity.



Figure 1. Photocatalytic performances of post-anodization modified AAO samples that were afterwards coated with a photocatalyst by ALD. (a) TiO₂-functionalized samples show stable photocatalytic activities for all three post-anodization treatments. (b) Coating Fe₂O₃ as a chemically less stable photocatalyst onto AAO structures demonstrates a dependence of the photocatalytic performance stability on the previously applied treatment.

Electrolyte ions present in the Al₂O₃ matrix of the as-prepared AAO can potentially react with the surface when activated by charge carriers of the photocatalytic processes. In this way, the photocatalyst is chemically altered and the photocatalytic activity is influenced. Exploring new photocatalytic or other functional materials coated onto nanostructured templates by ALD necessitates a chemically stable and known template to accurately characterize the materials' properties. Hence, we studied the influence of common post-anodization treatments on the photocatalytic performance of AAO templates to obtain a more detailed understanding of the surface chemistry changes.

3.2. Photocatalytic Performance and Compositional Characterization of Surface Modified AAO.

The influence of five different post-anodizations of AAO structures on their photocatalytic performance is investigated to identify treatments which stabilize the surface chemistry for

application of AAO samples as templates. Taking frequent treatments of AAO structures into account, we assessed the effects of AAO thermal annealing, exposure to trimethylaluminum (TMA), and immersion into water H₂O, H₂O₂, or H₃PO₄ compared to an as-prepared AAO structure. While the photocatalytic activity is decreasing for an as-prepared AAO sample (Figure 2a) within three consecutive measurements $(1.05 \pm 0.12 \text{ h}^{-1})$, it can be stabilized by certain postanodization treatments. Decreasing photocatalytic activities in consecutive measurements are typically caused by the change of the chemical state of the structures' surface or by structural decomposition.^{37–39} Since Al₂O₃ is a chemically stable material and no additional photocatalyst material is applied here, saturation or removal of contamination electrolyte ions are possible reasons for the decreasing activity. These species provide unsaturated sites within the alumina matrix and can therefore lead to undesired side-reactions where they react with other compounds or they can be removed from the structure by dissolution in aqueous media as discussed above. The side-reactions occur until all accessible contaminations have either reacted to stable species or are removed from the Al₂O₃ matrix, for example by dissolving them in a pore filling medium. For TMA pulse treatment, the photocatalytic activities still show high variance within three measurements $(1.01 \pm 0.14 \text{ h}^{-1})$. The H₂O treated AAO structure exhibits a clearly decreasing photocatalytic activity within consecutive measurements as also indicated by an increased standard deviation (0.97 \pm 0.18 h⁻¹). AAO samples immersed in H₂O₂ for 24 h or in H₃PO₄ for 1 min show the most stable photocatalytic performance over three measurements. Although the activity variation is slightly larger for the H₂O₂ treated samples $(1.11 \pm 0.05 \text{ h}^{-1})$ than for the H₃PO₄ treated sample $(0.98 \pm 0.02 \text{ h}^{-1})$, its mean activity is higher.



Figure 2. Photocatalytic performances of post-anodization modified AAO samples. (a) The photocatalytic activities remain constant or decrease over three consecutive measurements depending on the applied treatment. (b) Differences in the stability of the photocatalytic performances are also reflected in the mean value and standard deviation of the activity k.

The different photocatalytic activities probably originate from the different surface chemistry after post-anodization treatments corresponding to similar results which have previously been reported for TiO2.^{40,41} Based on this assumption, we investigated surface chemistry variations in detail with XPS measurements of the AAO structures after post-anodization treatments. These XPS measurements demonstrate changes of the present surface groups and their ratios depending on the respective post-anodization treatment (Figure 3). An as-prepared AAO sample (Figure 3a) features Al-OH groups (76.2 eV) and O-Al-O bonds (74.3 eV) at the Al_{2p} peak corresponding to the Al₂O₃ matrix and expected hydroxy groups at the surface.⁶ Different types of carbon-oxygen (286.0 eV and 288.5 eV) and carbon-carbon and carbon-hydrogen bonds (both 274.8 eV) can be identified at the C_{1s} peak which are probably caused by incorporated oxalate ions. These ion species originate from the inherent structure of the produced AAO, i.e., electrolyte ions built into the aluminum oxide during the anodization process.^{13,17} Hence, O-C=O, C-C, and C-H bonds at the AAO surface identified by the XPS measurements can be attributed to residues of oxalic acid (H₂C₂O₄) which was used as electrolyte herein. Moreover, HO-Al, O-C (both 532.9 eV), Al-O-Al, and O=C (both 531.4 eV) bonds are observed for the O_{1s} peak of the as-prepared structure. Note that some bonds cannot be distinguished as their peak energies are too close to each other. The

identified peak positions for all samples are summarized in **Table S1** in the Supporting Information.

Post-anodization treatments can reduce the amount of the contaminations as revealed by the XPS spectra. Thermal annealing predominantly removes -OH groups and oxalate ions from the Al-OH surface as shown in Figure 3b. Such behavior is in agreement with existing literature about the influence of annealing on the surface of Al₂O₃.^{17,20,22} Thermal annealing was previously reported of being capable to reduce PL intensities of AAO samples due to the thermal decomposition of the incorporated electrolyte ions during the annealing.^{20,22} Such treatment affects the complete alumina matrix and thus, results in a large amount of electrolyte decomposition. However, here the -OH groups are not completely removed which might be caused by the comparable low annealing temperature of 450 °C. For example, Han et al. reported that annealing temperatures of 500 °C are necessary to remove -OH groups.²² Although the subpeaks of the C_{1s} peak and the Al-OH contents are reduced for the sample annealed at 450 °C for 1 h, the photocatalytic activity could not be stabilized but instead shows a lower mean value. AAO structures exposed to TMA pulses reveal a strong reduction of the Al-OH signal which is caused by the reaction of TMA molecules with the -OH groups from the AAO surface to Al₂O₃ (Figure 3c). Since the gaseous precursor molecules can only react with functional groups located at the surface, only electrolyte ions being present at the surface can be saturated. Correspondingly, the Al-OH peak decreases but does not disappear. Also oxalate ions present at the surface might react with TMA forming aluminum oxalate complexes resembled by increased Al-O-Al contents. A reaction between oxalate ions and TMA molecules could result in decreasing O-C=O peak intensities at the structures' surface. The inconsistent photocatalytic activities of the TMA treated AAO sample might be caused by the decreased Al-OH content while carbon contaminations are present at a

similar amount compared to the as-prepared sample. Immersing AAO samples in aqueous media could dissolve oxalate ions incorporated into the AAO structure during anodization. XPS spectra of an AAO structure soaked in H₂O demonstrate a decreased Al-OH signal compared to the asprepared sample (Figure 3d). Moreover, the O-C=O content and C-O bond signal are decreasing. We assume that the H₂O post-anodization treatment dissolves oxalic acid molecules which might then partially react with the AAO surface to form Al-oxalate. Remaining oxalic acid species might be physisorbed at the surface. It was previously reported that treatments in aqueous solutions can lead to the dissociation of incorporated electrolyte ions in anodized metal oxides.⁴¹ In this way, the amount of ions inside the AAO matrix gets reduced. A H₂O treatment might be capable of removing electrolyte ions from the alumina matrix by dissolution, but the ions then present in solution cannot be further decomposed or chemically bound. Significant decrease of the photocatalytic performance of H₂O immersed AAO structures over consecutive measurements could be caused by the partial dissolution of oxalate species from the matrix during the postanodization treatment. However, since these species could not be decomposed in the H₂O treatment, they could have physisorbed at the surface and are degrading during the photocatalytic reaction resembled by decreasing activities with increasing measurement numbers.

If the aqueous solution contains oxidizing species such as H_2O_2 , the removed electrolyte ions can be further decomposed. The destruction of oxalate species by H_2O_2 results in the complete oxidation of the ions to carbon dioxide (CO₂).⁴² As depicted in Figure 3g, immersion of AAO into H_2O_2 removes Al-OH groups from the surface as indicated by the Al_{2p} peak profile. Moreover, the content of O-C=O groups decreases while Al-O-Al groups increase (C_{1s} and O_{1s} peaks). Oxalic acid species are likely dissolved in this treatment and could potentially react with Al-OH groups at the surface to form stable Al-oxalate complexes explaining the increasing Al-O-Al content. In addition, H₂O₂ could act as electron acceptor and thus accelerate the formation of Al-oxalate. The photocatalysis activity stabilization for the H₂O₂ treatment is probably caused by the saturation of surface groups and removal of electrolyte ions from the surface as observed in the XPS measurements. The proposed formation of Al-oxalate results in a stable surface chemistry which is not affected by the solution utilized in the photocatalysis measurements or the photocatalytic reactions themselves. Moreover, no additional washing out of electrolyte ions can occur because the ions are already removed, decomposed, or saturated after the post-anodization treatments. H₃PO₄ is often applied for pore-widening of AAO structures and thus, it is known that it selectively widens the pores by etching alumina.^{16,17} During the alumina dissolution, this etching process simultaneously releases the incorporated electrolyte species from the structure.¹⁶ Since aluminum ions are released into the solution by the etching, it is possible that they react with the dissolved electrolyte ions to form side-products such as aluminum oxalate. Figure 3f demonstrates decreasing peaks of O-C=O, C-O, and C-C/C-H bonds and a slight decrease of the OH-Al/O-C peak at 533.6 eV compared to the as-prepared sample. The latter one is still higher than for the H₂O and H₂O₂ treatment. Furthermore, the peak at 531.6 eV corresponding to Al-O-Al or O=C groups is increased compared to the as-prepared structure but lower than the for the other aqueous treatments. Since this peak energy is also characteristic for O=P, O-P, and Al-O-P groups, it cannot be unambiguously assigned to one of these groups for the H₃PO₄ treatment. Besides formation of Al-oxalate complexes, reactions of phosphoric acid with Al ions are also possible leading to the formation of Al-phosphate explaining peak increments in the XPS spectra. The Al_{2p} peak shows a similar ratio of both sub-peaks which was not observed for any of the other treatments. This is also caused by the additional groups featuring the same peak energies, namely Al-O-P at 76.5 eV as Al-OH and AlPO₄ at 74.4 eV as Al-O-Al groups. The additional P_{2p} peak also reveals the presence

of phosphor containing groups. Specifically, H_3PO_4 at 136.3 eV and $(PO_4)^{3-}$ and P-O-Al groups at 134.2 eV are detected. For samples immersed in H_3PO_4 , formation of phosphor containing aluminum groups might reduce the overall photocatalytic activity due to changes in the dye adsorption at the AAO surface. Hence, these structures feature a lower mean activity after three photocatalysis measurements. However, the activity variation is even lower than for the H_2O_2 treated sample which probably originates from stabilization of the surface chemistry by formation of Al-phosphate groups.



Figure 3. XPS measurements reveal the influence of different post-anodization treatments on the surface chemistry of AAO structures. The AAO samples are (a) as-prepared, (b) annealed at 450 °C for 1 h, (c) treated with 15 TMA pulses in an ALD system, (d) exposed to H_2O for 24 h, (e) immersed into H_2O_2 for 24 h followed by H_2O for 24 h, and (f) soaked into 5 wt% H_3PO_4 for 1 min.

The photocatalysis measurements of ALD-functionalized AAO structures presented in Figure 1 can be well explained with the results from the XPS study. TiO2-coating of as-prepared and postanodization surface modified AAO samples show stable photocatalytic activities over three measurements. The variations between the first and third measurement are very small and all tested templates benefit from the TiO₂ functionalization by exhibiting increased photocatalytic activities compared to the uncoated counterparts depicted in Figure 2. Hence, the photocatalytic performance is improved with TiO₂ coating, but the ratio when comparing the individual treatments remains constant - as-prepared and H₂O₂ modified templates demonstrate similar photocatalytic activities but the H₃PO₄ treated sample shows a lower activity. This is in good agreement with the high chemical stability of TiO2.³⁶ Contrary, the photocatalytic performance of Fe₂O₃-functionalized AAO structures is strongly influenced by the post-anodization surface treatment. As discussed above, as-prepared templates coated with Fe₂O₃ show decreasing activities over consecutive measurements which might be caused by the reaction of electrolyte ions in the as-prepared AAO structure that react with Fe₂O₃ when activated by charge carriers during the photocatalytic processes. This could induce chemical modification of Fe₂O₃ at the interface to the AAO template which could result in an activity decline over multiple measurements. The constant photocatalytic activities of H2O2 and H3PO4-treated AAO structures are maintained for Fe2O3 functionalization. Hence, improving the chemical stability of the templates' surface is beneficial for studying chemically less stable photocatalysts such as Fe₂O₃. Depositing Fe₂O₃ onto AAO templates modified with H₃PO₄ significantly boosts the photocatalytic performance compared to functionalizing a H₃PO₄ treated AAO structure with TiO₂. Coating Fe₂O₃ onto the treated AAO template might not only result in the growth of Fe₂O₃, but might also lead to the formation of iron phosphate or iron hydroxy phosphate compounds based on the presence of phosphate groups at the interface between the surface modified AAO template and the ALD prepared Fe_2O_3 layer.^{43–45} These materials also exhibit good photocatalytic activities as identified by previous studies.^{43–48} Local formation of iron phosphate or iron hydroxy phosphate at the AAO/Fe₂O₃ interface might explain the significant performance increase when H₃PO₄-treated AAO templates are functionalized with Fe₂O₃ instead of TiO₂.

As indicated by the XPS measurements, different post-anodization treatments reduce the content of Al-OH groups as well as C-O and C-H groups inherent in the AAO structures after fabrication. This study emphasizes that consideration of post-anodization treatments and their influence on the stability of AAO templates is crucial to ensure reliable and reproducible results. Consequently, these findings could further expand the utilization of AAO structures as templates for functional materials in the future.

CONCLUSION

To sum up, post-anodization treatments of AAO structures modify the surface chemistry as revealed by XPS measurements. Functionalizing post-anodization modified AAO samples with TiO_2 results in stable photocatalytic performances over consecutive measurements, because TiO_2 itself is a chemically very stable material. Thus, it is not influenced by the surface chemistry of the underlying AAO template. Contrary, the photocatalytic stability of AAO structures functionalized with Fe_2O_3 as a chemically less stable photocatalyst is significantly affected by the post-anodization treatment. Functional groups originating from electrolyte ions incorporated into the AAO matrix during anodization can be reduced by different treatments. Modifications of the

surface chemistry by these treatments determine the photocatalytic behavior of the respective AAO template structures. Especially the stability of the photocatalytic activity over consecutive measurements can be enhanced when aqueous solutions containing H_2O_2 or H_3PO_4 are utilized. These results could assist the characterization of new functional materials in the future by employing chemically stable nanostructured templates, such as post-anodization modified AAO.

Bibliography

- Chaikittisilp, W.; Yamauchi, Y.; Ariga, K. Material Evolution with Nanotechnology, Nanoarchitectonics, and Materials Informatics: What Will Be the Next Paradigm Shift in Nanoporous Materials? *Adv. Mater.* 2022, *34* (7), 2107212. https://doi.org/10.1002/adma.202107212.
- (2) Benelmekki, M. *Nanomaterials The Original Product of Nanotechnology*; Morgan & Claypool Publishers: San Rafael, California, 2019.
- (3) Kumar, N.; Kumbhat, S. *Essentials in Nanoscience and Nanotechnology*; John Wiley & Sons Inc.: Hoboke, New Jersey, 2016.
- (4) Ibhadon, A. O.; Fitzpatrick, P. Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts* **2013**, *3* (1), 189–218. https://doi.org/10.3390/catal3010189.
- (5) Beydoun, D.; Amal, R.; Low, G.; McEvoy, S. Role of Nanoparticles in Photocatalysis. J. Nanoparticle Res. 1999, 1 (4), 439–458. https://doi.org/10.1023/A:1010044830871.
- (6) Md Jani, A. M.; Losic, D.; Voelcker, N. H. Nanoporous Anodic Aluminium Oxide: Advances in Surface Engineering and Emerging Applications. *Prog. Mater. Sci.* 2013, 58 (5), 636–704. https://doi.org/10.1016/j.pmatsci.2013.01.002.
- (7) Lim, S. Y.; Hedrich, C.; Law, C. S.; Abell, A. D.; Blick, R. H.; Furlan, K. P.; Zierold, R.; Santos, A. Nanoporous Anodic Alumina Photonic Crystals for Sunlight Harvesting Applications: A Perspective. Sol. RRL 2022, 2200480. https://doi.org/10.1002/solr.202200480.
- (8) Lim, S. Y.; Law, C. S.; Liu, L.; Markovic, M.; Hedrich, C.; Blick, R. H.; Abell, A. D.; Zierold, R.; Santos, A. Electrochemical Engineering of Nanoporous Materials for Photocatalysis: Fundamentals, Advances, and Perspectives. *Catalysts* 2019, 9 (12), 988. https://doi.org/10.3390/catal9120988.
- (9) Jing, L.; Zhou, W.; Tian, G.; Fu, H. Surface Tuning for Oxide-Based Nanomaterials as Efficient Photocatalysts. *Chem. Soc. Rev.* **2013**, *42* (24), 9509–9549. https://doi.org/10.1039/c3cs60176e.
- (10) Sapoletova, N. A.; Kushnir, S. E.; Ulyanov, A. N.; Valeev, R. G.; Boytsova, O. V.; Roslyakov, I. V.; Napolskii, K. S. Effect of Post-Treatment on Photocatalytic Activity of Anodic Titania Photonic Crystals. *Opt. Mater.* 2023, 144, 114350. https://doi.org/10.1016/j.optmat.2023.114350.

- (11) Santos, A.; Kumeria, T.; Losic, D. Nanoporous Anodic Aluminum Oxide for Chemical Sensing and Biosensors. *TrAC - Trends Anal. Chem.* 2013, 44, 25–38. https://doi.org/10.1016/j.trac.2012.11.007.
- (12) Kumeria, T.; Santos, A.; Losic, D. Nanoporous Anodic Alumina Platforms: Engineered Surface Chemistry and Structure for Optical Sensing Applications. *Sens. Switz.* 2014, *14* (7), 11878–11918. https://doi.org/10.3390/s140711878.
- (13) Lee, W.; Park, S. J. Porous Anodic Aluminum Oxide: Anodization and Templated Synthesis of Functional Nanostructures. *Chem. Rev.* 2014, 114 (15), 7487–7556. https://doi.org/10.1021/cr500002z.
- (14) Santos, A. Nanoporous Anodic Alumina Photonic Crystals: Fundamentals, Developments and Perspectives. J. Mater. Chem. C 2017, 5 (23), 5581–5599. https://doi.org/10.1039/c6tc05555a.
- (15) Le Coz, F.; Arurault, L.; Datas, L. Chemical Analysis of a Single Basic Cell of Porous Anodic Aluminium Oxide Templates. *Mater. Charact.* 2010, 61 (3), 283–288. https://doi.org/10.1016/j.matchar.2009.12.008.
- (16) Han, H.; Park, S. J.; Jang, J. S.; Ryu, H.; Kim, K. J.; Baik, S.; Lee, W. In Situ Determination of the Pore Opening Point during Wet-Chemical Etching of the Barrier Layer of Porous Anodic Aluminum Oxide: Nonuniform Impurity Distribution in Anodic Oxide. ACS Appl. Mater. Interfaces 2013, 5 (8), 3441–3448. https://doi.org/10.1021/am400520d.
- (17) Santos, A.; Kumeria, T.; Wang, Y.; Losic, D. In Situ Monitored Engineering of Inverted Nanoporous Anodic Alumina Funnels: On the Precise Generation of 3D Optical Nanostructures. *Nanoscale* 2014, 6 (17), 9991–9999. https://doi.org/10.1039/C4NR01422G.
- (18) Xu, D.; Zhen, C.; Zhao, H. Microstructure and Photoluminescence Properties of Anodized Aluminum Oxide Films Treated by Argon Ion. *Ceram. Int.* **2021**, *47* (10), 14382–14389. https://doi.org/10.1016/j.ceramint.2021.02.017.
- (19) Gopal Khan, G.; Singh, A. K.; Mandal, K. Structure Dependent Photoluminescence of Nanoporous Amorphous Anodic Aluminium Oxide Membranes: Role of F+ Center Defects. *J. Lumin.* 2013, 134, 772–777. https://doi.org/10.1016/j.jlumin.2012.06.050.
- (20) Li, G. H.; Zhang, Y.; Wu, Y. C.; Zhang, L. D. Wavelength Dependent Photoluminescence of Anodic Alumina Membranes. J. Phys. Condens. Matter 2003, 15 (49), 8663–8671. https://doi.org/10.1088/0953-8984/15/49/034.
- (21) Gao, T.; Meng, G.; Zhang, L. Blue Luminescence in Porous Anodic Alumina Films: The Role of the Oxalic Impurities. J. Phys. Condens. Matter 2003, 15 (12), 2071–2079. https://doi.org/10.1088/0953-8984/15/12/324.
- (22) Han, Y.; Cao, L.; Xu, F.; Chen, T.; Zheng, Z.; Qian, K.; Huang, W. Quantitative Investigation in the Influence of Oxalic Impurities on Photoluminescence Properties of Porous AAOs. *Mater. Chem. Phys.* **2011**, *129* (3), 1247–1251. https://doi.org/10.1016/j.matchemphys.2011.06.008.
- (23) Li, G. H.; Zhang, Y.; Wu, Y. C.; Zhang, L. D. Photoluminescence of Anodic Alumina Membranes: Pore Size Dependence. *Appl. Phys. Mater. Sci. Process.* 2005, 81 (3), 627–629. https://doi.org/10.1007/s00339-004-2640-z.
- (24) Karunakaran, C.; Magesan, P.; Gomathisankar, P.; Vinayagamoorthy, P. Photocatalytic Degradation of Dyes by Al2O3-TiO2 and ZrO2-TiO2 Nanocomposites. *Mater. Sci. Forum* 2013, 734, 325–333. https://doi.org/10.4028/www.scientific.net/MSF.734.325.

- (25) Araoyinbo, A. O.; Derman, M. N.; Rahmat, A.; Rafezi Ahmad, K. Organic Dye Degradation with TiO2 Catalyst/AAO Template in the Presence of H2O2. *Adv. Mater. Res.* 2013, 795, 649–653. https://doi.org/10.4028/www.scientific.net/AMR.795.649.
- (26) Zhang, J.; Tian, B.; Wang, L.; Xing, M. *Photocatalysis Fundamentals, Materials and Applications*; Springer Open Ltd: Singapore, 2018.
- (27) Ahmed, S. N.; Haider, W. Heterogeneous Photocatalysis and Its Potential Applications in Water and Wastewater Treatment: A Review. *Nanotechnology* 2018, 29 (34). https://doi.org/10.1088/1361-6528/aac6ea.
- (28) Fox, M. A.; Dulay, M. T. Heterogeneous Photocatalysis. *Chem. Rev.* **1993**, *93* (1), 341–357. https://doi.org/10.1021/cr00017a016.
- (29) Mills, A.; Le Hunte, S. An Overview of Semiconductor Photocatalysis. J. Photochem. Photobiol. Chem. 1997, 108 (1), 1–35. https://doi.org/10.1016/S1010-6030(97)00118-4.
- (30) Herrmann, J. M. Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants. *Catal. Today* **1999**, *53* (1), 115–129. https://doi.org/10.1016/S0920-5861(99)00107-8.
- (31) George, S. M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110* (1), 111–131. https://doi.org/10.1021/cr900056b.
- (32) Bae, C.; Shin, H.; Nielsch, K. Surface Modification and Fabrication of 3D Nanostructures by Atomic Layer Deposition. *MRS Bull.* 2011, 36 (11), 887–897. https://doi.org/10.1557/mrs.2011.264.
- (33) Knez, M.; Nielsch, K.; Niinistö, L. Synthesis and Surface Engineering of Complex Nanostructures by Atomic Layer Deposition. *Adv. Mater.* 2007, *19* (21), 3425–3438. https://doi.org/10.1002/adma.200700079.
- (34) Cremers, V.; Puurunen, R. L.; Dendooven, J. Conformality in Atomic Layer Deposition: Current Status Overview of Analysis and Modelling. *Appl. Phys. Rev.* 2019, 6 (2), 021302. https://doi.org/10.1063/1.5060967.
- (35) Hedrich, C.; Burson, A. R.; González-García, S.; Vega, V.; Prida, V. M.; Santos, A.; Blick, R. H.; Zierold, R. Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide. *Adv. Mater. Interfaces* 2023, *10* (36), 2300615. https://doi.org/10.1002/admi.202300615.
- (36) Zhang, Y.; Jiang, Z.; Huang, J.; Lim, L. Y.; Li, W.; Deng, J.; Gong, D.; Tang, Y.; Lai, Y.; Chen, Z. Titanate and Titania Nanostructured Materials for Environmental and Energy Applications: A Review. *RSC Adv.* 2015, 5 (97), 79479–79510. https://doi.org/10.1039/c5ra11298b.
- (37) Li, J.; Wu, N. Semiconductor-Based Photocatalysts and Photoelectrochemical Cells for Solar Fuel Generation: A Review. *Catal. Sci. Technol.* 2015, 5 (3), 1360–1384. https://doi.org/10.1039/c4cy00974f.
- (38) Weng, B.; Qi, M.; Han, C.; Tang, Z.; Xu, Y. Photocorrosion Inhibition of Semiconductor-Based Photocatalysts: Basic Principle, Current Development, and Future Perspective. ACS Catal. 2019, 9, 4642–4687. https://doi.org/10.1021/acscatal.9b00313.
- (39) Chen, S.; Huang, D.; Xu, P.; Xue, W.; Lei, L.; Cheng, M.; Wang, R.; Deng, R. Semiconductor-Based Photocatalysts for Photocatalytic and Photoelectrochemical Water Splitting: Will We Stop with Photocorrosion ? J. Mater. Chem. Mater. Energy Sustain. 2020, 8, 2286–2322. https://doi.org/10.1039/C9TA12799B.
- (40) Trochowski, M.; Kobielusz, M.; Mróz, K.; Surówka, M.; Hämäläinen, J.; Iivonen, T.; Leskelä, M.; Macyk, W. How Insignificant Modifications of Photocatalysts Can Significantly

Change Their Photocatalytic Activity. J. Mater. Chem. A 2019, 7 (43), 25142–25154. https://doi.org/10.1039/C9TA09400H.

- (41) Monteiro, M. C. O.; Schmuki, P.; Killian, M. S. Tuning Anatase Surface Reactivity toward Carboxylic Acid Anchor Groups. *Langmuir* 2017, 33 (49), 13913–13922. https://doi.org/10.1021/acs.langmuir.7b03044.
- (42) Chung, D.-Y.; Kim, E.-H.; Shin, Y.-J.; Yoo, J.-H.; Choi, C.-S.; Kim, J.-D. Decomposition of Oxalate by Hydrogen Peroxide in Aqueous Solution. J. Radioanal. Nucl. Chem. Lett. 1995, 201 (6), 495–507. https://doi.org/10.1007/BF02162727.
- (43) Guo, W.; Cao, Y.; Zhang, Y.; Wang, L.; Kong, L. Synthesis of Porous Iron Hydroxy Phosphate from Phosphate Residue and Its Application as a Fenton-like Catalyst for Dye Degradation. J. Environ. Sci. 2022, 112, 307–319. https://doi.org/10.1016/j.jes.2021.05.033.
- (44) Zhang, Y.; Zhao, S.; Mu, M.; Wang, L.; Fan, Y.; Liu, X. Eco-Friendly Ferrocene-Functionalized Chitosan Aerogel for Efficient Dye Degradation and Phosphate Adsorption from Wastewater. *Chem. Eng. J.* 2022, 439, 135605. https://doi.org/10.1016/j.cej.2022.135605.
- (45) Arshadi, M.; Zandi, H.; Akbari, J.; Shameli, A. Ferrocene Functionalized Nanoscale Mixed-Oxides as a Potent Phosphate Adsorbent from the Synthetic and Real (Persian Gulf) Waters. J. Colloid Interface Sci. 2015, 450, 424–433. https://doi.org/10.1016/j.jcis.2015.03.026.
- (46) Yu, D.; Wu, C.; Kong, Y.; Xue, N.; Guo, X.; Ding, W. Structural and Catalytic Investigation of Mesoporous Iron Phosphate. J. Phys. Chem. C 2007, 111 (39), 14394–14399. https://doi.org/10.1021/jp0728930.
- (47) Wagh, A. S.; Jeong, S. Y. Chemically Bonded Phosphate Ceramics: III, Reduction Mechanism and Its Application to Iron Phosphate Ceramics. J. Am. Ceram. Soc. 2003, 86 (11), 1850–1855. https://doi.org/10.1111/j.1151-2916.2003.tb03571.x.
- (48) Mimouni, I.; Yahya, M.; Bouziani, A.; Naciri, Y.; Maarouf, F.; Alaoui El Belghiti, M.; El Azzouzi, M. Iron Phosphate for Photocatalytic Removal of Ibuprofen from Aqueous Media under Sun-like Irradiation. J. Photochem. Photobiol. Chem. 2022, 433, 114170. https://doi.org/10.1016/j.jphotochem.2022.114170.

Photocatalytic Performance Stabilization of Anodic Aluminum Oxide based Photocatalysts by Post-Anodization Surface Modification

Supporting Information

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Post-anodization treatment		Al _{2p} peak energies /eV	C _{1s} peak energies /eV	O _{1s} peak energies /eV	P _{2p} peak energies /eV	
	As-prepared	74.3, 76.2	274.8, 286.5, 289.3	531.4, 532.9	-	
	Annealed	74.3, 76.9	284.8, 286.6, 288.8	531.2, 533.0	-	
	TMA pulses	74.3	284.8, 286.2, 289.3	531.3, 532.9	-	
	H ₂ O	74.3, 76.4	284.8, 286.3, 289.0	531.7, 533.6	-	
	H ₂ O ₂	74.5	284.8, 286.1, 289.3	531.7, 532.9	-	
	H ₃ PO ₄	74.4, 76.5	284.8, 286.8, 290.6	531.6, 533.6	134.2, 136.3	

Table S1. XPS pe	ak energies	of the sub	opeaks	identified	l for eacl	ı sample.
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7.3. Publication III

Harnessing Slow Light in Optoelectronically Engineered Nanoporous Photonic Crystals for Visible Light-Enhanced Photocatalysis

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Author contributions: S.Y.L. and C.H. contributed equally. C.H. fabricated the ALD-functionalized NAA-PCs and conducted the AFM measurements. S.Y.L., L.J, C.S.L. conducted optical characterization, photocatalysis measurements, and SEM imaging. M.C. conducted the spectroscopic ellipsometry. S.Y.L., C.H., C.S.L., M.C., R.Z., A.S. performed the data analysis. R.Z. and A.S. conceived the project. A.D.A., R.H.B., R.Z., A.S. supervised the project and acquired funding. All authors conducted proofreading and approved the manuscript.



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Harnessing Slow Light in Optoelectronically Engineered Nanoporous Photonic Crystals for Visible Light-Enhanced Photocatalysis

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photocatalysis under visible–NIR illumination. Photocatalytic breakdown of methylene blue (MB) with a visible absorbance band is used as a benchmark reaction to unveil the mechanism of slow light-enhanced photocatalysis in TiO_2 –NAA-DBRs with a tunable photonic stop band (PSB) and thickness of TiO_2 . Assessment of the optical arrangement between MB's absorbance band and the PSB of TiO_2 –NAA-DBRs is used to identify and quantify slow light contributions in driving this model photocatalytic breakdown reaction. Our findings reveal that photo-



degradation rates rely on both the spectral position of PSB and thickness of the semiconductor. The performance of these photocatalysts is the maximum when the red edge of the PSB is spectrally close to the red or blue boundary of the MB's absorbance band and to dramatically decrease within the absorbance maximum of MB due to light screening by dye molecules. It is also demonstrated that TiO_2 -NAA-DBRs featuring thicker photoactive TiO_2 layers can harvest more efficiently incident slow light by generating extra pairs of charge carriers on the semiconductor coating's surface. The crystallographic phase of TiO_2 in the functional coatings is found to be critical in determining the performance of these model photocatalyst platforms, where the anatase phase provides ~69% higher performance over its amorphous TiO_2 form. This study provides opportunities toward the development of energy-efficient photocatalysts for environmental remediation and energy generation and other optoelectronic applications.

KEYWORDS: heterogeneous photocatalysis, nanoporous anodic alumina, photonic crystals, atomic layer deposition, photonic stop band, titanium dioxide

1. INTRODUCTION

Emerging global challenges in energy consumption and generation and emissions of toxic pollutants to the environment have led to exponentially increasing medical conditions associated with pollution and dramatic climatic phenomena. Addressing these issues will require the development of sustainable, ecological, safe, and energy-efficient technologies. Of all the emerging technologies available, heterogeneous photocatalysis—"photocatalysis"—is a sustainable and energy-efficient light-driven process, which makes it possible to transform clean sunlight energy into electron—hole pairs (e⁻— h⁺, charge carriers) when incident photons interact with the surface of semiconductors. Photoexcited e⁻—h⁺ pairs localized on the semiconductors' surface can then be harnessed to drive secondary reactions¹ for applications such as water purification, ^{2,3} air treatment,⁴ clean hydrogen (H₂) energy generation, ^{5,6} and carbon dioxide (CO₂) reduction.⁷ However, the

bench-to-field enterprise of translating fundamental knowledge in basic photocatalysis science into practical technologies for real-world applications remains challenging. Photocatalytic performance of the existing photocatalyst platforms is severely constrained by factors such as generation efficiency and recombination of charge carriers, surface reactivity, and inefficient use of high irradiance spectral regions of the solar spectrum (*i.e.*, visible and NIR, which account for ~47 and ~51% of sunlight energy, respectively).⁸ As such, significant efforts have been devoted on developing advanced materials for

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Figure 1. Engineering of TiO_2 -NAA-DBRs by combining anodization and ALD. (a) Structure of NAA-DBRs engineered with changing period length (L_{TP}) and thickness of the TiO_2 layer (t_{TiO_2}) modified by combined variation of the anodization period and number of ALD cycles. (b) Chemical and electronic structure of TiO_2 -NAA-DBRs under light illumination in water. (c) Optical transmission of a representative TiO_2 -NAA-DBRs with PSB and its blue and red boundaries (edges) where the velocity of incoming photons is represented as fast and slow across the spectrum, with the inset showing a digital image of the TiO_2 -NAA-DBR. (NB: TiO_2 -NAA-DBR fabricated with an anodization period, $T_P = 1200$ s; thickness of the deposited TiO_2 layer, $t_{TiO_2} = 0.5$ nm; and medium filling the nanopores = air). (d) Digital pictures provide a visual demonstration of the light-driven breakdown of MB by TiO_2 -NAA-DBRs under visible-NIR illumination (NB: change in color from blue to transparent indicates successful degradation of these organic molecules).

effective electron-hole separation and increasing surface reduction-oxidation reaction sites for visible light-driven photocatalysis *via* approaches such as substitutional doping,^{9,10} deposition of co-catalysts,^{11,12} and nanostructural engineering of semiconductors.^{13,14} Of all these, engineering nanostructural engineering of semiconductor materials in porous photonic crystals (PCs) enables new ways of harnessing interactions between atoms and incident electromagnetic waves for photocatalysis. These platform materials provide (i) dynamic paths to enhance the transfer of photopromoted electrons and holes, (ii)

a high number of functional redox centers with a high specific surface area, and (iii) a nanoporous architecture that provides enhanced flow of reduction-oxidation species.¹⁵ Rational design of nanoporous semiconductor PCs also enables enhanced photon-semiconductor interactions through optical phenomena such as multiple scattering, Bragg diffraction, slow light, light recirculation, and surface plasmons.¹⁶⁻¹⁸

Zheng *et al.* demonstrated that titanium dioxide (TiO_2) inverted opal PCs featuring a photonic stop band (PSB) at 660 nm outperform benchmark P25 TiO₂ nanoparticles by ~52% in



Figure 2. Fabrication and structural characterization of NAA-DBRs produced by STPA. (a) Full-view anodization profile to fabricate NAA-DBRs with $T_{\rm P} = 1400$ s and $N_{\rm P} = 150$ pulses. (b) Magnified view of current density and voltage pulses of the blue rectangle of (a) with the description of anodization parameters (*i.e.*, $J_{\rm min}$, $T_{\rm max}$, $t_{\rm min}$, $t_{\rm max}$, and $T_{\rm P}$). (c) Illustration of NAA-DBRs' architecture (left) with a definition of their geometric features [right; nanopore diameter ($D_{\rm P}$) and period length ($L_{\rm TP}$)]. (d) Top-view FEG-SEM image of an NAA-DBR showing nanopores with a $D_{\rm P}$ of 15 ± 2 nm (scale bar = 500 nm). (e) Full-view cross-sectional FEG-SEM image of an NAA-DBR generated by STPA profiles (CA = initial constant anodization step) (scale bar = 3 μ m). (f) Magnified-view cross-sectional FEG-SEM image of an NAA-DBR with details of porosity modulations with $L_{\rm TP} = 214 \pm 22$ nm (*i.e.*, denoted by red arrows and horizontal dotted lines) (scale bar = 500 nm).

breaking down methylene blue (MB)-a model organic with the maximum optical absorption at 664 nm—under visible light irradiation.¹⁹ Enhancements in optically driven breaking down were attributed to "slow light" effect, which is a characteristic light-matter interaction in PC structures where incident photons are dramatically slowed at the blue and red boundaries of the PC's PSB—wavelength ranges within which light flow is forbidden by the PC.¹⁸⁻²⁰ The number of photon-to-semiconductor atom interactions at the PSB's blue and red boundaries increases and increases the number of incident photons absorbed by the semiconducting material, enabling photocatalytic enhancements.¹³ This approach can be further enhanced by deposition of co-catalysts (i.e., noble metal and semiconductors) via decoration with nanoparticles, 21-23 atomic layer deposition (ALD),²⁴⁻²⁶ and sol-gel method.²⁷⁻²⁹ For instance, Sopha et al. demonstrated a photocatalytic enhancement of ~72% in photodegrading MB under UV light illumination after precisely depositing TiO₂ nanotubes with uniform TiO₂ coatings of 11 nm thickness by ALD.²⁴ Organic breakdown enhancements were attributed to the efficient charge carrier separation of the ALD-derived TiO₂ coating, which is strongly supported by a high specific surface area of TiO2 nanotubes. Although nanoporous semiconductor PCs such as TiO₂ inverse opals and TiO₂ nanotubes are widely employed for photocatalytic reactions, the fabrication of these PCs has intrinsic constraints and drawbacks such as poor controllability of the optical features of PC's PSB, long processing time (i.e.,

 TiO_2 inverse opals),^{13,30,31} and light scattering associated with asymmetric etching of the nanotubes over extended exposure to hydrofluoric acid electrolytes (*i.e.*, TiO₂ nanotubes fabricated by electrochemical oxidation of titanium).^{32,33}

Recent efforts have focused on developing new forms of nanoporous semiconductor PCs to address these limitations for maximizing photocatalytic efficiency. Among these, anodization of aluminum enables the development of nanoporous anodic alumina (NAA)-based PCs based on engineered optical features throughout the spectrum.³⁴⁻⁴⁰ Although NAA is an electronic insulator (*i.e.*, electronic band gap $\sim 9 \text{ eV}$) and cannot be directly applied in photocatalysis,⁴¹ functionalizing the nanoporous structure of NAA-PCs with light-responsive semiconductor layers has opened a new pathway to overcome this drawback. Photocatalytic breakdown of model organic pollutants under visible-NIR light illumination by TiO2-functionalized NAA-PCs has been recently demonstrated. These model PC structures include gradient index filters (GIFs),⁴² distributed Bragg reflectors (DBRs),^{43,44} optical microcavities (μ QVs),⁴⁵ and broadband DBRs (BDBRs).46 Nevertheless, the sol-gel method used to deposit photoactive TiO₂ layers on the surface of these NAA-PCs has limited controllability in the thickness and homogeneity of the deposited semiconductor layers.

Herein, we present TiO_2 -functionalized NAA-based DBRs optoelectronically engineered by combining pulse anodization and ALD for enhanced photocatalysis. The architecture of TiO_2 -NAA-DBRs was engineered by judicious modification of

input anodization period and surface functionalization (*i.e.*, thickness of ALD-deposited TiO_2 layers) (Figure 1a). The optoelectronic and chemical properties of the resulting TiO_2 –NAA-DBRs were comprehensively characterized (Figure 1b,c). Photocatalytic efficiency of TiO_2 –NAA-DBRs was analyzed through visible–NIR light-induced breakdown of MB (Figure 1d). Analysis of spectral arrangement of MB's absorbance band and the red boundary of TiO_2 –NAA-DBRs' PSB was comprehensively studied to identify and estimate photocatalytic enhancement attributed to slow light.

2. EXPERIMENTAL SECTION

2.1. Materials. Circular aluminum (Al) chips (99.9997% purity, 0.5 mm thickness) with a diameter of 200 mm were purchased from Goodfellow Cambridge Ltd. (UK). Copper(II) chloride (CuCl₂), MB ($C_{16}H_{18}ClN_3S$, MB), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2) were acquired from Sigma-Aldrich (Australia). Perchloric acid (HClO₄), titanium tetraisopropoxide ($C_{12}H_{28}O_4Ti$, TTIP), 4-chlorophenol (ClC₆H₄OH, 4-CP), sulfuric acid (H₂SO₄), and ethanol (C_2H_5OH , EtOH) were supplied by Merck Chemicals (Germany). Milli-Q water (18.2 M Ω cm) was used to prepare all aqueous solutions.

2.2. Fabrication of NAA-DBRs. NAA-based DBRs were fabricated by stepwise pulse anodization (STPA).⁴³ Circular Al chips were sequentially cleaned with EtOH and H₂O at room temperature for 15 min under sonication and air stream-dried. Electropolishing of circular aluminum chips was performed in a mixture electrolyte with a composition of 4:1 (v/v) EtOH/ HClO₄ at 5 °C and 20 V for 3 min under stirring. After this, aluminum chips were anodized by a current density input profile in 1.1 M H₂SO₄ electrolyte modified with 25 vol % of EtOH at -1 °C. Ethanol prevented the aqueous-based acid electrolyte from freezing at -1 °C while minimizing the progressive etching of the NAA structure during anodization.⁴⁷ Circular aluminum chips were then electrochemically oxidized in custom-built electrochemical reactors under controlled temperature conditions. The anodizing electrolyte was constantly stirred at ~300 rpm throughout the anodization process. Current density-time profiles were generated using a LabVIEW application. Figure 2a,b shows details of an anodization profile with a visual description of the anodization parameters in the input current density profile. A constant current density step at 1.120 mA cm⁻² was performed for 10 min to stabilize the growth rate of the anodic film. Anodization was then automatically changed to the STPA mode. In this step, the input current density was stepwise pulsed between high $(J_{max} = 1.120 \text{ mA cm}^{-2})$ and low $(J_{min} =$ 0.280 mA cm⁻²) values of current density for 150 pulses (N_p). The anodization period (T_p) or time between consecutive pulses (eq 1) was varied from 900 to 1400 s with a step of 100 s.

$$T_{\rm p} = t_{\rm max} + t_{\rm min} \tag{1}$$

where t_{max} and t_{min} are the times for $J_{\text{max}} = 1.120 \text{ mA cm}^{-2}$ and $J_{\text{min}} = 0.280 \text{ mA cm}^{-2}$, respectively, and the time ratio $(t_{\text{max}}/t_{\text{min}})$ was set to 1:4.

2.3. Optoelectronic Functionalization of NAA-DBRs. The surface of nanopores in NAA-DBRs was coated with semiconducting layers of TiO_2 via ALD.^{48,49} TiO_2 deposition was performed in a customized ALD reactor operated in a stop-flow mode. The system was heated to 150 °C and a constant nitrogen (6.0) flow of 2.5 L h⁻¹ was pumped as a carrier gas. Milli-Q water at room temperature and TTIP heated to 85 °C were used as precursors with a pulse time of 0.05 and 2 s,

respectively. Duration of exposure and pumping was set to 60 and 90 s for these half-reactions, respectively. In one complete ALD cycle, 0.03 \pm 0.006 nm of TiO₂ was deposited. Three different thicknesses of deposited TiO₂ layers (t_{TiO} = 0.5, 1, and 2 nm) were produced by systematic modification in the number of ALD cycles applied (i.e. ALD cycles = 20, 36, and 58, respectively). Deposited film thicknesses were confirmed by analyzing deposited layers on planar reference substrates (i.e., silicon chips) by optical ellipsometry using a SENpro ellipsometer (Sentech Instruments, Germany), where the reference substrates were coated by the same processes used to modify the NAA-DBRs. To elucidate the impact of the crystallographic phase of TiO_2 on the photocatalytic efficiency of TiO₂-NAA-DBRs, TiO₂-NAA-DBRs with T_P = 1200 s and $t_{\text{TiO}_2} = 2 \text{ nm}$ (corresponding to 58 cycles) were annealed at 450 °C on a hot plate for 1 h under an ambient atmosphere.

2.4. Optical Characterization of NAA-DBRs. Before acquisition of transmission spectra, the Al substrate remaining after anodization was selectively etched at the backside of TiO2-NAA-DBRs in a reactant mixture solution of HCl-CuCl₂, using a 5 mm-diameter circular mask. Transmission spectra of these TiO₂-NAA-DBRs in air and water were measured at normal, from 200 to 900 nm, using a UV-visible spectrophotometer (Cary 300, Agilent, USA). Optical characteristics of the PSB of these TiO₂-NAA-DBRs, namely, position of central wavelength, λ_{PSB} ; full width at half-maximum, FWHM_{PSB}; intensity, I_{PSB} ; and red-edge positions, $\lambda_{\text{PSB-red}}$, were estimated by fitting the PSB to Gaussian fittings. The absorbance spectrum of 5 mg L^{-1} of MB in a plastic cuvette of 10 mm path length was acquired using a UV-visible spectrophotometer. TiO₂-NAA-DBRs in air were also characterized using digital images acquired in a Canon EOS 700D digital camera under natural illumination.

2.5. Assessment of Photocatalytic Efficiency of TiO₂-NAA-DBRs. Photocatalytic efficiency of TiO₂-NAA-DBRs produced with changing $T_{\rm P}$ (*i.e.*, $T_{\rm P}$ = 900 to 1400 s with $\Delta T_{\rm P}$ = 100 s) and t_{TiO_2} (*i.e.*, t_{TiO_2} = 0, 0.5, 1, and 2 nm) was assessed using light-induced breakdown of MB, with a distinctive absorbance band (λ_{Abs-MB} = 664 nm) in the visible spectrum, as a model photocatalytic reaction system (Figure S1a— Supporting Information). 8 mL mixtures containing 5 mg L⁻¹ of MB and 100 mM H₂O₂ were pipetted into quartz containers. TiO₂-NAA-DBRs were kept normal to the light source, using customized holders. TiO2-NAA-DBRs were dipped into the reactant mixture in the dark and stirred to reach the equilibrium between adsorption and desorption on the photocatalyst surface. Light-induced breakdown reactions were performed within dark reactors connected to halogen lamps of 150 W (3000 lumen), simulating visible-NIR light. The optical absorbance of the reactant mixture at 664 nm was quantified every 15 min by UV-visible spectroscopy. Concentration of the model organic at these reaction times was calculated from the linear correlation between the absorbance maximum intensity and concentration of MB (Figure S2-Supporting Information). The Langmuir-Hinshelwood kinetic model was used to describe the kinetics of heterogeneous photocatalytic reactions. Under the conditions of our study (*i.e.*, $[MB] < 10^{-3}$ M), this kinetic model follows a pseudo-first-order kinetics, making it possible to quantify the photocatalytic conversion ratio (C_t/C_o) and kinetic constant (k) of the model reaction using eq 2^5

$$\ln(C_t/C_o) = kt \tag{2}$$

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Figure 3. Analysis of the chemical composition of TiO₂-NAA-DBRs produced by a combination of STPA and ALD. (a) EDX spectra of TiO₂-NAA-DBRs produced with $T_{\rm P}$ = 1400 s and varying thicknesses of optoelectronic TiO₂ coatings ($t_{\rm TiO_2}$). (b) Analysis of relative percentages of Ti atoms by EDX in TiO₂-NAA-DBRs produced with varying t_{TiO_2} shown in (a). The inset contains digital images depicting color of these TiO₂-NAA-DBRs. (c) Schematics illustrating the chemical composition of TiO_2 -NAA-DBRs produced with varying t_{TiO_2} = 0, 0.5, 1, and 2 nm.





Figure 4. Optical engineering of TiO₂–NAA-DBRs by modification of fabrication parameters and media filling the nanopores. (a,b) Optical transmission of TiO₂–NAA-DBRs produced with $T_{\rm p} = 1400$ s and varying $t_{\rm TiO_2}$, in air and water, respectively. (c) Definition of PSB's features of TiO₂–NAA-DBRs with baseline (y_0), central wavelength position ($\lambda_{\rm PSB}$), intensity ($I_{\rm PSB}$), position of blue and red edges ($\lambda_{\rm PSB-blue}$ and $\lambda_{\rm PSB-red}$), and full width at half-maximum (FWHM_{PSB}) (medium: air). (d,e) Linear dependence of $\lambda_{\rm PSB}$ with $T_{\rm p}$ for NAA-DBRs in air and water, respectively (left), and bar charts showing the slope of $\lambda_{\rm PSB}$ with $T_{\rm p}$ for TiO₂–NAA-DBRs fabricated with a $t_{\rm TiO_2}$ of 0, 0.5, 1, and 2 nm (right). (f) Linear correlation of $\lambda_{\rm PSB-red}$ with $T_{\rm p}$ for NAA-DBRs produced with $t_{\rm TiO_2} = 0$ nm in water (left) and a bar chart showing the slope for the linear shift of $\lambda_{\rm PSB-red}$ with $T_{\rm p}$ for TiO₂–NAA-DBRs produced with a $t_{\rm TiO_2}$ of 0, 0.5, 1, and 2 nm (right). (g) Digital images showing variation of color of TiO₂–NAA-DBRs with $T_{\rm p}$ and $t_{\rm TiO_2}$.

where C_t is the concentration of MB (in mg L⁻¹) at illumination time *t* (in h) and C_o is the concentration of MB (in mg L⁻¹) after stirring in the dark for 30 min.

Light-induced breakdown rates (*r*) were calculated as the product of the kinetic constant (*k*) and the initial concentration of MB after 30 min in the dark (C_{dark}), as described in eq 3⁵⁰

$$r = k \cdot C_{\text{dark}} \tag{3}$$

where average values of C_{dark} for MB after 30 min adsorption onto TiO₂-NAA-DBRs were estimated to be 5 ± 2% (0.23 ± 0.09 mg L⁻¹) of C_{o} .

To fully understand the photocatalytic degradation mechanism in TiO₂–NAA-DBRs, light-induced breakdown of MB in the absence of H₂O₂ was investigated. Light-induced breakdown of 4-CP ($\lambda_{Abs-4-CP} = 225 \text{ nm}$) (Figure S1b—Supporting Information), a colorless and resilient organic pollutant, by TiO₂–NAA-DBRs produced with $T_P = 1200 \text{ s}$ and $t_{TiO_2} = 0.5 \text{ nm}$ under controlled visible–NIR light irradiation conditions was also studied as a control experiment to elucidate the photocatalytic breakdown mechanism. Concentration of 4-CP at specific time intervals was calculated from a calibration line establishing a correlation between 4-CP concentration and its absorbance maximum intensity (Figure S2—Supporting Information).

2.6. Chemical and Structural Characterization of NAA-DBRs. NAA-DBRs were characterized by field emission gun scanning electron microscopy (FEG-SEM Quanta 450, FEI, USA). FEG-SEM images were analyzed using ImageJ.⁵¹ Freshly prepared and TiO₂-functionalized NAA-DBRs were analyzed by energy-dispersive X-ray (EDX) spectroscopy during FEG-SEM characterization, to determine their elemental chemical composition.

3. RESULTS AND DISCUSSION

3.1. Fabrication and Structural Characterization of NAA-DBRs. Figure 2a depicts a full-view anodization profile applied to fabricate NAA-DBRs with $T_{\rm p}$ = 1400 s. A magnified view of this anodization profile shows that the output voltage pulses follow closely the input current density pulses with a short time lag ($\sim 0-13$ s) attributed to the presence of a barrier oxide layer $(\sim 15 \text{ nm})^{40}$ at the bottom NAA, which regulates the transfer of electrons and ionic species (Figure 2b). Full and magnified views of anodization profiles used to produce NAA-DBRs with $T_{\rm p}$ = 900 to 1400 s with $\Delta T_{\rm p}$ = 100 s are compiled in Figure S3 (Supporting Information), demonstrating that the anodization conditions and parameters make it possible to effectively translate input current density pulses into in-depth modulations of porosity in NAA. Figure 2c illustrates the architecture of NAA-DBR with key structural features such as nanopore diameter $(D_{\rm P})$ and period length $(L_{\rm TP})$ in NAA-DBRs.

Figure 2d-f shows representative top- and cross-sectionalview FEG-SEM images of an NAA-DBR produced with $T_{\rm P}$ = 1400 s. The top-view FEG-SEM image depicts randomly distributed nanopores all over the surface of NAA-DBRs, with a $D_{\rm P}$ of 15 ± 2 nm (Figure 2d). Cross-sectional examination of the NAA-DBR features stacked layered structures of NAA with stepwise porosity modulation generated by STPA (Figure 2e). A magnified view of this FEG-SEM image shows details of nanopores that follow precisely the STPA profile applied, with an average $L_{\rm TP}$ (indicated by red arrows and horizontal dotted lines) measured to be 214 ± 22 nm (Figure 2f). This geometric feature can be structurally engineered by T_P to spectrally control the optical features of NAA-DBRs.^{40,43,44}

3.2. Chemical Composition Analysis of TiO₂-NAA-DBRs. NAA-DBRs were coated with optoelectronic coatings of TiO₂ by ALD. The TiO₂ coating provides the essential photocatalytic properties for NAA-DBRs, the chemical structure of which will otherwise be electronically insulating due to the large energy band gap of Al_2O_3 (~9 eV). Figure 3a displays the elemental composition of TiO2-NAA-DBRs fabricated with different t_{TiO} of 0, 0.5, 1, and 2 nm. Elements present in the asproduced and TiO₂-functionalized NAA-DBRs include Al, Ti, O, and S atoms, where Al, Ti, and O atoms correspond to amorphous aluminum oxide (Al₂O₃) and titanium dioxide (TiO_2) , and S atoms are introduced into Al₂O₃ from the sulfuric acid-based electrolyte throughout anodization. Figure 3b reveals that the relative percentage of Ti atoms increases from 0 ± 0 to 22 \pm 2% when $t_{\rm TiO_2}$ increases from 0 to 2 nm, respectively. Digital image analysis shows the change in interferometric color of the as-produced NAA-DBRs to TiO_2 -NAA-DBRs with t_{TiO_2} = 0.5 nm from orange to light brown. Further increase in t_{TiO} , did not change the interferometric color of TiO2-NAA-DBRs. These analyses demonstrate successful deposition and incremental thickness of thin optoelectronic TiO₂ coatings onto the surfaces of NAA-DBRs by ALD (Figure 3c).

3.3. Optical Engineering of TiO₂-NAA-DBRs. The characteristic PSB of TiO2-NAA-DBRs can be tuned with precision by judiciously manipulating anodization and surface functionalization parameters. Figure 4a shows the optical transmission spectrum of TiO2-NAA-DBRs fabricated with a $t_{\rm TiO_2}$ of 0, 0.5, 1, and 2 nm, in air. It is apparent that the central position (λ_{PSB}) and full width at half-maximum (FWHM_{PSB}) of the PSB of TiO₂-NAA-DBRs slightly red shifts from 486 \pm 17 to 506 \pm 18 nm and narrows from 68.2 \pm 6.8 to 38.2 \pm 3.8 nm with increasing t_{TiO} , respectively, while its intensity (I_{PSB}) remains relatively constant ($I_{PSB} \sim 74.3 \pm 2.8$ a.u.). A similar trend is observed for TiO_2–NAA-DBRs in water, where $\lambda_{\rm PSB}$ and FWHM_{PSB} of the characteristic PSB of TiO₂-NAA-DBRs slightly red shifts from 517 ± 20 to 531 ± 20 nm and narrows from 39.0 \pm 3.9 to 22.8 \pm 2.2 nm with increasing $t_{\text{TiO},i}$ respectively. I_{PSB} also remains relatively constant (*i.e.*, ~14.4 \pm 2.5 a.u.) (Figure 4b). Optical transmission spectra of TiO_2 -NAA-DBRs as a function of $T_{\rm P}$ in air and water also reveal a similar trend (Figures S4 and S5-Supporting Information, respectively). These results are attributable to the increase in the index of refraction (*n*) within nanopores after coating (*i.e.*, n_{TiO_2}) = 2.61 RIU > $n_{Al_{2}O_{3}}$ = 1.77 RIU) as well as the physical reduction of the nanopore diameter with progressive increasing deposition of thin TiO₂ layers. When changing the medium inside the nanopores from air to water, significant changes in the optical features of the TiO₂–NAA-DBRs' PSB are observed, where λ_{PSB} red shifts at an average rate of 27 ± 4 nm, FWHM_{PSB} narrows at an average rate of 19.4 \pm 7.1 nm, and I_{PSB} decreases at a rate of 59.9 ± 2.4 a.u. These changes are attributed to the change in the index of refraction of the medium filling the nanopores from air $(n_{\text{air}} = 1.00 \text{ RIU})$ to water $(n_{\text{water}} = 1.33 \text{ RIU})$, as well as absorption of incoming light by water molecules infiltrated into the nanopores. The optical characteristics of TiO₂-NAA-DBRs' PSB are graphically described in Figure 4c, where the two optical features, blue and red boundary (edge) of the PSB, associated with the photocatalytic breakdown enhancement of TiO2-



Figure 5. Light-induced breakdown assessment of MB by TiO₂–NAA-DBRs with combined T_P and t_{TiO_2} modification. (a–c) Kinetics of light-induced breakdown MB by TiO₂–NAA-DBRs fabricated with varying T_P and t_{TiO_2} (NB: black dotted line denotes the light-induced breakdown of MB in a control NAA-based DBR without functional coating). (d–f) Bar charts of kinetic constant (k, left) and reaction rate (r, right) for light-induced degradation of MB by TiO₂–NAA-DBRs produced with a t_{TiO_2} of 0.5, 1, and 2 nm, respectively, under visible–NIR irradiation (NB: insets display the chemical structure of MB molecules and error bars are standard deviation from three experiments).

NAA-DBRs by "slow light" effects are denoted. Figure 4d presents a linear relationship between $\lambda_{\rm PSB}$ and $T_{\rm P}$ for TiO₂– NAA-DBRs with $t_{\rm TiO_2} = 0$ nm (*i.e.*, as-produced NAA-DBRs), where $\lambda_{\rm PSB}$ is red-shifted at a rate of 0.41 ± 0.04 nm s⁻¹ with the anodization period. The bar chart shows that the linear fitting slope for TiO₂–NAA-DBRs with a $t_{\rm TiO_2}$ from 0.5 to 2 nm is comparable to that of the as-produced NAA-DBRs (*i.e.*, 2–8%). The trend for these analyses is also similar for TiO₂–NAA- DBRs infiltrated with water (*i.e.*, reacting medium), where $\lambda_{\rm PSB}$ of the as-produced NAA-DBRs is red-shifted at a rate of 0.51 ± 0.03 nm s⁻¹ with the anodization period, and the slope of the linear fittings for TiO₂–NAA-DBRs with a $t_{\rm TiO_2}$ from 0.5 to 2 nm only differs minimally (*i.e.*, 0–4%) (Figure 4e). Figure S6 (Supporting Information) compiles the linear fittings for the dependence of $\lambda_{\rm PSB}$ on $T_{\rm P}$ for TiO₂–NAA-DBRs with a $t_{\rm TiO_2}$ from 0 to 2 nm in air and water. It should be noted that the slope

of the linear fittings displayed for TiO₂-NAA-DBRs infiltrated with water is higher than that of air. Therefore, it can be concluded that although $T_{\rm P}$ and the medium inside the nanopores of TiO2-NAA-DBRs play significant roles in engineering TiO₂-NAA-DBRs' λ_{PSB} , this optical feature is weakly dependent on t_{TiO_2} . In this study, photocatalytic reactions were conducted in aqueous solutions. As such, it is critical to determine the red boundary position of TiO₂-NAA-DBRs' PSB in water, since this is the spectral region where incident photons interact with the semiconductor coating to generate charge carriers involved in photocatalytic reactions. Red-boundary slow light increases the number of photon-to-semiconductor interactions in these photonic structures, enabling a means of harnessing this optoelectronic phenomenon to boost photocatalytic rates.^{43,46} The red boundary of TiO₂–NAA-DBRs' PSB is estimated using eq 4

$$\lambda_{\text{PSB-red}} = \lambda_{\text{PSB}} + \left(\frac{1}{2} \times \text{FWHM}_{\text{PSB}}\right) \tag{4}$$

Figure 4f presents the correlation between $\lambda_{\text{PSB-red}}$ and T_{P} , where $\lambda_{PSB-red}$ red shifts linearly with the anodization period at 0.56 ± 0.02 nm s⁻¹ for the as-produced NAA-DBRs. Logically, the slope of the linear correlation between $\lambda_{PSB-red}$ and T_P is comparable between the as-produced NAA-DBRs and $\mathrm{TiO_2-}$ NAA-DBRs with a t_{TiO_2} from 0.5 to 2 nm (*i.e.*, 1–4%). Figure 4g shows digital images of TiO2-NAA-DBRs featuring changing interferometric colors with $T_{\rm P}$ and $t_{\rm TiO,2}$ in air. The as-produced NAA-DBRs produced with a distinct anodization period display an array of colors in air (i.e., purple, green, dark green-yellow, light green-yellow, orange, and orange, for $T_{\rm P}$ = 900, 1000, 1100, 1200, 1300, and 1400 s). This feature is found to undergo a red shift with $T_{\rm P}$ due to the change in the PSB's position throughout the visible spectrum. A similar red-shift trend is also observed for TiO₂-NAA-DBRs produced with increasing $T_{\rm P}$ and $t_{\rm TiO_2}$ from 0.5 to 2 nm. When the surface of the as-produced NAA-DBRs is coated with 0.5 nm TiO₂ semiconducting layers, the interferometric color undergoes a slight red shift. This result can be ascribed to the change in the local index of refraction of the PC structure and the associated shift in λ_{PSB} . However, no apparent change in interferometric color is found when t_{TiO_2} is further increased from 0.5 to 2 nm in TiO₂-NAA-DBRs. For instance, while the color of NAA-DBRs fabricated with $T_{\rm p}$ = 1300 s red shifts from orange to light brown color when the surface is coated with 0.5 nm of TiO₂ (*i.e.*, $\lambda_{PSB} = 674$ to 692 nm with $\Delta \lambda_{\text{PSB}} = 18$ nm), further increase in t_{TiO} , shows that the interferometric color remains relatively unchanged (*i.e.*, λ_{PSB} = 692 to 701 nm and $\Delta \lambda_{PSB} = 9$ nm), due to a reduced shift in $\Delta \lambda_{\rm PSB}$.

3.4. Photocatalytic Assessment of TiO₂-NAA-DBRs. The photocatalytic efficiency of TiO₂-functionalized NAA-DBRs featuring varying period length and thickness of semiconductor coating was assessed through light-induced breakdown of an MB under an illumination consisting of visible-NIR light. The absorbance band maximum of MB (*i.e.*, $\lambda_{Abs-MB} = 664$ nm) was used as an indicator to quantify the kinetic constant (k) and reaction rate (r)—breakdown performance indicators—of the model photocatalytic reaction driven by visible-NIR irradiation in TiO₂-NAA-DBRs. The spectral distribution of the light source was ~0.1% UV, ~64.9% visible, and ~35.0% NIR (Figure S7—Supporting Information). H₂O₂ solution was introduced to the reacting mixture to photogenerate extra electron-hole carriers in TiO₂-NAA-DBRs for photodegradation of MB. Figure 5a-c shows the pseudo-firstorder kinetic trend for the light-induced breakdown of MB by TiO₂-NAA-DBRs produced with t_{TiO_2} = 0.5, 1, and 2 nm, respectively, where the slope of the linear fittings corresponds to the kinetic constant. Control experiments performed with the as-produced NAA-DBRs (*i.e.*, denoted by the dotted black lines) show that there is no light-induced breakdown reaction in the absence of photoactive TiO₂ layers (*i.e.*, k = 0 h⁻¹). This indicates that photodegradation of MB is entirely driven by the TiO₂ coatings within these NAA-DBRs. Figure 5d-f (left) and Table S1 (Supporting Information) compile k values obtained in bar charts and table, respectively. Their product with C_{dark} which corresponds to the reaction rates, is summarized in Figure 5d-f (right) in the form of bar charts. The k value for TiO_2 -NAA-DBRs with t_{TiO_2} = 0.5 nm and T_P = 900, 1000, 1100, 1200, 1300, and 1400 s was 0.86 ± 0.19 , 1.23 ± 0.22 , 1.07 ± 0.18 , 3.95 \pm 0.68, 1.72 \pm 0.18, and 1.33 \pm 0.37 h⁻¹, respectively (Figure 5d). The best-performing photocatalyst platforms for $t_{\text{TiO}_2} = 0.5$ nm (*i.e.*, TiO₂-NAA-DBRs with $T_{\rm P}$ = 1200 s) provide a ~56-78% higher performance than that of other TiO₂-functionalized NAA-based DBRs featuring shorter or longer $T_{\rm P}$.

When the nanopores of NAA-DBRs were coated with 1 nm optoelectronic TiO₂ coatings, the kinetic constant for $T_{\rm P}$ = 900, 1000, 1100, 1200, 1300, and 1400 s was 2.15 ± 0.15 , 1.14 ± 0.23 , 0.47 ± 0.08 , 1.64 ± 0.22 , 0.35 ± 0.13 , and $0.58 \pm 0.17 \text{ h}^{-1}$, respectively (Figure 5e). The highest kinetic constant value was provided by TiO₂-functionalized NAA-based DBRs with $T_{\rm p}$ = 900 s, with a \sim 24–84% higher efficiency than that of those nanoporous DBRs fabricated with longer $T_{\rm P}$. This trend is also similar for TiO₂-NAA-DBRs with t_{TiO_2} = 2 nm, where the photocatalytic efficiency of TiO2-modified NAA-based DBRs with $T_{\rm P} = 900 \text{ s}$ (*i.e.*, $k = 2.85 \pm 0.30 \text{ h}^{-1}$) is ~14–78% higher than that of TiO2-modified NAA-based DBRs fabricated with a longer anodization period (*i.e.*, $T_{\rm P} = 1000$ s, $k = 1.02 \pm 0.18$ h⁻¹; $T_{\rm p} = 1100 \text{ s}, k = 0.62 \pm 0.07 \text{ h}^{-1}; T_{\rm p} = 1200 \text{ s}, k = 1.46 \pm 0.14$ h⁻¹; $T_{\rm P}$ = 1300 s, k = 2.44 ± 0.28 h⁻¹; and $T_{\rm P}$ = 1400 s, k = 2.20 ± 0.36 h⁻¹) (Figure 5f). The trends observed for these k values associated with the photoinduced breakdown of MB by TiO₂-NAA-DBRs with changing $T_{\rm P}$ at $t_{\rm TiO_2}$ = 0.5, 1, and 2 nm were relatively similar to their reaction rates, where r was $r_{\text{max}} = 0.90 \pm$ 0.16, 0.49 \pm 0.03, and 0.65 \pm 0.07 mg L⁻¹ h⁻¹ and $r_{\rm min}$ = 0.20 \pm 0.04, 0.08 \pm 0.03, and 0.14 \pm 0.02 mg L⁻¹ h⁻¹ for $t_{\text{TiO}} = 0.5, 1$, and 2 nm, respectively. Assessment of the spectral position between the MB's absorbance band and TiO2-NAA-DBRs' PSB provides a means of elucidating how "slow light" effects can be rationally engineered to harvest photons efficiently and enhance photocatalytic reactions. The propagation of incoming photons is forbidden in this region of the PSB. As such, photons within this spectral region cannot be efficiently used for driving photocatalytic reactions. Nevertheless, photons around the blue and red boundaries of the PCs' PSB-left and right regions of the band—can be harnessed to boost photocatalytic reaction rates. The speed of incoming photons localized in the high and low (*i.e.*, PSB's red and blue boundary, respectively) dielectric parts of the PC's structures is strongly reduced. Slow light localized at the PSB's red edge increases the number of interactions between photons and semiconductor within PC structures, enabling additional light-induced generation of e⁻h⁺ pairs by ALD-deposited TiO₂ coatings on the nanopores of NAA-DBRs.^{43,46} To elucidate photocatalytic enhancements



Figure 6. Effect of the fabrication parameters and the crystallinity on the light-induced efficiency of TiO_2 –NAA-DBRs to breakdown MB. (a–c) Relative optical alignment of PSB's red-edge TiO₂-functionalized NAA-based DBRs ($\lambda_{\text{PSB-red}}$) fabricated with varying anodization period and thickness of functional coating in water and MB's absorbance band, with the corresponding *k* values for different t_{TiO_2} of 0.5, 1, and 2 nm, respectively. (d) Photocatalytic degradation kinetics of MB by TiO₂–NAA-DBRs fabricated with $T_P = 1200$ s and $t_{\text{TiO}_2} = 2$ nm, and different crystallographic phases of TiO₂ (NB: black dotted line indicates the photoinduced breakdown of MB by a control NAA-based DBR with no functional TiO₂ coating). (e) Bar chart summarizing the kinetic constant values of MB by TiO₂–NAA-DBRs synthesized with different TiO₂ crystal phases. Insets display the interferometric color of the respective TiO₂–NAA-DBRs in air (NB: error bars indicate the standard deviation from three experiments).

associated with slow light, we analyzed optical alignment of MB's band and PSB's red boundary of TiO₂-NAA-DBRs with a combinational variation of anodization period and functional coating deposition time in water and correlated these with their corresponding k values (Figure 6a-c and Table S1—Supporting Information). Analysis of $\lambda_{PSB-red}$ of TiO₂–NAA-DBRs with t_{TiO_2} = 0.5, 1, and 2 nm indicated that $\lambda_{\text{PSB-red}}$ remains practically constant (*i.e.*, maximum deviation of ~2%) for individual $T_{\rm P}$ values used in our study. The position of the red edge of TiO₂-NAA-DBRs' PSB with the anodization period was estimated to be $542 \pm 1 (900 \text{ s})$, $592 \pm 8 (1000 \text{ s})$, $637 \pm 8 (1100 \text{ s})$, 685 ± 6 $(1200 \text{ s}), 767 \pm 3 (1300 \text{ s}), \text{ and } 823 \pm 6 \text{ nm} (1400 \text{ s}).$ Therefore, variance of k for TiO₂-functionalized NAA-based DBRs fabricated with fixed $T_{\rm P}$ (*i.e.*, $\lambda_{\rm PSB-red}$) and varying $t_{\rm TiO_2}$ can be exclusively attributed to the effect of the semiconductor layer thickness. Figure 6a shows that when $\lambda_{PSB-red}$ of TiO₂-NAA-DBRs with $T_{\rm p}$ = 1200 s is located within the red boundary of MB's absorbance band and away from its maximum (~21 nm away), a maximum kinetic constant (k_{max}) of 3.95 \pm 0.68 h⁻¹ is achieved for t_{TiO_2} = 0.5 nm. Photocatalytic efficiency of TiO₂modified NAA-based DBRs engineered with other $T_{\rm P}$ is found to be ~56-78% lower. This is particularly apparent for those PCs fabricated with $T_{\rm P}$ < 1200 s, where the red boundary of TiO₂-NAA-DBRs' PSB is within the absorbance maximum of MB. This could be attributed to the screening effect, by which MB prevents incoming light from flowing across the reacting mixture before electromagnetic waves can interact with functional semiconductor layer of these NAA-based DBRs to generate reactive species. Our observations indicate that the lightinduced breakdown efficiency of TiO2-functionalized NAAbased DBRs fabricated with $T_{\rm P}$ longer than 1200 s undergoes a slight recovery with respect to that of their counterparts produced with a shorter anodization period despite having their PSB's red boundary at a position that is far away from the absorbance band of MB (~103–159 nm). This slight photocatalytic enhancement can be ascribed to the geometric features (*i.e.*, pore length, L_P) of the overall PC structure. When total thicknesses of the PC structures increases, the light absorption of the overall composite structure enhances due to the increased area of the semiconductor.^{52,53} Figure 6b indicates that when $\lambda_{\text{PSB-red}}$ of TiO₂-modified NAA-based DBRs fabricated with T_{P} = 900 s and $t_{\text{TiO}_2} = 1$ nm is closely located to MB's blue boundary of absorbance and away from its maximum (\sim 122 nm), a



Figure 7. Investigation of the photocatalytic degradation mechanism in TiO_2 -functionalized NAA-DBRs. (a) Kinetics of light-induced breakdown of MB by these model composite PC structures showing the effect of H_2O_2 (NB: black dotted line indicates breakdown of MB in an NAA-based DBR with no TiO_2 coating). (b) Absorbance spectra of MB over illumination time from 0 to 1 h with an interval of 0.25 h photodegraded by a TiO_2 -functionalized NAA-DBR fabricated with an anodization period of 1200 s and a coating thickness of 0.5 nm. (c) Comparative kinetics of light-induced breakdown of MB and 4-CP by model TiO_2 –NAA-DBRs (NB: black dotted line indicates breakdown of MB and 4-CP in a model nanoporous PC with no TiO_2 coating).

maximum kinetic constant of $2.15 \pm 0.15 \text{ h}^{-1}$ is achieved. The photocatalytic performance of this system is found to dramatically decrease (\sim 78%) with increasing $T_{\rm P}$ when the PSB's red boundary of these model semiconductor PCs enters within the higher absorbance intensity of the absorbance band of MB until $T_{\rm P}$ = 1100 s. This is associated with MB's screening effect. The second highest k value is provided by TiO₂functionalized NAA-based DBRs produced with an anodization period of 1200 s ($k = 1.64 \pm 0.22$ h⁻¹). This observation is in excellent correlation with results obtained for TiO2-NAA-DBRs shown in Figure 6a. The photoinduced breakdown of MB by TiO₂-NAA-DBRs decreases with further increase in $T_{\rm P}$ by ${\sim}72 \pm 18\%$. This trend is further confirmed when analyzing the results for TiO2-modified NAA-based DBRs produced with TiO₂ functional layers with a nominal thickness of 2 nm (Figure 6c). These PCs achieve a maximum kinetic constant of 2.85 \pm 0.30 h⁻¹ when the PSB's red boundary is within MB's blue boundary (*i.e.*, TiO_2 -NAA-DBRs fabricated with $T_p = 900$). When $\lambda_{PSB-red}$ is positioned within the absorbance band of MB (*i.e.*, $T_{\rm P}$ 1000 and 1100 s), the photodegradation efficiency of TiO₂-NAA-DBRs decreases by \sim 78% due to screening effect. As the PSB's red boundary of ALD-coated NAA-DBRs is progressively positioned further away from the absorbance band of MB (*i.e.*, $T_{\rm P}$ = 1200 and 1300 s; ~21–103 nm), the photocatalytic performance of TiO₂-NAA-DBRs undergoes a recovery of ~86% of the maximum k value. It can be concluded that when the red boundary of the PSB of TiO₂-NAA-DBRs is positioned nearby MB's red or blue absorbance boundaries, the best light-induced breakdown efficiency by these composite PC structures is achieved for specific t_{TiO_2} (Figure 6a-c). The highest photoinduced breakdown efficiency of TiO2-NAA-DBRs with $t_{\text{TiO}_2} = 0.5$, 1, and 2 nm follows the order $t_{\text{TiO}_2} = 0.5 >$ 2 > 1 nm. These findings indicate that the thinnest TiO₂ layers (*i.e.*, $t_{\text{TiO}_2} = 0.5 \text{ nm}$) in TiO₂-NAA-DBRs is the most optimal $t_{\rm TiO_2}$ for utilizing slow light effects in enhancing the photocatalytic performance when compared to thicker TiO₂ layers (*i.e.*, t_{TiO} = 1 and 2 nm). The kinetic constant values with t_{TiO} = 0.5, 1, and 2 nm for all anodization periods were estimated to be

 1.69 ± 1.14 , 1.05 ± 0.72 , and $1.76 \pm 0.87 \text{ h}^{-1}$, respectively. The overall best photoinduced breakdown efficiency is achieved by the thickest TiO₂ coatings deposited *via* ALD (*i.e.*, $t_{TiO_2} = 2$ nm). This result could be attributable to additional e⁻-h⁺ pairs generated from the bulk of the semiconductor coating. However, our results demonstrate that thinner layers would be more favorable to harness slow photons. The morphology of thin films grown within nanoporous materials via ALD might also lead to the formation of multiple clusters of the semiconductor—through a Volmer–Weber growth mecha-nism—rather than a continuous thin film.^{54,55} This might in part determine the photocatalytic efficiency of the composite semiconductor structure. Analysis of surface roughness in model ALD-grown TiO₂ layers deposited on silicon wafers demonstrate that the longer the deposition time, the smoother the surface of the semiconductor film (Figure S8-Supporting Information). However, further studies will be needed to fully characterize the morphology of ALD-deposited TiO₂ layers within NAA-DBRs. Another important factor that contributes to the efficiency of semiconductors in photocatalysis is their crystallographic phase. Figure 6d shows the light-induced breakdown kinetics of MB by TiO2-NAA-DBRs fabricated with an anodization period of 1200 s and an ALD coating time of 2 nm with different crystallographic phases of TiO_2 (*i.e.*, amorphous and anatase). The slope of the linear fittings, k, is summarized into bar charts in Figure 6e. The crystallographic phase of ALD-modified TiO₂ layers in pristine TiO₂-NAA-DBRs is amorphous. When TiO₂-NAA-DBRs were annealed at 450 °C, the crystallographic phase of TiO₂ was transformed into the anatase phase. Our analysis indicates that transformation of the crystallographic phase of TiO₂ from amorphous to anatase significantly enhances the photocatalytic performance of TiO₂-NAA-DBRs, from 1.12 \pm 0.11 to 3.65 \pm 0.37 h⁻¹ (*i.e.*, ~69% enhancement). This result could be ascribed to the crystal facets in anatase TiO₂.^{45,56,57} Holes and electrons have tendencies to be trapped within the crystal facets of anatase TiO₂, enabling efficient separation between these charge carriers for boosting photocatalytic reactions and improving the photocatalytic performance. A digital image showing the interferometric

color change in TiO_2 -NAA-DBRs from amorphous (*i.e.* orange) to anatase (*i.e.*, white) phase indicates successful transformation of the crystallographic phase of TiO_2 .

3.5. Mechanism of Light-Induced Breakdown of MB by TiO₂–NAA-DBRs. A combinational photoinduced breakdown mechanism is proposed to explain the degradation of MB by TiO₂-functionalized NAA-based DBRs driven by visible–NIR excitation (Figure 7). Upon light irradiation, photoexcited electron-hole pairs are generated in the conduction and valence bands (CB and VB) of the TiO₂ coating, respectively. Photoexcited electronic holes oxidize H₂O molecules in the reactant mixture. This in turn generates OH[•] radicals on the photocatalyst, which can subsequently transform and degrade the organic molecule into CO₂ and H₂O. Simultaneously, photogenerated electrons react with H2O2 added to produce OH[•] radicals and OH⁻ ions. These species undergo more oxidation, leading to extra OH• radicals by light-excited electronic holes in the VB of the semiconductor coating. Figure 7a presents the light-induced breakdown of MB by a TiO2modified NAA-based DBR ($T_{\rm P}$ = 1200 s and $t_{\rm TiO_2}$ = 0.5 nm) without and with hydrogen peroxide in the reacting mixture (*i.e.*, at $[H_2O_2] = 0$ and 100 mM). MB degrades up to some extent with no hydrogen peroxide in the solution, where the quantified kinetic constant is 1.04 ± 0.03 and 3.95 ± 0.68 h⁻¹ at $[H_2O_2] = 0$ and 100 mM, respectively. As such, this mechanism alone cannot explain the whole light-driven breakdown of MB molecules by these TiO2-functionalized nanoporous PCs. The electronic band gap of TiO₂ coatings of varying thickness was determined via optical ellipsometry (Figure S9-Supporting Information). Our results indicate that the electronic band gap relies on the thickness of the ALD-deposited TiO₂ coating, with values ranging from ~3.675 eV at 2.0 nm to ~3.700 eV at 0.5 nm. These values would suggest that the average electronic band gap of the TiO_2 coatings used in our study (*i.e.*, 0.5, 1.0, and 2.0 nm) is ~3.7 eV (~335 nm, UV-A range of the spectrum). As such, these functional TiO_2 coatings cannot directly harvest visible photons for photocatalysis. However, we have previously demonstrated that alignment of the characteristic red edge of the PSB of TiO2-functionalized NAA-based PCs just above the electronic band gap of TiO₂ (*i.e.*, \sim 400–450 nm, low visible spectral range) results in a photocatalytic efficiency enhancement.45 Another contributing mechanism would involve dye sensitization, where singlet and triplet states in MB molecules would be induced by intersystem crossing when the dyesensitized TiO2-NAA-DBRs are illuminated by visible-NIR irradiation.46,58 The subsequent process contains photogenerated e⁻ injected into the CB of the semiconductor coating, where these e⁻ reduce chemically absorbed oxidant O₂ groups on the surface of the semiconducting coating to produce superoxide radical anions O_2^- and OH^\bullet radicals. These species would also play an important role in the light-induced breakdown of organic molecules. Figure 7b depicts the absorbance band of MB photodegraded by representative TiO_2 -NAA-DBRs over illumination time (t) from 0 to 1 h with an interval of 0.25 h. Before irradiation of visible-NIR light, two absorbance maxima of MB were measured at 622 and 664 nm, which corresponds to dimers and monomers, respectively. Upon light irradiation, these absorbance peaks of MB slightly blue shift their position with increasing *t*, from 0 to 0.5 h (*i.e.*, from 622 to 621 nm and from 664 to 661 nm, respectively), before these peaks merged into a single peak (*i.e.*, 634 nm) at t =0.75 h. The single absorbance maximum of MB further blue

shifts with increasing t to 1 h (*i.e.*, 629 nm). Zhang *et al.*⁵⁹ studied the light-induced oxidizing N-demethylation of MB in TiO₂ suspensions driven by ultraviolet light. MB was suggested to undergo stepwise N-demethylation (*i.e.*, one methyl group is removed one at a time), in which these were confirmed by the gradual absorbance maximum of MB shifting toward the blue region of the spectrum. Estimated Gaussian fittings and values of the two absorbance peaks of MB have also been summarized in Figure S10 and Table S2 (Supporting Information). It is found that enhanced photocatalysis rates of TiO2-NAA-DBRs by visible-NIR light excitation are critically determined by the spectral alignment between the PSB's red boundary ($\lambda_{PSB-red}$) of TiO₂-functionalized NAA-DBRs and the MB's optical absorbance band. At the PSB's red boundary, photon propagation through the PC structure is slowed dramatically. This extends the lifespan of visible photons within the semiconducting layer and increases the frequency of photon-semiconductor interactions, generating additional e^--h^+ pairs to accelerate photocatalytic reactions. When $\lambda_{PSB-red}$ of TiO₂-functionalized NAA-DBRs is positioned closely to the red or blue boundaries of the MB absorbance band, the light-driven breakdown efficiency of these composite PC structures to decompose MB is achieved for specific t_{TiO_2} . This enhancement is attributable to slow light effect. However, when $\lambda_{\text{PSB-red}}$ of TiO₂–NAA-DBRs is under the maximum optical absorbance of MB, the screening effect by MB molecules dramatically worsens the overall capability of the composite PC structure to breakdown MB molecules upon photonic activation. It is also found that the longer total pore length of TiO₂-NAA-DBRs may play a minor role in improving the light-induced breakdown efficiency of these PCs when the PSB's red boundary is far away from the absorbance band of MB. While TiO₂-NAA-DBRs fabricated with t_{TiO_2} = 0.5 nm provide the most optimal t_{TiO_2} for harnessing slow photons, additional e^--h^+ pairs from a thicker semiconducting TiO₂ layer in TiO₂-NAA-DBRs (*i.e.*, $t_{TiO_2} = 2 \text{ nm}$) can also contribute to the increase in overall light-induced breakdown efficiency of these composite PC structures. Analysis of the effect of the crystal phase of titanium dioxide functional coatings on the breakdown efficiency of TiO2-NAA-DBRs reveals that anatase semiconducting TiO₂ layers can achieve superior photocatalytic performances than their amorphous TiO2-NAA-DBR analogues.

Figure 7c presents the light-driven breakdown of 4-CP and MB by a representative nanoporous composite DBR. The breakdown efficiency of TiO2-NAA-DBRs to break 4-CP is significantly lower when compared to that of MB ($k_{4\text{-CP}}$ = 0.24 \pm 0.02 h⁻¹ and $k_{\rm MB} = 3.95 \pm 0.68$ h⁻¹, respectively), which is expected as 4-CP are much more resilient molecules.⁶⁰ The absorbance maxima of 4-CP and MB are 225 and 664 nm, respectively. Therefore, the photodegradation of 4-CP does not rely on the slow photon enhancement since the absorbance maximum of 4-CP is located far away from the red and blue edges of the composite nanoporous PC. It is also important to note that in contrast to positively charged MB molecules, 4-CP molecules are negatively charged and thus pushed away by the negatively charged surface of titanium oxide under the conditions of study. This, as a result, prevents 4-CP molecules from being efficiently absorbed onto the surface of TiO₂-NAA-DBRs and reduces the light-driven breakdown efficiency of these model semiconductor PCs. Nevertheless, TiO₂-functionalized NAA-based DBRs are still able to photodegrade 4-CP under visible-NIR irradiation. Kim and Choi⁶⁰ investigated the visible

Table 1. Comparison of Kinetic Constant (k) for the Light-Induced Breakdown of MB by Various Benchmark TiO ₂ -Base	d
Photocatalysts Excited by Visible Light	

photocatalyst	P25 TiO ₂ nanoparticles	TiO ₂ inverse opal	TiO ₂ –NAA- BDBRs	TiO ₂ –NAA- GIFs	TiO ₂ –NAA- µQVs	TiO ₂ –NAA- DBRs	TiO ₂ –NAA- DBRs
optical mechanism		slow photon	slow photon	slow photon	light recirculation	slow photon	slow photon
TiO ₂ deposition method			sol-gel	sol-gel	sol-gel	sol-gel	ALD
k (h ⁻¹)	0.64	1.32	1.12	2.10	3.55	3.04	3.95
$\begin{array}{c} \textbf{catalyst loading} \\ (\text{mg } \text{L}^{-1}) \end{array}$	200	200					
effective surface area (cm ²)		5	1	1	1	1	1
power (W)	500	500	150	150	150	150	150
$\begin{array}{c} \textbf{MB concentration} \\ (\text{mg } \text{L}^{-1}) \end{array}$	5	5	5	5	5	5	5
references	19	19	46	42	45		this study

light-driven breakdown reaction of 4-CP in water, using TiO_2 powder. Their observations show that the visible light reactivity is attributable to complexation of phenolic compounds on the surface of TiO_2 . According to this light-induced breakdown mechanism, direct transfer of electrons from the semiconductor to the surface-complexed phenol groups upon absorption of visible photons is the driving force through which oxidative degradation of 4-CP occurs.

3.6. Benchmarking of TiO₂-NAA-DBRs. Table 1 compiles the visible light-driven breakdown efficiency of benchmark photocatalyst platforms in breaking MB molecules. It is apparent that NAA-based DBRs functionalized with TiO₂ coatings via ALD provide better light-induced breakdown efficiency (~84%) than that of conventional P25 TiO_2 nanoparticles due to their constrained ability to only absorb UV light for driving photocatalytic reactions.¹⁹ It is also found that our model composite PCs have superior performance to that of TiO₂-based inverse opals to breakdown MB under light induction, with 67% enhancement.¹⁹ Nevertheless, a direct comparison would not be appropriate due to differences in conditions (i.e., catalyst loading, power of illumination, and effective surface area). We have recently engineered various NAA-based photocatalyst platforms and studied their lightdriven breakdown efficiency to destroy MB and other organics. These NAA-based photocatalyst platforms include PC structures such as GIFs, 42 DBRs, 43,44 $\mu \rm QVs, ^{45}$ and BDBRs, 46 the inner surface of which was functionalized with light-active TiO₂ coatings via the sol-gel approach. Since similar experimental conditions are employed, direct performance comparison between these NAA-based photocatalyst platforms is possible. It is apparent that TiO₂-functionalized NAA-DBRs developed in this study perform significantly better than TiO₂-NAA-BDBRs (72%) produced via sol-gel.⁴⁶ ALD-TiO₂-NAA-DBRs also outperform TiO₂-NAA-GIFs in breaking down MB molecules, with an enhancement of 47% due to a more efficient light collection associated with the spectrally broad PSB of NAA-DBRs.⁴² While TiO₂-NAA-DBRs outperform TiO₂-NAA- μ QVs in light-driven breakdown of MB, the photocatalytic enhancement is small (10%).⁴⁵ This result could be associated with the recirculation of incoming visible-NIR photons and their strong confinement within the composite PC structure.

Different surface functionalization techniques for TiO_2 – NAA-DBRs reveal that the light-driven breakdown efficiency of TiO_2 –NAA-DBRs fabricated by ALD is superior to those fabricated with the sol–gel method (23%).⁴³ This result could be associated with the more precise control over the thickness, composition, and homogeneity of TiO₂ layers achieved by ALD when compared to their counterparts deposited *via* the sol–gel method. To summarize, the photocatalytic comparison in this study demonstrates that ALD-TiO₂–NAA-DBRs are promising photocatalyst platforms to boost photocatalytic reactions by rationally managing photons at the nanoscale.

4. CONCLUSIONS

We have generated new insights into the development of highperforming photocatalytic platforms that can harness slow light to maximize generation of charge carriers under visible-NIR illumination. NAA-DBRs with highly versatile and controllable optical properties were fabricated by STPA and used as model PC platforms to identify enhancements in breakdown efficiency associated with slow light effects. Modification of NAA-DBRs with thin, functional, optoelectronic, and semiconducting layers of titanium dioxide by atomic layer deposition enabled enhanced optoelectronic conversion rates for boosting photocatalytic reactions. The combined effect of anodization and thickness of ALD TiO₂ layers on the light-induced breakdown efficiency of TiO₂-NAA-DBRs were studied using the photodegradation of MB as a model reaction under visible-NIR light. Analysis of relative optical alignment of the absorbance band of MB, PSB's red boundary, and the corresponding light-driven breakdown efficiencies was used to elucidate the mechanistic contribution of slow light effect in these reactions driven by TiO₂-NAA-DBRs. Our study demonstrates that when the PSB's red boundary of TiO₂-NAA-DBRs is positioned near the red or blue edge of the absorbance band of MB, the photocatalytic efficiency is the maximum. The maximum breakdown rate of MB was achieved by TiO2-functionalized NAA-based DBRs fabricated with an anodization period of 1200 s and a coating thickness of 0.5 nm (*i.e.*, $k = 3.95 \pm 0.68 \text{ h}^{-1}$). However, the screening effect by MB molecules worsens the light-induced breakdown efficiency when TiO₂-NAA-DBRs' red edge is positioned within the spectral region of maximum absorbance of MB. Our results indicate that NAA-based PCs featuring thinner TiO₂ coatings achieve the highest photocatalytic efficiency associated with slow light effect. However, the overall breakdown efficiency of TiO2-NAA-DBRs with thicker semiconductor layers is higher in the broad visible spectrum due to extra electron-hole pairs generated from the bulk of the TiO₂ layer in TiO₂-NAA-DBRs. It is also found that at those regions far from the absorbance band of MB, longer total pore length and anatase crystal phase also contribute to the

improvement of the resulting light-driven breakdown efficiency of TiO $_2$ –NAA-DBRs.

Our findings indicate that TiO_2 -NAA-DBRs fabricated by STPA and ALD are promising photocatalyst platforms that can outperform other benchmark photocatalysts in photodegradation of organic molecules. These findings provide exciting venues to rationally design and engineer light-matter interactions in PC semiconductors for multiple light-harvesting applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c03320.

Absorbance spectrum of MB molecules, calibration line correlating MB concentration and absorbance intensity, STPA profiles used to fabricate NAA-DBRs with varying anodization period $(T_{\rm P})$, transmission spectra of TiO₂– NAA-DBRs produced with varying TiO₂ thickness $(t_{\rm TiO_2})$ and $T_{\rm P}$ in air and water, dependence of the central position of characteristic PSB with $t_{\rm TiO_2}$ and $T_{\rm P}$ of TiO₂– NAA-DBRs in air and water, spectrum of simulated solar light irradiation used in our study, summary of photocatalytic performance and red edge of characteristic PSB of TiO₂–NAA-DBRs as a function of $t_{\rm TiO_2}$ and $T_{\rm P}$, measurement data and analysis of the optical spectroscopic ellipsometry, and Gaussian fittings and values of the absorbance band of MB over illumination time (PDF)

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Notes

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REFERENCES

(1) Fox, M. A.; Dulay, M. T. Heterogeneous Photocatalysis. *Chem. Rev.* **1993**, *93*, 341–357.

(2) Lee, S.-Y.; Park, S.-J. TiO₂ Photocatalyst for Water Treatment Applications. J. Ind. Eng. Chem. **2013**, 19, 1761–1769.

(3) Mills, A.; Davies, R. H.; Worsley, D. Water Purification by Semiconductor Photocatalysis. *Chem. Soc. Rev.* **1993**, *22*, 417–425.

(4) Ren, H.; Koshy, P.; Chen, W.-F.; Qi, S.; Sorrell, C. C. Photocatalytic Materials and Technologies for Air Purification. *J. Hazard. Mater.* **2017**, 325, 340–366.

(5) Hisatomi, T.; Domen, K. Reaction Systems for Solar Hydrogen Production via Water Splitting with Particulate Semiconductor Photocatalysts. *Nat. Catal.* **2019**, *2*, 387–399.

(6) Liao, C.-H.; Huang, C.-W.; Wu, J. C. S. Hydrogen Production from Semiconductor-based Photocatalysis via Water Splitting. *Catalysts* **2012**, *2*, 490–516.

(7) Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic Conversion of CO_2 into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv. Mater.* **2014**, *26*, 4607–4626.

(8) Qu, Y.; Duan, X. Progress, Challenge, and Perspective of Heterogeneous Photocatalysts. *Chem. Soc. Rev.* 2013, 42, 2568-2580.
(9) Liu, G.; Wang, L.; Yang, H. G.; Cheng, H.-M.; Lu, G. Q. Titania-Based Photocatalysts. *Crewith* Doping and Hoterostructuring I.

Based Photocatalysts-Crystal Growth, Doping and Heterostructuring. J. Mater. Chem. 2010, 20, 831–843.

(10) Khaki, M. R. D.; Shafeeyan, M. S.; Raman, A. A. A.; Daud, W. M. A. W. Application of Doped Photocatalysts for Organic Pollutant Degradation—A Review. *J. Environ. Manage.* **2017**, *198*, 78–94.

(11) Wang, M.; Ye, M.; Iocozzia, J.; Lin, C.; Lin, Z. Plasmon-Mediated Solar Energy Conversion via Photocatalysis in Noble Metal/Semiconductor Composites. *Adv. Sci.* **2016**, *3*, 1600024.

(12) Meng, A.; Zhang, L.; Cheng, B.; Yu, J. Dual Cocatalysts in TiO₂ Photocatalysis. *Adv. Mater.* **2019**, *31*, 1807660.

(13) Likodimos, V. Photonic Crystal-Assisted Visible Light Activated TiO₂ Photocatalysis. *Appl. Catal., B* **2018**, *230*, 269–303.

(14) Zhou, X.; Liu, N.; Schmuki, P. Photocatalysis with TiO_2 Nanotubes: "Colorful" Reactivity and Designing Site-Specific Photocatalytic Centers into TiO_2 Nanotubes. *ACS Catal.* **2017**, *7*, 3210– 3235.

(15) Lim, S. Y.; Law, C. S.; Liu, L.; Markovic, M.; Hedrich, C.; Blick, R. H.; Abell, A. D.; Zierold, R.; Santos, A. Electrochemical Engineering of

465 - 473.

Nanoporous Materials for Photocatalysis: Fundamentals, Advances, and Perspectives. *Catalysts* 2019, 9, 988.

(16) Gibbs, H. M.; Khitrova, G.; Koch, W. Exciton-Polariton Light-Semiconductor Coupling Effects. *Nat. Photonics* **2011**, *5*, 273–282.

(17) Raja-Mogan, T.; Ohtani, B.; Kowalska, E. Photonic Crystals for Plasmonic Photocatalysis. *Catalysts* **2020**, *10*, 827.

(18) Liu, J.; Zhao, H.; Wu, M.; Van der Schueren, B.; Li, Y.; Deparis, O.; Ye, J.; Ozin, G. A.; Hasan, T.; Su, B.-L. Slow Photons for Photocatalysis and Photovoltaics. *Adv. Mater.* **201**7, *29*, 1605349.

(19) Zheng, X.; Meng, S.; Chen, J.; Wang, J.; Xian, J.; Shao, Y.; Fu, X.; Li, D. Titanium Dioxide Photonic Crystals with Enhanced Photocatalytic Activity: Matching Photonic Band Gaps of TiO₂ to the Absorption Peaks of Dyes. *J. Phys. Chem. C* **2013**, *117*, 21263–21273. (20) Baba, T. Slow Light in Photonic Crystals. *Nat. Photonics* **2008**, *2*,

(21) Kim, K.; Thiyagarajan, P.; Ahn, H.-J.; Kim, S.-I.; Jang, J.-H. Optimization for Visible Light Photocatalytic Water Splitting: Gold-Coated and Surface-Textured TiO₂ Inverse Opal Nano-Networks. *Nanoscale* **2013**, *5*, 6254–6260.

(22) Temerov, F.; Pham, K.; Juuti, P.; Mäkelä, J. M.; Grachova, E. V.; Kumar, S.; Eslava, S.; Saarinen, J. J. Silver-Decorated TiO_2 Inverse Opal Structure for Visible Light-Induced Photocatalytic Degradation of Organic Pollutants and Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2020**, *12*, 41200–41210.

(23) Lee, K.; Hahn, R.; Altomare, M.; Selli, E.; Schmuki, P. Intrinsic Au Decoration of Growing TiO_2 Nanotubes and Formation of a High-Efficiency Photocatalyst for H₂ Production. *Adv. Mater.* **2013**, *25*, 6133–6137.

(24) Sopha, H.; Krbal, M.; Ng, S.; Prikryl, J.; Zazpe, R.; Yam, F. K.; Macak, J. M. Highly Efficient Photoelectrochemical and Photocatalytic Anodic TiO_2 Nanotube Layers with Additional TiO_2 Coating. *Appl. Mater. Today* **2017**, *9*, 104–110.

(25) Sopha, H.; Baudys, M.; Krbal, M.; Zazpe, R.; Prikryl, J.; Krysa, J.; Macak, J. M. Scaling Up Anodic TiO₂ Nanotube Layers for Gas Phase Photocatalysis. *Electrochem. Commun.* **2018**, *97*, 91–95.

(26) Alessandri, I.; Zucca, M.; Ferroni, M.; Bontempi, E.; Depero, L.
E. Tailoring the Pore Size and Architecture of CeO₂/TiO₂ Core/Shell Inverse Opals by Atomic Layer Deposition. *Small* 2009, *5*, 336–340.
(27) Namigata, H.; Watanabe, K.; Okubo, S.; Hasegawa, M.; Suga, K.;

Nagao, D. Double-Inverse-Opal-Structured Particle Assembly as a Novel Immobilized Photocatalytic Material. *Materials* **2020**, *14*, 28.

(28) Qiu, J.; Jin, Z.; Liu, Z.; Liu, X.; Liu, G.; Wu, W.; Zhang, X.; Gao, X. Fabrication of TiO_2 Nanotube Film by Well-Aligned ZnO Nanorod Array Film and Sol-Gel Process. *Thin Solid Films* **2007**, *515*, 2897–2902.

(29) Liu, Y.; Liu, R.; Liu, C.; Luo, S.; Yang, L.; Sui, F.; Teng, Y.; Yang, R.; Cai, Q. Enhanced photocatalysis on TiO_2 Nanotube Arrays Modified with Molecularly Imprinted TiO_2 Thin Film. *J. Hazard. Mater.* **2010**, *182*, 912–918.

(30) Curti, M.; Schneider, J.; Bahnemann, D. W.; Mendive, C. B. Inverse Opal Photonic Crystals as a Strategy to Improve Photocatalysis: Underexplored Questions. *J. Phys. Chem. Lett.* **2015**, *6*, 3903–3910.

(31) Stein, A.; Wilson, B. E.; Rudisill, S. G. Design and Functionality of Colloidal-Crystal-Templated Materials – Chemical Applications of Inverse Opals. *Chem. Soc. Rev.* **2013**, *42*, 2763–2803.

(32) Lee, K.; Mazare, A.; Schmuki, P. One-Dimensional Titanium Dioxide Nanomaterials: Nanotubes. *Chem. Rev.* **2014**, *114*, 9385– 9454.

(33) Paramasivam, I.; Jha, H.; Liu, N.; Schmuki, P. A Review of Photocatalysis using Self-organized TiO_2 Nanotubes and Other Ordered Oxide Nanostructures. *Small* **2012**, *8*, 3073–3103.

(34) Santos, A. Nanoporous Anodic Alumina Photonic Crystals: Fundamentals, Developments and Perspectives. J. Mater. Chem. C 2017, 5, 5581–5599.

(35) (a) Masuda, H.; Ohya, M.; Nishio, K.; Asoh, H.; Nakao, M.; Nohtomi, M.; Yokoo, A.; Tamamura, T. Photonic Band Gap in Anodic Porous Alumina with Extremely High Aspect Ratio Formed in Phosphoric Acid Solution. *Jpn. J. Appl. Phys.* **2000**, *39*, L1039– L1041. (b) Masuda, H.; Ohya, M.; Asoh, H.; Nishio, K. Photonic Band Gap in Naturally Occurring Ordered Anodic Porous Alumina. Jpn. J. Appl. Phys. 2001, 40, L1217–L1219.

(36) Liu, L.; Lim, S. Y.; Law, C. S.; Acosta, L. K.; Jin, B.; Abell, A. D.; Marsal, L. F.; Ni, G.; Santos, A. Optical Engineering of Nanoporous Photonic Crystals by Gaussian-Like Pulse Anodization. *Microporous Mesoporous Mater.* **2021**, 312, 110770.

(37) Lim, S. Y.; Law, C. S.; Jiang, L.; Acosta, L. K.; Bachhuka, A.; Marsal, L. F.; Abell, A. D.; Santos, A. Enhancing Forbidden Light Propagation in Nanoporous Anodic Alumina Gradient-Index Filters by Alcohol Additives. *ACS Appl. Nano Mater.* **2020**, *3*, 12115–12129.

(38) Law, C. S.; Lim, S. Y.; Abell, A. D.; Marsal, L. F.; Santos, A. Structural Tailoring of Nanoporous Anodic Alumina Optical Microcavities for Enhanced Resonant Recirculation of Light. *Nanoscale* **2018**, *10*, 14139–14152.

(39) Santos, A.; Pereira, T.; Law, C. S.; Losic, D. Rational Engineering of Nanoporous Anodic Alumina Optical Bandpass Filters. *Nanoscale* **2016**, *8*, 14846–14857.

(40) Chen, Y.; Santos, A.; Ho, D.; Wang, Y.; Kumeria, T.; Li, J.; Wang, C.; Losic, D. On The Generation of Interferometric Colors in High Purity and Technical Grade Aluminum: An Alternative Green Process for Metal Finishing Industry. *Electrochim. Acta* **2015**, *174*, 672–681.

(41) Lee, C.-Y.; Schmuki, P. Engineering of Self-Organizing Electrochemistry: Porous Alumina and Titania Nanotubes. In *Electrochemical Engineering across Scales: From Molecules to Processes*; Alkire, R. C., Bartlett, P. N., Lipkowski, J., Eds.; John Wiley & Sons: Weinheim, 2015; Vol. 15, pp 145–192.

(42) Lim, S. Y.; Law, C. S.; Markovic, M.; Kirby, J. K.; Abell, A. D.; Santos, A. Engineering the Slow Photon Effect in Photoactive Nanoporous Anodic Alumina Gradient-Index Filters for Photocatalysis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 24124–24136.

(43) Lim, S. Y.; Law, C. S.; Markovic, M.; Marsal, L. F.; Voelcker, N. H.; Abell, A. D.; Santos, A. Rational Management of Photons for Enhanced Photocatalysis in Structurally-Colored Nanoporous Anodic Alumina Photonic Crystals. *ACS Appl. Energy Mater.* **2019**, *2*, 1169–1184.

(44) Lim, S. Y.; Law, C. S.; Liu, L.; Markovic, M.; Abell, A. D.; Santos, A. Integrating Surface Plasmon Resonance and Slow Photon Effects in Nanoporous Anodic Alumina Photonic Crystals for Photocatalysis. *Catal. Sci. Technol.* **2019**, *9*, 3158–3176.

(45) Liu, L.; Lim, S. Y.; Law, C. S.; Jin, B.; Abell, A. D.; Ni, G.; Santos, A. Light-Confining Semiconductor Nanoporous Anodic Alumina Optical Microcavities for Photocatalysis. *J. Mater. Chem. A* **2019**, *7*, 22514–22529.

(46) Liu, L.; Lim, S. Y.; Law, C. S.; Jin, B.; Abell, A. D.; Ni, G.; Santos, A. Engineering of Broadband Nanoporous Semiconductor Photonic Crystals for Visible-Light-Driven Photocatalysis. *ACS Appl. Mater. Interfaces* **2020**, *12*, 57079–57092.

(47) Wang, Y.; Santos, A.; Evdokiou, A.; Losic, D. Rational Design of Ultra-Short Anodic Alumina Nanotubes by Short-Time Pulse Anodization. *Electrochim. Acta* **2015**, *154*, 379–386.

(48) Kubrin, R.; Pasquarelli, R. M.; Waleczek, M.; Lee, H. S.; Zierold, R.; do Rosário, J. J.; Dyachenko, P. N.; Montero Moreno, J. M.; Petrov, A. Y.; Janssen, R.; Eich, M.; Nielsch, K.; Schneider, G. A. Bottom-up Fabrication of Multilayer Stacks of 3D Photonic Crystals from Titanium Dioxide. ACS Appl. Mater. Interfaces 2016, 8, 10466–10476.

(49) Pasquarelli, R. M.; Lee, H. S.; Kubrin, R.; Zierold, R.; Petrov, A. Y.; Nielsch, K.; Schneider, G. A.; Eich, M.; Janssen, R. Enhanced Structural and Phase Stability of Titania Inverse Opals. *J. Eur. Ceram. Soc.* **2015**, *35*, 3103–3109.

(50) Diamantopoulou, A.; Sakellis, E.; Gardelis, S.; Tsoutsou, D.; Glenis, S.; Boukos, N.; Dimoulas, A.; Likodimos, V. Advanced Photocatalysts Based on Reduced Nanographene Oxide- TiO_2 Photonic Crystal Films. *Materials* **2019**, *12*, 2518.

(51) Abràmoff, M. D.; Magalhaes, P. J.; Ram, S. J. Image Processing with ImageJ. *Biophotonics Int.* **2004**, *11*, 36–42.

(52) Santos, A.; Balderrama, V. S.; Alba, M.; Formentín, P.; Ferré-Borrull, J.; Pallarès, J.; Marsal, L. F. Nanoporous Anodic Alumina Barcodes: Toward Smart Optical Biosensors. *Adv. Mater.* **2012**, *24*, 1050–1054. (53) Brzózka, A.; Brudzisz, A.; Hnida, K.; Sulka, G. D. Chemical and Structural Modifications of Nanoporous Alumina and Its Optical Properties. In *Electrochemically Engineered Nanoporous Materials: Methods, Properties and Applications*; Losic, D., Santos, A., Eds.; Springer International Publishing: Cham, 2015; Vol. 220, pp 219–288.

(54) Wiegand, C. W.; Faust, R.; Meinhardt, A.; Blick, R. H.; Zierold, R.; Nielsch, K. Understanding the Growth Mechanisms of Multilayered Systems in Atomic Layer Deposition Process. *Chem. Mater.* **2018**, *30*, 1971–1979.

(55) George, S. M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110*, *111*–131.

(56) Luttrell, T.; Halpegamage, S.; Tao, J.; Kramer, A.; Sutter, E.; Batzill, M. Why is Anatase a Better Photocatalyst than Rutile?—Model Studies on Epitaxial TiO₂ Films. *Sci. Rep.* **2014**, *4*, 4043.

(57) Zhou, W.; Sun, F.; Pan, K.; Tian, G.; Jiang, B.; Ren, Z.; Tian, C.; Fu, H. Well-Ordered Large-Pore Mesoporous Anatase TiO₂ with Remarkably High Thermal Stability and Improved Crystallinity: Preparation, Characterization, and Photocatalytic Performance. *Adv. Funct. Mater.* **2011**, *21*, 1922–1930.

(58) Li, Y.; Kunitake, T.; Fujikawa, S. Efficient Fabrication and Enhanced Photocatalytic Activities of 3D-Ordered Films of Titania Hollow Spheres. *J. Phys. Chem. B* **2006**, *110*, 13000–13004.

(59) Zhang, T.; Oyama, T.; Aoshima, A.; Hidaka, H.; Zhao, J.; Serpone, N. Photooxidative N-demethylation of Methylene Blue in Aqueous TiO₂ Dispersions under UV Irradiation. *J. Photochem. Photobiol.*, A **2001**, 140, 163–172.

(60) Kim, S.; Choi, W. Visible-Light-Induced Photocatalytic Degradation of 4-Chlorophenol and Phenolic Compounds in Aqueous Suspensions of Pure Titania: Demonstrating the Existence of a Surface-Complex Mediated Path. *J. Phys. Chem. B* **2005**, *109*, 5143–5149.

Supporting Information

Harnessing Slow Light in Optoelectronically Engineered Nanoporous Photonic Crystals for Visible Light-Enhanced Photocatalysis

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Figure S1. Optical absorbance spectrum of 5 mg L⁻¹ aqueous solution of: (a) methylene blue (MB) and (b) 4-chlorophenol (4-CP). The absorbance band maxima for MB and 4-CP were at λ_{abs-MB} = 664 nm and at $\lambda_{abs-4-CP}$ = 225 nm, respectively (NB: absolute absorbance intensity of MB and 4-CP at the central position of the absorbance band maxima were ~2.8 and 1.0 a.u., respectively).



Figure S2. Linear correlation between absorbance maximum intensity and concentration of methylene blue (MB) and 4-chlorophenol (4-CP) (NB: concentration range from 0.00244 to 10 mg L⁻¹). The linear correlation for MB and 4-CP were: Abs_{MB} (a.u.) = 0.1697 [*MB*] (mg L⁻¹) and Abs_{4-CP} (a.u.) = 0.0478 [4-CP] (mg L⁻¹), respectively. The R^2 value for MB and 4-CP were 0.99923 and 0.99980, respectively.



Figure S3. Full-view and magnified view of stepwise pulse anodization (STPA) profiles used to fabricate NAA–DBRs with anodization period (T_P) of: (a) 900 s, (b) 1000 s, (c) 1100 s, (d) 1200 s, (e) 1300 s and (f) 1400 s.



Figure S4. Transmission spectra of TiO₂–NAA–DBRs produced with varying TiO₂ thicknesses (t_{TiO2}) of 0, 0.5, 1 and 2 nm, and anodization period (T_P) of: (a) 900 s, (b) 1000 s, (c) 1100 s, (d) 1200 s, (e) 1300 s and (f) 1400 s (NB: media = air).



Figure S5. Transmission spectra of TiO_2 –NAA–DBRs produced with varying TiO_2 thicknesses (t_{TiO2}) of 0, 0.5, 1 and 2 nm, and anodization period (T_P) of: (a) 900 s, (b) 1000 s, (c) 1100 s, (d) 1200 s, (e) 1300 s and (f) 1400 s (NB: media = water).



Figure S6. Linear correlation of the central position of characteristic PSB (λ_{PSB}) and anodization period (T_P) of TiO₂–NAA–DBRs produced with varying TiO₂ thicknesses (t_{TiO2}) and media infiltration into the nanopores: (a) 0 nm in air, (b) 0.5 nm in air, (c) 1 nm in air, (d) 2 nm in air, (e) 0 nm in water, (f) 0.5 nm in water, (g) 1 nm in water and (h) 2 nm in water.



Figure S7. Spectrum of simulated visible–NIR light irradiation source used for photocatalysis in our study (i.e. 0.1% UV (350–400 nm), 64.9 % visible (400–750 nm), and 35.0% NIR (800–1025 nm)). The irradiation spectrum was measured using an optical fiber spectrometer (USB 4000, Ocean Optics, USA).



ALD-Coated Silicon Substrate ($t_{TIO2} = 0.5$ nm)



ALD-Coated Silicon Substrate ($t_{\tau_{102}} = 1.0$ nm)





ALD-Coated Silicon Substrate ($t_{\pi 02}$ = 2.0 nm)

Figure S8. Atomic force microscopy characterization of model TiO2 films deposited onto silicon wafers at different deposition times/ALD cycles under the same conditions used in our study with: (a) bare silicon wafer, (b) $t_{TiO2} = 0.5$ nm, (c) $t_{TiO2} = 1.0$ nm, and (d) $t_{TiO2} = 2.0$ nm. (NB: the maximum surface roughness determined by AFM where 1.71, 2.18, 1.77, and 1.21 nm, respectively).



Figure S9. Spectral ellipsometry of TiO₂ thin films demonstrating the dependence of the electronic band gap on the film thickness deposited via ALD. The TiO₂ films were deposited onto a planar silicon substrate by ALD using the same process as described for the TiO₂–NAA–DBRs. The number of applied ALD cycles was modified to produce TiO₂ thicknesses of 2.5 nm, 8.5 nm, 15.5 nm, and 18.5 nm. TiO₂ films were characterized with a spectroscopic ellipsometer (Semilab SE-2000) at room temperature, and at an incident angle of 70°, in the visible-near infrared regions. The ellipsometric parameters Ψ and Δ are measured in the range of 0.55–5 eV. The optical constants of TiO₂ are fitted using Semilab's SEA software with the Forouhi-Bloomer (F-B) dispersion model,¹⁻² and the goodness of the fit was considered when the root mean square error (RMSE) was less than 1.

1. Fujiwara, H., *Spectroscopic Ellipsometry. Principles and Applications*. John Wiley and Sons Ltd.: England, 2007.





Figure S10. Estimated Gaussian fittings of the absorbance of double-peak (deconvoluted) feature of MB photodegraded by TiO₂–NAA–DBRs fabricated with T_P = 1200 s and $t_{T/O2}$ = 0.5 nm at an illumination time (*t*) of (a) 0 h, (b) 0.25 h, (c) 0.5 h, (d) 0.75 h and (e) 1 h.

T _P (s)	t _{τio2} = 0.5 nm		t _{τio2} = 1 nm		t _{TiO2} = 2 nm	
	$\lambda_{PSB-red}$ (nm)	<i>k</i> (h⁻¹)	$\lambda_{PSB-red}$ (nm)	k (h ⁻¹)	$\lambda_{PSB-red}$ (nm)	k (h ⁻¹)
900	540 ± 14	0.86 ± 0.19	543 ± 14	2.15 ± 0.15	542 ± 14	2.85 ± 0.30
1000	594 ± 15	1.23 ± 0.22	599 ± 15	1.14 ± 0.23	584 ± 15	1.02 ± 0.18
1100	646 ± 16	1.07 ± 0.18	634 ± 16	0.47 ± 0.08	632 ± 16	0.62 ± 0.07
1200	688 ± 17	3.95 ± 0.68	678 ± 17	1.64 ± 0.22	689 ± 17	1.46 ± 0.14
1300	770 ± 19	1.72 ± 0.18	766 ± 19	0.35 ± 0.13	764 ± 19	2.44 ± 0.28
1400	826 ± 21	1.33 ± 0.37	816 ± 20	0.58 ± 0.17	826 ± 21	2.20 ± 0.36

Table S1. Compilation of k and $\lambda_{PSB-red}$ for photodegradation of MB by TiO₂–NAA–DBRs produced with varying T_P and t_{TiO2} .

Table S2. Estimated absorbance maximum of the photodegradation of double-peak feature of MB by TiO₂–NAA–DBRs produced with T_P = 1200 s and t_{TiO2} = 0.5 nm over various illumination time (*t*).

t (h)	Wavelength (nm)			
	Peak 1	Peak 2		
0	622 ± 6	664 ± 1		
0.25	623 ± 7	663 ± 1		
0.5	621 ± 11	661 ± 2		
t (h)	Merged Peak			
0.75	634 ± 1			
1	629 ± 1			

7.4. Publication IV

Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide

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Author contributions: C.H., A.R.B., S.G.-G. prepared the ALD-functionalized AAO-PhCs. C.H., A.R.B., V.V., A.S., R.Z. performed the data analysis. C.H. wrote the manuscript. C.H., A.R.B., V.V., A.S., R.Z. revised the manuscript. C.H. and R.Z. conceptualized the study. V.V., V.M.P., A.S., R.H.B., R.Z. acquired funding. V.V., R.H.B., R.Z. supervised the study. All authors conducted proofreading and approved the manuscript.



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Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide

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Photonic crystals (PhCs) are interesting structures for photocatalytic applications because of their capability of harnessing distinct forms of light-matter interactions within the PhCs. Of all these, overlapping one of the photonic stopband's (PSB) edge with the absorption of the PhC material or adsorbed molecules improves their excitation and generated charge carriers can subsequently induce photocatalytic reactions. The PSB position of anodic aluminum oxide PhCs (AAO-PhCs) can be easily adjusted by modifying the anodization profile. Herein, AAO-PhCs are designed to match the band gap of a model semiconductor enabling a general photocatalytic activity enhancement independent of the chemical to be decomposed. Fe₂O₃, as an example photocatalyst, is coated onto AAO-PhCs to demonstrate efficient photocatalytic systems by utilizing the slow photon effect. Tailored Fe₂O₃-AAO-PhCs with their PSB edge at 564 nm matching the Fe₂O₃ band gap exhibit generally enhanced degradation of three different organic dyes while a significant activity decrease is observed when the PSB edge does not overlap with the Fe₂O₃ absorption. Furthermore, photocatalyst degradation can be reduced down to only 4% activity loss over six consecutive measurements by an ultra-thin alumina coating.

1. Introduction

Purification of water is particularly important nowadays to ensure the supply of drinking water to society, especially in light of major challenges such as climate change and overpopulation. $^{\left[1,2\right] }$ Access to drinking water has been defined as Sustainable Development Goal (SDG) number 6 by the United Nations.^[3] Thus, cheap, reusable, sustainable, and decentralized water purification systems are urgently needed. Photocatalysts came into focus over the last decades as they use sunlight to induce chemical reactions, e.g., degradation various pollutants in water.^[4–8] Since the discovery of photocatalysis, titanium dioxide (TiO₂) has become the benchmark photocatalytic material due to its availability, inertness, stability, and good photocatalytic properties

in different processes.[9-12] However, it

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suffers from insufficient use of the solar light spectrum since UV light-which is only 5-10% of the sunlight spectrum at the Earth's surface-is required to initiate photocatalytic processes in TiO2.[13] Besides strategies to tune the excitation of TiO₂ toward the visible range such as doping or creation of oxygen vacancy defects,^[14] other photocatalytically active materials, namely various oxides, sulfides, and nitrides, or combinations among them are also intensively studied.^[6,7,15-19] Iron (III) oxide (hematite, Fe₂O₃), for example, is a promising photocatalyst because it is abundant on Earth and its electronic band gap is located in the visible region of the electromagnetic spectrum (≈1.7–3.1 eV).^[17,20,21] Accordingly, irradiance-rich sunlight spectral regions can be harvested to excite iron oxide and thereby induce photocatalytic reactions such as oxidative water purification. Moreover, Fe₂O₃ is a non-toxic material, which could be applied in the decontamination of drinking water. Nevertheless, the generation of charge carriers in Fe₂O₃ is often inefficient or the fast charge carrier recombination prevents the induction of reactions by the charge carrier.^[22-24] To overcome this limitation, combining Fe_2O_3 with other semiconductors to form heterojunctions has been demonstrated as an approach to improve charge carrier separation.^[22,25,26] Alternatively, engineering light-matter interactions between incoming light and Fe₂O₃ by tailoring the structure of the semiconductor also provides an effective means of increasing the generation yield of charge carriers. This approach also applies to many other semiconductors featuring low charge carrier generation rates. For example, the so-called slow photon effect in photonic crystals (PhCs) can be rationally engineered for this purpose.[27-29]

PhCs are structures composed of periodically arranged materials with different dielectric constants. These periodic variations within the structures result in photonic stopbands (PSBs)-also denoted as photonic band gaps-wherein photons with the respective wavelength cannot propagate through the PhC and are therefore reflected at the PhC's surface.[30-33] At the blue and red edges of the PhC's PSB, the group velocity of photons is strongly reduced, which is referred to as the slow photon effect (Figure 1a). These photons have more time to interact with the PhC material and thus, the interaction probability between incident photons and atoms of the material is increased.^[27,28,34] Consequently, charge carrier generation in semiconductor-based PhCs can be enhanced by utilizing the slow photon effect when one edge of the PSB is aligned with the electronic band gap of the semiconductor. PhCs can be realized in one, two, or three dimensions.^[31,32] Especially two- and three-dimensional PhCs are interesting for photocatalytic applications because they can consist of porous structures that provide high surface areas and, accordingly, many possible reaction sites. The most common semiconductor-based three-dimensional PhC structures are inverse opals, which are characterized by a semiconductor matrix around hollow spheres.^[12,27,28,34-36] However, PhCs can also be fabricated by tailoring the anodization of aluminum.^[37-40] Anodic aluminum oxide (AAO) structures consist of cylindrical, self-organized, highly ordered pores inside electrochemically prepared aluminum oxide. The pores of AAO feature distinct geometrical parameters, namely pore diameter, interpore distance, and pore length, which can be adjusted by tuning the electrochemical anodization parameters.^[39,41-43] Specifically, the application of pulse-like anodization approaches modifies the pore morwww.advmatinterfaces.de

phology from straight to periodically diameter-modulated structures (Figure 1b). Such modulated structures act as PhCs and their PSB can be precisely tailored across the UV to IR spectral range through judicious input anodization parameters.^[3740]

On the one hand, tuning the PSB position of semiconductorfunctionalized AAO-PhCs to overlap the PSB edge with the absorption wavelength of chemical pollutants boosts the photodegradation efficiency of these platforms.^[29,44.46] The photocatalytic activity of such tailor-made aligned AAO-PhCs is enhanced by the slow photon effect for the specific chemical, but it decreases when the photocatalytic decomposition of compounds with absorption bands off-side the PSB edge is tested. In the latter case, the slow photon effect no longer enhances the activity because the PSB edge is misaligned with the compounds' absorption maximum.

On the other hand, Liu et al. reported an enhanced photocatalytic degradation of organic dyes serving as model water pollutants when the PSB edge matches the band gap of TiO_2 , which was coated onto the AAO-PhC structure by sol–gel chemistry. However, TiO_2 excitation requires irradiation by UV light. To use the visible range of the electromagnetic spectrum, a semiconductor with a fitting band gap must be employed to increase the photocatalytic activity of a functionalized AAO-PhC. Thus, Fe₂O₃ is utilized in this study as a photocatalytically active semiconductor featuring a band gap in the visible region.^[23,24]

Ideal photocatalysts for purification systems should be durable, meaning they can be utilized multiple times without significant loss of their photocatalytic activity.^[4,52] Altering and destruction of Fe₂O₃ upon irradiation, and consequently, a corresponding reduction of their photocatalytic performance is often observed for this photocatalyst material.^[11,53,54] This phenomenon is denoted as photocorrosion or photodissolution since structural changes and decomposition processes of the Fe₂O₃ are induced by the illuminating (solar) light applied in photocatalytic processes to excite the semiconductor. Hence, the photocatalyst surface has to be protected to avoid such degradation, which could, for example, be realized by coating ultra-thin layers of metal oxides on top of the Fe₂O₃ film.^[11,53-60]

Apart from the PSB edge alignment with the semiconductor band gap, the film thickness of the semiconductor might be crucial for optimizing the photocatalytic performance of semiconductor-coated AAO-PhCs because it determines the charge carrier dynamics within the semiconductor as well as the mass transfer of photocatalytic reactants within the pores.^[11,20,22-24] Specifically, the minority charge carrier diffusion length in Fe₂O₃ is only a few nanometers^[20] whereby a low film thickness of Fe₂O₃ is therefore beneficial to achieve high photocatalytic activities. On the contrary, thicker films of at least a few tens of nanometers are required to ensure complete absorption of the incident sunlight by Fe2O3.^[20,47] Tailor-made functionalized AAO-PhCs provide new opportunities to balance these opposing effects by structural engineering of the nanostructure. Fe₂O₃ thin films deposited in the pores possess low thicknesses in the radial direction of the pores (i.e., diameter) while they cover a few tenths of micrometers in the pores' axial direction (i.e., length). Herein, atomic layer deposition (ALD) of Fe_2O_3 is applied to enable precise control over the deposited film thickness on the sub-nanometer scale.^[48-51] Accordingly, ALD is wellsuited as a functionalization technique to develop composite



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Figure 1. Schematic of photonic crystals, their optical properties, and the construction of Fe_2O_3 -functionalized anodic aluminum oxide photonic crystals. a) Due to the periodic modulation of the refractive index, a PhC exhibits a photonic stopband (PSB) which does not allow light propagation of specific wavelengths within the structure. Incoming light of this spectral region is reflected at the samples' surface. Due to the slow photon effect, light–matter interactions within the PhC are increased at the blue and red edges of the PSB (marked in the scheme). The position of the PSB edges can be tuned by controlling the preparation process to overlap with either the absorption of a dye (continuous grey line) or with the band gap of a semiconductor (dashed grey line), corresponding to the red and the blue edge, respectively. Depending on this alignment, the slow photon effect enhances the light absorption within the PhC structure by accelerating the excitation of the dye (upper right scheme) or of the semiconductor (lower right scheme). b) An AAO-PhC is exemplarily shown, featuring periodic diameter modulations of the pores. c) The AAO-PhC template is fabricated by pulse-like anodization of aluminum. Herein, the structures' surface is subsequently coated via atomic layer deposition of Fe_2O_3

semiconductor–AAO PhCs to study the photocatalytic performance of the structure with respect to the Fe_2O_3 film thickness.

In this work, we demonstrate how the photocatalytic activity of Fe₂O₃ coatings in structurally engineered AAO-PhCs can be enhanced by making use of the slow photon effect when the structures' PSB edge is aligned with the band gap of the semiconductor. Fe₂O₃-AAO-PhCs are prepared by pulse-like anodization of aluminum and subsequent ALD coating of Fe₂O₃ with different thicknesses (Figure 1c). Moreover, ultra-thin aluminum oxide (Al₂O₃) layers are also deposited onto optimized Fe₂O₃-AAO-PhCs by ALD to avoid photocorrosion and extend the lifetime of the semiconductor over repeated photocatalytic cycles. Fe₂O₃-AAO-PhCs' optical properties are characterized by UV-vis reflection measurements, and the photocatalytic performances are assessed with respect to the Fe₂O₃ film thickness. Specifically, Fe₂O₃-AAO-PhCs are immersed into aqueous solutions of model organic dyes-methylene blue (MB), rhodamine B (RhB), and methyl orange (MO)-and irradiated by visible light to analyze their photocatalytic degradation of the dyes. The structures' PSB characteristics and Fe_2O_3 film thicknesses are related to photocatalytic performances.

2. Results and Discussion

2.1. Fabrication and Optical Characterization of AAO-PhCs

AAO-PhCs with PSB edges located at wavelengths that match the Fe₂O₃ band gap are produced by applying rectangular current density pulses during the electrochemical oxidation of aluminum in oxalic acid ($H_2C_2O_4$, 0.3 M) electrolyte, as shown in **Figure 2**. The voltage signal response (output) of the aluminum chip anodized under these conditions follows the rectangular current density pulses with distortion of the pulse shape. The output pulses resemble a capacitor response with increase and decrease that follows the input current density with a certain temporal delay due to the recovery process of the barrier layer oxide at the

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Figure 2. Fabrication and characterization of AAO-PhCs by pulse-like anodization in oxalic acid. a) Rectangular current pulses are applied to the aluminum chip after an initial constant current period. The voltage at the sample follows the pulse behavior with distortion of the pulse shape due to the recovery effects of the barrier oxide layer. b) UV-vis reflection measurements reveal the PSB position of AAO-PhCs. The PSB position redshifts when the pores are infiltrated with H_2O compared to air due to the increased refractive index of the medium. The dashed lines indicate the positions of the PSB maximum (green line), the PSB blue edge (blue line), and the PSB red edge (red line). The PSB maximum is obtained by a Gaussian fit of the data, while the PSB edges are defined as the inflection points of the reflection peak. c,d) Photographs of the AAO-PhC samples. The AAO sample is indicated by the brown dotted circle. The aluminum backside of the sample is wet-chemically removed in (d), whereby the green color in reflection becomes visible.

bottom side of the nanopores (i.e., growth front of the anodic film).^[61-64] Moreover, the pulses are also asymmetric in shape. These pulses result in the formation of gradient-index filter-like structures, which are characterized by a smooth variation of pore diameter in depth (scanning electron microscope (SEM) images are shown in Figure S1, Supporting Information).^[29,65,66] Such AAO structures exhibit PSBs in the visible light range, as exemplarily shown in Figure 2b. The PSB position is determined by the pulse period ($t_{\rm pulse}$) and undergoes a red shift when the pores are infiltrated with water (H₂O) compared to air. The increment of the refractive index of the pore-filling medium (i.e., change from air to H_2O ^[67] leads to an increment of the effective refractive index of the filled AAO structure and simultaneous reflection intensity decrease. Analysis of the PSB properties is shown for the measurement in H₂O by the dashed lines. The blue line indicates the PSB blue edge, the red line resembles the PSB red edge, and the green line is the position of the PSB maximum (i.e., its maximum in intensity). Note, the inflection points of smoothed reflection data are calculated as the PSB edges ($\lambda_{\text{PSB,blue}}$; $\lambda_{\text{PSB,red}}$), while the peak maximum wavelength of a Gaussian fit defines the PSB maximum position λ_{PSB} . When the aluminum backside of the AAO-PhCs sample is present (Figure 2c), samples produced with $t_{\text{pulse}} = 275$ s appear yellow in an optical photograph. When the

aluminum backside of the underlying chip is removed, the refractive index contrast between the AAO-PhC and the background is higher and the green color reflected by the structures' PSB becomes visible, as demonstrated in Figure 2d.

Tuning t_{pulse} in the anodization or coating the samples with different thicknesses of Fe2O3 by ALD after their production modifies the PSB positions. Since the photocatalytic performance of semiconductor-modified AAO-PhCs is assessed in an aqueous medium, the structures' optical properties are characterized when the pores are infiltrated with deionized water (DI-H₂O). Figure 3a depicts the reflection spectra of as-produced, DI-H₂Oinfiltrated AAO-PhCs fabricated with $t_{\rm pulse}$ of 175, 270, 275, 300, 335, and 450 s, respectively. Note, the PSB characteristics are denoted as $\lambda_{\rm PSB}$ ($\lambda_{\rm PSB, blue};$ $\lambda_{\rm PSB, red}),$ where the PSB maximum wavelength λ_{PSB} is calculated by a Gaussian fitting while the inflection points of the PSB define the blue ($\lambda_{\text{PSB,blue}}$) and red edges ($\lambda_{\rm PSB,red}$). Here, the $\lambda_{\rm PSB}$ and the PSB edges change from 455 nm $(\lambda_{\text{PSB,blue}} = 428 \text{ nm}; \lambda_{\text{PSB,red}} = 477 \text{ nm})$ up to 858 nm (844 nm; 883 nm) with increasing pulse duration (Figure 3b) at a measured average rate of 1.5 \pm 0.1 nm s⁻¹. Since the reflection intensity of the samples applied in the photocatalysis measurements in this study (fabricated with $t_{pulse} = 270$ s and $t_{pulse} = 275$ s) are in the same absolute range, an effect of the PSB reflection intensity

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Figure 3. Optical properties of AAO-PhCs anodized by applying different pulse durations and coated with Fe₂O₃ by ALD after production. a) Normalized reflection spectra of samples anodized with varying pulse durations show a red shifting of the PSB position upon increasing the pulse duration. b) The PSB maximum wavelength depends linearly on the applied pulse duration t_{pulse} with a slope of 1.5 ± 0.1 nm s⁻¹. The error of the fit is 0.97. c) The PSB position is almost independent of the applied ALD cycle number for AAO-PhCs anodized with tpulse = 275 s and subsequently coated with Fe₂O₃ by ALD Here, the error bars denote the blue and red edge of the PSB while the data point represents the PSB maximum position λ_{PSB} . d) Depositing ultra-thin Al₂O₃ layer on AAO-PhCs prepared with 275 s pulse duration and previously coated by 385 cycles Fe₂O₃ does not significantly influence the PSB positions. (Reflection spectra for the samples characterized in (c,d) are shown in Figure S3 (Supporting Information).

on the photocatalytic performance for comparing the samples is herein not expected.

The PSB maximum wavelength and the blue and red edge of AAO-PhCs produced by 275 s pulse duration and coated with different cycle numbers of Fe_2O_3 by ALD are shown in Figure 3c. Within one Fe_2O_3 ALD cycle, 0.016 \pm 0.003 nm Fe_2O_3 are deposited and, accordingly, the applied ALD cycle numbers of 0, 77, 154, 231, 308, 385, and 462 cycles correspond to nominal film thicknesses of 0, 1, 2, 3, 4, 5, and 6 nm Fe₂O₃, respectively. Thicknesses of ALD-deposited films were analyzed by spectral ellipsometry on planar silicon reference substrates (Figure S2, Supporting Information). The AAO-PhCs exhibit similar PSB properties after ALD coating with a few nm of Fe₂O₃ and an overcoating by an ultra-thin aluminum oxide layer (Figure 3d), all in the range of the error obtained during AAO-PhC fabrication. Analysis of the AAO-PhCs' optical properties reveals that the PSB edges of samples coated with 77, 231, 385, and 462 Fe₂O₃ cycles by ALD overlap with the electronic band gap of Fe₂O₃ of \approx 2.2 Ev,^[23,24] which corresponds to a wavelength of \approx 564 nm. Here, a specific wavelength value is given for each PSB edge, whereby the "edge" region, which is essential for the slow photon effect, extends over a few nanometers. In Figure S3 (Supporting Information), the influence of Fe₂O₃ and Al₂O₃ coating on the PSB characteristics of AAO-PhCs fabricated with pulse durations of 270 and 335 s are shown compared to uncoated samples.

AAO-PhCs produced with similar pulse-like anodization approaches have previously been reported in literature.^[29,40,44-46,61,64-86] These structures show different PSB characteristics, namely position, width, intensity, and shape, depending on the anodization conditions. The herein presented profile utilizing rectangular current pulses in $H_2C_2O_4$ leads to similar AAO-PhCs as the existing approaches regarding the PSB reflection intensity and width. For example, reflection intensities reported in literature vary between 10% and 95%, depending on the applied conditions, while full width at half-maximum (FWHM) values from 16 nm up to 202 nm are observed.^[65,67,73,81,82]

To functionalize AAO-PhCs produced in $H_2C_2O_4$ with a photocatalytic active material, in literature the structures were coated with TiO₂ by sol–gel chemistry.^[29,44,45,80,85] It was reported that the coating red-shifted the PSB position of the samples due to the higher refractive index of TiO₂ compared to that of anodic Al_2O_3 .^[29,80] Furthermore, the coating reduced the AAO-PhC pore diameter, which induced a red shift of the PSB position. In 2021, Lim et al. deposited thin layers of TiO₂ onto AAO-PhCs by ALD, with film thicknesses below 2 nm. Since the thicknesses are much lower and better controlled than for sol–gel deposition processes, none of these samples significantly shifted the PSB position. Similarly, herein only slight shifts of the PSB positions were observed for AAO-PhCs anodized with pulse durations of

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Figure 4. Photocatalytic performances of Fe₂O₃-AAO-PhCs functionalized by different ALD cycle numbers. The photocatalytic activity depends on the pulse duration applied in anodization and the number of Fe₂O₃ cycles of the ALD process. For both AAO-PhC types anodized with different pulse durations t_{pulse} , the deposited Fe₂O₃ film thickness in combination with the PSB characteristics determines the photocatalytic performance. Analysis of the PSB edge positions with respect to the Fe₂O₃ band gap reveals that the highest activity is achieved when the PSB blue edge overlaps with the semiconductor band gap due to the slow photon effect. Note that the AAO-PhC coated by 385 ALD cycles for both sample types is most effective in photocatalytically degrading MB.

270, 275, and 335 s after coating with iron oxide and/or $\rm Al_2O_3$ by ALD.

2.2. Photocatalytic Activity of Fe₂O₃-AAO-PhCs

The photocatalytic performance of Fe₂O₃-functionalized AAO-PhCs with PSB edges located in the region of the Fe₂O₃ band gap depends on the Fe₂O₃ ALD cycle numbers. The Fe₂O₃ thickness, which corresponds to the different ALD cycles, is known to affect the charge carrier generation and recombination.^[11] For Fe₂O₃-AAO-PhCs produced by 270 s pulse duration within anodization, the photocatalytic activity of MB degradation is the lowest (1.38 \pm 0.03 h⁻¹) for 154 ALD cycles, while the highest activity of 1.93 ± 0.02 h⁻¹ is observed for a sample coated with 385 cycles (Figure 4). As depicted in Figure 4, the alignment of the PSB edge with the Fe₂O₃ band gap is the best for the 385 ALD cycle sample, which shows the highest photocatalytic activity. However, the different photocatalytic performances depending on the ALD cycle numbers cannot be explained by only considering the PSB edge alignment to the Fe₂O₃ band gap. Instead, additional factors such as film thickness and surface roughness must be considered. It is reported in literature that the film thickness of semiconductors determines their charge carrier dynamics, i.e., charge carrier generation and recombination.^[11] For Fe₂O₃, fast charge carrier recombination and low carrier mobility are common drawbacks to its application in photocatalytic processes.[22-24]

Apart from determining the charge carrier dynamics, the deposited film thickness also influences the mass transfer of molecules into and out of the pores of AAO-PhCs. The ALDcoated material narrows the pore diameter increasing the pores' **Table 1.** Characterization of surface roughness of Fe_2O_3 layers deposited by ALD with different cycle numbers. The silicon/ silicon dioxide wafers were coated in the same ALD processes as the AAO-PhCs.

ALD cycle number	Film thickness /nm	Surface roughness /nm
0	0	1.71
77	1	3.83
154	2	2.02
231	3	1.83
308	4	1.55
385	5	1.53
462	6	1.52

aspect ratio. Thus, the diffusion of molecules taking part in the photocatalytic reaction within the pores gets increasingly constrained by the increasing ALD cycle number.^[87-89] Hence, it is expected that this diffusion limitation leads to a decrease in the photocatalytic activity when a certain film thickness is reached. The surface roughness of our ALD-deposited Fe₂O₃ films decreases with increasing cycle number, as summarized in Table 1. The atomic force microscopy (AFM) images of the different films are shown in Figure S3 (Supporting Information). Nucleation of individual Fe₂O₃ islands occurs via the Volmer-Weber growth mechanism, which will grow together with increasing ALD cycle number, resulting in a continuous Fe₂O₃ layer.^[48,90,91] Due to the higher roughness of 3.83 nm after 77 ALD cycles, the materials' surface area is higher for lower ALD cycle numbers meaning that more active surface sites are available for the photocatalytic reactions. Therefore, the photocatalytic activity is strongly increased for 77 Fe₂O₃ cycles compared to that of Fe₂O₃-functionalized AAO-PhCs with lower surface roughness. Interestingly, 154 ALD cycles still feature a higher surface roughness of 2.02 nm compared to that quantified in Fe₂O₃ films produced at higher cycle numbers (<1.55 nm), but this does not affect the photocatalytic reaction strongly.

Taking all these effects (i.e., PSB edge alignment, charge carrier dynamics, diffusion limitation, and surface roughness) into account, the photocatalytic activities of all Fe2O3-functionalized AAO-PhCs produced with a pulse duration of 270 s can be mechanistically explained by the following: Application of 77 ALD cycles results in a photocatalytic activity of 1.82 ± 0.07 h⁻¹ due to the high surface area of the Fe₂O₃ film caused by the large surface roughness of 3.83 nm. The influence of the surface area on the photocatalytic activity decreases with increasing ALD cycle number because the surface roughness-and thereby the available surface area—is reduced down to < 1.55 nm. For 154 cycles, the lowest activity of $1.38 \pm 0.03 \text{ h}^{-1}$ is observed. Note that the PSB edge is also not perfectly matched with the semiconductor band gap, contributing to the reduced effect. Further increasing the Fe₂O₃ cycles of the ALD process (231 and 308 cycles, respectively) results in an increased photocatalytic activity since the film thicknesses allow for more charge carrier generation without recombination, even though the optical properties are not optimized to make use of the slow photon effect. The highest activity of $1.93 \pm 0.02 \text{ h}^{-1}$ is observed for the sample coated by 385 cycles Fe_2O_3 because the film thickness seems to be optimal.

Specifically, enough charge carriers can be generated without recombination while mass transfer into and out of the pores is possible to a sufficient extent. A thicker Fe₂O₃ film (462 cycles) leads to reduced photocatalytic activity $1.71 \pm 0.02 \ h^{-1}$, which might be attributed to a combination of different effects. First, the thicker film might not be optimal regarding the charge carrier separation due to the fast recombination and low diffusion length of the generated charge carriers.^[20] Second, the mass transfer of MB molecules and degradation products might be limited due to the smaller pore diameter.

The ALD cycle number of deposited Fe₂O₃ also determines the photocatalytic activities of AAO-PhCs anodized by using a pulse period of 275 s (Figure 4). Similar to the samples anodized with 270 s pulse duration, surface roughness dominates the activity when comparing the AAO-PhC coated by 77 cycles Fe₂O₃ $(1.65 \pm 0.01 h^{-1})$ to the sample functionalized with 154 cycles $(1.61 \pm 0.01 h^{-1})$. Increasing the ALD cycle number to 231 raises the photocatalytic activity to $1.97 \pm 0.02 \text{ h}^{-1}$, which is probably caused by a combination of the film thickness increment and the alignment of the PSB to the semiconductor band gap. Since the PSB edge of the sample coated with 308 cycles does not overlap with the Fe₂O₃ absorption, the photocatalytic activity is lower $(1.72 \pm 0.04 h^{-1})$ than in the previous sample. The deviation of the PSB blue edge from the Fe₂O₃ band gap can be explained by variations of the anodization parameters such as temperature or electrolyte volume. Nevertheless, this deviation demonstrates the importance of precisely aligning the PSB edge with the semiconductor band gap to use the slow photon effect. The AAO-PhC functionalized by 385 ALD cycles features the highest activity (2.05 \pm 0.04 h⁻¹), as already observed in the AAO-PhCs produced by 270 s pulse duration. The PSB edge alignment enhances the photodegradation reaction by the slow photon effect. Apart from that, these AAO-PhCs' film thickness seems to be optimal regarding charge carrier generation, separation, and available pore diameter for mass transfer. Specifically, the generated charge carriers can induce MB photodegradation reactions before they vanish by recombination, which is a competitive process. Moreover, even though the AAO pore diameter is reduced by applying 385 Fe₂O₃ cycles in ALD, mass transfer of molecules taking part in the photoreaction within the pores is still possible to a sufficient amount. In contrast, further increase of the Fe₂O₃ thickness by using 462 ALD cycles reduces the AAO-PhCs' photocatalytic activity (1.60 \pm 0.02 h⁻¹) due to increasingly hindered diffusion of reactants.

To sum up, the photocatalytic performance of Fe_2O_3 -functionalized AAO-PhCs depends on the alignment of the PSB edge with the semiconductor band gap as well as on the deposited Fe_2O_3 film thickness. Precise control of the PSB edge position is crucial to enhance the photocatalytic activity by the slow photon effect. The Fe_2O_3 coating thickness needs to be optimized regarding the charge carrier dynamics and the mass transfer of molecules inside the AAO pores.

2.3. Photocatalytic Performance of $\rm Al_2O_3\mathchar`-Protected Fe_2O_3\mathchar`-AAO\mathchar`-PhCs$

Ideal photocatalysts should not only have high initial activity, but this should also be maintained over multiple repetitions of the ADVANCED MATERIALS INTERFACES

photocatalytic reactions. For Fe_2O_3 , maintaining the photocatalytic properties is often challenging, since photocorrosion—also referred to as photodissolution—is a common issue.^[11,53,54] This phenomenon describes the (partial) destruction of the material induced by irradiation utilized in photocatalytic processes to induce the charge carrier generation and, thereby, the reaction. To avoid this destruction of the structure and the corresponding decrease of its photocatalytic activity, the device has to be protected, for example, by coating another material on top.^[11,53,54,94]

The photocatalytic activity of Fe₂O₃-coated AAO-PhCs decreases with an increasing number of photocatalysis measurements due to photocorrosion of the material. Still, it can be avoided when the structures are protected by ultra-thin layers of Al_2O_3 , as shown in **Figure 5**. Repetition of photocatalysis measurements with AAO-PhCs anodized by employing 275 s pulse time and coated with 231 and 308 Fe₂O₃ cycles by ALD decreases the photocatalytic activity by 27% for both samples in their third measurements compared to the first ones (Figure 5a). This is probably caused by photocorrosion of the photocatalyst material, namely here Fe₂O₃, which has also been reported in pre-vious publications.^[54,93,95,96] A structural change at the surface of Fe₂O₃-AAO-PhCs is visible by SEM images taken after three photocatalysis measurements compared to the same sample before the first photocatalysis reaction (Figure 5b). As depicted in Figure 5c, the photocatalytic performance of AAO-PhCs functionalized with 385 cycles Fe₂O₃ can be stabilized when ultrathin Al₂O₃ layers are coated on top by ALD. Within one ALD cycle, 1.4 ± 0.03 Å of Al₂O₃ is deposited. Although ultra-thin Al₂O₃ films of 2, 4, 6, and 8 cycles are used as protection layers, they can prevent the structural decomposition (Figure 5d), which was already shown in literature for similar applications.^[55-60,97] The initial photocatalytic activity of Al₂O₃-protected Fe₂O₃-AAO-PhCs is lower than the unprotected one, but it remains constant for measurement repetitions and can outperform the unprotected structures after four measurements. For better comparison, the photocatalytic activity in Figure 5c is given as a percentage relative to the activity in the first measurement of the sample without the Al₂O₃ protection layer. With an increasing number of Al₂O₃ ALD cycles, the initial photocatalytic performance of the AAO-PhCs decreases and saturates at 54% (6 and 8 cycles). However, these activities are stable over three measurements in contrast to the sample without protective layer. Since the Fe₂O₃-AAO-PhC protected by 2 ALD cycles of Al₂O₃ features the highest initial activity of 67% when comparing the different numbers of Al₂O₃ ALD cycles, it was further used to test its performance over measurement repetitions compared to the unprotected sample. While the activity of the latter one is significantly decreasing with increasing measurement number by 44%, there is only a slight decrease of 4% in the activity of the structure protected by 2 ALD cycles. Furthermore, the absolute activity of the Fe₂O₃-AAO-PhC coated with 2 ALD cycles of Al₂O₃ is higher than that of the unprotected one from the fourth measurement onwards. Accordingly, an ultra-thin Al₂O₃ protection layer can stabilize the photocatalytic performance of Fe2O3-AAO-PhCs over multiple measurements by preventing photocorrosion of the photocatalytically active material. Since this stabilization is shown to be effective in terms of avoiding an activity decrease within six measurements, it is expected that the samples will be stable over multiple tests. Here it should be mentioned that, in contrast to the unprotected

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Figure 5. Photocorrosion and stabilized photocatalytic activity after depositing ultra-thin protection layers by ALD. a) The photocatalytic performance of AAO-PhCs functionalized with different ALD cycle numbers decreases with increasing measurement numbers due to photocorrosion of the Fe_2O_3 films. b) SEM images of the structures' top surface before and after photocatalysis measurements demonstrate structural changes of the sample. c) Protection of Fe_2O_3 -AAO-PhCs by ultra-thin layers of Al_2O_3 by ALD stabilizes their photocatalytic performance over increasing measurement numbers. Although the initial activity is decreased compared to the unprotected structure, coating only 2 cycles of Al_2O_3 onto the structure outperforms the bare Fe_2O_3 -AAO-PhC after four measurements. d) The SEM image of the sample protected by 2 cycles of Al_2O_3 was taken after photocatalysis measurements and showed no sample destruction at the surface.

 Fe_2O_3 -AAO-PhC, Photo-Fenton reactions can be suppressed on the Al_2O_3 -protected sample since less iron ions are present at the samples' surface.^[4] This might contribute to the observed reduction of the initial photocatalytic activity since the Photo-Fenton reaction would be beneficial for the overall apparent photocatalytic activity.

2.4. Photocatalytic Activity Enhancement for Degradation of Different Dyes

 Fe_2O_3 -AAO-PhCs with the PSB edge aligned with the Fe_2O_3 band gap possess a generally enhanced photocatalytic activity for photodegradation of different organic dyes, which is found to be independent of the model organic absorption characteristics. In contrast, existing literature reports mostly of titanium dioxide functionalized AAO-PhCs for photocatalytic decomposition of organic molecules (dyes and colorless compounds) using structures with the PSB edge aligned with one specific dye.^[29,44,45,85]

As presented in **Figure 6**, the photocatalytic performance of AAO-PhCs with the PSB edge aligned to the Fe_2O_3 band gap and coated with the optimized semiconductor layer, i.e., 385 cycles of Fe_2O_3 and 2 cycles of Al_2O_3 , features an increased activity compared to their uncoated counterparts for all three dyes. Depend-

ing on the dye, different activity enhancements by the factors 1.11 (MB), 1.49 (RhB), and 1.35 (MO) are observed. The slow photon effect can be effectively used for the photodegradation of all compounds because it is solely related to the Fe₂O₃-AAO-PhCs structure and materials. The activity enhancement also becomes clear when comparing the percentage removal of the dyes by the coated sample with the uncoated one. The uncoated sample decomposes $61 \pm 2\%$ of MB, $21 \pm 2\%$ RhB, and $16 \pm 2\%$ MO within one hour of reaction under the conditions used herein. The optimized Al₂O₃-protected Fe₂O₃-AAO-PhC shows dye removal of $68 \pm 2\%$ for MB, $29 \pm 2\%$ for RhB, and $22 \pm 2\%$ for MO. When the activity increase is based on the adjustment of the AAO-PhCs' PSB edge with the absorption of an organic molecule, the slow photon effect will only work for degrading these specific molecules. In Figure 6, such properties are observed for the Fe₂O₃-AAO-PhC with its PSB edge overlapping the absorption maximum of MB. For degrading MB, the photocatalytic performance of the Fe₂O₃/Al₂O₃ functionalized sample is enhanced compared to the pristine sample by a factor of 1.07 due to the slow photon effect. The performance is only slightly increased because the PSB red edge overlaps with the MB absorption maximum, thus causing screening of incoming light by the MB molecules. As expected, no activity increase can be observed for decomposing RhB because the optical properties of the dye and the PhC structure

IDVANCED

SCIENCE NEWS _____ www.advancedsciencenews.com SB @ MB, coated

RhB

dye



Wavelength /nm

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Figure 6. The degradation of different organic dyes as model pollutants of water demonstrates the general activity enhancement by the slow photon effect when the PSB of AAO-PhCs is aligned with the band gap of the semiconductor photocatalyst. The Fe_2O_3 -functionalized samples are coated by 385 cycles of Fe_2O_3 and 2 cycles of Al_2O_3 . a) Fe_2O_3 -functionalized AAO-PhCs with the PSB edge matching the Fe_2O_3 band gap show significantly enhanced photocatalytic performance for degrading different organic dyes compared to the uncoated AAO-PhC structure. Only minor differences are observed for AAO-PhCs featuring a PSB edge at the absorption maximum of methylene blue. Note that the percent activity normalized to the photocatalytic activity of the coated sample with the PSB edge located at the Fe_2O_3 band gap is compared. The quantitative values of the activity for this sample are displayed for the different dyes. b) Absorbance spectra of the other organic dyes show the spectral alignment of the AAO-PhCs' PSB characteristics with respect to the different dyes and the band gap of Fe_2O_3 . The labeling of the AAO-PhCs denotes the PSB edge position (at the Fe_2O_3 band gap or at the MB absorption) and whether the structure is coated with Fe_2O_3 (c.) or not (unc.).

(b)

Absorbance la.u.

do not match at all. The difference in the photocatalytic performance for the MO degradation of the coated AAO-PhC compared to its uncoated counterpart is within the measurement accuracy as the overall absolute activity is much lower than for the other dyes. Such small concentration changes are within the statistical error associated with the detector used in the UV–vis measurement. Moreover, calculations of the dye removal rates demonstrate that there is no significant difference between the Fe₂O₃-functionalized AAO-PhC and the uncoated sample when the PSB edge overlaps with the absorption of MB. Specifically, the functionalized sample is capable of degrading 46 ± 2% MB, 22 ± 2% RhB, and 14 ± 2% MO while the uncoated AAO-PhC decomposes 43 ± 2% MB, 21 ± 2% RhB, and 15 ± 2% MO within one hour.

The photocatalytic activity enhancement for degrading different organic compounds with the same Fe₂O₃-AAO-PhC proves that aligning the PSB edge with the semiconductor band gap results in a generally applicable slow photon effect, which is independent of the molecules to be degraded. The herein presented results of Fe₂O₃-AAO-PhCs are phenomenological in agreement with similar previously reported types of PhC structures, namely Fe₂O₃ inverse opals^[92,98] and TiO₂-functionalized AAO-PhCs.^[80] Furthermore, our study demonstrates the combination of Fe₂O₃ as a low-cost, visible light active photocatalyst with AAO-PhCs as widely tailorable template structures.

3. Conclusion

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(a)

 Fe_2O_3 -AAO-PhCs were fabricated by combining pulsed aluminum anodization with ALD. The structures' optical and photocatalytic properties were systematically investigated by varying the period duration of the pulse-like anodization and the number of ALD cycles for Fe_2O_3 deposition by ALD. Optimized structures with the PSB edge overlapping with the semiconductor band gap were tested with further photocatalysis measurements and additional ultra-thin coatings of $\mathrm{Al}_2\mathrm{O}_3$ were applied as protective layers.

Previous literature reports mostly matched a PSB edge of AAO-PhCs with the absorption maximum of one chemical to be degraded. This approach facilitates the excitation of molecules of the respective chemical adsorbed at the AAO-PhCs surface by the slow photon effect. However, there is no activity increase for photocatalytic decomposition of different compounds when the PSB edge positions do not match their absorption profile. In contrast, we have demonstrated a general photocatalytic activity enhancement of semiconductor functionalized AAO-PhCs for degrading various organic compounds when the PhCs' PSB edge is aligned with the band gap of a semiconductor in the visible range of the electromagnetic spectrum. This activity enhancement is caused by the slow photon effect in the PhC structure, i.e., stimulated excitation of the semiconductor. Thus, it is independent of the chemical being degraded and its sensitivity to the PSB edge positions was shown. Moreover, Fe₂O₃ was first applied as a semiconductor coating for tailored AAO-PhCs and we proved an increased photocatalytic performance by employing the slow photon effect. The ALD-deposited Fe₂O₃ film thickness was optimized with respect to the structures' optical properties, charge carrier dynamics, and mass transfer of molecules within the porous structure to allow for high photocatalytic reaction rates. Furthermore, coating ultra-thin layers of Al2O3 onto the Fe2O3-AAO-PhC structures maintained the photocatalytic properties over multiple measurements and could avoid photocorrosion of the Fe₂O₃ film. Preparing Fe₂O₃-AAO-PhCs which feature higher absolute reflection intensities at their PSB might further increase the photocatalytic activity of these structures in the future as the interaction probability between incoming photons and the semiconductor will be further increased. Such higher reflection intensities can, for example, be realized by wet-chemical pore widening subsequent to the anodization of AAO-PhCs.^[76,77]

Due to their pore structure, AAO-PhC samples could be fabricated as through-hole membranes by removing the remaining aluminum and opening the pore bottoms after anodization.^[43,99]

aluminum and opening the pore bottoms after anodization.^[43,99] Such tailor-made through-hole AAO-PhC membranes functionalized with a semiconductor by ALD and aligned regarding their PSB edge position and band gap, respectively, might be utilized for water purification by filtration in combination with in situ photocleaning. Besides Fe₂O₃, ALD offers a large variety of cheap and earth-abundant photocatalysts to be deposited, such as titanium dioxide, zinc oxide, or tungsten oxide.^[48] Coating AAO-PhCs with these materials or combinations of them might allow for even more efficient use of solar light for photocatalytic reactions. Moreover, the application of semiconductor-functionalized AAO-PhCs in photoelectrochemical processes could expand the utilization of such structures and provide low-cost and easyto-manufacture material platforms for reactions such as water splitting.

4. Experimental Section

Materials: Aluminum (Al) chips (99.9997%, thickness 0.5 cm, 2 cm diameter) were purchased from Goodfellow GmbH (Germany). Oxalic acid (H₂C₂O₄), perchloric acid (HClO₄), ethanol (C₂H₅OH, EtOH), isopropyl alcohol (IPA), hydrochloric acid (HCl), copper (II) chloride dihydrate (CuCl₂ · 2 H₂O), nitric acid (HNO₃), methylene blue (C₁₆H₁₈ClN₃S, MB), rhodamine B (C₂₈H₃₁ClN₂O₃, RhB), methyl orange (C₁₄H₁₄N₃NaO₃S, MO), and hydrogen peroxide (H₂O₂) were supplied by Merck Chemicals (Germany) and used as received. Ferrocene (C₁₀H₁₀Fe, Cp₂Fe) was purchased from Alfa Aesar (Germany). Trimethylaluminum (C₃H₉Al, TMA) was received from Strem Chemicals (France). Milli-Q water (>16 MΩ cm, DI-H₂O) was used to prepare the aqueous solutions and as a precursor in the aluminum oxide ALD process.

Fabrication of AAO-PhCs: AAO-PhCs were produced by rectangular pulse anodization of Al under current density control conditions. Before anodization, the Al chips were cleaned for 30 min, respectively, in IPA and DI-H2O and dried with a nitrogen stream. Afterward, electropolishing of the Al chips in 1:4 (v:v) solution of HClO₄ and EtOH was conducted for 3 min at 20 V and 5 °C. Anodization was carried out in 0.3 M H₂C₂O₄ aqueous solution at 6°C. The applied anodization profile began with a constant current period t_{const} for 60 min at a current density j_{const} of 4.2 mA cm⁻¹ to initiate the formation of pores. Subsequently, 150 rectangular current pulses were applied. These consisted of alternating low and high current density levels $j_{\text{low}} = 0.6 \text{ mA cm}^{-1}$ and $j_{\text{high}} = 4.2 \text{ mA cm}^{-1}$ applied over the periods t_{low} and t_{high} , respectively. The low current density period was four times as long as the one of high current density, and the duration of one rectangular pulse t_{pulse} was calculated by the sum of t_{low} and t_{high} . The number of rectangular current pulses N_{rp} multiplied with the individual pulse duration t_{pulse} defined the total time over which the rectangular pulses were applied (t_{rp}). AAO-PhCs with different pulse durations, namely, 175, 270, 275, 300, 335, and 450 s, were anodized. After anodization, the AAO-PhC samples were washed with DI-H₂O and dried under nitrogen (N_2) flow. They were immersed into 30 wt.% $\rm H_2O_2$ for 24 h, rinsed with DI-H₂O, and dried with N₂ stream.

ALD Coating of AAO-PhCs: ALD functionalization of AAO-PhCs was performed in a home-built ALD system operated under stop-flow conditions. Nitrogen (6.0, SOL) was used as carrier gas with a constant flow of 2.5 l h⁻¹. For depositing Fe₂O₃, the system temperature was 200 °C. Cp₂Fe heated to 130 °C and ozone (O₃) at room temperature (generated by an OzoneLab OL80W ozone generator; Ozone Services, Canada, from O₂ (5.0) by Westfalen) were used as precursors with pulse times of 1.5 s and 0.08 s, respectively. Exposure and pump times were 60 and 90 s during the Cp₂Fe half-reaction. In the O₃ half-reaction, exposure and pump durations of 30 and 90 s, respectively, were applied. Note, the O₃ half-reaction was repeated twice within one ALD cycle of Fe₂O₃ deposition to ensure

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sufficient O₃ diffusion within the reaction chamber without venting the system. The growth per cycle (GPC) for Fe₂O₃ deposition was 0.016 \pm 0.003 nm. To functionalize the AAO-PhCs, 77, 154, 231, 308, 385, and 462 cycles were applied to achieve different film thicknesses.

ALD of Al₂O₃ was conducted at 150 °C system temperature utilizing TMA and DI-H₂O at room temperature as precursors. Both half-reactions consisted of 0.05 s precursor pulse, 60 s exposure, and 90 s pumping. The GPC was 0.14 ± 0.003 nm, and 2, 4, 6, or 8 cycles of Al₂O₃ deposition were conducted to generate an ultra-thin protection layer at the Fe₂O₃ coated samples with optimized film thickness.

The film thicknesses obtained within the respective ALD process were characterized by spectroscopic ellipsometry (SENpro ellipsometer, Sentech Instruments, Germany) on planar silicon reference substrates that were coated within the same ALD process as the AAO-PhCs. Atomic force microscopy (AFM) characterization of model Fe₂O₃ films was conducted using a Dimension 3100 Atomic Force Microscope (Bruker, USA) to determine the surface roughness of the films. The measurements were conducted on Fe₂O₃ films deposited onto silicon wafers applying ALD cycle numbers under the same conditions used in the study.

Optical Characterization: Optical characterization of AAO-PhCs was conducted by UV-vis spectroscopy in transmission and reflection using a Flame Extended Range Spectrometer (OceanOptics, Germany). Previously, the Al backsides of the AAO-PhC samples were removed by etching in a saturated $CuCl_2/HCl$ solution. Only the Al area below the AAO was removed by defining it with a Kapton mask featuring a circular hole at the AAO position. Transmission spectra were measured in a home-built setup consisting of a deuterium-halogen light source DH-2000-BAL (OceanOptics, Germany), whose light was guided by a glass-fiber cable through a collimator to the sample, which was placed in normal incidence. The transmitted light was collected by a collimator and guided by a glass-fiber cable until it reached a Flame Extended Range Spectrometer (OceanOptics, Germany). Reflection measurements were conducted using the deuteriumhalogen light source DH-2000, a glass-fiber cable, and the Flame Extended Range Spectrometer (OceanOptics, Germany) for data acquisition at normal incidence. The reflection measurements were conducted for AAO-PhCs filled with air and DI-H₂O. The spectral range for all measurements was 220 to 1020 nm with a resolution of 1 nm.

OriginPro 2021 software was used to analyze the PSB properties. The peak central wavelength was determined as PSB position by applying a Gaussian peak fit of the reflection data. To identify the PSB edges, the reflection data were smoothened using 200 data points, the second derivative was calculated, and the intersection points with the x-axis defined the PSB edge positions.

Photocatalytic Characterization: The photocatalytic activity of AAO-PhCs was studied by the degradation of organic dyes as model pollutants of water under simulated solar light irradiation. AAO-PhCs were mounted into a custom-built reaction chamber made of polyether ether ketone (PEEK) featuring a glass window for light irradiation. The sample was placed at normal incidence to a LE.5211 light source (Euromex Microscopen bv, Netherlands) generating visible-near infrared light (SI). The AAO-PhC was exposed to the solution inside the reaction chamber which was a mixture of 8 mL 2.5 mg L^{-1} dye solution and 200 mm $H_2O_2.$ The solution was filled into the reaction chamber one hour before starting the photocatalysis measurement. The chamber was kept in darkness to enable adsorption-desorption equilibrium of the dye molecules at the AAO-PhC surface. Methylene blue, rhodamine B, and methyl orange were used as dyes featuring different absorption maxima, namely 664 nm (MB), 551 nm (RhB), and 446 nm (MO). After starting the illumination of the sample inside the dye solution, the absorbance of the reaction solution was measured by UV-vis spectroscopy every 5 min during 1 h total degradation time. A halogen light source HL-2000 (OceanOptics, Germany) and a Flame Extended Range Spectrometer (OceanOptics, Germany) were utilized for the UV-vis transmission measurement. whereby 1 mL of the reaction solution was pipetted into a cuvette, analyzed, and pipetted back into the reaction chamber. According to Lambert-Beer's law, the dye concentration is linearly proportional to its absorbance and can therefore be calculated after calibration with known concentrations. The dye degradation efficiency of AAO-PhCs was analyzed assuming Langmuir-Hinshelwood

kinetics, which typically describes photocatalytic reactions in heterogeneous phases. For diluted solutions (concentration smaller than 10^{-3} M), the Langmuir–Hinshelwood model could be simplified to pseudo-first-order kinetics and the apparent rate constant *k* was obtained from analyzing the concentration decrease over time (Equation 1):

$$\ln\left(\frac{c}{c_0}\right) = -k \times t \tag{1}$$

Here, the concentration of the dye after certain time steps is characterized by c, c_0 denotes the dye concentration at the beginning of the measurement (t = 0 h), and t is the reaction time.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

anodic aluminum oxide, atomic layer deposition, photocatalysis, photonic crystals, slow photon effect

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- M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, A. M. Mayes, *Nature* **2008**, *452*, 301.
- [2] X. Qu, J. Brame, Q. Li, P. J. J. Alvarez, Acc. Chem, Res. 2013, 46, 834.
- [3] The Sustainable Development Goals Report 2020, UN DESA, New York 2022.
- [4] R. S. Jack, G. A. Ayoko, M. O. Adebajo, R. L. Frost, *Environ. Sci. Pollut. Res.* 2015, 22, 7439.
- [5] N. Kumar, S. Kumbhat, Essentials in Nanoscience and Nanotechnology, John Wiley & Sons Inc., Hoboken, New Jersey 2016.



www.advmatinterfaces.de

- [6] W. Y. Teoh, J. A. Scott, R. Amal, J. Phys. Chem. Lett. 2012, 3, 629.
- [7] M. B. Tahir, G. Nabi, M. Rafique, N. R. Khalid, Int. J. Environ. Sci. Technol. 2017, 14, 2519.
- [8] Y. Zhang, Z. Jiang, J. Huang, L. Y. Lim, W. Li, J. Deng, D. Gong, Y. Tang, Y. Lai, Z. Chen, RSC Adv. 2015, 5, 79479.
- [9] J. Zhang, P. Zhou, J. Liu, J. Yu, Phys. Chem. Chem. Phys. 2014, 16, 20382.
- [10] O. Carp, Prog. Solid State Chem. 2004, 32, 33.
- [11] J. Li, N. Wu, Catal. Sci. Technol. 2015, 5, 1360.
- [12] J. Zhang, B. Tian, L. Wang, M. Xing, Photocatalysis Fundamentals, Materials and Applications, Springer Open Ltd, Singapore 2018.
- [13] R. L. Mckenzie, P. J. Aucamp, A. F. Bais, L. O. Björn, M. Ilyas, S. Madronich, *Photochem. Photobiol. Sci.* 2011, 10, 182.
- [14] Y. Nam, J. H. Lim, K. C. Ko, J. Y. Lee, J. Mater. Chem. A 2019, 7, 13833.
- [15] H. Chang, C. Su, C.-H. Lo, L.-C. Chen, T.-T. Tsung, C.-S. Jwo, Mater. Trans. 2004, 45, 3334.
- [16] S. Shen, S. A. Lindley, X. Chen, J. Z. Zhang, Energy Environ. Sci. 2016, 9, 2744.
- [17] P. Singh, K. Sharma, V. Hasija, V. Sharma, S. Sharma, P. Raizada, M. Singh, A. K. Saini, A. Hosseini-Bandegharaei, V. K. Thakur, *Mater. To-day* **2019**, *14*, 100186.
- [18] S. Grushevskaya, I. Belyanskaya, O. Kozaderov, Materials (Basel) 2022, 15, 4915.
- [19] C. Xia, H. Wang, J. K. Kim, J. Wang, Adv. Funct. Mater. 2021, 31, 1.
- [20] D. A. Wheeler, G. Wang, Y. Ling, Y. Li, J. Z. Zhang, *Energy Environ. Sci.* 2012, 5, 6682.
- [21] D. H. Sliney, Eye 2016, 30, 222.
- [22] O. Akhavan, Appl. Surf. Sci. 2010, 257, 1724.
- [23] K. L. Hardee, A. J. Bard, J. Electrochem. Soc. 1977, 124, 215.
- [24] J. K. Leland, A. J. Bard, J. Phys. Chem. 1987, 91, 5076.
- [25] M. J. Kang, C. W. Kim, Appl. Sci. Converg. Technol. 2020, 29, 200.
- [26] A. Trenczek-Zajac, M. Synowiec, K. Zakrzewska, K. Zazakowny, K. Kowalski, A. Dziedzic, M. Radecka, ACS Appl. Mater. Interfaces 2022, 14, 38255.
- [27] J. I. L. Chen, G. Von Freymann, S. Y. Choi, V. Kitaev, G. A. Ozin, J. Mater. Chem. 2008, 18, 369.
- [28] J. Liu, H. Zhao, M. Wu, B. Van Der Schueren, Y. Li, O. Deparis, J. Ye, G. A. Ozin, T. Hasan, B.-L. Su, Adv. Mater. 2017, 29, 1605349.
- [29] S. Y. Lim, C. S. Law, M. Markovic, J. K. Kirby, A. D. Abell, A. Santos, ACS Appl. Mater. Interfaces 2018, 10, 24124.
- [30] G. Guida, A. De Lustrac, A. C. Priou, Prog. Electromagn. Res. 2003, 41, 1.
- [31] E. Yablonovitch, J. Opt. Soc. Am. B 1993, 10, 283.
- [32] J. D. Joannopoulos, S. G. Johnson, J. N. Winn, R. D. Meade, *Pho-tonic Crystals Molding the Flow of Light*, Princeton University Press, Princeton, New Jersey 2008.
- [33] C. M. Soukoulis, Nanotechnology 2002, 13, 420.
- [34] J. I. L. Chen, G. Von Freymann, S. Y. Choi, V. Kitaev, G. A. Ozin, Adv. Mater. 2006, 18, 1915.
- [35] B. E. A. Saleh, M. C. Teich, Fundamentals of Photonics, John Wiley & Sons, Inc., Hoboken 2019.
- [36] J. F. Galisteo-López, M. Ibisate, R. Sapienza, L. S. Froufe-Pérez, Á. Blanco, C. López, Adv. Mater. 2011, 23, 30.
- [37] S. Y. Lim, C. S. Law, L. Liu, M. Markovic, C. Hedrich, R. H. Blick, A. D. Abell, R. Zierold, A. Santos, *Catalysts* **2019**, *9*, 988.
- [38] C. S. Law, S. Y. Lim, A. D. Abell, N. H. Voelcker, A. Santos, Nanomaterials 2018, 8, 788.
- [39] A. Santos, J. Mater. Chem. C 2017, 5, 5581.
- [40] B. Wang, G. T. Fei, M. Wang, M. G. Kong, L. De Zhang, Nanotechnology 2007, 18, 365601.
- [41] A. M. Md Jani, D. Losic, N. H. Voelcker, Prog. Mater. Sci. 2013, 58, 636.
- [42] A. Santos, M. J. Deen, L. F. Marsal, Nanotechnology 2015, 26, 042001.
- [43] W. Lee, S.-J. Park, Chem. Rev. 2014, 114, 7487.

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- [44] S. Y. Lim, C. S. Law, M. Markovic, L. F. Marsal, N. H. Voelcker, A. D. Abell, A. Santos, ACS Appl. Energy Mater. 2019, 2, 1169.
- [45] S. Y. Lim, C. S. Law, L. Liu, M. Markovic, A. D. Abell, A. Santos, Catal. Sci. Technol. 2019, 9, 3158.
- [46] S. Y. Lim, C. Hedrich, L. Jiang, C. S. Law, M. Chirumamilla, A. D. Abell, R. H. Blick, R. Zierold, A. Santos, ACS Catal. 2021, 11, 12947.
- [47] S. C. Riha, M. J. Devries Vermeer, M. J. Pellin, J. T. Hupp, A. B. F. Martinson, ACS Appl. Mater. Interfaces 2013, 5, 360.
- [48] S. M. George, Chem. Rev. 2010, 110, 111.
- [49] C. Bae, H. Shin, K. Nielsch, *MRS Bull.* **2011**, *36*, 887.
- [50] M. Knez, K. Nielsch, L. Niinistö, Adv. Mater. 2007, 19, 3425.
- [51] V. Cremers, R. L. Puurunen, J. Dendooven, Appl. Phys. Rev. 2019, 6, 021302.
- [52] S. N. Ahmed, W. Haider, Nanotechnology 2018, 29, 342001.
- [53] B. Weng, M.-Y. Qi, C. Han, Z.-R. Tang, Y.-J. Xu, ACS Catal. 2019, 9, 4642.
- [54] S. Chen, D. Huang, P. Xu, W. Xue, L. Lei, M. Cheng, R. Wang, X. Liu, R. Deng, J Mater Chem A Mater 2020, 8, 2286.
- [55] M. Leskela, E. Salmi, M. Ritala, Mater. Sci. Forum 2017, 879, 1086.
- [56] J. Lu, J. W. Elam, P. C. Stair, Acc. Chem. Res. 2013, 46, 1806.
- [57] W.-J. Lee, S. Bera, H. Woo, H. G. Kim, J.-H. Baek, W. Hong, J.-Y. Park, S.-J. Oh, S.-H. Kwon, *Chem. Mater.* **2022**, *34*, 5949.
- [58] Y. S. Jung, A. S. Cavanagh, L. A. Riley, S.-H. Kang, A. C. Dillon, M. D. Groner, S. M. George, S.-H. Lee, *Adv. Mater.* **2010**, *22*, 2172.
- [59] I. D. Scott, Y. S. Jung, A. S. Cavanagh, Y. Yan, A. C. Dillon, S. M. George, S.-H. Lee, *Nano Lett.* **2011**, *11*, 414.
- [60] M. Liu, X. Xie, L. Chen, X. Wang, Y. Cheng, F. Lu, W.-H. Wang, J. Yang, X. Du, J. Zhu, H. Liu, H. Dong, W. Wang, H. Liu, *J. Mater. Sci. Technol.* 2016, *32*, 489.
- [61] J. Rasmussen, Plat. Surf. Finish. 2002, 89, 43.
- [62] J. O'Sullivan, G. Wood, Proc. Roy. Soc. Ser. A: Math. Phys. Sci. 1970, 317, 511.
- [63] W. Lee, R. Scholz, U. Gösele, Nano Lett. 2008, 8, 2155.
- [64] M. M. Rahman, L. F. Marsal, J. Pallarès, J. Ferré-Borrull, ACS Appl. Mater. Interfaces 2013, 5, 13375.
- [65] L. K. Acosta, F. Bertó-Roselló, E. Xifre-Perez, A. Santos, J. Ferré-Borrull, L. F. Marsal, ACS Appl. Mater. Interfaces 2019, 11, 3360.
- [66] C. S. Law, S. Y. Lim, L. Liu, A. D. Abell, L. F. Marsal, A. Santos, *Nanoscale* **2020**, *12*, 9404.
- [67] J. Lee, K. Bae, G. Kang, M. Choi, S. Baek, D.-S. Yoo, C.-W. Lee, K. Kim, RSC Adv. 2015, 5, 71770.
- [68] W. J. Zheng, G. T. Fei, B. Wang, L. De Zhang, Nanoscale Res. Lett. 2009, 4, 665.
- [69] P. Yan, G. T. Fei, G. L. Shang, B. Wu, L. De Zhang, J. Mater. Chem. C 2013, 1, 1659.
- [70] T. Kumeria, A. Santos, M. M. Rahman, J. Ferré-Borrull, L. F. Marsal, D. Losic, ACS Photonics 2014, 1, 1298.
- [71] T. Kumeria, M. M. Rahman, A. Santos, J. Ferré-Borrull, L. F. Marsal, D. Losic, ACS Appl. Mater. Interfaces 2014, 6, 12971.

- [72] J. Ferré-Borrull, J. Pallarès, G. Macías, L. Marsal, Materials (Basel) 2014, 7, 5225.
- [73] G. Macias, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, Nanoscale Res. Lett. 2014, 9, 315.
- [74] Y. Wang, Y. Chen, T. Kumeria, F. Ding, A. Evdokiou, D. Losic, A. Santos, ACS Appl. Mater. Interfaces 2015, 7, 9879.
- [75] G. L. Shang, Y. Zhang, G. T. Fei, Y. Su, L. De Zhang, Ann. Phys. 2016, 528, 288.
- [76] S. Y. Lim, C. S. Law, L. F. Marsal, A. Santos, Sci. Rep. 2018, 8, 1.
- [77] C. S. Law, S. Y. Lim, A. D. Abell, L. F. Marsal, A. Santos, Nanoscale 2018, 10, 14139.
- [78] C. S. Law, S. Y. Lim, A. Santos, *Sci. Rep.* 2018, *8*, 4642.
- [79] S. E. Kushnir, K. S. Napolskii, Mater. Des. 2018, 144, 140.
- [80] L. Liu, S. Y. Lim, C. S. Law, B. Jin, A. D. Abell, G. Ni, A. Santos, ACS Appl. Mater. Interfaces 2020, 12, 57079.
- [81] G. Szwachta, B. Januszewska, M. Wlodarski, M. Norek, Appl. Surf. Sci. 2023, 607, 155031.
- [82] L. K. Acosta, F. Bertó-Roselló, E. Xifre-Perez, C. S. Law, A. Santos, J. Ferré-Borrull, L. F. Marsal, ACS Appl. Mater. Interfaces 2020, 12, 19778.
- [83] L. Liu, S. Yee, C. Suwen, L. K. Acosta, B. Jin, A. D. Abell, L. F. Marsal, G. Ni, A. Santos, *Microporous Mesoporous Mater.* 2020, 312, 110770.
- [84] W. Lee, J.-C. Kim, Nanotechnology 2010, 21, 485304.
- [85] L. Liu, S. Y. Lim, C. S. Law, B. Jin, A. D. Abell, G. Ni, A. Santos, J. Mater. Chem. A 2019, 7, 22514.
- [86] J. Ferré-Borrull, M. M. Rahman, J. Pallarès, L. F. Marsal, Nanoscale Res. Lett. 2014, 9, 416.
- [87] B. I. Stefanov, B. S. Blagoev, L. Österlund, B. R. Tzaneva, G. V. Angelov, Symmetry 2021, 13, 1456.
- [88] S. Haschke, Y. Wu, M. Bashouti, S. Christiansen, J. Bachmann, Chem-CatChem 2015, 7, 2455.
- [89] S. Schlicht, S. Haschke, V. Mikhailovskii, A. Manshina, J. Bachmann, *ChemElectroChem* 2018, 5, 1259.
- [90] C. Argile, G. E. Rhead, Surf. Sci. Rep. 1989, 10, 277.
- [91] M. Fondell, Synthesis and Characterisation of Ultra Thin Film Oxides for Energy Applications, Uppsala University, 2014.
- [92] H. Zhu, Y. Zhang, J. Zhu, Y. Li, S. Jiang, N. Wu, Y. Wei, J. Zhou, Y. Song, J. Mater. Chem. A 2020, 8, 22929.
- [93] D. Beydoun, R. Amal, G. K. Low, S. Mcevoy, J. Phys. Chem. B 2000, 104, 4387.
- [94] N. K. R. Eswar, S. A. Singh, J. Heo, J. Mater. Chem. A 2019, 7, 17703.
- [95] D. Beydoun, R. Amal, G. Low, S. Mcevoy, J. Mol. Catal. A: Chem. 2002, 180, 193.
- [96] M. I. Litter, M. A. Blesa, Can. J. Chem. 1992, 70, 2502.
- [97] A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen, Nat. Mater. 2011, 10, 456.
- [98] H. Xie, Y. Li, S. Jin, J. Han, X. Zhao, J. Phys. Chem. C 2010, 114, 9706.
- [99] L. Zaraska, G. D. Sulka, M. Jaskula, J. Solid State Electrochem. 2011, 15, 2427.

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Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide

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Supporting Information

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Figure S1. SEM images of AAO-PhCs produced with a pulse period of t_{pulse} 275 s. (a) The top-view SEM image indicates the presence of unordered, cylindrical-shaped pores featuring an average diameter of 32 ± 23 nm of the pores at the AAO-PhC surface. (b) The periodic diameter modulation of the pores in depth is shown in cross-section SEM. According to the voltage pulses, the structures' pore diameter is constantly modulated in depth between 15 ± 6 nm and 30 ± 5 nm. Periodicities of these diameter modulations are set by the rectangular current density pulse duration t_{pulse} .





Figure S2. Film thicknesses of Fe_2O_3 and Al_2O_3 layers deposited by ALD were determined by spectral ellipsometry. Note, planar silicon wafers were used as substrates for the ellipsometry measurements. (a) The Fe_2O_3 process is characterized by a growth rate of 0.016 ± 0.003 nm per ALD cycle. (b) The herein used Al_2O_3 deposition process features a growth per cycle of 0.14 ± 0.003 nm.



Figure S3. Optical properties of AAO-PhCs anodized by applying different pulse durations and coated with Fe₂O₃ by ALD after production. (a) Reflection spectra of Fe₂O₃-AAO-PhCs anodized with t_{pulse} = 275 s and coated with different cycles of Fe₂O₃. (b) Reflection spectra of AAO-PhCs produced with t_{pulse} = 275 s, coated with 385 cycles Fe₂O₃ and subsequently protected by ultra-thin Al₂O₃ coatings by applying different numbers of ALD cycles. (c) Reflection spectra and (d) PSB properties analysis of AAO-PhCs prepared with 270 s pulse duration and functionalized by Fe₂O₃. (e) Reflection data and (f) PSB

characteristics of samples fabricated with t_{pulse} = 335 s without coating and after coating by 385 cycles Fe₂O₃ and 2 cycles Al₂O₃.



Figure S4. AFM images of Fe_2O_3 films deposited by different ALD cycle numbers corresponding to Table 1. The AFM measurements were done on Fe_2O_3 films of the respective cycle number deposited onto planar silicon wafers. Note, dust particles were excluded from the surface roughness analysis.



7.5. Publication V

Enhanced photocatalytic properties and photo-induced crystallization of TiO_2 -Fe₂O₃ inverse opals fabricated by atomic layer deposition

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Author contributions: C.H. and N.T.J. contributed equally. C.H. and N.T.J. fabricated the bilayer and multilayer IOs. N.T.J. and L.G.M. conducted the optical characterization, acquired SEM images, and conducted the XRD measurements. C.H. and N.T.J. conducted the photocatalytic characterization. C.H., N.T.J., L.G.M., V.d.L., S.Y.G.G., R.Z., K.P.F. performed the data analysis. C.H. wrote the manuscript. C.H., N.T.J., L.G.M., V.d.L, S.Y.G.G., R.Z., K.P.F. revised the manuscript. R.Z. and K.P.F. conceptualized the project. S.Y.G.G., R.H.B., R.Z., K.P.F. acquired funding and supervised the project. All authors conducted proofreading and approved the manuscript.

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Enhanced Photocatalytic Properties and Photoinduced Crystallization of TiO₂-Fe₂O₃ Inverse Opals Fabricated by Atomic Layer Deposition

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application in solar-driven photocatalysis. Previous studies have shown that semiconductor heterojunctions and nanostructuring can broaden the TiO2's photocatalytic spectral range. Semiconductor heterojunctions are interfaces formed between two different semiconductor materials that can be engineered. Especially, type II heterojunctions facilitate charge separation, and they can be obtained by combining TiO_2 with, for example, iron(III) oxide (Fe₂O₃). Nanostructuring in the



form of 3D inverse opals (IOs) demonstrated increased TiO2 light absorption efficiency of the material, by tailoring light-matter interactions through their photonic crystal structure and specifically their photonic stopband, which can give rise to a slow photon effect. Such effect is hypothesized to enhance the generation of free charges. This work focuses on the above-described effects simultaneously, through the synthesis of $TiO_2-Fe_2O_3$ IOs via multilayer atomic layer deposition (ALD) and the characterization of their photocatalytic activities. Our results reveal that the complete functionalization of TiO_2 IOs with Fe_2O_3 increases the photocatalytic activity through the slow photon effect and semiconductor heterojunction formation. We systematically explore the influence of Fe₂O₃ thickness on photocatalytic performance, and a maximum photocatalytic rate constant of 1.38 \pm 0.09 h⁻¹ is observed for a 252 nm template TiO₂-Fe₂O₃ bilayer IO consisting of 16 nm TiO₂ and 2 nm Fe₂O₃. Further tailoring the performance by overcoating with additional TiO₂ layers enhances photoinduced crystallization and tunes photocatalytic properties. These findings highlight the potential of TiO_2 -Fe₂O₃ IOs for efficient water pollutant removal and the importance of precise nanostructuring and heterojunction engineering in advancing photocatalytic technologies.

KEYWORDS: atomic layer deposition, inverse opal, photocatalysis, photoinduced crystallization, semiconductor heterostructure, multilayer thin films

1. INTRODUCTION

Solar-driven photocatalysis has emerged as a promising selfsustainable technology for removing water pollutants by harnessing solar energy to decompose organic contaminants.¹⁻³ Among various photocatalysts, titanium dioxide (TiO_2) is a benchmark material based on its excellent chemical stability, biocompatibility, and photocatalytic activity under ultraviolet (UV) light irradiation.4-7 However, its wide band gap prevents the utilization of visible light, which constitutes the majority of the sunlight spectrum, and thereby limits its practical applications. In recent years, efforts have been made to improve the light harvesting of TiO₂ by various strategies, such as doping with other elements, formation of semiconductor heterostructures, or nanostructuring of the material.^{6–8} The latter approach is based on increasing the surface area and light trapping in such structures.

Inverse opals (IOs) are an example of a nanostructured material characterized by a periodically ordered porous structure. They offer the possibility to tune light-matter interactions within the structure based on their photonic crystal (PhC) structure.9,10 PhCs feature so-called photonic stopbands (PSBs), i.e., spectral regions in which light of the

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Figure 1. Schematic drawing of the fabrication of $TiO_2-Fe_2O_3$ IOs and their shell composition. (a) Different steps in the fabrication process show (i) self-assembly of PS spheres, (ii) an assembled PS sphere opal template, and (iii) a TiO_2 inverse opal after ALD coating and burn-out of the polymer template. The latter scheme presents cuts through the front row of spheres to visualize the hollow inside and gaps connecting neighboring macropores. (b) The TiO_2 IO structure presented in (i) and (ii) is further modified by ALD functionalization to produce (iii) $TiO_2-Fe_2O_3$ bilayer IOs and (iv) $TiO_2-Fe_2O_3-TiO_2$ multilayer IOs.

respective wavelength cannot propagate through the structure and thus, the light is reflected by the PhC three-dimensional (3D) structure.^{9,11} The PSB position is determined by the composition and geometry of the PhC, namely the refractive indices of the utilized materials and the structural parameters, such as template size and spacing.^{9,12,13} Hence, modifications of the IO's structural parameters enable the tuning of the PSB position and allow, for instance, to position it across the whole UV to infrared range. Note, the group velocity of photons inside a PhC is strongly reduced at the PSB edges due to the slow photon effect.^{14,15} This effect leads to an increment of the interaction probability of photons with the PhC material.

Consequently, the generation of free charge carriers by absorption of photons in a semiconductor photocatalyst nanostructured within an IO 3D structure can be enhanced when the material's electronic band gap is aligned with the PhC's PSB edge and, thus, potentially boost its' photocatalytic performance. Another approach to further improve the activity of a photocatalyst is to facilitate charge separation. Combining different semiconductors results in heterojunctions at the interfaces, which tune the migration of free charge carriers through the structure.^{8,16} Specifically, type II heterojunctions of two semiconductors direct electrons (e⁻) and holes (h⁺) to the different materials, thereby, separating them and reducing their recombination. For example, iron(III) oxide (Fe_2O_3) as a visible light-active semiconductor photocatalyst can be combined with TiO₂ to improve charge separation and to widen the light absorption range, potentially leading to a further increase in photocatalytic performance. Fe₂O₃ is abundant on Earth, cheap, and nontoxic, rendering it a promising candidate for photocatalytic applications.^{17,18} However, inherent limitations such as inefficient charge carrier generation or fast recombination of photogenerated charge carriers need to be overcome.¹⁹⁻²¹ Previous reports about TiO_2 -Fe₂O₃ heterostructure thin films and Fe₂O₃ coated TiO₂ nanostructures prove the concept of enhancing the photocatalytic properties by adding Fe₂O₃ as visible light absorbing material to TiO₂ due to semiconductor heterojunction formation.^{19,22–32}

Moreover, Liu et al. and Pylarinou et al. reported further improvement of the photocatalytic activity of TiO_2 IOs when

decorating them with Fe₂O₃ nanoparticles or nanoclusters, respectively, based on the slow photon effect when the PSB edge is aligned with the Fe_2O_3 band gap.^{33,34} Liu et al. synthesized the nanoparticles at the TiO₂ IOs by a hydrothermal method, while Pylarinou et al. utilized a chemisorption-calcination-cycle technique to deposit Fe₂O₃ nanoclusters.^{33,34} However, coating TiO₂ IOs with Fe₂O₃ films to encapsulate the complete TiO₂ film has not been reported yet. Such structure could affect the photocatalytic performance because only either Fe₂O₃ or TiO₂ is in contact with the environment, thereby further increasing the importance of charge carrier separation. Since Fe₂O₃ often suffers from a short hole diffusion length of only a few nanometers and, thus, limited charge carrier separation, precise control over the film thickness is essential.^{6,18} Besides forming semiconductor heterojunctions to facilitate charge separation, the fabrication of Fe_2O_3 thin films by atomic layer deposition (ALD) allows for very defined thicknesses based on the self-limiting reactions during the ALD process.³⁵ Hence, the Fe₂O₃ film thickness can be optimized for maximum photocatalytic performance.

Here, we report on the synthesis of $TiO_2 - Fe_2O_3$ multilayer inverse opals by ALD and assessment of their photocatalytic properties. We demonstrate that the complete functionalization of TiO_2 IOs with Fe_2O_3 by ALD enhances their photocatalytic properties by concomitantly forming semiconductor heterojunctions (material combination) and activating the slow photon effect (nanostructuring into IOs). In addition, the influence of the Fe₂O₃ thickness on the photocatalytic performance of TiO2-Fe2O3 bilayer IOs is studied to further improve the efficient utilization of photogenerated charge carriers. Moreover, TiO2-Fe2O3 IOs are overcoated with another TiO2 thin film by ALD to investigate the effect on the photocatalytic performance. These TiO₂-Fe₂O₃-TiO₂ multilayer IOs exhibit reduced photocatalytic activities compared to the bilayer IOs due to nonoptimal heterojunction configuration leading to the charge carriers' trapping. However, the TiO₂-Fe₂O₃-TiO₂ multilayer IOs provoke photoinduced crystallization of the amorphous TiO₂ layers to anatase, which enhances their photocatalytic properties.

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Figure 2. Characterization of the structural integrity and composition by SEM and EDX. (a) and (b) demonstrate the typical IO structure for (a) 16 nm TiO₂ IO and (b) 20 nm TiO₂-2 nm Fe₂O₃, both fabricated with 252 nm PS template size. (c) an EDX scan along a 20 nm TiO₂-2 nm Fe₂O₃ cross-section reveals a homogeneous distribution of iron and titanium. (d) Fe₂O₃-coated IOs present needle-like structures and larger particles at their top surface.

2. EXPERIMENTAL SECTION

2.1. Materials. Mucasol solution was purchased from Brand GmbH (Germany), and 5 w/v% aqueous polystyrene (PS) particles' dispersions with particle sizes of 150 ± 3 nm and 252 ± 6 nm were acquired from microParticles GmbH (Germany). Ultrapure "Milli-Q" water (>16 M\Omega cm, H₂O) was utilized as oxidant precursor for the ALD cycles and to prepare aqueous dispersions for colloidal self-assembly performed on borosilicate glass cover slides from Paul Marienfeld GmbH (Germany). Methylene blue (C₁₆H₁₈ClN₃S, MB, CAS 122965–43–9), and hydrogen peroxide (H₂O₂, CAS 7722–84–1) were supplied by Sigma-Aldrich (Germany), while titanium tetraisopropoxide (TTIP, CAS 546–68–9) and ferrocene (C₁₀H₁₀Fe, Cp₂Fe, CAS 102–54–5) were purchased from Alfa Aesar (Germany). Nitrogen (6.0) was received from SOL (Germany), and oxygen (5.0) was supplied by Westfalen (Germany), respectively.

2.2. Fabrication of TiO₂-Fe₂O₃ Inverse Opals. Preparation of TiO2-Fe2O3 IOs starts with the colloidal self-assembly of PS particles, followed by coating of the self-assembled direct opal structures with TiO₂ by ALD, removal of the PS template, functionalization with Fe₂O₃ by ALD, and optionally depositing another TiO2 layer by ALD (Figure 1). The colloidal self-assembly process is performed by vertical convective self-assembly of PS particles on top of glass substrates that are immersed into PTFE beakers containing 25 mL of PS particle dispersion (0.75 mg/mL) and placed inside a humidity chamber (HCP108, Memmert) at 55 °C and 70% relative humidity for 90 h. Previously to immersion, the glass substrates were ultrasonically cleaned in 0.1 vol % aqueous mucasol solution for 1 h, brushed with mucasol solution, and rinsed with ultrapure H₂O. The clean substrates were dried with a nitrogen stream and plasma treated using a RF plasma barrel etcher for 20 min (Polaron PT7160, VG Microtech). The resulting colloidal selfassembled PS template structures were coated with TiO₂ by ALD in a custom-built reactor (Hamburg University of Technology, Integrated Materials Systems Group). The ALD process was operated in stopflow mode at 95 °C and with 2 Nl/h nitrogen flow, starting after 3 h

of prevacuum. TTIP as titanium precursor was heated to 85 °C, and H₂O as oxygen precursor was kept at room temperature. During an ALD cycle, the precursors were pulsed, exposed, and purged for 1, 30, and 90 s (TTIP) and 0.2, 30, and 90 s (H₂O), respectively, resulting in a growth per cycle (GPC) of 0.4 Å. TiO₂ cycles were repeated until the desired coating thicknesses of 16 and 20 nm were obtained. After ALD coating, the PS templates were removed by burn-out in a muffle furnace in air, where samples were heated to 500 °C at a rate of 0.3 $^\circ\text{C/min},$ kept at 500 $^\circ\text{C}$ for 30 min, and naturally cooled down to room temperature. The obtained TiO₂ IOs were further functionalized with Fe₂O₃ in another custom-built ALD reactor (Universität Hamburg, CHyN). The Fe₂O₃ ALD process utilized Cp₂Fe at 100 °C and O₃ at room temperature (generated from O₂ by an OzoneLab OL80W ozone generator; Ozone Services, Canada) as precursors and was operated in stop-flow mode at 200 °C. Pulse, exposure, and purge times were 2, 60, and 90 s for Cp₂Fe and 0.08, 30, and 90 s for O₃, respectively. The O₃ half-cycle was twice repeated within one ALD cycle, and the GPC of Fe₂O₃ deposition was determined to be 0.16 Å. Fe₂O₃ coating thicknesses targeted 10 ALD pulses, 2 and 4 nm. To prepare TiO2-Fe2O3-TiO2 multilayer IOs, another TiO2 ALD process with the same parameters described above was applied. Here, TiO₂ thicknesses of only 2 nm were deposited.

2.3. Structural and Optical Characterization. Microstructural characterization was conducted with a Zeiss Supra 55 VP scanning electron microscope (SEM), both in top and cross-section view, obtained after sectioning the IOs' substrates with a glass cutter. Energy-dispersive X-ray spectroscopy (EDX) measurements were acquired with an Oxford Instruments EDX SDD detector. Optical properties were analyzed with UV/vis spectroscopy in reflection mode utilizing a Flame Extended Range Spectrometer while irradiating the samples with a deuterium-halogen light source DH-2000 (Ocean-Optics, Germany). Reflection measurements were conducted at normal incidence for IOs filled with air and H₂O. Their PSB positions were analyzed with OriginPro 2021 software by applying Gaussian fits to obtain the PSB central wavelength, while the PSB edges were

(a) 1.0 (b) 0.4 150 nm template 16 nm TiO₂+4 nm Fe₂O₃ 16 nm TiO₂+4 nm Fe₂O₃+2 nm air H₂O ∘/a.u. °o emplate nm TiO₃+4 nm Fe₃O Reflectance /a.u. 16 nm TiO.+4 nm Fe.O.+2 nm Reflectance la 0.0 0.0 400 800 1000 1000 600 400 600 800 Wavelength /nm Wavelength /nm

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Figure 3. Optical properties of the prepared IOs. (a) The template size of 16 nm TiO₂ IOs determines the PSB position, which is characterized by the PSB central wavelength (green dashed line), the PSB blue edge (blue dashed line), and the PSB red edge (red dashed line) as exemplarily shown for one measurement. Infiltrating the IOs with H₂O redshifts the PSB due to the higher refractive index of the pore-filling medium. (b) $TiO_2-Fe_2O_3$ IOs and $TiO_2-Fe_2O_3-TiO_2$ multilayer IOs with 150 nm template size feature PSBs around the electronic band gap of TiO₂. Templates of 252 nm lead to $TiO_2-Fe_2O_3$ IOs and $TiO_2-Fe_2O_3-TiO_2$ multilayer IOs with PSBs overlapping with the Fe₂O₃ band gap. The measurements were conducted in aqueous environment.

determined as inflection points of the PSBs and obtained from reflection data smoothed using 200 data points. X-ray diffraction patterns were obtained with a Bruker D8 Discover diffractometer. Grazing incidence diffraction (GID) configuration was used with the X-ray source fixed at an angle of 0.5° , and the detector moved along the range from 10° to 60° with a step size of 0.01° and a step time of 5 s. Phase identification was performed using commercial software from Bruker (Diffrac.EVA 5.1) and the powder diffraction file database (PDF-2 Release 2020 RDB).

2.4. Photocatalytic Characterization. The photocatalytic performance of TiO2-Fe2O3 IOs was assessed by monitoring the photocatalytic degradation of methylene blue (MB) as a model pollutant of water. A sample was mounted in a custom-built photocatalysis cell consisting of polyether ether ketone (PEEK) and a soda-lime glass window. The cell was filled with 8 mL MB solution (2.5 mg/L), which included 200 mM H_2O_2 and was kept in darkness for 1 h to obtain the adsorption-desorption equilibrium of molecules at the sample surface. Afterward, the cell was illuminated with UVvisible light from a Euromex LE.5211 light source equipped with a Philips 64230 FO halogen bulb and the MB absorbance was measured every 5 min. This analysis was conducted by UV-vis spectroscopy after pipetting 1 mL of the MB solution into a cuvette and placing it in the UV-vis absorbance setup consisting of a halogen light source HL-2000 (OceanOptics, Germany), glass fibers, a cuvette holder, and a Flame Extended Range Spectrometer (OceanOptics, Germany). The analyzed volume was then transferred back into the photocatalysis cell. Irradiation of the photocatalysis cell was blocked during the absorbance measurements. For further studying the MB degradation pathway, 100 mM isopropyl alcohol (IPA) as a hole scavenger was added to 8 mL MB solution (2.5 mg/L). The further processing was the same as for the H2O2-containing solution. Based on Lambert-Beer's law, the measured MB absorbance was converted to the concentration and the photocatalytic MB degradation was examined by assuming Langmuir-Hinshelwood kinetics:³⁶

$$\ln\!\!\left(\frac{c}{c_0}\right) = -k \cdot t$$

In this equation, c describes the concentration of the MB solution at the time t, c_0 is the concentration at the measurement start (t = 0 h), and k denotes the apparent photocatalytic rate constant, which measures the photocatalytic activity of a sample. Unless otherwise stated, photocatalytic measurements were repeated three times for each sample to calculate the photocatalytic activity's mean value and standard deviation. Note, the samples stayed in the same photocatalysis cell for the consecutive measurements to ensure the same positioning for all measurements.

A 400 nm long-pass filter and a 425 nm short-pass filter were installed between the light source and a sample, respectively, to assess

the influence of the irradiation spectrum on the photocatalytic performance. For these measurements and the study with IPA containing solutions the samples and photocatalysis cells were new assembled. Their activity was normalized to the measured performance under the standard conditions (2.5 mg/L MB, 200 mM H_2O_2 , full illumination spectrum) in this assembly.

3. RESULTS AND DISCUSSION

3.1. Structural and Optical Characterization. The fabricated IOs show, in general, good structural integrity, as exemplarily depicted in Figure 2. SEM images of all samples are presented in Figure S1 in the Supporting Information. Topview and cross-section SEM images reveal a 3D PhC structure with ordered domains and hollow shells, characteristic of the IOs (Figures 2a and 2b). However, vacancies and stacking faults are also visible. These are typical defects of IO structures originating from the self-assembly of the PS particle templates.^{38,39} EDX analysis of the TiO_2 -Fe₂O₂ IOS EDX analysis of the TiO₂-Fe₂O₃ IOs templates.3 demonstrates coherent signals of iron and titanium throughout the structure (Figure 2c). Since the hereby practiced ALD processes cannot produce elemental iron and titanium, these signals originate from their oxides.^{35,40} For the TiO₂-Fe₂O₃ bilayer IOs, bigger flakes and needles at the top surface of the PhC are observed (Figure 2d). EDX analysis indicates that they consist of iron oxide, probably arising from the Fe₂O₃ ALD process as detachments from the ALD reactor walls. The template with a smaller PS particle diameter of 150 nm presents a challenge for the ALD precursor penetration and homogeneous diffusion within the 3D structure. Hence, structural defects of the IO structure are observed at some spots (Figure S1).

The fabricated IOs feature PSBs in the UV to the visible range of the electromagnetic spectrum corresponding to their structural characteristics, i.e., PS template particle size defining the template size, composition of the shell, and thicknesses of the ALD coated materials (shell thickness of the IO). Figure 3a displays the PSB positions of pure TiO_2 IOs at normal incidence and their dependence on both the size of the PS spheres utilized as templates and the medium inside the pores. Increasing the PS particle diameter drives a redshift of the PSB position based on the increased spacing of the structure. The characterization of the optical properties not only in air, but also in an aqueous environment is crucial as the photocatalytic reactions will also take place in aqueous media and the PSB

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Figure 4. (a) The photocatalytic activity of $TiO_2-Fe_2O_3$ bilayer IOs depends on the TiO_2 and Fe_2O_3 coating thicknesses and the template size due to the alignment of the PSB with the semiconductor band gap to utilize the slow photon effect for performance enhancement. Each sample was measured three times. (b) Schematic drawing of the band structure and charge carrier movement in $TiO_2-Fe_2O_3$ bilayer IOs. Based on the type II heterojunction, photogenerated holes inside the valence band (VB) migrate toward the Fe₂O₃ layers and can induce an oxidation reaction at the catalyst's surface. Electrons in the conduction band (CB) either get inside the TiO_2 layer or are scavenged by H_2O_2 , which is added to the reaction solution.

position needs to be tailored for this. Comparing the reflection spectra of TiO₂ IOs in air to the TiO₂ IOs filled with H₂O reveals a PSB redshift as the refractive index of H₂O is higher $(1.33)^{41}$ than the refractive index of air (1.00).^{42,43} For the TiO₂-Fe₂O₃ bilayer IOs, the layer composition determines their PSB position, as presented in Figure 3b. Nevertheless, only slight shifts of the PSB positions are observed for TiO₂-Fe₂O₃-TiO₂ multilayer IOs compared to TiO₂-Fe₂O₃ bilayer IOs. The PSBs of all samples overlap with the respective semiconductor band gaps, i.e., TiO₂ for 150 nm template size and Fe₂O₃ for 252 nm template size, as indicated in Figure 3b and Figure S2.

3.2. Photocatalytic Performance. 3.2.1. TiO₂ and TiO₂-Fe₂O₃ Inverse Opals. Pure 16 nm TiO₂ IOs with 150 nm template size exhibit a higher photocatalytic activity of 0.98 \pm $0.01 h^{-1}$ than their counterparts with 252 nm template size $(0.86 \pm 0.02 \text{ h}^{-1})$ due to the expected activity enhancement by the slow photon effect (Figure 4a). The individual photocatalytic activities during three consecutive measurements are shown in Figure S3 and the MB concentration decline of the individual measurements is depicted in Figure S4. The PSB blue edge of the 150 nm template size TiO_2 IO overlaps with the band edge of TiO_2 at around 376 nm⁴⁴ (as illustrated in Figure 3a) and thus, the slow photon effect results in an improved photocatalytic performance. Although larger template sizes should lead to facilitated mass transfer of dye molecules into and reaction products out of the structure, this effect is overweighed by the mismatch of the PSB position concerning the TiO₂ band gap. Hence, as expected, the slow photon effect does not enhance the photocatalytic performance in 252 nm template TiO₂ IOs.

Additional layers of Fe_2O_3 significantly increase the photocatalytic activity of the IOs compared to the reference IO with only TiO₂ (Figure 4a). This is associated with increased light absorption and facilitation of charge carrier separation. The location of the Fe_2O_3 band gap at ~2.2 eV expands the absorption spectrum of the IOs to wavelengths smaller than ~564 nm.^{20,21} Furthermore, coating Fe_2O_3 onto the TiO₂ IOs results in the formation of heterojunctions at the materials interfaces, which should allow for efficient separation of the generated electron/hole pairs. The band alignment of Fe_2O_3 and TiO₂ is ambiguous in literature since both type I

and type II heterojunctions have been reported for such heterostructures. $^{22,23,25,27-29,34,45}$ Accordingly, the heterojunction type depends on the fabrication method and further sample specifications, such as geometry. Based on the publications by Cao et al. and Yang et al. about ALD-based functionalization of $\rm TiO_2$ powders coated with $\rm Fe_2O_3$ thin films and synthesis of TiO2-Fe2O3 thin film heterostructures, respectively, we assume that our samples feature type II heterojunctions (Figure 4b).^{22,31} Hence, photogenerated electrons move toward the conduction band (CB) of TiO₂. At the same time, holes migrate to the valence band (VB) of Fe₂O₃ and can induce oxidation reactions in molecules adsorbed at the material surface. This charge carrier separation reduces the recombination of the free charge carriers and results in an improved photocatalytic performance. Free electrons can, in principle, also contribute to the degradation of organic pollutants by inducing reactions in adsorbed molecules. H₂O₂ was added to the reaction solution to aid the generation of radicals necessary for the photocatalytic decomposition. However, H₂O₂ also acts as an electron scavenger; thus, H₂O₂ molecules at the photocatalysts' surface could trap free electrons.¹⁹ These electrons will then contribute to the photocatalytic degradation of the organic dye instead of moving toward the CB of the inner TiO₂ layer. Although these two competing processes (electron migration to the TiO₂ layer and electron trapping by H_2O_2 at the surface) cannot be clearly distinguished by the dye degradation measurements, both of them lead to a better separation of photogenerated charge carriers in the photocatalyst and hence, to an enhancement of the photocatalytic activity. Assessment of the dye degradation of the 252 nm template sample with 16 nm TiO₂-2 nm Fe₂O₃ coating with a MB solution containing 100 mM IPA revealed a decrease of the activity to 26% compared to the H_2O_2 -containing solution (Figure S5). IPA is used as hole scavenger and the decreasing activity upon its' presence demonstrates that photogenerated holes are crucial for inducing the MB destruction in our samples.

A general increase of the photocatalytic activity for the 252 nm template compared to the smaller one is expected for $TiO_2-Fe_2O_3$ bilayer IOs due to the slow photon effect, as in this case, the IO structural PSB was designed to match the band gap of the Fe₂O₃. The PSB edge of the larger template

size samples overlaps with the band gap of Fe_2O_3 , which allows for enhancement of the photocatalytic performance by the slow photon effect in Fe_2O_3 as observed for all $TiO_2-Fe_2O_3$ bilayer IOs (Figure 4a).

Furthermore, the performance also depends on the Fe₂O₃ coating thickness. A rise of the Fe₂O₃ coating thickness from 10 ALD pulses to 2 nm improves the sample' photocatalytic activity based on the material's additional light absorption. An optimum activity of 1.38 \pm 0.09 h⁻¹ is demonstrated for TiO₂-Fe₂O₃ bilayer IOs composed of 16 nm TiO₂ and 2 nm Fe_2O_3 in comparison to 0.86 \pm 0.02 h⁻¹ of the single TiO₂ IO. The photocatalytic performance is reduced when the illumination spectrum is limited to specific spectral regions (Figure S6). Specifically, the utilization of a 400 nm long-pass filter eliminates UV radiation. In this case, the photocatalytic performance of the 252 nm template sample consisting of 16 nm TiO₂ and 4 nm Fe₂O₃ is reduced to 75% compared to the standard conditions. Further modification is observed when a 425 nm short-pass filter is applied. Here, the spectral range between 425 and 530 nm is suppressed and wavelengths higher than 530 nm are attenuated, while wavelengths shorter than 425 nm are transmitted without intensity alteration. With this short-pass filter, the samples' activity decreases to 66%, demonstrating the importance of visible light radiation for inducing photocatalytic reactions by the presented heterostructure IOs. Please note that the sample was only tested once in each measurement configuration.

Nevertheless, a further increase to 4 nm Fe_2O_3 thickness reduces the photocatalytic activity. Although the thicker coating could absorb more light, it simultaneously reduces the gap size between neighboring shells, which might limit the diffusion of dye molecules and reaction products within the IO structure.⁴⁶ Thus, the photocatalytic performance declines as measured for both template sizes. The higher diffusion path length for charge carriers within the 4 nm Fe₂O₃ coating could also result in higher charge carrier recombination rates, leading to decreasing activities with increasing thickness. Such performance decline with increasing Fe₂O₃ content was also observed by Pylarinou et al.³⁴ for TiO₂-Fe₂O₃ thin film heterostructure samples. Similar photocatalytic activities to the TiO₂-Fe₂O₃ bilayer IOs of 16 nm TiO₂ and 4 nm Fe₂O₃ are obtained for samples consisting of 20 nm TiO₂ and 2 nm Fe₂O₃. ALD coating onto an assembled opal template structure presents a maximum coating thickness of ~7.7% of the template sphere diameter because the tetrahedral gaps, i.e., the smallest interconnecting pores between neighboring macropores, close at this thickness.⁴⁷ Hence, the template sizes used herein correspond to a theoretically estimated maximum coating of 11.6 and 19.4 nm for 150 and 252 nm templates, respectively. For the TiO₂ deposition onto the opal templates, further material deposition can only occur by material transport through the octahedral gaps or at the outer surfaces of the IO, which are in contact with the environment. Since both template size IOs studied herein are coated with the same TiO₂ thickness, the 150 nm template IO already reached the theoretical estimated maximum coating after the first ALD coating, while IOs consisting of 252 nm templates still have open tetrahedral gaps after the TiO2 deposition. During the Fe₂O₃ ALD process, the tetrahedral gaps of the 252 nm template size also get very small or even close.

Nevertheless, since the Fe_2O_3 coating is conducted by utilizing TiO_2 IO structures as template instead of the PS opal, this template provides open channels between neighboring shells at the shell contact points.³⁹ Thus, material diffusion through these contact points is still possible after the closure of the tetrahedral gaps by the Fe₂O₃ coating. Additional Fe₂O₃ coating may influence the charge carrier separation in the structure because the diffusion of molecules within the structure is reduced due to the tetrahedral gap closures. The slightly decreasing activities for the thicker coating, i.e., 20 nm TiO₂ and 2 nm Fe₂O₃, support the assumption that diffusion limitation affects the photocatalytic properties because 2 nm Fe₂O₃ was the best-performing thickness for TiO₂ IOs of 16 nm.

Functionalizing TiO₂ IOs with Fe₂O₃ by ALD outperforms the photocatalytic performance of previously reported structures, namely TiO₂ IOs modified with Fe₂O₃ by hydrothermal methods or chemisorption-calcination and Fe $_2O_3$ -functionalized Ti O_2 nanostructures. 22,23,26,28,33,34 This comparison considers samples of Fe₂O₃-coated TiO₂ particles or inverse opals tested by photocatalytic dye degradation. Nevertheless, the exact value of the photocatalytic activity kdepends strongly on the reaction conditions, such as illumination power, illumination spectrum, temperature, catalyst loading, type of dye, and additives in the reaction solution, which are summarized in Table S1. Hence, it is setupspecific and we, therefore, compare here the qualitative evolution of the photocatalytic activities upon Fe₂O₃ functionalization within publications on Fe₂O₃-modified TiO₂ IOs. Our results of enhanced photocatalytic performances of $TiO_2~IOs~upon~functionalization~with~Fe_2O_3~agree~with~previous~reports~by~Liu~et~al.~and~Pylarinou~et~al.^{33,34}$ In detail, Liu et al. observed an increase in the photocurrent density by up to 50% when TiO₂ IOs were modified with Fe₂O₃ nanoparticles by the hydrothermal method. Similarly, Pylarinou et al. reported increased photocatalytic activities and photocurrent densities when they modified TiO₂ IOs with FeO_x nanoclusters by chemisorption-calcination cycles. Moreover, they showed that the enhancement depends on the utilized iron oxide content. They attributed the maximum improvement for low iron oxide contents to the efficient charge carrier separation in combination with the utilization of the slow photon effect. High iron oxide loadings resulted in a performance decline due to increased surface recombination of photogenerated charge carriers. However, the processes involved in the photocatalytic and photoelectrochemical reaction with the structures of the two aforementioned publications differ from those in this work. Since both references functionalized TiO₂ IOs with iron oxide particles or clusters, TiO₂ surfaces are still in contact with the reaction solution and charges accumulated at the TiO₂ film can induce reactions in the aqueous surrounding.

In contrast, our $TiO_2-Fe_2O_3$ bilayer IOs prepared by ALD consist of continuously capped TiO_2 by the Fe_2O_3 layers. Thus, charge transfer from the photocatalyst structure toward the solution is only possible via the Fe_2O_3 surfaces. To the best of our knowledge, such configuration of Fe_2O_3 -modified TiO_2 IOs has yet to be reported. Significant enhancement of the photocatalytic performance of TiO_2 powder coated with Fe_2O_3 by ALD was reported by Cao et al.²² Similar to our results, they observed an optimum coating thickness of ~2.6 nm Fe_2O_3 for the photocatalytic degradation of methyl orange as an organic dye. The structures formed type II heterojunctions, effectively improving the separation of photogenerated charge carriers by reducing their recombination. Further, the IOs fabricated herein present nanostructured materials that could



Figure 5. (a) The mean photocatalytic activity of $TiO_2-Fe_2O_3-TiO_2$ multilayer IOs after three measurements depends on the composition and template size but shows a significant standard deviation. (b) The individual activities during seven consecutive measurements of 16 nm TiO_2-2 nm Fe_2O_3-2 nm TiO_2 and 16 nm TiO_2-4 nm Fe_2O_3-2 nm TiO_2 multilayer IOs for the 252 nm template increase during the first four measurements, slightly decrease in the following two measurements and are stable afterward. (c) The band structure of $TiO_2-Fe_2O_3-TiO_2$ multilayer IOs depicts trapping of photogenerated holes inside the Fe_2O_3 layers due to adding another TiO_2 layer. Electrons in the CB move toward the TiO_2 layers, and those located in the outer layers can induce reductive reactions in the surrounding electrolyte or get scavenged by H_2O_2 molecules. (d) XRD patterns show anatase TiO_2 peaks for Fe_2O_3 functionalized TiO_2 IOs after photocatalysis measurements. Multilayer structures exhibit significantly higher peak intensities, indicating that this composition provokes photoinduced crystallization of the TiO_2 layers.

prevent potentially hazardous leaching of photocatalytic nanoparticles into the environment.⁴⁸ The interconnected porous structure of IOs provides a stable framework and thus, can be considered as nanostructured solids with "bulk-like" properties regarding the high stability of the structure and adhesion to the substrate during operation.⁴⁹

3.2.2. TiO₂-Fe₂O₃-TiO₂ Multilayer Inverse Opals. Depositing an additional TiO₂ thin film onto the previously presented TiO2-Fe2O3 IOs leads to TiO2-Fe2O3-TiO2 multilayer IOs exhibiting unstable photocatalytic activities over consecutive measurements with a reduced average performance (Figure 5a). Specifically, the activities increase within the first four measurements, then slightly decrease for two measurements, and are stable for the following trial (Figure 5b). This behavior is observed for all studied TiO_2 -Fe₂O₃-TiO₂ multilayer IOs independent of the Fe₂O₃ coating thickness and the template size. Note, the average performance is calculated from the first three measurements to compare the multilayer IOs to the TiO₂-Fe₂O₃ bilayer IOs. The multilayer IOs with 150 nm template size feature average activities of 0.83 \pm 0.12 h⁻¹ and 1.00 \pm 0.14 h⁻¹ for samples composed of 16 nm TiO₂-2 nm Fe₂O₃-2 nm TiO₂ and 16 nm TiO₂-4 nm Fe₂O₃-2 nm TiO₂, respectively. In contrast, bilayer IOs of the same template size exhibit higher activities of $1.24 \pm 0.01 \text{ h}^{-1}$ $(16 \text{ nm TiO}_2-2 \text{ nm Fe}_2\text{O}_3)$ and $1.13 \pm 0.04 \text{ h}^{-1}$ (16 nm TiO_2-4 nm Fe₂O₃). The MB concentration decrease within the seven photocatalysis measurements of TiO₂-Fe₂O₃-TiO₂

multilayer IOs is shown in Figure S8. The individual photocatalytic performances for the 150 nm template multilayer IOs are depicted in Figure S7. Template sizes of 252 nm also result in decreased activities of 0.93 ± 0.20 h⁻¹ and 0.81 ± 0.21 h⁻¹ for samples consisting of 16 nm TiO₂-2 nm Fe₂O₃-2 nm TiO₂ and 16 nm TiO₂-4 nm Fe₂O₃-2 nm TiO₂, respectively, compared to the bilayer samples of this template size which show photocatalytic activities of 1.38 ± 0.09 h⁻¹ for 16 nm TiO₂-2 nm Fe₂O₃ and 1.25 ± 0.05 h⁻¹ for 16 nm TiO₂-4 nm Fe₂O₃.

These results demonstrate that the photocatalytic properties of a multilayer arrangement of TiO₂ and Fe₂O₃ not depend on the thicknesses of the individual layers but rather on the template size. The TiO₂-Fe₂O₃-TiO₂ multilayer IOs exhibit lower activities than those observed for TiO₂-Fe₂O₃ bilayer IOs. The significant decrease in the average photocatalytic activity of multilayer IOs after three measurements compared to the TiO₂-Fe₂O₃ bilayer IOs can be attributed to two effects. First, photo-Fenton reactions at the Fe₂O₃ surface can no longer contribute to MB degradation because TiO₂ overcoats Fe_2O_3 .¹ Second, the nonoptimal heterojunction configuration in the multilayer IOs could lead to a performance decline. Although electrons migrate toward the TiO₂ layers and the 2 nm outer TiO₂ film, the holes could be trapped inside the Fe_2O_3 layers (see schematic drawing in Figure 5c). Organic dye degradation is often mainly driven by oxidative processes involving holes, but both charge carrier types can contribute to

the decomposition. The H_2O_2 added to the dye solution herein also acts as an electron scavenger and, therefore, could use the electrons generated in the outer TiO₂ layers to induce photocatalytic reactions. However, electrons that migrate from the Fe₂O₃ layers toward the inner TiO₂ layer and the holes trapped in the Fe₂O₃ layers are not available for photocatalytic reactions. Correspondingly, the photocatalytic activity is strongly reduced compared to TiO₂-Fe₂O₃ bilayer IOs. IPA was utilized as hole scavenger for the 16 nm TiO₂-4 nm Fe₂O₃-2 nm TiO₂ trilayer IO to elucidate the influence of holes on the photocatalytic performance (Figure S5). With 100 mM IPA, the activity decreases to 27%, revealing that holes that migrate from the outer TiO₂ layer to the TiO₂ surface significantly contribute to the dye degradation in the surrounding MB solution.

3.2.3. In Situ Photoinduced Crystallization of TiO₂. The configuration of TiO₂-Fe₂O₃-TiO₂ multilayer IOs provokes photoinduced crystallization of TiO₂ as characterized by XRD measurements (Figure 5d). The above-mentioned trapped holes contribute to the photoinduced crystallization of the inner TiO₂ layer, which is enhanced by multilayer IOs (Figure 5d). While the TiO_2 IO is still amorphous after the photocatalytic performance measurements, the TiO₂-Fe₂O₃ bilayer IO with 4 nm Fe₂O₃ coating features a slight peak at 25° corresponding to the anatase main peak (PDF 00-064-0863). Utilizing the Scherrer equation with a shape factor of 0.9 gives an estimated average crystallite size of 9.2 nm.⁵⁰ The $TiO_2 - Fe_2O_3 - TiO_2$ multilayer IO reveals intense peaks of the anatase phase and one peak, which indicates either brookite or hematite. The anatase (101) peak at $\sim 25^{\circ}$ indicates crystallite sizes of 19.2 and 20.4 nm for the sample composed of 16 nm TiO_2-4 nm Fe_2O_3-2 nm TiO_2 after three and seven measurements, respectively. All peaks are present after three photocatalysis measurements and remain constant after seven measurements.

Moreover, the crystallite size is in the same range as the thickness of the inner TiO2 layer. Control experiments with Fe₂O₃ coated samples before the photocatalysis measurements (Figure 5d) and another control after 17 h in the reaction solution in darkness (Figure S9), i.e., the accumulated duration of 7 measurements, showed only shallow intense peaks in the XRD patterns corresponding to a crystallite size of 3.3 nm. As indicated by the crystallite sizes, crystallite growth occurs mainly within the first three measurements for which increasing activities are observed. Thus, we assume that Fe₂O₃ incorporation triggers the crystallization under illumination. The photoinduced crystallization is amplified for TiO₂-Fe₂O₃-TiO₂ multilayer IOs as the additional material interfaces and charge carrier trapping can facilitate the crystallization. It was previously reported that Fe ions inside the TiO₂ lattice can create oxygen vacancies.^{51,52} These defects can serve as nucleation sites for the crystallization of the TiO_{2} film due to charge imbalances and structural distortion. In the TiO₂-Fe₂O₃-TiO₂ multilayer IOs, Fe ions present local defects in the amorphous TiO₂ lattice at the interfaces of the TiO_2 and Fe_2O_3 layers. In addition, the energy absorbed by the material during photoexcitation can also contribute to the crystallization process by providing the energy required for the crystallization.⁵³ The photogenerated charge carriers can transfer energy to neighboring atoms, which can promote structural rearrangement such as crystallization.

 TiO_2 crystallization observed in this work is probably promoted by the band alignment of the individual materials.

For TiO₂-Fe₂O₃ bilayer IOs, the material interfaces, oxygen vacancies, and charge carriers already elicit crystallization of small parts of the TiO₂ as indicated by the minor peak in the XRD pattern. Adding another TiO₂ layer to the structure, i.e., the outer TiO_2 layers in case of the TiO_2 -Fe₂O₃-TiO₂ trilayer IOs, increases the number of material interfaces and confines photogenerated charge carriers to certain areas of the photocatalyst structure. Since holes migrate to the VB of Fe_2O_3 (Figure 5c), they are trapped inside the trilayer structure. Hence, these holes increase charge imbalances at the Fe₂O₃/TiO₂ interfaces. In this way, they create additional nucleation sites for crystallization, and the required activation energy can be obtained from further photogenerated charge carriers in the material. Note, in contrast to the trilayer IOs, holes are not trapped in bilayer IO structures because they can move toward the Fe₂O₃ surface surrounded by the electrolyte and release their energy by inducing oxidation reactions in molecules adsorbed at the Fe₂O₃ surface. Both effects, the increased number of interfaces and the charge carrier trapping inside the multilayer structure are hypothesized to contribute to the strong photoinduced crystallization of the inner TiO₂ layer in the TiO₂-Fe₂O₃-TiO₂ multilayer IOs. This photoinduced crystallization into the anatase phase improves the photocatalytic performance of the structures due to the higher inherent photocatalytic activity of anatase compared to amorphous TiO2.4 In addition, photoinduced crystallization could help to avoid shrinkage of porous structures and strong atom diffusion at interfaces, which are typical structural alterations induced by thermal crystallization.⁵⁴ The increasing photocatalytic activities of the TiO2-Fe2O3-TiO2 multilayer IOs within the first four measurements correspond to the crystallization of the TiO2. The presence of oxygen vacancies, as introduced by the Fe₂O₃ layers, promotes charge carrier transport in TiO_2 and improves the photocatalytic proper-ties. ${}^{51,52,55-57}$ Assuming that oxygen vacancies trigger the crystallization and are responsible for the high photocatalytic activity, a decline in their concentration would result in a reduced photocatalytic performance. Assuming that the oxygen vacancy content reaches a maximum during the crystallization process and decreases and vanishes in the final stage of the TiO₂ crystallization, fits with the fact that the photocatalytic activity first increases and then slightly decreases until a stable performance is observed for the anatase structure. In situ XRD at a synchrotron during the photocatalysis characterization of the trilayer IOs could shed light on the details of the crystallization mechanism.

The emergence of photoinduced crystallization of TiO₂ in TiO₂-Fe₂O₃ multilayered structures was not previously reported. It could enable the fabrication of crystalline materials on templates unsuited for high-temperature treatments. This could, for example, be realized by incorporating ultrathin Fe₂O₃ layers into thicker TiO₂ films to generate oxygen vacancies inside the complete TiO₂ layer effectively. ALD is a commonly used technique to fabricate delta-doped structures based on self-limiting reactions. Moreover, ALD-based processing allows further combining Fe₂O₃-incorporated TiO₂ with other semiconductor photocatalyst layers to separate photogenerated charge carriers as presented herein for the $TiO_2 - Fe_2O_3$ bilayer IOs. The observed photoinduced crystallization also emphasizes the influence of semiconductor heterojunctions on photocatalytic performance, structural stability, and possible tailoring. Hence, the formation of
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semiconductor heterostructures could further expand the application of photoinduced crystallization in various fields.⁵⁸

4. CONCLUSION

Modifying TiO₂ inverse opals with conformal Fe₂O₃ layers prepared by ALD significantly enhanced the photocatalytic properties due to additional visible light absorption and efficient separation of photogenerated charges with a photocatalytic degradation rate improvement of 27% compared to pure TiO₂ IOs. Aligning the IOs' PSB edge with the electronic band gap of Fe2O3 enabled further improvement of the photocatalytic performance by 60% due to the slow photon effect. Optimization of the Fe_2O_3 thickness resulted in a maximum activity of 1.38 \pm 0.09 h^{-1} for $TiO_2-Fe_2O_3$ bilayer IOs consisting of 16 nm TiO₂ and 2 nm Fe₂O₃ coating. TiO₂-Fe₂O₃-TiO₂ multilayer IOs demonstrated reduced photocatalytic activities due to the nonoptimal band structure alignment of the individual layers. Nevertheless, the band structure provoked photoinduced crystallization of TiO₂, resulting in an increase of the photocatalytic activity within the first four photocatalysis measurements due to anatase formation, which is known to enhance the performance compared to amorphous TiO₂. In the future, in situ XRD at a synchrotron during the photocatalysis characterization could be conducted to elucidate the mechanism of photoinduced crystallization in detail. Moreover, fine-tuning the structural and optical properties of PhCs, e.g., by optimizing the IO thickness, in combination with precise adjustment of semiconductor heterostructures could further improve photocatalysts' performance.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c10831.

SEM images of all samples, optical properties of the prepared IOs, individual photocatalytic activities of TiO_2 IOs and $TiO_2-Fe_2O_3$ bilayer IOs during three consecutive measurements, dye concentration decrease during three consecutive photocatalysis measurements for TiO_2 IOs and $TiO_2-Fe_2O_3$ bilayer IOs, photocatalytic activities over seven measurements of multilayer IOs prepared with 150 nm template size, dye concentration decrease during seven consecutive photocatalysis measurements for $TiO_2-Fe_2O_3-TiO_2$ multilayer IOs, and XRD pattern of a multilayer IO exposed to the reaction solution without illumination for 17 h (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Jack, R. S.; Ayoko, G. A.; Adebajo, M. O.; Frost, R. L. A Review of Iron Species for Visible-Light Photocatalytic Water Purification. *Environ. Sci. Pollut. Res.* **2015**, *22* (10), 7439–7449.

(2) Kumar, N.; Kumbhat, S. Essentials in Nanoscience and Nanotechnology; John Wiley & Sons Inc.: Hoboken, NJ, 2016.

(3) Teoh, W. Y.; Scott, J. A.; Amal, R. Progress in Heterogeneous Photocatalysis: From Classical Radical Chemistry to Engineering Nanomaterials and Solar Reactors. *J. Phys. Chem. Lett.* **2012**, 3 (5), 629–639.

(4) Zhang, J.; Zhou, P.; Liu, J.; Yu, J. New Understanding of the Difference of Photocatalytic Activity among Anatase, Rutile and Brookite TiO2. *Phys. Chem. Chem. Phys.* **2014**, *16* (38), 20382–20386.

(5) Carp, O.; Huisman, C. L.; Reller, A. Photoinduced Reactivity of Titanium Dioxide. *Prog. Solid State Chem.* **2004**, 32 (1–2), 33–177. (6) Li, J.; Wu, N. Semiconductor-Based Photocatalysts and Photoelectrochemical Cells for Solar Fuel Generation: A Review. *Catal. Sci. Technol.* **2015**, 5 (3), 1360–1384.

(7) Zhang, J.; Tian, B.; Wang, L.; Xing, M. *Photocatalysis Fundamentals, Materials and Applications*; Springer Open Ltd: Singapore, 2018.

(8) Li, H.; Zhou, Y.; Tu, W.; Ye, J.; Zou, Z. State-of-the-Art Progress in Diverse Heterostructured Photocatalysts toward Promoting Photocatalytic Performance. *Adv. Funct. Mater.* **2015**, *25* (7), 998– 1013.

(9) Aguirre, C. I.; Reguera, E.; Stein, A. Tunable Colors in Opals and Inverse Opal Photonic Crystals. *Adv. Funct. Mater.* **2010**, *20* (16), 2565–2578.

(10) Galisteo-Lõpez, J. F.; Ibisate, M.; Sapienza, R.; Froufe-Pérez, L. S.; Blanco, Ú.; Lõpez, C. Self-Assembled Photonic Structures. *Adv. Mater.* **2011**, 23 (1), 30–69.

(11) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. Photonic Crystals: Putting a New Twist on Light. *Nature* **1997**, 386 (6621), 143–149.

(12) López, C. Materials Science Aspects of Photonic Crystals. Adv. Mater. 2003, 15 (20), 1679–1704.

(13) Schroden, R. C.; Al-Daous, M.; Blanford, C. F.; Stein, A. Optical Properties of Inverse Opal Photonic Crystals. *Chem. Mater.* **2002**, *14* (8), 3305–3315.

(14) Chen, J. I. L.; Von Freymann, G.; Choi, S. Y.; Kitaev, V.; Ozin, G. A. Amplified Photochemistry with Slow Photons. *Adv. Mater.* **2006**, *18* (14), 1915–1919.

(15) Chen, J. I. L.; Von Freymann, G.; Choi, S. Y.; Kitaev, V.; Ozin, G. A. Slow Photons in the Fast Lane in Chemistry. *J. Mater. Chem.* **2008**, *18* (4), 369–373.

(16) Grushevskaya, S.; Belyanskaya, I.; Kozaderov, O. Approaches for Modifying Oxide-Semiconductor Materials to Increase the Efficiency of Photocatalytic Water Splitting. *Materials* **2022**, *15*, 4915. (17) Singh, P.; Sharma, K.; Hasija, V.; Sharma, V.; Sharma, S.; Raizada, P.; Singh, M.; Saini, A.K.; Hosseini-Bandegharaei, A.; Thakur, V.K. Systematic Review on Applicability of Magnetic Iron-Oxides Integrated Photocatalysts for Degradation of Organic Pollutants in Water. *Mater. Today* **2019**, *14*, 100186.

(18) Wheeler, D. A.; Wang, G.; Ling, Y.; Li, Y.; Zhang, J. Z. Nanostructured Hematite: Synthesis, Characterization, Charge Carrier Dynamics, and Photoelectrochemical Properties. *Energy Environ. Sci.* **2012**, *5*, 6682–6702.

(19) Akhavan, O. Thickness Dependent Activity of Nanostructured TiO 2 $/\alpha$ - Fe 2 O 3 Photocatalyst Thin Films. *Appl. Surf. Sci.* 2010, 257 (5), 1724–1728.

(20) Hardee, K. I.; Bard, A. J. Semiconductor Electrodes: X. Photoelectrochemical Behavior of Several Polycrystalline Metal Oxide Electrodes in Aqueous Solutions. *J. Electrochem. Soc.* **1977**, *124* (124), 215–224.

(21) Leland, J. K.; Bard, A. J. Photochemistry of Colloidal Semiconducting Iron Oxide Polymorphs. J. Phys. Chem. **1987**, 91, 5076–5083.

(22) Cao, Y.-Q.; Zi, T.-Q.; Zhao, X.-R.; Liu, C.; Ren, Q.; Fang, J.-B.; Li, W.-M.; Li, A.-D. Enhanced Visible Light Photocatalytic Activity of Fe2O3 Modified TiO2 Prepared by Atomic Layer Deposition. *Sci. Rep.* **2020**, *10*, 13437.

(23) Trenczek-Zajac, A.; Synowiec, M.; Zakrzewska, K.; Zazakowny, K.; Kowalski, K.; Dziedzic, A.; Radecka, M. Scavenger-Supported Photocatalytic Evidence of an Extended Type I Electronic Structure of the TiO2@Fe2O3Interface. ACS Appl. Mater. Interfaces **2022**, *14* (33), 38255–38269.

(24) Alves da Silva, J.; Borges dos Santos, G.; Stumpf Madeira, V.; de Almeida Ramalho, M. L.; Ouriques Brasilero, I. L.; Marinho Cahino, A. Use of Fe2O3-TiO2 in Solar Photo-Fenton Process for the Phenol Degradation. *Engevista* **2018**, 757–771.

(25) Baldovi, H. G. Optimization of α -Fe2O3 Nanopillars Diameters for Photoelectrochemical Enhancement of α -Fe2O3-TiO2 Heterojunction. *Nanomaterials* **2021**, *11* (8), 2019.

(26) Hiltunen, A.; Ruoko, T.-P.; Iivonen, T.; Lahtonen, K.; Ali-Löytty, H.; Sarlin, E.; Valden, M.; Leskelä, M.; Tkachenko, N. Design Aspects of All Atomic Layer Deposited TiO $_2$ – Fe $_2$ O $_3$ Scaffold-Absorber Photoanodes for Water Splitting. *Sustain. Energy Fuels* **2018**, 2 (9), 2124–2130.

(27) Hitam, C. N. C.; Jalil, A. A. A Review on Exploration of Fe 2 O 3 Photocatalyst towards Degradation of Dyes and Organic Contaminants. *J. Environ. Manage.* **2020**, *258*, No. 110050.

(28) Peng, L.; Xie, T.; Lu, Y.; Fan, H.; Wang, D. Synthesis, Photoelectric Properties and Photocatalytic Activity of the Fe2O3/ TiO2 Heterogeneous Photocatalysts. *Phys. Chem. Chem. Phys.* **2010**, *12* (28), 8033.

(29) dela Rosa, F. M.; Popovic, M.; Papac Zjacic, J.; Radic, G.; Kraljic Rokovic, M.; Kovacic, M.; Farre, M. J.; Genorio, B.; Lavrencic Stangar, U.; Kusic, H.; Loncaric Bozic, A.; Petrovic, M. Visible-Light Activation of Persulfate or H2O2 by Fe2O3/TiO2 Immobilized on Glass Support for Photocatalytic Removal of Amoxicillin: Mechanism, Transformation Products, and Toxicity Assessment. *Nanomaterials* **2022**, *12*, 4328.

(30) Aritonang, A. B.; Selpiana, H.; Wibowo, M. A.; Warsidah, W.; Adhitiawarman, A. PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING Fe2O3-TiO2/KAOLINITE UNDER VISIBLE LIGHT. J. Kim. Dan Pendidik. Kim. **2022**, 7 (3), 277–286.

(31) Yang, X.; Liu, R.; Du, C.; Dai, P.; Zheng, Z.; Wang, D. Improving Hematite-Based Photoelectrochemical Water Splitting with Ultrathin TiO $_2$ by Atomic Layer Deposition. ACS Appl. Mater. Interfaces **2014**, 6 (15), 12005–12011.

(32) Zandi, O.; Klahr, B. M.; Hamann, T. W. Highly Photoactive Ti-Doped α -Fe2O3 Thin Film Electrodes: Resurrection of the Dead Layer. *Energy Environ. Sci.* **2013**, *6* (2), 634–642.

(33) Liu, J.; Sun, C.; Fu, M.; Long, J.; He, D.; Wang, Y. Enhanced Photochemical Catalysis of TiO2 Inverse Opals by Modification with ZnO or Fe2O3 Using ALD and the Hydrothermal Method. *Mater. Res. Express* **2018**, *5*, No. 025509.

(34) Pylarinou, M.; Toumazatou, A.; Sakellis, E.; Xenogiannopoulou, E.; Gardelis, S.; Boukos, N.; Dimoulas, A.; Likodimos, V. Visible Light Trapping against Charge Recombination in FeOx-TiO2 Photonic Crystal Photocatalysts. *Materials* **2021**, *14*, 7117.

(35) Martinson, A. B. F.; Devries, M. J.; Libera, J. A.; Christensen, S. T.; Hupp, J. T.; Pellin, M. J.; Elam, J. W. Atomic Layer Deposition of Fe2O3 Using Ferrocene and Ozone. *J. Phys. Chem. C* **2011**, *115* (10), 4333–4339.

(36) Ollis, D. F. Kinetic Disguises in Heterogeneous Photocatalysis. *Top. Catal.* **2005**, 35 (3–4), 217–223.

(37) Gaya, U. I. Heterogeneous Photocatalysis Using Inorganic Semiconductor Solids; Springer: Berlin Heidelberg, 2014.

(38) Vogel, N.; Retsch, M.; Fustin, C.-A.; Del Campo, A.; Jonas, U. Advances in Colloidal Assembly: The Design of Structure and Hierarchy in Two and Three Dimensions. *Chem. Rev.* **2015**, *115* (13), 6265–6311.

(39) Furlan, K. P.; Larsson, E.; Diaz, A.; Holler, M.; Krekeler, T.; Ritter, M.; Petrov, A. Y.; Eich, M.; Blick, R.; Schneider, G. A.;

ACS Applied Materials & Interfaces

Greving, I.; Zierold, R.; Janßen, R. Photonic Materials for High-Temperature Applications: Synthesis and Characterization by X-Ray Ptychographic Tomography. *Appl. Mater. Today* **2018**, *13*, 359–369. (40) Rahtu, A.; Ritala, M. Reaction Mechanism Studies on Titanium Isopropoxide–Water Atomic Layer Deposition Process. *Chem. Vap. Depos.* **2002**, *8* (1), 21.

 $(\overline{41})$ Daimon, M.; Masumura, A. Measurement of the Refractive Index of Distilled Water from the Near-Infrared Region to the Ultraviolet Region. *Appl. Opt.* **2007**, *46* (18), 3811–3820.

(42) Birch, K. P.; Downs, M. J. An Updated Edlén Equation for the Refractive Index of Air. *Metrologia* **1993**, *30* (3), 155–162.

(43) Lee, J.; Bae, K.; Kang, G.; Choi, M.; Baek, S.; Yoo, D. S.; Lee, C. W.; Kim, K. Graded-Lattice AAO Photonic Crystal Heterostructure for High Q Refractive Index Sensing. *RSC Adv.* **2015**, 5 (88), 71770–71777.

(44) Lim, S. Y.; Hedrich, C.; Jiang, L.; Law, C. S.; Chirumamilla, M.; Abell, A. D.; Blick, R. H.; Zierold, R.; Santos, A. Harnessing Slow Light in Optoelectronically Engineered Nanoporous Photonic Crystals for Visible Light-Enhanced Photocatalysis. *ACS Catal.* **2021**, *11* (21), 12947–12962.

(45) Kment, S.; Riboni, F.; Pausova, S.; Wang, L.; Wang, L.; Han, H.; Hubicka, Z.; Krysa, J.; Schmuki, P.; Zboril, R. Photoanodes Based on TiO2 and Alpha-Fe2O3 for Solar Water Splitting - Superior Role of 1D Nanoarchitectures and of Combined Heterostructures. *Chem. Soc. Rev.* **2017**, *46*, 3716–3769.

(46) Hedrich, C.; Burson, A. R.; González-García, S.; Vega, V.; Prida, V. M.; Santos, A.; Blick, R. H.; Zierold, R. Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide. *Adv. Mater. Interfaces* **2023**, *10*, 2300615.

(47) Míguez, H.; Tétreault, N.; Yang, S. M.; Kitaev, V.; Ozin, G. A. A New Synthetic Approach to Silicon Colloidal Photonic Crystals with a Novel Topology and an Omni-Directional Photonic Bandgap: Micromolding in Inverse Silica Opal (MISO). *Adv. Mater.* **2003**, *15* (7–8), 597–600.

(48) Eremin, D. B.; Ananikov, V. P. Understanding Active Species in Catalytic Transformations: From Molecular Catalysis to Nanoparticles, Leaching, "Cocktails" of Catalysts and Dynamic Systems. *Coord. Chem. Rev.* **2017**, *346*, 2–19.

(49) Namigata, H.; Watanabe, K.; Okubo, S.; Hasegawa, M.; Suga, K.; Nagao, D. Double-Inverse-Opal-Structured Particle Assembly as a Novel Immobilized Photocatalytic Material. *Materials* **2021**, *14* (1), 28.

(50) Holzwarth, U.; Gibson, N. The Scherrer Equation versus the "Debye-Scherrer Equation. *Nat. Nanotechnol.* **2011**, *6* (9), 534–534.

(51) Nair, R. V.; Gummaluri, V. S.; Matham, M. V.; C, V. A Review on Optical Bandgap Engineering in TiO ₂ Nanostructures via Doping and Intrinsic Vacancy Modulation towards Visible Light Applications. J. Phys. Appl. Phys. **2022**, 55 (31), 313003.

(52) Pan, X.; Yang, M.-Q.; Fu, X.; Zhang, N.; Xu, Y.-J. Defective TiO2 with Oxygen Vacancies: Synthesis, Properties and Photocatalytic Applications. *Nanoscale* **2013**, *5* (9), 3601.

(53) Krylova, G.; Na, C. Photoinduced Crystallization and Activation of Amorphous Titanium Dioxide. J. Phys. Chem. C 2015, 119 (22), 12400–12407.

(54) Pasquarelli, R. M.; Lee, H. S.; Kubrin, R.; Zierold, R.; Petrov, A. Y.; Nielsch, K.; Schneider, G. A.; Eich, M.; Janssen, R. Enhanced Structural and Phase Stability of Titania Inverse Opals. *J. Eur. Ceram. Soc.* **2015**, *35* (11), 3103–3109.

(55) Li, J.; Su, W.; Li, J.; Wang, L.; Ren, J.; Zhang, S.; Cheng, P.; Hong, H.; Wang, D.; Zhou, Y.; Mi, W.; Du, Y. Orientational Alignment of Oxygen Vacancies: Electric-Field-Inducing Conductive Channels in TiO ₂ Film to Boost Photocatalytic Conversion of CO ₂ into CO. *Nano Lett.* **2021**, *21* (12), 5060–5067.

(56) Pham, H. H.; Wang, L.-W. Oxygen Vacancy and Hole Conduction in Amorphous TiO ₂. *Phys. Chem. Chem. Phys.* **2015**, 17 (1), 541–550.

www.acsami.org

(57) Andronic, L.; Enesca, A. Black TiO2 Synthesis by Chemical Reduction Methods for Photocatalysis Applications. *Front. Chem.* **2020**, *8*, No. 565489.

(58) Bretos, I.; Jiménez, R.; Ricote, J.; Calzada, M. L. Low-Temperature Crystallization of Solution-Derived Metal Oxide Thin Films Assisted by Chemical Processes. *Chem. Soc. Rev.* **2018**, 47 (2), 291–308.

Supporting Information

Enhanced photocatalytic properties and photoinduced crystallization of TiO₂-Fe₂O₃ inverse opals fabricated by atomic layer deposition

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Figure S1. SEM micrographs of TiO₂-Fe₂O₃ IOs and TiO₂-Fe₂O₃ multilayer IOs fabricated with different layer thicknesses and template sizes.



Figure S2. Optical properties of all prepared IOs measured in aqueous environment. The samples were prepared with PS particle template sizes of (a) 150 nm and (b) 252 nm.



Figure S3. Individual photocatalytic activities of three consecutive measurements for TiO₂ IOs and TiO₂-Fe₂O₃ bilayer IOs. Different TiO₂ and Fe₂O₃ thicknesses were tested for template sizes of (a) 150 nm and (b) 252 nm. The



Figure S4. Dye concentration decrease during three consecutive photocatalysis measurements for $TiO_2 IOs$ and TiO_2 -Fe₂O₃ bilayer IOs. The data represents the MB degradation by (a) 16 nm TiO_2 IOs, (b) 16 nm TiO_2 -10 pulses Fe₂O₃, (c) 16 nm TiO_2 -2 nm Fe₂O₃, (d) 16 nm TiO_2 -4 nm Fe₂O₃, and (e) 20 nm TiO_2 -2 nm Fe₂O₃.



Figure S5. Assessment of the photocatalytic activities with MB solution containing 100 mM IPA as hole scavenger. Both, the 16 nm TiO_2-2 nm Fe_2O_3 bilayer IO and the 16 nm TiO_2-4 nm Fe_2O_3-2 nm TiO_2 trilayer IO demonstrate significant reduction of their photocatalytic activity compared to standard conditions. Each sample was measured three times with IPA containing solution.



Figure S6. Photocatalytic activities under standard illumination conditions without a filter, with a 400 nm longpass (LP) filter, and with a 425 nm shortpass (SP) filter, respectively. (a) Activities of the 16 nm TiO_2-4 nm Fe_2O_3 bilayer IO normalized to the illumination without filter. The sample was measured once with each illumination spectra. (b) Optical illumination spectra of the light source with and without filters.

Sample Fabrication		Organic pollutant	Illumination	Photocatalytic	reference	
	method			activity k		
Fe ₂ O ₃ -coated TiO ₂	Coating by ALD	Methyl orange	300 W Xe lamp	97.4 % removal	22	
powder		4 mg/L	with 420 nm	after 1.5 h		
			shortpass filter			
Fe_2O_3 -coated TiO_2	Hydrothermal	Rhodamine B	8 W daylight white	52 % removal	23	
nanocrystals	method	$50 \ \mu M, \ H_2O_2$	LED	after 1 h		
Fe_2O_3 -coated TiO_2	ALD	PEC	150 W Xe lamp		26	
nanoporous		characterization				
structures						
Fe ₂ O ₃ -coated TiO ₂	Hydrothermal	Orange II 20 mg/L	500 W Xe lamp	54 % removal	28	
microrod powder	method		with 420 nm	after 3 h		
			shortpass filter			
Fe ₂ O ₃ -coated TiO ₂	TiO_2 IO by ALD,	PEC	300 W Xe lamp		33	
IO	Fe_2O_3 coating	characterization				
	hydrothermal					
	method					
Fe ₂ O ₃ -decorated	TiO_2 IO by sol-gel	salicylic acid	150 W Xe lamp	~0.9 h⁻¹, 75 %	34	
TiO ₂ IO	method, Fe_2O_3			removal after 1.5 h		
	decoration by					
	chemisorption					
	calcination cycles					
TiO_2 - Fe_2O_3	ALD	Methylene blue	150 W halogen	1.38 h⁻¹; 65 %	This study	
multilayer IOs		2.5 mg/L	lamp	removal after 1 h		

Table S1. Comparison of the reaction conditions and photocatalytic performances of Fe_2O_3 -functionalized TiO_2 nanostructures.



Figure S7. The individual activities during seven consecutive measurements of 150 nm template size 16 nm TiO_2-2 nm Fe_2O_3-2 nm TiO_2 and 16 nm TiO_2-4 nm Fe_2O_3-2 nm TiO_2 multilayer IOs show the same behavior as the 252 nm template size, namely increase during the first four measurements, slight decline in the following two measurements, and stable performance afterwards.



Figure S8. MB concentration decrease during seven consecutive measurements of (a) 16 nm TiO_2-2 nm Fe_2O_3-2 nm TiO_2 and (b) 16 nm TiO_2-4 nm Fe_2O_3-2 nm TiO_2 multilayer IOs.



Figure S9. XRD pattern of a TiO_2 -Fe₂O₃ multilayer IO composed of 16 nm TiO_2 , 4 nm Fe₂O₃, and 2 nm TiO_2 . The sample was kept in the reaction solution for 17 h in darkness and does not show peaks indicating crystalline TiO_2 phases.

7.6. Publication VI

Nanoporous Anodic Alumina Photonic Crystals for Sunlight Harvesting Applications: A Perspective

Siew Yee Lim, **Carina Hedrich**, Cheryl Suwen Law, Andrew D. Abell, Robert H. Blick, Kaline P. Furlan, Robert Zierold, and Abel Santos

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Nanoporous Anodic Alumina Photonic Crystals for Sunlight Harvesting Applications: A Perspective

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Nanoporous anodic alumina (NAA) fabricated by anodization of aluminum is a versatile platform material with tailorable geometric, optical, and chemical features for specific light-based technologies and applications. Recent advances in anodization technology have enabled a new generation of NAA-based photonic crystals (PCs)—periodic dielectric nanoporous structures that selectively allow, forbid, and confine the flow of incoming electromagnetic waves of specific wavelengths across their structure. NAA–PCs provide exciting new opportunities to engineer light-matter interactions with versatility across the broad spectrum, from UV to IR. But despite these fundamental advances, demonstrations of sunlight-harvesting technologies based on NAA–PCs are still limited. Herein, an up-to-date summary of recent advances in NAA–PC technology is provided, and proof-of-concept demonstrations and future pathways to propel this versatile platform material across sunlight-harvesting technologies such as photocataly-sis, photoelectrocatalysis, photothermal energy conversion, and solar cells are discussed.

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1. Introduction

The world population is projected to reach 9.8 billion by 2050.^[1] Underpinning such a drastic population growth, and its associated demands on resources and environmental impact will require integrated approaches to ensuring water security, sustainable agriculture, and green energy generation. Solar light is a critical natural resource that can drive the sustainable development of our society by addressing emerging global challenges such as renewable energy supply, climate change, environmental pollution, and green chemical synthesis processes.^[2] Theoretically, the amount of sunlight that strikes the surface of the earth in two hours could supply the annual consumption of energy by the entire world.^[3] As such, fundamental and applied developments of technologies that

can efficiently harness sunlight and convert photons radiated by the sun into electrical, thermal, and chemical energy are urgently needed. But existing materials suffer from a range of physical barriers that limit their photon-to-energy conversion efficiency performance. These include limited generation of electronhole charge carriers, fast recombination of photo-generated charge carriers, constrained surface reactivity, and inability to harness high irradiance sunlight regions in the visible and NIR spectrum (i.e., \approx 98% of sunlight energy).^[4–7] Therefore, research efforts have focused on developing advanced materials with engineered properties specifically devised to address these intrinsic limitations. These include: 1) modification of the electronic bandgap by doping and addition of co-catalysts atoms to harvest visible-NIR photons;^[8] 2) combination of semiconductors with plasmonic structures to concentrate electromagnetic fields and increase localized temperature;^[9] 3) increment of surface reactive sites by combining distinct forms of porous and carbon-based platform materials (e.g., nanotubes, graphene, etc.) with external atoms;^[10] and 4) structural engineering of materials at the nanoscale to modify their photonic bandgap and extend exciton diffusion length.^[11,12] These engineering approaches and combinations of them have demonstrated promising potential to maximize the efficiency of existing materials for harvesting sunlight photons. Of all these, engineering the structure of materials such as semiconductors at the nanoscale in the form of photonic crystals (PCs) provides novel paths for increasing photon-to-energy conversion rates by modulating

the way in which these materials interact with solar electromagnetic waves.^[13] In particular, nanoporous PCs are ideal structures for sunlight harvesting applications because these enable: 1) light trapping capabilities to increase the frequency of photon-atom interactions; 2) channels that favor the flow of reactive species involved in photon-to-energy reactions; 3) high number of reactive sites associated with their high specific surface area; 4) extended exciton diffusion length and minimized recombination rate of electron-hole pairs; 5) and capability to harvest sunlight photons across high irradiance spectral regions.^[14] Importantly, to rationally design the structure of materials at the nanoscale in the form of PCs also makes it possible to harness a range of optical phenomena not attainable by other nanostructures. These include light confinement and constructive recirculation, slow photons, multiple scattering, Bragg diffraction, surface plasmons, and hybrid photonic-plasmonic modes (e.g., Tamm plasmons).^[14] Nanoporous anodic alumina (NAA) fabricated by electrochemical oxidation (anodization) of aluminum is an ideal platform material for photonic technologies and applications.^[15] The structure of NAA consists of arrays of well-defined, self-organized, hexagonally distributed cylindrical nanopores embedded in a matrix of alumina (aluminum oxide, Al₂O₃). The key aspect of this platform material is its nanoporous structure, which can be tailor-engineered in a multidimensional fashion, using a fully scalable, cost-competitive approach compatible with existing micro- and nanofabrication for integration into functional systems and devices.^[16] Optically, NAA is an effective medium in which spatial changes of porosity enable a direct approach to precisely modulate the distribution of effective refractive index in 1D, 2D, or 3D.^[17] Advances in pulse anodization-periodic modulation of input anodizing potential or current density-have provided new opportunities to generate in-depth, periodic modulations of porosity along NAA's nanopores, increasing the tuneability

degree of its effective medium and thus enabling new forms of light–matter interactions in this platform materials.^[18]

This approach has resulted in a variety of NAA-PCs, the most representative examples of which are gradient index filters (NAA-GIFs),^[19] optical microcavities (NAA-µQVs),^[20] distributed Bragg reflectors (NAA-DBRs),[21] and broadband distributed Bragg reflectors (NAA-BDBRs).^[22] These NAA-PC structures have paved the way to expand the applicability of NAA across a range of photonic technologies requiring versatile control of electromagnetic waves such as photocatalysis, photoelectrocatalysis, optical encoding, sensing and biosensing, and lasing.^[23] But more fundamental and applied advances are needed if we are to fully develop the potential of NAA-based photonic technologies for sunlight harvesting applications. In this perspective, we focus on recent developments in NAA-PC technology and its application in sunlight harvesting disciplines (Figure 1). We provide insights into how incoming electromagnetic waves can be judiciously manipulated in NAA-PCs by engineering their structure and optoelectronic properties through distinct pulse anodization approaches and functionalization methods. We provide an up-to-date overview of recent advances in this field, and a comprehensive analysis and prospective outlook on potential research lines that we believe will drive this highly dynamic and promising discipline across sunlight technologies.

2. Structure and Fabrication of NAA-PCs

2.1. NAA Structure and Formation

NAA is a matrix of alumina (aluminum oxide, Al_3O_2) with embedded arrays of hexagonally arranged cells containing a straight cylindrical pore at their center, which grows



Figure 1. Nanoporous anodic alumina (NAA) in sunlight harvesting applications.



Figure 2. Structure and fabrication of NAA. a) Schematics describing the main geometric features of NAA (i.e., nanopore diameter or filling factor— D_P , interpore distance or lattice constant— D_{Int} , and nanopore length— L_P), and top view (scale bar: 1 µm), bottom view (1 µm), and general and magnified (inset) cross-sectional view (scale bars: 250 and 50 nm, respectively) field emission scanning electron microscopy (FEG-SEM) images of NAA produced by the two-step anodization process in 0.3 M oxalic acid electrolyte at 40 V. Adapted with permission.^[232] Copyright 2022, American Chemical Society. b) Fabrication diagram describing the two-step anodization process with: aluminum substrate, nanopore nucleation (initial stage of the first anodization step), nanopore growth, chemical wet etching to remove the sacrificial anodic layer, and nanopore development (second anodization step). Adapted with permission.^[232] Copyright 2022, American Chemical Society.

perpendicularly to the underlying aluminum substrate (Figure 2a). Lithography-free, self-organized formation of highly ordered NAA structures can be achieved by the so-called two-step anodization process under mild conditions-top-down electrochemical oxidation of aluminum in acid electrolytes at moderate electrolyte temperature and anodizing voltage or current density (Figure 2b).^[15] During the first anodization step, nanopores nucleate across the surface of the anodic oxide film and grow in depth through a mechano-electrochemical process driven by the input electric field. Under specific conditions, nanopores self-organize progressively inside the anodic film to minimize the mechanical stress induced by the oxide-to-metal volume expansion between adjacent nanopores at their bottom tips, which are closed by a hemispherical cap-the barrier oxide layer (i.e., anodic oxide growth front). After \approx 24 h, the anodic film features hexagonally arranged nanopores at its bottom. However, this organization is constrained to the bottom side of the anodic oxide film at the interface oxide-metal. So, the resultant anodic oxide film is then chemically dissolved in an aqueous mixture of acids to expose the underlying aluminum substrate patterned with highly ordered concavities, which are a negative replica of the bottom side of the original anodic film. The application of a second anodization step under the same conditions as those of the first step results in nanopore nucleation at the center of each concavity across the patterned aluminum substrate (i.e., one nanopore per concavity). After nucleation, nanopores grow and propagate at normal direction to the aluminum substrate with straight coherency, from top to bottom, following the original honeycomb-like arrangement.

The formation and dissolution of anodic oxide at the barrier oxide layer located at the nanopore bottom tips of NAA is determined by the electrochemical reactions shown in **Equation (1)–(6)**:

1) Formation of anodic oxide at the aluminum-alumina interface

$$\mathrm{Al} \to \mathrm{Al}_{(\mathrm{ov})}^{3+} + 3\mathrm{e}^{-} \tag{1}$$

$$2\mathrm{Al}_{(\mathrm{ox})}^{3+} + 3\mathrm{O}_{(\mathrm{ox})}^{2-} \to \mathrm{Al}_2\mathrm{O}_3 \tag{2}$$

$$2Al_{(ox)}^{3+} + 3HO_{(ox)}^{-} \rightarrow Al_2O_3 + 3H_{(aq)}^{+} \tag{3}$$

2) Dissolution of anodic oxide at the alumina-electrolyte interface $% \left({{{\left[{{{\left[{{{\left[{{{c}} \right]}} \right]}}} \right]}_{\rm{c}}}}_{\rm{c}}}} \right)$

$$Al_2O_3 + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(liq)} \tag{4}$$

$$3O^{2-}_{(ox)} \to O_{2(gas)} + 4e^- \tag{5}$$

$$2H_2O_{(liq)} \to O_{(ox)}^{2-} + OH_{(ox)}^- + 3H_{(aq)}^+$$
 (6)

The structure of self-organized NAA is geometrically characterized by the interpore distance (or lattice constant— D_{Int}) and nanopore diameter (or filling factor— D_P) (Figure 2a). These geometric features are tunable by the input anodizing profile and post-fabrication treatments (i.e., pore widening by wet chemical etching).^[16]

2.2. NAA as an Effective Medium Platform

The concept of using highly ordered NAA structures as platforms to develop 2D NAA-based photonic crystals (NAA–PCs) was first introduced by Masuda and coworkers (**Figure 3**a).^[24–26] In their pioneering studies, they utilized nanoindentation by lithographically produced master stamps to pattern the surface of aluminum substrates with highly ordered indentations, the function

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Figure 3. Optical properties of 2D nanoporous anodic alumina photonic crystals (2D NAA–photonic crystals (PCs)). a) In-plane optical properties of 2D NAA–PCs with *x*–*y*–*z* directions. b) Illustration describing the flow of incoming photons traveling in the *z*- and *x*-directions across the effective medium of 2D NAA–PC structures featuring straight nanopores, where light is selectively forbidden to flow through the PC structure in the in-plane direction (*x*-axis) (NB: low and high effective refractive index, $n_{\text{eff-low}}$ and $n_{\text{eff-loh}}$). c) Transmission spectra at *z* (left) and *x* (right) direction across the 3D NAA–PC structure, with a graphical description of optical features of photonic stopband: baseline (γ_0), central wavelength (λ_{PSB}), full width at half maximum (FWHM_{PSB}), intensity (I_{PSB}), and photonic stopband (PSB's) blue and red edge positions (λ_{Blue} and λ_{Red}).

of which was to act as nucleation sites for nanopore growth. Upon anodization under specific potentials matching the indentation period, ideally ordered arrays of nanopores with a high aspect ratio grow from these indentations (one nanopore per indentation) with straight coherency, following the pattern

pre-established by the master stamp. 2D NAA-PCs exhibit a characteristic optical feature across their spectrum, the so-called photonic stopband (PSB), which represents those spectral regions within which the PC structure selective inhibits the flow of photons of specific wavelengths when incoming electromagnetic waves propagate across the cross-section of the NAA-based, air-hole array structure (Figure 3b).^[17] The features of the characteristic PSB of NAA (i.e., central wavelength position (λ_{PSB}), full width at half-maximum (FWHM_{PSB}), intensity (I_{PSB}), and quality factor (Q)) rely intrinsically on the geometric features of air-holes in 2D NAA-PCs (i.e., lattice constant and filling factor) (Figure 3c). This dependence makes it possible to tailor the position of NAA's PSB by engineering its interpore distance and nanopore diameter through anodization and pore widening treatment. But despite various successes to increase the interpore distance in NAA by extending anodizing potentials in different acid electrolytes and anodization regimes, the range of available lattice constant is limited from \approx 50 to \approx 700 nm. This limitation in turn constraints the spectral range of PSBs in 2D NAA-PCs within the UV-visible region.^[16]

So, research efforts focused on devising alternative anodization strategies to overcome this intrinsic constraint and expand the spectral range of NAA-PCs across the broad spectrum. Lee and coworkers introduced the so-called "pulse-like anodization" -periodic modulation of input anodizing voltage or current density profile.^[18a] This class of anodization approach enables the in-depth modulation of nanopores in NAA during anodization and thus extends our ability to engineer NAA's PSB across a broader range of spectral regions, with multidimensionality (i.e., 1D and 3D), which are features not attainable by the twostep anodization process (Figure 4a). Further to that, pulse anodization also makes it possible to engineer distinct forms of PC structures to harness other classes of light-matter interactions in NAA-PCs such as light confinement and recirculation, and omnidirectional reflection.^[20,22] Pioneering studies in pulse-like anodization harnessed anodizing voltage or current density pulses switched between two anodization regimes (i.e., mild anodization (MA) and hard anodization (HA)).^[18a] Briefly, MA is performed at the moderate anodizing voltage/current density and yields a slow, almost linear anodic oxide growth rate $(\approx 3-8 \,\mu\text{m h}^{-1})$. Conversely, HA is characterized by high anodizing voltage/current density and yields a fast, non-linear oxide growth rate (\approx 50–70 µm h⁻¹), which decreases exponentially with the thickness of the anodic film.^[16] Critically, the porosity of NAA films produced in MA and HA in the oxalic acid electrolyte is ≈ 10 and $\approx 3\%$, respectively. As such, when the input anodizing voltage/current density is switched between MA and HA regimes via pulse anodization, the inner porosity of NAA oscillates between \approx 10 and \approx 3%. This structural engineering process is translated into highly uniform, periodic modulations of nanopore diameter along the nanopore axis, from top to bottom within the anodic oxide film (Figure 4b).^[18b,27] But despite its advantages, MA-HA pulse anodization also has technical constraints such as the recovery time delay between anodizing input and output response during the HA-to-MA transition associated with the thick barrier oxide layer of NAA under HA, the extensive Joule's heat generated during HA, the low porosity level under HA conditions, and the dependence of oxide growth rate with nanopore length under HA regime.^[18e,28,29] Lee and Kim

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Figure 4. Mild–hard (MA–HA) pulse anodization. a) Schematic showing the fabrication of 1D NAA–PCs featuring modulated pores in depth via MA–HA pulse anodization (left), and voltage (input) and current density (output) MA–HA pulse anodization profile with: MA pulse $U_{MA} = 25$ V and $\tau_{MA} = 180$ s; and HA pulse $U_{HA} = 35$ V and $\tau_{HA} = 0.1$ s). Adapted with permission.^[18a] Copyright 2006, Nature Publishing Group. b) Cross-sectional SEM image of an NAA–PC featuring nanopore modulations in depth generated during the MA–HA pulse anodization profile shown in (a) (left) and magnified view of white rectangle showing details of NAA stacks (right). Adapted with permission.^[18d] Copyright 2008, Nature Publishing Group. c) Illustration of the modified MA–HA pulse anodization process devised by Lee and Kim to tailor-engineer the structure of NAA (left) and cross-sectional SEM image of the resulting structure with details of nanopore modulations along the nanopore length (scale bar: 500 nm). Adapted with permission.^[18d] Copyright 2010, IOP Publishing Ltd.

overcame this limitation by a series of multi-step anodizing voltage pulses with varying period and amplitude, in which the input potential is gradually increased prior to reaching the HA potential stage (Figure 4c).

This approach enables a more controllable methodology to tailor and modulate the nanopore structure of NAA in depth, with a high degree of directional coherency and precision. Although the revised pulse anodization method addresses some intrinsic limitations of conventional MA–HA pulse anodization (i.e., slow current/voltage recovery and input–output time delay, uncontrollable oscillatory kinetic behavior) and some studies successfully realized 1D and 3D NAA–PCs via MA–HA pulse anodization, this technology remains challenging.^[21d,e] In an alternative study, Wang and coworkers devised a more

controllable form of pulse anodization, in which anodizing voltage or current density pulses are applied entirely within the MA regime.^[19a] Despite the slow anodic oxide growth rate under mild anodization conditions (i.e., \approx 3–8 µm h⁻¹), MA pulse anodization has been demonstrated as a highly controllable and versatile approach to generate multidimensional NAA-based PC structures with precisely engineering optical properties for specific applications.^[19,20] Subsequent advances in this form of pulse anodization resulted in a variety of anodization profiles (e.g., sinusoidal, stepwise, pseudo-stepwise, sawtooth, Gaussian-like, etc.) to produce a new generation of 1D NAA–PCs with versatile PSBs across UV–visible–NIR spectrum. These include Fabry–Pérot interferometers (NAA–FPIs), distributed Bragg reflectors (NAA–DBRs), gradient-index filters (NAA–GIFs), apodized

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gradient-index and distributed Bragg reflectors (Apo–NAA–GIFs and Apo–NAA–DBRs), linear variable distributed Bragg reflectors (NAA–LVDBRs), broadband distributed Bragg reflectors (NAA–BDBRs), and microcavities (NAA–µQVs) (**Figure 5**).

2.3. Types of NAA-PC Structures

NAA–DBRs produced by stepwise pulse anodization are a class of PC structures formed by stacked dielectric layers of NAA featuring high and low effective refractive indexes. The PSB of NAA–DBRs is characteristically broad and centered at the Bragg wavelength, which corresponds to the minimum of transmissivity of the PSB. The central wavelength of the PSB is determined by the optical thickness of each NAA stack (i.e., product of effective refractive index and physical thickness).

In their seminal study, Sulka and Hnida utilized pulse anodization with alternating MA and HA voltages to build stacks of NAA layers with low and high porosities to generate NAA– DBR structures.^[21] The reflection spectrum of NAA–DBRs featured two broad PSBs (i.e., first and second order) with central wavelengths located at \approx 1800 and \approx 3800 nm in the NIR and IR regions, respectively. The optical properties of these NAA-based PC structures were mechanistically validated by simulations implementing an effective medium model representing an ideal DBR structure. In a subsequent study, using a combination of MA–HA pulse anodization with limited current density output under voltage control conditions and wet chemical etching,



Figure 5. NAA as a platform material to develop PCs, with illustrations showing representative NAA–PC structures: Fabry–Pérot interferometer (NAA–FPI), distributed Bragg reflector (NAA–DBR), gradient–index filters (NAA–GIF), apodized NAA–PCs (Apo–NAA–GIF/DBR), optical microcavity (NAA– μ QV), and hybrid plasmonic–photonic Tamm system (TMM–NAA–PC).

Martin et al. fabricated 3D NAA-DBRs with a network of interconnected nanopores. The PSB of 3D NAA-DBRs in their reflection and transmission spectra was broad and centered at \approx 650 nm. Tunability of the central wavelength of the PSB was demonstrated by systematic modification of the periodicity in the input MA-HA pulse anodization profile (i.e., period length of MA layers), and by selective infiltration of the nanoporous PC structure with liquids of varying refractive index.^[30] Wang et al. produced NAA-DBRs through a pseudo-stepwise anodization process combining hybrid voltage pulses featuring straight and sinusoidal sections. These pulses were translated into nanopores with straight and branched sections, respectively. The PSB of these NAA-based PCs was in the visible range and was found to blue shift, from 700 to 525 nm, upon chemical etching for 15 min. A gradual blue shift of PSB was also observed in the interferometric color displayed by these NAA-DBRs with the etching time.^[19a] Zheng and coworkers demonstrated that the spectral position of NAA-DBRs' PSB can also be tuned across the visible spectrum by modifying the temperature of the anodizing electrolyte, where the PSB undergoes a blue shift in position when the anodization temperature decreases from 14 to 7 °C.^[31] Recent research efforts have focused on improving the properties of PSB in terms of intensity, bandwidth, and band edges, as well as controllability of PSB position over a broader range of wavelengths (Figure 6a). These include new anodization waveforms, implementation of voltage compensation modes, and manipulation of anodization parameters.^[21c,32-41] NAA-DBRs often feature vivid interferometric colors, which correspond to the PSB spectral position within the visible and denote a highly efficient reflection of light by these PC structures as compared to other forms of NAA-based PCs. The structural and optical characteristics of NAA-DBRs have been systematically studied by varying a range of anodization parameters such as anodization period, time, and electrolyte temperature with the objective of optimizing and tuning the features of their PSB across UV-visible–NIR spectrum.^[21g,h,22a,42-49] Among these studies, a new type of NAA-DBRs with an ultra-broad PSB bandwidth of \approx 153 nm, known as broadband NAA–DBRs, has been generated by a double exponential pulse anodization approach in which the period in the input anodizing pulses is increased with varying anodizing time.^[22b] NAA–GIFs are a type of NAA–PCs in which the effective refractive index of NAA varies smoothly and periodically in depth, along the length of the nanopore. As a result, these PC structures exhibit a PSB that is narrower than that of their NAA–DBR counterparts by a factor of $\pi/4.^{[50]}$ Yan et al. fabricated NAA-GIFs by an input sinusoidal anodization current density profile.^[51] It was demonstrated that the PSB of NAA-GIFs narrowed its bandwidth by changing the period between sinusoidal pulses, while its position shifted with the peak-to-peak current density or amplitude of the input sinusoidal wave. Kumeria et al. generated NAA-GIFs using a total chargecontrolled pseudo-sinusoidal anodization approach, which was optimized in terms of the total charge per pulse (i.e., integrated current density per voltage pulse), voltage pulse form, and the number of pulses. The effective medium of NAA-GIFs was then mechanistically described by the Looyenga-Landau-Lifshitz effective medium approximation model.^[52,53] Macias et al. developed a sinusoidal current profile with small current density variation to modulate the porosity of NAA along the pore axis with no

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Figure 6. Structural engineering of high-quality NAA–PCs by MA pulse anodization. a) Fabrication of NAA–distributed Bragg reflectors (DBRs) by MA pulse anodization with voltage pulses consisting of a linear increase followed by a constant voltage for a duration controlled by a total charge Q_0 , and linear decrease of voltage, and PSBs of NAA–DBRs produced at: 1) $Q_0 = 0$ C with cone-like pores and 2) $Q_0 = 4$ C with cylindrical pores. Adapted with permission.^[35] Copyright 2013, American Chemical Society. b) Fabrication of NAA–GIFs by current density-controlled sinusoidal pulse anodization with: 1) cross-sectional FEG-SEM images showing nanopores of NAA–GIFs modulated in-depth with varying anodization period, and 2) tunability of PSB of NAA–GIFs by anodization period across UV–visible–NIR spectrum and digital pictures showing their interferometric color. Adapted with permission. ^[19b] Copyright 2016, Royal Society of Chemistry. c) Fabrication of NAA– μ QVs by cyclic anodization with voltage versus optical path length modulation with: i) sinusoidal wave modulation of NAA– μ QVs with a defect layer introduced by a phase shift in the anodization profile, and ii) transmission (top) and reflection (bottom) spectra of NAA– μ QVs produced at different structure lengths showing their corresponding resonance bands. Adapted with permission. ^[20g] Copyright 2020, Royal Society Chemistry. d) Engineering of Tamm plasmon cavities based on hybrid photonic–plasmonic NAA structures with: i) fabrication of NAA–PCs by Gaussian-like pulse anodization, ii) cross-sectional FEG-SEM view of NAA–PCs showing the progressive modulation of nanopores in-depth, and iii) generation of Tamm resonances by broadening of PSB of NAA–PCs and deposition of gold layer. Adapted with permission.^[79] Copyright 2021, American Chemical Society.

branching. The PSB of as-produced NAA–GIFs was found to red-shift from 500 to 700 nm when the period length of the PC structure (i.e., distance between nanopore modulations) increased with the anodization period, and to blue-shift from 460 to 425 nm when the overall refractive index of the NAA–GIF decreased after a pore widening treatment.^[54] Santos et al. performed a detailed study about the effect of different anodization parameters (i.e., anodization period, amplitude, offset, electrolyte temperature, and pore widening time) on

the characteristic PSB of NAA–GIFs produced by sinusoidal pulse anodization under current density control.^[19b] The effect of each anodization parameter on the characteristic PSB of NAA–GIFs was systematically analyzed, demonstrating full tuneability of this optical feature across the UV–visible–NIR spectral region (Figure 6b). Building on the foundations established by this study, other studies explored distinct forms of sinusoidal pulse anodization to further improve the narrow bandwidth of NAA–GIFs. These include multi-sinusoidal anodization,

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integration of apodization functions with sinusoidal anodization, feedback regime on the rate of chemical etching, and further optimization of electrolyte concentration, temperature, and composition.^[19c,d,e,f,55-61] NAA-GIFs were also used as PC platforms to generate linear variable bandpass filters (NAA-LVBPFs) by progressive pore widening of the original PC structure in phosphoric acid solution to engineer the effective medium both laterally and in depth.^[62] Another form of 1D NAA-PCs are optical microcavities (NAA-µQVs), which are PC structures that confine light to small volumes by resonant recirculation of electromagnetic waves within two highly reflecting mirrors. The fabrication of NAA-µQVs involves the introduction of defect modes in the PC structure by various approaches. The defect mode results in the appearance of a sharp resonance band at the center of the characteristic PSB. One of the methods to create defects in 1D NAA-PCs is by incorporating a thin layer of nanopores with constant porosity between two highly reflective NAA-DBRs or NAA-GIFs. Yan et al. created a planar defect in NAA-PCs by inserting a constant voltage in periodic voltage waveforms. The resulting NAA-µQVs had a resonance band with an FWHM of \approx 18 nm after optimizing the thickness of the defect layer.^[20a] Lee et al. fabricated NAA– μ QVs made up of two lattices: one with constant optical thickness periodicity and one with a gradual change in optical thickness. The graded lattice was engineered by progressive asymmetric modulation of the effective medium of NAA in depth through a periodically modulated input voltage following a sinusoidal decaying ramp.^[20b] Wang et al. demonstrated the fabrication of NAA-µQVs under voltage control MA conditions by shifting the phase of anodization waveform between two Bragg mirrors. The phase of the effective refractive index of the bottom DBR was shifted with respect to that of the top DBR to create an optical interference between the two DBR structures, resulting in a narrow resonance peak with an FWHM of $\approx 14 \text{ nm.}^{[20c]}$

Law et al. applied an apodized stepwise pulse anodization with a logarithmic negative function to produce NAA-µQVs. Due to the asymmetrically modulated effective refractive index in depth following a logarithmic change in current density amplitude, the transmission spectra of NAA-µQVs were characterized by a broad PSB with an intense and narrow resonance band (i.e., Q of \approx 113) at its central position.^[20f] Subsequent studies focused on the optimization of NAA– μ QVs to improve the quality of light confinement, using modified approaches such as the use of different waveforms, voltage modulation as a function of optical path length, and optimization of anodization conditions (Figure 6c).^[20d,e,g,h,63-65] More recently, the combination of NAA-PCs produced by Gaussian-like pulse anodization with thin films of gold has enabled the generation of Tamm plasmon resonances in NAA photonic-plasmonic hybrid structures (TMM-NAA-PCs).^[66-78] Tran et al. fabricated NAA-GIFs by Gaussian pulse anodization, followed by a pore widening treatment and deposition of a thin layer of gold (Figure 6d). The transmission spectrum of this NAA-based Tamm plasmon system featured a well-resolved, narrow, and intense Tamm resonance band associated with the strong and selective confinement of photons between the gold layer and dielectric PC system.^[79] The TMM-NAA-PC system was demonstrated as a suitable platform technology for sensing applications.



2.4. Advantages and Challenges of NAA-PC Technology

Research efforts in the past decade have significantly advanced NAA-PC technology and enhanced the capability and potential of this unique material across photonic technologies, broadening the horizon of NAA-PCs across various disciplines such as optoelectronics, optical sensing, photovoltaics, and photocatalysis. Despite these advances, there remain fundamental challenges to facilitating the integration of this material into fully functional systems and devices. For instance, an intrinsic constraint of NAA when compared to its porous silicon or titanium dioxide counterparts is its low refractive index, which has been reported to vary from ≈ 1.7 to 2.3.^[19d] As a result, NAA-based PCs require an extended minimum thickness (≈10 µm) to maximize lightmatter interactions through multiple scattering across an increasing number of stacks of NAA. This intrinsic constraint in turn limits the integrability of this technology in applications requiring thin film thicknesses. Future efforts should focus on increasing the inherent refractive index of NAA to reduce the required thickness of NAA-PC structures. This could be accomplished by adding dopant elements in the anodization electrolyte or in the aluminum substrate prior to anodization, which can then be incorporated into the structure of NAA during the anodization process. Alternatively, the effective refractive index of NAA can be locally increased by depositing layers of materials with high refractive index such as titanium dioxide and silicon dioxide (Table 1).

3. Functionalization of NAA-PCs

As-produced NAA is a dielectric material based on anodic aluminum oxide (Al₂O₃) with a wide electronic bandgap located within the range 5.1–8.8 eV, which corresponds to the UV–C spectrum (i.e., wavelength of 141–243 nm).^[80,81] As such, NAA-based PCs cannot be directly used to harvest incident sunlight since the solar radiation arriving at the earth's surface does not contain any UV–B/C radiation (i.e., 100–280 nm).^[82] However, this intrinsic constraint can be overcome by functionalizing the inner surface of NAA with a variety of photoactive materials or by template synthesis of nanostructures based on semiconductors and other types of light-harvesting materials. Optoelectronic functionalization of NAA–PC structures can be achieved through different methods such as sol–gel process, electrodeposition, sputter deposition, chemical vapor deposition (CVD), and atomic-layer deposition (ALD). These will be outlined and described in detail throughout this section of the perspective.

3.1. Sol-Gel Method

The sol–gel process is a wet-chemical technique to deposit nonmetallic materials.^[83–85] In general, a precursor solution—often consisting of a metal alkoxide precursor—is hydrolyzed to form a sol. This colloidal solution is then altered to a gel, which is an interconnected, porous network of colloidal particles. Further treatment such as drying and sintering generates a dense, solid phase of the material.^[85–87] When a template is infiltrated with the sol prior to gelation, the gel and the subsequent film formation occur on the surface of the template, leading to the

 $\ensuremath{\text{Table 1.}}\xspace$ A summary of different forms of NAA–PCs and their characteristics.

NAA–PC Structure	Characteristics	References
NAA–DBR	Produced by stepwise pulse anodization	[21,30–49]
	Stepwise distribution of effective refractive index and thickness in depth between high and low values	
	Broad PSB centered at Bragg wavelength	
NAA–GIF	Produced by sinusoidal pulse anodization Sinusoidal modulation of effective refractive index in depth	[19b,c,d,e,f, 23b,51–61]
	Narrow PSB with bandwidth $\pi/4$ narrower than that of DBRs	
NAA-µQV	Produced by stepwise, sinusoidal, or apodized pulse anodization by generating cavity section sandwiched between two highly reflective DBRs or a phase shift between mirrors Symmetric or asymmetric modulation of effective refractive index	[20,63–65, 234]
	Narrow and sharp resonance band within PSB	
Apo–NAA–GIF Apo–NAA–DBR	Produced by sinusoidal or stepwise pulse anodization modified with apodization function in amplitude with anodization time	[20f,55]
	Apodized modulation of effective medium	
	Narrow PSB with suppression of characteristics sidelobes	
NAA-BPF	Produced by pseudo-stepwise pulse anodization with progressive modification of anodization period	[22a]
	Stepwise, progressive modulation of effective medium	
	Number and position of PSBs correspond to each stacked BPF	
NAA-LVBPF	Produced by sinusoidal pulse anodization followed by wet chemical etching	[62]
	Tunable PSB as functions of anodization period and etching time	
	Displayed color and PSB position gradient along the etching path	
Other forms of NAA–PCs	Produced by Gaussian-like pulse anodization (e.g., Gaussian, Lorentzian, Laplacian, and logarithmic)	[66–78]
	Varied modulation of effective refractive index in depth	
	Tunable PSB across UV-visible-NIR spectrum	
Hybrid plasmonic– photonic structures	Tamm plasmon structure with an asymmetric cavity formed by a gold film and a dielectric NAA-DBR	[79]
	Well-resolved, intense Tamm resonance band in PSB	

formation of a solid thin film (**Figure 7**a,b). Sol–gel is a lowtemperature deposition method widely used to produce metaloxide-based coatings, the composition of which can be precisely tuned through various synthesis routes to obtain different material properties.^[84,85] For example, dense films, aerogels, or xerogels can be realized by this technique. However, many metal alkoxide precursors are expensive and this deposition technique suffers from poor control over the thickness and composition homogeneity of the resultant film.^[85,88] Despite these limitations, the sol–gel method has been extensively used for decades to functionalize the inner surface of NAA-based structures including NAA–PCs. In the context of sunlight harvesting applications, the most extensively used functional semiconductor coating deposited via sol–gel is titanium dioxide (TiO₂). Sol–gel-deposited TiO₂ functional coatings have been integrated with various forms of NAA–PC structures (i.e., NAA–GIFs, NAA–DBRs, and NAA– μ QVs) to enable photocatalytic reactions such as degradation of organic pollutants (vide infra).^[38,47,58,64]

3.2. Electrodeposition

Wet-chemical electrodeposition method uses electrochemical reactions to coat materials with films of conductive and semiconductive compounds.^[89–91] Materials such as pure metals and alloys,^[89,91] elemental semiconductors, and composites^[90] can be deposited by this technique.

Typically, a conductive film working as a cathode is immersed into an electrolyte solution, whereas the anode consists either of the coating material or a conductive material that is inert to electrochemical oxidation reaction (e.g., platinum). In the latter case, the electrolyte must contain dissolved precursors of the material to be deposited.^[89-91] Application of an electrochemical potential or current between the two electrodes drives electrochemical reactions at cathode (reduction) and anode (oxidation). The reduction reaction at the cathode results in the deposition of material over the surface of this electrode, where the consumed charge density determines the amount of deposited material according to the Faraday law.^[92] As such, electrodeposition is a simple yet precise deposition technique, which allows tunable and fast deposition rates over a variety of substrates and templates of up to several tens of micrometers per hour.^[90,92] Electrodeposition within porous templates such as NAA can also be realized. However, a pore opening or barrier oxide layer thinning step must be applied prior to electrodeposition-to overcome the electrically insulating nature of the barrier oxide layer (BOL). The most extensively used technique to deposit conductive materials via electrodeposition within NAA structures involves the removal of the BOL via wet or dry chemical etching and the generation of a conductive film at the bottom side of the anodic film via sputter deposition-to create a conductive film (i.e., cathode). After this modification, electrodeposition of conductive materials within the nanopores of NAA can be performed by potentiostatic or galvanostatic methods (Figure 7c). The resulting structures can range from nanotubes to nanowires, depending on the degree of filling or deposition of material within the nanopores. Alternatively, the BOL at the bottom of the nanopores can be thinned down by progressive reduction of the anodizing potential or current density at the final stage of the anodization process.^[93] For instance, stepwise reduction of the anodizing potential results in the formation of branched pores with decreasing diameter and thinner BOL. After this BOL thinning process, electrodeposition can be directly performed inside the nanopores



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Figure 7. Schematic representation of an NAA–PC nanopore modified by different functionalization techniques. a) As-prepared nanopore featuring a periodic diameter modulation. b) Functionalization by the sol–gel process results in a dense film at the entire surface. c) Application of electrodeposition requires opening of the nanopore at the backside and deposition of a conductive layer as back contact prior to coating the nanopore (NB: the deposition of material starts from the conductive layer and, depending on the process parameters, the result is either nanowires or nanotubes. d) For electroless deposition, the nanopore surface must be modified with catalytic seeds to achieve a complete functionalized of the surface with a thin film of material. e) Sputter deposited material covers the top surface and to a small extent the inner side of the nanopore. f,g) Chemical vapor deposition (CVD) and atomic-layer deposition (ALD) result in a thin film coating, the conformal degree of which relies on the technique (low for CVD and high for ALD).

by using the underlying aluminum as an electrode without the need for additional backside opening and metallization.^[91] In the context of sunlight harvesting applications, electrodeposition of metals in combination with semiconductors within NAA-FPIs is the most extensively reported approach to date.^[94–97] For example, Kemell et al.^[94] and Tan et al.^[97] grew arrays of nickel and gold nanowires within NAA templates by electrodeposition, respectively, and combined these nanostructures with layers of semiconductors deposited via ALD to generate composite nanostructures for photocatalysis. Haschke et al. deposited nickel as a back contact for the preparation of electrodes consisting of nanotubes deposited by ALD.^[95,96] It is also important to note that direct electrodeposition can be current-/electrode-directed or surface-directed, at which the chemistry of the interface between nanopore wall and electrolyte is tuned. Furthermore, electrodeposition of oxides, such as titanium dioxide from ionic liquids and aqueous electrolytes has been reported for planar substrates. However, the use of this electrodeposition approach within nanoporous materials is yet to be investigated.^[98,99] Although electrodeposition of nanowires or nanotubes into NAA-PC structures has not yet been investigated, the combination of metals deposited via electrodeposition with semiconductor coatings could provide new opportunities to harness hybrid plasmonic-photonic phenomena to maximize photon-to-electron conversion rates across a range of sunlight harvesting applications.

3.3. Electroless Deposition

Electroless deposition (also called electroless or chemical plating) enables the deposition of metals onto complex, shaped substrates

without an additional supply of external energy such as heat, light, or current. Electroless deposition can be performed by employing two different reaction mechanisms: 1) galvanic displacement reaction and 2) reduction via a reducing agent in aqueous solutions or ionic liquids (Figure 7d). $^{[100]}$ In the galvanic displacement pathway, a redox reaction takes place between metal ions with a stronger noble metal character in an electrolyte solution and metal ions with a weaker noble metal character in a substrate. Electron transfer between metal ions in the solution and metal atoms in the substrate leads to the chemical reduction of metal ions and a concomitant dissolution of the less noble metal in the substrate during the reaction. Note that a reducing agent is necessary when the electroless deposition is to be performed on an insulating/non-conductive substrate. Therein, the reducing agent is first oxidized at the surface such that electrons can then be transferred to metal ions in the electrolyte, resulting in an electroless deposition process. Reducing agents can be of organic nature, such as glyoxylic acid, dimethylamine borane, hydrazine, formaldehyde, or inorganic compounds (e.g., sodium hypophosphite or silver and palladium nanoparticles), which can be used as catalysts to drive a subsequent electroless deposition at the surface of the template. For instance, the oxidation of complexed metal ions (i.e., Co^{2+} to Co^{3+}) could be used to reduce other metals (e.g., Ag, Pt) to coat the substrate or template.^[101,102] One advantage of electroless plating over other deposition techniques is its simplicity in terms of instrumentation. Furthermore, substrates of various materials and shapes, including nanoporous templates with high aspect ratios, can be coated with functional materials via this deposition technique. However, often a pretreatment to achieve nano-sized catalytic



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3.4. Physical Deposition

Physical deposition-commonly known as sputtering or sputter deposition—is a deposition technique in which atoms of a material are removed from a target with the assistance of an electric field. After removal, atoms are accelerated by the applied electric field to create a beam of highly energetic particles (typically ions), which are subsequently implanted onto a substrate material.^[117-120] Momentum transfer during the ion bombardment at the substrate provokes the mechanical release of the substrate's material. Extracted atoms move toward the sample stage and subsequently, they precipitate at the sample surface and form a coating. $^{\left[118-120\right] }$ The mechanical removal of the material allows for sputter deposition of a wide range of materials such as pure metals and alloys,[117-120] and semiconductors,^[119,120] whereby the stoichiometry of the target material is mostly preserved.^[118,119] Note that by varying the atmosphere and temperature during the sputtering process, in operando oxidation and nitridation of the deposited material can be achieved. The sputtering rate (i.e., the number of released target atoms per sputtering time) is characteristic for each material and might vary within the range of tens to hundreds Ångströms per second.^[119] Accordingly, the deposited film thickness can be finely adjusted by controlling the sputtering time and conditions (e.g., temperature). Since the coating is generated by released target atoms, the maximum deposition depth into the substrate's features is limited to a few hundreds of nanometers. Owing to the high aspect ratio of the pores in NAA, deposition of functional coatings via sputtering is constrained to the top surface and to a limited penetration distance inside the inner surface of the pores (Figure 7e). The utilization of sputter deposition onto NAA structures has mainly three purposes: 1) to provide a conductive layer on either the backside or top surface of NAA membranes (metals, especially gold, are typically deposited for this purpose); 2) to provide or further improve the material's properties such as catalytic or plasmonic activity;^[121–124] 3) to modify the intrinsic optical properties of NAA-based PCs^[38,79,123–127]. In the latter configuration, both the sputtered metal coating and the NAA-PC can be precisely engineered to attain specific interactions with incoming photons. For example, Tran et al. demonstrated that combining NAA-PCs with plasmonically active gold films deposited onto the top surface of the dielectric nanoporous PC via sputtering results in the generation of hybrid plasmon-polariton modes, the so-called "Tamm plasmon resonances," in which photons of predefined energies are trapped between both optical elements.^[79]

3.5. ALD

ALD is a chemical vapor deposition technique based on sequential, self-limiting reactions between gaseous precursors and solid surfaces.^[128–131] ALD provides precise control over the thickness of deposited thin films within the Ångström range, and can be grown up to several hundreds of nanometers. At least two material precursors must react alternately with the template surface during a thermal ALD processe, which is the most widespread class of ALD processes used to functionalize NAA structures. A typical cycle of such a

distinct electroless approaches.^[103–106] Electroless deposition of functional coatings with well-defined properties and characteristics requires precise control over the process parameters (e.g., ion concentrations, buffer, pH-value, temperature) to control surface chemistry and composition, shape/size, and crystallinity of the deposited material. In NAA templates, a variety of metals has been deposited by electroless plating, such as palladium-which is often used as seed material for the subsequent electroless deposition of other materials, silver, copper, nickel, and cobalt.^[107-110] Electroless deposition also provides a precise means of tuning the morphology of the resultant coating, from nanotubes to nanowires, by increasing the deposition time or by a post-deposition treatment. Electroless deposition of gold in NAA structures has resulted in optical platforms for plasmon surface-enhanced Raman scattering (SERS)-based sensing applications.^[111,112] Catalytic conversion of 4-nitrophenol into 4-aminophenol has been demonstrated by Yu et al. by employing gold nanotubes (GNTs) prepared by electroless plating inside NAA structures.^[113] The authors demonstrated that the pH value during the electroless plating is critical in controlling the formation of clusters/particles and the resultant structure of the GNTs. GNTs in NAA structures featuring smaller cluster sizes achieved significantly higher catalytic activity as compared to rougher functional coatings. Similarly, copper nanoparticles have been electroless deposited into chitosanfunctionalized NAA membranes showing a significantly improved catalytic decomposition of methyl blue compared to pure or only chitosan-functionalized particles.^[114] Silver nanoparticles coated in an electroless fashion into polydopamine-coated NAA membranes achieved remarkable catalytic activity during the reduction of o-nitroaniline compared to their silver- or poly-dopamine-coated counterparts.^[115] Despite these advances, none of the above-mentioned studies harnessed the optical properties of NAA structures to stimulate catalytic enhancements via photocatalytic activation. The combination of plasmonic and photonic effects with functional coatings and particles deposited via electroless deposition can enable new efficient forms of light-matter interactions to boost photocatalytic reactions driven by photons. However, to the best of our knowledge, this combination is yet to be explored. Previous studies on planar substrates have shown that noble metal nanoparticles deposited onto semiconductor titania interfaces can increase the catalytic efficiency by utilizing local surface plasmon resonances (SPRs) to induce and enhance photosensitization.^[116] Since the Fermi level of noble metals is lower than that of titania, photogenerated electrons can be quickly transferred from the TiO₂ conduction band to the noble metal particles in contact with the functional semiconductor. In contrast, photo-excited holes remain in the valence band of titania, which in turn reduces the probability of electron-hole recombination and maximizes the utilization of electrons to drive photocatalytic reactions.

seeds at the surface of the substrate material is needed to start the

catalyzed reaction of the desired functional coating. Electroless deposition has been mainly used to plate metals and metal alloys

due to their well-defined and simple redox reactions. However,

metal oxides such as indium tin oxide, iron oxide, manganese

oxide, and lead oxide have been successfully deposited using





process consists of two half-reactions. The first half-reaction pulses the first material precursor into the reaction chamber, where the precursor reacts with the template's surface resulting in an intermediate surface functionality.^[128-131] Afterward, the chamber is purged to remove unreacted precursor molecules and by-products generated from the reaction. The second half-reaction exposes the second precursor into the chamber to react with the modified surface chemistry of the template in the first half-reaction. When the reaction has finished, the remaining precursor and by-products are pumped away. Ideally, one monolayer of material is deposited within such an ALD cycle. Although this cannot be fully achieved due to steric hindrance, incomplete reactions, or inhibiting by-products, the growth per cycle (GPC) denotes the material thickness deposited within one ALD cycle and is constant within the so-called ALD window-a parameter set of temperature, precursor type, pulse lengths, and substrate type.^[128-131] As such, the deposited film thickness can be controlled by repeating ALD cycles until the desired value is obtained. However, the low GPC of 0.1 to 3 Å limits the application of ALD to deposition of a few tenths of nanometers considering reasonable process durations.^[128–130] Despite this limitation, the ALD technique is a very advantageous approach for functionalizing NAA templates. Due to the self-limiting nature of the reactions at the surface, NAA structures can be coated with highly conformal films of a broad variety of materials—this includes complex shaped or high aspect ratio NAA-PC structures (Figure 7g).^[128-132] Various materials such as oxides, sulfides, nitrides, and pure metals can be deposited by ALD.^[128-133] ALD has been combined with NAA because of its uniform and very accurate coating control in terms of film quality and thickness. Different applications of ALD-modified NAA structures in the field of solar energy harvesting have been reported to date. For example, ALDdeposited titanium dioxide TiO2 coatings combined with silver functionalization within NAA structures have been explored for photochemical reduction reactions.^[94,134-138] The photoelectrochemical (PEC) properties of NAA functionalized with ALD-deposited antimony sulfide-nickel oxide structures, titanium dioxide, zinc oxide, and antimony sulfide were investigated for solar cells.^[139-143] All these studies focused on NAA structures featuring straight nanopores. To date, ALD in NAA-PC structures has only been reported in two publications. Pitzschel et al. deposited silicon dioxide and iron oxide layers into NAA structures with nanopore modulations along the growth axis.^[144] Analysis of the magnetic properties of these structures revealed that these rely strongly on the position of diameter modulations in NAA. More recently, Lim et al. demonstrated the application of ALD-coated NAA-PCs in photocatalysis.^[49] In their study, NAA-DBRs were coated with different thicknesses of TiO₂ and used as model PC platforms to study photocatalytic reactions. Their observations demonstrated an enhanced photocatalytic degradation of a model dye when the PSB red edge is close to the edges of the dye absorption owing to the so-called slow photon effect. Furthermore, it was found that the deposited layer thickness of the semiconductor affects the photocatalytic activity by determining the efficiency of free charge carrier generation.

3.6. CVD

CVD is a deposition technique where precursors in the gas phase are either reacted or dissociated in a continuous flow, while byproducts are pumped out of the reactor chamber (Figure 7f). The main steps during the deposition process are the adsorption of intermediate reactants or precursors on the heated substrate surface, followed by diffusion on the surface, heterogeneous reaction at the gas-solid interface, nucleation, growth, and coalescence of the film. The chemical reactions or dissociation can be further activated through heat, light, plasma, or catalytic sites at the substrates, thereby giving rise to several different types of CVD processes such as thermal, metalorganic, lowpressure, hot-filament, light-activated, plasma-enhanced, and catalyst-assisted CVD.^[145] The major difference between CVD and physical deposition methods, such as sputtering, is the multidirectional deposition instead of a line-of-site impingement deposition. This enables CVD coatings to further penetrate and coat the inner surface of the NAA structures and provide conformal growth up to a certain nanopore aspect ratio-the ratio of nanopore length to its diameter. However, since the transport is limited by molecular diffusion and the deposition rate is usually linked to the local precursor partial pressure, eventually, the precursor moving down along the NAA pores will be consumed by the reaction on the walls, while a lower deposition rate will be observed at the bottom resulting in a non-conformal or uneven coating.^[146] This in turn can hinder the conformal internal coating of NAA structures featuring a high aspect ratio. Since film growth in the CVD process depends on the precursor(s) characteristics and on aspects such as flow rate, pressure, temperature, and the presence of reaction enhancers (e.g., plasma), the thickness limit for conformal deposition is often the result of a complex interplay between all these parameters. Despite these limitations, CVD has been successfully and extensively used to deposit functional coatings of a variety of materials onto a range of NAA structures. For example, Wang et al. have demonstrated that ultra-thin carbon films (\approx 5 nm thick) can be deposited onto the pores of NAA with a nanopore length of 1.64 µm, leading to enhanced broadband absorption and an increase in the saturation of the interference color in the visible range.^[147] Following a different approach, Tavakoli et al.^[148] and Waleed et al.^[149] have shown the CVD growth of methylammonium and cesium halides onto Pb previously electrodeposited into the nanopores of NAA to form hybrid composite materials. The fabricated hybrid NAA-perovskites nanowires (NWs) structures showed an enhanced photoresponse suitable for solar cells or photodetectors. Hybrid NAA-NW structures were also the focus of Fan et al.,^[150] who fabricated ZnO NWs into NAA structures by laser ablation-assisted CVD. The resultant structures showed a photoresponse upon UV irradiation (300-425 nm). Direct application in a p-n heterojunction solar cell was presented by Zhang et al.^[151] for an InP NW-NAA structure, where the NWs were deposited by metalorganic CVD. The Cu₂O/ InP-NAA p-n heterojunction solar cell attained a 1.55% power conversion efficiency (PCE) with a photocurrent density of 5.47 mA cm⁻², and a fill factor of about 47%. Meanwhile, Dhahri et al.^[152] and Ghrib et al.^[153] have used plasma-enhanced CVD to deposit nanocrystalline silicon on top of NAA structures.

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The resultant composite structure showed tuneability of optical properties with deposition temperature and time. Plasmaenhanced CVD has also been used to produce Pd–NAA hybrid materials for plasmonic photocatalysis by Kim et al.^[154] CVD has also been used to generate free-standing nanostructures such as nanotubes, nanowires, and nanodots using NAA as a template (later removed) for photocatalysis, plasmonic solar cells,^[155,156] and other applications aside from sunlight harvesting, thus not mentioned here, but covered in other reviews.^[157–159]

3.7. Further Techniques to Generate Hybrid Photonic Crystal Structures

Another approach to functionalizing NAA and tailoring its properties for sunlight harvesting systems is the fabrication of integrated hybrid material systems comprised of NAA structures in combination with other materials and structures capable of manipulating radiation. Some of these include 3D photonic crystals (e.g., opals or inverted opals) and plasmonic nanoparticles (Figure 8). Earlier works by Lu et al.^[160] and Cui et al.^[161] demonstrated the potential incorporation of NAA structures into silicon solar cells fulfilling the function of a passivating layer, replacing thin film stacks of SiO₂/SiN_x, SiO₂/AlO_x, and AlO_x deposited by ALD or plasma-enhanced CVD (PECVD). In both works, the authors have used a smart in situ light-induced anodization process to generate the NAA template from Al films incorporated in the Si solar cell stack. Their results show that NAA films can effectively passivate *p*-type silicon wafers to a level similar to PECVD or ALD thin film stacks, reaching interface state and fixed charge densities of $1\times 10^{10}\,\text{cm}^{-2}$ eV^{-1} and $2\times 10^{11} \text{ cm}^{-2},$ respectively. Qin et al. $^{[162,163]}$ and Wu et al. $^{[164]}$ have investigated the integration of NAA structures into Si solar cells for enhanced light absorption. Preliminary simulation $results^{[162,163]}$ showed a potential increase of ${\approx}23\%$ in light absorption in the wavelength range 280-1100 nm when using NAA as a light trapping layer, whereas the solar cell's

short-circuit current density was found to increase up to 131% when a double trap NAA system is used. The experimental realization of such systems where NAA thin films act as light-trapping and anti-reflection layers also showed an increase in the short-circuit current density and in the PCE, although at a lower level than that previously predicted by simulations.^[164]

This improvement was found to be dependent on the NAA lattice period, thickness, and nanopore diameter, where further developments were foreseen by the authors. Enhanced light absorption was also observed for integrated systems based on nanoparticles-infiltrated NAA. In the work by Li et al.^[165] carbon black nanoparticles were deposited inside the nanopores of NAA by airbrush spraying from a suspension. This hybrid material was then mounted on top of a p-type nanoporous Si substrate. The resultant integrated material shows a very efficient absorption of ${\approx}97\%$ of infrared radiation in the 2.5–15.3 μm range. Alternatively, Zhou et al.^[166] used sputtering to decorate the nanopores of NAA structures with Au nanoparticles, leading to a hybrid system with a 200 nm-10 µm broadband optical absorption with an efficiency of 99%. This capability was associated with strong multiple scattering inside the NAA pores combined with a low refractive index and high density of optical modes. The fabrication of integrated material systems with plasmonic nanoparticles is also suitable for photocatalysis applications, even though current demonstrations focus mostly on biosensing^[167] and surface-enhanced Raman scattering.^[168] The experimental realization of such structures is done by self-assembly of nanoparticles at the solvent interface followed by transfer and dewetting of electron-beam-evaporated gold films, respectively. In both cases, the resultant nanoparticles are located on the top surface of the NAA structure. An inverse approach with TiO2-coated NAA membranes fabricated on top of self-assembled SiO₂ beads was explored by Chung et al.^[169] These hybrid structures showed a 20% and 40% increase in methylene blue photocatalytic degradation in comparison to planar TiO2 and TiO2-coated NAA. The authors associate the



Figure 8. Hybrid materials based on NAA. a,b) NAA mounted as: a) passivation layer and b) anti-reflective layer in Si-based solar cells. c–e) NAAnanoparticle hybrid materials where nanoparticles are either: c) fully infiltrated within the NAA template, d) infiltrated within the NAA template and in the form of a film on its top, and e) deposited on top of the NAA template. f–h) NAA-nanostructures hybrid materials where the nanostructures are grown on top of the NAA template as: f) flakes, g) nanopillars or nanowires, and h) mesoporous films. (i and j) NAA–3D opal photonic crystals hybrids with illustrations showing representative i) NAA–opal and j) NAA–inverse opal structures.



increased performance with the higher surface area of the hybrid 3D system. Photocatalysis was also the focus of Najma et al., who fabricated ZnO-NAA free-standing membranes by hydrothermal growth of nanosheets on top of NAA membranes.^[170] The authors associated enhanced photocatalytic performances and antibacterial activity with the mass production and transfer of oxygen species and Zn^{2+} in combination with the high aspect ratio of the NAA membranes. Latest works have shown the capability of light-responsiveness (photocurrent generation) for integrated systems comprising NAA and 3D structures such as nanopillars,^[171] 3D opal photonic crystal,^[172] and periodically ordered mesoporous carbon nanostructures.^[173] TiO₂ nanopillars-NAA hybrid systems were fabricated by interfacial superassembly of a solution containing TTIP and Pluronic P123 template onto previously PMMA-infiltrated NAA films to grow the nanopillars on top of the nanoporous structure. The characterization focuses on ion transport but points out a potential application as an active device in energy conversion. Osmotic energy conversion is also the application targeted by Gao et al.,^[173] where mesoporous carbon-based structures are assembled on top of NAA structures by evaporation-induced self-assembly followed by calcination at 450 °C. The fabricated nanofluidic heterojunction converts salinity gradients into electricity, with a maximum power density value of 3.46 W m², outperforming many commercial membranes. In comparison, charged polystyrene opals with carboxylic or amino functionalization assembled on top of the NAA by drop $cast^{[172]}$ achieve a maximum value of 3.16 W m^2 ; however, with different performances regarding maximum power density depending on the functionalization and structural arrangement of the opals. This interesting result combined with the multitude of processes available to fabricate 3D opal photonic crystal structures,^[174] including recent advances in 3D printing combined with self-assembly,^[175] and 3D structures of optically relevant metal oxides produced by ALD^[176-179] opens the path for potential future developments in this highly dynamic field. Alternative approaches include changing the electrolyte from acidic to alkaline (i.e., sodium tetraborate) to increase the range of lattice constant (i.e., 250-600 nm) on curved surfaces without oxide burning.^[180] Another interesting feature of the resultant NAA structures is that, in contrast to their conventional counterparts produced in acid electrolytes, their nanopore walls are not flat but feature spiky needles, which grow perpendicularly to the nanopore axis. Consequently, these nanopores have a larger surface area compared to their flat counterparts, which could be harnessed to maximize specific surface area-dependent processes after functionalization. Another example of this is the combination of anodization with nanopatterning processes such as the generation of monolayers of self-assembled polystyrene spheres for pre-structuring the top surface aluminum, which upon anodization leads to a moth-eye-like array at the backside.^[181] This artificial structure can then be functionalized to generate a moth-eye-like array of titania or silver nanorods, which can be applied in photocatalysis and sensing applications. Note that some of the articles mentioned in this section do not directly demonstrate sunlight harvesting application, but radiation manipulation and radiation interaction tuning, which are promising capabilities of functionalized NAA structures and hybrid integrated material systems later discussed in the perspective section.



4. Sunlight Harvesting Applications of NAA-PCs

4.1. NAA–PCs in Solar Cells

Solar cells, also known as "photovoltaics," are semiconductor devices that convert solar energy into electricity by the photovoltaic (PV) effect.^[182] A basic solar cell consists of n- and p-type semiconductor materials sandwiched in between negative and positive electrodes, respectively. When sunlight illuminates the solar cell, incoming photons carrying energy higher than that of the bandgap of the semiconductor are absorbed by the material to generate electron-hole (e⁻/h⁺) pairs (charge carriers or excitons). If an external circuit is formed at the n- and p-type sections of the cell, the difference in voltage drives electrons from the p-n junction to produce electrical power. Although solar cells are a renewable energy source that provides many advantages such as simplicity in design and installation, sustainability, and low maintenance, the applicability of conventional solar cells is limited by the low PCE. This limitation is mainly attributed to: 1) thermalization of energy loss in the form of heat dissipation through crystal lattice vibration and 2) inefficient absorption of high irradiance sunlight photons of lower energy than that of the bandgap of the semiconductors.^[183] So, research efforts have aimed at addressing these intrinsic limitations to enhance PCE in solar cells through distinct approaches. In the context of this perspective, the integration of NAA-PCs into solar cell systems has been explored to break through some of these technological bottlenecks, harnessing the unique geometric, optical, thermal, and electrically insulative properties of NAA to maximize photon-to-electron conversion rates in solar cell systems. In particular, NAA-based Fabry-Pérot interferometers (NAA-FPIs) have been integrated into PV cells as scaffolds for PV materials,^[184,185] radiative coolers,^[186] electrodes,^[184,187] and antireflective coatings.^[163,164,188] NAA-FPIs are composed of straight cylindrical nanopores featuring a homogeneous distribution of effective refractive index in depth.^[23a] In PV cells. the characteristic barrier oxide layer at the bottom side of NAA-FPIs is often selectively etched to provide a physical connection between the n- and p-type sections of the PV cell (Figure 9).^[163,164,184–186,188] Kwon et al. developed a semitransparent, highly efficient, 1D nanostructured perovskite solar cells integrating an NAA-FPI as an insulating scaffold layer (Figure 9a).^[185] NAA-FPIs are used as a template to geometrically conform the PV cell precursors to generate vertically aligned perovskite pillars, eliminating the possibility of shunting current. The presence of NAA-FPIs in these PV cells also enables the precise control of the perovskite layer deposition, modulation of average variable transmittance without parasitic scattering, and suppression of internal ion diffusion while allowing critical improvements in long-term stability under continuous irradiation. The optimized solar cell device can achieve a relatively high PCE of 9.6%. Using a similar concept, Montero-Rama et al. prepared a perovskite solar cell in which NAA-FPIs were used to contain the components of the device (i.e., titanium dioxide-TiO2, methylammonium lead iodide-MAPbI3, and spiro-OMeTAD) and the aluminum substrate on its backside functions as the cathode.^[184] Despite achieving a low PCE of 0.06%, this study demonstrated that NAA-FPIs can be filled with multiple materials to engineer their structure at the

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Figure 9. Applicability of NAA in solar cell applications. a) NAA–Fabry–Pérot interferometers (FPIs) as scaffolds for the development of semitransparent parallelized nanopillar perovskite solar cells with: i) scheme showing the fabrication process of perovskite solar cell with NAA–FPIs conforming perovskite material; ii) structural and optical characterization of device performance of semitransparent nanopillar-structured perovskite solar cell with an ITO cathode. Adapted with permission.^[185] Copyright 2016, WILEY-VCH. b) NAA–FPIs as radiative coolers in crystalline silicon (c-Si) solar cells: i) schematics showing the energy balance for solar cells; ii) measured (filled circles) and simulated (shaded areas) steady-state temperatures of the solar cell at various solar irradiation with and without NAA–FPIs; and iii) photovoltaic performance modeling of the solar cell output electricity and enhanced efficiency in representative cities in China. Adapted with permission.^[186] Copyright 2022, Elsevier. c) NAA–FPIs as antireflective coatings on the surface of polycrystalline silicon (pc-Si) solar cells: i) Illustration showing the light-trapping and light-scattering effect of NAA–FPIs; ii) schematic illustrating the facilitation of charge carrier separation by the light scattering effect of NAA–FPIs; iii) device performance with current density versus voltage curves for pc-Si solar cells with and without NAA–FPIs. Adapted with permission.^[164] Copyright 2017, Elsevier.

nanoscale and use the aluminum substrate on its backside as an ohmic contact. On the other hand, El-Said et al. used the aluminum substrate of NAA–FPIs containing Cu impurities as the photoanode in dye-sensitized solar cells (DSSCs).^[187]

These composite PC structures immobilize the organic dye and, upon light illumination, a relatively high PCE of 12.3% is achieved. Tang et al.^[186] fabricated transparent NAA–FPIs as radiative cooler elements for crystalline silicon (c-Si) solar cells (Figure 9b). NAA–FPIs are directly encapsulated on solar absorbers to create a compact and efficient photovoltaic cooling system. This solar cell architecture allows a temperature drop of \approx 35.6 K in contrast to that of bare Si wafers (i.e., up to 137.4 °C), even in humid conditions. PV cells with integrated NAA–FPIs show a PCE enhancement of \approx 6% when compared to commercial PV cells. A solar cell photovoltaic performance model in seven representative cities across China for solar cells integrating these





NAA structures has also been reported. Solar cell systems with NAA–FPIs show an increased output energy of 16.5 kW h (a m²)⁻¹ in Lhasa when compared with commercial PV cells, demonstrating the potential use of NAA–FPIs as radiative coolers in solar cells. NAA–FPIs have also been used as antireflective coatings in Si solar cells.^[163,164,188] These antireflectors can be placed at the front,^[164] back,^[188] and on both sides^[163] of the solar cells. Figure 9c presents the function of NAA–FPIs as antireflectors and the resulting photovoltaic performance in Si solar cells.^[164] Antireflective coatings based on NAA–FPIs provide: 1) light trapping effect to increase optical absorption of the Si layers, and 2) light scattering effect to facilitate charge carrier separation within the Si layers. As a result, the PCE of commercial PV cells integrating NAA–FPIs are 12% superior to those without NAA–FPIs. Although the most widely NAA–PC structures used for solar

cell applications are NAA–FPIs, recent studies have demonstrated that other forms of structurally engineered NAA–PCs can be excellent platforms for the development of antireflective coatings for solar cells. Choi et al. fabricated NAA–GIFs by asymmetric pulse anodization under potentiostatic conditions (Figure 10).^[189] The resulting NAA–GIFs were demonstrated to have super broadband and omnidirectional antireflection properties, with minimal reflection at any angle of incidence. The application of NAA–GIFs onto the front surface of polymer solar cells revealed that the PCE of these solar cell systems reached a 10.0–5.0% enhancement as compared to the solar cell counterpart without NAA–GIF coating. Table 2 collates all solar cell systems integrating NAA–PCs, summarizing their PCE and main characteristics.

These studies reveal that NAA–PCs are promising candidates for solar cell applications because of their optical properties (i.e.,



Figure 10. Fabrication of NAA gradient-index filters (NAA–GIFs) and integration into polymer solar cells. a) anodization profile consisting of asymmetric stepwise potentiostatic pulses and schematic showing details of the structure of NAA–GIFs; and b) device performance with current density versus voltage curves (left) and power conversion efficiency (right) at different angles of incidence. Adapted with permission.^[189] Copyright 2017, WILEY-VCH.

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antireflection and light trapping), which in turn make it possible to elongate the optical path length in the active semiconducting layer of the cell for PCE enhancement. Most of these studies use NAA-FPIs as the antireflective coating in PV cells. Thus, it is suggested that other NAA-PC structures, particularly NAA-µQVs, could be integrated into solar cells for improvement in PCE since these PC structures provide the capability to efficiently recirculate and trap incoming photons with energies within the resonance band of these PC structures. While NAA-PCs, particularly NAA-FPIs, are highly beneficial as scaffolds for PV materials, NAA-FPIs are found to be less suitable as the cathode of the solar cell. Although the use of NAA-FPI with Cu impurities as photoanode provides relatively high PCE, the dye-sensitized solar cell is susceptible to poor performances at high temperature and the thermal properties of NAA-FPIs in this type of solar cell have not been investigated. The increased operating temperature in solar cells due to partial solar-to-heat energy conversion would adversely affect the material reliability and charge carrier recombination rate.^[190,191] This would subsequently reduce the efficiency and lifetime of the solar cells. The integration of NAA-FPIs into crystalline Si solar cell as radiative coolers has demonstrated relatively high PCE under various climatic conditions. All of the studies used one sun light intensity (100 mW cm^{-2}) to mimic natural sunlight but no real-life climatic conditions have been explored. Therefore, studies on the effect of temperature, wind speed, relative humidity, and solar irradiation on PCE of solar cells integrated with NAA-PCs should be performed in the future to further assess the real-life potential of this unique material across these applications.

4.2. NAA-PCs in Photocatalysis

Heterogeneous photocatalysis—"photocatalysis"—is a sustainable light-driven process in which photons (electromagnetic waves) interact with atoms (matter, photoactive materials) to produce electron–hole (e^-/h^+) pairs, which then can be harnessed to drive secondary reactions.^[192] Photoactive materials for photocatalysis include semiconductors with well-defined energy bandgaps, in which the bandgap of the photocatalyst material needs to be smaller than the energy of the incoming sunlight photons. Since photocatalytic reactions take place at the surface of the



photoactive material, a high specific surface area is essential to increase the number of active sites to maximize the efficiency of photocatalytic reactions. NAA has a wide energy bandgap (i.e., \approx 7–9 eV), which prevents it from being directly used as a photocatalyst under sunlight illumination. However, recent advances have demonstrated that the integration of functionalized NAA-PCs into photocatalyst platforms can provide new pathways for increasing photon-to-electron conversion rates and enhancing photocatalytic reactions by overcoming some of the intrinsic limitations of benchmark photocatalyst platforms. Several studies have demonstrated successful photocatalytic applications of semiconductor-based NAA-FPIs, including CO2 reduction,^[193] bacteria disinfection, $^{[170]}$ and photodegradation of organic pollutants in air $^{[194]}$ and water. $^{[138,195-197]}$ The main function of NAA-FPIs in these systems is to serve as a supporting layer for photocatalyst materials to ensure the mechanical robustness of the composite material and the capillary flow of the gas or water matrices through the nanopores of the NAA-FPIs to facilitate the mass transport of molecules involved in the photocatalytic reactions. Structural engineering of NAA-PCs have also demonstrated promising results in enhancing photodegradation of organic pollutants when the surface of these PC structures is functionalized with semiconductors such as titanium dioxide (TiO₂) (Figure 11). TiO₂-functionalized NAA-PC structures include TiO₂-NAA-GIFs,^[58] TiO₂-NAA-DBRs,^[47] TiO₂-NAA-µQVs,^[64] and TiO₂-NAA-BDBRs^[22b] (Figure 11a). TiO2-NAA-PCs are fabricated by a range of anodization approaches followed by a functionalization step to coat the inner surface of NAA with TiO₂ photoactive layers through the sol-gel and ALD methods. TiO2-NAA-PCs feature characteristic PSBs within which the propagation of incoming photons is forbidden by the PC structure (Figure 11b).

Therefore, photons within this spectral region cannot be efficiently used for enhancing photocatalytic reactions. Nevertheless, various NAA–PC structures also offer a range of optical phenomena beneficial for photocatalysis, including Bragg diffraction, multiple scattering, slow photons, light confinement, and constructive recirculation. The most widely exploited optical phenomena of all to boost photocatalytic reaction rates in TiO₂–NAA–PCs is the so-called "slow photon" effect.^[198] The speed of incoming photons localized in the low and high dielectric parts of the PC's structure (i.e., blue and

Table 2.	Comparison	of power	conversion	efficiency	(PCE)	for solar	cell system	integrating	NAA–PCs.
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NAA-PC	Function in solar cell	Type of solar cell	Configuration of solar cell	Intensity [mW cm ⁻²]	PCE [%]	References
NAA–FPI with Cu impurities	Photoanode	Dye-sensitized	Dye/NAA–FPI with Cu impurities/Al/TiN/Si	100	12.3	[187]
NAA-FPI	Antireflection coating (front and rear)	Thinfilm c-Si	NAA-FPI/ITO/c-Si/NAA-FPI/Ag	100	11.0	[163]
NAA-FPI	Antireflection coating (front)	pc-Si	NAA–FPI/Ag/SiN _x :H/pc-Si (n-i-p)/NAA–FPI/Al	100	11.5	[164]
NAA-FPI	Antireflection coating (rear)	Si	Si/NAA-FPI/(Si/SiO ₂)-DBR	100	12.5	[188]
NAA-FPI	Radiative cooler	c-Si	_	100	11.9	[186]
NAA-FPI	Cathode and scaffold	Perovskite	(WO3/Ag)/spiro-OMeTAD/MAPbI3/TiO2/NAA-FPI/Al	100	0.06	[184]
NAA-FPI	Scaffold	Perovskite	ITO/MoO _x /spiro-OMeTAD/AAO+perovskite/c-TiO ₂ /FTO	100	9.6	[185]
NAA–GIF	Antireflective coating (front)	Polymer	$\label{eq:NAA-GIF} \begin{split} NAA-GIF/adhesive/glass/(ITO/TiO_2\ NPs)/PTB7\text{-}Th:PC_{71}\\ BM/(V_2O_5/Ag)/encapsulated\ glass \end{split}$	100	10.0	[189]

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Figure 11. Photocatalytic capabilities of representative TiO_2 –NAA–PC structures in the photodegradation of organic dye molecules (from top to bottom: TiO_2 –NAA–DIF; TiO_2 –NAA–DBR; TiO_2 –NAA–QV; and TiO_2 –NAA–DBR). a) Schematic showing details of the nanoporous structure of TiO_2 –NAA–PCs. b) Representative optical transmission spectra of TiO_2 –NAA–PCs showing blue and red edges of the PSB or resonance band, where photons at the red and blue edges slow down their group velocity after interacting with the PC structure. c) Relative optical alignment of red edges of the PSB $(\lambda_{PSB-red})$ or resonance band (λ_R) of TiO_2 –NAA–PCs fabricated with varying anodization periods (T_P) in water and the absorbance spectrum of organic dye molecules (RhoB Rhodamine B; MB methylene blue; MO methyl orange), with the corresponding *k* values. TiO_2 –NAA–GIF: Adapted with permission.^[58] Copyright American Chemical Society. TiO_2 –NAA–DBR: Adapted with permission.^[64] Copyright 2019, Royal Society of Chemistry. TiO_2 –NAA–BDBR: Adapted with permission.^[22b] Copyright 2020, American Chemical Society.

red edges of the PC's PSB—left and right regions of the band, respectively) is strongly reduced. Slow photons localized at the red edge of the PSB increase the number of photon-to-surface interactions within the PC structures, resulting in the generation of additional e^--h^+ pairs, which can be subsequently used for driving photocatalytic reactions. In contrast $TiO_2-NAA-\mu QVs$ can harness the slow photon effect along with confinement and constructive resonant recirculation of light to drive and



further enhance photocatalytic reaction rates by combining two optical phenomena in one single PC platform. Light trapping between the two highly reflective mirrors of TiO2-NAA-µQVs occurs within a narrow spectral range-bandwidth of the resonance band-in which the number of interactions between photons and TiO₂ increases, boosting the generation of charge carriers at those spectral regions where light is poorly absorbed by the photoactive TiO₂ (i.e., visible–NIR spectrum). The photocatalytic performance of these TiO2-NAA-PCs was assessed by studying the photodegradation of organic dyes (i.e., Rhodamine B-RhoB, methylene blue-MB, and methyl orange-MO) with well-defined absorbance bands across different spectral regions under visible-NIR illumination.^[64] To elucidate the effect of slow photons and light confinement in enhancing photocatalytic reactions, the relative spectral distance between red edges of the PSB $(\lambda_{PSB-red})$ or resonance band (λ_R) of these TiO₂-NAA-PCs fabricated with varying anodization period $(T_{\rm P})$ in water, and the absorbance band of organic pollutants, using the photocatalytic degradation rate (k) as an indicator (Figure 11c). The maximum photocatalytic performance (k_{max}) of TiO₂-NAA-GIFs and TiO₂-NAA–BDBRs are found to be 0.39 and 0.73 h^{-1} for the photodegradation of RhoB and MO, respectively. $\lambda_{PSB-red}$ for these k_{max} values is positioned such that it partially overlaps with the blue edge of the absorbance band of the organic dyes and these photocatalytic enhancements are ascribed to slow photon effects. The photocatalytic performance of TiO2-NAA-GIFs and TiO2-NAA-BDBRs with $\lambda_{PSB-red}$ positioned at other spectral ranges is found to significantly decrease, particularly when $\lambda_{PSB-red}$ is aligned with the absorbance maximum of RhoB and MO, respectively (i.e., $\lambda_{Abs-RhoB} = 554$ and $\lambda_{Abs-MO} = 464$ nm). This decay in performance was attributed to the "screening effect", by which RhoB and MO molecules prevent incoming light from interacting with the functional TiO₂ layers of these NAA-PCs to generate reactive species to drive these photocatalytic reactions. In contrast, the maximum photocatalytic performance of TiO2-NAA-DBRs (i.e., $k_{\text{max}} = 3.04 \text{ h}^{-1}$) is achieved when $\lambda_{\text{PSB-red}}$ almost overlaps with the absorbance maximum of MB (i.e., λ_{Abs-} $_{\text{RhoB}} = 664 \text{ nm}$), while *k* values decrease with the increasing spectral distance between $\lambda_{PSB-red}$ and the absorbance band of MB. A similar result was obtained for the photocatalytic degradation of MB by TiO₂–NAA– μ QVs, which achieve a k_{max} of 3.55 h⁻¹ when $\lambda_{\rm R}$ is positioned near to the absorbance maximum of MB. Thus, these findings demonstrate that TiO2-based NAA-PCs are promising photocatalyst platforms to drive photocatalytic reactions by rationally designing and engineering light-matter interactions in porous PC structures. Other approaches have also explored the use of noble metal films^[38] and different deposition methods for photoactive TiO₂ layers^[49] to further improve the photocatalytic performance of TiO₂-based NAA-PC photocatalyst platforms. Lim et al.^[38] explored the potential of gold (Au)-coated TiO₂-NAA-DBRs as photocatalyst platforms to enhance photocatalytic reactions by integrating slow light effect and SPR. Photocatalytic improvements associated with these two optical phenomena in Au-TiO2-NAA-DBRs were investigated by monitoring the photodegradation of MB under visible-NIR irradiation. This study demonstrated that slow light effect plays a major role in the efficiency of photocatalytic degradation rates when compared to SPR effect due to the localized nature of generated surface plasmons in the Au layer deposited on the



top surface of TiO2-NAA-DBRs. Lim et al.^[49] also used a different approach to analyze the effect of surface functionalization of NAA-DBRs with TiO2 for photocatalysis. NAA-DBRs were surface-functionalized with a TiO₂ layer deposited via ALD, and used as photocatalyst platforms to harness slow photons for photocatalytic degradation of MB under visible-NIR illumination. The combinational effect of anodization parameters and thickness of ALD-functionalized TiO₂ layers on the photocatalytic reaction rates were investigated. This study also provides a comprehensive explanation of the mechanism for photocatalytic degradation of MB by TiO2-NAA-DBRs under visible-NIR illumination, which can be extended to other types of TiO2-NAA-PC structures (Figure 12). These findings indicate that a combinational light-induced breakdown mechanism is responsible for the photodegradation of MB molecules. Upon light illumination, $e^{-}h^{+}$ pairs are photogenerated in the conduction and valence band of the TiO₂ layers, respectively (Figure 12a). Charge carriers then react with redox species and radicals (i.e., OH) formed on the TiO₂ layers coating the inner surface of the nanopores, which subsequently further oxidize the reactant mixture adsorbed onto or close to the photoactive TiO₂ layer into clean CO2 and H2O molecules. Figure 12b depicts an illustration of the photocatalytic degradation of MB by TiO2-NAA-DBRs under light irradiation. The photocatalytic enhancement in the photodegradation of MB by TiO2-NAA-DBRs is found to be critically determined by the relative optical distance between $\lambda_{PSB-red}$ and the absorbance band of MB associated with the slow photon effect (Figure 12c). This optical mechanism extends the lifetime of visible-NIR photons within the photoactive TiO₂ layers coating the inner surface of NAA-DBRs. As such, the number of photon-atom interactions increases, resulting in a higher generation of charge carriers to drive the photocatalytic reactions. Since adsorption of MB molecules onto different TiO2-NAA-DBRs under dark conditions may vary, photocatalytic degradation is assessed in the form of photocatalytic reaction rates (r) (Figure 12d).

Crystallinity of TiO2 structures is also found to affect the conductivity, reactive sites, and lifetime of e⁻-h⁺ pairs, which subsequently improve the overall photocatalytic performance of TiO₂–NAA–DBRs (Figure 12e).^[49] TiO₂–NAA–DBRs featuring anatase phase are demonstrated to outperform their counterparts containing the amorphous phase of TiO₂ due to the higher tendency to confine e^--h^+ pairs for photocatalysis. This study also demonstrates that without the addition of H₂O₂ in the reactant solution, MB molecules can still be partially degraded by the photocatalyst platform (Figure 12f). Therefore, the photocatalytic degradation mechanism cannot alone be explained by the slow photon effect and its contribution to the photoinduced breakdown of MB by TiO₂-NAA-DBRs. Another contributing mechanism would involve dye sensitization, where singlet and triplet states are generated in MB molecules by intersystem crossing when MB molecules are illuminated with visible-NIR light. The e⁻ photogenerated from this process are then injected into the conduction band of the TiO₂ layers, where the chemically adsorbed oxidant O₂ groups are reduced to produce O₂⁻ and \times OH radicals on the surface of TiO₂ layers. These redox species and radicals are also responsible for the photocatalytic degradation of MB molecules. Figure 12g explains the dye sensitization mechanism by demonstrating N-demethylation of MB



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Figure 12. Investigation of the photoinduced breakdown mechanism for the photocatalytic degradation of MB by TiO_2 –NAA–DBRs driven by visible–NIR illumination. a) Schematic showing architectural, chemical, and electronic structure of TiO_2 –NAA–DBRs under light irradiation in water. b) Digital images showing a visual depiction of the photodegradation of MB by TiO_2 –NAA–DBRs under light illumination. c) Representative relative optical alignment of PSBs' red edge of TiO_2 –NAA–DBRs fabricated with varying T_P in water and the absorbance spectrum of MB, with corresponding photocatalytic performance (k). d) Reaction rate for photocatalytic degradation of MB by representative TiO_2 –NAA–DBRs under light illumination. e) Bar chart showing the photocatalytic performance of TiO_2 –NAA–DBRs with different TiO_2 crystal phases. f) Photocatalytic degradation kinetics of MB by TiO_2 –NAA–DBRs showing the effect of the presence of hydrogen peroxide (H_2O_2). g) Absorbance bands of MB over illumination time from 0 to 1 h with an interval of 0.25 h photodegraded by representative TiO_2 –NAA–DBRs. h) Photocatalytic degradation kinetics of 4-chlorophenol (4-CP) and MB by representative TiO_2 –NAA–DBRs. Adapted with permission.^[49] Copyright 2021, American Chemical Society.

(i.e., one methyl group is removed at a time) through a gradual blue shift in the absorbance maximum of MB until the two peaks merge into a single peak at an illumination time of >0.75 h. The photocatalytic degradation of 4-chlorophenol (4-CP) by TiO₂–NAA–DBRs was also investigated to elucidate if the photocatalytic degradation mechanism for this organic molecule, a model transparent compound, is affected by slow photon effect and sensitization (Figure 12h). It was found that TiO₂–NAA–DBRs are still able to photodegrade 4-CP under visible–NIR illumination due to the complexation of phenolic compounds on the surface of TiO₂ layers, where e^- are directly transferred from surface-complexed phenol groups into the conduction band of TiO₂ layers deposited on NAA–DBRs under illumination.^[199]

Therefore, the light-induced breakdown mechanism is inferred to be attributable to a combination of slow photon and sensitization mechanisms on the semiconducting layers of these composite photonic crystals. Other factors that affect the photocatalytic performance of TiO₂–NAA–DBRs include the total pore length of the PC structures and the charge of the organic dye molecules, where the former factor will increase the available reactive sites while the latter will increase or decrease the effective absorption of molecules on the surface of the semiconductor coating. **Table 3** compiles all structurally engineered TiO₂-functionalized NAA–PCs developed for photocatalytic degradation of various organic pollutants, including a summary of the photocatalytic performances of these systems in terms of kinetic constant



values (k). Since the effective surface area of TiO2-NAA-PCs, power of illumination, and concentration of organics in these studies were the same, a direct comparison between the photocatalytic degradation performances of TiO2-NAA-PCs in terms of light-induced breakdown of organic pollutants is possible. The slow photon effect has been the most widespread optical phenomenon integrated with TiO2-NAA-PCs (i.e., TiO2-NAA-GIFs, TiO2-NAA-DBRs, and TiO2-NAA-BDBRs) to photodegrade model organic pollutants. When we compare the photocatalytic performances of these composite PC structures, TiO₂-NAA-DBRs generally are superior to other counterpart NAA-based PC structures. This could be attributable to a more efficient collection of photons associated with the broad and intense characteristic PSB of NAA-DBR structures as well as a better relative spectral alignment between the red edge of the PSB and the absorbance band of organic pollutants. However, TiO₂-NAA-µQVs provide superior photocatalytic degradation rates when compared to these other TiO2-NAA-PCs due to the strong confinement and recirculation of incoming photons across those spectral regions within the resonance band. When TiO2-NAA-DBRs are coated with Au layers, the photocatalytic enhancement is lower than that of TiO2-NAA-DBRs without Au coating. This shows that the slow photon and SPR effects need to be rationally coupled to efficiently harness both optical phenomena in TiO2-based NAA-PC photocatalyst platforms. ALD-functionalized TiO2-NAA-DBRs demonstrated higher k values when compared to their sol-gel TiO2-NAA-DBRs and Au-TiO2-NAA-DBRs counterparts in the photodegradation of MB. This result could be attributed to the better controlled thickness, composition, and homogeneity of the TiO₂ layers deposited onto the inner surface of NAA-DBRs by the ALD method. Reusability is a fundamental aspect of the development of photocatalyst platforms for real-life applications. TiO2-NAA-DBRs, TiO₂-NAA-µQVs, and TiO₂-NAA-BDBRs have demonstrated the outstanding photostability of these composite PC structures to be reused in the photocatalytic degradation of organic pollutants without losing performance after five cycles. To summarize, these studies have demonstrated the successful applicability of TiO2-NAA-PCs as photocatalyst platforms for highly efficient photocatalysis. However, these studies have so far been focused on photocatalytic degradation of organic pollutants in water, particularly organic dyes, which can self-sensitize into harmless compounds upon light illumination.



Future investigations of photocatalytic degradation of organics should focus on colorless and resilient compounds with absorbance bands in the UV and visible regions of the solar spectrum. Moreover, different photoactive materials and semiconductors should be explored to investigate the contributions from other factors in the photocatalytic efficiency of these model photocatalytic platforms. These include quantum efficiency, electron mobility, electrochemical properties, energy bandgap, and chemical stability. More fundamental research assessing the capabilities and limitations of the proposed surface-functionalized NAA-PC platforms with different functional layers should be performed in the future. These studies should evaluate aspects such as photon-to-electron conversion rate, photosensitivity, reproducibility, chemical selectivity, and stability. Since the type of semiconductor and noble metal deposition methods affect the photocatalytic performance of TiO2-NAA-PCs, other chemical modification techniques could enable better alignments between photonic, electronic, and plasmonic characteristics. The use of surface-functionalized NAA-PCs developed in these studies has been mainly focused on photocatalytic degradation of single organic pollutants in pure form. To translate NAA-PC technology into fully functional prototypes for real-life multiplexed photocatalytic applications, the photocatalytic performance of surface-functionalized NAA-PCs should be assessed in decontamination of a wide range of complex organic pollutants, including real-life samples such as wastewater, groundwater, drinking water, and extracts from contaminated soil. It is also important to note that the versatility of surface-modified NAA-PCs should also be demonstrated for other photocatalytic applications, including clean hydrogen fuel generation, carbon dioxide reduction, and air purification.

4.3. NAA-PCs in Photoelectrochemistry

PEC applications are based on the same charge carrier generation process as photocatalysis (i.e., excitation of a semiconductor by incoming photons). But, in contrast to photocatalysis, in PEC recombination is strongly reduced by integrating the semiconductors into an external circuit leading to spatial separation of the free charge carriers and thus increasing the reaction efficiency.^[200–202] Semiconductor materials can absorb photons with energy larger than that of the semiconductor's electronic bandgap. Such absorption process creates electron–hole pairs

Table	3. Comparison of Ti	O ₂ -functionalized NAA–PC-b	ased photocatalyst	s with: optical pheno	mena, TiO ₂ depos	sition method, e	effective surface area
(SA),	power of illumination	(P), organic concentration	(C _{organic}), photocat	talytic performance (k	x), and reusability	(R) after five ph	iotocatalytic cycles.

Photocatalyst	Optical mechanism	TiO ₂ deposition method	SA [cm ²] P	P [W]	$ [W] \qquad C_{\rm organic} \\ [mg \ L^{-1}] $	<i>k</i> [h ⁻¹]				R [%]	References
						MB	МО	RhoB	4-CP		
TiO ₂ –NAA–GIFs	Slow photon	Sol-gel	1	150	5	2.10	0.25	0.39	-	-	[58]
TiO ₂ –NAA–DBRs	Slow photon	Sol-gel	1	150	5	3.04	0.32	0.35	0.15	96	[47]
TiO ₂ –NAA–µQVs	Light recirculation	Sol-gel	1	150	5	3.55	0.77	1.34	-	98	[64]
TiO ₂ –NAA–BDBRs	Slow photon	Sol-gel	1	150	5	1.12	0.73	0.24	-	91	[22b]
Au-TiO ₂ –NAA–DBRs	Slow photon and surface plasmon	Sol-gel	1	150	5	2.45	-	-	-	-	[38]
TiO ₂ –NAA–DBRs	Slow photon	ALD	1	150	5	3.95	-	-	0.24	-	[49]

 $(e^{-}h^{+} pairs)$ as free charge carriers. The negatively charged electrons are excited from the valance band (VB) to the conduction band (CB) of the semiconductor, leaving positively charged holes in the VB.^[200,202] Both charge carriers electrons, and holes, can induce secondary processes such as chemical reactions due to their strongly reducing and oxidizing properties, respectively. Reduction and oxidation reactions take place at the semiconductors' surface where molecules are adsorbed. However, in this process, many charge carriers are not able to reach the surface of the semiconductor because they undergo recombination. The integration of an external circuit around semiconductors photoelectrodes makes it possible to address this constraint by externally providing the necessary electrons to perform redox reactions through photoelectrochemistry.^[200,202] The working electrode in a PEC device consists of a semiconductor bonded to a conductive material. Upon illumination under electromagnetic radiation of specific wavelengths, the semiconductor material in the working electrode generates electrons and holes. The electrical conductor bonded to the semiconductor connects the working electrode with a counter electrode, which typically consists of a noble metal such as platinum. Both electrodes are immersed into an electrolyte solution containing the chemical species that are to be oxidized/reduced by PEC reactions. Furthermore, a potential or current is applied between the electrodes to spatially separate the generated ($e^{-}h^{+}$ pairs) based on their charges.^[200,202] When the semiconductor gets in contact with the electrolyte solution, its electronic bands bend at the semiconductor surface. The formation of this Schottky junction equilibrates the electrochemical potential difference between semiconductor and electrolyte as shown in Figure 13. Depending on the (intrinsic) doping state of the semiconductor, band bending occurs either upwards or downwards for n-type and p-type semiconductors, respectively.^[202] The bent area is denoted as the space charge layer or depletion layer wherein the majority charge carries-electrons in n-type and holes in p-type semiconductors—are depleted. Application of a potential between the electrodes of a PEC device can further enhance and drive this effect. Due to the band bending, e^--h^+ pairs are separated after their generation according to their charges. For n-type semiconductors, holes accumulate at their surface (Figure 13a)



while electrons move towards the surface of a *p*-type semiconductor (Figure 13b). The respective minority charge carriers are removed from the working electrode by electrical transport along the electric connector towards the counter electrode.^[202] After separation, both carrier types induce redox reactions at their respective electrode. Since holes facilitate oxidations, these take place at the working electrode in the case of an n-type semiconductor and at the counter electrode for p-type semiconductors. For the reduction reactions induced by the electrons, it is vice versa-at the counter electrode for n-type and working electrode for p-type semiconductors. This spatial separation of both reactions minimizes e⁻-h⁺ recombination and therefore significantly increases the PEC reaction efficiency compared to photocatalytic processes.^[200,202] As for photocatalytic reactions, an increase in the semiconductor effective surface area provides more active sites for redox reactions since these occur at the semiconductor's surface. Consequently, the PEC activity of a nanostructured semiconductor material is higher compared to its flat, thin film counterpart for the same macroscopic area. Hence, NAA is well-suited as a working electrode material for PEC devices owing to its high specific surface area and its functional surface, which can be precisely tailored with semiconductors and metals through a wide range of functionalization techniques (vide supra). Several publications have used NAA as a template to synthesize nanowires or rods for PEC applications. To this end, different semiconductors such as copper(I) oxide (Cu₂O),^[203,204] copper tungsten oxide (CuWO₄),^[205] copper bismuth oxide (Cu_2BiO_4) ,^[206] copper indium selenide (CuInSe₄),^[207] iron(III) oxide,^[208] silver metal (Ag),^[209] and also heterostructures of Fe₂O₃-Cu₂O,^[210] and nickel-bismuthvanadate (BiVO₄)^[211] have been deposited as nanowires or nanorods by electrodeposition into NAA structures featuring straight pores. Additionally, nanowire and nanotube arrays made of Cu₂ZnSnS₄^[212] and iron titanate (Fe₂TiO₅),^[213] respectively, have been deposited by solution-based techniques within NAA. In all these studies, arrays of free-standing nanowires, nanorods, and nanotubes were obtained upon selective dissolution of the NAA template. Such an approach increases the accessible specific surface area of nanostructures for PEC reactions. However, no tailorable light-matter interaction can be engineered to



Figure 13. Schottky junctions formed at the surface of a semiconductor to equilibrate the energy difference between the semiconductor Fermi level (E_F) and the redox potential of the electrolyte (E_{redox}). Band bending occurs: a) upward for n-type semiconductors and b) downward for *p*-type semiconductors. The depletion layer (DL) influences the movement of photogenerated e^--h^+ pairs. a) In n-type semiconductors, h^+ are accumulated at the surface and can induce oxidation reactions in the electrolyte while e^- are transported away from the interface. b) Electrons accumulate at the surface of p-type semiconductors and can reduce adsorbed molecules there.





maximize photon-to-electron conversion rates at specific spectral regions.^[200,202] An alternative configuration to free-standing nanostructures is to deposit functional materials onto NAA structures by ALD for PEC applications and preserve the NAA template as support for thin films.^[214–217] Since ALD provides high conformality, the inner surface of NAA nanopores is precisely coated and heterostructures such as coaxial junctions can be realized. Jiao et al. applied molybdenum sulfide (MoS₂) and functionalized NAA as a photoelectrochemical biosensor for microRNA-155—a biomarker in the diagnostic and therapy of cancer.^[214] The working principle of this system is based on photoexcitation of MoS₂ and simultaneous change in ion-transmitting current due to immobilization microRNA over the NAA template.

The PEC sensing system achieves an ultrasensitive detection range of 0.01 fM to 0.01 nM and an ultralow detection limit of 3 aM Photoelectrocatalysis—particularly water splitting—is broadly considered a PEC process. Barr et al. fabricated coaxial nanotubular heterostructures made of p-type nickel(II) oxide (*p*-NiO) and intrinsic antimony sulfide (i-Sb₂S₃) (**Figure 14**a) and optimized the design of the system to further improve photoelectrochemical water splitting efficiency.^[139,140] Under illumination, the composite NAA structure exhibited a current density of 0.15 mA cm⁻² at a potential of 1 V against a silver/silver chloride (Ag/AgCl) reference electrode. According to the layer arrangement of the heterostructure (i.e., type II semiconductor heterojunction), a transfer of electrons photogenerated within the i-Sb₂S₃ to the electrolyte is expected. However, this effect could not be observed. Unexpectedly, injection of holes from the underlying p-NiO into the electrolyte occurred. Analysis of the structure showed that the i-Sb₂S₃ layer shrank and got discontinuous upon annealing during the ALD deposition. To prevent this, further optimization of the sample design will be required.^[139,140] The Bachmann group studied the influence of different geometrical parameters (e.g., nanopore diameter and length) to improve the PEC properties of Fe₂O₃-coated NAA structures.^[95,96,215,216] They first reported on the electrochemical characterization of Fe2O3-functionalized NAA structures with different pore diameters and observed an increase in the current density with increasing diameter.^[216]



Figure 14. Photoelectrochemical (PEC) applications are demonstrated for different semiconductor heterostructures. a) A NAA/*p*-NiO/i-Sb₂S₃ photoanode is designed to efficiently separate generated charge carriers as schematically shown in (i) and (ii). iii) Since the i-Sb₂S₃ layer shrank during annealing, hole injection from the underlying *p*-NiO layer into the electrolyte influenced the PEC properties. (iv) Nevertheless, an increase in the photocurrent density is observed under illumination. Reproduced with permission.^[140] Copyright 2015, Elsevier. b) i) Charge carrier separation in NAA/SnO₂/Fe₂O₃/ IrO₂ structures, ii) improved current density compared to systems consisting of only one or two of these materials. iii) Irradiation with simulated solar light revealed different photocurrent increases of anodes consisting of: a) Fe₂O₃, b) Fe₂O₃/IrO₂, c) SnO₂/Fe₂O₃, and d) SnO₂/Fe₂O₃/IrO₂. Reproduced with permission.^[96] Copyright 2019, Wiley-VCH.

Furthermore, they used this NAA architecture design to establish a model system for studying mass and charge transport at the electrode. Haschke et al. continued this work to optimize Fe₂O₃-coated NAA structures and improved the electrocatalytic current densities by annealing the structures prior to the PEC characterization.^[215] Additionally, they observed the existence of an optimal pore length of 17 µm and a pore diameter of \approx 160 nm for efficient water splitting, where the highest current density of 1.8 mA cm⁻² was achieved at an operational 0.69 V overpotential.^[95] Compared to a control as-prepared planar electrode, the current density was found to increase by a factor of 1000 through nanostructuring. Following this optimization of the electrochemical properties of NAA templates functionalized with Fe₂O₃, Bachmann and his team fabricated similar heterostructures consisting of tin(IV) oxide (SnO₂), Fe₂O₃, and iridium(IV) oxide (IrO₂).^[96] This heterostructure is designed to separate the photoexcited charge carriers in the Fe₂O₃ layer efficiently, as depicted in Figure 14b.

Generated electrons are transferred to the SnO₂ layer while holes will move across the IrO2 layer towards the electrolyte and induce oxidation reactions there. A steady-state current density of 1.36 mA $\rm cm^{-2}$ was achieved at 0.48 V, which is a 17-fold increase compared to pure Fe₂O₃. The lower overpotential of 0.38 V reveals a 0.57 mA cm⁻² current density corresponding to an enhancement by a factor of 188 compared to the bare Fe₂O₃ structure. Moreover, the SnO₂/Fe₂O₃/IrO₂ electrodes show long-term stability for at least 15 h and the onset photocurrent is reduced by 300 mV against Ag/AgCl reference electrode. Utilization of NAA-PC structures has not yet been reported for PEC applications. Nevertheless, it should be relatively easy to realize since the basic structure is the same as for the reported straight pores. In addition, NAA-PCs would allow for further improvement of solar light harvesting by tailor engineering the optical properties of the composite structures to maximize semiconductor excitation.

4.4. NAA-PCs in Photothermal Conversion

Solar light can be harnessed to heat materials by the so-called photothermal effect. In this process, photons are absorbed by the material and excited electrons relax toward their ground state via transitions to lower energetic vibrational states.^[218-220] Such transitions are accompanied by the release of heat, which subsequently can be used for different purposes, for example, water purification, CO2 conversion, or spectroscopy.^[220-224] Efficient sunlight-to-thermal energy conversion requires a broad absorption range over the solar spectrum. This is already present in many metals and metal compounds but can be further tuned by nanostructuring these materials.^[218-220] The size and shape of structural features at the nanoscale determine the solar harvesting capabilities of a material by modulating the way in which it interacts with electromagnetic waves. In particular, nanoporous materials can be engineered to reduce the reflection of incoming light and increase the optical absorption of photons for conversion processes.^[219] To date, several studies have explored the use of NAA structures as templates for different photothermal solar harvesting applications. Zhang et al. polymerized polyaniline nanoparticles (NPs) in situ into NAA films

featuring straight nanopores to realize a broadband absorption platform composite material.^[225] They observed efficient photothermal conversion by irradiating the structures with artificial sunlight (power 1000 W m⁻²). Integration of these NAA structures into a commercial thermoelectric generator based on the Seebeck effect revealed an output voltage of 180 mV compared to 0.8 mV by the commercial system for a similar temperature difference. The application of gold-coated NAA microcantilevers for infrared (IR) spectroscopy has been reported by Lee et al. as shown in Figure 15a.^[226] Thin Au films were deposited onto both surfaces of NAA structures and the effect of NAA nanopore size and Au coating thickness were systematically investigated. NAA structures featuring 70 nm nanopores in diameter and 40 nm thick Au films showed the highest photothermal response, which was found to strongly increase when compared to the same uncoated NAA structure. Additionally, the molecular detection sensitivity in photothermal IR spectroscopy was found to increase by one order of magnitude for acetone detection when the functionalized microcantilever was applied. Lou et al. achieved a high photothermal carbon dioxide (CO₂) hydrogenation rate by sputter depositing cobalt (Co) NPs onto NAA structures.^[121] The CO₂ conversion rate of the system reached 1666 mmol g_{Co}^{-1} h⁻¹, which is the highest reported for Co-based systems. Dark amorphous TiO_x nanotube arrays were investigated by Liu et al. for solar thermal conversion.[227] NAA structures were functionalized by TiO_x deposition via ALD at 10 nm coating thickness. The resulting composite structures featured a broadband absorption. When compared to uncoated NAA structures, the surface temperature of the TiO_x-coated structures achieved a solar thermal conversion efficiency enhancement of 85.3%. The integration of plasmonic structures in combination with NAA templates can further improve the solar conversion efficiency of photothermal processes by harnessing localized surface plasmon resonances (LSPR) at the nanoscale. Irradiating plasmonic materials with light wavelengths at least equal to their size excites collective, resonant oscillations of conduction electrons at the material-dielectric interface due to the oscillating electromagnetic field of the incoming light.^[220–222] LSPR energy is locally released by internal scattering processes, which in turn heat the local environment of the platform material.^[221] Deposition of NPs consisting of various materials such as titanium nitride (TiN),^[228,229] zirconium nitride,^[228] hafnium nitride,^[228] silver,^[230] and nickel,^[224,231] and co-deposition of gold and TiO₂ NPs^[196] leads to increased sunlight-to-energy conversion efficiencies for water vaporization and desalination. These applications are studied by floating functionalized NAA membranes (open pores) on top of a water reservoir containing salt species and illuminating the NAA structure with artificial sunlight (Figure 15b). Local heating of the composite NAA structure associated with LSPR upon illumination causes water evaporation.

The vapor condenses at the containers' cover plate and the purified liquid water is guided toward another reservoir. Nickel NPs deposited onto NAA templates by sputtering enable a high absorptivity of 97% in the wavelength range of 400–2500 nm.^[231] Such membranes feature a vapor generation efficiency (VGE) of 0.9 kg m⁻² h⁻¹ with an increased surface temperature under solar illumination compared to that of bare NAA. Cheng et al. observed an enhancement of desalination rate
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water vaporization setup

(b)

(c) plasmonic NP functionalized NAA membranes for water vaporization



(d) Co-Ni composite NP modified NAA-PCs as solar thermal absorption structures



Figure 15. Functionalized NAA structures are used for different photothermal applications. a) Au-coated NAA microcantilevers showed enhanced IR response and were utilized for IR spectroscopy. i) Scheme of the structure design and ii) increasing photothermal IR signal with increasing Au coating thickness. Reproduced with permission.^[226] Copyright 2017, AIP Publishing. b) Schematic of a water vaporization setup using plasmonic functionalization of NAA membranes. Reproduced with permission.^[228] Copyright 2020, American Chemical Society. c) i) Deposition of plasmonic NPs into NAA membranes to increase localized surface temperature under illumination. ii) The optical properties of the different materials could be related to the water evaporation rate. Reproduced with permission.^[228] Copyright 2020, American Chemical Society. d) Co–Ni NP coated NAA–PCs were designed to reduce the reflection in the IR range to be used as solar thermal absorption materials. i) Schematic of the PC structure and ii) reflectance spectra of samples coated by Cu–Ni composite NPs under different deposition conditions. Reproduced with permission.^[224] Copyright 2017, Elsevier.



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photothermal materials and NAA–PCs would boost the efficiency of solar-to-thermal energy conversion.

5. Conclusions and Perspective

Tailor-engineered NAA-PC structures with tunable optical properties are ideal platform material candidates to tackle future challenges in solar energy conversion via efficient light harvesting and rational management of photons at the nanoscale. Despite being limited by its electrically insulating composition, NAA-PCs can be combined with a broad range of functionalization techniques to adjust their optoelectronic properties through the deposition of photoactive materials onto the inner surface of their nanopores or plasmonic structures in the form of nanoparticles and films. Pioneering studies summarized in this perspective indicate the potential of NAA-PC technology across several sunlight harvesting fields including solar cells, photocatalysis, photoelectrocatalysis, and photothermal conversion. Recent advances in pulse-like anodization have enabled the realization of a new variety of NAA-based photonic structures and systems with precisely engineered optoelectronic properties for specific light technologies and applications. For example, the structure and composition of NAA can be judiciously engineered to align photonic and electronic band gaps to maximize photon-atom interactions. Optoelectronic engineering can in turn boost the generation of charge carriers to drive distinct processes and reactions by harnessing a range of light-matter interactions such as slow light, light recirculation and confinement, hybrid plasmonicphotonic modes, and omnidirectional inhibition of light reflection. Of all the disciplines reviewed in this perspective, it is apparent that photocatalysis has been the most developed to date. In particular, the combination of distinct forms of NAA-PCs with functional layers of titanium dioxide deposited via the sol-gel method and ALD have demonstrated that these composite photonic structures achieve superior photocatalytic performances to those of benchmark materials (e.g., nanoparticles) and analogue photonic systems (i.e., opal and inverted opal structures). The rational design of NAA-PC photocatalysts provides new opportunities to harness photons at the nanoscale to drive photodegradation processes of model organics with well-defined absorption bands in the UV and visible spectral ranges. Despite these advances, there remain fundamental and applied questions regarding the applicability of semiconductor-functionalized NAA-PCs to drive other photocatalytic reactions and processes in gas and liquid phases such as water splitting to generate hydrogen and oxygen gas, reduction of carbon dioxide to carbon monoxide, synthesis of ammonia, bacterial and viral disinfection, and degradation of emerging resilient toxicants such as perfluoroalkyl and polyfluoroalkyl substances. The use of other semiconductors and carbonbased materials is also to be explored in this field. NAA-based structures have also found applicability in solar cells as scaffolds for photovoltaic materials, radiative coolers, electrodes, and antireflective coatings. However, most of these applications used NAA featuring straight cylindrical nanopores with a homogeneous distribution of the effective refractive index. The combination of other forms of NAA-PCs would benefit sunlight harvesting in photovoltaic devices by enabling: i) precise alignment of photonic

bon is utilized.^[230] TiN NPs are also reported to improve water vapor generation through NAA structures.^[228,229] Kaur et al. systematically investigated the influence of NAA nanopore diameter and TiN sputter deposition thickness of this system. With increasing nanopore diameter, the hydrophilicity of the membrane increased, whereby water transport through the pores gets more effective. Regarding photothermal applications, NAA membranes with 300 nm pore diameter coated by 80 nm TiN showed the highest performance. Illumination of such TiN NP functionalized membrane raised its surface temperature, making it possible to reach a VGE of 92%. Another publication by Traver et al. reported a VGE of 78% for TiN NP decorated NAA.^[228] In that study, the NPs were drop-casted onto one NAA membrane surface while vacuum was applied on the opposite side to soak NPs into the pores. This study also investigated NPs of zirconium nitride (ZrN) and hafnium nitride (HfN) as plasmonic materials and could correlate the VGE to the absorptivity of the respective structure (Figure 15c). ZrN-functionalized NAA structures featured a VGE of 88%, whereas it was 95% for HfN. Correspondingly, the water surface temperate increased to 40.5, 41.0, and 49.7 °C and evaporation rates were $1.1\pm0.05,$ $1.27\pm0.04,~{\rm and}~1.36\pm0.03~{\rm kg}\,{\rm m}^{-2}\,{\rm h}^{-1}$ for TiN, ZrN, and HfN at a material loading of 2.5 g ${\rm m}^{-2},$ respectively. Wei et al. also demonstrated that an NAA-PC structure can reduce the IR reflection of a copper-nickel functionalized membrane for solar thermal absorption purposes (Figure 15d).^[224] The NAA-PCs were produced via pulse-like anodization and copper-nickel composite NPs were electrodeposited into the nanopores. This composite material served as a solar heat absorption layer featuring a high absorptivity. The PC geometry could be tuned to significantly lower IR reflection at the structure's surface to further improve the solar thermal absorption properties. Another raising application of NAA-PC technology across solar-to-thermal energy conversion is sky radiative cooling systems. In a pioneering study, Fu et al. used NAA-FPIs as a passive radiative cooling optical coating.^[232] The structure of NAA films was optimized to achieve high absorbance with nearly no loss in the far-IR atmospheric window. The authors reported a cooling power density for this system in the range of 64 W m^{-2} at ambient temperature and 70% humidity under a sunlight radiance of AM1.5. The NAA-FPI films were capable of reducing the temperature to 2.6 °C below the ambient temperature of air. In a similar study, Liu et al. developed a composite optical film with NAA-FPIs filled with silica nanoparticles.^[232] The resultant film technology is capable of reducing the temperature to 8.9 and 8.4 °C below the ambient air temperatures at night and day, respectively. Despite these advances, there remains a broad range of opportunities to integrate NAA-based PC structures for solarto-thermal energy conversion processes. To date, most of these proof-of-concept studies have focused on NAA as a template to nanostructure thermo-responsive materials and enhance their performance by increasing optical absorption and minimizing reflection. However, the integration of NAA-PC structures such as DBRs and µQVs would provide new opportunities to harness other optical phenomena such as slow photons and light confinement. It is our opinion that such systems integrating

by a factor of 1000 compared to direct seawater desalination

when an NAA membrane functionalized with silver NPs and car-



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and electronic bandgaps; ii) more efficient forms of light-matter interactions to increase the frequency of photon-to-electron conversion rates through strong light confinement or multiple Bragg scattering; iii) reduction of the recombination rate of charge carriers by nanostructuring of p- and n-type semiconductors to minimize exciton length using interdigitated configurations. Additionally, the integration of other optical phenomena such as surface plasmons and hybrid plasmonic-photonic modes could further boost photon-to-electron transitions by strongly localizing incident electromagnetic fields within specific spectral windows. Similarly, photoelectrocatalysis systems integrating NAA structures have focused on using these as templates or scaffolds to grow semiconductor nanoparticles, nanotubes, and nanowires, and exploiting the resultant composite materials to maximize electric-field driven photocatalytic processes. However, the function of NAA in these systems so far has been passive. If we consider the promising performances reported for semiconductor NAA-PC systems in photocatalysis and the similarities between photocatalysis and photoelectrocatalysis, it is reasonable to infer that the incorporation of NAA-PC structures could provide a new degree of efficiency in these systems by maximizing the collection photons of specific energies through structurally engineered light-matter interactions. Distinct forms of NAA-PC structures have also found promising applicability in solar-to-thermal energy conversion systems. Particularly, the use of NAA in combination with semiconductor coatings and plasmonic structures have made it possible to harness localized surface plasmon resonances to increase the local temperature and maximize conversion of sunlight photons into heat energy. Nevertheless, other controllable forms of hybrid plasmonic-photonic modes such as Tamm plasmons remain unexplored. In summary, all studies mentioned in this perspective indicate that NAA-PCs are a promising platform technology for sunlight harvesting applications. But despite some progresses, this field is at its early development stages and there remain many fundamental and applied questions regarding the integrability of these photonic structures into functional systems for sunlight technologies. Developments in the field have focused on NAA-based structures featuring straight nanopores, which are the most basic form of photonic crystal structure. However, advances in pulse-like anodization have realized novel forms of NAA-PCs, which have already demonstrated superior performances than that of analogue systems in specific applications such as photocatalysis. Additionally, strategies aiming at creating novel hybrid NAA structures might be of special interest due to their potential to attain more flexible sunlight harvesting capabilities. It is also important to note that NAA-PCs still suffer from intrinsic constraints such as a low refractive index, which requires NAA-PCs to have critical thicknesses above those of thin film technologies. As this perspective indicates, NAA-PCs are also compatible with additive manufacturing, which makes it possible to engineer unique photonic crystal heterostructures in combination with opal and inverted opal photonic crystals, nanoporous metals, and 3D-printed structures. Based on all the evidence outlined throughout this perspective, it is our opinion that this is just the beginning, and we remain strongly convinced that there is still plenty of room to spread the applicability of this iconic technology across sunlight harvesting applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

light-matter interactions, nanoporous anodic alumina, photonic crystals, photon-to-electron conversion, sunlight harvesting, surface functionalization

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- United Nations, Department of Economic and Social Affairs, Population Division, World Population Prospects 2019: Highlights (ST/ESA/SER.A/423), 2019.
- [2] S. Suresh, Nature 2012, 490, 337.
- [3] D. R. Myers, Fundamentals of Solar Radiation, CRC Press, Boca Raton, FL 2013, pp. 1–13.
- [4] M. Stolterfoht, A. Armin, S. Shoaee, I. Kassal, P. Burn, P. Meredith, Nat. Commun. 2016, 7, 11944.
- [5] D. Bartesaghi, I. del Carmen Pérez, J. Kniepert, S. Roland, M. Turbiez, D. Neher, L. J. A. Koster, *Nat. Commun.* 2014, *6*, 7083.
- [6] X. Liu, P. R. Coxon, M. Peters, B. Hoex, J. M. Cole, D. J. Fray, Energy Environ. Sci. 2014, 7, 3223.
- [7] B. Oregan, M. Grätzel, Nature 1991, 353, 737.
- [8] Y.-Z. Zheng, X. Tao, Q. Hou, D.-T. Wang, W.-L. Zhou, J.-F. Chen, Chem. Mater. 2011, 23, 3.
- [9] S. K. Cushing, N. Wu, J. Phys. Chem. Lett. 2016, 7, 666.
- [10] D. D. Tune, J. G. Shapter, Energy Environ. Sci. 2013, 6, 2572.
- [11] C. F. Guo, T. Sun, F. Cao, Q. Liu, Z. Ren, Light: Sci. Appl. 2014, 3, 161.
- [12] M. T. Sajjad, A. Ruseckas, D. W. Samuel, Matter 2020, 3, 341.
- [13] a) E. Yablonovitch, Phys. Rev. Lett. 1987, 58, 2059; b) S. John, Phys. Rev. Lett. 1987, 58, 2486.
- [14] S. Y. Lim, C. S. Law, L. Liu, M. Markovic, C. Hedrich, R. H. Blick, A. D. Abell, R. Zierold, A. Santos, *Catalysts* **2019**, *9*, 988.
- [15] a) H. Masuda, K. Fukuda, Science 1995, 268, 1466; b) H. Masuda,
 F. J. Hasegwa, Electrochem. Soc. 1997, 144, L127; c) H. Masuda,
 K. Yada, A. Osaka, Jpn. J. Appl. Phys. 1998, 37, L1340;
 d) O. Jessensky, F. Müller, U. Gösele, Appl. Phys. Lett. 1998, 72, 1173.
- [16] a) W. Lee, J.-S. Park, Chem. Rev. 2014, 114, 7487; b) G. D. Sulka, in Nanostructured Materials in Electrochemistry, Wiley-VCH Verlag, Hoboken, NJ 2008, pp. 1–116.
- [17] A. Santos, J. Mater. Chem. C 2017, 5, 5581.
- [18] a) W. Lee, R. Ji, U. Gösele, K. Nielsch, Nat. Mater. 2006, 5, 741;
 b) W. Lee, R. Scholz, U. Gösele, Nano Lett. 2008, 8, 2155;

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c) K. Schwirn, W. Lee, R. Hillebrand, M. Steinhart, K. Nielsch, U. Gösele, ACS Nano 2008, 2, 302; d) W. Lee, K. Schwirn, M. Steinhart, E. Pippel, R. Scholz, U. Gösele, Nat. Nanotechnol. 2008, 3, 234; e) W. Lee, J. C. Kim, U. Gösele, Adv. Funct. Mater. 2010, 20, 21; f) W. Lee, J. C. Kim, Nanotechnology 2010, 21, 485304.

- [19] a) B. Wang, G. T. Fei, M. Wang, M. G. Kong, L. D. Zhang, Nanotechnology 2007, 18, 365601; b) A. Santos, J. H. Yoo, C. V. Rohatgi, T. Kumeria, Y. Wang, D. Losic, Nanoscale, 2016, 8, 1360; c) S. E. Kushnir, T. Y. Pchelyakova, K. S. Napolskii, J. Mater. Chem. C 2018, 6, 12192; d) S. Y. Lim, C. S. Law, L. Jiang, L. K. Akosta, L. F. Marsal, A. D. Abell, A. Santos, ACS Appl. Nano Mater. 2020, 3, 12115; e) L. K. Akosta, F. Berto-Rosello, E. Xifré-Pérez, A. Santos, J. Ferré-Borrull, L. F. Marsal, ACS Appl. Mater. Interfaces 2019, 11, 3360; f) C. S. Law, S. Y. Lim, L. Liu, A. D. Abell, L. F. Marsal, A. Santos, Nanoscale 2020, 12, 9404.
- [20] a) P. Yan, G.-T. Fei, H. Li, G.-L. Shang, B. Wu, L.-D. Zhang, Chin. J. Chem. Phys. 2014, 27, 121; b) J. Lee, K. Bae, G. Kang, M. Choi, S. Baek, D.-S. Yoo, C.-W. Lee, K. Kim, RSC Adv. 2015, 5, 71770; c) Y. Wang, Y. Chen, T. Kumeria, F. Ding, A. Evdokiou, D. Losic, A. Santos, ACS Appl. Mater. Interfaces 2015, 7, 9879; d) G. L. Shang, G. T. Fei, L. D. Zhang, J. Phys. D: Appl. Phys. 2015, 48, 435304; e) C. S. Law, S. Y. Lim, A. D. Abell, L. M. Marsal, A. Santos, Nanoscale 2018, 10, 14139; f) C. S. Law, S. Y. Lim, R. M. Macalincag, A. D. Abell, A. Santos, ACS Appl. Nano Mater. 2018, 1, 4418; g) Y.-Y. An, J. Wang, W.-M. Zhou, H.-X. Jin, J.-F. Li, Wang, C.-W. Superlattice. Microst. 2018, 119. 1; h) S. E. Kushnir, T. Y. Komarova, K. S. Napolskii, J. Mater. Chem. C 2020, 8, 3991; i) L. K. Acosta, C. S. Law, S. Y. Lim, A. D. Abell, L. F. Marsal, A. Santos, ACS Appl. Mater. Interfaces 2021, 13, 14394.
- [21] a) W. J. Zheng, G. T. Fei, B. Wang, Z. Jin, L. D. Zhang, Mater. Lett.
 2009, 63, 706; b) W. J. Zheng, G. T. Fei, B. Wang, L. D. Zhang, Nanoscale Res. Lett. 2009, 4, 665; c) Y. Su, G. T. Fei, Y. Zhang, P. Yan, H. Li, G. L. Shang, L. D. Zhang, Mater. Lett. 2011, 65, 2693; d) G. D. Sulka, K. Hnida, Nanotechnology 2012, 23, 075303; e) J. Martín, M. Martín-González, J. F. Fernández, O. Caballero-Calero, Nat. Commun. 2014, 5, 5130; f) L. Yisen, C. Yi, L. Zhiyuan, H. Xing, L. Yi, Electrochem. Commun. 2011, 13, 1336; g) Y. Chen, A. Santos, Y. Wang, T. Kumeria, C. Wang, J. Li, D. Losic, Nanoscale 2015, 7, 7770; h) Y. Chen, A. Santos, Y. Wang, T. Kumeria, J. Li, C. Wang, D. Losic, ACS Appl. Mater. Interfaces 2015, 7, 19816.
- [22] a) A. Santos, T. Pereira, C. S. Law, D. Losic, *Nanoscale* 2016, *8*, 14846;
 b) L. Liu, S. Y. Lim, C. S. Law, B. Jin, A. D. Abell, G. Ni, A. Santos, *ACS Appl. Mater. Interfaces* 2020, *12*, 57079.
- [23] a) C. S. Law, S. Y. Lim, A. D. Abell, N. H. Voelcker, A. Santos, Nanomaterials 2018, 8, 788; b) A. Santos, C. S. Law, T. Pereira, D. Losic, Nanoscale 2016, 8, 8091; c) H. Masuda, M. Yamada, F. Matsumoto, S. Yokoyama, S. Mashiko, M. Nakao, K. Nishio, Adv. Mater. 2006, 18, 213; d) S. Yokoyama, T. Nakahama, S. Mashiko, M. Nakao, M. Yamada, K. Nishio, H. Masuda, Appl. Phys. Lett. 2005, 87, 191101.
- [24] H. Masuda, M. Ohya, H. Asoh, M. Nakao, M. Nohtomi, T. Tamamura, Jpn. J. Appl. Phys. 1999, 38, L1403.
- [25] H. Masuda, M. Ohya, K. Nishio, H. Asoh, M. Nakao, M. Nohtomi, A. Yokoo, T. Tamamura, *Jpn. J. Appl. Phys.* **2000**, *39*, L1039.
- [26] H. Masuda, M. Ohya, H. Asoh, K. Nishio, Jpn. J. Appl. Phys. 2001, 40, L1217.
- [27] W. Lee, R. Scholz, U. Gösele, Nano Lett. 2008, 8, 2155.
- [28] K. Schwirn, W. Lee, R. Hillebrand, M. Steinhart, K. Nielsch, U. Gösele, ACS Nano 2008, 2, 302.
- [29] W. Lee, J. C. Kim, Nanotechnolgy 2010, 21, 485304.
- [30] J. Martin, M. Martín-González, J. Francisco Fernandez, O. Caballero-Calero, Nat. Commun. 2014, 5, 5130.



- [31] W. J. Zheng, G. T. Fei, B. Wang, L. D. Zhang, Nanoscale Res. Lett. 2009, 4, 665.
- [32] G. L. Shang, G. T. Fei, Y. Zhang, P. Yan, S. H. Xu, H. M. Ouyang,
 L. D. Zhang, *Sci. Rep.* 2014, *4*, 3601.
- [33] Y. Su, G. T. Fei, Y. Zhang, H. Li, P. Yan, G. L. Shang, L. D. Zhang, J. Opt. Soc. Am. B 2011, 28, 2931.
- [34] Z.Y. Ling, S.S. Chen, X. Hu, Y. Li, Chin. Phys. Lett. 2009, 26, 054213.
- [35] M. M. Rahman, L. F. Marsal, J. Pallarès, J. Ferré-Borrull, ACS Appl. Mater. Interfaces 2013, 5, 13375.
- [36] T. Kumeria, A. Santos, M. M. Rahman, J. Ferré-Borrull, L. F. Marsal, D. Losic, ACS Photonics 2014, 1, 1298.
- [37] G. Wang, J. Wang, S-Y. Li, J-.W. Zhang, C-.W. Wang, Superlattices Microstruct. 2015, 86, 546.
- [38] S. Y. Lim, C. S. Law, L. Liu, M. Markovic, A. D. Abell, A. Santos, Catal. Sci. Technol. 2019, 9, 3158.
- [39] S. Zhang, Q. Xu, S. Feng, C. Sun, Q. Peng, T. Lan, Opt. Mater. 2019, 98, 109488.
- [40] E. Bialek, M. Włodarski, M. Norek, Materials 2020, 13, 3185.
- [41] E. Bialek, M. Włodarski, M. Norek, Materials 2020, 13, 5622.
- [42] Y. Liu, Y. Chang, Z. Ling, X. Hu, Y. Li, Electrochem. Commum. 2011, 13, 1336.
- [43] Y. Chen, A. Santos, Y. Wang, T. Kumeria, D. Ho, J. Li, C. Wang, D. Losic, *Sci. Rep.* **2015**, *5*, 12893.
- [44] Y. Chen, A. Santos, D. Ho, Y. Wang, T. Kumeria, J. Li, C. Wang, D. Losic, *Electrochim. Acta* **2015**, *174*, 672.
- [45] C. S. Law, S. Y. Lim, A. Santos, Sci. Rep. 2018, 8, 4642.
- [46] V. S. Gorelik, S. O. Klimonsky, V. V. Filatov, K. S. Napolskii, Opt. Spectrosc. 2016, 120, 534.
- [47] S. Y. Lim, C. S. Law, M. Markovic, L. F. Marsal, N. H. Voelcker, A. D. Abell, A. Santos, ACS Appl. Energy Mater. 2019, 2, 1169.
- [48] K. S. Napolskii, A. A. Noyan, S. E. Kushnir, Opt. Mater. 2020, 109, 110317.
- [49] S. Y. Lim, C. Hedrich, L. Jiang, C. S. Law, M. Chirumamilla, A. D. Abell, R. H. Blick, R. Zierold, A. Santos, ACS Catal. 2021, 11, 12947.
- [50] E. Lorenzo, C. J. Oton, N. E. Capuj, M. Ghulinyan, D. Navarro-Urrios, Z. Gaburro, L. Pavesi, Appl. Opt. 2005, 44, 5415.
- [51] P. Yan, G. T. Fei, G. L. Shang, B. Wu, L. D. Zhang, J. Mater. Chem. C 2013, 1, 1659.
- [52] T. Kumeria, M. M. Rahman, A. Santos, J. Ferré-Borrull, L. F. Marsal, D. Losic, Anal. Chem. 2014, 86, 1837.
- [53] T. Kumeria, M. M. Rahman, A. Santos, J. Ferré-Borrull, L. F. Marsal, D. Losic, ACS Appl. Mater. Interfaces 2014, 6, 12971.
- [54] G. Macias, J. Ferré-Borrull, J. Pallarès, L. F. Marsal, Nanoscale Res. Lett. 2014, 9, 315.
- [55] A. Santos, C. S. Law, D. C. L. Wong, T. Pereira, D. Losic, Nanoscale 2016, 8, 18360.
- [56] M. Nemati, A. Santos, C. S. Law, D. Losic, Anal. Chem. 2016, 88, 5971.
- [57] C. Eckstein, C. S. Law, S. Y. Lim, S. Kaur, T. Kumeria, J. Ferré-Borrull, A. D. Abell, L. F. Marsal, A. Santos, J. Mater. Chem C 2019, 7, 12278.
- [58] S. Y. Lim, C. S. Law, M. Markovic, J. K. Kirby, A. D. Abell, A. Santos, ACS Appl. Mater. Interfaces 2018, 10, 24124.
- [59] P. Kapruwan, L. K. Acosta, J. Ferré-Borrull, L. F. Marsal, Nanomaterials 2021, 11, 730.
- [60] L. K. Acosta, C. S. Law, A. Santos, J. Ferré-Borrull, L. F. Marsal, APL Photonics 2022, 7, 026108.
- [61] S. Gunenthiran, J. Wang, W. Zhao, C. S. Law, S. Y. Lim, J. A. McInnes, H. Ebendorff-Heidepriem, A. D. Abell, Z. T. Alwahabi, A. Santos, ACS Photonics 2022, 9, 1226.
- [62] S. Sukarno, C. S. Law, A. Santos, Nanoscale 2017, 9, 7541.
- [63] Y.-Y. An, J. Wang, W.-M. Zhou, H.-X. Jin, J.-F. Li, C.-W. Wang, Superlattices Microstruct. 2018, 119, 1.

www.advancedsciencenews.com

- [64] L. Liu, S. Y. Lim, C. S. Law, B. Jin, A. D. Abell, G. Ni, A. Santos, J. Mater. Chem. A 2019, 7, 22514.
- [65] X-.G. Wang, J. Wang, J.-F. Li, D-.W. Tao, W-.M. Zhou, Y. Li, C-.W. Wang, Opt. Mater. 2020, 105, 109982.
- [66] C. S. Law, A. Santos, M. Nemati, D. Losic, ACS Appl. Mater. Interfaces 2016, 8, 13542.
- [67] S. Y. Lim, C. S. Law, L. F. Marsal, A. Santos, Sci. Rep. 2018, 8, 9455.
- [68] S. E. Kushnir, K. S. Napolskii, Mater. Des. 2018, 144, 140.
- [69] V. S. Gorelik, P. P. Sverbil, V. V. Filatov, D. Bi, G. T. Fei, S. H. Xu, Photonics Nanostruct. 2018, 32, 6.
- [70] S. Abbasimofrad, M. A. Kashi, M. Noormohammadi, A. Ramazani, J. Phys Chem. Solids 2018, 118, 221.
- [71] A. I. Sadykov, S. E. Kushnir, I. V. Roslyakov, A. E. Baranchikov, K. S. Napolskii, *Electrochem. Commun.* **2019**, *100*, 104.
- [72] S. Zhang, Q. Xu, S. Feng, C. Sun, Q. Peng, T. Lan, Opt. Mater. 2019, 987, 109488.
- [73] L. K. Acosta, F. Bertó-Roselló, E. Xifre-Perez, C. S. Law, A. Santos, J. Ferré-Borrull, L. F. Marsal, ACS Appl. Mater. Interfaces 2020, 12, 19778.
- [74] M. Ashurov, V. Gorelik, K. Napolskii, S. Klimonsky, Photonic Sens. 2020, 10, 147.
- [75] C. Sun, S. Hao, Z. Wang, Q. Xu, Y. Wang, Q. Peng, T. Lan, Opt. Mater. 2020, 104, 109937.
- [76] L. Liu, S. Y. Lim, C. S. Law, L. K. Acosta, B. Jin, A. D. Abell, L. F. Marsal,
- G. Ni, A. Santos, *Microporous Mesoporous Mater.* 2021, 312, 110770.
 [77] H. Wei, Q. Xu, D. Chen, M. Chen, M. Chang, X. Ye, *Opt. Mater.* 2021, 122, 111722.
- [78] X.-G. Wang, J. Wang, Z.-J. Jiang, D.-W. Tao, X.-Q. Zhang, C.-W. Wang, *Appl. Surf. Sci.* 2021, 544, 148881.
- [79] H. N. Q. Tran, N. D. A. Le, Q. N. Le, C. S. Law, S. Y. Lim, A. D. Abell, A. Santos, ACS Appl. Mater. Interfaces 2021, 14, 22747.
- [80] S. Canulescu, K. Rechendorff, C. N. Borca, N. C. Jones, K. Bordo, J. Schou, L. Pleth Nielsen, S. V. Hoffmann, R. Ambat, *Appl. Phys. Lett.* 2014, 104, 121910.
- [81] E. O. Filatova, A. S. Konashuk, J. Phys. Chem. C 2015, 119, 20755.
- [82] C. A. Gueymard, Sol. Energy 2004, 76, 423.
- [83] L. L. Hench, J. O. N. K. West, Chem. Rev. 1990, 90, 33.
- [84] J. Livage, Curr. Opin. Solid State Materials Sci. 1997, 2, 132.
- [85] A. C. Pierre, in *Introduction to Sol-Gel Processing*, 2nd ed. Springer Nature Cham, Switzerland 2020.
- [86] O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Ravinovich, S. Sampath, *Chem. Mater.* **1997**, *9*, 2354.
- [87] J. Zarzycki, J. Sol-Gel Sci. Technol. 1997, 8, 17.
- [88] J. D. Mackenzie, Mater. Sci. 1988, 100, 162.
- [89] Y. D. Gamburg, G. Zangari, in Theory and Practice of Metal Electrodeposition. Springer, New York 2011.
- [90] D. Lincot, Thin Solid Films 2005, 487, 40.
- [91] F. Nasirpouri, in *Electrodeposition of Nanostructured Materials*. Springer, New York **2017**.
- [92] L. P. Bicelli, B. Bozzini, C. Mele, L. D'Urzo, Int. J. Electrochem. Sci. 2008, 3, 356.
- [93] W. J. Stepniowski, M. Moneta, K. Karczewski, M. Michalska-Domanska, T. Czujko, J. M. C. Mol, J. G. Buijnsters, J. Electroanal. Chem. 2018, 809, 59.
- [94] M. Kemell, V. Pore, J. Tupala, M. Ritala, M. Leskelä, Chem. Mater. 2007, 19, 1816.
- [95] S. Haschke, D. Pankin, Y. Petrov, S. Bochmann, A. Manshina, J. Bachmann, *ChemSusChem* 2017, 10, 3644.
- [96] S. Haschke, Y. Zhuo, S. Schlicht, M. K. S. Barr, R. Kloth, M. E. Dufond, L. Santinacci, J. Bachmann, Adv. Mater. Interfaces 2019, 6, 1801432.
- [97] L. K. Tan, A. S. Maria Chong, X. S. Eric Tang, H. Gao, J. Phys. Chem. C 2007, 111, 4964.

- [98] S. Patra, S. Bruyère, P. L. Taberna, F. Sauvage, ECS Electrochem. Lett. 2014, 3, 16.
- [99] B. Endrödi, E. Kecsenovity, K. Rajeshwar, C. Janáky, ACS Appl. Energy Mater. 2018, 1, 851.
- [100] A. Lahiri, G. Pulletikurthi, F. Endres, Front. Chem. 2019, 7, 85.
- [101] M. Selvam, Trans. Inst. Met. Finish. 2010, 88, 198.
- [102] L. Tamasauskaite-Tamasiunaite, Y. Dordi, E. Norkus,
 I. Stankeviciene, A. Jagminiene, A. Naujokaitis, L. Tumois,
 V. Buzas, L. Maciulis, *Materials* 2021, *14*, 1893.
- [103] M. Boehme, E. Ionescu, G. Fu, W. Ensinger, *Beilstein J. Nanotechnol.* 2011, 2, 119.
- [104] M. B. Sassin, A. N. Mansour, K. A. Pettigrew, D. R. Rolison, J. W. Long, ACS Nano 2010, 4, 4505.
- [105] W. Mindt, J. Electrochem. Soc. 1971, 118, 93.
- [106] W. Mindt, J. Electrochem. Soc. 1970, 117, 615.
- [107] A. Johansson, J. Appl. Phys. 2004, 96, 5189.
- [108] S. Z. Chu, H. Kawamura, M. Mori, J. Electrochem. Soc. 2008, 155, D414.
- [109] S-.H. Zhang, Z-.X. Xie, Z-.Y. Jiang, X. Xu, J. Xiang, R-.B. Huang, L-.S. Zheng, *Chem. Commun.* **2004**, 1106.
- [110] W. Wang, N. Li, X. Li, W. Geng, S. Qiu, Mater. Res. Bull. 2006, 41, 1417.
- [111] C. Mu, J-.P. Zhang, D. Xu, Nanotechnology 2009, 21, 015604.
- [112] K. Liu, P. R. Ohodnicki, Z. Kong, S. S. Lee, H. Du, Nanotechnology 2019, 30, 405704.
- [113] Y. Yu, K. Kant, J. G. Shapter, J. Addai-Mensah, D. Losic, Microporous Mesoporous Mater. 2012, 153, 131.
- [114] M. Jinsenji, A. Tajiri, Y. Nishimura, M. Bachman, G-.P. Li, O. Takai, J. Electrochem. Soc. 2019, 166, D470.
- [115] B. Celen, D. Ekiz, E. Piskin, G. Demirel, J. Mol. Catal. A: Chem. 2011, 350, 97.
- [116] M. Perera, L. A. Wijenayaka, K. Siriwardana, D. Dahanayake, K. M. Nalin de Silva, RSC Adv. 2020, 10, 29594.
- [117] B. Window, Surf. Coat. Technol. 1995, 71, 93.
- [118] D. Depla, S. Mahieu, J. E. Greene, in *Handbook of Deposition Technologies for Films and Coatings*, (Ed: P. M. Martin) 3rd ed., Vol. 13, Elsevier, Amsterdam 2010, pp. 253.
- [119] V. S. Smentkowski, Prog. Surf. Sci. 2000, 64, 1.
- [120] P. J. Kelly, R. D. Arnell, Vacuum 2000, 56, 159.
- [121] D. Lou, A. B. Xu, Y. Fang, M. Cai, K. Lv, D. Zhang, Z. Wang, Y. Huang, C. Li, L. He, *ChemNanoMat* 2021, 7, 1008.
- [122] K. Bae, J. Lee, G. Kang, D. S. Yoo, C. W. Lee, K. Kim, RSC Adv. 2015, 5, 103052.
- [123] J. Xue, Z.K. Zhou, Z. Wei, R. Su, J. Lai, J. Li, C. Li, T. Zhang, X-.H. Wang, Nat. Commun. 2015, 6, 8906.
- [124] Y. Yu, Z. Ji, S. Zu, B. Du, Y. Kang, Z. Li, Z. Zhou, K. Shi, Z. Fang, Adv. Funct. Mater. 2016, 26, 6394.
- [125] C. V. Manzano, D. Ramos, L. Pethö, G. Bürki, J. Michler, L. Philippe, J. Phys. Chem. C 2018, 122, 957.
- [126] X. Zhu, C. Zhao, W. Zhang, B. Zhang, M. Sun, X. Chen, V. I. Belotelov, Y. Song, *Coatings* **2021**, *11*, 1123.
- [127] L. Feng, P. Huo, Y. Liang, T. Xu, Adv. Mater. 2020, 32, 1903787.
- [128] S. M. George, Chem. Rev. 2010, 110, 111.
- [129] V. Miikkulainen, M. Leskelä, M. Ritala, R. L. Puurunen, J. Appl. Phys. 2013, 113, 021301.
- [130] R. L. Puurunen, J. Appl. Phys. 2005, 97, 121301.
- [131] V. Cremers, R. L. Puurunen, J. Dendooven, Appl. Phys. Rev. 2019, 6, 021302.
- [132] M. Knez, K. Nielsch, L. Niinistö, Adv. Mater. 2007, 19, 3425.
- [133] M. Leskelä, M. Ritala, Thin Solid Films 2002, 409, 138.
- [134] L. K. Tan, M. K. Kumar, W.W An, H. Gao, ACS Appl. Mater. Interfaces 2010, 2, 498.



www.advancedsciencenews.com

- [135] M. Kemell, E. Härkönen, V. Pore, M. Ritala, M. Leskelä, Nanotechnology 2010, 21, 035301.
- [136] W. T. Chang, Y. C. Hsueh, S. H. Huang, K. I. Liu, C. C. Kei, T. P. Perng, J. Mater. Chem. A 2013, 1, 1987.
- [137] Y. C. Liang, C. C. Wang, C. C. Kei, Y. C. Hsueh, W. H. Cho, T. P. Perng, J. Phys. Chem. C 2011, 115, 9498.
- [138] H-.S. Chen, P-.H. Chen, S-.H. Huang, T-.P. Perng, Chem. Commun. 2014, 50, 4379.
- [139] M. Barr, L. Assaud, Y. Wu, J. Bachmann, L. Santinacci, ECS Trans. 2015, 66, 119.
- [140] M. K. S. Barr, L. Assaud, Y. Wu, C. Laffon, P. Parent, J. Bachmann, L. Santinacci, *Electrochim. Acta* **2015**, *179*, 504.
- [141] T. R. B. Foong, Y. Shen, X. Hu, A. Sellinger, Adv. Funct. Mater. 2010, 20, 1390.
- [142] A. B. F. Martinson, J. W. Elam, J. T. Hupp, M. J. Pellin, Nano Lett. 2007, 7, 2183.
- Y. Wu, L. Assaud, C. Kryschi, B. Capon, C. Detavernier, L. Santinacci, J. Bachmann, J. Mater. Chem. A 2015, 3, 5971.
- [144] K. Pitzschel, J. M. M. Moreno, J. Escrig, O. Albrecht, K. Nielsch, J. Bachmann, ACS Nano 2009, 3, 3463.
- [145] L. Sun, G. Yuan, L. Gao, J. Yang, M. Chhowalla, M. H. Gharahcheshmeh, K. K. Gleason, Y. S. Choi, B. H. Hong, Z. Liu, Nat. Rev. Methods Primers 2021, 1, 5.
- [146] W. B. Wang, N. N. Chang, T. A. Codding, G. S. Girolami, J. R. Abelson, J. Vac. Sci. Technol., A 2014, 32, 51512.
- [147] X. H. Wang, T. Akahane, H. Orikasa, T. Kyotani, Y. Y. Fu, Appl. Phys. Lett. 2007, 91, 11908.
- [148] M. M. Tavakoli, A. Waleed, L. Gu, D. Zhang, R. Tavakoli, B. Lei,
 W. Su, F. Fang, Z. Fan, *Nanoscale* 2017, *9*, 5828.
- [149] A. Waleed, M. M. Tavakoli, L. Gu, S. Hussain, D. Zhang, S. Poddar,
 Z. Wang, R. Zhang, Z. Fan, *Nano Lett.* 2017, *17*, 4951.
- [150] Z. Fan, D. Dutta, C-.J. Chien, H-.Y. Chen, E.C. Brown, P-.C. Chang, J.G. Lu, Appl. Phys. Lett. 2006, 89, 213110.
- [151] J. Zhang, L. Jin, S. Li, J. Xie, F. Yang, J. Duan, T.-H. Shen, H. Wang, J. Mater. Sci. Technol. 2015, 31, 634.
- [152] S. Dhahri, E. Fazio, M. Ghrib, F. Neri, K. El Khirouni, H. Ezzaouia, J. Alloys Compd. 2017, 699, 991.
- [153] M. Ghrib, M. Gaidi, T. Ghrib, N. Khedher, M. Ben Salam, H. Ezzaouia, *Appl. Surf. Sci.* 2011, 257, 9129.
- [154] Y-.S. Kim, V. P. Godbole, J-.H. Cho, G. Khang, H-.S. Shin, Curr. Appl. Phys. 2006, 6, 58.
- [155] W-.J. Ho, P-.Y. Cheng, K-.Y. Hsiao, Appl. Surf. Sci. 2015, 354, 25.
- [156] W-.J. Ho, K-.Y. Hsiao, C-.H. Hu, T-.W. Chuang, J-.J. Liu, Y-.H. Chen, *Thin Solid Films* **2017**, *631*, 64.
- [157] H. Zhao, M. Zhou, L. Wen, Y. Lei, Nano Energy 2015, 13, 790.
- [158] Q. Xu, G. Meng, F. Han, Prog. Mater. Sci. 2018, 95, 243.
- [159] M. Pérez-Page, E. Yu, J. Li, M. Rahman, D. M. Dryden, R. Vidu, P. Stroeve, Adv. Colloid Interface Sci. 2016, 234, 51.
- [160] P. H. Lu, K. Wang, Z. Lu, A. J. Lennon, S. R. Wenham, IEEE J. Photovoltaics 2013, 3, 143.
- [161] J. Cui, Z. Ouyang, Z. Hameiri, X. Wang, A. J. Lennon, IEEE J. Photovoltaics 2015, 5, 1020.
- [162] F. Qin, H. Zhang, C. Wang, J. Zhang, C. Guo, Opt. Commun. 2014, 331, 325.
- [163] F. F. Qin, H. M. Zhang, C. X. Wang, J. J. Zhang, C. Guo, Opt. Laser Technol. 2015, 75, 93.
- [164] L. Wu, H. Zhang, F. Qin, X. Bai, Z. Ji, D. Huang, Opt. Commun. 2017, 385, 205.
- [165] H. Li, L. Wu, H. Zhang, W. Dai, J. Hao, H. Wu, F. Ren, C. Liu, ACS Appl. Mater. Interfaces 2020, 12, 4081.
- [166] L. Zhou, Y. Tan, D. Ji, B. Zhu, P. Zhang, J. Xu, Q. Gan, Z. Yu, J. Zhu, Sci. Adv. 2016, 2, 1501227.
- [167] L. Li, Y. Liang, X. Zong, Y. Liu, Opt. Express 2020, 28, 695.

- [168] J. Dong, Y. Wang, Q. Wang, Y. Cao, Q. Han, W. Gao, Y. Wang, J. Qi, M. Sun, *Nanotechnology* **2022**, *33*, 135501.
- [169] C. K. Chung, K. T. Tu, C. Y. Chang, Y. C. Peng, Surf. Coat. Technol. 2019, 361, 170.
- [170] B. Najma, A. K. Kasi, J. Khan Kasi, A. Akbar, S. M. A. Bokhari, I. R. C. Stroe, *Appl. Surf. Sci.* 2018, 448, 104.
- [171] X. Zhang, L. Xie, S. Zhou, H. Zeng, J. Zeng, T. Liu, Q. Liang, M. Yan,
 Y. He, K. Liang, L. Zhang, P. Chen, L. Jiang, B. Kong, ACS Cent. Sci.
 2022, 8, 361.
- [172] T. Xiao, J. Ma, Z. Liu, B. Lu, J. Jiang, X. Nie, R. Luo, J. Jin, Q. Liu, W. Li, J. Zhai, J. Mater. Chem. A 2020, 8, 11275.
- [173] J. Gao, W. Guo, D. Feng, H. Wang, D. Zhao, L. Jiang, J. Am. Chem. Soc. 2014, 136, 12265.
- [174] N. Vogel, M. Retsch, C-.A. Fustin, A. Del Campo, U. Jonas, Chem. Rev. 2015, 115, 6265.
- [175] B. F. Winhard, S. Haugg, R. Blick, G. A. Schneider, K. P. Furlan, J. Colloid Interface Sci. 2021, 597, 137.
- [176] K. P. Furlan, T. Krekeler, M. Ritter, R. Blick, G. A. Schneider, K. Nielsch, R. Zierold, R. Janßen, Adv. Mater. Interfaces 2017, 4, 1700912.
- [177] K. P. Furlan, E. Larsson, A. Diaz, M. Holler, T. Krekeler, M. Ritter, A. Y. Petrov, M. Eich, R. Blick, G. A. Schneider, I. Greving, R. Zierold, R. Janßen, Appl. Mater. Today 2018, 13, 359.
- [178] M. Waleczek, J. Dendooven, P. Dyachenko, A. Y. Petrov, M. Eich, R. H. Blick, C. Detavernier, K. Nielsch, K. P. Furlan, R. Zierold, *Nanomaterials* **2021**, *11*, 1053.
- [179] R. J. Gehensel, R. Zierold, G. Schaan, G. Shang, A. Y. Petrov, M. Eich, R. Blick, T. Krekeler, R. Janssen, K. P. Furlan, *J. Eur. Ceram. Soc.* 2021, 41, 4302.
- [180] M. Iwai, T. Kikuchi, R. O. Suzuki, Sci. Rep. 2021, 11, 7240.
- [181] Y. Hu, Z. Wang, M. Zhang, S. Wang, S. Li, G. Chen, Nano Lett. 2021, 21, 250.
- [182] T. Zhang, H. Yang, in Handbook of Energy Efficiency in Buildings: A Life Cycle Approach, Vol. 1 (Eds: F. Asdrubali, U. Desideri), Butterworth-Heinemann, Oxford, UK 2019, Ch 7.
- [183] W. Yang, X. Li, D. Chi, H. Zhang, X. Liu, Nanotechnology 2014, 25, 482001.
- [184] M. P. Montero-Rama, A. Viterisi, J. Ferré-Borrull, L. F. Marsal, *Energy Sci. Eng.* 2021, 10, 30.
- [185] H-.C. Kwon, A. Kim, H. Lee, D. Lee, S. Jeong, J. Moon, Adv. Energy Mater. 2016, 6, 1601055.
- [186] H. Tang, Z. Zhou, S. Jiao, Y. Zhang, S. Li, D. Zhang, J. Zhang, J. Liu,
 D. Zhao, Sol. Energy Mater. Sol. Cells 2022, 235, 111498.
- [187] W. A. El-Said, M. Abdel-Shakour, A. M. Abd-Elnaiem, Mater. Lett. 2018, 222, 126.
- [188] X. Sheng, J. Liu, N. Coronel, A. M. Agarwal, J. Michel, L. C. Kimerling, IEEE Photonics Technol. Lett. 2017, 22, 1394.
- [189] K. Choi, Y. Yoon, J. Jung, C. W. Ahn, G. J. Lee, Y. M. Song, M. J. Ko,
 H. S. Lee, B. Kim, I-S. Kang, *Adv. Opt. Mater.* 2017, *5*, 1600616.
- [190] S. Dubey, J. N. Sarvaiya, B. Seshadri, *Energy Procedia* 2013, 33, 311.
 [191] P. Hacke, S. Spataru, K. Terwilliger, G. Perrin, S. Glick, S. Kurtz,
- J. Wohlgemuth, in *IEEE 42nd Photovoltaic Specialist Conf.*, Vol. 5 IEEE, Piscataway, NJ **2015**, pp. 1549–1553.
- [192] M. A. Fox, M. T. Dulay, Chem. Rev. 1993, 93, 341.
- [193] M. M. Kandy, V. G. Gaikar, Mater. Res. Bull. 2018, 102, 440.
- [194] B. I. Stefanov, B. S. Blagoev, L. Österlund, B. R. Tzaneva, G. V. Angelov, Symmetry 2021, 13, 1456.
- [195] X. Qu, D. Xie, L. Gao, L. Cao, F. Du, J. Mater. Sci. 2015, 50, 21.
- [196] Y. Liu, J. Lou, M. Ni, C. Song, J. Wu, N. P. Dasgupta, P. Tao,
 W. Shang, T. Deng, ACS Appl. Mater. Interfaces 2016, 8, 772.
- [197] Y. Liu, H. Meng, X. Yu, Y. Zhu, Y. Zhang, Mater. Technol. Adv. Func. Mater. 2015, 30, A84.
- [198] T. Baba, Nat. Photonics 2008, 2, 465.



www.advancedsciencenews.com

- [199] S. Kim, W. Choi, J. Phys. Chem. B 2005, 109, 5143.
- [200] E. Zarei, R. Ojani, J. Solid State Electrochem. 2017, 21, 305.
- [201] S. Zhong, Y. Xi, Q. Chen, J. Chen, S. Bai, Nanoscale 2020, 12, 5764.
- [202] G. G. Bessegato, T. T. Guaraldo, J. F. de Brito, M. F. Brugnera, M. V. B. Zanoni, *Electrocatalysis* 2015, 6, 415.
- [203] R. Inguanta, C. Sunseri, S. Piazza, Electrochem. Solid-State Lett. 2007, 10, 2.
- [204] N. Nasori, T. Dai, X. Jia, A. Rubiyanto, D. Cao, S. Qu, Z. Wang, Z. Wang, Y. Lei, J. Semicond. 2019, 40, 6.
- [205] N. Nasori, D. Cao, Z. Wang, U. Farahdina, A. Rubiyanto, Y. Lei, *Molecules* 2021, 26, 2900.
- [206] N. Nasori, A. Rubiyanto, E. Endarko, J. Phys. Conf. Ser. 2019, 1373, 012016.
- [207] P.-K. Hung, T.-H. Lin, M.-P. Houng, J. Electrochem. Soc. 2014, 161, D79.
- [208] A. Mao, G. Y. Han, J. H. Park, J. Mater. Chem. 2010, 20, 2247.
- [209] S. Vilayurganapathy, M. I. Nandasiri, A. G. Joly, P. Z. El-Khoury, T. Varga, G. Coffey, B. Schwenzer, A. Pandey, A. Kayani, W. P. Hess, S. Thevuthasan, *Appl. Phys. Lett.* 2013, 103, 161112.
- [210] M. J. Kang, C. W. Kim, Appl. Sci. Converg. Technol. 2020, 29, 200.
- [211] M. Lei, J. Liu, Y. Huang, Y. Dong, S. Zhou, H. Zhao, Z. Wang, M. Wu, Y. Lei, Z. Wang, *Nanotechnology* **2019**, *30*, 445403.
- [212] J. S. Santos, P. dos Santos Araújo, Y.B. Pissolitto, P.P. Lopes, A. P. Simon, M. de Souza Sikora, F. Trivinho-Strixino, *Materials* 2021, 14, 383.
- [213] H. Zhang, J. H. Kim, J. H. Kim, J. S. Lee, Adv. Funct. Mater. 2017, 27, 1702428.
- [214] S. Jiao, L. Liu, J. Wang, K. Ma, J. Lv, Small 2020, 16, 2001223.
- [215] S. Haschke, Y. Wu, M. Bashouti, S. Christiansen, J. Bachmann, ChemCatChem 2015, 7, 2455.
- [216] J. Gemmer, Y. Hinrichsen, A. Abel, J. Bachmann, J. Catal. 2012, 290, 220.

[217] Y. H. Chang, C. M. Liu, C. Chen, H. E. Cheng, Nanoscale Res. Lett. 2012, 7, 231.

www.solar-rrl.com

- [218] Y. Zhao, A. Dunn, J. Lin, D. Shi, in Novel Nanomaterials for Biomedical, Environmental and Energy Applications, Elsevier Inc., Amsterdam 2018, pp. 415.
- [219] P. Wang, Environ. Sci. Nano 2018, 5, 1078.
- [220] D. Shin, G. Kang, P. Gupta, S. Behera, H. Lee, A. M. Urbas, W. Park,
 K. Kim, Adv. Opt. Mater. 2018, 6, 1800317.
- [221] C. Zhang, H. Q. Liang, Z. K. Xu, Z. Wang, Adv. Sci. 2019, 6, 1900883.
- [222] S. L. Wu, H. Chen, H. L. Wang, X. Chen, H. C. Yang, S. B. Darling, Environ. Sci. Water Res. Technol. 2021, 7, 24.
- [223] H. Chen, S-.L. Wu, H-.L. Wang, Q-.Y. Wu, H-.C. Yang, Adv. Energy Sustain. Res. 2021, 2, 2000056.
- [224] H. Wei, H. Hu, M. Chang, Y. Zhang, D. Chen, M. Wang, Ceram. Int. 2017, 43, 12472.
- [225] S. Zhang, Z. Wu, Z. Liu, Y. Lv, Z. Hu, Energies 2022, 15, 1354.
- [226] D. Lee, I. Chae, O. Kwon, K-.H. Lee, C. Kim, S. Kim, T. Thundat, Appl. Phys. Lett. 2017, 110, 011901.
- [227] Y. Liu, H. Song, Z. Bei, L. Zhou, C. Zhao, B. S. Ooi, Q. Gan, Nano Energy 2021, 84, 105872.
- [228] E. Traver, R. A. Karaballi, Y. E. Monfared, H. Daurie, G. A. Gagnon, M. Dasog, ACS Appl. Nano Mater. 2020, 3, 2787.
- [229] M. Kaur, S. Ishii, S. L. Shinde, T. Nagao, Opt. InfoBase Conf. Pap. 2018, Part F125.
- [230] S. Cheng, S. Zhan, Z. Wu, G. Nie, S. Wu, J. Hu, J. Li, S. Hu, Y. Zhang, Y. Liu, J. Alloys Compd. 2019, 791, 380.
- [231] H. Gong, X. Liu, G. Liu, Z. Lin, X. Yu, L. Zhou, Nanophotonics 2020, 9, 1539.
- [232] J. Wang, C. S. Law, S. Gunenthiran, H. N. Q. Tran, K. N. Tran, S. Y. Lim, A. D. Abell, A. Santos, ACS Appl. Mater. Interfaces 2022, 14, 21181.
- [233] P. Yan, G. T. Fei, Y. Su, G. L. Shang, H. Li, B. Wu, L. D. Zhang, *Electrochem. Solid-State Lett.* **2011**, *15*, K23.



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- [1] Carina Hedrich, Davy Deduytsche, Robin R. Petit, Tobias Krekeler, Jun Peng, Martin Ritter, Jolien Dendooven, Christophe Detavernier, Robert H. Blick, and Robert Zierold. Tuning the Crystallization Temperature of Titanium Dioxide Thin Films by Incorporating Silicon Dioxide via Supercycle Atomic Layer Deposition. *Surfaces and Interfaces*, 57:105696, 2025.
- [2] Carina Hedrich, Robin R. Petit, Matthias M. Minjauw, Anna R. Burson, Christophe Detavernier, Jolien Dendooven, Robert H. Blick, and Robert Zierold. How Surface Treatments of Anodic Aluminum Oxide Alter the Photocatalytic Performance. in preparation, 2024.
- [3] Siew Yee Lim, Carina Hedrich, Lin Jiang, Cheryl Suwen Law, Manohar Chirumamilla, Andrew D. Abell, Robert H. Blick, Robert Zierold, and Abel Santos. Harnessing Slow Light in Optoelectronically Engineered Nanoporous Photonic Crystals for Visible Light-Enhanced Photocatalysis. ACS Catalysis, 11(21):12947–12962, 2021.
- [4] Carina Hedrich, Anna R. Burson, Silvia González-García, Víctor Vega, Victor M. Prida, Abel Santos, Robert H. Blick, and Robert Zierold. Enhancing the Photocatalytic Activity by Tailoring an Anodic Aluminum Oxide Photonic Crystal to the Semiconductor Catalyst: At the Example of Iron Oxide. Adv Materials Inter, page 2300615, September 2023.
- [5] Carina Hedrich, Nithin T. James, Laura G. Maragno, Valéria de Lima, Sergio Yesid Gómez González, Robert H. Blick, Robert Zierold, and Kaline P. Furlan. Enhanced photocatalytic properties and photo-induced crystallization of TiO₂-Fe₂O₃ inverse opals fabricated by atomic layer deposition. ACS Applied Materials & Interfaces, 16:46964–46974, 2024.
- [6] Siew Yee Lim, Carina Hedrich, Cheryl Suwen Law, Andrew D Abell, Robert H Blick, Kaline P Furlan, Robert Zierold, and Abel Santos. Nanoporous Anodic Alumina Photonic Crystals for Sunlight Harvesting Applications: A Perspective. Solar RRL, page 2200480, 2022.
- [7] Francesco Caddeo, Sophie Medicus, Carina Hedrich, Marco Krüger, Sani Y. Harouna-Mayer, Robert H. Blick, Robert Zierold, and Dorota Koziej. Enhancing Charge Transport in CuBi₂O₄ Films: The Role of a Protective TiO₂ ALD Coating Probed by Impedance Spectroscopy. Adv Materials Inter, page 2400263, June 2024.
- [8] Stefanie Haugg, Carina Hedrich, Robert H. Blick, and Robert Zierold. Subtractive Low-Temperature Preparation Route for Porous SiO₂ Used for the Catalyst-Assisted Growth of ZnO Field Emitters. *Nanomaterials*, 11(12):3357, December 2021.
- [9] Stefanie Haugg, Carina Hedrich, Robert Zierold, and Robert H Blick. Field emission characteristics of ZnO nanowires grown by catalyst-assisted MOCVD on free-standing inorganic nanomembranes. J. Phys. D: Appl. Phys., 55(25):255104, June 2022.
- [10] Stefanie Haugg, Carina Hedrich, Luis-Felipe Mochalski, Isabel González Díaz-Palacio, Robert Zierold, and Robert H. Blick. Enhancement of Field Emission Properties of Carbon Nanotube Forests by Direct Growth on Titanium Nitride-Coated Substrates. In 2023 IEEE 36th International Vacuum Nanoelectronics Conference (IVNC), pages 122–124, Cambridge, MA, USA, July 2023. IEEE.
- [11] Stefanie Haugg, Luis-Felipe Mochalski, Carina Hedrich, Isabel González Díaz-Palacio, Kristian Deneke, Robert Zierold, and Robert H. Blick. Field Emission from Carbon Nanotubes on Titanium Nitride-Coated Planar and 3D-Printed Substrates. *Nanomaterials*, 14(9):781, April 2024.
- [12] N.L. Panwar, S.C. Kaushik, and Surendra Kothari. Role of renewable energy sources in environmental protection: A review. *Renewable and Sustainable Energy Reviews*, 15(3):1513–1524, April 2011.
- [13] Atika Qazi, Fayaz Hussain, Nasrudin Abd. Rahim, Glenn Hardaker, Daniyal Alghazzawi, Khaled Shaban, and Khalid Haruna. Towards Sustainable Energy: A Systematic Review of Renewable Energy Sources, Technologies, and Public Opinions. *IEEE Access*, 7:63837–63851, 2019.
- [14] Phebe Asantewaa Owusu and Samuel Asumadu-Sarkodie. A review of renewable energy sources, sustainability issues and climate change mitigation. *Cogent Engineering*, 3(1):1167990, December 2016.
- [15] Antoni Salvatore Arico, Peter Bruce, Bruno Scrosati, Jean-Marie Tarascon, and Walter van Schalkwijk. Nanostructured materials for advanced energy conversion and storage devices. *Nature Materials*, 4(May):366–377, 2005.
- [16] Xiuzhen Zheng and Liwu Zhang. Photonic nanostructures for solar energy conversion. *Energy Environ. Sci.*, 9(8):2511–2532, 2016.
- [17] Van Tan Tran, Huu-Quang Nguyen, Young-Mi Kim, Gyeongsik Ok, and Jaebeom Lee. Photonic–Plasmonic Nanostructures for Solar Energy Utilization and Emerging Biosensors. *Nanomaterials*, 10(11):2248, November 2020.
- [18] Zakya H. Kafafi, Raúl J. Martín-Palma, Ana F. Nogueira, Deirdre M. O'Carroll, Jeremy J. Pietron, Ifor D. W. Samuel, Franky So, Nelson Tansu, and Loucas Tsakalakos. The role of photonics in energy. J. Photon. Energy, 5(1):050997, October 2015.
- [19] Steven M. George. Atomic layer deposition: An overview. Chemical Reviews, 110(1):111–131, 2010.
- [20] Ville Miikkulainen, Markku Leskelä, Mikko Ritala, and Riikka L Puurunen. Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends. *Journal of Applied Physics*, 113(2), 2013.
- [21] Riikka L Puurunen. Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum / water process. Journal of Applied Physics, 97(12):121301–121301–52, 2005.
- [22] Véronique Cremers, Riikka L. Puurunen, and Jolien Dendooven. Conformality in atomic layer deposition: Current status overview of analysis and modelling. *Applied Physics Reviews*, 6(2):021302, 2019.

- [23] E Yablonovitch. Photonic band-gap structures. J. Opt. Soc. Am. B, 10(2):283–295, 1993.
- [24] J. D. Joannopoulos, Pierre R. Villeneuve, and Shanhui Fan. Photonic crystals: Putting a new twist on light. Nature, 386(6621):143–149, 1997.
- [25] C. M. Soukoulis. The history and a review of the modelling and fabrication of photonic crystals. *Nanotechnology*, 13(3):420–423, 2002.
- [26] G. Guida, A. de Lustrac, and A. Priou. An introduction to photonic band gap (PBG) materials. Progress in Electromagnetics Research, 41:1–20, 2003.
- [27] John D. Joannopoulos, Steven G. Johnson, Joshua N. Winn, and Robert D. Meade. Photonic Crystals Molding the Flow of Light. Princeton University Press, Princeton, New Jersey, 2008.
- [28] Jing Liu, Heng Zhao, Min Wu, Benoit Van der Schueren, Yu Li, Olivier Deparis, Jinhua Ye, Geoffrey A. Ozin, Tawfique Hasan, and Bao Lian Su. Slow Photons for Photocatalysis and Photovoltaics. Advanced Materials, 29(17):1605349, 2017.
- [29] Jennifer I.L. Chen, Georg Von Freymann, Sung Yeun Choi, Vladimir Kitaev, and Geoffrey A. Ozin. Slow photons in the fast lane in chemistry. *Journal of Materials Chemistry*, 18(4):369–373, 2008.
- [30] Alex Lonergan and Colm O'Dwyer. Many Facets of Photonic Crystals: From Optics and Sensors to Energy Storage and Photocatalysis. Adv Materials Technologies, 8(6):2201410, March 2023.
- [31] Kaline P. Furlan, Tobias Krekeler, Martin Ritter, Robert Blick, Gerold A. Schneider, Kornelius Nielsch, Robert Zierold, and Rolf Janßen. Low-Temperature Mullite Formation in Ternary Oxide Coatings Deposited by ALD for High-Temperature Applications. Advanced Materials Interfaces, 4(23):1–8, 2017.
- [32] Kaline P. Furlan, Emanuel Larsson, Ana Diaz, Mirko Holler, Tobias Krekeler, Martin Ritter, Alexander Yu Petrov, Manfred Eich, Robert Blick, Gerold A. Schneider, Imke Greving, Robert Zierold, and Rolf Janßen. Photonic materials for high-temperature applications: Synthesis and characterization by X-ray ptychographic tomography. *Applied Materials Today*, 13:359–369, 2018.
- [33] Alberto Gomez-Gomez, Diego Ribas Gomes, Benedikt F. Winhard, Laura G. Maragno, Tobias Krekeler, Martin Ritter, and Kaline P. Furlan. Mullite photonic glasses with exceptional thermal stability for novel reflective thermal barrier coatings. J Mater Sci, 58(32):12993–13008, August 2023.
- [34] Jan Plutnar and Martin Pumera. Applications of Atomic Layer Deposition in Design of Systems for Energy Conversion. Small, 17(39):2102088, October 2021.
- [35] N. K.R. Eswar, Satyapaul A. Singh, and Jaeyeong Heo. Atomic layer deposited photocatalysts: Comprehensive review on viable fabrication routes and reactor design approaches for photo-mediated redox reactions. *Journal of Materials Chemistry A*, 7(30):17703–17734, 2019.
- [36] Tuo Wang, Zhibin Luo, Chengcheng Li, and Jinlong Gong. Controllable fabrication of nanostructured materials for photoelectrochemical water splitting via atomic layer deposition. *Chem. Soc. Rev.*, 43(22):7469–7484, February 2014.
- [37] Qing Peng, Jay S. Lewis, Paul G. Hoertz, Jeffrey T. Glass, and Gregory N. Parsons. Atomic layer deposition for electrochemical energy generation and storage systems. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 30(1):010803, January 2012.
- [38] J A Van Delft, D Garcia-Alonso, and W M M Kessels. Atomic layer deposition for photovoltaics: Applications and prospects for solar cell manufacturing. *Semicond. Sci. Technol.*, 27(7):074002, July 2012.
- [39] Md. Anower Hossain, Kean Thong Khoo, Xin Cui, Geedhika K Poduval, Tian Zhang, Xiang Li, Wei Min Li, and Bram Hoex. Atomic layer deposition enabling higher efficiency solar cells: A review. *Nano Materials Science*, 2(3):204–226, September 2020.
- [40] UN DESA. The Sustainable Development Goals Report 2020. Technical report, UN DESA, New York, 2022.
- [41] Markku Leskelä and Mikko Ritala. Atomic layer deposition (ALD): From precursors to thin film structures. *Thin Solid Films*, 409:138–146, 2002.
- [42] Mato Knez, Kornelius Nielsch, and Lauri Niinistö. Synthesis and surface engineering of complex nanostructures by atomic layer deposition. Advanced Materials, 19(21):3425–3438, 2007.
- [43] Hyungjun Kim, Han Bo Ram Lee, and W. J. Maeng. Applications of atomic layer deposition to nanofabrication and emerging nanodevices. *Thin Solid Films*, 517(8):2563–2580, 2009.
- [44] Changdeuck Bae, Hyunjung Shin, and Kornelius Nielsch. Surface modification and fabrication of 3D nanostructures by atomic layer deposition. MRS Bulletin, 36(11):887–897, 2011.
- [45] Cefe López. Materials Aspects of Photonic Crystals. Advanced Materials, 15(20):1679–1704, 2003.
- [46] Alain C Pierre. Introduction to Sol-Gel Processing. Springer Nature Switzerland AG, Cham, 2020.
- [47] Jerzy Zarzycki. Past and Present of Sol-Gel Science and Technology. Journal of Sol-Gel Science and Technology, 8(1-3):17–22, 1997.
- [48] O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, and S. Sampath. Sol-Gel Materials in Electrochemistry. *Chemistry of Materials*, 9(11):2354–2375, 1997.

- [49] Jacques Livage. Sol-gel processes. Current Opinion in Solid State & Metrials Science, 2(132-138):132-138, 1997.
- [50] John D Mackenzie. APPLICATIONS OF THE SOL-GEL PROCESS. Materials Science, 100:162–168, 1988.
- [51] Yuliy D Gamburg and Giovanni Zangari. Theory and Practice of Metal Electrodeposition. Springer, New York, 2011.
- [52] Daniel Lincot. Electrodeposition of semiconductors. Thin Solid Films, 487(1-2):40-48, 2005.
- [53] Farzad Nasirpouri. Electrodeposition of Nanostructured Materials. Springer, 2017.
- [54] Luisa Peraldo Bicelli, Benedetto Bozzini, Claudio Mele, and Lucia D'Urzo. A review of nanostructural aspects of metal electrodeposition. *International Journal of Electrochemical Science*, 3(4):356–408, 2008.
- [55] Abhishek Lahiri, Giridhar Pulletikurthi, and Frank Endres. A review on the electroless deposition of functional materials in ionic liquids for batteries and catalysis. *Frontiers in Chemistry*, 7(FEB):1–13, 2019.
- [56] B Window. Recent advances in sputter deposition. Surface and Coatings Technology, 71:93–97, 1995.
- [57] D Depla, S Mahieu, and J E Greene. Sputter Deposition Processes. In Peter M Martin, editor, Handbook of Deposition Technologies for Films and Coatings, volume 13, pages 253–296. Elsevier, 2010.
- [58] Vincent S. Smentkowski. Trends in sputtering. Progress in Surface Science, 64(1):1-58, 2000.
- [59] P. J. Kelly and R. D. Arnell. Magnetron sputtering: A review of recent developments and applications. Vacuum, 56(3):159–172, 2000.
- [60] S. M. Rossnagel. Thin film deposition with physical vapor deposition and related technologies. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 21(5):S74–S87, September 2003.
- [61] Tansel Karabacak and Toh Ming Lu. Enhanced step coverage by oblique angle physical vapor deposition. *Journal of Applied Physics*, 97(12), 2005.
- [62] Christoph Grüner, Susann Liedtke, Jens Bauer, Stefan G. Mayr, and Bernd Rauschenbach. Morphology of Thin Films Formed by Oblique Physical Vapor Deposition. ACS Appl. Nano Mater., 1(3):1370–1376, March 2018.
- [63] Luzhao Sun, Guowen Yuan, Libo Gao, Jieun Yang, Manish Chhowalla, Meysam Heydari Gharahcheshmeh, Karen K. Gleason, Yong Seok Choi, Byung Hee Hong, and Zhongfan Liu. Chemical vapour deposition. *Nat Rev Methods Primers*, 1(1):5, January 2021.
- [64] Wenjiao B. Wang, Noel N. Chang, Tracey A. Codding, Gregory S. Girolami, and John R. Abelson. Superconformal chemical vapor deposition of thin films in deep features. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 32(5):051512, September 2014.
- [65] Jan Otto Carlsson and Peter M. Martin. Chemical Vapor Deposition. Elsevier Ltd., 2010.
- [66] Riikka L. Puurunen. A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy. Chemical Vapor Deposition, 20(10-11-12):332–344, December 2014.
- [67] Matthieu Weber, Anne Julbe, André Ayral, Philippe Miele, and Mikhael Bechelany. Atomic Layer Deposition for Membranes: Basics, Challenges, and Opportunities. *Chemistry of Materials*, 30(21):7368–7390, 2018.
- [68] Seong Keun Kim, Gyu-Jin Choi, and Cheol Seong Hwang. Controlling the Composition of Doped Materials by ALD: A Case Study for Al-Doped TiO₂ Films. *Electrochemical and Solid-State Letters*, 11(7), 2008.
- [69] Ville Miikkulainen, Katja Väyrynen, Kenichiro Mizohata, Jyrki Räisänen, Marko Vehkamäki, and Mikko Ritala. Photoassisted atomic layer deposition of oxides employing alkoxides as single-source precursors. *Journal of Vacuum Science & Technology* A: Vacuum, Surfaces, and Films, 37(6):060911, November 2019.
- [70] Siva Krishna Karuturi, Lijun Liu, Liap Tat Su, Yang Zhao, Hong Jin Fan, Xiaochen Ge, Sailing He, and Alfred Tok Iing Yoong. Kinetics of Stop-Flow Atomic Layer Deposition for High Aspect Ratio Template Filling through Photonic Band Gap Measurements. J. Phys. Chem. C, 114(35):14843–14848, September 2010.
- [71] Adriaan J. M. Mackus, Joel R. Schneider, Callisto MacIsaac, Jon G. Baker, and Stacey F. Bent. Synthesis of Doped, Ternary, and Quaternary Materials by Atomic Layer Deposition: A Review. *Chem. Mater.*, 31(4):1142–1183, February 2019.
- [72] H.-J. Gossmann and E. F. Schubert. Delta doping in silicon. Critical Reviews in Solid State and Materials Sciences, 18(1):1–67, January 1993.
- [73] Eli Yablonovitch. Inhibited spontaneous emission in solid-state physics and electronics. *Physical Review Letters*, 58(20):2059–2062, 1987.
- [74] Sajeev John. Strong localization of photons in certain disordered dielectric superlattices. Phys. Rev. Lett., 58(23):2486–2489, June 1987.
- [75] J D Joannopoulos, Pierre R Villeneuve, and Shanhni Fan. Photonic Crystals. Solid State Communications, 102(2):165–173, 1997.
- [76] Kurt Busch and Sajeev John. Photonic band gap formation in certain self-organizing systems. Physical Review E Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics, 58(3):3896–3908, 1998.

- [77] Steven G. Johnson, Pierre R. Villeneuve, Shanhui Fan, and J. D. Joannopoulos. Linear waveguides in photonic-crystal slabs. *Phys. Rev. B*, 62(12):8212–8222, September 2000.
- [78] Jiatong Liu, Cuifeng Sun, Ming Fu, Jie Long, Dawei He, and Yongsheng Wang. Enhanced Photochemical Catalysis of TiO₂ Inverse Opals by Modification with ZnO or Fe₂O₃ using ALD and the Hydrothermal Method. *Materials Research Express*, 5:025509, 2018.
- [79] Wenshan Cai and Vladimir Shalaev. Optical Metamaterials: Fundamentals and Applications. Springer, New York, 2010.
- [80] Moran Wang and Ning Pan. Predictions of effective physical properties of complex multiphase materials. *Materials Science and Engineering R: Reports*, 63(1):1–30, 2008.
- [81] Tuck C. Choy. Effective Medium Theory: Principles and Applications. Oxford University Press, Oxford, 2016.
- [82] Bahaa E. A. Saleh and Malvin Carl Teich. Fundamentals of Photonics. John Wiley /& Sons, Inc., Hoboken, 2019.
- [83] Jiao Wang, Gaoshan Huang, and Yongfeng Mei. Modification and Resonance Tuning of Optical Microcavities by Atomic Layer Deposition. *Chemical Vapor Deposition*, 20(4-5-6):103–111, June 2014.
- [84] Juan F. Galisteo-Lõpez, Marta Ibisate, Riccardo Sapienza, Luis S. Froufe-Pérez, Úlvaro Blanco, and Cefe Lõpez. Selfassembled photonic structures. Advanced Materials, 23(1):30–69, 2011.
- [85] Georg von Freymann, Vladimir Kitaev, Bettina V. Lotsch, and Geoffrey A. Ozin. Bottom-up assembly of photonic crystals. *Chemical Society Reviews*, 42(7):2528–2554, 2013.
- [86] Woo Lee and Sang Joon Park. Porous anodic aluminum oxide: Anodization and templated synthesis of functional nanostructures. *Chemical Reviews*, 114(15):7487–7556, 2014.
- [87] Abdul Mutalib Md Jani, Dusan Losic, and Nicolas H. Voelcker. Nanoporous anodic aluminium oxide: Advances in surface engineering and emerging applications. *Progress in Materials Science*, 58(5):636–704, 2013.
- [88] Siew Yee Lim, Cheryl Suwen Law, Lina Liu, Marijana Markovic, Carina Hedrich, Robert H. Blick, Andrew D. Abell, Robert Zierold, and Abel Santos. Electrochemical engineering of nanoporous materials for photocatalysis: Fundamentals, advances, and perspectives. *Catalysts*, 9(12):988, 2019.
- [89] Junxian Gao, Wenjie Tian, Huayang Zhang, and Shaobin Wang. Engineered inverse opal structured semiconductors for solar light-driven environmental catalysis. *Nanoscale*, 14(39):14341–14367, 2022.
- [90] Hideki Masuda and Kenji Fukuda. Ordered Metal Nanohole Arrays Made by a Two-Step Replication of Honeycomb Structures of Anodic Alumina. *Science*, 268(5216):1466–1468, June 1995.
- [91] Cheryl Suwen Law, Siew Yee Lim, Andrew D. Abell, Nicolas H. Voelcker, and Abel Santos. Nanoporous anodic alumina photonic crystals for optical chemo-and biosensing: Fundamentals, advances, and perspectives. *Nanomaterials*, 8(10):788, 2018.
- [92] Tushar Kumeria, Abel Santos, and Dusan Losic. Nanoporous anodic alumina platforms: Engineered surface chemistry and structure for optical sensing applications. *Sensors (Switzerland)*, 14(7):11878–11918, 2014.
- [93] Abel Santos, Mohamed Jamal Deen, and Lluis F. Marsal. Low-cost fabrication technologies for nanostructures: State-of-the-art and potential. *Nanotechnology*, 26(4):042001, 2015.
- [94] Abel Santos. Nanoporous anodic alumina photonic crystals: Fundamentals, developments and perspectives. Journal of Materials Chemistry C, 5(23):5581–5599, 2017.
- [95] Tushar Kumeria, Abel Santos, Mohammad Mahbubur Rahman, Josep Ferré-Borrull, Lluís F. Marsal, and Dusan Losic. Advanced Structural Engineering of Nanoporous Photonic Structures: Tailoring Nanopore Architecture to Enhance Sensing Properties. ACS Photonics, 1(12):1298–1306, 2014.
- [96] Hee Han, Sang Joon Park, Jong Shik Jang, Hyun Ryu, Kyung Joong Kim, Sunggi Baik, and Woo Lee. In situ determination of the pore opening point during wet-chemical etching of the barrier layer of porous anodic aluminum oxide: Nonuniform Impurity Distribution in Anodic Oxide. ACS Applied Materials and Interfaces, 5(8):3441–3448, 2013.
- [97] Alaa M Abd-Elnaiem, Zain Elabdeen A Mohamed, Sayed Elshahat, and Mohamed Almokhtar. Recent Progress in the Fabrication of Photonic Crystals Based on Porous Anodic Materials. *Energies*, 16:4032, 2023.
- [98] Jean Rasmussen. Pulse anodizing of aluminum: The recovery effect. Plating and Surface Finishing, 89(1):43–45, 2002.
- [99] Mohammad Mahbubur Rahman, Lluis F. Marsal, Josep Pallarès, and Josep Ferré-Borrull. Tuning the photonic stop bands of nanoporous anodic alumina-based distributed bragg reflectors by pore widening. ACS Applied Materials and Interfaces, 5(24):13375–13381, 2013.
- [100] JP O'Sullivan and GC Wood. Morphology and mechanism of formation of porous anodic films on aluminum. Proc Roy Soc Ser A Math Phys Sci, 317(1731), 1970.
- [101] Woo Lee, Roland Scholz, and Ulrich Gösele. A continuous process for structurally weil-defined Al₂O₃ nanotubes based on pulse anodization of aluminum. *Nano Letters*, 8(8):2155–2160, 2008.
- [102] Cheryl Suwen Law, Siew Yee Lim, and Abel Santos. On the Precise Tuning of Optical Filtering Features in Nanoporous Anodic Alumina Distributed Bragg Reflectors. Scientific Reports, 8(1):1–16, 2018.

- [103] Cheryl Suwen Law, Siew Yee Lim, Lina Liu, Andrew D. Abell, Lluis F. Marsal, and Abel Santos. Realization of high-quality optical nanoporous gradient-index filters by optimal combination of anodization conditions. *Nanoscale*, 12(17):9404–9415, 2020.
- [104] Siew Yee Lim, Cheryl Suwen Law, Marijana Markovic, Lluís F. Marsal, Nicolas H. Voelcker, Andrew D. Abell, and Abel Santos. Rational Management of Photons for Enhanced Photocatalysis in Structurally-Colored Nanoporous Anodic Alumina Photonic Crystals. ACS Applied Energy Materials, 2(2):1169–1184, 2019.
- [105] Siew Yee Lim, Cheryl Suwen Law, Lluís F. Marsal, and Abel Santos. Engineering of hybrid nanoporous anodic alumina photonic crystals by heterogeneous pulse anodization. *Scientific Reports*, 8(1):1–16, 2018.
- [106] Vygantas Mizeikis, Irmantas Mikulskas, Roland Tomašiunas, Saulius Juodkazis, Shigeki Matsuo, and Hiroaki Misawa. Optical characteristics of two-dimensional photonic crystals in anodic aluminum oxide films. Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers, 43(6 A):3643–3647, 2004.
- [107] Guoliang Shang, Dongxue Bi, Vladimir Semenovich Gorelik, Guangtao Fei, and Lide Zhang. Anodic alumina photonic crystals: Structure engineering, optical properties and prospective applications. *Materials Today Communications*, 34:105052, March 2023.
- [108] Ewelina Białek, Grzegorz Szwachta, Miron Kaliszewski, and Małgorzata Norek. Charge density-versus time-controlled pulse anodization in the production of PAA-based DBRs for MIR spectral region. *Energies*, 14(16):1–14, 2021.
- [109] Ye Wang, Yuting Chen, Tushar Kumeria, Fuyuan Ding, Andreas Evdokiou, Dusan Losic, and Abel Santos. Facile synthesis of optical microcavities by a rationally designed anodization approach: Tailoring photonic signals by nanopore structure. ACS Applied Materials and Interfaces, 7(18):9879–9888, 2015.
- [110] Grzegorz Szwachta, Blanka Januszewska, Maksymilian Włodarski, and Małgorzata Norek. From gradient-index to step-index filters: A switch between the two types of photonic crystals induced by the amplitude and period of sinusoidal function applied during high-temperature anodisation of aluminium. *Applied Surface Science*, 607(September), 2023.
- [111] Grzegorz D. Sulka and Katarzyna Hnida. Distributed Bragg reflector based on porous anodic alumina fabricated by pulse anodization. *Nanotechnology*, 23(7), 2012.
- [112] Laura K. Acosta, Francesc Bertó-Roselló, Elisabet Xifre-Perez, Abel Santos, Josep Ferré-Borrull, and Lluis F. Marsal. Stacked Nanoporous Anodic Alumina Gradient-Index Filters with Tunable Multispectral Photonic Stopbands as Sensing Platforms. ACS Applied Materials and Interfaces, 11(3):3360–3371, 2019.
- [113] Laura K. Acosta, Francesc Bertó-Roselló, Elisabet Xifre-Perez, Cheryl Suwen Law, Abel Santos, Josep Ferré-Borrull, and Lluis F. Marsal. Tunable Nanoporous Anodic Alumina Photonic Crystals by Gaussian Pulse Anodization. ACS Applied Materials and Interfaces, 12(17):19778–19787, 2020.
- [114] Cheryl Suwen Law, Siew Yee Lim, Andrew D. Abell, Lluís F. Marsal, and Abel Santos. Structural tailoring of nanoporous anodic alumina optical microcavities for enhanced resonant recirculation of light. *Nanoscale*, 10(29):14139–14152, 2018.
- [115] Jungmin Lee, Kyuyoung Bae, Gumin Kang, Minjung Choi, Seunghwa Baek, Do Sik Yoo, Chang Won Lee, and Kyoungsik Kim. Graded-lattice AAO photonic crystal heterostructure for high Q refractive index sensing. *RSC Advances*, 5(88):71770– 71777, 2015.
- [116] Siew Yee Lim, Cheryl Suwen Law, Lina Liu, Marijana Markovic, Andrew D. Abell, and Abel Santos. Integrating surface plasmon resonance and slow photon effects in nanoporous anodic alumina photonic crystals for photocatalysis. *Catalysis Science and Technology*, 9(12):3158–3176, 2019.
- [117] Yan-ling Liu, Jian Zhu, Jian-jun Ki, and Jun-wu Zhao. Gold nanotubes: Synthesis, properties and biomedical applications. *Microchimica Acta*, 187:612, 2020.
- [118] Lina Liu, Siew Yee, Cheryl Suwen, Laura K Acosta, Bo Jin, Andrew D Abell, Lluis F Marsal, Gang Ni, and Abel Santos. Optical engineering of nanoporous photonic crystals by Gaussian-Like pulse anodization. *Microporous and Mesoporous Materials*, 312:110770, 2020.
- [119] Sixiang Liu, Junlong Tian, and Wang Zhang. Fabrication and application of nanoporous anodic aluminum oxide: A review. Nanotechnology, 32(22):222001, 2021.
- [120] Wen Jun Zheng, Guang Tao Fei, Biao Wang, and Li De Zhang. Modulation of Transmission Spectra of Anodized Alumina Membrane Distributed Bragg Reflector by Controlling Anodization Temperature. *Nanoscale Research Letters*, 4(7):665–667, 2009.
- [121] Loïc Assaud, Johannes Schumacher, Alexander Tafel, Sebastian Bochmann, Silke Christiansen, and Julien Bachmann. Systematic increase of electrocatalytic turnover at nanoporous platinum surfaces prepared by atomic layer deposition. *Journal of Materials Chemistry A*, 3(16):8450–8458, 2015.
- [122] Maïssa K.S. Barr, Loïc Assaud, Yanlin Wu, Carine Laffon, Philippe Parent, Julien Bachmann, and Lionel Santinacci. Engineering a three-dimensional, photoelectrochemically active p-NiO / i-Sb₂S₃ junction by atomic layer deposition. *Electrochimica Acta*, 179:504–511, 2015.
- [123] M. Barr, L. Assaud, Y. Wu, J. Bachmann, and L. Santinacci. Atomic Layer Deposition of i-Sb₂S₃/p-NiO Thin Layers into Anodic Alumina Membranes for Photoelectrochemical Water Splitting. *ECS Transactions*, 66(6):119–126, 2015.
- [124] Wen Ting Chang, Yang Chih Hsueh, Sheng Hsin Huang, Kuang I. Liu, Chi Chung Kei, and Tsong Pyng Perng. Fabrication of Ag-loaded multi-walled TiO₂ nanotube arrays and their photocatalytic activity. *Journal of Materials Chemistry A*, 1(6):1987– 1991, 2013.

- [125] Hsueh Shih Chen, Po Hsun Chen, Sheng Hsin Huang, and Tsong Pyng Perng. Toward highly efficient photocatalysis: A flow-through Pt@TiO₂@AAO membrane nanoreactor prepared by atomic layer deposition. *Chemical Communications*, 50(33):4379–4382, 2014.
- [126] Marianna Kemell, Viljami Pore, Jere Tupala, Mikko Ritala, and Markku Leskelä. Atomic layer deposition of nanostructured TiO₂ photocatalysts via template approach. *Chemistry of Materials*, 19(7):1816–1820, 2007.
- [127] Marianna Kemell, Emma Härkönen, Viljami Pore, Mikko Ritala, and Markku Leskelä. Ta₂O₅-and TiO₂-based nanostructures made by atomic layer deposition. *Nanotechnology*, 21(3):035301, 2010.
- [128] Yu Chuan Liang, Chih Chieh Wang, Chi Chung Kei, Yang Chih Hsueh, Wen Hao Cho, and Tsong Pyng Perng. Photocatalysis of Ag-loaded TiO₂ nanotube arrays formed by atomic layer deposition. *Journal of Physical Chemistry C*, 115(19):9498–9502, 2011.
- [129] M. J. Pellin, P. C. Stair, G. Xiong, J. W. Elam, J. Birrell, L. Curtiss, S. M. George, C. Y. Han, L. Iton, H. Kung, M. Kung, and H. H. Wang. Mesoporous catalytic membranes: Synthetic control of pore size and wall composition. *Catalysis Letters*, 102(3-4):127–130, 2005.
- [130] Stefanie Schlicht, Sandra Haschke, Vladimir Mikhailovskii, Alina Manshina, and Julien Bachmann. Highly Reversible Water Oxidation at Ordered Nanoporous Iridium Electrodes Based on an Original Atomic Layer Deposition. *ChemElectroChem*, 5(9):1259–1264, 2018.
- [131] P. C. Stair, C. Marshall, G. Xiong, H. Feng, M. J. Pellin, J. W. Elam, L. Curtiss, L. Iton, H. Kung, M. Kung, and H. H. Wang. Novel, uniform nanostructured catalytic membranes. *Topics in Catalysis*, 39(3-4):181–186, 2006.
- [132] Julia Gemmer, Yvonne Hinrichsen, Annik Abel, and Julien Bachmann. Systematic catalytic current enhancement for the oxidation of water at nanostructured iron(III) oxide electrodes. *Journal of Catalysis*, 290:220–224, 2012.
- [133] Martin Waleczek, Jolien Dendooven, Pavel Dyachenko, Alexander Y. Petrov, Manfred Eich, Robert H. Blick, Christophe Detavernier, Kornelius Nielsch, Kaline P. Furlan, and Robert Zierold. Influence of alumina addition on the optical properties and the thermal stability of titania thin films and inverse opals produced by atomic layer deposition. *Nanomaterials*, 11(4), 2021.
- [134] Jeffrey S. King, Elton Graugnard, and Christopher J. Summers. Photoluminescence modification by high-order photonic bandsin TiO₂/ZnS:Mn multilayer inverse opals. *Applied Physics Letters*, 88(8):081109, February 2006.
- [135] Heloisa G. Campos, Kaline P. Furlan, Daniel E. Garcia, Robert Blick, Robert Zierold, Manfred Eich, Dachamir Hotza, and Rolf Janssen. Effects of processing parameters on 3D structural ordering and optical properties of inverse opal photonic crystals produced by atomic layer deposition. Int J Ceramic Engine & Sci, 1(2):68–76, July 2019.
- [136] H. Míguez, N. Tétreault, S.M. Yang, V. Kitaev, and G.A. Ozin. A New Synthetic Approach to Silicon Colloidal Photonic Crystals with a Novel Topology and an Omni-Directional Photonic Bandgap: Micromolding in Inverse Silica Opal (MISO). Advanced Materials, 15(7-8):597–600, April 2003.
- [137] J. López Medina, J. Vazquez Arce, P. Pizá-Ruiz, N. Nedev, M.H. Farías, and H. Tiznado. HfO₂:Y₂O₃ ultrathin nanolaminate structures grown by ALD: Bilayer thickness and annealing temperature effects on optical properties. *Ceramics International*, 48(12):17564–17575, June 2022.
- [138] E.G. Lizarraga-Medina, D.L. Caballero Espitia, J. Jurado Gonzalez, J. López, H. Marquez, O.E. Contreras López, and H. Tiznado. Al₂O₃-Y₂O₃ nanolaminated slab optical waveguides by atomic layer deposition. *Optical Materials*, 103:109822, May 2020.
- [139] J. López, A. Sotelo, F.F. Castillón, R. Machorro, N. Nedev, M.H. Farías, and H. Tiznado. Influence of the bilayer thickness on the optical properties of Al₂O₃-Y₂O₃ dielectric nanolaminate films grown by thermal atomic layer deposition. *Materials Research Bulletin*, 87:14–19, March 2017.
- [140] Adriana Szeghalmi, Michael Helgert, Robert Brunner, Frank Heyroth, Ulrich Gösele, and Mato Knez. Atomic layer deposition of Al₂O₃ and TiO₂ multilayers for applications as bandpass filters and antireflection coatings. *Appl. Opt.*, 48(9):1727, March 2009.
- [141] G E Testoni, W Chiappim, R S Pessoa, M A Fraga, W Miyakawa, K K Sakane, N K A M Galvão, L Vieira, and H S Maciel. Influence of the Al₂O₃ partial-monolayer number on the crystallization mechanism of TiO₂ in ALD TiO₂ /Al₂O₃ nanolaminates and its impact on the material properties. J. Phys. D: Appl. Phys., 49(37):375301, September 2016.
- [142] Lilit Ghazaryan, Shiti Handa, Paul Schmitt, Vivek Beladiya, Vladimir Roddatis, Andreas Tünnermann, and Adriana Szeghalmi. Structural, optical, and mechanical properties of TiO₂ nanolaminates. *Nanotechnology*, 32(9):095709, February 2021.
- [143] Ling-Shan Gao, Qing-Yuan Cai, Er-Tao Hu, Qiu-Yu Zhang, Yu-Ting Yang, Yun-Bo Xiong, Bao-Jian Liu, Wei-Bo Duan, Tian-Yan Yu, and Ding-Quan Liu. Optimization of optical and structural properties of Al₂O₃/TiO₂ nano-laminates deposited by atomic layer deposition for optical coating. *Opt. Express*, 31(8):13503, April 2023.
- [144] Marcel Mayer, Kahraman Keskinbora, Corinne Grévent, Adriana Szeghalmi, Mato Knez, Markus Weigand, Anatoly Snigirev, Irina Snigireva, and Gisela Schütz. Efficient focusing of 8 keV X-rays with multilayer Fresnel zone plates fabricated by atomic layer deposition and focused ion beam milling. J Synchrotron Rad, 20(3):433–440, May 2013.
- [145] J. López, J. Martínez, N. Abundiz, D. Domínguez, E. Murillo, F.F. Castillón, R. Machorro, M.H. Farías, and H. Tiznado. Thickness effect on the optical and morphological properties in Al₂O₃/ZnO nanolaminate thin films prepared by atomic layer deposition. *Superlattices and Microstructures*, 90:265–273, February 2016.

- [146] Wenbin Niu, Lele Zhang, Yunpeng Wang, and Shufen Zhang. Multicolored one-dimensional photonic crystal coatings with excellent mechanical robustness, strong substrate adhesion, and liquid and particle impalement resistance. J. Mater. Chem. C, 7(12):3463–3470, 2019.
- [147] Yu-Zhu Gu, Hong-Liang Lu, Yang Geng, Zhi-Yuan Ye, Yuan Zhang, Qing-Qing Sun, Shi-Jin Ding, and David Wei Zhang. Optical and microstructural properties of ZnO/TiO₂ nanolaminates prepared by atomic layer deposition. *Nanoscale Res Lett*, 8(1):107, December 2013.
- [148] Jiao Wang, Gaoshan Huang, and Yongfeng Mei. Modification and Resonance Tuning of Optical Microcavities by Atomic Layer Deposition. *Chemical Vapor Deposition*, 20(4-5-6):103–111, June 2014.
- [149] D. P. Gaillot, E. Graugnard, J. Blair, and C. J. Summers. Dispersion control in two-dimensional superlattice photonic crystal slab waveguides by atomic layer deposition. *Applied Physics Letters*, 91(18):181123, October 2007.
- [150] Charlton J. Chen, Chad A. Husko, Inanc Meric, Ken L. Shepard, Chee Wei Wong, William M. J. Green, Yurii A. Vlasov, and Solomon Assefa. Deterministic tuning of slow-light in photonic-crystal waveguides through the C and L bands by atomic layer deposition. *Applied Physics Letters*, 96(8):081107, February 2010.
- [151] Xiaodong Yang, Charlton J. Chen, Chad A. Husko, and Chee Wei Wong. Digital resonance tuning of high-Q/Vm silicon photonic crystal nanocavities by atomic layer deposition. *Applied Physics Letters*, 91(16):161114, October 2007.
- [152] Davy P. Gaillot, Olivier Deparis, Victoria Welch, Brent K. Wagner, Jean Pol Vigneron, and Christopher J. Summers. Composite organic-inorganic butterfly scales: Production of photonic structures with atomic layer deposition. *Phys. Rev. E*, 78(3):031922, September 2008.
- [153] I. M. Povey, D. Whitehead, K. Thomas, M. E. Pemble, M. Bardosova, and J. Renard. Photonic crystal thin films of GaAs prepared by atomic layer deposition. *Applied Physics Letters*, 89(10):104103, September 2006.
- [154] E. Graugnard, D. P. Gaillot, S. N. Dunham, C. W. Neff, T. Yamashita, and C. J. Summers. Photonic band tuning in twodimensional photonic crystal slab waveguides by atomic layer deposition. *Applied Physics Letters*, 89(18):181108, October 2006.
- [155] Z. A. Sechrist, B. T. Schwartz, J. H. Lee, J. A. McCormick, Rafael Piestun, W. Park, and S. M. George. Modification of Opal Photonic Crystals Using Al₂O₃ Atomic Layer Deposition. *Chem. Mater.*, 18(15):3562–3570, July 2006.
- [156] Robert Vaßen, Maria Ophelia Jarligo, Tanja Steinke, Daniel Emil Mack, and Detlev Stöver. Overview on advanced thermal barrier coatings. *Surface and Coatings Technology*, 205(4):938–942, November 2010.
- [157] Jungwan Cho, Joonsuk Park, and Jihwan An. Low thermal conductivity of atomic layer deposition yttria-stabilized zirconia (YSZ) thin films for thermal insulation applications. *Journal of the European Ceramic Society*, 37(9):3131–3136, August 2017.
- [158] Alex Omo Ibhadon and Paul Fitzpatrick. Heterogeneous photocatalysis: Recent advances and applications. *Catalysts*, 3(1):189–218, 2013.
- [159] Ankita Rani, Rajesh Reddy, Uttkarshni Sharma, Priya Mukherjee, Priyanka Mishra, Aneek Kuila, Lan Ching Sim, and Pichiah Saravanan. A Review on the Progress of Nanostructure Materials for Energy Harnessing and Environmental Remediation, volume 8. Springer Berlin Heidelberg, 2018.
- [160] Ebrahim Zarei and Reza Ojani. Fundamentals and some applications of photoelectrocatalysis and effective factors on its efficiency: A review. *Journal of Solid State Electrochemistry*, 21(2):305–336, 2017.
- [161] Shuxian Zhong, Yamin Xi, Qin Chen, Jianrong Chen, and Song Bai. Bridge engineering in photocatalysis and photoelectrocatalysis. *Nanoscale*, 12(10):5764–5791, 2020.
- [162] Guilherme Garcia Bessegato, Thaís Tasso Guaraldo, Juliana Ferreira de Brito, Michelle Fernanda Brugnera, and Maria Valnice Boldrin Zanoni. Achievements and Trends in Photoelectrocatalysis: From Environmental to Energy Applications. *Elec*trocatalysis, 6(5):415–441, 2015.
- [163] Ximin Cui, Qifeng Ruan, Xiaolu Zhuo, Xinyue Xia, Jingtian Hu, Runfang Fu, Yang Li, Jianfang Wang, and Hongxing Xu. Photothermal Nanomaterials: A Powerful Light-to-Heat Converter. *Chem. Rev.*, 123(11):6891–6952, June 2023.
- [164] Yuan Zhao, Andrew Dunn, Jou Lin, and Donglu Shi. Photothermal Effect of Nanomaterials for Efficient Energy Applications. In Novel Nanomaterials for Biomedical, Environmental and Energy Applications, pages 415–434. Elsevier Inc., 2018.
- [165] Athil S. Al-Ezzi and Mohamed Nainar M. Ansari. Photovoltaic Solar Cells: A Review. ASI, 5(4):67, July 2022.
- [166] Shruti Sharma, Kamlesh Kumar Jain, and Ashutosh Sharma. Solar Cells: In Research and Applications—A Review. MSA, 06(12):1145–1155, 2015.
- [167] Marye Anne Fox and Maria T. Dulay. Heterogeneous Photocatalysis. Chemical Reviews, 93(1):341–357, 1993.
- [168] Andrew Mills and Stephen Le Hunte. An overview of semiconductor photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 108(1):1–35, 1997.
- [169] Rafaela B.P. Marcelino and Camila C. Amorim. Towards visible-light photocatalysis for environmental applications: Band-gap engineering versus photons absorption—a review. *Environmental Science and Pollution Research*, 26(5):4155–4170, 2019.
- [170] M. B. Tahir, G. Nabi, M. Rafique, and N. R. Khalid. Nanostructured-based WO₃ photocatalysts: Recent development, activity enhancement, perspectives and applications for wastewater treatment. *International Journal of Environmental Science and Technology*, 14(11):2519–2542, 2017.

- [171] Svetlana Grushevskaya, Irina Belyanskaya, and Oleg Kozaderov. Approaches for Modifying Oxide-Semiconductor Materials to Increase the Efficiency of Photocatalytic Water Splitting. *Materials*, 15:4915, 2022.
- [172] Peng Wang. Emerging investigator series: The rise of nano-enabled photothermal materials for water evaporation and clean water production by sunlight. *Environmental Science: Nano*, 5(5):1078–1089, 2018.
- [173] Dongheok Shin, Gumin Kang, Prince Gupta, Saraswati Behera, Hyungsuk Lee, Augustine M. Urbas, Wounjhang Park, and Kyoungsik Kim. Thermoplasmonic and Photothermal Metamaterials for Solar Energy Applications. Advanced Optical Materials, 6(18):1–26, 2018.
- [174] Andrew G. Scheuermann and Paul C. McIntyre. Atomic Layer Deposited Corrosion Protection: A Path to Stable and Efficient Photoelectrochemical Cells. J. Phys. Chem. Lett., 7(14):2867–2878, July 2016.
- [175] Akira Fujishima and Kenichi Honda. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature, 238(5358):37–38, July 1972.
- [176] Shuying Dong, Jinglan Feng, Maohong Fan, Yunqing Pi, Limin Hu, Xiao Han, Menglin Liu, Jingyu Sun, and Jianhui Sun. Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: A review. *RSC Advances*, 5(19):14610–14630, 2015.
- [177] Jiangtian Li and Nianqiang Wu. Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: A review. Catalysis Science and Technology, 5(3):1360–1384, 2015.
- [178] Irshad Ahmad, Yanhong Zou, Jiaying Yan, Yuyu Liu, Shazia Shukrullah, Muhammad Yasin Naz, Humaira Hussain, Waheed Qamar Khan, and N.R. Khalid. Semiconductor photocatalysts: A critical review highlighting the various strategies to boost the photocatalytic performances for diverse applications. *Advances in Colloid and Interface Science*, 311:102830, January 2023.
- [179] Huijie Wang, Xin Li, Xiaoxue Zhao, Chunyan Li, Xianghai Song, Peng Zhang, Pengwei Huo, and Xin Li. A review on heterogeneous photocatalysis for environmental remediation: From semiconductors to modification strategies. *Chinese Journal* of Catalysis, 43(2):178–214, February 2022.
- [180] Joseph A. Singh, Nuoya Yang, and Stacey F. Bent. Nanoengineering Heterogeneous Catalysts by Atomic Layer Deposition. Annual Review of Chemical and Biomolecular Engineering, 8(1):41–62, 2017.
- [181] Necmi Biyikli and Ali Haider. Atomic layer deposition: An enabling technology for the growth of functional nanoscale semiconductors. Semiconductor Science and Technology, 32(9):93002, 2017.
- [182] Brandon J. Oneill, David H.K. Jackson, Jechan Lee, Christian Canlas, Peter C. Stair, Christopher L. Marshall, Jeffrey W. Elam, Thomas F. Kuech, James A. Dumesic, and George W. Huber. Catalyst design with atomic layer deposition. ACS Catalysis, 5(3):1804–1825, 2015.
- [183] Umar Ibrahim Gaya. Heterogeneous Photocatalysis Using Inorganic Semiconductor Solids. Springer Berlin Heidelberg, Heidelberg, 2014.
- [184] David F. Ollis. Kinetic Disguises in Heterogeneous Photocatalysis. Topics in Catalysis, 35(3-4):217–223, 2005.
- [185] David F. Ollis. Kinetics of photocatalyzed reactions: Five lessons learned. Frontiers in Chemistry, 6(AUG):1-7, 2018.
- [186] A. V. Petukhov. Effect of molecular mobility on kinetics of an electrochemical Langmuir-Hinshelwood reaction. *Chemical Physics Letters*, 277(5-6):539–544, 1997.
- [187] R L Mckenzie, P J Aucamp, A F Bais, M Ilyas, S Madronich, M Norval, R M Lucas, A P Cullen, F R De Gruijl, J Longstreth, Y Takizawa, J C Van Der Leun, M M Caldwell, S D Flint, S A Robinson, J F Bornman, E W Helbling, C E Williamson, R C Worrest, R G Zepp, N D Paul, B Sulzberger, X Tang, S R Wilson, K R Solomon, M Shao, S Madronich, A L Andrady, H Hamid, A Torikai, P J Aucamp, and R Lucas. Ozone depletion and climate change: Impacts on UV radiation. *Photochemical* and Photobiological Sciences, 10(2):173, 2011.
- [188] Rito Yanagi, Tianshuo Zhao, Devan Solanki, Zhenhua Pan, and Shu Hu. Charge Separation in Photocatalysts: Mechanisms, Physical Parameters, and Design Principles. ACS Energy Lett., 7(1):432–452, January 2022.
- [189] M. Humayun, F. Raziq, A. Khan, and W. Luo. Modification strategies of TiO₂ for potential applications in photocatalysis: A critical review. *Green Chemistry Letters and Reviews*, 11(2):86–102, 2018.
- [190] Haijin Li, Yong Zhou, Wenguang Tu, Jinhua Ye, and Zhigang Zou. State-of-the-Art Progress in Diverse Heterostructured Photocatalysts toward Promoting Photocatalytic Performance. Adv Funct Materials, 25(7):998–1013, February 2015.
- [191] Younes Ahmadi and Ki-Hyun Kim. Modification strategies for visible-light photocatalysts and their performance-enhancing effects on photocatalytic degradation of volatile organic compounds. *Renewable and Sustainable Energy Reviews*, 189:113948, January 2024.
- [192] D. Beydoun, R. Amal, G. Low, and S. McEvoy. Role of nanoparticles in photocatalysis. *Journal of Nanoparticle Research*, 1(4):439–458, 1999.
- [193] Narendra Kumar and Sunita Kumbhat. Essentials in Nanoscience and Nanotechnology. John Wiley & Sons Inc., Hoboke, New Jersey, 2016.
- [194] Maria Benelmekki. Nanomaterials The Original Product of Nanotechnology. Morgan & Claypool Publishers, San Rafael, California, 2019.

- [195] L. E. Brus. Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. *The Journal of Chemical Physics*, 80(9):4403–4409, 1984.
- [196] Arnim Henglein. Small-Particle Research: Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles. Chemical Reviews, 89(8):1861–1873, 1989.
- [197] Horst Weller. Colloidal Semiconductor Q-Particles: Chemistry in the Transition Region Between Solid State and Molecules. Angewandte Chemie International Edition in English, 32(1):41–53, 1993.
- [198] Siew Yee Lim, Cheryl Suwen Law, Marijana Markovic, Jason K. Kirby, Andrew D. Abell, and Abel Santos. Engineering the Slow Photon Effect in Photoactive Nanoporous Anodic Alumina Gradient-Index Filters for Photocatalysis. ACS Applied Materials and Interfaces, 10(28):24124–24136, 2018.
- [199] Lina Liu, Siew Yee Lim, Cheryl Suwen Law, Bo Jin, Andrew D. Abell, Gang Ni, and Abel Santos. Engineering of Broadband Nanoporous Semiconductor Photonic Crystals for Visible-Light-Driven Photocatalysis. ACS Applied Materials and Interfaces, 12(51):57079–57092, 2020.
- [200] Heling Zhu, Yajuan Zhang, Jingqian Zhu, Yuhuan Li, Saihua Jiang, Na Wu, Yu Wei, Jinming Zhou, and Yanlin Song. Crackfree hematite inverse opal photo-anodes for enhancing photo-electrochemical water splitting. *Journal of Materials Chemistry* A, 8:22929–22937, 2020.
- [201] Hao Xie, Yuanzhi Li, Shaofen Jin, Jianjun Han, and Xiujian Zhao. Facile Fabrication of 3D-Ordered Macroporous Nanocrystalline Iron Oxide Films with Highly Efficient Visible Light Induced Photocatalytic Activity. *Journal of Physical Chemistry C*, 114:9706–9712, 2010.
- [202] Jie Long, Ming Fu, Caixia Li, Cuifeng Sun, Dawei He, and Yongsheng Wang. High-quality ZnO inverse opals and related heterostructures as photocatalysts produced by atomic layer deposition. *Applied Surface Science*, 454:112–120, October 2018.
- [203] Hamsasew Hankebo Lemago, Nour Khauli, Dóra Hessz, Tamás Igricz, Cserháti Csaba, Eszter Baradács, Bence Parditka, Zoltán Erdélyi, and Imre Miklós Szilágyi. Fabrication of Zno-Al2o3 Inverse Opals with Atomic Layer Deposited Amorphous-Al2o3 for Enhanced Photocatalysis, 2023.
- [204] P. Birnal, M.C. Marco De Lucas, I. Pochard, F. Herbst, O. Heintz, L. Saviot, B. Domenichini, and L. Imhoff. Visible-light photocatalytic degradation of dyes by TiO₂–Au inverse opal films synthesized by Atomic Layer Deposition. *Applied Surface Science*, 609:155213, January 2023.
- [205] J. S. King, E. Graugnard, and C. J. Summers. TiO 2 Inverse Opals Fabricated Using Low-Temperature Atomic Layer Deposition. Advanced Materials, 17(8):1010–1013, April 2005.
- [206] P. Birnal, M.C. Marco De Lucas, I. Pochard, B. Domenichini, and L. Imhoff. Photocatalytic properties of atomic layer deposited TiO₂ inverse opals and planar films for the degradation of dyes. *Applied Surface Science*, 512:145693, May 2020.
- [207] Khai Pham, Segolene Pelisset, Niko Kinnunen, Petri Karvinen, Tommi K. Hakala, and Jarkko J. Saarinen. Controlled photocatalytic activity of TiO₂ inverse opal structures with atomic layer deposited (ALD) metal oxide thin films. *Materials Chemistry* and Physics, 277:125533, February 2022.
- [208] Myungjun Kim, Joobong Lee, Seonhee Lee, Seongrok Seo, Changdeuck Bae, and Hyunjung Shin. Nanotubular Heterostructure of Tin Dioxide/Titanium Dioxide as a Binder-Free Anode in Lithium-Ion Batteries. *ChemSusChem*, 8(14):2363–2371, July 2015.
- [209] Ji Young Park, Jeong Hwan Han, and Byung Joon Choi. High-performance of ZnO/TiO₂ heterostructured thin-film photocatalyst fabricated via atomic layer deposition. *Journal of Vacuum Science & Technology A*, 42(3):032404, May 2024.
- [210] Mahmoud Sayed, Jiaguo Yu, Gang Liu, and Mietek Jaroniec. Non-Noble Plasmonic Metal-Based Photocatalysts. *Chem. Rev.*, 122(11):10484–10537, June 2022.
- [211] Gillian Collins, Alex Lonergan, David McNulty, Colm Glynn, Darragh Buckley, Changyu Hu, and Colm O'Dwyer. Semiconducting Metal Oxide Photonic Crystal Plasmonic Photocatalysts. Adv Materials Inter, 7(8):1901805, April 2020.
- [212] Junling Lu, Baosong Fu, Mayfair C. Kung, Guomin Xiao, Jeffrey W. Elam, Harold H. Kung, and Peter C. Stair. Coking- and Sintering-Resistant Palladium Catalysts Achieved Through Atomic Layer Deposition. *Science*, 335(6073):1205–1208, March 2012.
- [213] D.F. Zambrano, R. Villarroel, R. Espinoza-González, N. Carvajal, A. Rosenkranz, A.G. Montaño-Figueroa, M.J. Arellano-Jiménez, M. Quevedo-Lopez, P. Valenzuela, and W. Gacitúa. Mechanical and microstructural properties of broadband antireflective TiO₂/SiO₂ coatings for photovoltaic applications fabricated by magnetron sputtering. *Solar Energy Materials and Solar Cells*, 220:110841, January 2021.
- [214] Chenxu He, Baozhu Tian, and Jinlong Zhang. Thermally stable SiO₂-doped mesoporous anatase TiO₂ with large surface area and excellent photocatalytic activity. *Journal of Colloid and Interface Science*, 344(2):382–389, April 2010.
- [215] Yan Su, Jiansheng Wu, Xie Quan, and Shuo Chen. Electrochemically assisted photocatalytic degradation of phenol using silicon-doped TiO2 nanofilm electrode. *Desalination*, 252(1-3):143–148, March 2010.
- [216] Yu-Hong Zhang and Armin Reller. Phase transformation and grain growth of doped nanosized titania. Materials Science and Engineering: C, 19(1-2):323–326, January 2002.
- [217] S. Schipporeit, M. Jerman, and D. Mergel. Crystallization and conductivity of large-domain Nb-doped TiO₂ films prepared by electron beam evaporation. *Thin Solid Films*, 754:139299, July 2022.

- [218] H. Sankur and W. Gunning. Crystallization and diffusion in composite TiO₂-SiO₂ thin films. *Journal of Applied Physics*, 66(10):4747–4751, November 1989.
- [219] Huang-Wei Pan, Shun-Jin Wang, Ling-Chi Kuo, Shiuh Chao, Maria Principe, Innocenzo M. Pinto, and Riccardo DeSalvo. Thickness-dependent crystallization on thermal anneal for titania/silica nm-layer composites deposited by ion beam sputter method. *Opt. Express*, 22(24):29847, December 2014.
- [220] D R G Mitchell, G Triani, D J Attard, K S Finnie, P J Evans, C J Barbé, and J R Bartlett. Atomic layer deposition of TiO₂ and Al₂O₃ thin films and nanolaminates. *Smart Mater. Struct.*, 15(1):S57–S64, February 2006.
- [221] Ofelia Durante, Veronica Granata, Joshua Neilson, Giovanni Carapella, Francesco Chiadini, Riccardo DeSalvo, Roberta De Simone, Vincenzo Fiumara, Vincenzo Pierro, Innocenzo Mario Pinto, Antonio Vecchione, Rosalba Fittipaldi, Fabrizio Bobba, and Cinzia Di Giorgio. Investigation of crystallization in nanolayered TiO₂-based superlattices. *Surfaces and Interfaces*, 41:103309, October 2023.
- [222] Christoph W. Wiegand, René Faust, Alexander Meinhardt, Robert H. Blick, Robert Zierold, and Kornelius Nielsch. Understanding the Growth Mechanisms of Multilayered Systems in Atomic Layer Deposition Process. *Chemistry of Materials*, 30(6):1971–1979, 2018.
- [223] J W Elam, D Routkevitch, and S M George. Properties of ZnO/Al₂O₃ Alloy Films Grown Using Atomic Layer Deposition Techniques. *Journal of The Electrochemical Society*, 2003.
- [224] Michael Reinke, Yury Kuzminykh, and Patrik Hoffmann. Surface Reaction Kinetics of Titanium Isopropoxide and Water in Atomic Layer Deposition. J. Phys. Chem. C, 120(8):4337–4344, March 2016.
- [225] Jorge Luis Vazquez-Arce, Tibor Suta, Bálint Fodor, László Makai, Oscar Contreras, Amin Bahrami, Kornelius Nielsch, and Hugo Tiznado. Optical Properties of TiO₂ Grown by Atomic Layer Deposition Using Various Oxidizing Agents: The Ellipsometry Analysis of Absorption Properties. Adv Materials Inter, page 2400269, July 2024.
- [226] Xin Min Du and Rui M. Almeida. Effects of thermal treatment on the structure and properties of SiO₂-TiO₂ gel films on silicon substrates. J Sol-Gel Sci Technol, 8(1-3):377–380, February 1997.
- [227] George Christidis, Olga B. Fabrichnaya, Stefan M. Koepfli, Erik Poloni, Joel Winiger, Yuriy M. Fedoryshyn, Andrey V. Gusarov, Mariia Ilatovskaia, Ivan Saenko, Galina Savinykh, Valery Shklover, and Juerg Leuthold. Photonic response and temperature evolution of SiO₂/TiO₂ multilayers. *J Mater Sci*, 56(33):18440–18452, November 2021.
- [228] Takahiro Nakayama. Structure of TiO2₂/SiO₂ Multilayer Films. J. Electrochem. Soc., 141(1):237–241, January 1994.
- [229] Abbas Hodroj, Odette Chaix-Pluchery, Marc Audier, Ulrich Gottlieb, and Jean-Luc Deschanvres. Thermal annealing of amorphous Ti–Si–O thin films. J. Mater. Res., 23(3):755–759, March 2008.
- [230] Romy Dwipa Y. Away, Chika Takai-Yamashita, Takayuki Ban, and Yutaka Ohya. Photocatalytic properties of TiO₂-Si₂2 sandwich multilayer films prepared by sol-gel dip-coating. *Thin Solid Films*, 720:138522, February 2021.
- [231] Rui M. Almeida and Eva E. Christensen. Crystallization behavior of SiO₂-TiO₂ sol-gel thin films. J Sol-Gel Sci Technol, 8(1-3):409–413, February 1997.
- [232] Guillermo Calleja, David P. Serrano, Raúl Sanz, and Patricia Pizarro. Mesostructured SiO₂-doped TiO₂ with enhanced thermal stability prepared by a soft-templating sol-gel route. *Microporous and Mesoporous Materials*, 111(1-3):429–440, April 2008.
- [233] Zungang Zhu, Shengcai Wu, Yongfu Long, Lu Zhang, Xin Xue, Yue Yin, and Benjun Xu. Phase-transition kinetics of silicon-doped titanium dioxide based on high-temperature X-ray-diffraction measurements. *Journal of Solid State Chemistry*, 303:122544, November 2021.
- [234] Jinfeng Zhang, Peng Zhou, Jianjun Liu, and Jiaguo Yu. New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO₂. *Physical Chemistry Chemical Physics*, 16(38):20382–20386, 2014.
- [235] Zhenbiao Dong, Dongyan Ding, Ting Li, and Congqin Ning. Facile fabrication of Si-doped TiO₂ nanotubes photoanode for enhanced photoelectrochemical hydrogen generation. *Applied Surface Science*, 436:125–133, April 2018.
- [236] Kesong Yang, Ying Dai, and Baibiao Huang. First-principles calculations for geometrical structures and electronic properties of Si-doped TiO₂. *Chemical Physics Letters*, 456(1-3):71–75, April 2008.
- [237] Anaimalai Ramamoorthy Arul, Thirumalaisamy Esvaramoorthy Manjulavalli, and Rajendran Venckatesh. Visible light proven Si doped TiO₂ Nanocatalyst for the Photodegradation of Organic dye. *Materials Today: Proceedings*, 18:1760–1769, 2019.
- [238] M. Magnozzi, S. Terreni, L. Anghinolfi, S. Uttiya, M.M. Carnasciali, G. Gemme, M. Neri, M. Principe, I. Pinto, L.-C. Kuo, S. Chao, and M. Canepa. Optical properties of amorphous SiO₂-TiO₂ multi-nanolayered coatings for 1064-nm mirror technology. *Optical Materials*, 75:94–101, January 2018.
- [239] N. S. Gluck, H. Sankur, J. Heuer, J. DeNatale, and W. J. Gunning. Microstructure and composition of composite SiO₂/TiO₂ thin films. *Journal of Applied Physics*, 69(5):3037–3045, March 1991.
- [240] Abel Santos, Tushar Kumeria, and Dusan Losic. Nanoporous anodic aluminum oxide for chemical sensing and biosensors. *TrAC - Trends in Analytical Chemistry*, 44:25–38, 2013.
- [241] Abel Santos, Tushar Kumeria, Ye Wang, and Dusan Losic. In situ monitored engineering of inverted nanoporous anodic alumina funnels: On the precise generation of 3D optical nanostructures. *Nanoscale*, 6(17):9991–9999, 2014.

- [242] Dayin Xu, Congmian Zhen, and Hao Zhao. Microstructure and photoluminescence properties of anodized aluminum oxide films treated by argon ion. *Ceramics International*, 47(10):14382–14389, May 2021.
- [243] François Le Coz, Laurent Arurault, and Lucien Datas. Chemical analysis of a single basic cell of porous anodic aluminium oxide templates. *Materials Characterization*, 61(3):283–288, March 2010.
- [244] Gobinda Gopal Khan, Ashutosh K. Singh, and Kalyan Mandal. Structure dependent photoluminescence of nanoporous amorphous anodic aluminium oxide membranes: Role of F+ center defects. *Journal of Luminescence*, 134:772–777, 2013.
- [245] Yanyan Zhang, Zhelong Jiang, Jianying Huang, Linda Y. Lim, Wenlong Li, Jiyang Deng, Dangguo Gong, Yuxin Tang, Yuekun Lai, and Zhong Chen. Titanate and titania nanostructured materials for environmental and energy applications: A review. RSC Advances, 5(97):79479–79510, 2015.
- [246] Bo Weng, Ming-yu Qi, Chuang Han, Zi-rong Tang, and Yi-jun Xu. Photocorrosion Inhibition of Semiconductor-Based Photocatalysts: Basic Principle, Current Development, and Future Perspective. ACS Catalysis, 9:4642–4687, 2019.
- [247] Sha Chen, Danlian Huang, Piao Xu, Wenjing Xue, Lei Lei, Min Cheng, Rongzhong Wang, and Rui Deng. Semiconductorbased photocatalysts for photocatalytic and photoelectrochemical water splitting: Will we stop with photocorrosion ? Journal of Materials Chemistry A: Materials for energy and sustainability, 8:2286–2322, 2020.
- [248] Mariana C. O. Monteiro, Patrik Schmuki, and Manuela S. Killian. Tuning Anatase Surface Reactivity toward Carboxylic Acid Anchor Groups. *Langmuir*, 33(49):13913–13922, December 2017.
- [249] Mateusz Trochowski, Marcin Kobielusz, Krystian Mróz, Marcin Surówka, Jani Hämäläinen, Tomi Iivonen, Markku Leskelä, and Wojciech Macyk. How insignificant modifications of photocatalysts can significantly change their photocatalytic activity. J. Mater. Chem. A, 7(43):25142–25154, 2019.
- [250] Dong-Yong Chung, Eung-Ho Kim, Young-Joon Shin, Jae-Hyung Yoo, Cheong-Song Choi, and Jong-Duk Kim. Decomposition of oxalate by hydrogen peroxide in aqueous solution. *Journal of Radioanalytical and Nuclear Chemistry Letters*, 201(6):495– 507, December 1995.
- [251] Weilin Guo, Yin Cao, Yi Zhang, Lijun Wang, and Lingxue Kong. Synthesis of porous iron hydroxy phosphate from phosphate residue and its application as a Fenton-like catalyst for dye degradation. *Journal of Environmental Sciences*, 112:307–319, February 2022.
- [252] M. Arshadi, H. Zandi, J. Akbari, and A. Shameli. Ferrocene functionalized nanoscale mixed-oxides as a potent phosphate adsorbent from the synthetic and real (Persian Gulf) waters. *Journal of Colloid and Interface Science*, 450:424–433, July 2015.
- [253] Yongmin Zhang, Shanjuan Zhao, Meng Mu, Lushan Wang, Ye Fan, and Xuefeng Liu. Eco-friendly ferrocene-functionalized chitosan aerogel for efficient dye degradation and phosphate adsorption from wastewater. *Chemical Engineering Journal*, 439:135605, July 2022.
- [254] Ibtihal Mimouni, Mohamed Yahya, Asmae Bouziani, Yassine Naciri, Fatima-ezzahra Maarouf, Mohammed Alaoui El Belghiti, and Mohammed El Azzouzi. Iron phosphate for photocatalytic removal of Ibuprofen from aqueous media under sun-like irradiation. Journal of Photochemistry and Photobiology A: Chemistry, 433:114170, December 2022.
- [255] Arun S. Wagh and Seung Y. Jeong. Chemically Bonded Phosphate Ceramics: III, Reduction Mechanism and Its Application to Iron Phosphate Ceramics. *Journal of the American Ceramic Society*, 86(11):1850–1855, November 2003.
- [256] Dinghua Yu, Cheng Wu, Yan Kong, Nianhua Xue, Xuefeng Guo, and Weiping Ding. Structural and Catalytic Investigation of Mesoporous Iron Phosphate. J. Phys. Chem. C, 111(39):14394–14399, October 2007.
- [257] Lina Liu, Siew Yee Lim, Cheryl Suwen Law, Bo Jin, Andrew D. Abell, Gang Ni, and Abel Santos. Light-confining semiconductor nanoporous anodic alumina optical microcavities for photocatalysis. *Journal of Materials Chemistry A*, 7(39):22514–22529, 2019.
- [258] K. P. Birch and M. J. Downs. An updated Edlén equation for the refractive index of air. *Metrologia*, 30(3):155–162, 1993.
- [259] Masahiko Daimon and Akira Masumura. Measurement of the refractive index of distilled water from the near-infrared region to the ultraviolet region. Applied Optics, 46(18):3811–3820, 2007.
- [260] Tim Luttrell, Sandamali Halpegamage, Junguang Tao, Alan Kramer, Eli Sutter, and Matthias Batzill. Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO₂ films. *Scientific Reports*, 4:1–8, 2015.
- [261] Yuanzhi Li, Toyoki Kunitake, and Shigenori Fujikawa. Efficient Fabrication and Enhanced Photocatalytic Activities of 3D-Ordered Films of Titania Hollow Spheres. J. Phys. Chem. B, 110(26):13000–13004, July 2006.
- [262] Tianyong Zhang, Toshiyuki Oyama, Akio Aoshima, Hisao Hidaka, Jincai Zhao, and Nick Serpone. Photooxidative Ndemethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation. *Journal of Photochemistry and Photobiology A: Chemistry*, 140(2):163–172, 2001.
- [263] Tianyong Zhang, Toshiyuki Oyama, Satoshi Horikoshi, Hisao Hidaka, Jincai Zhao, and Nick Serpone. Photocatalyzed Ndemethylation and degradation of methylene blue in titania dispersions exposed to concentrated sunlight. *Solar Energy Materials and Solar Cells*, 73(3):287–303, 2002.
- [264] Soonhyun Kim and Wonyong Choi. Visible-Light-Induced Photocatalytic Degradation of 4-Chlorophenol and Phenolic Compounds in Aqueous Suspension of Pure Titania: Demonstrating the Existence of a Surface-Complex-Mediated Path. J. Phys. Chem. B, 109(11):5143–5149, March 2005.

- [265] Jean Marie Herrmann. Heterogeneous photocatalysis: Fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today*, 53(1):115–129, 1999.
- [266] Suzushi Nishimura, Neal Abrams, Bradley A. Lewis, Lara I. Halaoui, Thomas E. Mallouk, Kurt D. Benkstein, Jao Van de Lagemaat, and Arthur J. Frank. Standing wave enhancement of red absorbance and photocurrent in dye-sensitized titanium dioxide photoelectrodes coupled to photonic crystals. *Journal of the American Chemical Society*, 125(20):6306–6310, 2003.
- [267] Jennifer I.L. Chen, Georg Von Freymann, Sung Yeun Choi, Vladimir Kitaev, and Geoffrey A. Ozin. Amplified photochemistry with slow photons. Advanced Materials, 18(14):1915–1919, 2006.
- [268] Jennifer I.L. Chen, Georg Von Freymann, Vladimir Kitaev, and Geoffrey A. Ozin. Effect of disorder on the optically amplified photocatalytic efficiency of titania inverse opals. *Journal of the American Chemical Society*, 129(5):1196–1202, 2007.
- [269] Jennifer I.L. Chen, Edward Loso, Naazia Ebrahim, and Geoffrey A. Ozin. Synergy of slow photon and chemically amplified photochemistry in platinum nanocluster-loaded inverse titania opals. *Journal of the American Chemical Society*, 130(16):5420– 5421, 2008.
- [270] Min Wu, Yu Li, Zhao Deng, and Bao Lian Su. Three-dimensionally ordered macroporous titania with structural and photonic effects for enhanced photocatalytic efficiency. *ChemSusChem*, 4(10):1481–1488, 2011.
- [271] Sheng-Li Chen, Ai-Jun Wang, Chun-Tian Hu, and Chao Dai. Enhanced Photocatalytic Performance of Nanocrystalline TiO₂ Membrane by Both Slow Photons and Stop-band Reflection of Photonic Crystals. *AIChE Journal*, 58(2):568–572, 2012.
- [272] Zhongyu Cai, Zhigang Xiong, Xianmao Lu, and Jinghua Teng. Insitu gold-loaded titania photonic crystals with enhanced photocatalytic activity. *Journal of Materials Chemistry A*, 2(2):545–553, 2014.
- [273] Xing Zhang, Yang Liu, Shuit Tong Lee, Shihe Yang, and Zhenhui Kang. Coupling surface plasmon resonance of gold nanoparticles with slow-photon-effect of TiO₂ photonic crystals for synergistically enhanced photoelectrochemical water splitting. *Energy and Environmental Science*, 7(4):1409–1419, 2014.
- [274] Jae Hyo Han, Anna V. Shneidman, Do Yoon Kim, Natalie J. Nicolas, Jessi E. S. van der Hoeven, Michael Aizenberg, and Joanna Aizenberg. Highly Ordered Inverse Opal Structures Synthesized from Shape-Controlled Nanocrystal Building Blocks. *Angewandte Chemie*, 2021.
- [275] Martha Pylarinou, Alexia Toumazatou, Elias Sakellis, Evangelia Xenogiannopoulou, Spiros Gardelis, Nikos Boukos, Athanasios Dimoulas, and Vlassis Likodimos. Visible Light Trapping against Charge Recombination in FeO_x-TiO₂ Photonic Crystal Photocatalysts. *Materials*, 14:1–17, 2021.
- [276] Sugang Meng, Danzhen Li, Peng Wang, Xiuzhen Zheng, Jinxiu Wang, Jing Chen, Jialin Fang, and Xianzhi Fu. Probing photonic effect on photocatalytic degradation of dyes based on 3D inverse opal ZnO photonic crystal. *RSC Advances*, 3(38):17021– 17028, 2013.
- [277] Jing Liu, Jun Jin, Yu Li, Hua Wen Huang, Chao Wang, Min Wu, Li Hua Chen, and Bao Lian Su. Tracing the slow photon effect in a ZnO inverse opal film for photocatalytic activity enhancement. *Journal of Materials Chemistry A*, 2(14):5051–5059, 2014.
- [278] Liang Zhou, Juying Lei, Lingzhi Wang, Yongdi Liu, and Jinlong Zhang. Highly Efficient Photo-Fenton Degradation of Methyl Orange Facilitated by Slow Light Effect and Hierarchical Porous Structure of Fe₂O₃-SiO₂ Photonic Crystals. Applied Catalysis B: Environmental, 2017.
- [279] Damon A Wheeler, Gongming Wang, Yichuan Ling, Yat Li, and Jin Z Zhang. Nanostructured hematite: Synthesis, characterization, charge carrier dynamics, and photoelectrochemical properties. *Energy and Environmental Science*, 5:6682–6702, 2012.
- [280] Pardeep Singh, Kirti Sharma, Vasudha Hasija, Sheetal Sharma, Pankaj Raizada, Mahavir Singh, Adesh K. Saini, Ahmad Hosseini-Bandegharaei, and Vijay Kumar Thakur. Systematic review on applicability of magnetic iron-oxides integrated photocatalysts for degradation of organic pollutants in water. *Materials Today*, 14:100186, 2019.
- [281] O. Akhavan. Thickness dependent activity of nanostructured TiO₂/α-Fe₂O₃ photocatalyst thin films. Applied Surface Science, 257(5):1724–1728, 2010.
- [282] Kenneth I Hardee and Allen J Bard. Semiconductor Electrodes: X. Photoelectrochemical Behavior of Several Polycrystalline Metal Oxide Electrodes in Aqueous Solutions. *Journal of The Electrochemical Society*, 124:215–224, 1977.
- [283] Jonathan K Leland and Allen J Bard. Photochemistry of Colloidal Semiconducting Iron Oxide Polymorphs. Journal of Physical Chemistry, 91:5076–5083, 1987.
- [284] C. Argile and G. E. Rhead. Adsorbed layer and thin film growth modes monitored by Auger electron spectroscopy. Surface Science Reports, 10(6-7):277–356, 1989.
- [285] Mattis Fondell. Synthesis and Characterisation of Ultra Thin Film Oxides for Energy Applications. PhD thesis, Uppsala University, 2014.
- [286] Marta I. Litter and Miguel A. Blesa. Photodissolution of iron oxides. IV. A comparative study on the photodissolution of hematite, magnetite, and maghemite in EDTA media. *Canadian Journal of Chemistry*, 70(9):2502–2510, 1992.
- [287] Donia Beydoun, Rose Amal, Gary K Low, and Stephen Mcevoy. Novel Photocatalyst: Titania-Coated Magnetite . Activity and Photodissolution. *Journal of Physical Chemistry B*, 104(18):4387–4396, 2000.
- [288] Donia Beydoun, Rose Amal, Gary Low, and Stephen Mcevoy. Occurrence and prevention of photodissolution at the phase junction of magnetite and titanium dioxide. *Journal of Molecular Catalysis A: Chemical*, 180:193–200, 2002.

- [289] Russell S. Jack, Godwin A. Ayoko, Moses O. Adebajo, and Ray L. Frost. A review of iron species for visible-light photocatalytic water purification. *Environmental Science and Pollution Research*, 22(10):7439–7449, 2015.
- [290] Nicolas Vogel, Markus Retsch, Charles-André Fustin, Aranzazu Del Campo, and Ulrich Jonas. Advances in Colloidal Assembly: The Design of Structure and Hierarchy in Two and Three Dimensions. *Chem. Rev.*, 115(13):6265–6311, July 2015.
- [291] Liming Zhai, Bin Zhang, Haitao Li, Min Jiang, Xinchun Yang, Zhuo Li, Shichao Zhao, and Yong Qin. The Deposition of Isolated Fe(3+) Species in Mesoporous Silicon for Oxidation of Cyclohexane. *ChemCatChem*, page e202300887, November 2023.
- [292] Ana Katharina Steffens. Semiconductor Heterostructures to Tune Tailor-made Nanoporous Photocatalysts. *Bachelor's Thesis*, Universität Hamburg, 2023.
- [293] S. Canulescu, K. Rechendorff, C. N. Borca, N. C. Jones, K. Bordo, J. Schou, L. Pleth Nielsen, S. V. Hoffmann, and R. Ambat. Band gap structure modification of amorphous anodic Al oxide film by Ti-alloying. *Applied Physics Letters*, 104(12):1–5, 2014.
- [294] Elena O. Filatova and Aleksei S. Konashuk. Interpretation of the Changing the Band Gap of Al₂O₃ Depending on Its Crystalline Form: Connection with Different Local Symmetries. *Journal of Physical Chemistry C*, 119(35):20755–20761, 2015.
- [295] Yan Qiang Cao, Tao Qing Zi, Xi Rui Zhao, Chang Liu, Qiang Ren, and Jia Bin Fang. Enhanced visible light photocatalytic activity of Fe₂O₃ modified TiO₂ prepared by atomic layer deposition. *Scientific Reports*, pages 1–10, 2020.
- [296] O. Carp, C. L. Huisman, and A. Reller. Photoinduced reactivity of titanium dioxide. Progress in Solid State Chemistry, 32(1-2):33–177, 2004.
- [297] Anita Trenczek-Zajac, Milena Synowiec, Katarzyna Zakrzewska, Karolina Zazakowny, Kazimierz Kowalski, Andrzej Dziedzic, and Marta Radecka. Scavenger-Supported Photocatalytic Evidence of an Extended Type I Electronic Structure of the TiO₂ @Fe₂O₃ Interface. ACS Applied Materials and Interfaces, 14(33):38255–38269, 2022.
- [298] Arto Hiltunen, Tero-Petri Ruoko, Tomi Iivonen, Kimmo Lahtonen, Harri Ali-Löytty, Essi Sarlin, Mika Valden, Markku Leskelä, and Nikolai Tkachenko. Design aspects of all atomic layer deposited TiO₂–Fe₂O₃ scaffold-absorber photoanodes for water splitting. *Sustainable Energy Fuels*, 2(9):2124–2130, 2018.
- [299] Linlin Peng, Tengfeng Xie, Yongchun Lu, Haimei Fan, and Dejun Wang. Synthesis, photoelectric properties and photocatalytic activity of the Fe₂O₃/TiO₂ heterogeneous photocatalysts. *Phys. Chem. Chem. Phys.*, 12(28):8033, 2010.
- [300] Xiaoyang Pan, Min-Quan Yang, Xianzhi Fu, Nan Zhang, and Yi-Jun Xu. Defective TiO₂ with oxygen vacancies: Synthesis, properties and photocatalytic applications. *Nanoscale*, 5(9):3601, 2013.
- [301] Radhika V Nair, Venkata Siva Gummaluri, Murukeshan Vadakke Matham, and Vijayan C. A review on optical bandgap engineering in TiO₂ nanostructures via doping and intrinsic vacancy modulation towards visible light applications. J. Phys. D: Appl. Phys., 55(31):313003, August 2022.
- [302] Hieu H. Pham and Lin-Wang Wang. Oxygen vacancy and hole conduction in amorphous TiO₂. Phys. Chem. Chem. Phys., 17(1):541–550, 2015.
- [303] Luminita Andronic and Alexandru Enesca. Black TiO₂ Synthesis by Chemical Reduction Methods for Photocatalysis Applications. *Front. Chem.*, 8:565489, November 2020.
- [304] Junming Li, Wenxia Su, Jun Li, Lu Wang, Jun Ren, Sheng Zhang, Pengtao Cheng, Hong Hong, Dunhui Wang, Yong Zhou, Wenbo Mi, and Youwei Du. Orientational Alignment of Oxygen Vacancies: Electric-Field-Inducing Conductive Channels in TiO₂ Film to Boost Photocatalytic Conversion of CO₂ into CO. *Nano Lett.*, 21(12):5060–5067, June 2021.
- [305] Yuanxin Deng, Mingyang Xing, and Jinlong Zhang. An advanced TiO₂/Fe₂TiO₅/Fe₂O₃ triple-heterojunction with enhanced and stable visible-light-driven fenton reaction for the removal of organic pollutants. *Applied Catalysis B: Environmental*, 211:157–166, August 2017.
- [306] Zirui Lou, Yaguang Li, Hui Song, Zhizhen Ye, and Liping Zhu. Fabrication of Fe₂TiO₅/TiO₂ nanoheterostructures with enhanced visible-light photocatalytic activity. *RSC Adv.*, 6(51):45343–45348, 2016.
- [307] Higor A. Centurion, Mauricio A. Melo, Lucas G. Rabelo, Gustavo A.S. Alves, Washington Santa Rosa, Ingrid Rodríguez-Gutiérrez, Flavio L. Souza, and Renato V. Gonçalves. Emerging trends of pseudobrookite Fe₂TiO₅ photocatalyst: A versatile material for solar water splitting systems. *Journal of Alloys and Compounds*, 933:167710, February 2023.
- [308] Damián Monllor-Satoca, Mario Bärtsch, Cristian Fàbrega, Aziz Genç, Sandra Reinhard, Teresa Andreu, Jordi Arbiol, Markus Niederberger, and Joan Ramon Morante. What do you do, titanium? Insight into the role of titanium oxide as a water oxidation promoter in hematite-based photoanodes. *Energy Environ. Sci.*, 8(11):3242–3254, 2015.
- [309] Guillaume Seitz, Nicolas Penin, Léa Decoux, Alain Wattiaux, Mathieu Duttine, and Manuel Gaudon. Near the Ferric Pseudobrookite Composition (Fe₂TiO₅). *Inorg. Chem.*, 55(5):2499–2507, March 2016.
- [310] Chengcheng Li, Tuo Wang, Zhibin Luo, Shanshan Liu, and Jinlong Gong. Enhanced Charge Separation through ALD-Modified Fe₂O₃/Fe₂TiO₅ Nanorod Heterojunction for Photoelectrochemical Water Oxidation. *Small*, 12(25):3415–3422, 2016.
- [311] PengYi Tang, HaiBing Xie, Carles Ros, LiJuan Han, Martí Biset-Peiró, YongMin He, Wesley Kramer, Alejandro Pérez Rodríguez, Edgardo Saucedo, José Ramón Galán-Mascarós, Teresa Andreu, Joan Ramon Morante, and Jordi Arbiol. Enhanced photoelectrochemical water splitting of hematite multilayer nanowire photoanodes by tuning the surface state via bottom-up interfacial engineering. *Energy Environ. Sci.*, 10(10):2124–2136, 2017.

- [312] Adilson Candido da Silva, Monique Rocha Almeida, Mariandry Rodriguez, Alan Rodrigues Teixeira Machado, Luiz Carlos Alves de Oliveira, and Márcio César Pereira. Improved photocatalytic activity of δ-FeOOH by using H₂O₂ as an electron acceptor. Journal of Photochemistry and Photobiology A: Chemistry, 332:54–59, 2017.
- [313] Md. Ashraful Islam Molla, Ikki Tateishi, Mai Furukawa, Hideyuki Katsumata, Tohru Suzuki, and Satoshi Kaneco. Evaluation of Reaction Mechanism for Photocatalytic Degradation of Dye with Self-Sensitized TiO₂ under Visible Light Irradiation. Open Journal of Inorganic Non-metallic Materials, 07(01):1–7, 2017.
- [314] Jéssica Tamara Schneider, Daniele Scheres Firak, Ronny Rocha Ribeiro, and Patricio Peralta-Zamora. Use of scavenger agents in heterogeneous photocatalysis: Truths, half-truths, and misinterpretations. *Physical Chemistry Chemical Physics*, 22(27):15723–15733, 2020.
- [315] Yoshiaki Tamaki, Akihiro Furube, Miki Murai, Kohjiro Hara, Ryuzi Katoh, and M. Tachiya. Direct observation of reactive trapped holes in TiO₂ undergoing photocatalytic oxidation of adsorbed alcohols: Evaluation of the reaction rates and yields. *Journal of the American Chemical Society*, 128(2):416–417, 2006.
- [316] David Brinkley and Thomas Engel. Photocatalytic dehydrogenation of 2-propanol on TiO₂(110). *Journal of Physical Chemistry B*, 102(39):7596–7605, 1998.
- [317] Lawrence M Peter. Dynamic aspects of semiconductor photoelectrochemistry. Chemical Reviews, 90(5), 1990.
- [318] W. John Albery, Gerald J. O'Shea, and Alec L. Smith. Interpretation and use of Mott–Schottky plots at the semiconductor/electrolyte interface. J. Chem. Soc., Faraday Trans., 92(20):4083–4085, 1996.
- [319] K Gelderman, L Lee, and S W Donne. Flat-Band Potential of a Semiconcuctor: Using the Mott–Schottky Equation. Journal of Chemical Education, 84(4), 2007.
- [320] Josny Joy, Jinu Mathew, and Soney C. George. Nanomaterials for photoelectrochemical water splitting review. International Journal of Hydrogen Energy, 43(10):4804–4817, March 2018.
- [321] Sandra Haschke, Yanlin Wu, Muhammad Bashouti, Silke Christiansen, and Julien Bachmann. Engineering Nanoporous Iron(III) Oxide into an Effective Water Oxidation Electrode. *ChemCatChem*, 7(16):2455–2459, 2015.
- [322] Hussain Al-ekabi, Nick Serpone, Ezio Pelizzetti, Claudio Minero, Marye Anne Fox, and R. Barton Draper. Kinetic Studies in Heterogeneous Photocatalysis. 2. TiO₂-Mediated Degradation of 4-Chlorophenol Alone and in a Three-Component Mixture of 4-Chlorophenol, 2,4-Dichlorophenol, and 2,4,5-Trichlorophenol in Air-Equilibrated Aqueous Media. *Langmuir*, 5(1):250–255, 1989.
- [323] Yahui Shi, Jinhui Huang, Guangming Zeng, Wenjian Cheng, and Jianglin Hu. Photocatalytic membrane in water purification: Is it stepping closer to be driven by visible light? *Journal of Membrane Science*, 584:364–392, August 2019.
- [324] Pooria Sedigh Rahimabadi, Mehdi Khodaei, and Kaveenga R. Koswattage. Review on applications of synchrotron-based X-ray techniques in materials characterization. X-Ray Spectrometry, 49(3):348–373, May 2020.
- [325] Xiaosong Liu, Wanli Yang, and Zhi Liu. Recent Progress on Synchrotron-Based In-Situ Soft X-ray Spectroscopy for Energy Materials. Advanced Materials, 26(46):7710–7729, December 2014.
- [326] X Q Yang, X Sun, S J Lee, J McBreen, S Mukerjee, M L Daroux, and X K Xing. In Situ Synchrotron X-Ray Diffraction Studies of the Phase Transitions in Li_xMn₂O₄ Cathode Materials. *Electrochemical and Solid-State Letters*, 2:157–160, 1999.
- [327] Robert M. Pasquarelli, Hooi Sing Lee, Roman Kubrin, Robert Zierold, Alexander Yu Petrov, Kornelius Nielsch, Gerold A. Schneider, Manfred Eich, and Rolf Janssen. Enhanced structural and phase stability of titania inverse opals. *Journal of the European Ceramic Society*, 35(11):3103–3109, 2015.
- [328] Gillian Collins, Alex Lonergan, David McNulty, Colm Glynn, Darragh Buckley, Changyu Hu, and Colm O'Dwyer. Semiconducting Metal Oxide Photonic Crystal Plasmonic Photocatalysts. Adv Materials Inter, 7(8):1901805, April 2020.
- [329] Rodolfo Zanella, Suzanne Giorgio, Claude R. Henry, and Catherine Louis. Alternative methods for the preparation of gold nanoparticles supported on TiO₂. Journal of Physical Chemistry B, 106(31):7634–7642, 2002.
- [330] Kun Cao, Jiaming Cai, Xiao Liu, and Rong Chen. Review Article: Catalysts design and synthesis via selective atomic layer deposition. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 36(1):010801, January 2018.
- [331] Juan I. Mirena, Denis Constales, Johan Martens, Jolien Dendooven, Gregory S. Yablonsky, and Vladimir V. Galvita. TAP analysis of single and double peak responses during CO oxidation over Pt. *Catalysis Today*, 417:113673, May 2023.
- [332] Markku Leskelä, Mikko Ritala, and Ola Nilsen. Novel materials by atomic layer deposition and molecular layer deposition. MRS Bull., 36(11):877–884, November 2011.
- [333] Tomáš Imrich, Hana Krýsová, Michael Neumann-Spallart, and Josef Krýsa. Pseudobrookite (Fe₂TiO₅) films: Synthesis, properties and photoelectrochemical characterization. *Catalysis Today*, 413–415:113982, March 2023.
- [334] Jiujun Deng, Xiaoxin Lv, Jinyin Liu, Hui Zhang, Kaiqi Nie, Caihao Hong, Jiaou Wang, Xuhui Sun, Jun Zhong, and Shuit-Tong Lee. Thin-Layer Fe₂TiO₅ on Hematite for Efficient Solar Water Oxidation. ACS Nano, 9(5):5348–5356, May 2015.
- [335] Roman Kubrin, Robert M. Pasquarelli, Martin Waleczek, Hooi Sing Lee, Robert Zierold, Jefferson J. Do Rosário, Pavel N. Dyachenko, Josep M. Montero Moreno, Alexander Yu Petrov, Rolf Janssen, Manfred Eich, Kornelius Nielsch, and Gerold A. Schneider. Bottom-up Fabrication of Multilayer Stacks of 3D Photonic Crystals from Titanium Dioxide. ACS Applied Materials and Interfaces, 8(16):10466–10476, 2016.

- [336] Carina Hedrich. Tailor-made Anodic Aluminum Oxide Photonic Crystals for Application in Photocatalysis. *Master's Thesis*, Universität Hamburg, 2021.
- [337] Robert Zierold. Magnetite Nanotubes and Nickel Nanorods of Low Aspect Ratios: From Synthesis to Application in Ferrofluidic Suspensions. *Dissertation, Universität Hamburg*, 2013.
- [338] Nikolaos Voudoukis and Sarantos Oikonomidis. Inverse square law for light and radiation: A unifying educational approach. European Journal of Engineering Research and Science, 2(11):23, 2017.
- [339] Ammar Houas, Hinda Lachheb, Mohamed Ksibi, Elimame Elaloui, Chantal Guillard, and Jean Marie Herrmann. Photocatalytic degradation pathway of methylene blue in water. Applied Catalysis B: Environmental, 31(2):145–157, 2001.
- [340] Matthieu Petit, Lisa Michez, Jean Manuel Raimundo, Tuhiti Malinowski, and Philippe Dumas. An introduction to photocatalysis through methylene blue photodegradation. *European Journal of Physics*, 37(6), 2016.

Appendix

A.1. Experimental Setups

Home-built setups utilized for the experiments in this thesis are presented in the following sections. The setups for anodization, ALD, and UV/Vis were previously constructed in our group, but are nevertheless explained here as they are essential for sample fabrication and characterization in this work. ^[336, 337] The photocatalysis setup was designed and optimized by me in the frame of this thesis.

A.1.1. Anodization Setup

Aluminum anodization is carried out with a home-built anodization setup shown in Figure A.1. The setup consists of an anodization cell in which the Al sample is placed as anode and an anodization hat containing the cathode and a stirrer. In detail, the sample is mounted into the cell by clamping it between the cell bottom and a copper back plate. The cell is filled with the electrolyte and covered with the hat which contains a noble metal wire grid as cathode. The copper back plate of the cell has two functions: First, it provides the electrical contact to the Al sample that is required for electrochemical oxidation. Second, the cell is placed on the cooling plate and the copper back plate mediates the heat transfer to ensure a constant temperature of the electrolyte inside the cell. The cooling plate is connected to a chiller (Haake C25P Refrigerated Bath with Phoenix II Controller, Thermo Fisher) to allow for precise temperature control during anodization. Anodization can be conducted under potentiostatic or galvanostatic conditions. A Keithley 2400 sourcemeter is used as power supply and is connected to the anode and cathode. Applied potentiostatic or galvanostatic anodization profiles are controlled by a LabVIEW software developed by Prof. Abel Santos (University of Adelaide). Different profiles such as con-



Figure A.1. Photographs of the anodization setup showing (a) the complete setup with the assembled anodization cell and hat, (b) the anodization cell, and (c) the anodization hat.



Figure A.2. Exemplary pulse-like anodization profile applying rectangular current density pulses. The pulses are defined by the low and high current densities j_{low} and j_{high} and the duration at these values t_{low} and t_{high} which result in the pulse duration t_{pulse} .

stant voltage or pulse-like voltage or current density profiles are used depending on the desired pore wall morphology. Especially the pulse-like profiles (Figure A.2.) allow for tuning many parameters such as pulse shape, pulse duration, voltage/current amplitude, increase/decrease rate and shape, or number of pulse repetitions, to name a few. This versatile control renders precise tuning of the AAO-PhCs structural and hence, optical properties easily realizable.

A.1.2. Atomic Layer Deposition Systems

Three systems are utilized for ALD of different metal oxides. System 1 and 2 are homebuilt devices that are operated for Al_2O_3 and TiO_2 (both system 1) and Fe_2O_3 deposition (system 2).¹ A commercial ALD System (GEMStar, Arradiance) is used as third system for deposition of SiO₂ and TiO₂. All ALD processes are conducted under stop-flow conditions and use nitrogen (N₂) 6.0 as carrier gas during the ALD processes. The standard deposition parameters for the different materials are summarized in Table A.1 including temperature, carrier gas flow, precursor types, pulse times, exposure times, purge times, and growth per cycle (GPC) for each process.

¹The home-built ALD systems were constructed by Dr. Robert Zierold during his PhD thesis in 2009/2010. ^[337]

A.1.3. Photocatalysis Setup

The photocatalaysis setup was constructed and optimized for studying the degradation of organic dyes by photocatalyst-coated PhC structures. Based on previous work using AAO-PhCs as templates in combination with a Lumixo S light source as a solar simulator, ^[336] the following requirements for the photocatalysis setup have been identified:

- The light source emission spectrum should be mainly located in the visible range of the electromagnetic spectrum to avoid strong influence of the photoluminescence of Al₂O₃.
- Precise control of the distance between the light source and the sample is crucial as the light intensity decreases with the inverse square of the distance to the light source. ^[338]
- Only the sample area of interest should be exposed to the dye solution to prevent side-reactions from the Al frame or from the backside of the sample.
- The exposed sample area has to be precisely defined and sample exchange should easily be done.
- The sample has to be located at the end of the sample holder to avoid solution containing volume that is not irradiated during the measurements.
- The sample holder has to be inert against chemical reactions occurring in the photocatalysis measurements.

According to these criteria, the photocatalysis setup was built with a modified Euromex LE.5211 halogen light source, a custom-build photocatalysis cell, and a custom-made sample stage shown in Figure A.3.. The Euromex LE.5211 light source emits 98.8% of its spectrum in the visible range, i.e., 400 nm - 750 nm wavelength. Small fractions of 0.7% and 0.5% are emitted in the ultraviolet range (300 nm - 400 nm) and in the near-infrared range (750 nm - 900 nm), respectively. The light source was modified by mounting a pressurized air outlet directly above the bulb for additional cooling during operation. The photocatalysis cell is made of polyether ether ketone (PEEK) as an inert material. A sample is fixed in the cell by clamping it between the back plate and an oring whereby the utilized o-ring defines the exposed sample area. At the front site, the photocatalysis cell has a transparent window of soda-lime glass. The cell is filled with the dye solution which should be photocatalytically degraded and is then put onto the 3Dprinted sample stage made of polylactic acid (PLA). This stage is constructed in a way that first, the complete sample is centrally in the beam of the light source. Second, the stage ensures a fixed distance between the sample and light source. This is very important as the light intensity scales to the power of minus two with the radius from a light source. Accordingly, even small differences in the sample-light source distance strongly impact the light intensity at the sample surface which is related to the measured photocatalytic activity of the sample. Since the photocatalytic performance of different samples should

be studied in this setup, the light intensity must be kept constant. Herein, organic dye solutions are used as model systems to investigate the photocatalytic degradation capability of different samples. Such organic dyes serve as model pollutants of water and can be decomposed by both oxidative and reductive reaction pathways. ^[339]This allows for characterizing various materials especially metal oxide semiconductors without the need of adapting reaction conditions (electrolyte or buffer) or potentials as required for photoelectrochemical analysis techniques. Based on Lambert-Beer's law, the dye concentration *c* present in a solution can be calculated by measuring the solutions absorbance *A* after calibration of the setup: ^[340]

$$A = \lg\left(\frac{I}{I_0}\right) = -\varepsilon \cdot c \cdot d \tag{A.1}$$

In this equation, I denotes the light intensity after passing through the solution, I_0 is the initial light intensity, d is the distance through the solution, and ε denotes the molar attenuation coefficient of the solution. Examination of the absorbance is conducted by UV/Vis transmission spectroscopy. For this, 1 ml of the dye solution is filled into a cuvette and analyzed in the setup. The general procedure of a photocatalytic measurement is described in (Section A). Since heating effects of the solution by the light irradiation occur within the first 10 min of the measurement until a stable temperature is reached, this time is excluded from the data analysis by setting the data point 10 min after initiating the photocatalytic degradation as starting point t_0 for the analysis.



Figure A.3. Photographs of the photocatalysis setup showing (a) the complete setup including the external power supply for the fan, the pressurized air cooling, the light source, the sample holder, and the sample stage. (b) depicts a front and top view of the sample holder.

To analyze the efficiency of a photocatalyst, it is important to understand the kinetics behind the process. Heterogeneous photocatalysis typically occurs via the Langmuir-Hinshelwood mechanism or the Eley-Rideal mechanism. ^[167, 183–185] The Langmuir-Hinshelwood mechanism assumes that both reactant adsorb at the catalyst surface before reacting. After the adsorption which is described by a Langmuir isotherm, the catalyzed reaction occurs. ^[167, 183–185] In processes following the Eley-Rideal mechanism only one of the reactants is adsorbed at the catalyst surface. Hence, the reaction occurs between the adsorbed component and another reactant which is still present in the phase of the surrounding medium. ^[185] The dye concentration decrease by photocatalytic degradation is analyzed by assuming Langmuir-Hinshelwood kinetics. ^[167, 183–185] This photocatalytic reaction mechanism is applicable to heterogeneous photocatalytic systems where a solid photocatalyst is immersed into a liquid or gaseous medium containing the species which is being decomposed, i.e., analyte molecules. Specifically, in the case of Langmuir-Hinshelwood kinetics, it is assumed that analyte molecules undergo monolayer adsorption on the surface of the photocatalyst, forming an adsorption-desorption equilibrium, before initiating the photocatalytic reaction. The equation below describes the general reaction rate, i.e., concentration change over time:

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \kappa \cdot c \tag{A.2}$$

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\kappa \cdot K \cdot c}{1 + K \cdot c} \tag{A.3}$$

where *K* is the adsorption coefficient at the surface. This rate equation is not a first order type anymore, but for diluted solutions with concentrations much smaller than 10^{-3} mol l⁻¹ as typical the case for organic compound decomposition, it simplifies to Equation A.4 which is a pseudo first-order kinetics equation. ^[183–186]

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \kappa \cdot K \cdot c = k \cdot c \tag{A.4}$$

Here, k as the product of the reaction rate constant κ and the adsorption coefficient K denotes the apparent rate constant. Since k represents the rate constant of the degradation for a specific photocatalyst, it can be used as a measure for the photocatalytic activity of the photocatalyst.

Photocatalysis Measurement Procedure

The typical sequence of a photocatalytic measurement is described below.

Step	Time related to the photocataly- sis measurement start
1. Switching on the UV-vis lamp 1 h prior to starting the photocatalysis measurement. The bulb needs to warm up to provide stable light emission.	- 1 h
2. Mounting the sample in the photocatalysis sample holder (Figure A.3.(b)) 1 h before starting the measurement. This time is required to obtain adsorption-desorption equilibrium of the reactants at the catalysts' surface which is necessary for reactions according to Langmuir-Hinshelwood mechanism.	- 1 h
3. Switching on the photocatalysis lamp and opening the pressurized air valve 15 min before starting the measurements.	- 15 min
4. Calibrating the UV-Vis lamp for the absorption measurement in the software <i>OceanView</i> .	- 5 min
5. Measuring the absorption of 1 ml of the solution as 0 min point to start the photocatalysis measurement. Filling the solution back into the sample holder and placing the sample holder on the sample stage. Excluding light from the photocatalysis lamp during sample holder positioning by placing a black shutter plate between the lamp and sample holder. Finally, putting the black cap over the sample holder to exclude illumination from the room light.	0 min
6. 5 min after starting the measurement, interrupting the illumination by placing the shutter plate between sample holder and photocatalysis lamp. Pipetting 1 ml from the solution into the cuvette, measuring the absorption in the UV-Vis setup, and pipetting the solution back into the sample holder. Removing the shutter plate and starting the next 5 min degradation period.	+ 5 min
7. Repeating the procedure from 6. every 5 min for 70 min after starting the reaction	+ 10-70 min

A.1.4. UV/Vis Setups

UV/Vis measurements are conducted by utilizing light sources, cables, sampling accessory, and detectors from OceanOptics and custom-made 3D-printed structures. In Detail, transmission and reflection setups for solid samples and a absorbance measurement setup for liquids were construted during my Master's thesis in 2020/2021.^[336] For all setups data analysis is performed by using the software OceanView from OceanOptics. The transmission setup is built of a deuterium-halogen light source DH-2000 (OceanOptics), glass fiber cables (OceanOptics), collimators (OceanOptics), a self-build 3D-printed samples holder, and a Flame Extended Range Spectrometer (OceanOptics). Light from the deuterium-halogen light source is guided through a glass fiber cable and collimator to a sample which is fixed at the sample holder at normal incidence to the beam. The light transmitted through the sample is collected by a second collimator and guided through a glass fiber cable to the detector which is connected to the PC. The transmission measurement data is analyzed by using the Ocean View software with the following sampling parameters: 4 ms integration time, 20 scans to average, and a boxcar width of 5.

Two separate setups are utilized for reflection measurements under 0° and 45° incidence angle. The 0° incidence angle setup utilized the deuterium-halogen light source DH-2000 (OceanOptics) conncected to a bifurcated glass fiber cable (OceanOptics) that is positioned at 0° incidence in the reflectance sample holder(OceanOptics). The analyst end of the cable is mounted to the Flame Extended Range Spectrometer (OceanOptics) that is connected to the PC. Data acquisition is performed with 100 ms integration time, 5 scans to average, and a boxcar width of 7. At 45°, two glass fibe cables (OceanOptics) with collimators are used in combination with a 3D-printed sample holder. Sampling parameters of 500 ms, 5 scans per average, and boxcar width 7 are applied.

The absorbance setup consist of a halogen light source HL-2000 light (OceanOptics) connected to a glass fiber cable (OceanOptics). The cable is then fixed at the cuvette holder (OceanOptics) which also connects to the second cable and the Flame Extended Range Spectrometer (OceanOptics). A 1 ml cuvette is placed in the cuvette holder and it is covered by a home-made 3D-printed cap to exclude stray light from the surrounding. Data acquisition parameters are 100 μ s integrating time, 30 scans to average, and 10 boxcar width.

A.2. Experimental Parameters of QCM Measurements

The following ALD process parameters were used for the QCM study discussed in Chapter 3. SiO₂ deposition from tris(dimethylamino)silane (TDMAS) heated to 40 °C and ozone (O₃) at room temperature was combined with TiO₂ deposition from TTIP heated to 80 °C and either O₃ or H₂O as oxygen precursor (both at room temperature) for the TiO₂ growth. The ALD process was conducted with an Arradiance GEMStar XT system at a chamber temperature of 150 °C, a constant nitrogen (N₂) flow of 30 sccm, and in stop-flow mode. Precursor pulse, exposure, and purge durations for the individual ALD half-cycles were 0.1 s, 10 s, and 30 s; 2 s, 10 s, and 30 s; and 0.05 s, 10 s, and 30 s for TTIP, O₃, and H₂O, respectively for TiO₂ growth. SiO₂ deposition was performed by applying 0.05 s, 15 s, and 30 s for TDMAS and 2 s, 40 s, and 30 s for O₃. Growth rates of 0.30 Å for TiO₂ by using O₃, 0.42 Å for TiO₂ deposition with H₂O, and 0.84 Å for SiO₂ are obtained.

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