

**Experimental and theoretical studies on the
formation of highly luminescent II-VI, III-V and
core-shell semiconductor nanocrystals**

A dissertation
submitted to the University of Hamburg for the degree of
Doctor of Natural Sciences

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February 2002

The work described in this thesis was carried out in the Institute of Physical Chemistry, University of Hamburg in Prof. Dr. H. Weller group.

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For my Teachers

Acknowledgements

I want to thank *Prof. Dr. Horst Weller* for the invitation to join his working group, for very interesting research topic involving me in spending two years with my arms inserted into large drybox gloves, for providing excellent experimental facilities and for many useful discussions. An additional gratitude for his favour a friendly group atmosphere.

My special thanks go to my advisor, *Priv.-Doz. Dr. Markus Haase*, for providing me a freedom when I wanted it, as well as guidance when I needed it. His insight and advise were always valuable and appreciated. Additional thanks for prompt and perfect corrections of our manuscripts.

I am very thankful to *Dr. Andrey Rogach*, who probably was the main driving force of my enormous activities during last years.

Special appreciation goes to *Dr. Stephan Haubold*, who introduced me to the mysteries of Synthesis.

Priv.-Doz. Dr. Alexander Eychmüller is acknowledged for the interest in my work with aqueous quantum dots and for a number of fruitful comments and stimulating discussions. I want to thank *Dipl.-Ing. Andreas Kornowski* and *Sylvia Bartholdi-Nawrath* for excellent TEM and HRTEM images. *Dipl.-Chem Joanna Kolny* is acknowledged for the powder XRD measurements and *F. Bürli, B. Seydak* and *L. Ruth* – for technical support. I also thank *Holger Borchert* and the colleagues from HASYLAB/DESY, *Dr. Colm McGinley* and *Sorin Adam*, for XPS investigations and useful discussions.

The work described in this thesis was carried out in the Institute of Physical Chemistry, University of Hamburg, from April 2000 to January 2002, and was supported by the BMBF research project of the University of Hamburg and Philips. I thank our colleagues from Philips Research Laboratories (Aachen), *Dr. Dietrich Bertram*, *Dr. Helga Hummel* and *Volker Weiler*, for useful collaboration, stimulating discussions and hospitality.

I want to thank everyone in the nanochemistry group for making the lab an enjoyable and productive place to work. Special commendation goes to *Kirsten, Claudia, Kathrin, Herwig, Holger and Ivo*. I will remember you, always.

Retracing the long journey that led me in Hamburg, I am very grateful to the person who lit my path: *Dr. Nicolai Gaponik*. Without him, I would not be writing this thesis in this place today.

Finally, and most importantly, I thank my wife and friend, *Elena Shevchenko*, for more things than space allows, but mostly for her love and support.

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Notations

<>	Averaged value
DDA	Dodecylamine
FFT	Fast Fourier Transformation
FWHM	Full Width at Half Maximum
HDA	Hexadecylamine
HPL	Highly luminescent (fraction)
HRTEM	High Resolution Transmission Electron Microscopy
LED	Light Emitting Device
LPL	Lowly luminescent (fraction)
LSW	Lifshitz-Slyozov-Wagner (theory)
MA	2-Mercapto-ethylamine
NP	Nanoparticle
P-XRD	Powder X-Ray Diffraction
PL	Photoluminescence
QD	Quantum Dot
QE	Quantum Efficiency
RT	Room Temperature
SAXS	Small-angle X-Ray Scattering
TBP	Tri-n-butylphosphine
TEM	Transmission Electron Microscopy
TMS₃As	Tris-(trimethylsilyl)arsine
TMS₃P	Tris-(trimethylsilyl)phosphine
TGA	Thioglycolic acid
TOP	Tri-n-octylphosphine
TOPO	Tri-n-octylphosphine oxide
TOPS	Tri-n-octylphosphine sulfide
TOPSe	Tri-n-octylphosphine selenide
TOPTe	Tri-n-octylphosphine telluride
vol.	volume
wt.	weight
ZGR	Zero Growth Rate

Chapter 1

“...It’s wonderful to see the robustness of the physics and chemistry of materials, a field that continues to be amazingly creative. With the move towards nanoscience and self-assembly, this field is full of life.”

-Alan J. Heeger, winner of the Nobel Prize for Chemistry in 2000

Introduction

Chemistry and physics in the nanometer size range have experienced a great development in the last decade leading to the appearance of the new interdisciplinary field of nanoscience. The interest in nanoscale materials arises from the finding that many physical phenomena in both organic and inorganic materials have natural length scales between 1 and 100 nm (10^2 - 10^7 atoms). Below a certain threshold, the properties a material are determined not only by its composition, but also by the size. For instance, if the physical size of a semiconductor material lies in the range of ~ 1 -20 nm, i.e., is much smaller than the natural radius of the electron-hole pair (Wannier exciton) in a semiconductor (Bohr radius), additional energy is required to "confine" the excited carriers within the material leading to drastic changes of its electronic and optical properties. Tuning of the properties can be achieved by controlling the physical size of materials in one (quantum wells), two (quantum wires) and three (quantum dots, QDs) dimensions. There are two distinct routes to produce QDs: in the “physical” approach they are grown by lithographic or molecular beam techniques. In the “bottom up”, or “chemical” approach they are synthesized by methods of colloidal chemistry in a solvent medium, and are usually called “nanocrystals”.

In quantum dots, atomic-like electronic energy levels are formed due to the charge carrier confinement [1]. In very small dots, the spacing of the electronic states is much greater than the available thermal energy (strong confinement). Upon UV-excitation these quantum dots show strong fluorescence that is a pronounced function of size, providing the advantage of continuous spectral tunability over a wide spectral range simply by changing the size of the nanocrystal (Figure 1.1) [2].



Figure 1.1. *Size-dependent change of the photoluminescence color of colloidal solutions of CdSe nanocrystals passivated with a ZnS shell. The smallest (~ 1.7 nm) CdSe particles emit blue, the largest (~ 5 nm) – red.*

Because of strong luminescence (“band edge emission”) in combination with their high chemical flexibility (colloidal nanocrystals can be handled like ordinary chemical substances), luminescent semiconductor nanocrystals are currently investigated as emitting materials for thin film light-emitting devices [3], optical amplifier media for telecommunication networks [4], and for biological labeling [5]. Research is now under way to incorporate quantum dots into devices ranging from low-threshold lasers and solar cells to quantum computers. A new field of research has recently been emerged on the use of individual monodisperse nanocrystals as building blocks for the fabrication of artificial quantum dot superstructures and the investigation of the collective properties of these.

The synthesis of monodisperse nanocrystals of desired sizes and properties is a first and very important step being a pre-requisite of their further investigation and use in practice. This theses deals with the development of advanced synthetic routes toward various

luminescent nanomaterials. The synthesis and luminescent behaviour of various II-VI, III-V and core-shell nanocrystals prepared both *via* organometallic and aqueous approaches are discussed in Chapters 2-4. Chapter 5 describes the self-assembly of chemically synthesized monodisperse nanocrystals into two-dimensional and three-dimensional arrays and colloidal crystals, where individual nanocrystals play the role of building blocks – artificial atoms in the next level of hierarchy.

Despite of the progress in the synthesis of nanomaterials with high luminescent efficiencies, there is still a lack of theoretical understanding of the processes occurring during the formation of nanocrystalline matter in colloidal solutions. Further progress depends on our ability to understand and control the parameters governing the desired properties of colloiddally grown nanocrystals. A theory of the evolution of an ensemble of nanoparticles growing in colloidal solution is presented in Chapter 6. In Chapter 7 the variation of the photoluminescence efficiency within various ensembles of colloiddally grown II-VI and III-V semiconductor nanocrystals is described for the first time and studied both experimentally and theoretically.

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Chapter 2

Luminescent materials based on quantum-sized CdSe crystallites

Highly monodisperse CdSe nanocrystals were prepared in a three-component hexadecylamine – trioctylphosphine oxide – trioctylphosphine (HDA-TOPO-TOP) mixture. This modification of the conventional organometallic synthesis of CdSe nanocrystals in TOPO-TOP provides much better control over the growth dynamics resulting in strongly reduced broadening of the particle size distribution during growth. The room temperature quantum efficiency of the band edge luminescence of CdSe nanocrystals can be significantly improved to 40-70% by passivation of the CdSe surface with inorganic (CdS or ZnS) or organic (alkylamines) shells. The resulting highly luminescent CdSe/ZnS core-shell nanocrystals were used for preparation of luminescent nanocrystal – polymer composites with polylaurylmethacrylate. The superior luminescent properties of CdSe-related core-shell nanocrystals make these materials attractive for various optoelectronic and tagging applications.

2.1. Introduction

CdSe nanocrystals (also referred to as quantum dots) are probably the most extensively investigated object among chemically grown semiconductor nanoparticles since the introduction of the concept of the “size quantization effect” in the earlier eighties [1,2]. This is caused to large extent by the existence of a very successful preparation method for high-

quality CdSe nanocrystals, i.e., arrested precipitation in high boiling mixtures of trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) [3,4]. The term “high quality quantum dots” has been recently defined as follows [5]: the achievement of desired particle sizes over the largest possible range, narrow size distributions, good crystallinity, desired surface properties and, in case of luminescent materials, high quantum yield. CdSe nanocrystals prepared by the TOPO-TOP route and size-separated after synthesis meet all these requirements apart from the last – high luminescence quantum yield, which does not exceed 5-15% for as-prepared particles [6-8]. The luminescence quantum efficiency can be sufficiently improved by growing hetero-epitactically an inorganic shell of a wide-bandgap semiconductor around the particles [6-9]. The conventional techniques used for the latter, however, allow to prepare only very small amounts of core-shell nanoparticles. Other problems of the TOPO-TOP synthesis are the irreproducible growth dynamics and the irreproducible shape of the CdSe nanocrystals presumably caused by an uncertain composition of the coordinating solvent. Technical grade TOPO (90%, Aldrich), for instance, provides better conditions for the growth of CdSe nanocrystals than distilled TOPO [10].

Taking into account the growing demand on highly luminescent semiconductor nanocrystals for light-emitting devices [11-13] and tagging applications [14,15], we tried to improve the conventional organometallic TOPO-TOP synthesis by introducing an additional coordinating component – hexadecylamine (HDA) – to the TOPO-TOP mixture.

2.2. TOPO-TOP and HDA-TOPO-TOP stabilized CdSe nanocrystals

CdSe nanocrystals were prepared by a modified high temperature organometallic synthesis based on the recipe given by Murray et al. [3] All manipulations were performed using standard air-free techniques. HDA, TOPO and TOP were purified by distillation. In a typical synthesis of TOPO-TOP capped CdSe nanocrystals, a portion of stock solution prepared by mixing 1 mmol of TOPSe [3,4] and 1.35 mmol of dimethylcadmium with 5 mL of TOP was rapidly injected into 10 g of TOPO vigorously stirred and heated to 300°C. In the synthesis of HDA-TOPO-TOP capped CdSe nanocrystals the injection of stock solution was performed into a mixture of 10 g of TOPO (55 mol%) and 5 g of HDA (45 mol%) – see details in Appendix 1. In both cases, injection resulted in an immediate nucleation of nanoparticles displaying a broad adsorption maximum around 450 nm. Further growth occurred at 250-310°C, depending on the desired size of the nanocrystals.

Figure 2.1 shows the temporal evolution of absorption and PL spectra of CdSe nanocrystals monitored during their growth in the TOPO-TOP mixture at 300°C. The growth dynamics of the nanocrystals was monitored by taking samples from the reaction mixture at different instants of time. All samples were immediately cooled and diluted with toluene to stop particle growth and to provide optical densities appropriate for PL measurements. The band-edge luminescence of CdSe nanocrystals is strongly dependent on particle size what allows us to translate a given PL spectrum into a size distribution curve by assuming a δ function emission for each single size [16]. The general trend is that the width of PL spectrum decreases with narrowing of the particle size distribution. Analysis of experimental data shows that during the first 25 min the growth of CdSe nanocrystals occurred with narrowing of the particle size distribution with subsequent broadening of the size distribution at later stages of heating. Such behavior was reported in the literature and was called “focusing” and “defocusing” of the nanocrystal size distribution [16]. A more detailed description of growth kinetics of the TOPO-TOP capped CdSe nanocrystals will be presented in Chapter 7. After synthesis, size-selective precipitation using n-butanol and methanol as solvent and non-solvent, respectively, was employed to isolate nearly monodisperse fractions of TOPO-TOP capped CdSe nanocrystals with perfect crystallinity (Figure 2.1). Usually, size selective precipitation was performed as following: a sample of as-prepared CdSe nanocrystals with a broad size distribution was dispersed in n-butanol and methanol was added dropwise until the initially clear solution becomes slightly turbid. The largest nanocrystals in the sample exhibit the greatest attractive van der Waals forces and tend to aggregate before the smaller nanocrystals [17]. The aggregates consisting of the largest nanocrystals present in the sample can be isolated by centrifuging or filtration through a 0.2 μm PTFE membrane filter and re-dissolved in non-polar organic solvents (toluene, hexane, chloroform, etc.). Subsequently, a small amount of additional non-solvent was added to the supernatant to precipitate the second size-selected fraction. Repetition of this procedure for several times allows obtaining up to ~10 size-selected fractions from one portion of the CdSe crude solution.

When the reaction mixture contained HDA in addition to TOP and TOPO, the ratio between TOPO and HDA strongly affected the growth kinetics. The general tendency was that with increasing HDA content the initial particle size and the growth rate decreased. In mixtures containing more than about 80 mol% of HDA, precipitation of CdSe nanocrystals was observed above 200°C. To prepare CdSe nanocrystals with sizes above 4.5-5.0 nm, additional injections of stock solution were required.

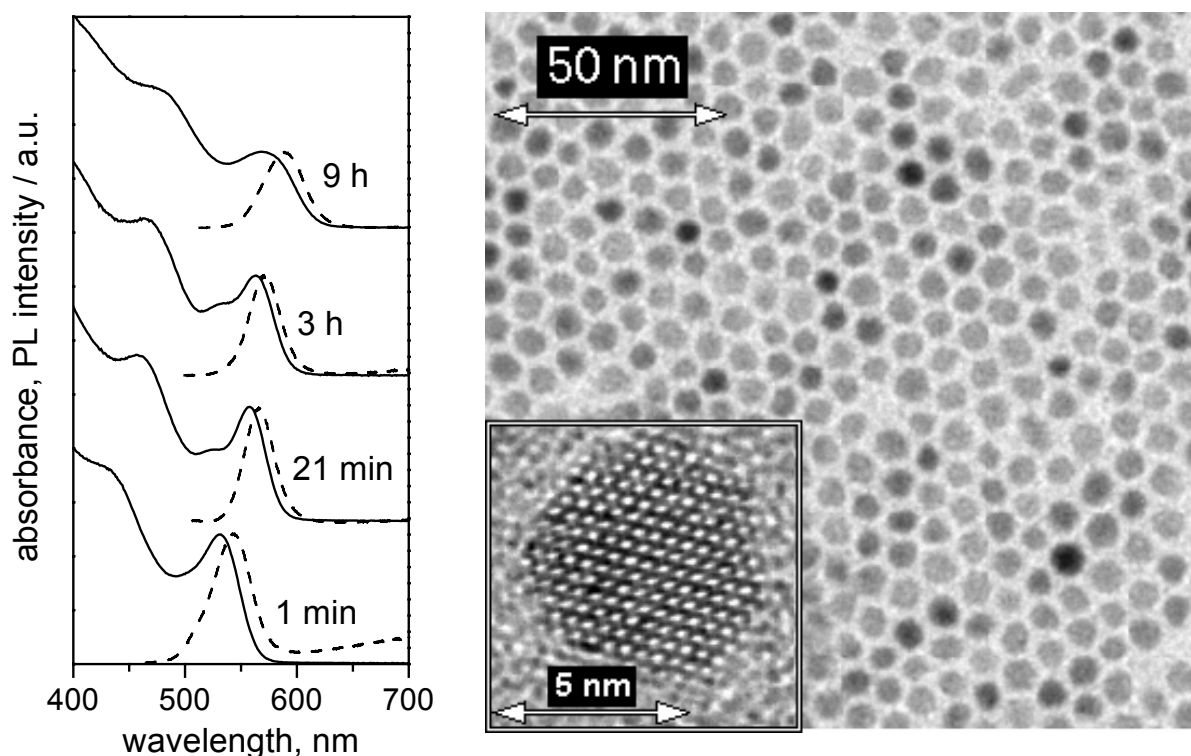


Figure 2.1. Temporal evolution of absorption and PL spectra of TOPO-TOP capped CdSe nanocrystals at 300°C (left). TEM overview and HRTEM images of a size-selected fraction of TOPO-TOP capped CdSe nanocrystals (right).

A set of absorption and photoluminescence spectra displaying the growth of CdSe nanocrystals in the stabilizing HDA-TOPO-TOP mixture at 300°C is shown in Figure 2.2. Up to 5 electronic transitions are resolved in absorption spectra, indicating very narrow size distributions of the CdSe nanocrystals. The *in situ* particle size distributions are comparable with those of the best CdSe samples obtained *via* the TOPO-TOP synthesis followed by several stages of size-selective precipitation [3,6,16].

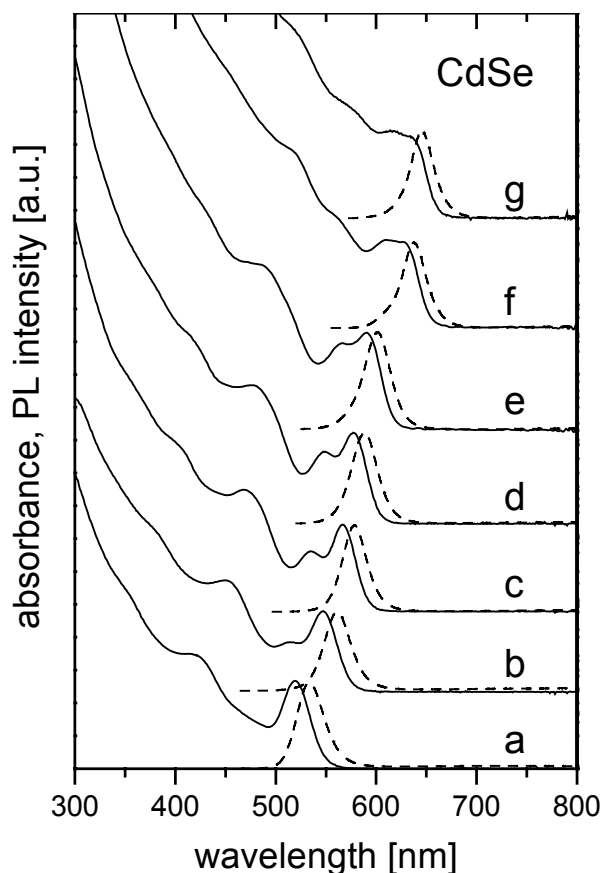


Figure 2.2. Room temperature absorption and emission spectra of CdSe nanocrystals monitored during the growth at 300°C.

Figure 2.3a shows the evolution of the mean particle size during growth of the CdSe nanocrystals at 300°C. The growth rate decreased gradually and the growth almost terminated when the particles diameter reached ~ 4.5 nm. A comparatively low injection temperature (300°C) and the use of purified solvents resulted in very reproducible growth kinetics of the CdSe nanocrystals. The evolution of the particle size distribution during the growth at 300°C was estimated from the absorption and PL spectra as described above [see also details in Refs.16,18] and shown in Figure 2.3b. As the size distributions estimated from optical spectra are systematically broader than the real ones [16], we present the relative values of standard deviation (σ) normalized to a starting value (σ_0) observed immediately after injection of the stock solution. The inset in Figure 2.3b shows a size histogram of a sample with average size of 4.1 nm with standard deviation of $\sim 4\%$, as measured from HRTEM images. In contrast to the growth of CdSe nanocrystals in TOPO-TOPO, very fast “focusing” of the size distribution was observed during the particle growth in HDA-TOPO-TOPO and no “defocusing” after long-term heating at 300°C. The absence of “defocusing” means that the narrowest size distribution corresponds to the largest size achievable at a given growth temperature. As a result, stepwise

growth (1 h at 250°C + 1 h at 280°C + 1 h at 310°C) allowed to reproducibly reach size distributions with a standard deviation below 5%. Additional injections of stock solution were required to obtain larger CdSe nanocrystals which slightly broadened the size distribution (Figure 2.3b). This broadening is most probably caused by the high (300°C) growth temperature resulting partly in new nucleation of nanocrystals. On the other hand, very slow (1 drop per 30 s) additional injection at 280°C into a solution of CdSe nanocrystals primarily grown at 310°C resulted in an even further narrowing of the size distribution. For all crude solutions of CdSe nanocrystals, i.e. without particle size selection, the full width at half maximum (FWHM) of the band edge PL spectra were in the range of 27-31 nm.

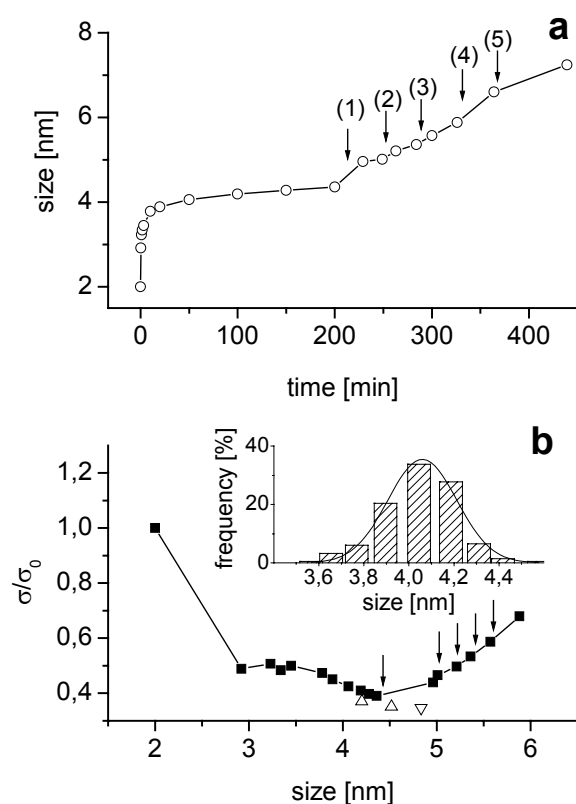


Figure 2.3. (a) Temporal dependence of the mean particle size during the growth of CdSe nanocrystals at 300°C. (b) The relative particle size distribution of growing CdSe nanocrystals: (■) during continuous growth at 300°C; (Δ) obtained after stepwise growth (1 h 250°C + 1 h 280°C) and (1 h 250°C + 1 h 280°C + 1 h 310°C); (∇) obtained after slow additional injection of 0.4 mL of the stock solution at 280°C to the stepwise grown nanocrystals. The insert shows a size histogram of CdSe nanocrystals with average size of $\sim 4.05 \pm 4\%$ measured from HRTEM images for over 200 particles. Arrows indicate additional injections of stock solutions containing: (1)-(3) 50%; (4) 100%; (5) 140% of Cd and Se precursors compared to the initial amount of CdSe.

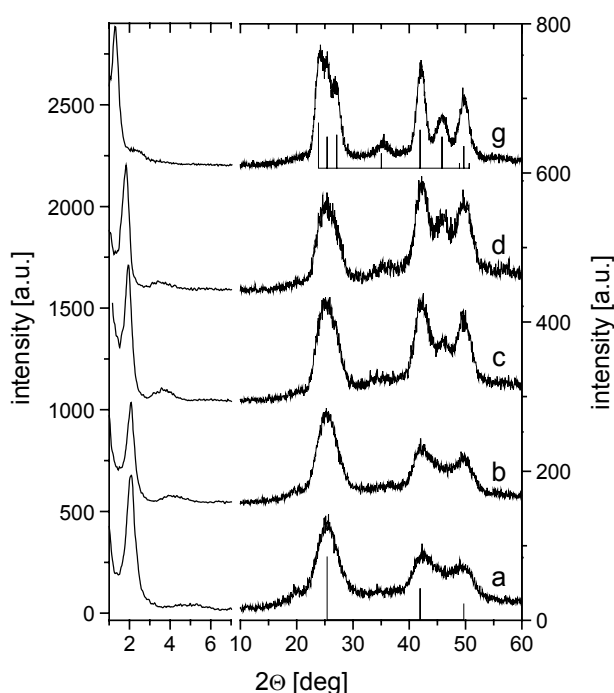


Figure 2.4. Small-angle and wide-angle powder X-ray diffractograms of a size series of CdSe nanocrystals (samples **a-d** and **g** from Figure 2.2). Vertical lines indicate bulk CdSe reflections (top: wurtzite, hexagonal; bottom: zinc blende, cubic).

Figure 2.4 shows small-angle and wide-angle powder XRD (P-XRD) patterns of CdSe nanocrystals of different sizes. As expected, the width of the diffraction peaks at wide angles is considerably broadened and increases with decreasing particle size. Nanocrystals with sizes above ~ 4.0 nm exhibit P-XRD patterns with diffraction peaks in accord with those of hexagonal CdSe (wurtzite phase). In the case of smaller CdSe nanocrystals the XRD patterns do not permit to distinguish between the cubic and the hexagonal phases unambiguously. As it is often observed for nanocrystalline samples with narrow particle size distributions, the P-XRD patterns also show a very well pronounced sharp first-order reflex in the small-angle region (Figure 2.4) which is caused by Bragg diffraction on the nanocrystals ordered in the powder. The intensity of this reflex was ~ 3 -5 times larger than that of the diffraction peaks at wide angles. Due to the exceptionally narrow size distribution of these CdSe nanocrystals, the second-order reflexes are also resolved (Figure 2.4).

HRTEM images of the CdSe nanocrystals (Figure 2.5) show nearly spherical crystalline particles with lattice plane distances identical to hexagonal CdSe. EDX measurements indicate compositions close to the ratios given by the bulk formula. The narrow size distribution of the particle sizes resulted in a 2D hexagonal arrangement of the CdSe

nanocrystals on the TEM grids. The ordered nanocrystal arrays were obtained simply by drying a drop of diluted colloidal solution on the carbon coated TEM grid.

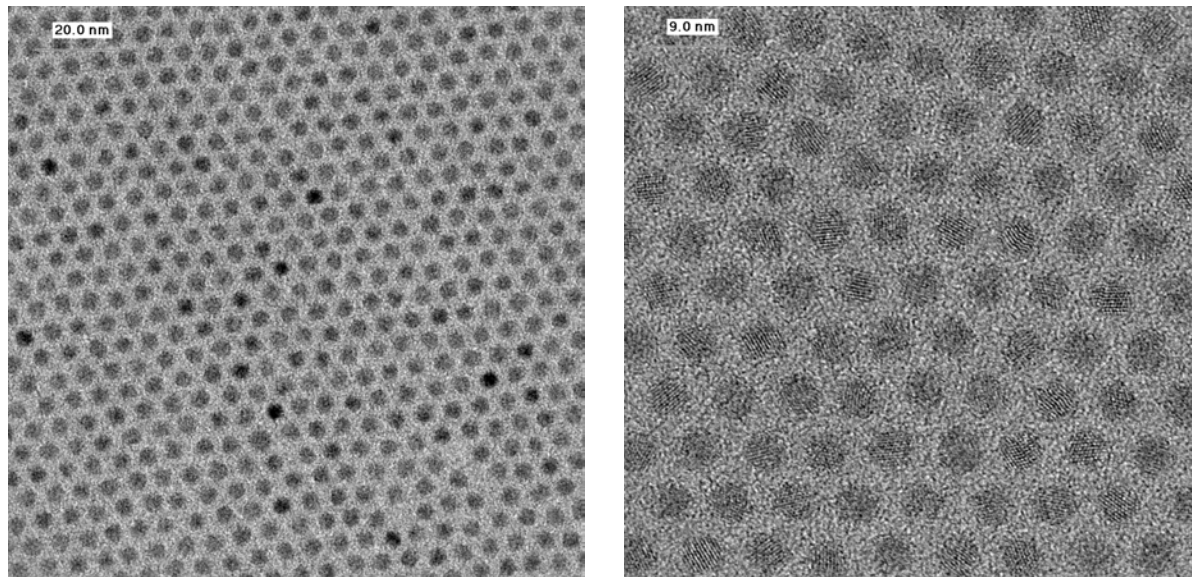


Figure 2.5. Typical TEM and HRTEM images of as-prepared HDA-TOPO-TOP CdSe nanocrystals.

The room temperature PL quantum efficiency (QE) of as-prepared CdSe nanocrystals was in the range of 10-25% and has a tendency to decrease with increasing particle size. However, the PL QE of the CdSe nanocrystals can be considerably improved by post-preparative surface passivation with an inorganic (ZnS) or organic (amines) shell. This is a strong hint that the PL efficiency losses are due to insufficient passivation of surface traps.

The post-preparative treatment of CdSe nanocrystals with primary amines, e.g. allylamine or dodecylamine (DDA) resulted in a significant improvement of the PL QE. The passivation of the CdSe surface with amines was performed by mixing 1 mL of the crude solution of CdSe nanocrystals (prepared in TOPO-TOP mixture) 5 mL of allylamine or DDA and subsequently stirring at 50°C (allylamine) or 100°C (DDA) for 24 h. The nanocrystals were precipitated with methanol and re-dispersed in hexane for optical measurements. The procedure led to a stable PL with QE of 40-50% in both cases, which is comparable to values for CdSe nanocrystals covered with inorganic shells. This enhancement of the band edge PL in comparison with TOPO-capped CdSe nanocrystals may be caused by strong bonding of the amines to the nanocrystal surface which resulting in better passivation. Less sterically

hindered amines may improve surface capping and, hence, the passivation of traps by creating larger capping densities [9].

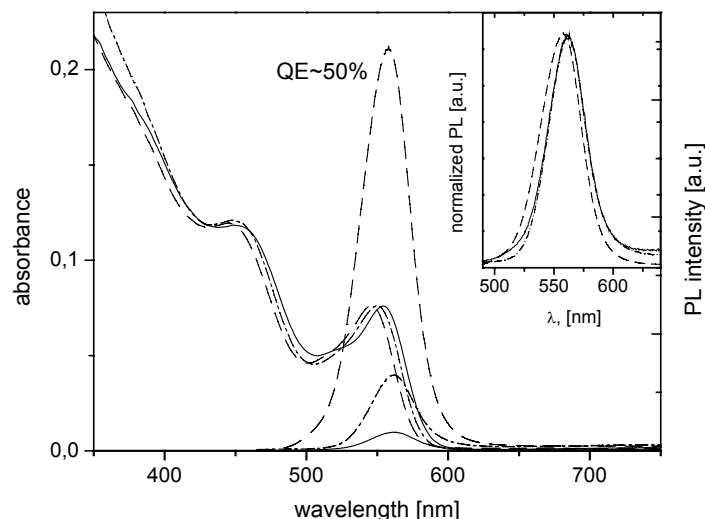


Figure 2.6. Room temperature absorption and emission spectra of TOPO-capped 3.7 nm CdSe nanocrystals before (solid lines) and after (dashed lines) surface exchange with allylamine. The spectra taken after partial reconstruction of the initial TOPO-TOP stabilizing shell are presented as dash-dot lines. The insert shows normalized PL spectra.

The influence of amines on the PL properties of CdSe nanocrystals has been further investigated by the substitution of TOPO at the surface of CdSe nanocrystals synthesized *via* the conventional TOPO-TOP synthesis. After treatment of the nanocrystals with allylamine or DDA the band edge PL increased by about an order of magnitude (Figure 2.6) and reached a QE of ~50%. This exchange of TOPO by amines at the surface of CdSe nanocrystals was accompanied by a slight blue shift of both the absorption spectrum onset and the maximum of the band edge PL band (Figure 2.6). Allylamine can be partially removed from the particle surface by precipitating the nanocrystals from the amine-TOPO-TOP solution, re-dissolving them in TOPO-TOP mixture and subsequently pumping off allylamine in vacuum at 60°C. This partial reconstruction of the initial TOPO/TOP surface was accompanied by a red shift of both, the absorption and the PL spectra (Figure 2.6). The blue shift during the exchange of TOPO with amine might be explained either by a slight decrease of the particle size caused by the removal of surface Cd and Se atoms with leaving TOPO molecules [3], or by a re-distribution of electronic density in the semiconductor core under the influence of passivating

groups. The reversibility of the spectral shift during the amine-to-TOPO exchange allows to suppose the latter explanation as responsible for the behavior observed.

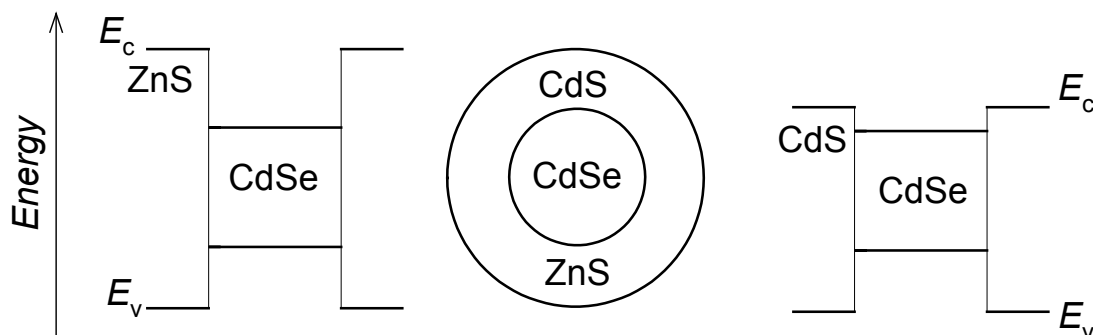
In summary, exceptionally monodisperse CdSe nanocrystals were synthesized by introducing alkylamines into the widely used TOPO-TOP synthesis. The use of purified stabilizing agents resulted in highly reproducible growth dynamics, shape and PL QE of CdSe nanocrystals. In the HDA-TOPO-TOP mixture, focusing of the particle size distribution is observed during particle growth so that no post-preparative size-selective precipitation is required. The surface of as-prepared CdSe nanocrystals can be passivated without isolating the nanocrystals from the crude solution by surface modification with alkylamines. It lead to stable and reproducible luminescence quantum efficiencies ~50% at room temperature.

2.3. Core-shell nanocrystals with CdSe cores: CdSe/CdS and CdSe/ZnS

The organometallic routes described in Section 2.2 result in nearly monodisperse perfectly crystalline CdSe nanoparticles capped with a shell of organic ligands (amines, TOPO and TOP). The organic molecules provide passivation of surface dangling bonds or coordination sites which form traps for photogenerated carriers. Surface passivation with organic molecules is necessary to achieve high PL quantum efficiencies. However, a bottleneck of this approach is the poor stability of the organic shell and, hence, the PL efficiency and its strong dependence on the nanocrystal surrounding. The TOPO-TOP stabilizing shell is rather labile and can be partially washed out during post preparative treatment. As an example, several repetitive size-selective precipitations allowed us to isolate TOPO-TOP capped CdSe nanocrystals with very narrow particle size distribution, but, after this treatment, the band edge PL usually decreased by approx. two orders of magnitude.

The next step towards the preparation of more robust highly luminescent quantum dots could be the passivation of the nanocrystal surface with an inorganic shell of a semiconductor with wider band gap, e.g., ZnS or CdS [6,8]. The lattice mismatch between CdSe and ZnS or CdS shell is small enough to allow epitaxial growth. In CdSe/ZnS and CdSe/CdS core-shell nanocrystals the large bandgap semiconductor forms a closed outer shell and the band edges of the core material lie between the band edges of the outer one (Scheme 2.1). The outer inorganic shell provides both high PL quantum efficiency due to passivation of charge carrier traps at the surface and improves chemical stability and photostability of the whole nanocrystal. Last two parameters are crucially important for all potential applications of the

nanocrystals. Chemical stability implies negligible changes of properties like particle size, solubility, PL efficiency, etc. after exposure of nanocrystal to various surroundings, e.g., ambient atmosphere. Photostability means stability of the particle properties under illumination.



Scheme 2.1. *Schematic representation of band structure of core shell CdSe/ZnS and CdSe/CdS nanocrystals*

To date, CdSe/ZnS and CdSe/CdS nanocrystals are, probably, the most successful examples of core-shell nanocrystals [6,8,9]. In both cases, values of 30-80% were reported for their PL efficiency, i.e., much higher than those observed for “bare” CdSe QDs [6,8]. CdSe/ZnS core-shell nanocrystals are more stable and processable as compared to CdSe/CdS, probably, due to the relatively large energy barrier at the CdSe - ZnS core-shell interface (Scheme 2.1.) resulting in perfect confinement of both electron and holes to the CdSe core [6]. On the other hand, as-prepared CdSe/CdS nanocrystals exhibited higher PL quantum yields: the best value reported was as high as 84% [8]. The experimental results indicate that in the excited state the hole is confined to the core and the electron is delocalized throughout the entire particle what makes CdSe/CdS nanocrystals attractive for use in optoelectronic devices [8].

The CdSe/CdS core-shell nanocrystals were synthesized according to the recipe proposed by Peng et al. [8]. The growth of the CdS shell resulted in significant improvement of the PL efficiency of the nanocrystals achieving 68% (Figure 2.7). The red shift observed in both absorption and PL spectra evidenced that some delocalization of wavefunctions of CdSe core takes place upon growth of the CdS shell. The growth of the CdS shell also considerably improves the nanocrystal stability. Even after storage of the CdSe/CdS nanocrystals at

ambient conditions for more than one year no remarkable changes of the nanocrystal size and PL efficiency were observed.

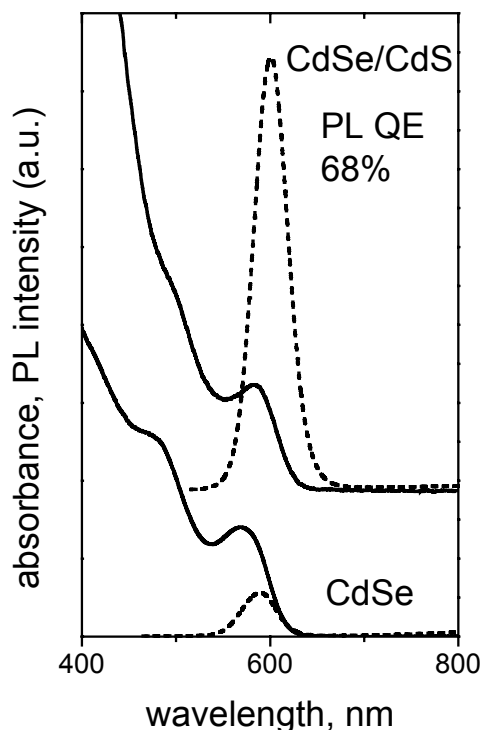


Figure 2.7. Room temperature absorption (solid lines) and emission (dashed lines) spectra of CdSe nanocrystals before and after growth of ~ 3 monolayers thick CdS shell.

The CdSe/ZnS core-shell nanocrystals were synthesized using colloidal CdSe cores prepared either in TOPO-TOP or in HDA-TOPO-TOP mixtures. Since CdSe quantum dots synthesized in the HDA-TOPO-TOP mixture showed an exceptionally narrow size distribution, no size selection and even no isolation of the CdSe nanocrystals from the crude solution was required for the synthesis of the core-shell particles. Moreover, rather high initial concentrations of CdSe cores can be used for the synthesis of the core-shell particles.

In a typical synthesis of CdSe/ZnS core-shell nanocrystals, 2.5 mL of the crude solution of CdSe nanocrystals (prepared as described in Section 2.2) were mixed with 5 g of TOPO and 2.5 g of HDA and heated to 220°C. The amount of Zn:S stock solution (see details in Appendix 1) necessary to obtain the desired shell thickness was calculated from the ratio between the core and shell volumes using bulk lattice parameters of CdSe and ZnS. This amount was then added dropwise to the vigorously stirred solution of CdSe nanocrystals. Figure 2.8 shows a set of absorption and PL spectra of CdSe/ZnS nanocrystals with different

thicknesses of the shells. A maximum of the PL QE (66%) was observed for a ~ 1.6 monolayers thick ZnS shell and was reproducibly 50% or above for a wide range of the shell thicknesses. Figure 2.9b shows a HRTEM image of CdSe/ZnS nanocrystals (1.6 monolayers of ZnS) synthesized from ~ 4.0 nm large CdSe cores shown in Figure 2.9a.

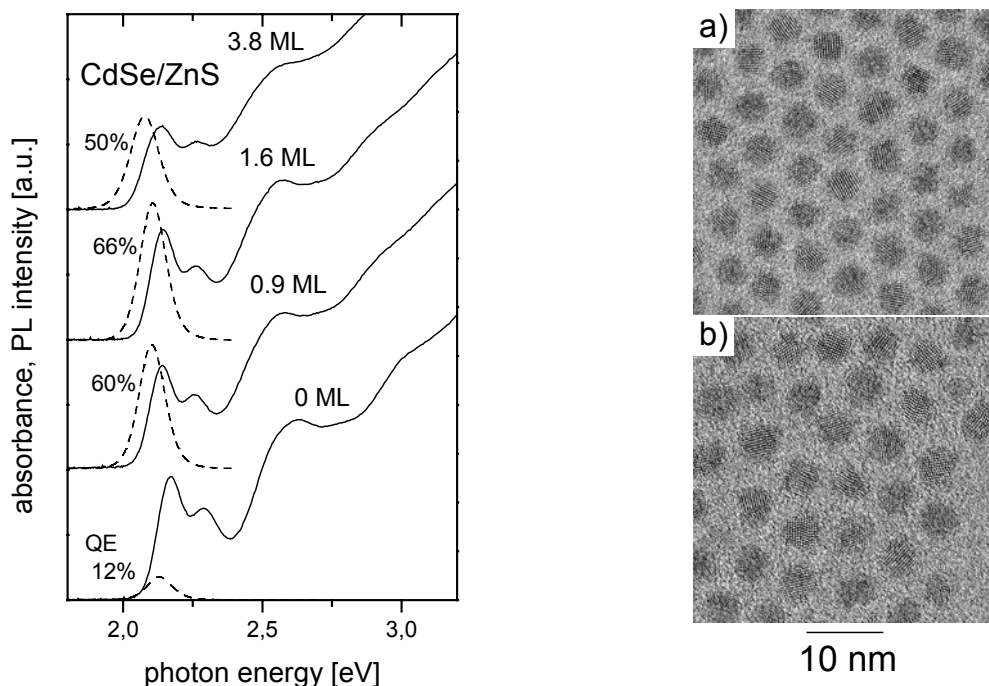


Figure 2.8. (left) Room temperature absorption and emission spectra of CdSe nanocrystals before and after growth of a ZnS shell of different thickness (in monolayers, ML).

Figure 2.9. (right) HRTEM images of (a) CdSe nanocrystals (sample c - see Figure 2.2) and (b) CdSe/ZnS core-shell nanoparticles (CdSe sample c covered with 1.6 monolayers of ZnS).

The emission wavelength of the CdSe/ZnS core-shell nanocrystals depend strongly on the size of the CdSe core and can be tuned from blue to red as shown in Figures 1.1 and 2.10. The narrow size distribution of CdSe nanocrystals prepared in using HDA-TOPO-TOP mixture (see Figures 2.2 and 2.5) instead of the conventional TOPO-TOP mixture, as well as proper control of the reaction conditions allowed us to prepare colloids with PL bands as narrow as 25-35 nm (FWHM) and room temperature PL quantum yields as high as 50-70%. (Figure 2.10)

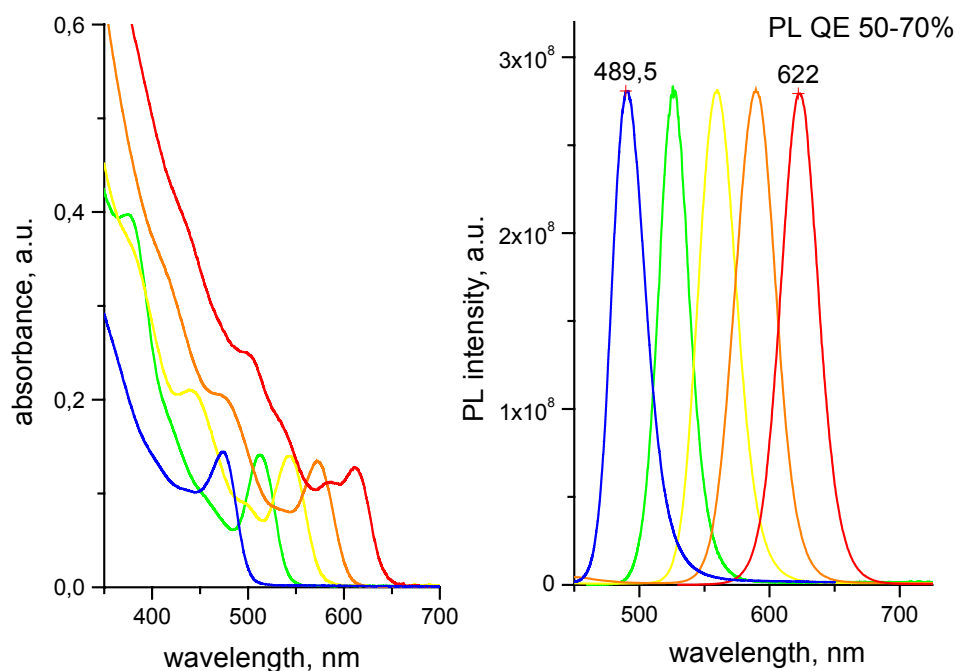


Figure 2.10. Room temperature absorption (left) and emission (right) spectra of CdSe/ZnS nanocrystals with different sizes of CdSe core and ~ 2 monolayers thick ZnS shell.

CdSe/ZnS core-shell nanocrystals exhibit high PL quantum efficiencies not only in the dissolved state, but also in close packed layers and in polymer matrixes [19]. Thus, nanocrystal-polymer composites have been prepared by mixing HDA-TOPO-TOP capped CdSe/ZnS nanocrystals with a mixture of laurylmethacrylate and dimethacrylate crosslinker and subsequent co-polymerization of the acrylate derivatives (Figure 2.11, see experimental details in Appendix I). Such composite materials combined processability and mechanical properties of the polylaurylmethacrylate matrix with the superior luminescent properties of CdSe/ZnS nanocrystals. The nanocrystals almost quantitatively retain their PL quantum efficiency after the polymerization of the matrix. Their strong luminescence, narrow emission bands and wide color tunability makes such quantum dot – polymer composites attractive for various scientific and commercial applications.

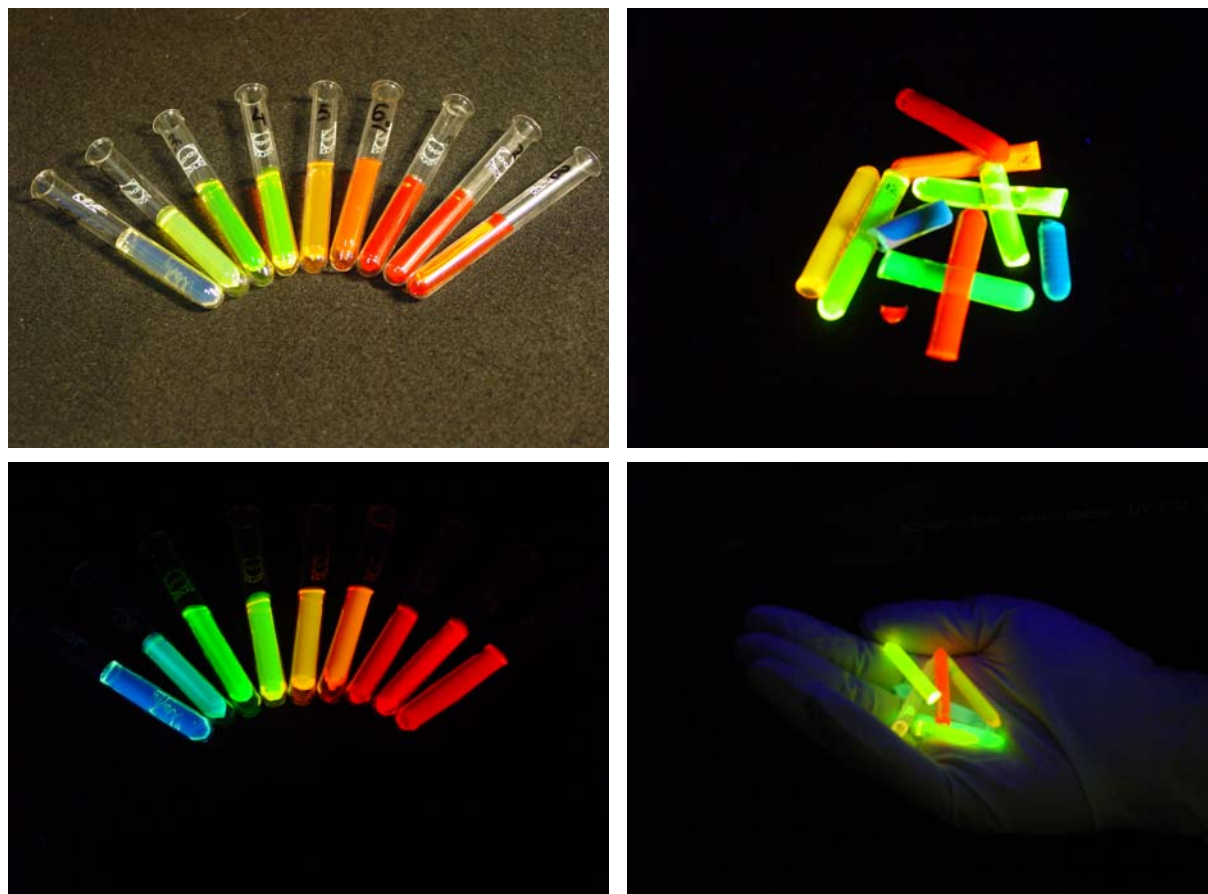


Figure 2.11. *Composites of luminescent CdSe/ZnS nanocrystals and polylaurylmethacrylate (PLMA)*

2.4. Conclusions

Highly crystalline CdSe nanocrystals have been synthesized by organometallic reactions in the presence of primary amines as effective capping agents. Fairly narrow particle size distributions are obtained already on the synthesis stage, which can be further improved by size selective precipitation. The use of amines generally allows to synthesize CdSe nanocrystals with sizes smaller than obtained in the conventional TOP-TOPO method by using the dodecylamine-TOP mixture, for instance, highly monodisperse CdSe nanocrystals with an average diameter of ~ 1.5 nm were obtained which exhibit bright blue emission peaked at 460 nm and a QE of 17%. Depending on the particle size, the band edge luminescence of CdSe nanocrystals with a mean size between 1.2-7.0 nm cover the whole

visible spectral range with room temperature quantum yields of 10-30%. The PL QE of amino-capped particles is markedly higher than that of TOPO-capped nanocrystals. Treatment of pre-synthesized TOPO-capped CdSe nanocrystals with primary amines allows to reach a quantum efficiency of the band edge luminescence as high as 40-60%. CdSe nanocrystals synthesized in the HDA-TOPO-TOP mixture can be successfully used as prepared for the synthesis of core-shell CdSe/CdS and CdSe/ZnS nanoparticles with high reaction yields and PL QE's of 50-70%. These features may be especially important for the use of CdSe nanocrystals for display and tagging applications.

2.5. References

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Chapter 3

Luminescent CdTe nanocrystals

Luminescent CdTe nanocrystals were synthesized *via* two different approaches. CdTe nanocrystals stabilized with long chain primary amines were prepared organometallically by reacting dimethylcadmium with different tellurium sources in mixtures of dodecylamine and trioctylphosphine as the coordinating and size regulating solvent. Colloids of crystalline CdTe nanoparticles with zincblende lattice display mean particle sizes between 2.5 and 7 nm. The particles show strong band edge photoluminescence shifting from green to red with increasing particle size. The photoluminescence quantum yield of amino-capped CdTe nanocrystals was as high as 65% at room temperature without covering the surface of the nanoparticles with a passivating inorganic shell.

In the second approach, luminescent CdTe nanocrystals were synthesized in aqueous solutions by a metathesis reaction between cadmium perchlorate and H_2Te gas. Different thiols were used to stabilize the CdTe nanocrystals and design their surface properties. These CdTe nanocrystals represent a new kind of highly-luminescent core-shell QD system with a naturally sulfur-capped surface (CdS shell) created by mercapto-groups covalently attached to surface cadmium atoms. The two routes for luminescent CdTe nanocrystals, organometallic and aqueous, are compared and their advantages and disadvantages are discussed.

3.1. Introduction

In contrast to CdS and CdSe nanocrystals which can be prepared either in aqueous solutions using thiols as stabilizing agents [1-5] or in high-boiling coordinating solvents like TOP-TOPO mixtures [6-8], only a few reports on non-aqueous chemical routes to CdTe

nanoparticles have been published [6, 9-12]. In a synthesis given by Bawendi et al., high quantum yields of about 50 % have been reached if a special tellurium compound (hexapropyl phosphorous triamide telluride) was used in the synthesis [12]. On the other hand, since the appearance of the first report on the aqueous synthesis of mercaptoethanol- and thioglycerol-capped CdTe nanocrystals in 1996 [4], sufficient progress has been made in the aqueous preparation of thiol-capped CdTe nanocrystals. The luminescence of these particles is very stable and covers almost the whole visible spectral range (500-730 nm) depending on the particle size. Several papers deal with characterization of thiol-capped CdTe nanocrystals [13,14] and their use for numerous applications. Worth to mention is the utilization of luminescent thiol-capped CdTe QDs in light-emitting devices (LEDs) [15-17], photonic crystals[18-21] and as biological labels [22,23]. Recent investigations have shown that this material may be attractive for light energy conversion [24].

In this Chapter, we report on a novel organometallic synthesis of CdTe nanocrystals using dodecylamine as a size regulating and stabilizing agent (Section 3.2). The synthesis allows obtaining a size series of highly luminescent CdTe nanoparticles whose emission colors cover the visible spectral range from green to red. If metallic tellurium is used as the tellurium source, the synthesis yields particles with a room temperature quantum yield reaching 65%.

In Section 3.3 we report on recent progress in the aqueous synthesis of thiol-capped CdTe nanocrystals and discuss their processability and optical properties, with an emphasis on procedures leading to highly luminescent (QE at room temperature of up to 40%) QDs. We also discuss the advantages and disadvantages of different thiols which determine as capping agents of CdTe QDs the surface properties of the nanocrystals. In Section 3.4 we discuss some advantages and disadvantages of the aqueous synthesis in comparison to the organometallic approach. In Section 3.5 we report on various approaches towards the transfer of luminescent CdTe nanocrystals from organic media into aqueous medium and from aqueous solution into non-polar organic solvents.

3.2. Organometallic synthesis of CdTe nanocrystals

Luminescent CdTe nanocrystals were synthesized in various stabilizing solvents using dimethylcadmium as cadmium precursor and either TOPTe or Te powder as the tellurium precursor [see Equation (3.1)]. The conventional TOPO-TOP stabilizing mixture do not yield

CdTe nanocrystals with high PL efficiency. Therefore, various other mixtures of different stabilizing agents were tested and the results obtained are summarized in Table 3.1.

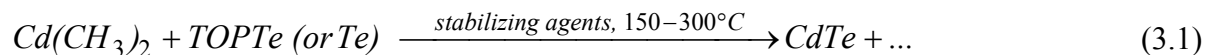


Table 3.1. Organometallic synthesis of CdTe nanocrystals

Stabilizing agents	Te source	Result	Solubility
TOPO/TOP (1:1)	TOPTe	+	Toluene, hexane
	Te	+	Toluene, hexane
TOP	TOPTe	+	Toluene, hexane
	Te	-	
TOPS	TOPTe	+	Toluene, hexane
DDA/TOP(5:1)	TOPTe	++	Toluene, hexane
DDA/TOP(1:1)	TOPTe	+	Toluene, hexane
	Te	++	Toluene, hexane
DDA/TOPO	TOPTe	+	Toluene, hexane
DDA/TBP	Te	+	Toluene, hexane
HDA/TOP(5:1)	TOPTe	+	Toluene, hexane
DOA/TOP (5:1); DOA – dioctylamine	TOPTe	-	
DMPU/TOP(5:1) ; DMPU – 2,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone	TOPTe	+	Toluene
TG; TG - 1-thioglycerol	TOPTe	+	Methanol, DMF
MTh/TOP(5:2); MTh - 1-methylthiophene	TOPTe	++	-
MTh/TOP(1:1)	Te	-	-
Ani/TOP(5:2); Ani – Aniline	TOPTe	++	Toluene

Figure 3.1. shows the average room temperature PL quantum efficiency obtained for CdTe nanocrystals prepared with different stabilizing agents. The nature of the stabilizing agents also affects the nanocrystal size and, as a result, the position of the PL band which can be tuned in the ranges presented in Fig. 3.1. by properly adjusting the growth conditions.

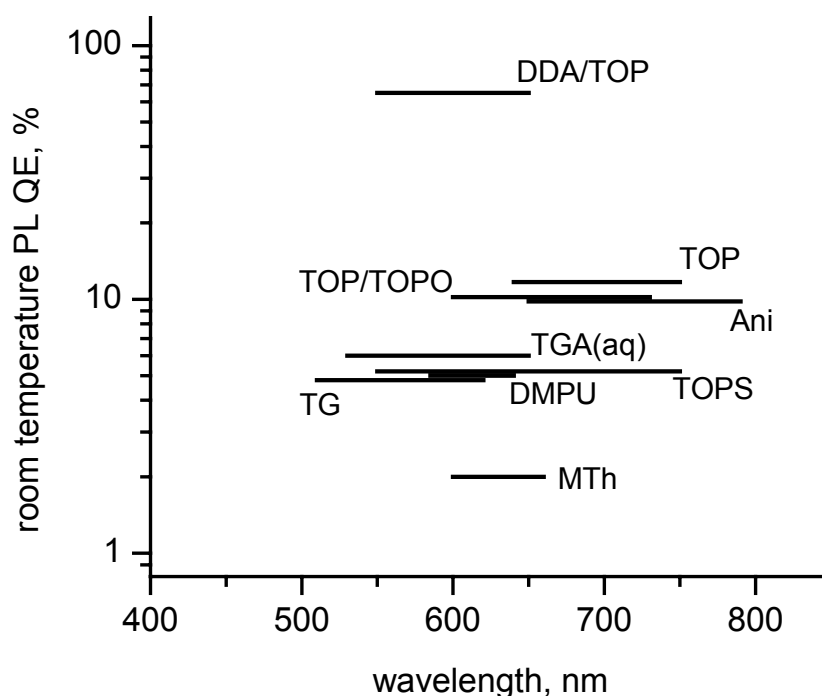


Figure 3.1. A comparison of the CdTe nanocrystals prepared using different stabilizing and size-regulating agents (see abbreviations in Table 3.1).

The highest PL efficiencies were achieved for CdTe nanocrystals synthesized in mixtures of dodecylamine and trioctylphosphine as the coordinating and size regulating solvents. A detailed description of the synthetic route is given in the Appendix 1.

Figure 3.2 shows the absorption and the photoluminescence spectra of CdTe nanoparticles synthesized in DDA-TOP mixture at different stages of particles growth (see Appendix 1.5, method B). The spectra shown are from samples taken from the reaction vessel without any further narrowing of their size distribution. They were diluted with toluene to provide the optical densities appropriate for PL measurements. A shift of the absorption edge and of the PL maximum towards longer wavelengths indicates growth of the CdTe nanocrystals during the heat treatment. The use of DDA as size-regulating and stabilizing agent resulted in quite narrow particle size distributions although we did not apply a hot injection technique. Prolonged heating (20 hours) of the nanoparticles at temperatures between 180-210°C significantly increased the quantum yield of the band edge PL, presumably owing to annealing of defects and improvement of the crystallinity. Nanoparticles

prepared by method A (see Appendix 1.5) finally exhibit a quantum yield of up to 65% at room temperature.

Similar to CdS and CdSe nanocrystals, the CdTe colloids also show a relatively weak PL band red-shifted from the absorption edge which, most probably, originates from the radiative recombination of electrons and holes trapped in defect (surface) states. Its intensity is strongly influenced by the presence of TOP and DDA in the colloidal solutions and complete suppression of the defect luminescence through surface modification of the nanocrystallites is currently investigated.

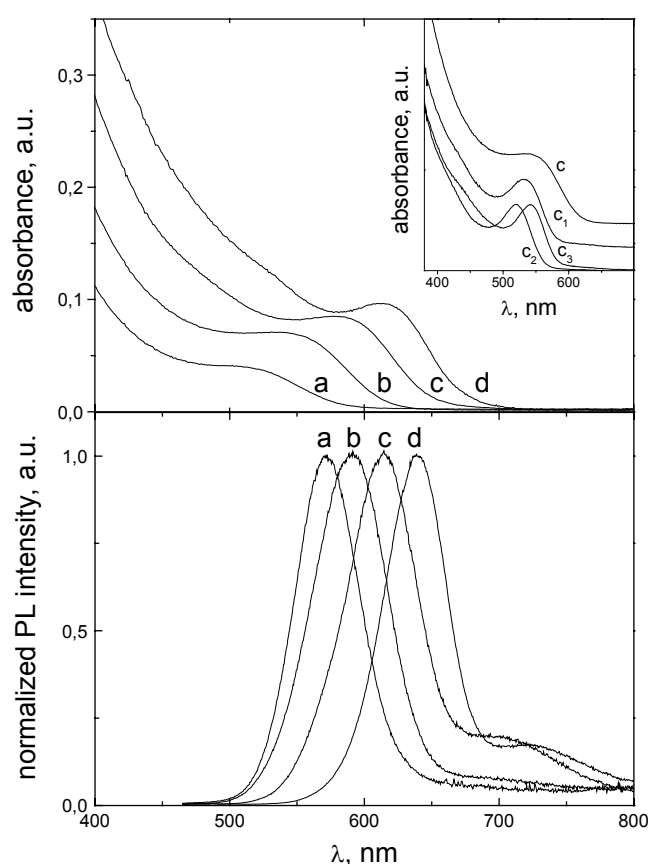


Figure 3.2 Absorption (top) and photoluminescence (bottom) spectra of CdTe nanocrystals recorded immediately after injection of the dimethylcadmium/tri-*n*-octylphosphine telluride mixture into DDA at 150°C (a) and after the particles growth for one hour at this temperature (b). Spectra (c) and (d) were measured after heating at 200°C for one hour and for 12 hours, respectively. The insert shows the absorption spectra of the reaction mixture (c) and of the samples after one (c_1) and two (c_2 , c_3) size-selective precipitations from toluene/methanol mixtures (The narrowing of the size distribution of CdTe nanocrystals is clearly recognized).

The resulting size distribution of the CdTe nanocrystals in the crude solution was calculated from SAXS data and is presented in Figure 3.3. The size distribution of nanocrystals in solution was calculated from the scattering data by means of indirect Fourier transformation [25]. The position of the pronounced maximum in the distribution corresponds to the weight-averaged mean radius of the CdTe nanocrystals. The value of about 2.2 nm agrees well with that estimated by TEM and XRD. The FWHM of the distribution curve of CdTe nanocrystals was ~ 2.3 nm, being considerably better than that observed for CdTe nanocrystals prepared in TOPO-TOP mixtures. Subsequent size selective precipitation using toluene and methanol as solvent and non-solvent, respectively, allows to further narrow down the size distribution.

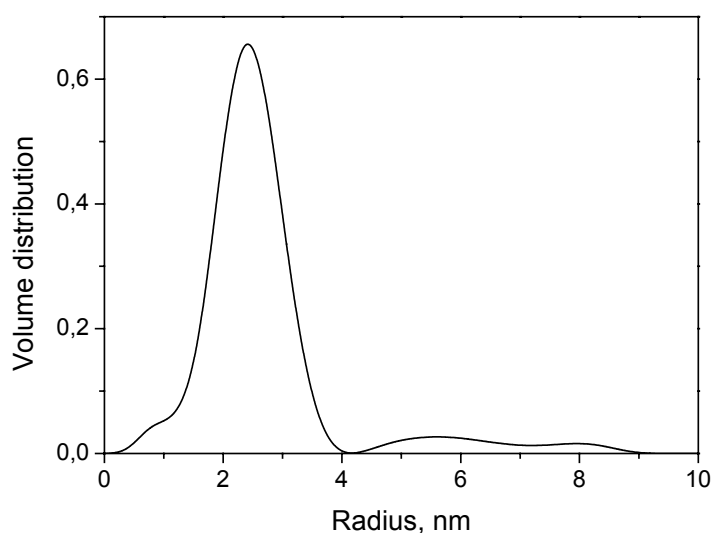


Figure 3.3. Size distribution of CdTe nanocrystals in the crude solution as calculated from SAXS measurements.

The inset in the Figure 3.2a shows absorption spectra of size selected samples of CdTe nanoparticles. The size distribution of the nanoparticles became narrower after size-selective precipitation resulting in a better resolution of the first electronic transition in the absorption spectra (from top to bottom). However, residual inhomogeneities of the size-selected samples are evident from the photoluminescence excitation (PLE) spectra (Figure 3.4). At a resolution of about 2 nm (emission and excitation monochromator) well-structured spectra are obtained displaying up to four transitions even at room temperature. Moreover, well pronounced anti-Stokes tails were observed in PLE spectra of CdTe nanocrystals (Figure 3.4). The nature of

the anti-Stokes PL in colloidal semiconductor nanocrystals was recently discussed [26] and it has been shown that sub-bandgap surface states are involved as intermediate states in the up-conversion process.

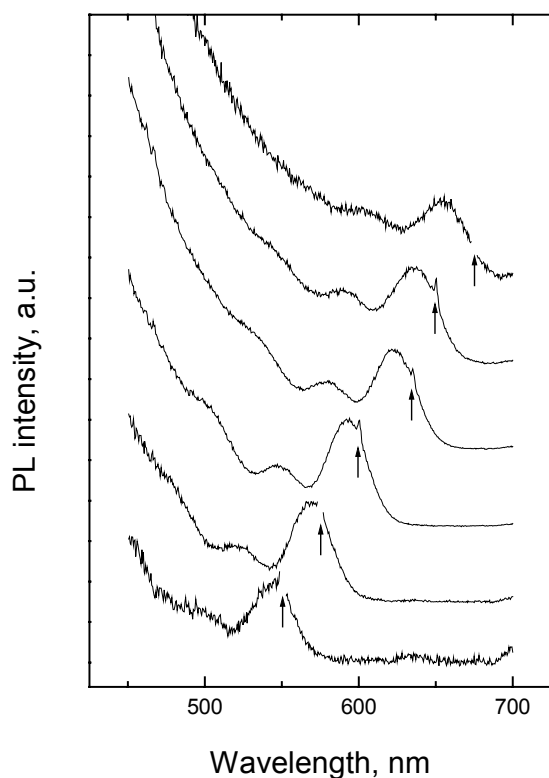


Figure 3.4. *Photoluminescence excitation spectra measured at different emission wavelengths as indicated by the arrows. The spectra correspond to different sizes of CdTe nanocrystals contained in the sample.*

Figure 3.5 shows small- and wide-angle powder X-ray diffraction data of size-selected CdTe nanoparticles. The positions of the diffraction peaks at wide angles match those of the cubic modification of bulk CdTe (zincblende phase). As expected, the width of the diffraction peaks is considerably broadened and decreases with increasing particle size. By using the Scherrer formula, the mean sizes of the nanocrystals can be calculated from the peak width at half-maximum. Particle sizes obtained from the width of the (111) reflection are depicted in the figure. As is often observed for samples with narrow particle size distribution, the XRD-pattern also shows a strong peak in the small-angle region which is caused by some short-range ordering of particles in the powder. By using the Bragg equation, the distance between nearest neighbors can be roughly calculated from the peak position assuming a local-range particle order and a liquid-like radial distribution function [3]. The calculated values given in Figure 3.5 are slightly larger than the particle sizes obtained from the Scherrer equation

indicating that the particles are separated from each other by a shell of organic ligands around the nanoparticles. The latter is in fact observed in transmission electron micrographs of the particles. An example is given in Figure 3.6 showing particles with absorption maximum at 605 nm. The image displays well separated particles with a mean size of 4.0 nm, the latter being in accord with the size calculated from the Scherrer equation. The Fourier transform of the image in fact confirms short-range ordering in the powder with a period of about 5.5 nm. The high resolution image given as inset shows lattice fringes for most particles indicating highly crystalline material. The EDX measurements indicate the presence of Cd, Te and P in the samples with the Cd:Te ratio being very close to 1:1.

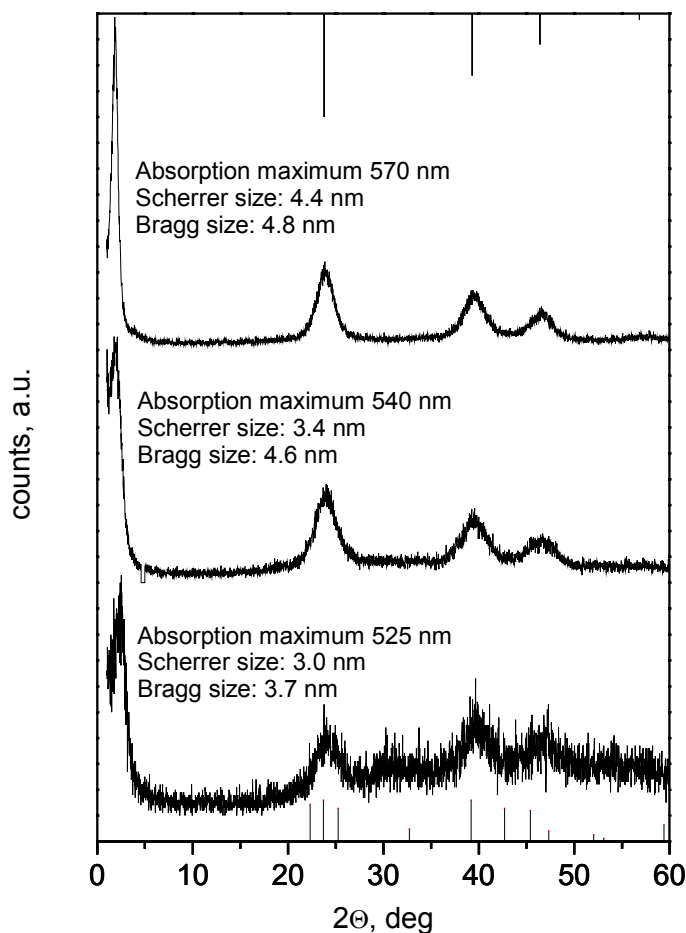


Figure 3.5. Powder X-ray diffraction data of size-selected fractions of CdTe nanocrystals. The particle sizes decrease from top to bottom; particle sizes were calculated from the Bragg equation and the Scherrer equation. The line spectra indicate the reflections of bulk CdTe (top: zinc blende, cubic; bottom: wurzite, hexagonal).

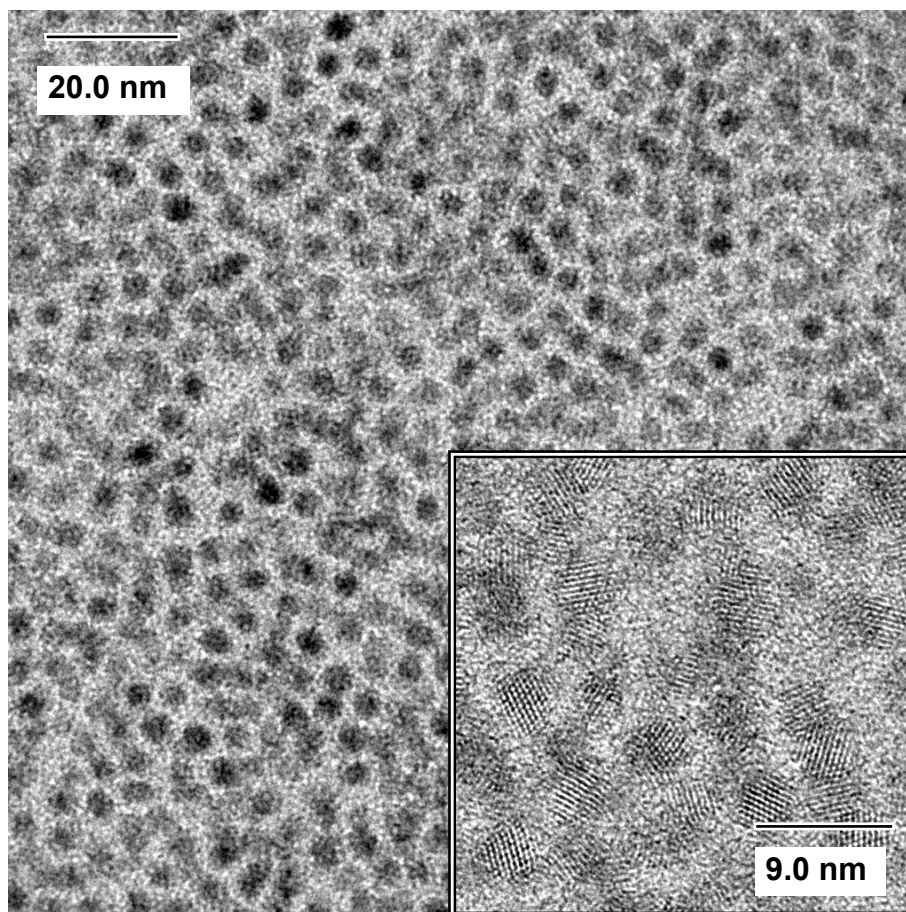


Figure 3.6. TEM overview image of a monolayer of CdTe nanocrystals. The insert shows a HRTEM image of single CdTe nanocrystals.

Thus, the use of DDA as coordinating solvent allows to synthesize highly crystalline CdTe nanoparticles showing size-dependent and very strong band edge PL. For the synthesis of these nanoparticles, dodecylamine was found to have several advantages over other amines. For instance, octylamine with its relatively low boiling point did not allow to use temperatures higher than 160-170°C and the particles tend to precipitate after several hours of heating. The use of dioctylamine as a solvent resulted in the immediate precipitation of the reaction products. Hexadecylamine provided good conditions for the growth of CdTe nanoparticles, but the particle size distribution obtained after prolonged heating was not as narrow as was achieved with DDA.

A proper choice of the tellurium source is another important point in the synthetic route developed. Thus, elemental tellurium slowly dissolving in the presence of TOP provides a constant source of highly diluted tellurium precursor. This method allows to grow CdTe nanocrystals at high temperatures but with extremely low rates controlled by the very slow

dissolution of tellurium. This probably results in a very low defect density which may be the reason for the very high room temperature PL quantum yield of 65 %.

3.3. Aqueous luminescent thiol-capped CdTe nanocrystals

3.3.1. Synthesis of thiol-stabilized CdTe nanocrystals

Figure 3.7a shows typical room temperature absorption and PL spectra of a size series of thiol-capped CdTe nanocrystals synthesized in aqueous medium (see experimental details in Appendix 1). The spectra were measured on as-prepared CdTe colloidal solutions which were taken from the refluxing reaction mixture at different intervals of time and diluted with water to provide the optical densities appropriate for PL measurements (about 0.1 at the excitation wavelength). All samples show a well resolved absorption maximum of the first electronic transition indicating a sufficiently narrow size distribution of the CdTe QDs. The maximum shifts to longer wavelengths with increasing size of the nanocrystals as a consequence of the quantum confinement. The room temperature PL excitation (PLE) spectra (Figure 3.7b) also display well resolved electronic transitions at higher energies and the pronounced tails of anti-Stokes PL. The nature of the anti-Stokes PL is, probably, similar to that suggested for InP and CdSe colloidal QDs [26]. From single dot spectroscopy performed on CdSe nanocrystals it is known that the emission of one particle with distinct size is basically a narrow line, therefore, the PLE technique allows the detection of luminescence emitted only by particles with selected size. The PL bands (Figure 3.7a) are located close to the absorption thresholds (so-called band-edge or "excitonic" photoluminescence) and are sufficiently narrow, ~0.15 eV during all stages of the particle growth (full width at half maximum, FWHM, ~35 nm for green-emitting particles being increased up to 55-60 nm for size fractions of largest CdTe nanocrystals). The position of the PL maximum of the smallest (~ 2 nm) luminescent CdTe QDs is located at 510 nm (green emission), whereas the largest (~ 6 nm) CdTe nanocrystals obtained emit in the near IR with a PL maximum at 730 nm. The whole spectral range between these two wavelengths is covered by the intermediate sizes of CdTe QDs.

The PL QE of as-synthesized CdTe nanocrystals depends on the nature of the stabilizing agent (Table 3.2) and lies typically between 3 and 11%, although values of 30-35% for 2-(dimethylamino)ethanethiol stabilized nanocrystals were attained. In most cases the quantum yield can be sufficiently improved by post-preparative treatments of the nanocrystals as will be shown below.

Table 3.2. Overview of the conditions used for the aqueous synthesis of CdTe nanocrystals, their properties and additional comments on their use.

Stabilizer	pH used for the synthesis	Stability* of CdTe QDs	Surface charge of CdTe QDs	Typical PL QE of as-prepared CdTe QDs	Additional comments
2-Mercapto-ethanol	11.2-11.8	Moderate	Slightly negative in alkaline	<1%	“Magic” clusters of the (supposed) formula $\text{Cd}_{54}\text{Te}_{32}(\text{SCH}_2\text{CH}_2\text{OH})_{32}^{8-}$ are formed [13]
1-Thioglycerol	11.2-11.8	Stable	Slightly negative in alkaline	3%	Have been used for synthesis of highly luminescent CdHgTe QDs and for electrophoretic deposition of closely-packed films [29]
Mixture of 1-Thioglycerol and 2,3-Dithioglycerol (1:1)	11.2-11.8	Moderate	Slightly negative in alkaline	6%	High affinity to different surfaces (gold, glass, latex, polymers <i>etc.</i>) [20]
Thioglycolic acid (TGA)	11.2-11.8	Stable	Negative	10%	Have been used for fabrication of LEDs by layer-by-layer (LbL) assembly [15,27] and for electrophoretic deposition into pores of artificial opals [21]. Can potentially be used for bio-conjugation and for the synthesis of QDs conjugates [23].
2-Mercapto-ethylamine (MA)	5.6-5.9	Moderate	Positive	10%	Can potentially be used for bio-conjugation and for the synthesis of QDs conjugates [23].
L-Cysteine	11.2-11.8	Moderate	Negative or positive depending on the pH	10%	Have been used for synthesis of conjugates with bovine serum albumin [22].
2-(dimethylamino)ethanethiol	5.0-6.0	Under investigation	Positive	30%	Under investigation

* “Stable” means here that colloidal solutions of CdTe QDs are stable for months and even years being stored under air in the dark at room temperature. “Moderate” means that colloidal solutions coagulate occasionally during the storage; however, they are generally stable for months as well. Independent of the stabilizer nature, CdTe QDs are generally stable (no oxidation, no or only very minor changes of the optical properties) for years in powder form and in closely packed or nanocrystal/polymer films being kept in the dark under air.

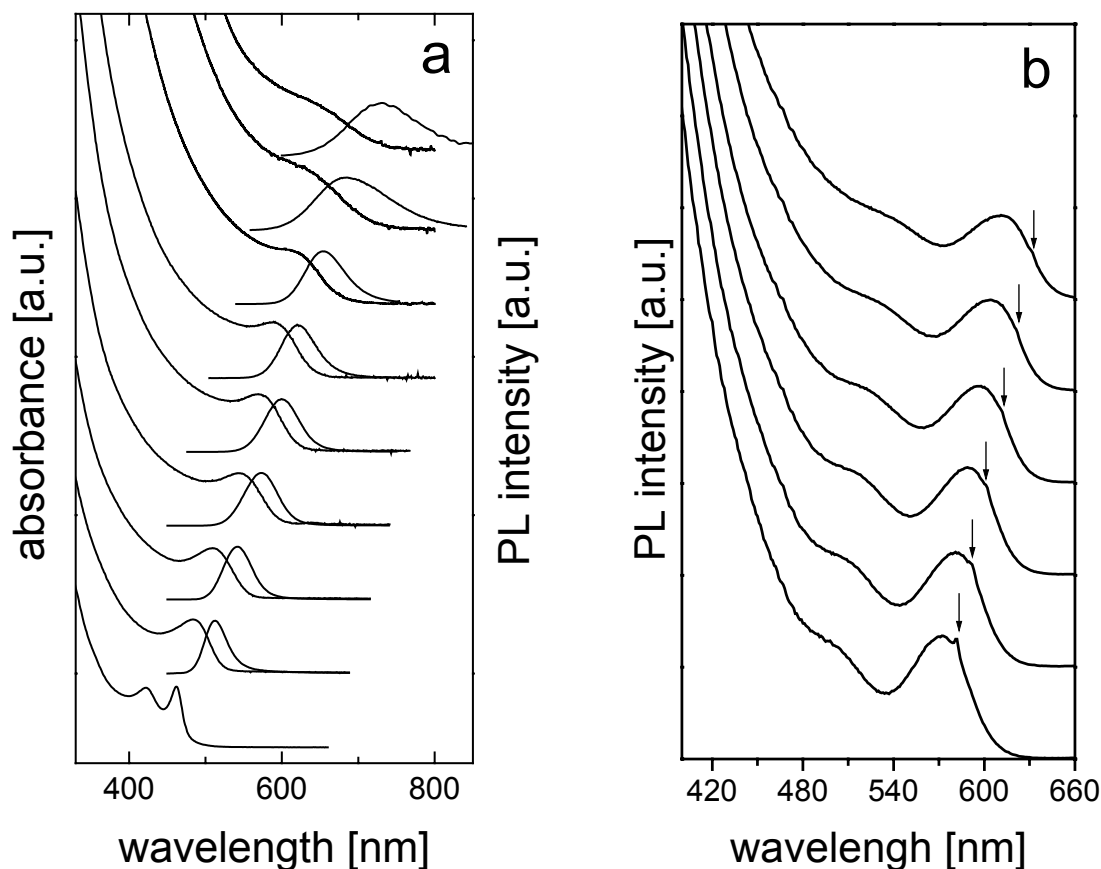


Figure 3.7. (a) Absorption and photoluminescence spectra ($\lambda_{\text{ex}} = 400 \text{ nm}$) of CdTe nanocrystals taken as prepared. The smallest nanoparticles stabilized by 2-mercaptoethanol possess only a weak broad emission, associated with surface traps (not shown in the figure). Nanocrystals with emission maxima above 670 nm were obtained by additional injections of Cd and Te precursors. (b) Photoluminescence excitation spectra of TGA-capped CdTe nanocrystals showing well-resolved maxima of high-energy electronic transitions. The emission wavelengths are indicated by arrows.

Table 3.2 provides an overview of different thiols used by us as capping agents for CdTe nanocrystals. As already mentioned above, the nature of the thiol influences the particle growth and the PL QE of as-synthesized CdTe nanocrystals. Besides that, each type of stabilizer has its own advantages and disadvantages allowing the use of CdTe nanocrystals capped by varying thiols for different purposes. This is also briefly summarized in Table 3.2. CdTe QDs stabilized by thioglycolic acid (TGA) and by mercaptoethylamine (MA) show efficient luminescence as prepared and possess either negative or positive surface charge because of the surface carboxylic or

amino groups respectively. The possibility to manipulate these nanocrystals, e.g. by the layer-by-layer technique or by electrophoresis [15,21] and to use the free functional groups of the capping molecules for conjugation with other molecules or QDs [23] makes them especially attractive for fabrication of functional materials. In the following sections, we mainly discuss the TGA- and MA-capped CdTe nanocrystals and describe ways of further improvement of their photoluminescence efficiency.

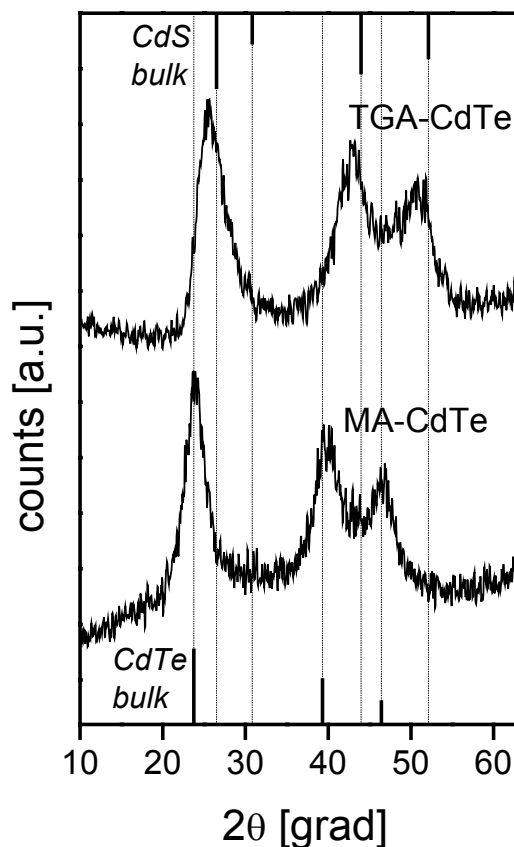


Figure 3.8. X-ray diffractograms of CdTe nanocrystals obtained in aqueous solutions in the presence of thioglycolic acid (TGA) and 2-mercaptoethylamine (MA).

Figure 3.8 shows XRD patterns obtained from powdered precipitated fractions of TGA- and MA-capped CdTe nanocrystals which are similar to those previously reported for thiol-capped CdTe nanocrystals [13,14,28]. The nanocrystals belong to the cubic (zinc blende) structure which is also the dominant crystal phase of bulk CdTe. However, the positions of the XRD reflexes of CdTe QDs synthesized under prolonged refluxing in the presence of thioglycolic acid (Figure 3.8) are intermediate between the values of the cubic CdTe and the

cubic CdS phases. As discussed in Ref. [29], prolonged refluxing of the aqueous colloidal solutions of CdTe nanocrystals in the presence of an excess of thiols in basic media leads to partial hydrolysis of the thiols and to the incorporation of the sulfur from the thiol molecules into the growing nanoparticles. Mixed CdTe(S) QDs, most probably with some gradient of sulfur distribution from inside the nanocrystals to the surface are formed under these conditions. Indeed, the smaller nanocrystals synthesized at moderate conditions (short refluxing time) show only slight deviations of the XRD reflexes from CdTe zinc blende diffraction patterns. The aqueous synthesis performed at comparatively low pH values (5.6 – 5.9) in the presence of 2-mercaptoethylamine as a stabilizer led to the formation of CdTe nanocrystals whose XRD patterns show only slight traces of a CdS phase (Figure 3.8).

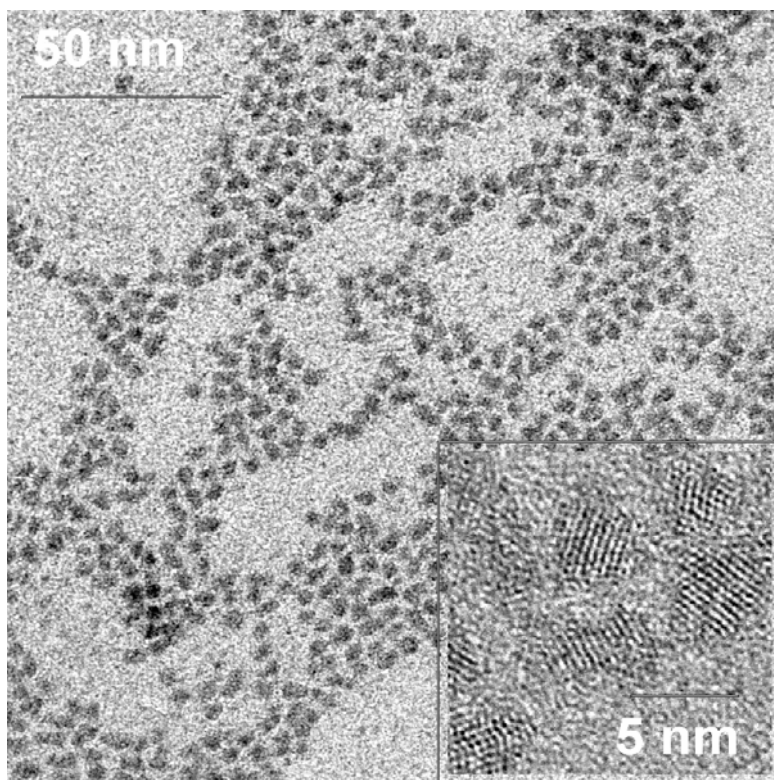


Figure 3.9. High-resolution TEM image of CdTe nanocrystals stabilized by thioglycolic acid. The particles were transferred from water to toluene in order to achieve their better separation on the TEM grids.

HRTEM investigations of CdTe nanocrystals grown at different conditions confirmed the XRD data. The longer the time of refluxing in the basic medium, the larger was the sulfur content in the mixed CdTe(S) nanocrystals as indicated by the lattice plane distances in the HRTEM images being intermediate between cubic CdTe and cubic CdS phases [29]. In

contrast, MA-capped CdTe nanocrystals synthesized at slightly acidic pH showed the lattice plane distances of the cubic CdTe phase. As is evident from Figure 3.9 the thiol-capped CdTe nanoparticles are crystalline, sufficiently monodisperse and well separated, with a mean size of ~4.5 nm which is in good accordance with the size calculated from the XRD data by the Scherrer equation.

Thus, both XRD and TEM investigations show that crystalline (cubic zinc blende structure) particles of either pure CdTe or mixed CdTe(S) phase are formed in the aqueous synthesis depending on the reaction conditions (pH value, duration of reflux, nature of stabilizer).

3.3.2. Photostability of thiol-capped CdTe nanocrystals

As indicated in Table 3.2, colloidal solutions of CdTe QDs being kept under air in the dark at room temperature are stable and do not change their optical properties for months and even years (depending on the nature of the stabilizer). However, the light sensitivity (photochemical stability) of aqueous CdTe colloids was found to be strongly dependent on the presence of oxygen and free stabilizer molecules in solution and can be greatly improved by keeping them under inert atmosphere. We have compared the room-temperature photostability of aqueous colloids of TGA-capped and MA-capped CdTe nanocrystals with the photostability of organometallically-synthesized CdTe QDs and TOPO-capped CdSe nanocrystals (see Chapter 2). The latter QDs were reported to be stable enough for, e.g., applications in light-emitting devices [30,31].

To investigate the photostability of CdTe nanocrystals in comparison with that of TOPO-TOP capped CdSe QDs, dilute colloidal solutions were irradiated for different time intervals with light of 450 W xenon lamp cut around 400 nm by a band pass filter having a bandwidth of ~40 nm and a peak transmission of ~40%. The optical densities of irradiated solutions of TGA-capped CdTe QDs in water and TOPO-capped CdSe QDs in toluene were adjusted to 0.15 at 400 nm. The absorption and the PL spectra of CdTe and CdSe nanocrystals were checked after different intervals of irradiation time. The long-term photostability of deaerated solutions of TGA-capped CdTe and TOPO-capped CdSe QDs was found to be comparable and very high. The photodegradation of TGA-capped CdTe QDs proceeded approx. 20-times faster in oxygen-saturated solutions. However, taking into account the rigid conditions of illumination their photostability even in this case was very high in comparison

with organometallically synthesized CdTe QDs and was comparable with the stability of TOPO-capped CdSe nanocrystals.

The mechanism of nanocrystal photodegradation seems to be different in the cases of TGA-capped CdTe and TOPO-capped CdSe nanocrystals. Both in airless and in oxygen-saturated solutions the illumination of CdTe nanocrystals led firstly to an improvement of their PL QE, followed by a gradual quenching of the PL intensity and finally to coagulation of the colloid. The temporal evolution of the absorption and the PL spectra of TGA-capped CdTe nanocrystals in aqueous solution will be also discussed in Chapter 7 (see Figure 7.8). The nanocrystals in the precipitate normally still luminesce. In the case of TOPO-capped CdSe nanocrystals the PL QE slowly went down during the illumination until the luminescence disappeared completely, while no coagulation was observed.

The photostability of MA-capped CdTe nanocrystals in aerated aqueous solutions was found to be lower compared to that of the TGA-capped CdTe QDs and no improvement of the PL QE was observed at initial stages of irradiation. The difference between the behavior of TGA- and MA-stabilized CdTe QDs originates most probably from their structural difference. The TGA-capped nanocrystals are essentially in the mixed CdTe(S) phase with sulfur enriched pre-surface layers, whereas MA-capped particles are almost pure CdTe. The irradiation promotes oxidation of unsaturated Te atoms which were recently identified as hole traps by optically detected magnetic resonance [32] and are known to be highly susceptible to oxidation [33]. This treatment leads to an improvement of the CdS shell around the CdTe core *via* substitution of oxidized surface Te sites by sulfur from the stabilizer molecules. The formation of such a shell enhances the PL efficiency of TGA-capped CdTe QDs at the initial stages of illumination and greatly inhibits the following photodegradation of the nanocrystals. In fact, an enhancement of the PL efficiency at initial stages of irradiation was also observed for CdSe/ZnS core-shell nanocrystals [34]. In the case of MA-stabilized CdTe QDs where sulfur atoms are hardly present in the crystalline structure, a complete outer CdS shell cannot be formed at the expense of thiol molecules of the stabilizing shell resulting in their faster photodegradation. The absence of a stabilizing CdS shell in the case of organometallically-synthesized CdTe nanocrystals whose surface is capped by TOP and amines [see Section 3.2.] causes a very quick loss of the photoluminescence in air as well.

In addition to the above mentioned processes, a photocatalytic oxidation of thiol molecules on the surface of nanocrystals can also take place as was shown for thiol-capped CdSe nanocrystals [35]. The thiol ligands on the surface of the QDs convert into disulfides under irradiation leading to precipitation of the nanocrystals if no new thiol ligands are

available in solution. This model correlates well with the behavior of the TGA-capped CdTe nanocrystals allowing the explanation of their higher photostability in presence of the excess of free thiol stabilizer in solution [36].

3.3.3. Selective photochemical etching

As was mentioned in Section 3.3.2, the photoluminescence efficiency of TGA-capped CdTe nanocrystals increases at the initial stages of photooxidation, presumably due to the removal of tellurium trap states and an improvement of the CdS shell. Further investigations of photochemical etching showed that this technique may not only be used to enhance the luminescence of CdTe nanocrystals but also to narrow their size distribution. The etching was carried out by illumination with a 450 W Xenon lamp in air-saturated solutions. The high-energy part of the lamp spectrum was cut off by optical filters in order to illuminate the samples near the absorption edges. Under these conditions an exposure for 5 days typically leads to both a ~3-fold improvement of the PL QE (up to 30%) and narrowing the PL band of the crude solutions of TGA-stabilized CdTe QDs (Figure 3.10).

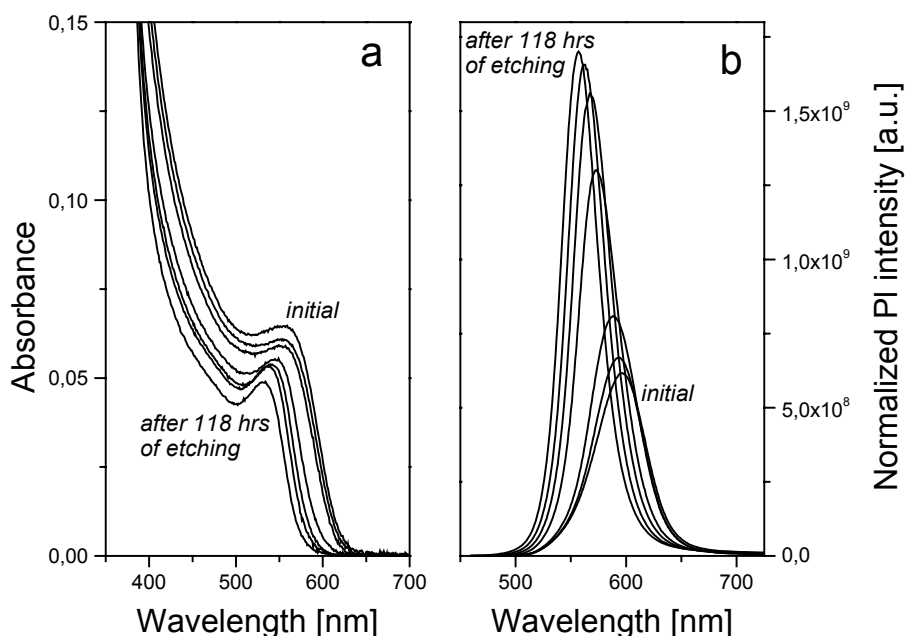


Figure 3.10. Evolution of absorption (left) and PL (right) spectra of TGA-stabilized CdTe nanocrystals exposed to selective photoetching. All PL spectra are normalized to the absorption at the excitation wavelength (450 nm).

In contrast, the photochemical etching under polychromatic light leads to an even stronger increase of the PL QE of up to 40% but is accompanied by a broadening of the photoluminescence and absorption bands owing to different rates of etching of different nanocrystals in the ensemble. We suggest that the improvement of the PL QE is due to the eliminating of defect states (or carrier traps) - most probably unsaturated surface tellurium atoms [32]. The nanocrystals possessing the most defect states dissolve primarily during photochemical etching. On the other hand, low defect QDs possessing only of a few (or single) Te traps do not completely degradate due to the passivating role of their CdS shell. Moreover, the vacancies formed can be successfully saturated by an excess of thiol molecules being available in solution.

The fractions of etched CdTe nanocrystals with PL QE of $\sim 40\%$ show a temporal stability against coagulation comparable with the initial solutions of the nanocrystals. The luminescence properties of the former as solid films (both casted and spin-coated) were found to be stable for at least 4 weeks under daylight conditions.

3.4. Aqueous synthesis vs organometallic approach: advantages and disadvantages

In this section we discuss some general advantages of the aqueous synthesis and compare some characteristics of thiol-capped CdTe nanocrystals with corresponding data of organometallically synthesized QDs. The comparison with organometallically synthesized QDs will be based both on their properties published in the literature and on our own experiences in the synthesis and handling of CdTe [Section 3.2.], CdSe and CdSe/ZnS [Chapter 2 and references therein], InP and InAs [Chapter 4 and references therein] nanocrystals.

Among the advantages of the aqueous synthesis its simplicity and high reproducibility should be mentioned first. Thus, colloids of CdTe nanocrystals with a particle size distribution about 10% can be prepared without the hot-injection technique which is necessary for the synthesis of nanocrystals in TOPO-TOP mixture (e.g., CdSe [6,37], CdTe [38], InAs [39]). As a result, the aqueous synthesis of thiol-capped nanocrystals can be carried out equally effective on a large scale, whereas the scaling up of the organometallic synthesis is difficult due to its poor reproducibility [40,41] and the use of extremely dangerous reactants (e.g. dimethylcadmium). Thiol-capped CdTe nanocrystals can be precipitated, washed and

kept in the dry state under ambient conditions as long as two years being retaining their stability and solubility in water.

Keeping in mind the potential importance of highly luminescent nanocrystals for large-scale applications, we also estimated the cost of equimolar amounts (with respect to the formula unit, i.e. CdTe and CdSe) of TGA-capped CdTe QDs and TOPO-capped CdSe nanocrystals whose luminescence efficiencies and photostabilities are similar. The costs of chemicals were compared using Aldrich's 2001 prices for most of the chemicals, Strem's 2001 price for dimethylcadmium and CERAC Inc.'s 2001 price for Al_2Te_3). The synthesis of CdSe QDs is about 8 times more expensive. In the case of organometallically prepared core/shell nanocrystals (e.g., CdSe/ZnS and CdSe/CdS) this difference reaches orders of magnitude.

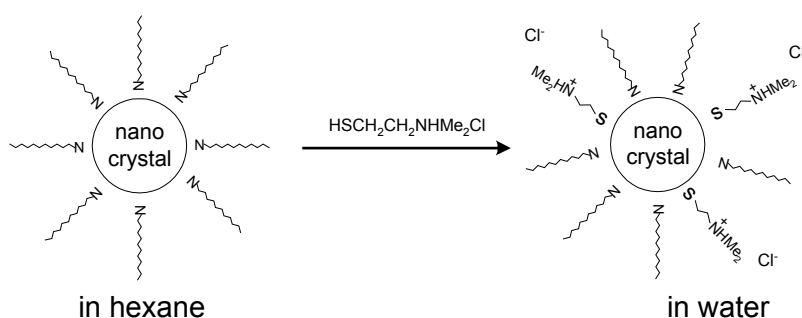
Nanocrystals synthesized by the aqueous approach do not possess the degree of crystallinity of the organometallically prepared QDs, where high annealing temperatures (200-360°C) are used during the synthesis. A very effective separation of nucleation and growth stages achieved in the organometallic synthesis by the so-called hot-injection technique allows to reach narrower size distributions of the nanocrystals in comparison with those prepared in aqueous solutions. However, the aqueous approach generally allows the synthesis of smaller QDs, both CdTe and CdSe, and the post-preparative size-selective precipitation procedure works more reproducibly in the case of aqueous colloids in terms of retaining the luminescence properties, as will be discussed in Chapter 7.

The possibility to control the surface charge and other surface properties of thiol-capped QDs simply by the choice of the stabilizing mercapto-compound with appropriate free functional groups is definitely important, especially when water soluble nanocrystals are needed, e.g. for fluorescent tagging applications. TGA-capped water-soluble CdTe nanocrystals with stable PL QE up to 40% reported in the present study might be an useful alternative in this case.

3.5. Transfer of luminescent CdTe nanocrystals from organics into aqueous medium and from aqueous solution into organics

Transfer of CdTe nanocrystals from organic solvents to water. Further functionalization and modification of organometallically synthesized amino-capped nanocrystals, in particularly their solubility in a variety of solvents can be realized by surface exchange of the amine capping groups. The possibility to make luminescent semiconductor nanocrystals water-soluble is of special interest due to their potential application as biological labels [22,34,42]. For this purpose we treated CdTe nanocrystals with N,N-dimethyl-2-mercaptoethylammonium chloride in order to attach these highly polar surface capping molecules to the nanocrystal surface (Scheme 3.2).

Scheme 3.2.



Highly luminescent semiconductor nanocrystals prepared in a nonaqueous medium can be readily transferred to water by the following procedure, which has to be carried out under nitrogen atmosphere. 20-50 mg of freshly prepared CdTe nanocrystals were precipitated from toluene solution by adding a small amount of methanol and were isolated by filtration through a 0.22 μm membrane filter. Nanocrystals collected on the membrane were immediately transferred to an aqueous 1 M solution of N,N-dimethyl-2-mercaptoethylammonium chloride. The mixture was left under stirring at room temperature for about 1 h until it became optically clear. Absorption spectra of nanocrystals transferred to water were identical to those of the same particles dispersed in toluene. The CdTe nanocrystals retained sufficiently strong band edge PL (QE 13-18% depending on the particle sizes) after being transferred in aqueous solution.

Under the mild conditions applied (room temperature), a complete exchange of stabilizing DDA molecules by thiol molecules is improbable. Nevertheless, it was possible to make the CdTe nanocrystals soluble in water and to retain a sufficiently high PL with QE up

to 18%. This value is comparable with those achieved for more complex water-soluble core-shell CdSe/CdS/SiO₂ and CdSe/ZnS nanocrystals used for biolabeling [34,43], and for thiol-capped CdTe nanocrystals synthesized in aqueous solutions (see Section 3.3).

Transfer of thiol-capped CdTe nanocrystals from aqueous solution to non-polar organic solvents. As was discussed in Section 3.3, the synthesis of CdTe nanocrystals in aqueous medium allows preparation of strongly luminescent nanocrystals of high quality. As an advantage of the aqueous synthesis the simplicity and the high reproducibility was mentioned. On the other hand, processing of water soluble nanocrystals is strongly restricted since they are incompatible with most common organic solvents and polymers, making it difficult to form high quality films by spin-coating or casting techniques, etc. Here we present a novel simple approach allowing transfer of thiol-capped CdTe nanocrystals from aqueous solution to non-polar organic solvents. The procedure is based on the partial exchange of surface stabilizer molecules with dodecanethiol. This process successfully transfers up to 90% of the nanoparticles is accompanied by only moderate changes of their optical properties.

In the typical phase transfer reaction, 1ml of an aqueous solution of either crude or size-selected CdTe nanocrystals stabilized with thioglycolic acid was placed into a vessel (Figure 3.11a) and 1ml of 1-dodecanethiol was added dropwise (Figure 3.11b). Then acetone was added to the upper organic phase (Figure 3.11b). The addition of about 2-3 ml acetone was found to be necessary to promote and accelerate the transport through the phase boundary. The exact amount of acetone depends on the nanocrystal size and has to be established experimentally. The CdTe nanocrystal start to transfer immediately after shaking and heating up to boiling point of acetone. Simultaneously, the volume of the organic phase decreases to ca. 1 ml indicating almost quantitative transfer of acetone to the bottom (aqueous) phase (Figure 3.11c). The efficiency of the phase transfer process was found to be directly dependent on the amount of acetone added. After isolation of the organic phase, methanol was added drop-wise to precipitate the CdTe nanocrystals. The isolated precipitate consists of CdTe nanocrystals capped with dodecanethiol and is readily soluble in toluene, hexane, chloroform, etc (Figure 3.11d). The photoluminescence efficiency of the initial aqueous CdTe nanocrystals is comparable with that of nanocrystals transferred in toluene (*cf.* Figures 3.11e and 3.11f) and is of about 12-15%. The absorption and the photoluminescence spectra of nanocrystals in toluene solutions are very similar to the ones in water.

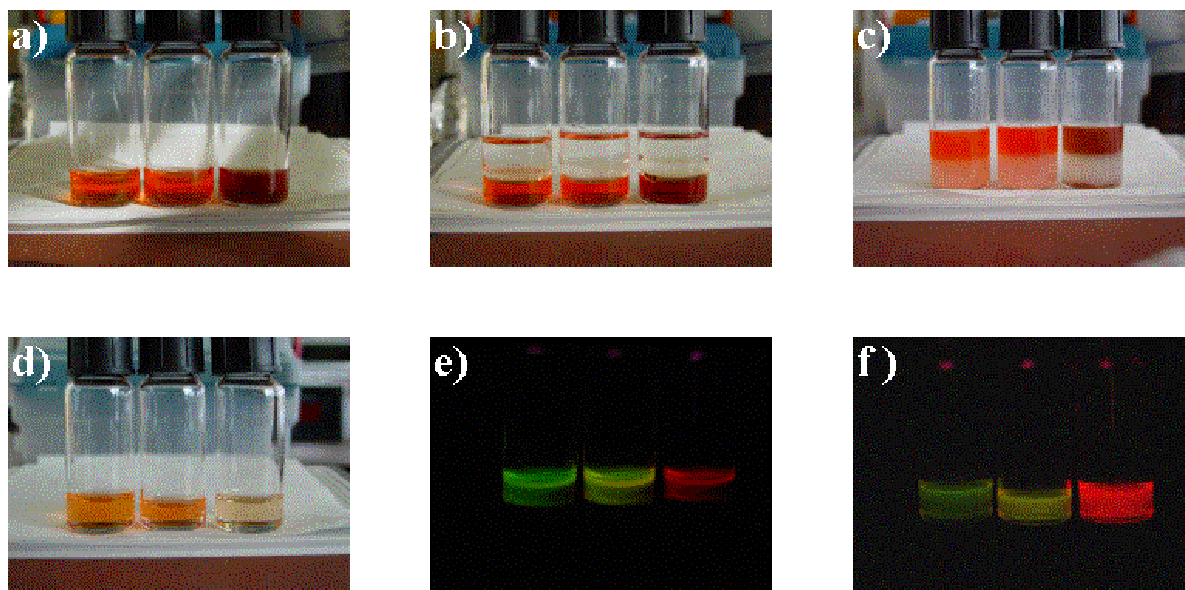


Figure 3.11. Phase transfer of aqueous thioglycolic acid capped CdTe nanocrystals to non-polar organic solvents: (a) initial aqueous solutions of CdTe nanocrystals with different particle size, (b) addition of dodecanethiol and acetone, (c) shaking and heating results in transfer of CdTe nanocrystals from aqueous medium to dodecanethiol phase, (d) the CdTe nanocrystals can be isolated from dodecanethiol and redispersed in a non-polar solvent (toluene). Images (e) and (f) shows photoluminescence of CdTe nanocrystals dispersed in water [initial colloidal solution, image (a)] and toluene [resulting solution, image (e)].

3.6. Conclusions

Highly luminescent CdTe nanocrystals were synthesized by the reaction of dimethylcadmium and metallic tellurium in a mixture of dodecylamine and trioctylphosphine. Fairly narrow particle size distributions have been obtained without using the “hot injection” technique to separate nucleation and growth of the nanoparticles. A series of nearly monodisperse crystalline CdTe nanoparticles with zincblende lattice and mean particle sizes between 2.5 and 7 nm were isolated by size-selective precipitation. The particles show strong band edge photoluminescence tunable in the visible spectral range from green to red and have been characterized by powder XRD, HRTEM, absorption and luminescence spectroscopy. A photoluminescence quantum yield of up to 65% is observed at room temperature without passivating the surface of the nanoparticles with an inorganic shell.

Thiol-capped CdTe nanocrystals represent a new kind of core-shell system with a naturally sulfur-capped surface (CdS shell) created by mercapto-groups covalently attached to the surface cadmium atoms. Under reaction conditions facilitating the formation of mixed CdTe(S) nanocrystals, as in case of the TGA-capped CdTe QDs, the sulfur-rich region is most probably stretched from the surface into the nanocrystal. Importantly, the synthesis of this kind of core-shell nanocrystals naturally occurs in one step during particle growth, as the sulfur originates from the stabilizing thiol molecules. The wave functions calculated for a CdTe/CdS system with the particle-in-a-box model [44] show a delocalization of the electron through the entire structure and the confinement of the hole in the CdTe core. The effective screening of the hole by the shell explains the high photostability of these nanocrystals, since the main photodegradation mechanism is the photooxidation of surface tellurium atoms requiring oxygen and holes [33]. The weak localization of electrons promotes the electronic accessibility of thiol-capped CdTe nanocrystals, allowing, e.g., an effective electron injection important for LED applications. The additional functional groups of the thiol capping molecules of the nanocrystals provides their water solubility, high processability and the surface charge desired.

3.7. References

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Chapter 4

Luminescent III-V nanocrystals

Luminescent InP, InAs and InAs/CdSe core-shell nanocrystals were prepared by organometallic approaches using long chain alkylamines, trioctylphosphine and trioctylphosphine oxide as stabilizing and size regulating agents. The nanocrystals were characterized by powder XRD, synchrotron XPS, HRTEM, absorption and luminescence spectroscopy. In the case of InP nanocrystals the use of amines allowed obtaining extremely small particles and improving the particle crystallinity and size distribution. Nearly monodisperse fractions of both InP and InAs nanocrystals were isolated by the size-selective precipitation technique. As prepared, InP nanocrystals exhibit very poor photoluminescent properties, however, their PL efficiency can be drastically enhanced by photoetching of the nanoparticle surface with certain fluorine compounds. This process was thoroughly studied applying the technique of photoelectron core level spectroscopy with synchrotron radiation and the possible origins of the luminescence improvement upon surface etching are discussed. A new technique of controllable size-selective photoetching of colloidal nanoparticles allowed the preparation of nearly monodisperse fractions of InP nanocrystals with room temperature PL quantum yields of 20-30%. The PL band was tunable from green to near-IR with increasing particle size. InAs/CdSe core-shell nanocrystals exhibit strong near-IR emission tunable from ~ 800 to 1500 nm with room temperature quantum efficiency of about 20%.

4.1. Introduction

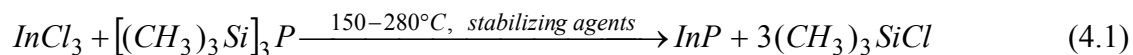
While II-VI semiconductor nanocrystals were studied extensively during last decade, much less information is available about their III-V analogous. The synthesis of colloidal III-V nanocrystals is more difficult than that of II-VI nanocrystals. The reason is that III-V semiconductors are more covalent compounds and high temperatures are usually required for their synthesis. In progressive, more covalent series of semiconductors, the synthesis of quantum dots by colloidal techniques becomes increasingly difficult[1]. Only a limited number of papers discussing the synthesis and characterization of InP [2-7], GaP [8] and InAs [9,10] nanocrystals begun to appear in the literature during last years. The strong interest to III-V nanocrystals arose from the expectations that these materials may exhibit even more pronounced quantum size effects than II-VI materials. Thus, III-V materials usually have relatively covalent bonding and direct band gap structure, larger bulk exciton radii and smaller effective masses what makes them promising candidates in various optoelectronic applications. Another potential interest to III-V nanocrystals is caused from “green chemical principles” dominating in chemistry during last years and based on the development of environmentally benign chemical methodologies and materials [11]. From this point of view some III-V compounds, e.g. InP, are more attractive than the cadmium-related II-VI ones.

A large step toward controllable synthesis of III-V nanocrystals was made by Nozik et al. which adapted the Well's dehalosilylation reaction [12] for synthesis of nanocrystalline InP colloids [2,8]. Alivisatos et al. have extended this approach to InAs quantum dots [9]. The luminescent properties of as-prepared InP and InAs nanocrystals are rather poor as compared to II-VI ones, however, several ways of improvement of the band edge luminescence were proposed. Thus, Micic et al. had developed etching of InP nanocrystals with HF resulting in strong enhancement of the PL efficiency [4,5,13]. The growth of an epitaxial shell of a higher band gap II-VI or III-V semiconductor on the core InAs nanocrystal also yielded strongly luminescent colloidal quantum dots [14,15]. InAs-based core-shell nanocrystals exhibit the PL band tunable in the near-IR spectral range, covering the wavelength region that is important for telecommunication applications [15].

In this chapter we report on various approaches for the organometallic synthesis and characterization of luminescent InP, InAs and InAs/CdSe nanocrystals. Thorough investigation of etching of the InP nanocrystal surface with some fluorine compounds which results in drastic enhancement of the PL efficiency allowed us to elucidate the etching mechanism and clarify the origin of surface traps quenching the luminescence of as-prepared InP nanocrystals.

4.2. Synthesis of monodisperse crystalline InP nanoparticles

InP nanocrystals were synthesized *via* Well's dehalosilylation reaction [12] in presence of stabilizing agents preventing growth of the bulk InP phase, as shown in Scheme 4.1 :



This reaction was applied for the preparation of InP nanocrystals using TOP [16], TOPO [3] and TOPO-TOP [1,2] as particle stabilizing agents. However, in all cases the reaction pathway involves a large energetic barrier resulting in a very slow particle nucleation stage [3]. As a consequence, no temporal separation of particle nucleation and growth *via* the hot-injection technique can be achieved and the control over the particle size distribution in the reaction mixture is poor in comparison with that of II-VI nanocrystals. The InP particles forming after the nucleation stage are usually amorphous and their annealing for 1-6 days at temperatures above 250°C is required to obtain crystalline InP nanoparticles [2,3].

We have tested various particle growth regimes and stabilizing agents (primary amines, TOPO, TOP, etc.) with a goal to make the synthesis of InP nanocrystals more controllable and versatile. As was shown in Chapters 2 and 3, introducing of primary amines in the stabilizing mixture allowed considerable improvement of size distributions of II-VI nanocrystals. Synthesis of InP nanocrystals in dodecylamine (DDA)-TOP mixtures [see the experimental details in Appendix 1] also allows obtaining narrower particle size distributions as compared to those prepared in TOPO, TOP and TOPO-TOP stabilizing mixtures. Figure 4.1a shows the evolution of absorption spectra of crude solution of InP nanocrystals during heating of the reaction mixture. Proper choice of the heating regime allows to tune the size of InP nanocrystals from ~1.5 to 3.5 nm with *in situ* particle size distribution of about 20%. Comparison of these values with those obtained by the TOP-TOPO synthesis [2,3] shows that the use of amines as stabilizing and size-regulating agent permits to obtain smaller InP nanocrystals with narrower size distribution than is achievable by the conventional TOPO-TOP method. DDA-capped InP nanocrystals show both the band edge luminescence and a PL band red-shifted from the absorption edge (inset to Figure 4.1a) which originates from the recombination of electrons and holes trapped in surface states and is commonly observed for as-prepared InP nanoparticles [3,8]. The overall PL quantum efficiency of DDA-capped InP nanocrystals, however, does not exceed 0.5%.

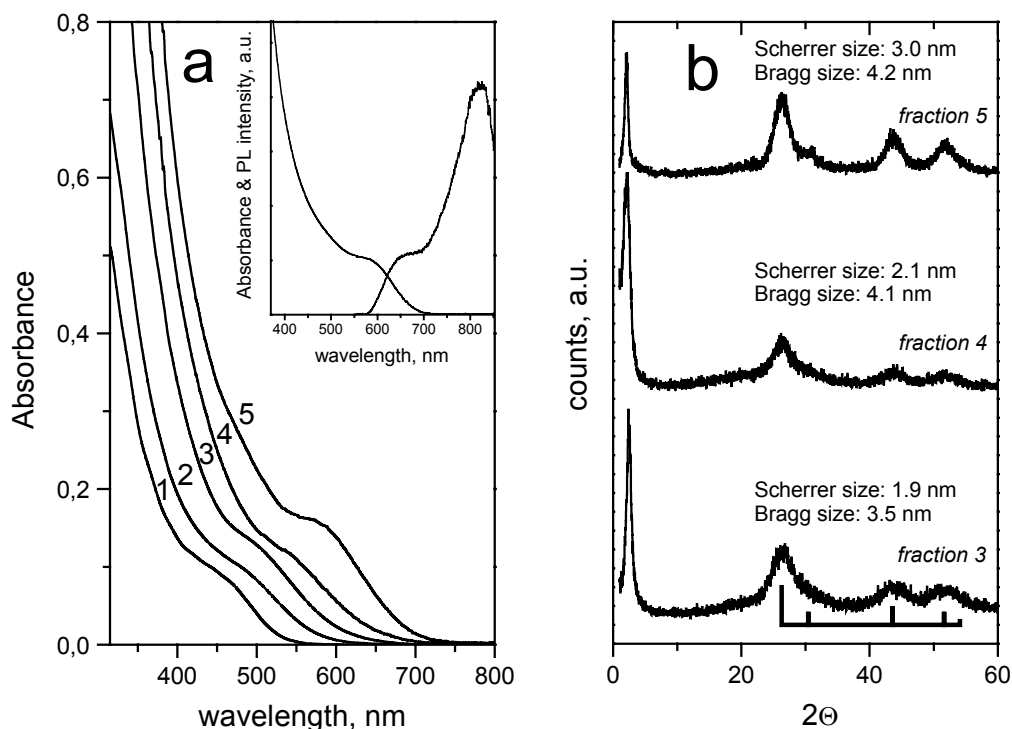


Figure 4.1. (a) Temporal evolution of absorption spectrum of InP nanocrystals growing in the crude solution. The spectra were measured after applying of subsequent annealing regimes (of the same sample): (1) 150°C, 5 min; (2) 150°C 40 min; (3) 150°C, 8h; (4) 180°C, 17h; (5) 240°C, 22h. Inset shows typical absorption and PL spectra of as-prepared InP nanocrystals. (b) Powder X-ray diffractograms of InP nanocrystal fractions 3, 4 and 5 shown in Figure 4.1a. The line spectrum gives the bulk InP (zinc blende, cubic) reflections.

The synthesis of InP nanocrystals in the DDA-TOP stabilizing mixture also allowed us to improve the particle crystallinity even at early stages of growth. Thus, Figure 4.1b shows P-XRD patterns measured on as-prepared InP nanocrystals after different annealing conditions. The DDA-TOP synthesized InP particles are crystalline after annealing at 150°C for 8 h, whereas, the synthesis of InP in conventional TOPO or TOPO-TOP stabilizing mixtures under these conditions yields amorphous particles exhibiting no reflexes in XRD pattern [2,3]. The positions of the diffraction peaks at wide angles match those of the bulk phase of cubic InP (zincblende phase). As expected, the width of the diffraction peaks is considerably broadened and increases with decreasing particle size. By using the Scherrer formula, the mean sizes of the nanocrystals can be estimated from the peak width at half-maximum. As is often observed for samples with narrow particle size distribution, the P-XRD

patterns also show a narrow peak in the small-angle region which is caused by short-range ordering of the nanocrystals in the powder. Assuming a dense packing of nearly monodisperse particles, the distance between nearest neighbors has been calculated using the Bragg equation [17]. The calculated values are slightly larger for all samples than the particle sizes obtained from the Scherrer equation. Overview TEM image (Figure 4.2) presents well separated nanocrystals with mean sizes being in accordance with the sizes calculated from the Scherrer equation. TEM images show that the difference in the particle sizes estimated from Scherrer and Bragg equations is caused by a shell of organic ligands about 1 nm thick, which separates particles from each other. EDX measurements indicate compositions close to an In:P ratio of 1:1. High resolution TEM images of amino-capped InP nanocrystals show crystalline nanoparticles with clearly resolved lattice fringes (Figure 4.2).

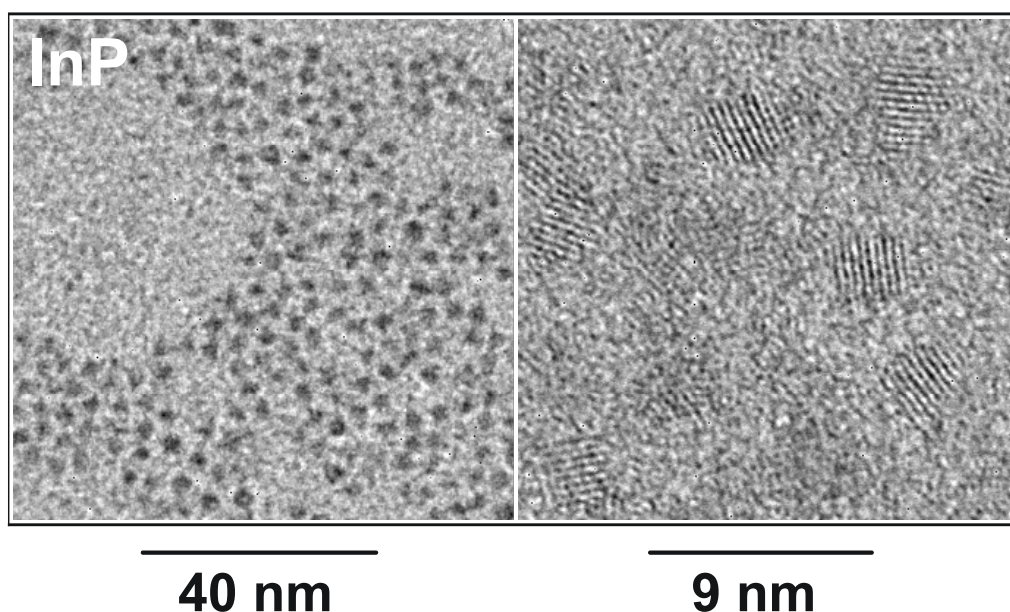


Figure 4.2. TEM overview (left) and HRTEM images (right) of InP nanocrystals synthesized in DDA-TOP mixture.

The synthesis of InP nanocrystals in TOPO-TOP was performed as described in Ref.[5] and usually allowed obtaining InP nanocrystals of larger sizes (from ~2.2 to 6 nm) than are achievable in the DDA-TOP mixture. Long-term (up to 3-5 days) annealing at 250-280°C provides a high degree of particle crystallinity (Figure 4.3). The broad size distribution of as-prepared TOPO-TOP InP nanocrystals (~25-30%) does not allow utilization of their size-dependent properties. However, the nanocrystal size distribution can be considerably improved by post-preparative size selective precipitation. Usually, size selective precipitation was performed as following: a sample of as-prepared InP nanocrystals with a broad size

distribution was dispersed in toluene and methanol was added dropwise until the initially clear solution becomes slightly turbid. The largest nanocrystals in the sample exhibit the greatest attractive van der Waals forces and tend to aggregate before the smaller nanocrystals [18]. The aggregates consisting of the largest nanocrystals present in the sample can be isolated by filtration through a 0.2 μm PTFE membrane filter and can be re-dissolved in non-polar organic solvents (toluene, hexane, chloroform, etc.). Subsequently, a small amount of additional non-solvent was added to the supernatant to precipitate the second size-selected fraction. Repetition of this procedure for several times allows obtaining up to ~ 10 size-selected fractions from one portion of the InP crude solution.

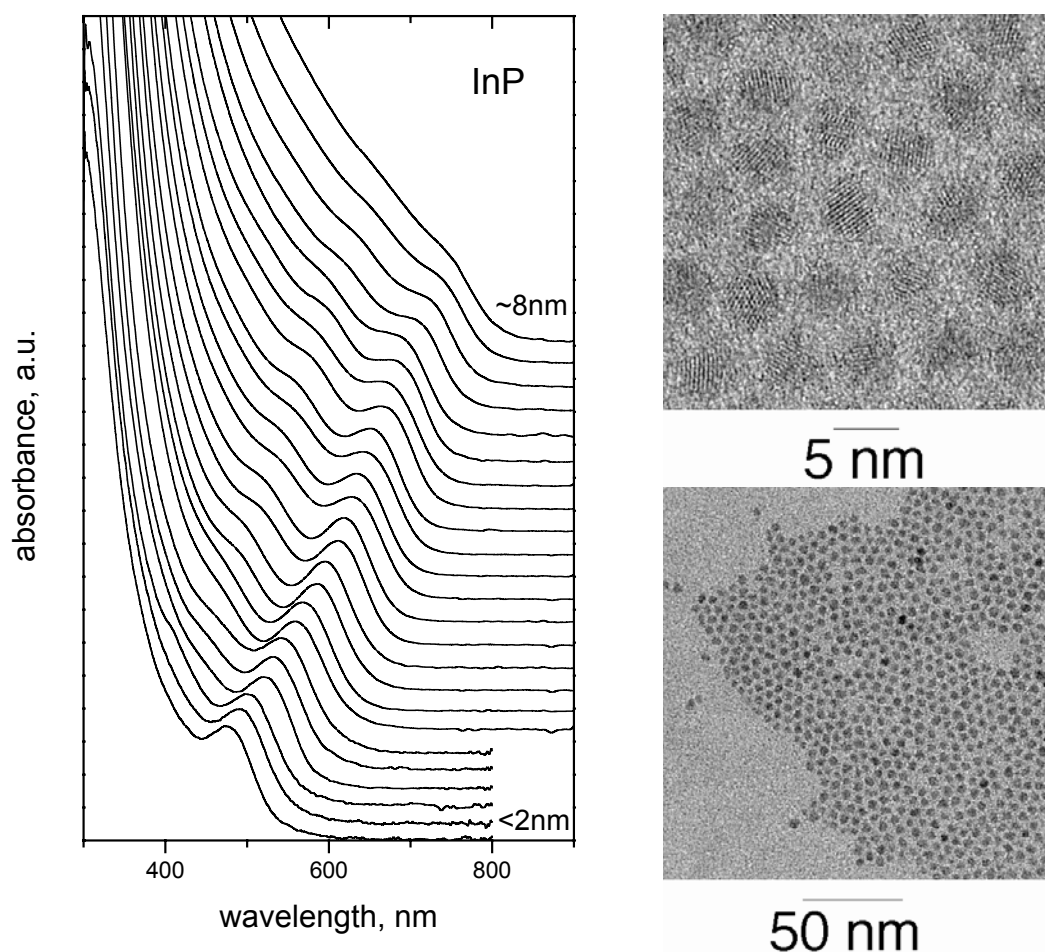


Figure 4.3. Size-dependent evolution of absorption spectra of TOPO-TOP capped InP colloidal quantum dots (left). TEM overview and HRTEM images of a size selected fraction of InP nanocrystals grown in TOPO-TOP mixture(right).

Figure 4.3 demonstrates the size-dependence of the absorption spectrum of monodisperse InP nanocrystals isolated as described above. All size selected fractions possess sharp excitonic transitions. TEM and HRTEM investigations show that carefully performed size selective precipitation allows to achieve size distributions narrower than of about 8-10% (Figure 4.3). Both as-prepared and size selected TOPO-TOP capped InP nanocrystals exhibit very poor luminescence composed of weak band edge luminescence and luminescence from deep traps. The luminescence intensity increases with oxidation of the nanocrystal surface. However, the room temperature PL quantum efficiency of oxidized nanocrystals does not exceed $\sim 0.01\%$. This value can be drastically improved *via* treatment of InP nanocrystal surface with certain fluorine compounds as will be discussed below.

4.3. Etching of InP nanocrystals with fluorine compounds resulting in a strong band edge luminescence

Their poor luminescent properties do not allow us to consider as-prepared InP nanocrystals as appropriate candidates for applications in optoelectronic devices. Low PL efficiency is usually a result of non-adequate passivation of the nanocrystal surface [19]. Non-passivated surface sites (often considered as so-called dangling bonds) may serve as traps for photogenerated carriers and can provide non-radiative recombination pathways. In principle, proper post-preparative modification of the particle surface can eliminate these traps. Recently, Micic et al. have proposed the very interesting procedure of treatment of InP nanocrystals with HF resulting in the appearance of strong band edge luminescence [13]. Upon HF treatment the particle becomes smaller and some modification of its surface results in drastic improvement of the luminescent properties. However, to the best of our knowledge, there is no satisfactory explanation of the “etching” processes occurring at the particle surface and resulting in luminescence enhancement. Moreover, the existing procedure for InP nanocrystals is extremely irreproducible with respect to the resulting PL quantum efficiency [20]. Here we attempted to systematically study InP nanocrystals surface treatments with different fluorine compounds.

4.3.1. Size dependent extinction coefficients of InP nanocrystals

In general, the concentration of colloidal nanoparticles can be determined very easily by optical absorption measurements if the molar extinction coefficient is known. Unfortunately, no information about the extinction coefficients of III-V nanocrystals is available. In order to estimate the values of the molar extinction coefficient of synthesized InP nanocrystals, we characterized thoroughly washed size-selected samples of TOPO-TOP capped InP nanocrystals by UV-Vis spectroscopy and subsequently dissolved the particles in aqueous HNO_3 digesting solution. The total indium concentration of each sample was determined by inductively coupled plasma mass spectroscopy (ICP MS). Once the metal concentrations were determined, the particle concentrations were calculated by using bulk lattice parameters and the average particle size. The latter was either determined from TEM images or from the known correlation between optical absorption and particle size [3,7] and by assuming a 1:1 ratio of In to P. The accuracy of this approach was of about 15% in case of CdSe and ZnSe nanocrystals [21].

Figure 4.4a shows the particle size dependence of the extinction coefficient corresponding to the molar concentration of InP units in the InP nanoparticles. The value of the extinction coefficient measured far from the absorption onset (350 nm) is almost size independent, whereas the extinction coefficient at the first absorption maximum decreases with increasing particle size (Figure 4.4a). To calculate the molar extinction coefficients (ϵ) of *InP-particles* of one size, the exact dependence of the band gap on the particle size (sizing curve) is required. Unfortunately, sizing curves reported for InP nanocrystals are controversial [3,7]. Comparison of literature values with our TEM and HRTEM investigations shows that the value of (ϵ) at the first absorption maximum increases with the particle size (Figure 4.4b). However, the size dependence is not as pronounced as the reported one for CdSe nanocrystals [22] where the extinction coefficient was proportional to the cube of the particle radius. In fact, measurements on colloidal CdS particles prepared in aqueous solution showed that the oscillator strength is not depending on the particle diameter if the size of the nanocrystals is smaller than the bulk exciton [23]. Our results demonstrate that InP nanocrystals exhibit a size dependence of (ϵ) lying in between the two limiting cases mentioned above. Figure 4.4c shows the absorption spectra of InP nanocrystals scaled with their molar extinction coefficients. Far from the absorption onset the value of ϵ is proportional to the number of InP unit cells in the nanocrystal what is rather convenient for the estimation of the particle concentration from the absorption spectra.

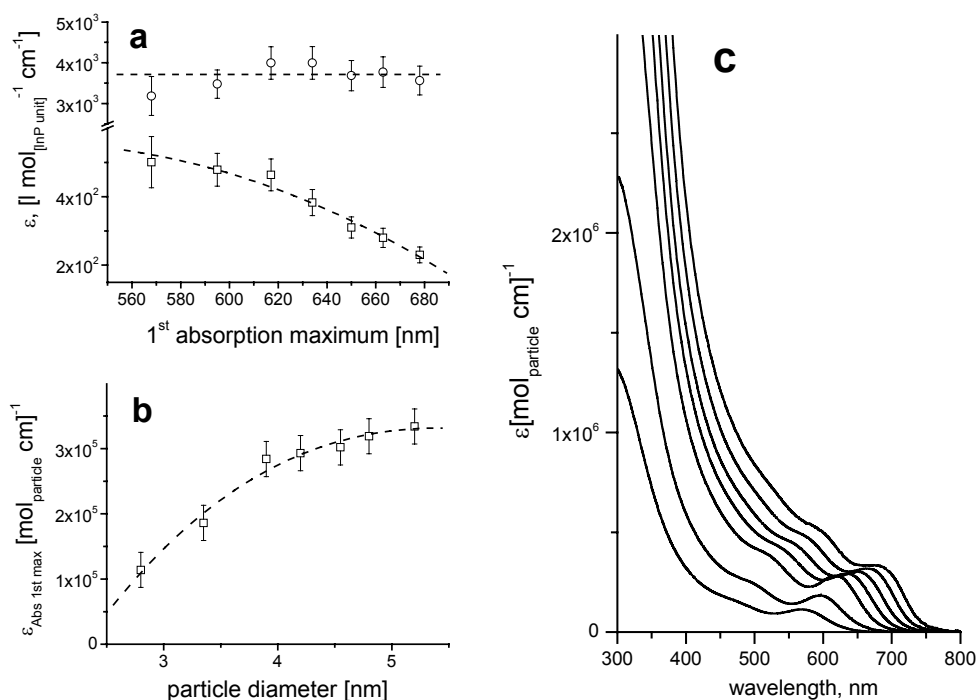


Figure 4.4 (a) the extinction coefficients referred to the concentration of InP units measured at 350 nm (○) and at the first absorption maximum (■) for different nanocrystal sizes; (b) molar extinction coefficient of InP nanocrystals at the first absorption maximum referred to the particle concentration; (c) absorption spectra of InP nanocrystals scaled with their molar extinction coefficients.

4.3.2. Photochemical nature of the etching of InP nanocrystal with fluorine compounds

In the first series of experiments, etching of InP nanocrystals under nitrogen atmosphere was performed without long-term exposure of the particles to daylight, i.e. under conditions typically used in the processing of nanoparticles. Figure 4.5 shows the evolution of the absorption and the PL spectra of InP nanocrystals after addition of different amounts of HF. The HF treatment increased the band edge PL by more than one order of magnitude whereas no significant changes were detected in the absorption spectra. However, the resulting PL quantum efficiency was still very low and did not exceed 0.2 - 0.5%. When the HF concentration in the etching solution was increased above a certain level, the PL efficiency started to decrease as shown in Figure 4.5. This behavior was observed for all InP nanocrystals, independent of their size.

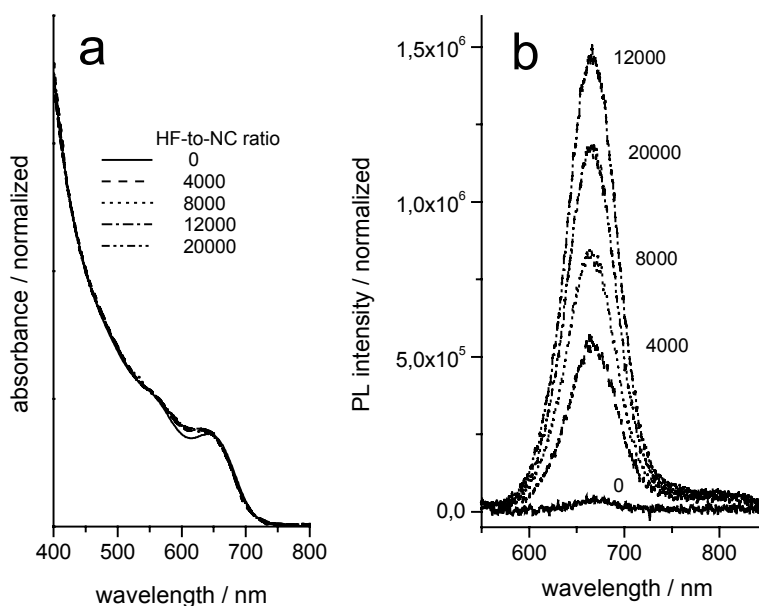


Figure 4.5. Anaerobic etching of InP nanocrystals with HF in darkness. Evolution of absorption (a) and PL (b) spectra upon the etching of InP nanocrystals with different amounts of HF. The numbers show approximate ratio of initial concentration of InP nanocrystals to HF molecules in the etching solution.

A much stronger increase of the band edge PL have been observed when the etching is performed under illumination of the solution with photons having an energy above the InP nanocrystals' band gap. Some experiments indicate that oxygen dissolved in the etching solution is also necessary for successful etching, however, to claim it unambiguously, more precise experiments under rigorously oxygen-free conditions are necessary. Illumination of the InP nanocrystals in the absence of HF does not result in any considerable improvement of the PL efficiency as shown in Figure 4.6a. The long term (days) contact of InP nanocrystals with HF in darkness does not considerably improve their PL efficiency even if the reaction mixture is heated to 40-50°C. In contrast, combining the HF treatment with the particle illumination results in strong band edge PL with room temperature quantum efficiencies as high as 20-35% (Figure 4.6a, see experimental details in Appendix 1). The photochemical nature of the HF-etching of InP nanocrystals is, probably, an explanation for the poor reproducibility of the conventional approach proposed by Micic et al. [4,13] - occasional illumination of the nanocrystals with daylight during etching resulted in strong PL of our samples. Figure 4.6 (Part b and c) show how the absorption and PL spectra depend on the initial ratio between InP nanocrystals and HF molecules in the case of particle etching under

illumination. Thus, effective treatment of $\sim 4.5\text{nm}$ particles requires about $3 \cdot 10^3 - 10^4$ HF molecules per one InP nanocrystal. The shape of the absorption spectrum also changes with this process as shown in Figure 4.6b. In fact, similar changes of the shape of the absorption spectra were detected in the PL excitation spectra of etched InP. This change is weaker if the particles are treated in the dark (Figure 4.5a) which may be a hint that some correlation between the shape of the absorption spectrum and PL efficiency exists.

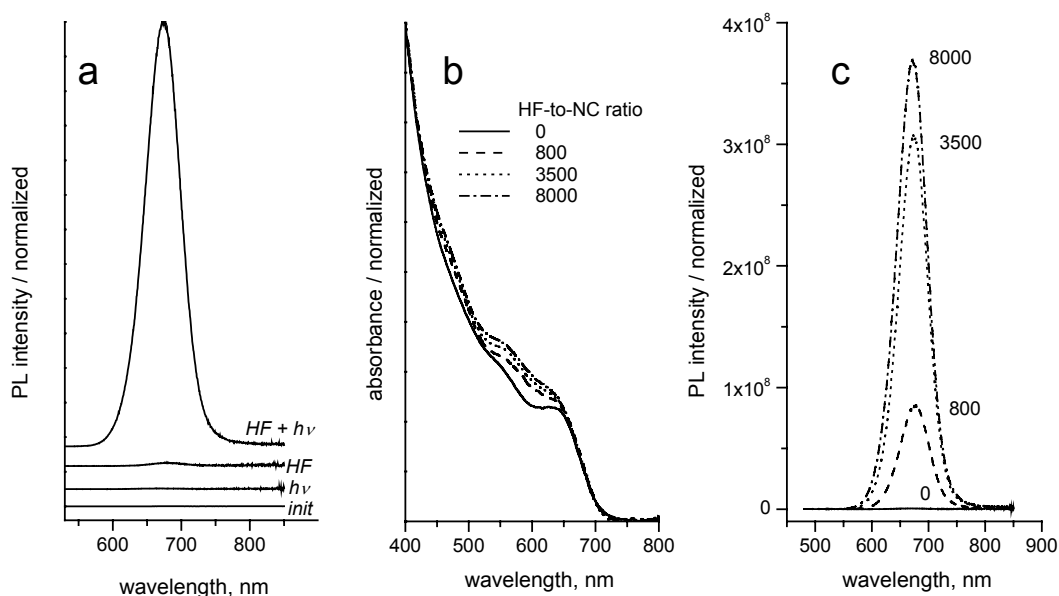


Figure 4.6. (a) Representative PL spectra measured for InP nanocrystals of the same size before (init) and after treatment with HF (HF, 40°C, 24h, ~ 3500 HF molecules per one InP particle), illumination in absence of HF ($h\nu$) and illumination in presence of HF (HF+ $h\nu$, ~ 3500 HF molecules per one InP particle). Evolution of absorption (b) and PL (c) spectra due to the photoetching of InP nanocrystals with different amounts of HF. Approximate numbers of HF molecules per one InP nanocrystal are shown. The etching solution was illuminated with the light of 450W xenon lamp passed through a cut-off filter (610 nm).

The luminescent InP nanocrystals can be isolated from the etching solution by precipitating them with acetonitrile and subsequent re-dissolution in a desired non-polar organic solvent. TEM and HRTEM images of the etched InP nanocrystals show that the nanocrystals retain after etching their monodispersity and crystallinity (Figure 4.7). EDX

measurements indicate an In to P ratio close to one and also indicate the presence of a small amount of fluorine (~ 10 atomic %) in the etched InP nanocrystals.

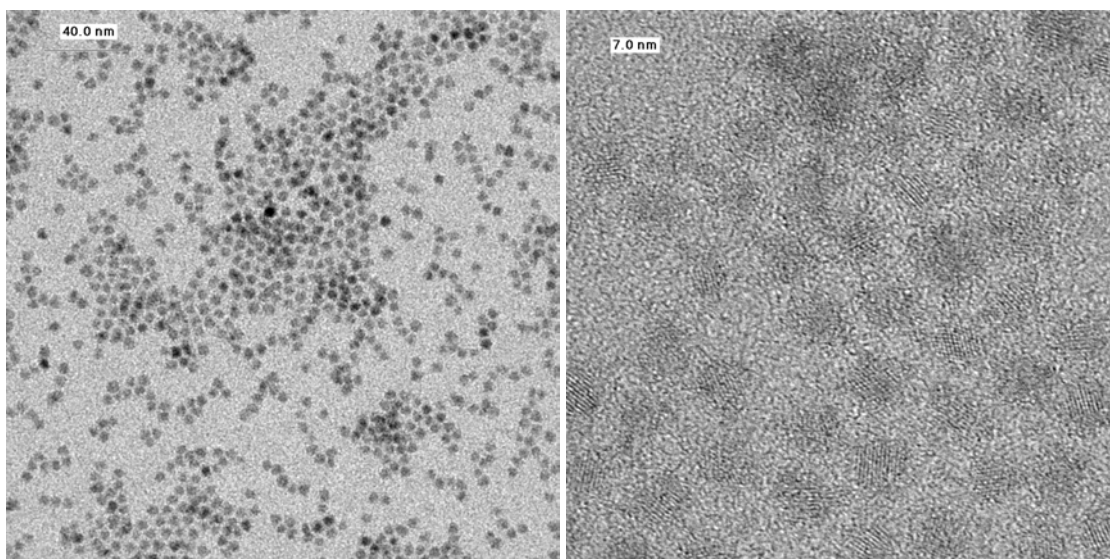


Figure 4.7. TEM overview (left) and HRTEM (right) images of the photoetched InP nanocrystals.

We have tested various fluorine compounds as etching agents for InP nanocrystals. Thus, we found that satisfactory PL efficiency can be achieved using HF, NH_4F , $\text{N}(\text{C}_4\text{H}_9)_4\text{F} \cdot 3\text{H}_2\text{O}$, pyridine poly(hydrogen fluoride) and HF-melamine complexes. Etching with $\text{KF} \cdot [18\text{-Crown-6}]$ and hexadecylamine hydrofluoride resulted in PL efficiencies of about 3-5% and n-hexylfluoride did not improve the PL efficiency of InP nanocrystals at all.

The size of the InP nanocrystals usually decreases during the etching process. The high PL efficiency is achieved after removal of ~ 1 InP monolayer from the nanocrystal surface [1,4,5,13]. The etching rate strongly decreases with increasing particle size, i.e. etching of smaller particles is much faster than etching of larger ones [1]. As a result, substantial broadening of the particle size distribution always accompanies the etching of InP nanocrystals with HF. The spectral width or “color purity” of the emission is proportional to the width of the particle size distribution. This means that high PL efficiency in combination with a narrow emission spectrum is difficult to achieve *via* HF-treatment of InP nanocrystals. This problem can be overcome if the so-called size-selective photoetching technique [24,25] is applied. This approach is based on the strong quantum confinement effect of our particles. Thus, smaller particles have their absorption onset shifted towards blue with respect to that of larger particles (see Figure 4.3.) and illumination of a nanocrystal ensemble through a filter

cutting off the short-wavelength light excites only the largest particles whereas the smallest ones do not absorb light (Figure 4.8a). As soon as the particle size decreases upon etching below a certain value, the absorption onset shifts towards wavelength blocked by the filter and the etching terminates. Application of this technique to InP allowed us to keep the particle size distribution narrow even at late stages of etching (Figure 4.8b). Moreover, careful titration of InP nanocrystals with HF etching solution in combination with size-selective particle photoexcitation allowed isolation of highly luminescent nearly monodisperse fractions of extremely small InP nanocrystals with a diameter below ~ 1.8 nm. These nanocrystals have the absorption maximum below 500 nm (Figure 4.8b) and emit in the green. To the best of our knowledge, preparation of so small luminescent InP nanocrystals has not been achieved *via* other approaches.

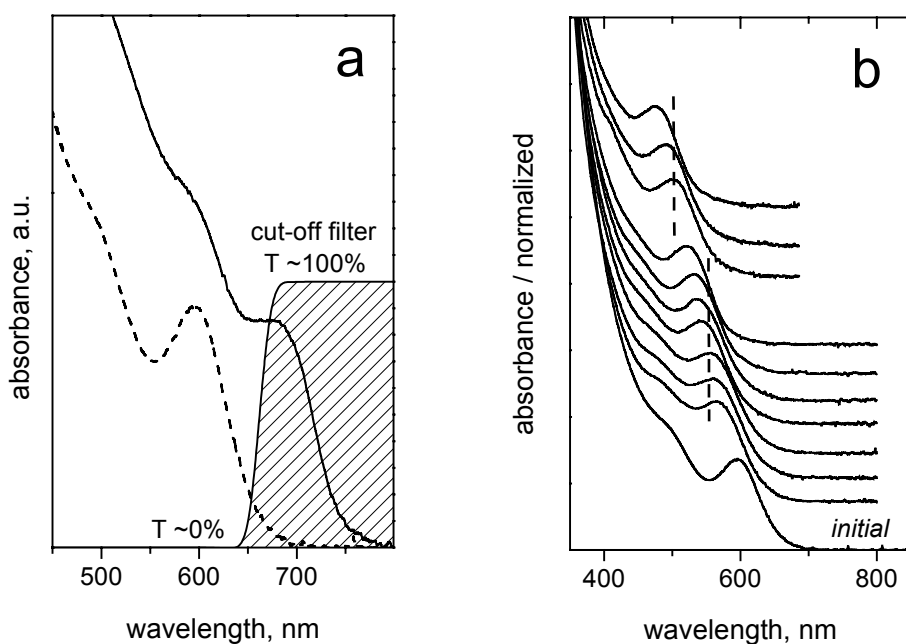


Figure 4.8. (a) Schematic representation of size-selective photoetching technique. The light passed through a cut-off filter selectively excites only the larger particles with absorption spectrum shown as a solid line whereas smaller particles (dash line) are not excited. (b) Evolution of absorption spectra during size-selective photoetching of InP nanocrystals. The vertical dashed lines show the filter cut-off wavelength.

The etching of InP nanocrystals in combination with size-selective particle photoexcitation permits us to tune the PL-band of highly luminescent colloidal particles from

green to the near-IR region (Figure 4.9). The room temperature PL quantum efficiency was typically about 20-30% for all particle sizes. Some samples exhibited PL efficiencies as high as about 40% showing that optimized experimental conditions (light intensity, concentration of etching agent, etc) allows the preparation of InP nanocrystals with superior luminescent properties.

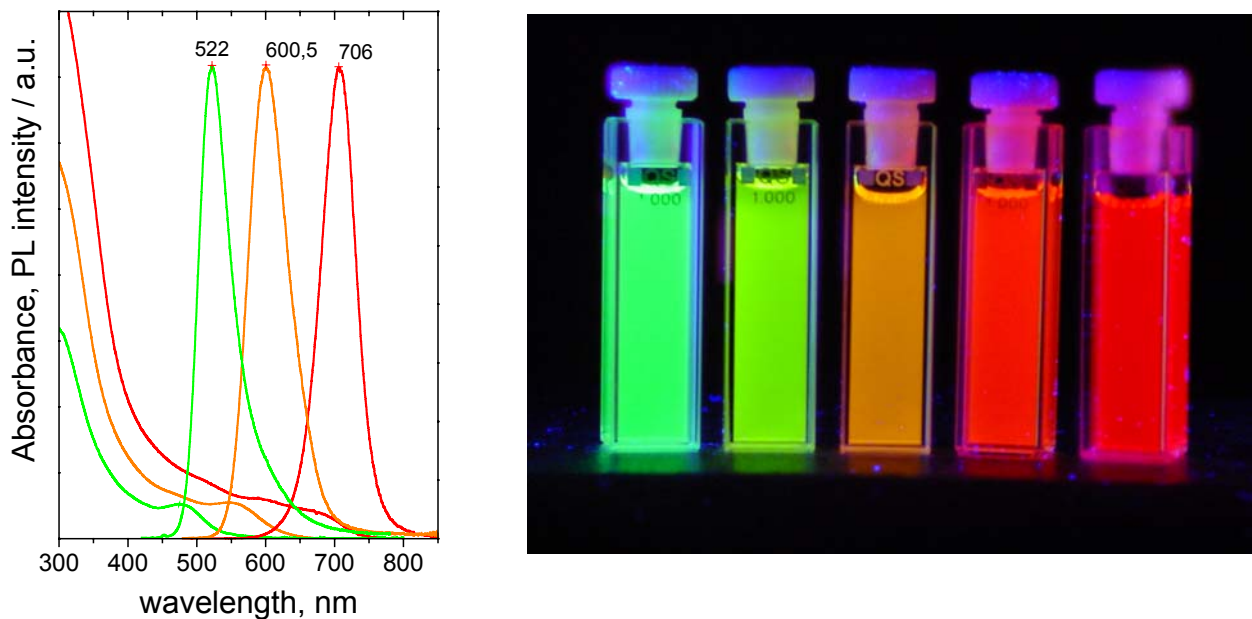


Figure 4.9. (left) Absorption and PL spectra of HF-etched InP nanocrystals. (right) Size-dependent change of the photoluminescence color of HF-etched InP nanocrystals. The smallest (~ 1.5 nm) particles emit green, the largest (~ 4 nm) – deep red.

4.3.3 Discussion of the etching mechanism

The photochemical nature of the etching process with HF molecules evidences that the carriers photogenerated within the InP nanocrystals play an important role. The behavior observed for InP nanocrystals is in accord with that reported for bulk InP, which does not dissolve in dilute HF solutions in dark, even under anodic bias [26-28]. On the other hand, photoelectrochemical etching of bulk InP in various acidic solutions (HF, HCl, H₂SO₄) has been a matter of thorough investigations [26-29]. Thus, it has been found, that in the first step

of dissolution, a hole is captured by an unbroken surface bond and a decomposition intermediate is formed [26,27]. Then, six elementary charges are required for the dissolution of one formula unit of InP. The rate of the process is determined (and limited) by the capture rate of the first hole. The overall photodissolution mechanism can be expressed as following [28]:



where $(x+y)=6$.

A similar mechanism may explain the strong enhancement of the band edge PL observed after photoetching of InP nanocrystals. In the first step, a photon is absorbed by an InP nanocrystal yielding an electron-hole pair (Figure 4.10). The poor PL quantum efficiency of as-prepared InP nanocrystals allows us to assume at least one efficient non-radiative recombination pathway *via* sub-bandgap states. Zunger et al. discussed the nature of these states in InP nanocrystals and have shown that both In and P surface dangling bonds provide surface states which lie within the band gap and are involved into the recombination process [30]. As was shown by Alivisatos et al., TOPO provides very effective passivation of In surface sites [3], whereas the passivation of P surface sites by TOPO or TOP seems to be doubtful. Therefore, it is reasonable to assume that the photogenerated hole is trapped by the phosphorus surface dangling bond (P-DB) activating it for a nucleophilic attack with a fluorine ion from the solution (Figure 4.10). The intermediate formed is unstable [26,27] and the process goes promptly until the phosphorus atom is converted to, e.g., PF_3 and is removed from the InP nanocrystal surface. The In sites thereby exposed to the surface are immediately passivated by TOPO present in the etching solution. The photogenerated electrons can react with some acceptors in the solution, e.g., dissolved oxygen.

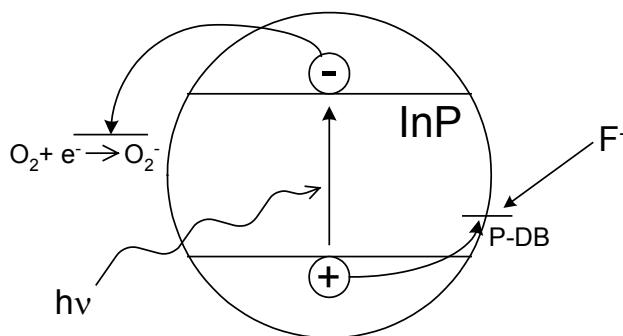


Figure 4.10. Schematic representation of mechanism of photochemical etching of InP nanocrystals.

In fact, a preferred dissolution of P-sites at the InP nanocrystal surface is also predictable from the relative stabilities of bulk InP faces against photoelectrochemical dissolution in HF solution. Thus, Kohl et al. found that the stability of InP faces decreases in the following direction: $(111) > (100) > (\bar{1}\bar{1}\bar{1})$ [29]. The (111) face having only In atoms on the surface is most stable whereas the $(\bar{1}\bar{1}\bar{1})$ face consisting of P atoms is the most unstable against HF treatment. The presence of capping agents like TOPO providing selective passivation of In sites will even increase the difference in stability of the (111) and $(\bar{1}\bar{1}\bar{1})$ faces.

The removal of P-sited from the nanocrystal surface will result in an In-rich nanocrystal surface which can be effectively passivated by TOPO present in the etching solution. Elimination of the surface traps associated with the P-dangling bonds results in strong enhancement of the band edge PL.

The model proposed above for HF-etched InP nanocrystals is in good agreement with the results obtained from X-Ray Photoelectron Spectroscopy (XPS) with synchrotron radiation. An advantage of using synchrotron radiation is that the excitation energy $h\nu$ can be varied over a large range. This provides the opportunity to vary the surface sensitivity of the experiment once photoelectrons from deeper layers escape easier with increasing excitation energy. The XPS experiments were performed at the undulator Beamline BW3 ($h\nu = 20\text{--}1800$ eV) at HASYLAB/DESY. The photoelectron spectra were taken at normal emission for the **In 3d** and **P 2p** core levels. The radiation incident angle is 45° . The photoelectrons from the **In 3d** and **P 2p** core levels are detected at kinetic energies that depend on the energy of the synchrotron radiation. A high kinetic energy allows the photoelectrons to escape from deeper portions of the sampler (*mean free path length*). Figure 4.11 shows XPS spectra of the **In 3d** core level for different excitation energies $h\nu$ measured both for as-prepared and HF-treated InP nanocrystals. In the case of as-prepared InP nanocrystals, fitting of the spectra with Voigt doublet function yields a bulk (b) and a surface component (s1) for the **In 3d** core level peaks. The surface component is assigned to surface atoms bonded to TOPO molecules. Its position (chemical shift) in the spectrum is similar to that of the **In** core level shifts in InP(110) native oxide [31,32]. After etching of the InP nanocrystals with HF, a new surface component (s2) appears in the **In 3d** lines. Its chemical shift value indicates the presence of F atoms on the nanocrystals' surface due to the HF treatment.

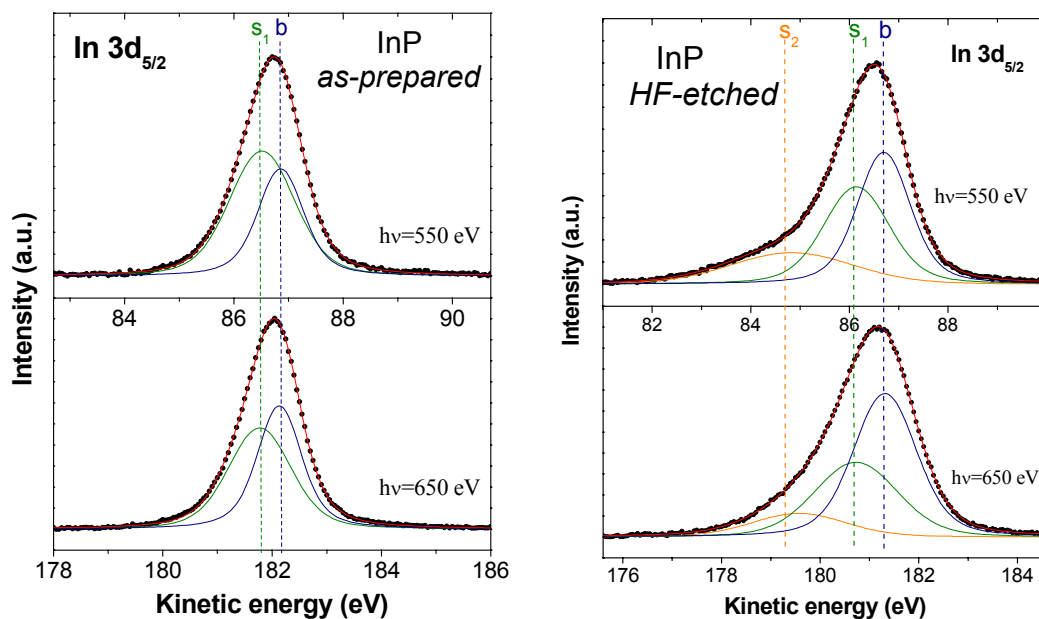


Figure 4.11. XPS spectra of **In 3d** core level for different excitation energies $h\nu$ obtained for as-prepared (left) and HF-treated (right) InP nanocrystals. The s_1 line is shifted by $\Delta E_{bind} = 0.4$ eV relative to the volume component b and s_2 line shift is $\Delta E_{bind} = 1.8$ eV.

More dramatic changes are induced by the HF treatment in the photoelectron spectra of the **P 2p** core level (Figure 4.12). In the case of as-prepared InP nanocrystals, the fitting procedure reveals one bulk (b) and two surface (s_1 and s_2) components. Surface component (s_1) probably represents the contribution of **P** surface atoms, whereas the (s_2) component reflects the signal of **P** atoms from the TOPO ligands. After etching of the nanocrystal surface with HF, a third (s_3) surface component is resolved. The value of chemical shift provides clear evidence of a new F bond contribution. In addition, the ratio between the intensities of the (s_1) and (s_2) surface components of a given sample decreases after the HF-treatment by a factor of 7. This is in accord with the removal of **P** surface atoms (s_1) and an increased amount of TOPO on the nanocrystal surface (s_2) (Figure 4.12). This behavior probably evidences the transition from a P-rich surface of as-prepared InP nanocrystals to an In-rich one during the treatment of the nanocrystal surface with HF.

Consequently, the non-radiative recombination pathway in as-prepared InP nanocrystals involves capture of a photogenerated hole by a surface trap connected to a P surface dangling bond.

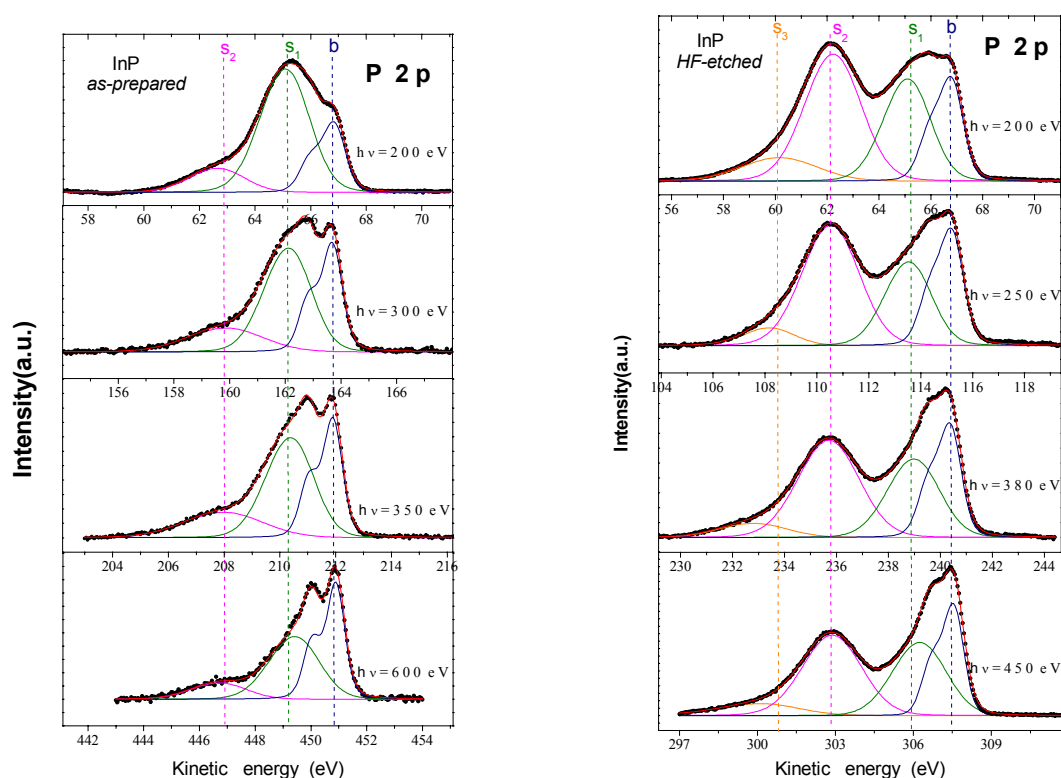
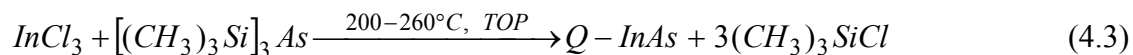


Figure 4.12. XPS spectra of **P 2p** core level for different excitation energies $h\nu$ obtained for *as-prepared* (left) and *HF-treated* (right) InP nanocrystals. The component *s1* is shifted by $\Delta E_{bind} = 1.1$ eV relative to the bulk component *b* and *s2* line shift is $\Delta E_{bind} = 4.4$ eV. The *s3* component is shifted $\Delta E_{bind} = 6.1$ eV with respect of the bulk contribution *b*.

4.4. Organometallic synthesis of IR-emitting InAs and InAs/CdSe core-shell nanocrystals

InAs nanocrystals were synthesized *via* the dehalosilylation reaction similar to InP nanocrystals [see experimental details in Appendix 1]:



Tris-(trimethylsilyl)arsine was used as the As precursor and was synthesized according to the literature method [16,33]. TOP has been chosen as the reaction medium since it was reported to be an appropriate stabilizing agent for InAs nanocrystals [9,16] providing good control of the particle growth and their size distribution. Application of the hot injection technique allowed successful separation of particle nucleation and growth yielding particle size distributions of $\sim 15\%$ during the nanocrystal growth. Crystallization of InAs nanocrystals proceeded much faster as compared to InP, therefore, no long term annealing was required to

obtain highly crystalline particles. To isolate nearly monodisperse fractions, size-selective precipitation was applied using toluene and methanol as solvent and non-solvent, respectively.

Figure 4.13a shows the evolution of the absorption spectrum of InAs nanocrystals upon increasing the particle size from ~ 1.8 to 4.5 nm. The band gap of bulk InAs is 0.46 eV at room temperature [34] corresponding to the absorption onset at $2.7\mu\text{m}$, therefore the excitonic transitions of InAs nanocrystals are observable in the near-IR spectral region. The absorption spectra possess several features indicating a high degree of particle monodispersity and crystallinity. A typical XRD pattern of colloiddally grown InAs nanocrystals shows that the positions of diffraction peaks at wide angles match those of the bulk phase of cubic InAs (Figure 4.13b). As expected, the width of the diffraction peaks is considerably broadened due to a small X-ray coherence length limited by the particle size. The HRTEM image shown in Figure 4.13c demonstrates well separated crystalline InAs particles with clearly resolved lattice fringes and shows a moderately broad size distribution. EDX measurements indicate compositions close to that given by the bulk formula.

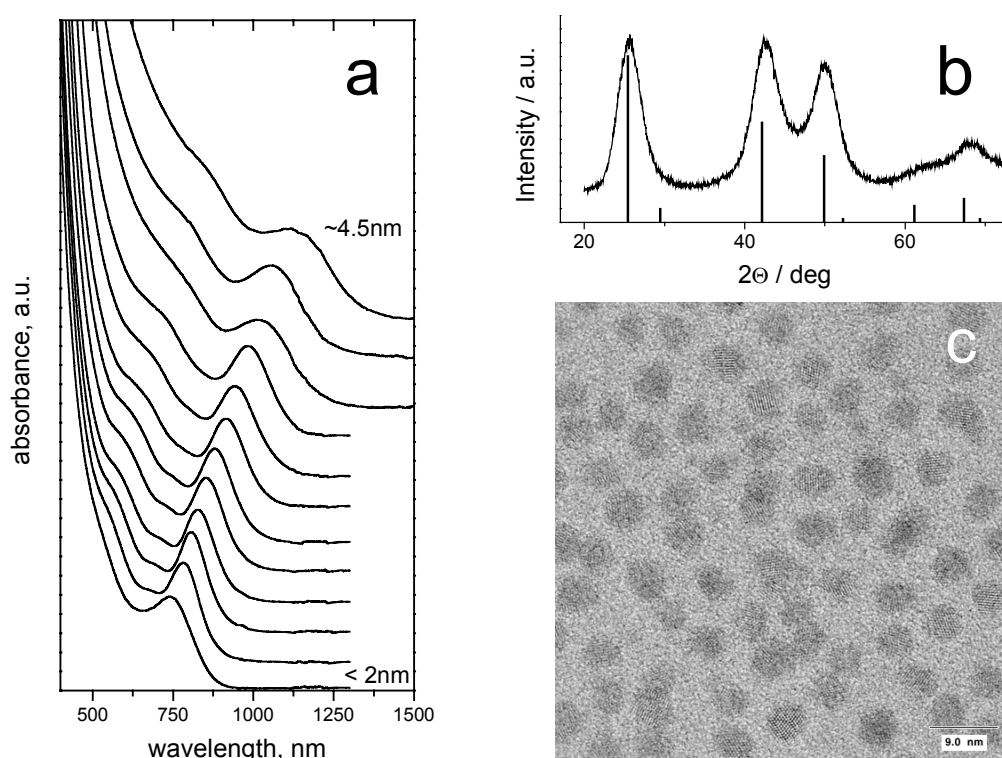


Figure 4.13. (a) Size-dependent evolution of absorption spectrum of InAs nanocrystals. (b) A typical powder X-ray diffractogram of InAs nanocrystals. The line spectrum gives the bulk InAs (zinc blende, cubic) reflections. (c) HRTEM image of a size selected fraction of InAs nanocrystals synthesized according to Scheme 4.3.

As-prepared InAs nanocrystals exhibit a band edge PL with a room temperature PL quantum efficiency of about 1% (see Chapter 7, Figures 7.1 and 7.3) The PL efficiency can be improved by more than one order of magnitude by growth of an epitaxial shell of either a II-VI (CdSe, ZnSe, ZnS) or wide-bandgap III-V (InP, GaAs) semiconductor on the surface of the InAs nanocrystals [14,15]. The resulting core-shell nanocrystals emit in the near-IR and exhibit a room temperature quantum efficiency of about 20% [15]. In order to investigate the origin of this strong improvement of the PL efficiency, InAs/CdSe core-shell nanocrystals were synthesized and investigated using photoelectron core level spectroscopy with synchrotron radiation.

InAs/CdSe nanocrystals with different sizes of the InAs core and the CdSe shell thickness were synthesized as described in Ref. [15], see experimental details in Appendix 1. Figure 4.14a shows the absorption and the PL spectra of InAs nanocrystals before and after growth of a CdSe shell with a thickness of ~ 2.1 monolayers. Here the photoluminescence has increased by about an order of magnitude. The exact measurement of the PL improvement is difficult in this case due to absorption of a significant portion of emitted light by the solvent (toluene). The features at ~ 0.90 and ~ 1.10 eV present on the emission spectra in Figure 4.14a are due to absorption bands of the solvent as it evidenced from the toluene transmission spectrum shown (on the same photon energy scale) for comparison. The shift towards longer wavelengths observed in the absorption and the PL spectrum indicates that some delocalization of the wavefunctions of the InAs core takes place into the CdSe shell. The growth of the CdSe shell also results in a considerable improvement of the nanocrystal stability against oxidation and photodegradation under daylight conditions. Figure 4.14b shows the evolution of XRD patterns upon growth of CdSe shell. Since the lattice mismatch between bulk InAs and CdSe is only about 0.001%, no shift of the reflexes was detected during the shell growth whereas the width of the reflexes decreased with increasing shell thickness. The latter indicates an epitaxial shell growth mechanism.

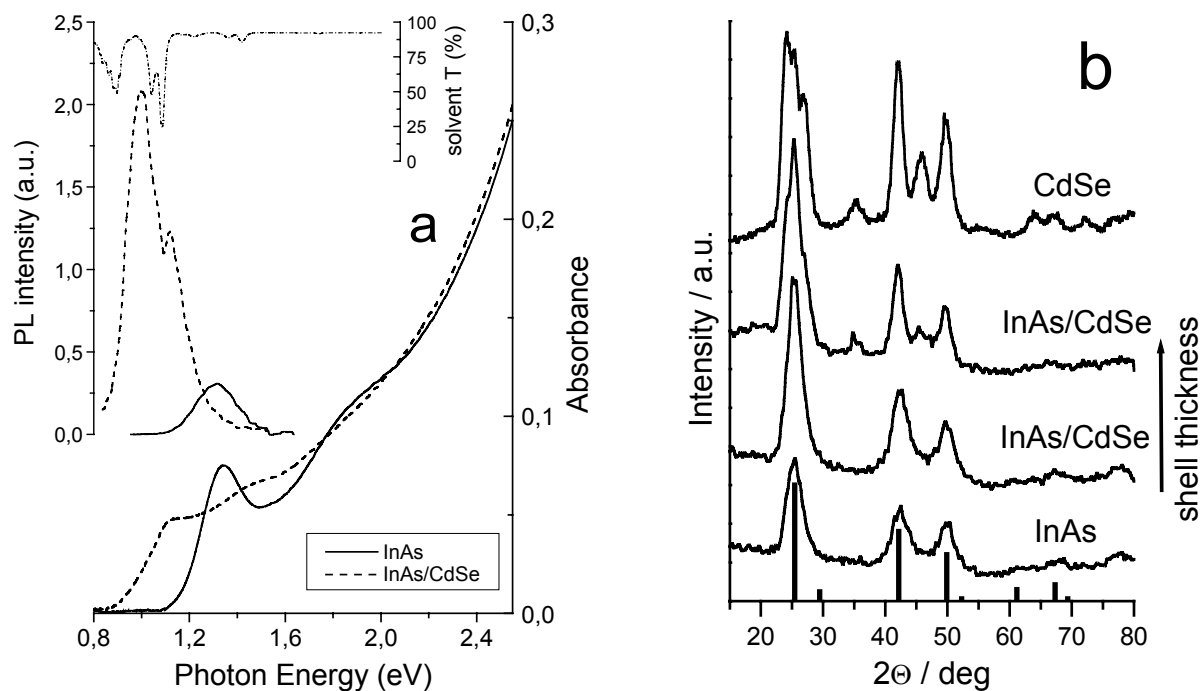


Figure 4.14. (a) Absorption and PL spectra of InAs (~ 2.9 nm in diameter) and InAs/CdSe core-shell nanocrystals with the CdSe shell thickness of ~ 9.3 nm. Transmission spectrum of solvent (toluene) is also shown. (b) Powder-XRD patterns of InAs, CdSe and InAs/CdSe nanocrystals. The thickness of CdSe shells is of ~ 1.5 and ~ 3.2 monolayers. The line spectrum gives the bulk InAs (zinc blende, cubic) reflections.

The technique of core-level photoemission spectroscopy with synchrotron radiation was also applied to study the internal interface in the InAs/CdSe core/shell nanocrystal system. It was found that As-Se and In-Se chemical bonds dominate the interface which we may describe as 'Se-rich'. Previously discovered In and As surface states of the pure InAs nanocrystals [35] are successfully removed by growth of the CdSe shell layer. This allows us to propose the physical origin for the improved photoluminescence yield of InAs/CdSe core shell nanocrystals as compared to that of the pure InAs system. In the latter, surface traps provide dark recombination channels for the Wannier excitons. These traps are removed by forming chemical bonds between both In and As surface atoms with the epitaxial shell layer. Surface states in the InAs nanocrystals are likely to be present on both anion and cation sites which implies that dark channel exciton recombination relies on charge traps for both electrons and holes. Highly IR-photoluminescent InAs/CdSe nanocrystals have useful applications in biological labelling experiments and are also essential for nanoscale optoelectronic devices. Our results should be useful toward a full description of how the

luminescence yield is optimised as well as for describing the relationship between electronic and crystal structure at a nanocrystal surface.

4.5. References

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Chapter 5

Crystallization of Monodisperse Nanocrystals in Ordered Two- and Three-Dimensional Superlattices

In this Chapter a new approach to crystallization of CdSe nanoparticles in ordered three-dimensional superlattices *via* controlled oversaturation is proposed. In regular 3D quantum dot arrays formed by this way, individual CdSe nanocrystals play the role of building blocks – artificial atoms in the next level of hierarchy. Two different types of crystals - irregular and perfectly faceted hexagonal can be prepared, depending on the nucleation rate.

5.1. Introduction

A new field of research has recently been emerged on the use of individual nanocrystals as building blocks for 2D or 3D superstructures and on the investigation of collective properties of these artificial quantum dot solids [1,2]. Crystallization followed by unambiguous determination of the exact position of each atom in the superstructure by single-crystal X-ray analysis is the most suitable way of their characterization. In fact, there are several successful attempts to build up colloidal crystals from molecular-like semiconductor clusters of exact composition, e.g. $[\text{Cd}_{17}\text{S}_4(\text{SC}_6\text{H}_5)_{28}]^{2-}$ [3], $[\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}]\cdot(\text{DMF})_4$ [4], $[\text{Cd}_{17}\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_{26}]$ [5], $[\text{Cd}_{32}\text{S}_{14}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_3)_{26}]\cdot(\text{H}_2\text{O})_4$ [6], $[\text{Cd}_{32}\text{Se}_{14}(\text{SeC}_6\text{H}_5)_{36}]\cdot(\text{P}(\text{C}_6\text{H}_5)_3)_4$ and $[\text{Hg}_{32}\text{Se}_{14}(\text{SeC}_6\text{H}_5)_{36}]\cdot(\text{P}(\text{C}_6\text{H}_5)_3)_4$ [7],

$[\text{Mo}_{154}(\text{NO})_{14}\text{O}_{420}(\text{OH})_{28}(\text{H}_2\text{O})_{70}]^{(25\pm 5)-}$ [8] and a family of Cu-Se clusters [9]. The strategy to fabricate superstructures from larger colloidal particles with a narrow, although a finite size distribution is a gentle destabilization of the colloidal dispersion; dispersive attractions of nanoparticles drive their self-organization and superlattice formation [1,2]. 3D colloidal crystals made from submicrometer size monodisperse silica[10,11] or latex[12,13] spheres as well as from silver nanoparticles[14,15] have been reported. The first and to the best of our knowledge the only example of a 3D semiconductor nanocrystal superlattice are stacked crystals 5 to 50 μm in size produced from CdSe quantum dots [2,16]. The crystallization was induced by pressure-and-temperature-controlled evaporation of the two-solvent mixture containing CdSe nanocrystals. The alignment of CdSe quantum dots in a face centered cubic (fcc) superlattice was very clearly shown by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction in the small- and wide-angle ranges.

In this Chapter we report on CdSe colloidal crystals whose growth was induced by slow diffusion of a non-solvent into a concentrated solution of CdSe nanocrystals, either directly or through a buffer layer with low, but not negligible solubility for nanocrystals. Both irregular-shaped colloidal crystals with sizes up to 200 μm and perfectly faceted hexagonal colloidal crystals with sizes of about 100 μm have been grown from monodisperse CdSe nanocrystals depending on the growth and nucleation rates.

5.2. Formation of 2D and 3D superlattices from monodisperse CdSe nanocrystals

CdSe nanocrystals have been synthesized either in a trioctylphosphine oxyde-trioctylphosphine (TOPO-TOP) or in a hexadecylamine (HDA)-TOPO-TOP mixture as described in Chapter 2. Fractions of nanocrystals with narrow ($\sim 4\%$) size distributions were carefully separated by the size-selective precipitation technique[17,18] and re-dissolved in toluene (see also experimental details in Appendix 1). Room temperature absorption and photoluminescence spectra of the size-selected nanocrystals used for crystallization are shown in Figure 5.1a. The absorption spectrum of a dilute colloidal solution of 3.5 nm diameter CdSe nanocrystals in toluene possesses sharp and well resolved electronic transitions indicating a narrow size distribution of nanoparticles being in the size quantization regime. The emission band of these CdSe nanocrystals in toluene solution (quantum efficiency $\sim 5\%$ at room temperature) is narrow and lies close to the absorption onset. Figure 5.1b shows the X-ray diffraction pattern of the CdSe nanocrystals indicating the hexagonal (wurtzite) phase.

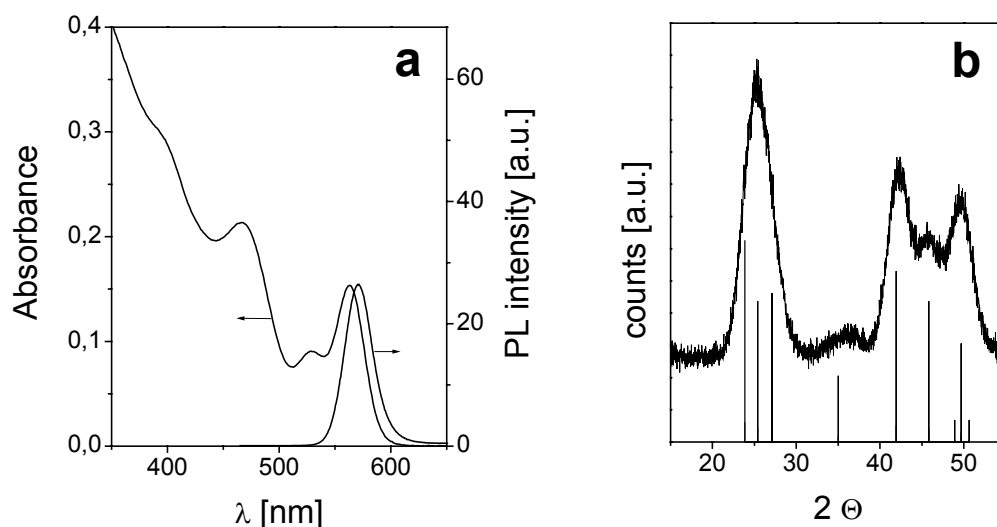


Figure 5.1. (a) Absorption and photoluminescence spectra of the dilute colloidal solution of 3.5 nm CdSe nanocrystals in toluene. (b) Powder X-ray diffraction pattern of 3.5 nm CdSe nanocrystals.

The crystallization of CdSe quantum dots has been carried out in vertically positioned glass tubes. The colloidal solution was slowly destabilized by diffusion of methanol into the system, a “non-solvent” commonly used for the precipitation of TOPO-capped CdSe nanocrystals [17,18]. The slow dilution with methanol resulted in nucleation of nanocrystals on the walls of the tubes and in the bulk of the solution. The spatial distribution of local oversaturations caused by the non-solvent diffusion determines, most probably, the quality of the colloidal crystals. To make the oversaturation front not as sharp as in the case of a direct solvent-non-solvent contact, we used a buffer layer of propanol-2 between the solution of CdSe nanocrystals and the methanol layer. The nucleation of nanocrystals was slower in this case. Figure 5.2a schematically outlines the two approaches. Crystalline nuclei visible with the naked eye started to form after about one to two weeks in both cases, and grew slowly to colloidal crystals during two months. Red-colored crystals formed in the absence of a buffer layer were 80-220 μm in size and can be described as irregularly shaped, although triangular or hexagonal shapes were observed more often than others (Figure 5.2b). In the presence of a buffer layer, single crystals grew in the form of perfectly faceted hexagonal platelets (Figure 5.2c). The orange-red colored platelets were very similar in size, about 100 μm in lateral dimension and 20 μm in depth. Each single colloidal crystal of such kind consists of more

than 10^{12} individual CdSe nanocrystals. The orange-red color of the colloidal crystals arises from the optical absorption of the 3.5 nm CdSe building blocks. The different color depth may be caused both by the different thickness of the nanocrystal superstructures. Moreover, the irregularly-shaped crystals shown in Figure 5.2b might be polymorphous so that the scattering of light at grain boundaries occurs. Interestingly enough, only the irregularly-shaped colloidal crystals were readily re-soluble in toluene, giving absorption and luminescence spectra corresponding to the isolated 3.5 nm CdSe nanocrystals. Perfectly faceted hexagonal platelets were much less soluble in toluene, hexane, and mixtures of these solvents and TOP. Presumably, the formation of these crystals was accompanied with some irreversible changes of the nanocrystal ligand shells.

There was enough material only in the case of irregular-shaped crystals to measure XRD spectra from the powdered crystals. Diffraction peaks at wide angles probing the internal structure of the quantum dots were as expected for wurtzite phase CdSe nanocrystals, indicating an isotropic distribution of colloidal crystallites in the powder. Reflexes in the small-angle region could not be assigned to a simple fcc, bcc, or hcp structure, indicating a polymorphous sample, which is probably also reflected by the irregular shape of the crystals.

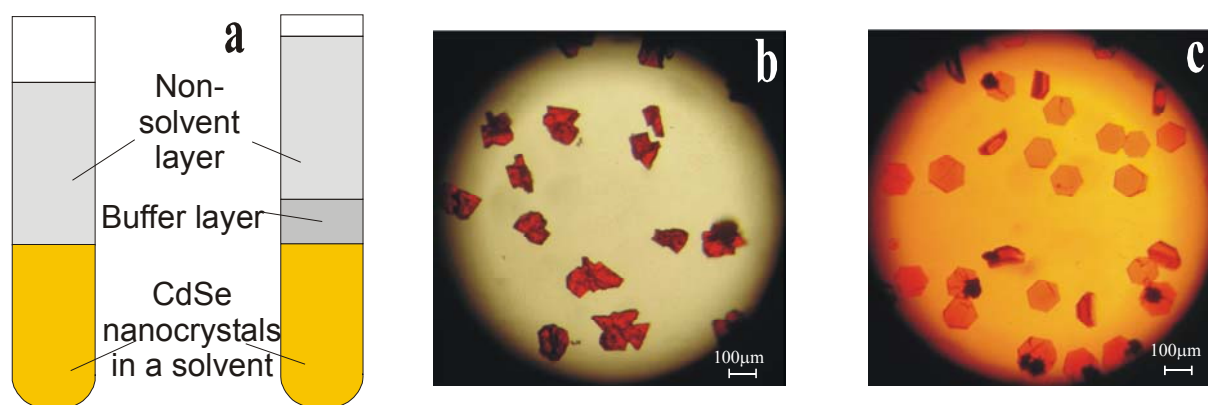


Figure 5.2. (a) Schematic outline illustrating the concept of the nucleation procedure. Left tube: the non-solvent (methanol) diffuses directly into colloidal solution of CdSe nanocrystals in toluene. Right tube: buffer layer of propanol-2 slows down diffusion of methanol.

(b,c) Optical micrographs of colloidal crystals of CdSe nanocrystals made by a digital camera through an objective of an optical microscope. (b) faster nucleation, irregular-shaped crystals; (c) slower nucleation, perfectly faceted hexagonal platelets.

The strong tendency of the nanocrystals to form highly ordered 2D and 3D arrays was obvious from transmission electron micrographs (Figures 5.3 and 5.4). For the TEM measurements, a droplet of colloid was applied to a TEM grid, the excess of solvent was removed with a filter paper and the grids were subsequently dried in a desiccator. Figure 5.3a presents a 2D arrangement of small (3.5 nm) CdSe nanocrystals [11]. These nearly spherical small nanocrystals are randomly oriented on the TEM grid, as it is seen from the lattice planes and from the isotropic ring in the correspondent FFT (inset in Figure 5.3a). Figure 5.3b shows a HRTEM image of an ordered 2D array of TOPO-capped faceted CdSe nanocrystals with a particle size of ~ 7 nm. The particles are slightly elongated along the c-axis of the wurtzite structure and are aligned on the TEM grid with the c-axes perpendicular to the substrate [19]. Remarkably, there is a certain preferred orientation of the lattice plane directions of these relative large CdSe nanocrystals, which is further confirmed by six distinct reflexes in the correspondent FFT pattern being characteristic for the (100) zone (inset in Figure 5.3b).

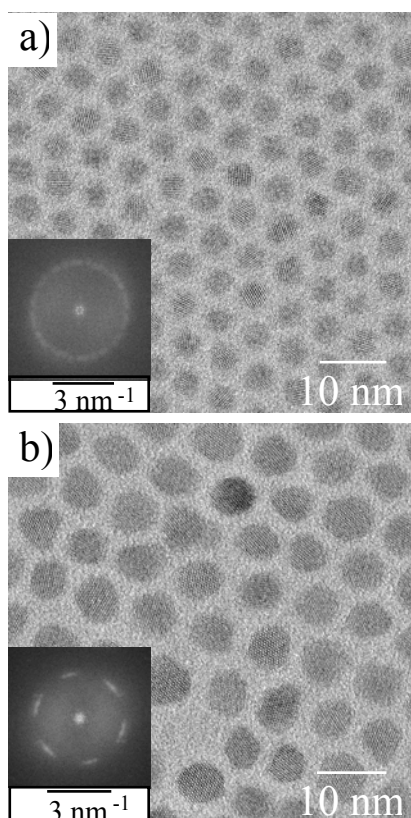


Figure 5.3. *High-resolution transmission electron microscope images of 2D arrangements of CdSe nanocrystals. (a) Fragment of an array of the 3.5 nm particles together with a correspondent FFT; (b) fragment of an array of the 7 nm particles together with a correspondent FFT.*

Figure 5.4a presents a TEM image of a 3D arrangement of the 3.5 nm TOPO-capped CdSe nanocrystals at low magnification. A close packing of up to seven layers of nanocrystals into 3D superlattice is observed. Further investigation of this superlattice showed two different arrangements of the CdSe nanoparticles, given in Figures 5.4b and 5.4c. The FFT patterns of these arrangements (given as insets) are consistent with those expected for the (100) and (110) projection of a fcc superlattice, respectively. Thus, TEM investigations on differently oriented packings of nanocrystals led to the assumption that the 3D alignment of particles is fcc-like. It has to be clarified whether this arrangement resembles the packing of CdSe nanoparticles in the colloidal crystals, too, or reflects the method of sample preparation on the TEM grid.

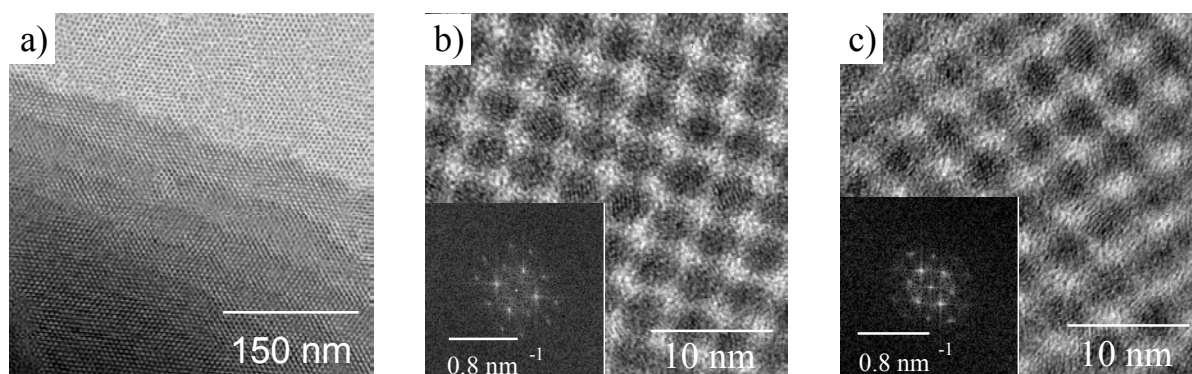


Figure 5.4. Transmission electron microscopy images of a 3D arrangement of the 3.5 nm CdSe nanocrystals. (a) overview picture of a fcc-like superlattice (b) (100) projection along the superlattice with a correspondent FFT; (c) (110) projection along the superlattice with a correspondent FFT.

In summary, two types of colloidal crystals of CdSe nanocrystals were prepared by the method of controlled oversaturation in solutions. The growth technique was based on slow diffusion of a non-solvent (methanol) into the bulk of a concentrated solution of monodisperse CdSe nanocrystals in toluene, either directly or through a buffer layer of a third component (propanol-2). Both irregular-shaped crystals and, for the first time, perfectly faceted hexagonal platelets with sizes of about 100 μm have been obtained depending on the conditions of crystal growth. In quantum dot solids formed by this way, individual CdSe nanocrystals playing the role of building blocks (artificial atoms in the next level of hierarchy) are aligned in a regular fcc-like 3D superlattice as confirmed by TEM.

5.3. References

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Chapter 6

Evolution of an ensemble of nanoparticles in a colloidal solution: theoretical study

In this Chapter the evolution of a nanosized particle in colloidal solution is studied theoretically. The model developed is based on the size dependence of the activation energies of the growth and dissolution processes and takes into account the mass transport. Using this model, Monte-Carlo simulations of the evolution of an ensemble of growing nanoparticles during Ostwald ripening have been performed, and conditions leading to either “focusing” or “defocusing” of the particle size distribution were found. The stationary particle size distribution inherent to the Ostwald ripening process in ensembles of nanoparticles less than 5 nm in radius is narrower and more symmetric than that predicted by the Lifshitz-Slyozov-Wagner theory for ensembles of larger (> 20 nm in radius) colloidal particles. The growth of nanoparticles in the diffusion-controlled regime results in better final size distributions as compared with those grown in the reaction-controlled regime. The dependence of the particle size distribution on a number of external and internal ensemble characteristics is studied and possible ways of controlling the particle size distribution are discussed.

6.1. Introduction

A lot of work was devoted to the preparation of high quality II-VI and III-V semiconductor quantum dots and investigation of their optical properties [see Chapters 2-4 and references therein]. On the other hand, there is a lack of theoretical understanding of the

processes occurring during the growth of nanoparticles (NPs) in colloidal solutions. Only a few reports deal with this important problem [1,2]. Peng et al. described the conditions when narrowing (“focusing”) and broadening (“defocusing”) of the particle size distribution occurs during the growth of several II-VI and III-V NPs [1]. The results were explained in the framework of a model developed by Sugimoto, describing the growth of a single colloidal particle at constant external surrounding and valid for micrometer-scale systems rather than nanometer-scale ones [3]. However, in the reaction vessel containing an ensemble of growing NPs at any instant of time a large number of colloidal particles compete for a finite amount of monomer, and the number of particles changes gradually due to the particle nucleation and dissolution processes. Here and below, we use the term “ensemble” to describe the whole population of particles presented in the colloidal solution at different instants of time. The term “monomer” refers to any molecular precursor(s) participating in the reversible act of adding/removing a molecular unit (e.g. Cd or Se atoms) to a NP (e.g. CdSe) in the reaction vessel.

An important point of the dynamics of the ensemble evolution is the intrinsic polydispersity of colloidal particles, which can result in Ostwald ripening. Ostwald ripening is the growth mechanism where smaller particles dissolve and the monomer thereby released is consumed by the large ones [4]. Lifshitz, Slyozov [5] and Wagner [6] have developed an elegant asymptotic solution for the evolution of an ensemble of particles during Ostwald ripening (LSW theory). The appearance of the LSW approach has stimulated several attempts to describe the Ostwald ripening analytically [7-10] and to verify the LSW and more recent theories experimentally [11-14]. Whereas in the stationary regime the competition of growing colloidal particles for monomers can be treated analytically by the LSW theory, no general solution exists for the earlier transient stages of the particle growth [8,15]. Extensive numerical simulations of Ostwald ripening were performed therefore to treat self-consistent models of the particle ensemble evolution [8,9,15-17].

In the present Chapter we present a model allowing to calculate the size evolution of a NP under reaction, diffusion, and mixed reaction-diffusion control (Section 6.2). We have performed a Monte Carlo simulation of Ostwald ripening of an ensemble of growing NPs (Sections 6.3. and 6.4). The conditions leading to “focusing” and “defocusing” of the particle size distribution under mixed diffusion-reaction control are investigated in Section 6.5. The dynamic distribution of single particle growth rates within an ensemble of nanoparticles will be discussed in Section 6.6.

6.2. Evolution of a single NP in a colloidal solution

The theory of Lifshitz, Slyozov and Wagner (LSW) provides an asymptotic solution for the evolution of an ensemble of particles during Ostwald ripening. However, this approach as well as further analytical models and numerical simulations of Ostwald ripening [8,9,11-17] fail in the description of ensembles of nanometer-sized particles as only two terms of the expansion of the Gibbs-Thompson equation were used:

$$C(r) = C_{flat}^0 \exp\left[\frac{2\gamma V_m}{rRT}\right] \approx C_{flat}^0 \left(1 + \frac{2\gamma V_m}{rRT}\right) \quad (6.1)$$

where $C(r)$ and C_{flat}^0 are the solubilities of a particle with radius r and of the bulk material, respectively; γ is the surface tension and V_m is the molar volume of the solid.

The coefficient $2\gamma V_m/(RT)$ called “capillary length” is usually of the order of 1 nm [11,14], and Eq. (6.1) satisfactorily describes the solubility of colloidal particles with radius larger than ~20 nm. For nanocrystals with $r=1-5$ nm the value of the capillary length is approaching the particle radius, and the particle solubility becomes strongly nonlinear against r^{-1} . On the other hand, the Gibbs-Thompson equation in its exact form is, probably, valid for very small particles: it was reported that the surface tension remains nearly constant for many interfaces even if the particle size is as small as ~1 nm [18].

Moreover, the chemical potential of nanoparticles and, as a result, the rate of the interface reactions also depend non-linearly on r^{-1} as will be described below. Both effects were not taken into account in the classical description of the reaction-controlled Ostwald ripening. Probably, the description of the ensemble taking into account the above mentioned effects cannot be done analytically in the framework of the existing mathematical approaches.

We start with a model describing the behavior of a single NP of radius r placed in an infinite volume of solution with a constant concentration of monomer, thereafter referred to as the bulk concentration $[M]$. The monomer can react with the surface, thereby adding a new unit to the particle (NP grows) or can leave the surface, thereby removing one unit (NP dissolves). Both processes occur along the reaction path including the activated complex with the chemical potential $^\ddagger\mu$ (Figure 6.1).

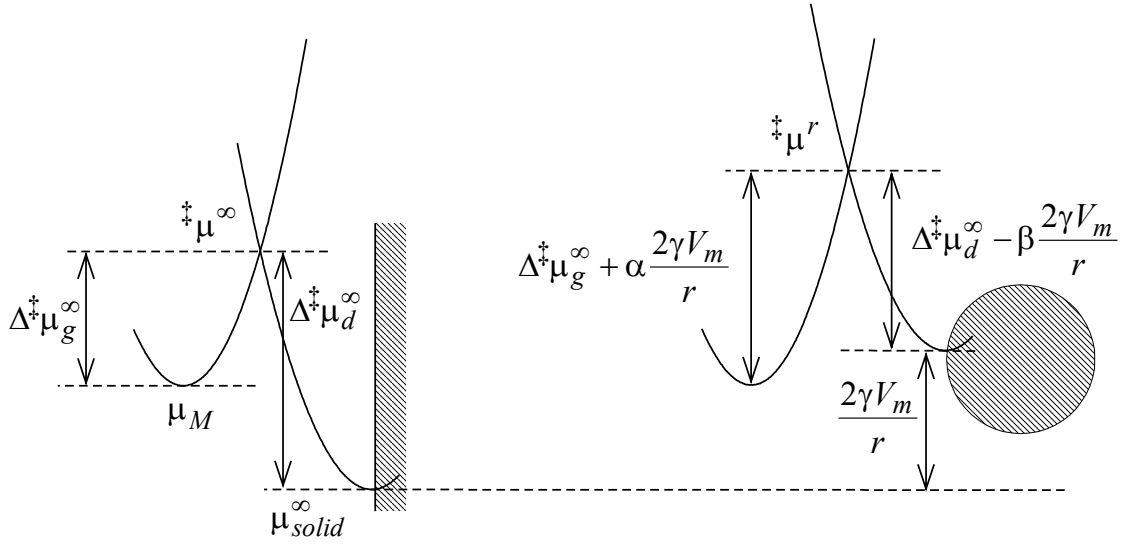


Figure 6.1. Schematic description of the size dependence of the activation energies for growth and dissolution processes.

The resulting activation energies for growth and dissolution of the NP are $\Delta^\ddagger\mu_g$ and $\Delta^\ddagger\mu_d$, respectively. The chemical potential of the solid depends on the curvature of the surface by means of the Kelvin equation [19], and the activation energy $\Delta^\ddagger\mu$ is a function of the particle radius:

$$\Delta^\ddagger\mu_g(r) = \Delta^\ddagger\mu_g^\infty + \alpha \frac{2\gamma V_m}{r} \quad (6.2)$$

$$\Delta^\ddagger\mu_d(r) = \Delta^\ddagger\mu_d^\infty - \beta \frac{2\gamma V_m}{r} \quad (6.3)$$

where α and β are the transfer coefficients ($\alpha + \beta = 1$); $\Delta^\ddagger\mu^\infty$ is an activation energy in the case of the flat interface.

In the framework of the theory of the activated complex, the rate constant can be expressed through the height of the activation barrier [19]:

$$k = B \exp(-\Delta^\ddagger\mu / RT) \quad (6.4)$$

where B is a constant with the same dimension as k .

Combining the size dependence of the rate constant of the surface reaction expressed via Eq.(6.4) with the expression for the steady-state diffusion toward a spherical particle [3], one can derive the equation describing the size dependent evolution of a nanoparticle under reaction, diffusion, and mixed reaction-diffusion control. Thus, the evolution of a single particle of radius r in a solution of monomer with constant concentration $[M]$ is given by the following equation (see details in the Appendix 2):

$$\frac{dr^*}{d\tau} = \frac{S - \exp\left[\frac{I}{r^*}\right]}{r^* + K \exp\left[\frac{\alpha}{r^*}\right]} \quad (6.5)$$

where $r^* = \frac{RT}{2\gamma V_m} r$ and $\tau = \frac{R^2 T^2 D C_{flat}^0}{4\gamma^2 V_m} t$ are dimensionless particle radius and time, respectively.

$K = \frac{RT}{2\gamma V_m} \frac{D}{k_g^{flat}}$ is the dimensionless parameter describing the type of the process involved, i.e. the ratio between the rates of a purely diffusion-controlled process (D is the diffusion coefficient of the monomer) and a purely reaction-controlled one (k_g^{flat} is a first-order reaction rate constant for the process of addition of a monomer to a flat interface – see Appendix 2 for details). Thus, a value of $K < 0.01$ corresponds to an almost pure diffusion-controlled process, $K > 100$ to a reaction-controlled one, and the range $0.01 < K < 100$ corresponds to the regime of mixed control with comparable contributions of both processes.

The dimensionless parameter $S = [M]_{bulk} / C_{flat}^0$ describes the oversaturation of the monomer in solution; α is the transfer coefficient of the activated complex ($0 < \alpha < 1$).

In the case of pure diffusion control, i.e. when $D \ll k_r^{flat}$ ($K \rightarrow 0$) and $r^* \gg 1$ Eq.(6.5) can be simplified to the equation obtained by Sugimoto [3] and applied by Peng [1] to explain the experimentally observed “focusing” and “defocusing” of the size distributions of growing II-VI and III-V semiconductor NPs:

$$\frac{dr}{dt} = \frac{2\gamma D V_m^2 C_{flat}^0}{r R T} \left(\frac{1}{r_{cr}} - \frac{1}{r} \right) \quad (6.6)$$

At “critical” radius r_{cr} the rate of dissolution is equal to the growth rate and the size of the NP is time-independent.

The growth rate of a single NP depends strongly on its radius and on the concentration of monomer in solution close to the NP surface. The size dependencies of the NP growth rate were calculated from Eq.(6.5) for different values of K and S and are presented in Figures 6.2a and 2b, respectively. A NP having a radius smaller than some critical radius r_{cr} has a negative growth rate, i.e. dissolves. The value of this “critical” radius corresponding to a net growth rate equal to zero can be easily evaluated from Eq.(6.5):

$$r_{ZGR} = \frac{2\gamma V_m}{RT \ln S} \quad (6.7)$$

where the index ZGR indicates “zero growth rate”.

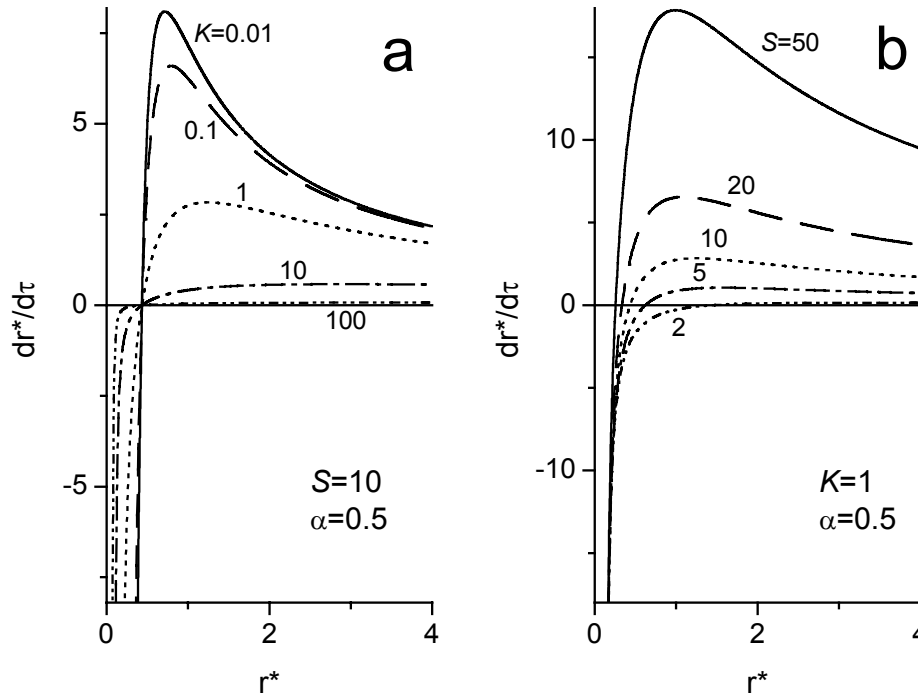


Figure 6.2. Growth rate vs. NP radius calculated from Eq. (6.5) for a single NP for different kinds of the kinetics control described by parameter K (a) and for different values of oversaturation S of the monomer (b).

During growth of a NP, some amount of monomer is consumed in the reaction and, in the case of a finite volume of the solution, the bulk concentration of monomer and the value of oversaturation S decreases gradually. This results in a shift of the critical radius toward larger NP size, and the growth rate of the NP decreases (Figure 6.2b).

6.3. Simulation of the ensemble of NPs

In Section 6.2 we described the size evolution of a single NP placed into an infinite volume of solution with fixed monomer concentration. As discussed in the Introduction, there is no general analytical solution describing all processes occurring during the evolution of the entire NP ensemble. For this reason, a Monte-Carlo simulation was applied to obtain statistical information about the ensemble behavior. Monte-Carlo modeling of the NP ensemble was rather straightforward and similar to those reported in Refs. [9,15]. We simulated a volume of $3 \cdot 10^{-12} \text{ cm}^3$ of the colloidal solution containing $5 \cdot 10^3 - 5 \cdot 10^4$ NPs which

is in reasonable agreement with the experimental conditions.[21-23] The numerical parameters used in the simulation procedure are presented in Table 6.1.

Table 6.1.: Values of numerical parameters used in the Monte Carlo simulations of NP ensembles

Parameter		value	Comments
Initial monomer oversaturation	S_0	1-1000	Constant (15) in Figures 6.3-6.6,6.11
Parameter describing the type of the control	K	$10^{-3} - 10^3$	$K \ll 1$ – diffusion-controlled process $K \gg 1$ – reaction-controlled process
Initial mean particle size	$\langle r \rangle$	1.0 nm	
Initial standard deviation of the particle size distribution	σ_0	5-35%	Normal distribution. Constant (20%) in Figures 6.3-6.5,6.7-6.9,6.11
Specific surface energy	γ	$5 \cdot 10^{-3} - 1 \text{ J m}^{-2}$	Constant (0.125 J m^{-2}) in Figures 6.3-6.5,6.7-6.9,6.11
Diffusion coefficient	D	$10^{-12} \text{ m}^2 \text{ s}^{-1}$	
Simulated volume of the colloidal solution	V_{sln}	$3 \cdot 10^{-12} \text{ m}^3$	
Number of simulated NPs	N	$5 \cdot 10^3 - 5 \cdot 10^4$	
Solubility of the monomer in equilibrium with a flat interface	C_{flat}^0	$10^{-2} \text{ mol m}^{-3}$	
Molar volume	V_m	$3.29 \cdot 10^{-5} \text{ m}^3$	The value corresponds to wurtzite CdSe
Transfer coefficients	α, β	0.5	
Number of time steps		$10^4 - 10^5$	

The evolution of each NP is described by Eq. (6.5). The volume fraction of the NPs for all growth stages was below 10^{-3} , so that no correction on the local particle surrounding was necessary [7]. The concentration of remaining monomer and the value of the monomer oversaturation S in the solution were calculated after each time step and were substituted into Eq. (6.5) to calculate the growth/dissolution rates of the next step. Different statistical parameters (oversaturation of monomer, NP concentration, mean particle size, standard deviation and the shape of size distribution, *etc.*) were monitored after each time step. The

number of NPs used in the simulation allowed to achieve appropriate error values for all statistical parameters.

Two different starting points were used for the simulations performed. In the first approach we considered the nucleation of NPs from an initially homogeneous solution containing a known concentration of monomer. We assumed that the NP nuclei appear in the solution with the rate described by the following equations [20]:

$$J_N = B_N \exp\left(-\frac{\Delta G^N}{RT}\right) \quad (6.8)$$

$$\Delta G^N = \frac{16\pi\gamma^3 V_m^2}{3(RT \ln S)^2} \quad (6.9)$$

where ΔG^N is the activation energy for homogeneous nucleation; B_N is the pre-exponential factor depending on many parameters such as desolvation of species *etc.*

In the second approach we simulated experimental conditions where the processes of nucleation and NP growth are completely separated. This situation is realized, e.g., in a so-called “hot-injection” technique of the NP synthesis [21], when the precursors (monomer) are injected into very hot solvent leading to explosive-like nucleation with a subsequent growth of NPs at lower temperature. In this case the simulation procedure can be started from a pre-formed ensemble of NPs with some known mean size and Gaussian particle size distribution, and do not take into account the nucleation of new nanocrystals during further growth. This approach does not require the knowledge of the precise kinetics of nucleation.

As no detailed information on the nucleation kinetics in colloidal solutions of real semiconductor NPs is available to date, the simulation of the growth dynamics which involves the above nucleation step might appear rather speculative. However, our calculations show that the influence of the initial conditions is negligibly small and does not affect further evolution of the NP ensemble if the rate of nucleation is much higher than the NP growth rate. This is in accord with the LSW theory predicting a unique shape of the particle size distribution for late stages of growth, being independent on the initial conditions [5].

Two different situations can be experimentally realized at initial stages of the NP growth. The first one occurs if almost all monomer has been involved in the nucleation process and nuclei produced are in the equilibrium with monomer. In this case S depends on the NP mean size and can be estimated from Eq.(6.7). The NP growth can occur only *via* the dissolution of small particles which provide the monomer necessary to form larger ones in the ensemble. This is the classic concept of Ostwald ripening. The situation is different if the nucleation is suppressed before major amount of monomer reacts. This case can be

experimentally realized either by the rapid injection of monomer with subsequent fast decrease of the temperature (“hot injection” method) [21], or if the nucleation rate J_N described by Eq. (6.8) drops much faster than S decreases. In both cases, large amounts of monomer remains in solution and their concentration is much higher than the equilibrium concentration for the nuclei presenting.

6.4. Ostwald ripening of nanoparticle ensemble

In order to describe the evolution of an ensemble of nanoparticles in colloidal solution, several processes occurring simultaneously have to be considered: the kinetics of the addition or/and the removal of monomer from the nanocrystals, changes of the particle concentration with time due to nucleation and dissolution processes, temporal evolution of the monomer concentration, etc.

LSW and the LSW-based modern theories describe the self-consistent behavior of colloidal particles during Ostwald ripening and predict formation of final ensembles with unique asymptotic particle size distributions. Thus, for a diffusion controlled coarsening the existence of a stationary regime was predicted by the LSW theory [5,6] and is characterized by the following parameters:

$$\text{coarsening rate } v = \frac{d \langle r \rangle^3}{dt} = \frac{8\gamma V_m^2 DC_{flat}^0}{9RT}, \quad (6.10)$$

limiting stationary size distribution

$$W(r/r_{cr}) = W(u) = \begin{cases} (3^4 e / 2^{5/3}) u^2 \exp[-1/(1-2u/3)] / [(u+3)^{7/3} (1.5-u)^{11/3}] & \text{if } 0 < u < 1.5, \\ 0 & \text{otherwise.} \end{cases} \quad (6.11)$$

with a cut-off at $u=1.5$. A particular feature of this LSW distribution is that $\langle r \rangle = r_{cr}$.

For the reaction-controlled coarsening, the equation describing an approximate stationary particle size distribution was obtained by Wagner [6]:

$$W(u) = \begin{cases} 2^7 3u(2-u)^{-5} \exp[-3u/(2-u)] & \text{if } 0 < u < 2, \\ 0 & \text{otherwise.} \end{cases} \quad (6.12)$$

where $\langle r \rangle = 8r_{cr}/9$.

As was mentioned above, the expansion of the Gibbs-Thompson equation used in LSW and other theories is non-valid for nanoscale systems where terms of higher order begin to play an increasingly important role with decreasing NP size. On the other hand, the Monte-

Carlo technique allows us to account any particle growth law for the simulation of temporal evolution of the NP ensemble. To study the NP growth under the most ideal conditions, we have assumed complete separation of nucleation and NP growth, which can be realized, e.g., by the “hot injection” method [21]. The characteristics of the starting NP ensemble (mean radius of NPs 1.0 nm with standard deviation of 20%) used for the simulation were similar to the ones experimentally observed in the synthesis of CdSe nanocrystals from organometallic precursors at 360°C [1]. An ensemble with similar parameters also forms at initial stages of the synthesis of CdTe nanocrystals in aqueous medium [24].

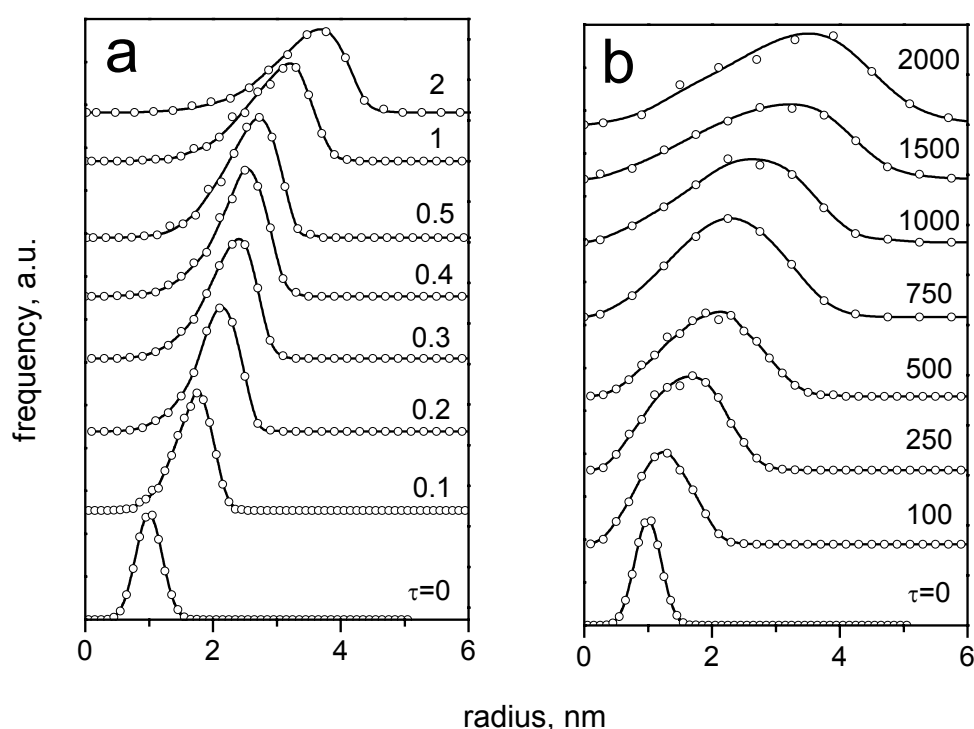


Figure 6.3. Temporal evolution of size distribution of the NP ensemble during the Ostwald ripening under (a) diffusion ($K=10^{-3}$) and (b) reaction ($K=10^3$) control.

Figure 6.3a shows the temporal evolution of the particle size distribution during diffusion-controlled Ostwald ripening ($K=0.001$). It is clearly seen that the initially symmetric normal particle radius distribution evolves in time toward the asymmetric negatively skewed one. Similar results were obtained when we varied the standard deviation of the initial normal distribution or even used non-gaussian, e.g., log-normal distributions. After a rather short transient period where the drastic changes in shape of the size distribution occurred, only

minor changes were evidenced for later stages of the NP growth. A set of size distribution curves calculated at different instants of time during the reaction-controlled Ostwald ripening ($K=10^3$) is presented in Figure 6.3b. In the case of reaction-controlled coarsening the particle size distributions were systematically broader as compared to those observed for diffusion-controlled growth. This observation can be explained with the size dependence of the NP growth rate presented in Figure 6.2a. The difference between r_{cr} and the radius of NP with maximal growth rate (r_{max}) increases gradually with K . Particles smaller than r_{cr} dissolve rapidly, at the same time particles larger than r_{max} have growth rates decreasing with r and, thus, their size distribution narrows down in time.

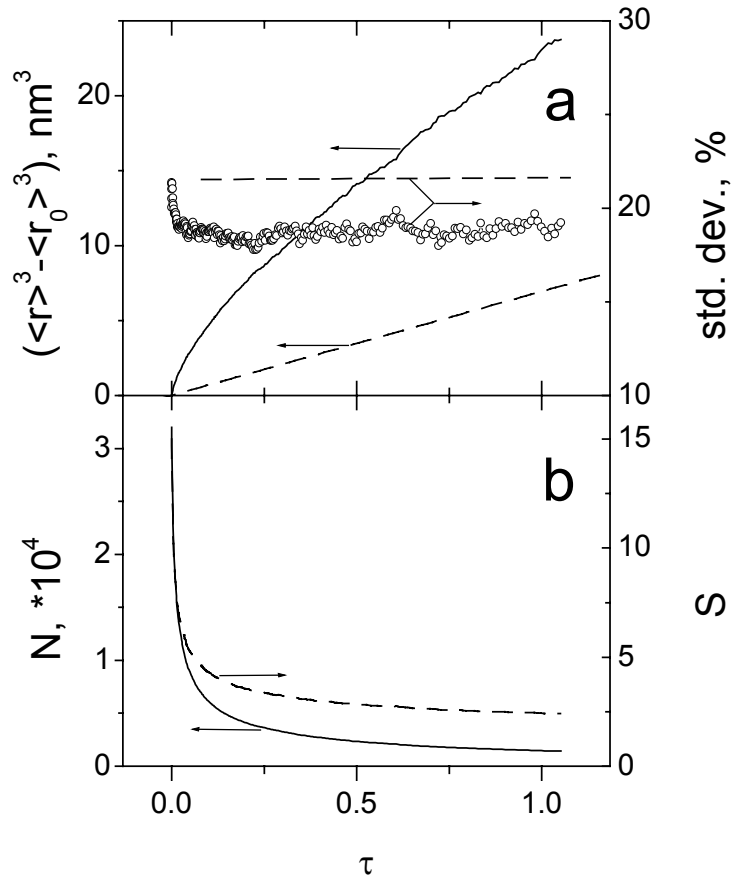


Figure 6.4. Diffusion-controlled Ostwald ripening ($S_0=15$, $K=10^{-3}$) of the NP ensemble. (a) Evolution of the mean particle radius and standard deviation of particle size distribution in time. Dashed lines correspond to LSW predicted ripening. (b) Change of the number of particles (N) and monomer oversaturation (S) during the ensemble evolution.

The temporal evolution of the mean particle size $\langle r \rangle$ and the standard deviation σ (in %) of the particle size distribution are presented in Figure 6.4a. The $\langle r \rangle^3$ vs. τ curve shows a

non-linear behavior during the particle growth in the whole studied range of $\langle r \rangle$ (1.0-3.0 nm), and the growth rate is much higher compared to that predicted by the LSW theory (Figure 6.4a). This is a result of both, the non-stationary regime of coarsening and the intrinsic non-validity of Eq.(6.10) for nanoscale systems. The value of σ (%) tends to a steady-state value of $18.7 \pm 1.0\%$ after a short transient behavior being strongly dependent on the initial conditions. The temporal changes of the oversaturation S and the particle concentration N are presented in Figure 6.4b. It is worth to mention that the temporal behavior of both S and N is very difficult to determine experimentally with reasonable accuracy.

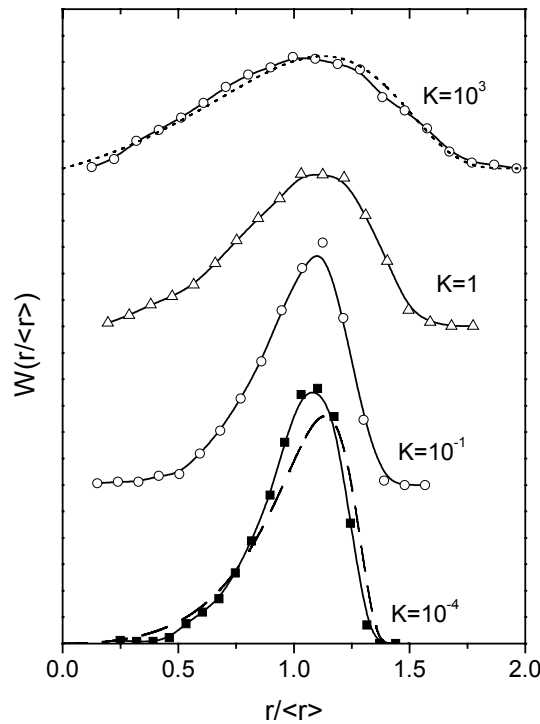


Figure 6.5. Stationary size distributions observed for the Ostwald ripening of the NP ensemble for different types of kinetics control described by parameter K in Eq.(6.5). The limiting distributions predicted by the LSW theory for diffusion- (dashed) and reaction-controlled (dotted) Ostwald ripening are shown for comparison.

To simulate Ostwald ripening under different contributions of the diffusion and the surface reaction, we varied the coefficient K in Eq.(6.5). For all values of K tested, the initial standard deviation of the particle size distribution (20%) changed drastically during initial stages of the nanocrystals growth. This transient behavior depended strongly on the parameters of the initial particle size distribution. After an increase of the mean radius from 1.0 nm (starting value) to ca. 1.5 nm, some saturation level of $\sigma(\%)$ was reached which was

rather stable during further growth, especially in the case of small and large values of K ($K < 0.1$ or $K > 1$). This final value of σ was strongly dependent on K , from 18% for $K < 0.01$ to 35% for $K > 100$. When the regime of stationary growth was attended, the further coarsening became self-similar with σ remaining almost constant and very slow change of the shape of the distribution curve. Figure 6.5 shows nearly stationary particle size distribution curves observed at later stages of Ostwald ripening under different contributions of diffusion and surface reaction as expressed by the coefficient K . The most pronounced difference was observed for $0.01 < K < 10$, whereas below and above this range the influence of K on the shape of the $\sigma(\%)$ vs $\langle r \rangle$ curve was minimal.

The limiting size distributions predicted by the LSW theory for the pure diffusion-limited and pure reaction-limited cases are shown as dashed lines in Figure 6.5 for comparison. In the case of diffusion-limited NP coarsening the size distribution is more symmetric and more narrow as compared to the predicted ones. The value of σ inherent to the LSW distribution is $\sim 21.5\%$. The simulations of Ostwald ripening of the NP ensembles presented in Figures 6.3-6.5 started from $\sigma = 20\%$ and led to the stationary values of σ of $18 \pm 1.5\%$. This fact is of interest because all previous corrections of the LSW resulted in broadening of the size distributions [8,11]. In fact, many experiments performed for ensembles of large colloidal particles or droplets showed the size distributions being generally broader than predicted by LSW theory for these systems [11]. On the other hand, semiconductor NPs synthesized in colloidal solutions whose growth occurs probably *via* the Ostwald ripening often showed the particle size distributions markedly below 20% [21-24]. However, it is worth to mention that the narrow particle size distributions observed could be a result of coarsening in a transient regime which will be discussed below.

The most convenient way to present the results of our Monte Carlo simulation for further discussion is plotting of $\sigma(\%)$ against $\langle r \rangle$. Both parameters can be determined experimentally and allow us to describe the intrinsic statistical behavior of the NP ensemble. Another important point of such presentation is the elimination of the dimensionless time, which is the combination of many external parameters such as mass transport coefficient, temperature *etc.* and usually is not critical in the NP synthesis.

To ensure that the size distributions narrower than those inherent for the LSW are not a result of the non-stationary transient behavior, we have simulated Ostwald ripening of NPs starting from ensembles with different initial values of σ . The effect of the initial size distribution of NPs on the further evolution of the ensemble is presented in Figure 6.6a for diffusion-controlled ($K = 0.01$) Ostwald ripening. Almost independent on the initial value of σ ,

the standard deviation during the NP growth tended asymptotically to a value in the range of 17-20% which is below 21.5 % predicted by the LSW. If σ of the initial size distribution was larger than 20%, the size distribution curve becomes narrower during Ostwald ripening, i.e., a “focusing” of the size distribution is observed (Figure 6.6a). This result dispels the conventional statement that Ostwald ripening results only in the broadening of size distributions. The transients from initial size distributions toward the stationary ones accompanied with broadening of the size distributions were much faster than transients accompanied with narrowing of the size distribution (Figure 6.6a). Simulations starting from very narrow initial size distributions resulted in more smooth and less noisy $\sigma(\%)$ vs. $\langle r \rangle$ curves, probably due to smaller deviations of the single particle trajectories during the Monte-Carlo simulation route.

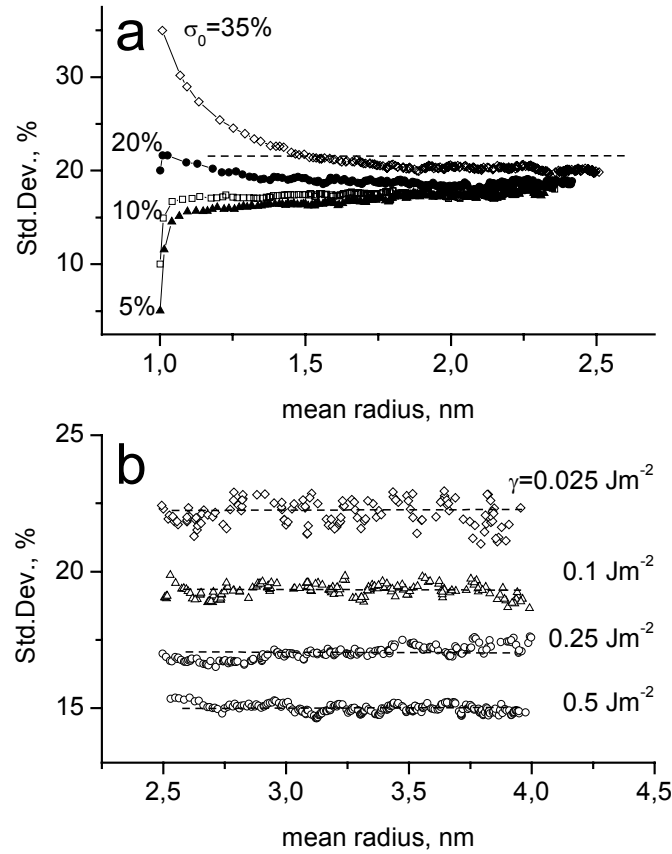


Figure 6.6. (a) Dependence of the standard deviation of the particle size distribution on the mean particle size during the Ostwald ripening for different values of initial width of particle size distributions. Horizontal dashed line corresponds to LSW predicted ripening. (b) Dependence of the stationary value of standard deviation of the size distribution on the surface tension for the diffusion-controlled coarsening of the NP ensemble. $S_0=15$, $K=10^{-2}$.

The reason why the stationary size distributions of NPs were narrower than predicted by the LSW theory lies, again, in the small radius of NPs. As was mentioned above, the particle growth law used in the LSW assumed $2\gamma V_m/(RT) \ll r$ and higher terms of the expansion of the Gibbs-Thompson equation (Eq.(6.1)) were omitted. However, if $2\gamma V_m/(RT) \approx r$ or even $>r$, these terms play a major role, accelerating the dissolution of particles with radii less than critical. This also results in acceleration of the coarsening rate, as was shown in Figure 6.4a.

Another feature of the Ostwald ripening of nanoscale systems which is determined by higher terms of the expansion of the Gibbs-Thompson equation is the dependence of the stationary standard deviation on the surface tension at the particle-solution interface. Figure 6.6b shows the stationary parts of $\sigma(\%)$ vs. $\langle r \rangle$ curves corresponding to different values of the surface tension. For the case of diffusion-controlled NP growth in Ostwald ripening regime the curves demonstrate an decrease of the stationary value of the standard deviation with increasing γ . If $2\gamma V_m/(RT)$ is markedly larger than r , a stationary value of σ as small as 15% can be achieved (Figure 6.6b).

The ratio of $2\gamma V_m/(RT)$ and r decreases during the NP growth, so that σ increases slowly and can achieve the LSW predicted value of 21.5% if the condition $2\gamma V_m/(RT) \ll r$ is satisfied at very late stages of particle coarsening. Under realistic experimental conditions, the mean size of NPs is usually tunable by not more than a factor of 3-4. In this case the ratio between $2\gamma V_m/(RT)$ and r and, as a result, the stationary value of σ remains nearly constant. A similar behavior was observed also for the reaction-controlled NP growth and for the growth under mixed-control.

Summarizing, our simulations show that Ostwald ripening in NP ensembles occurs faster and can result in narrower size distributions than in ensembles of micrometer-scale particles. The most narrow size distribution are achieved if particle growth takes place under strong diffusion control.

6.5. Growth of NPs at high oversaturation of the monomer: “focusing” and “defocusing” of particle size distribution

A particularly strong and fast focusing of the ensemble size distribution takes place if the solution initially contains a comparatively large amount of monomer. To treat this situation we simulated the evolution of NP ensembles with high initial oversaturations, where almost all particles were larger than r_{cr} . Figure 6.7 shows $\sigma(\%)$ vs. $\langle r \rangle$ curves for diffusion-controlled growth with different initial oversaturations S . The excess of monomer affected strongly the evolution of the size distribution during the initial stages of growth. A fast increase of the mean radius $\langle r \rangle$ accompanied by a strong narrowing of the size distribution is observed, followed by subsequent broadening almost without changes in $\langle r \rangle$ (Figure 6.7). The position and depth of the minimum of $\sigma(\%)$ depends on the initial oversaturation of monomer. The reaction conditions influencing this parameter can be optimized to produce NPs of desirable size with very narrow size distributions. The temporal evolutions of the size distributions are shown in Figures 6.8a and 6.8b for the diffusion-controlled and reaction-controlled growth, respectively. In both cases a stable growth regime, more than 10^2 times longer than the previous stage of rapid particle growth, was observed. This growth regime is characterized by a slow broadening of the particle size distribution and a mean particle size being nearly constant. For diffusion-controlled growth the mean radius $\langle r \rangle$ and $\sigma(\%)$ change with time as shown in Figure 6.9a; the evolution of the number of NPs N and the oversaturation S are given in Figure 6.9b. In all cases, the nanocrystals have initially positive growth rates and smaller nanocrystals grow faster than the larger ones. The number of particles remains nearly constant during the stage of “focusing” of the size distribution. During the “focusing” stage the size distribution remains nearly symmetric and is well fitted by a normal distribution. During defocusing the shape of this symmetric size distribution changes towards the asymmetric shape of the stationary size distribution. During the focusing stage the oversaturation decreases to some equilibrium value, and the number of nanocrystals starts to decrease due to the dissolution of the smallest particles. Finally, the Ostwald ripening mechanism governs the further evolution of the NP ensemble.

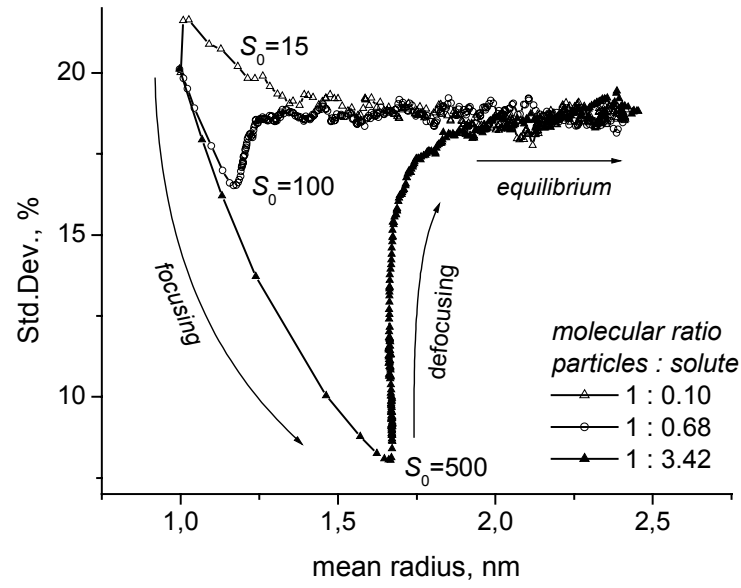


Figure 6.7. Dependence of the standard deviation of particle size distribution on the mean particle size for different initial oversaturations of monomer in the solution. Arrows show focusing, defocusing and equilibrium of the size distribution. $K=10^{-2}$

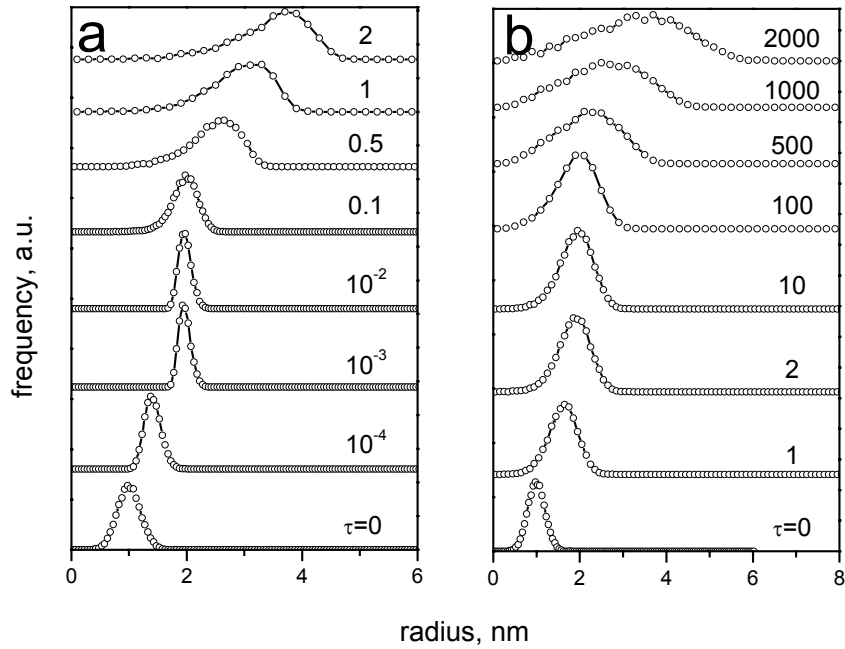


Figure 6.8. Temporal evolution of the size distribution of the NP ensemble at high initial oversaturation of monomer ($S_0=900$) under (a) diffusion ($K=10^{-3}$) and (b) reaction ($K=10^3$) control.

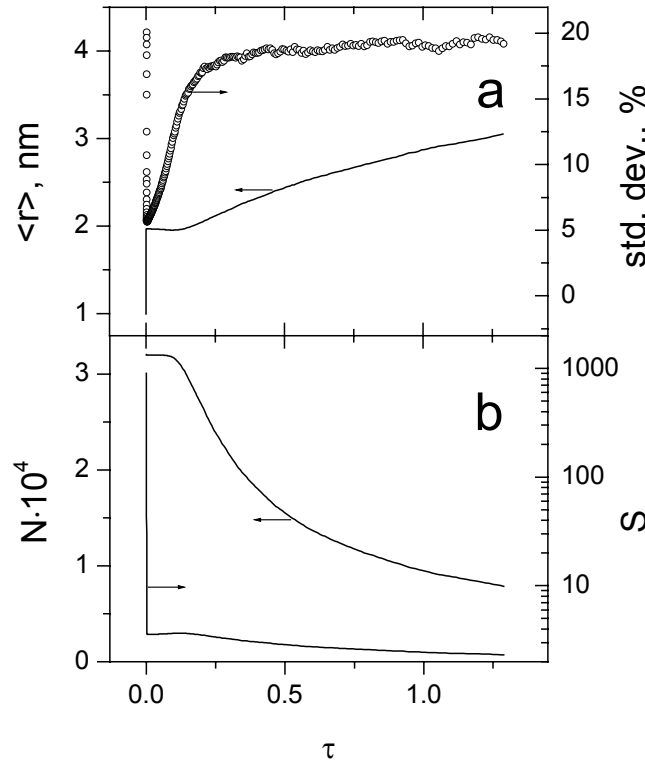


Figure 6.9. Temporal evolution of the NP ensemble with high initial monomer oversaturation ($S_0=900$, $K=10^{-3}$). (a) Evolution of the mean particle radius and standard deviation of their size distribution in time; (b) Changes of the number of particles (N) and monomer oversaturation (S) during the ensemble evolution.

6.6. Dynamic growth rate distribution within an ensemble of nanocrystals

As was shown in Section 6.2, the growth rate of a single nanocrystal depends strongly on its radius and on the concentration of monomer in solution close to the nanocrystal surface. The size dependencies of the nanocrystal growth rate were calculated from Eq. (6.5) for different values of S and are presented in Figure 6.10. The critical radius corresponding to a net growth rate equal to zero ($dr^*/d\tau = 0$) can be easily derived from Eq. (6.5) as shown by Eq. (6.7). Note that nanocrystals smaller than a critical radius, r_{ZGR} , have negative growth rates, i.e. they dissolve.

The zero growth rate in terms of a real ensemble of growing nanocrystals implies that the average rate of removal of matter from the nanocrystals is equal to the rate of addition of

monomer from solution to the nanocrystal surface. In a real experiment a large number of colloidal particles compete for a finite amount of monomer and the monomer is consumed during nanocrystal growth. As a result, the bulk concentration of monomer as well as the oversaturation S decrease gradually. This causes a shift of r_{ZGR} towards larger sizes and a decrease of the nanocrystal growth rate (Figure 6.10).

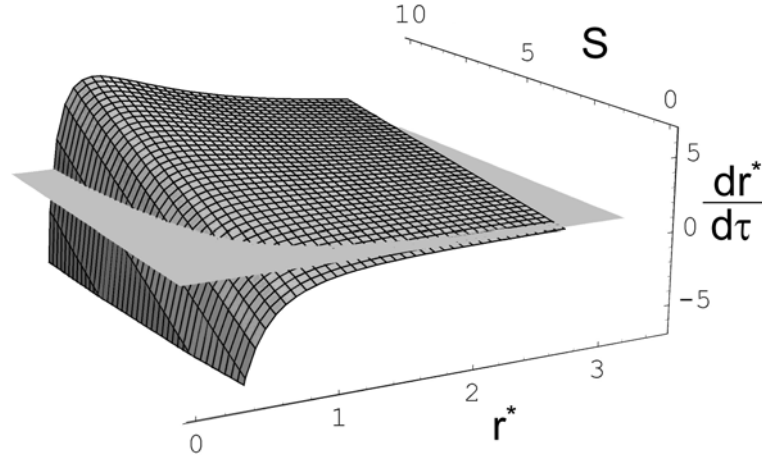


Figure 6.10. Growth rate vs. nanocrystal radius for different values of the monomer oversaturation S as calculated from Eq. (6.5) for a single nanocrystal under diffusion control ($K=0.01$). The gray plane corresponds to zero growth rate (ZGR) of the nanocrystal.

A general analytical solution describing all processes occurring during the evolution of the entire ensemble could not be obtained. As was predicted by the LSW theory and confirmed by our numerical simulations, the parameters of the initial size distribution of the nuclei do not affect the later stages of particle growth. After a short transient time, the ensemble evolves towards an unique particle size distribution independent of the initial conditions. In accord with the mechanism of Ostwald ripening, the largest particles in the ensemble have positive and the smallest have negative growth rates (Figure 6.10). In between these two cases there are particles having nearly zero net growth rate. In other words, at any given instant of time, the ratio between the concentration of monomer in solution and its equilibrium concentration is different for different nanocrystals in the ensemble and equals to zero for nanocrystals with a size corresponding to ZGR.

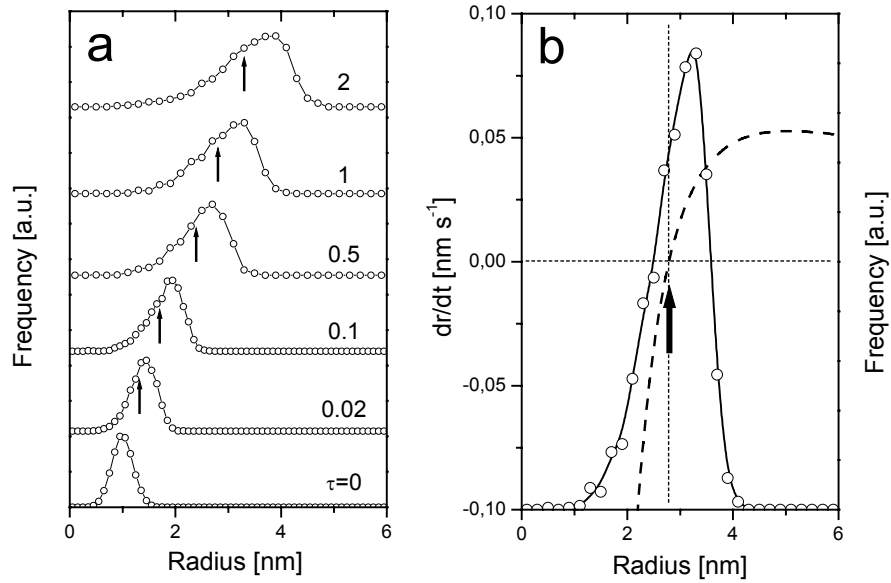


Figure 6.11. (a) Monte-Carlo simulations of the temporal evolution of an ensemble of nanocrystals during Ostwald ripening under diffusion control ($K=10^{-3}$). Arrows indicate the particle size for which the average particle growth rate is zero (ZGR).

(b) **Solid line and open circles:** “Stationary” particle size distribution after prolonged growth of an ensemble of nanoparticles: shape of the distribution becomes independent of time. **Dashed line:** Growth rate vs. particle size for a single nanoparticle. The arrow shows the particle size with zero average growth rate.

The main goal of the simulations performed was to establish the intrinsic distribution of the particle growth rates within an ensemble at different stages of its evolution. Figure 6.11a presents the temporal evolution of the nanocrystal size distribution during diffusion-controlled Ostwald ripening ($K=0.001$). As mentioned above, the initially symmetric normal particle radius distribution evolves in time towards an asymmetric negatively skewed one. Figure 6.11b shows a particle size distribution curve of the nanocrystal ensemble grown from a mean particle radius of 1.0 nm to 3.5 nm. The dashed line gives the size dependence of the single particle growth rate as calculated from Eq. (6.5) for the current value of oversaturation. The particle size corresponding to ZGR is marked by an arrow and is shifted from the maximum of the particle size distribution towards smaller particles. Coming back to Figure 6.11a, one can see that the particle radius corresponding to ZGR is situated at the left side of the ensemble size distribution at all stages of growth.

6.7. Summary and Outlook

A model has been developed describing the growth of a single nanoparticle in colloidal solution. The model takes into account the size dependence of the activation energies of the growth and dissolution processes as well as the mass transport of monomers towards the particle surface. Based on this model, we performed Monte-Carlo simulations of the evolution of an ensemble of growing nanoparticles allowing to identify the conditions that lead to either “focusing” or “defocusing” of the particle size distribution. At later stages of growth the shape of the particle size distribution becomes time-independent, as predicted by the LSW theory for the micrometer sized particles. As compared to micrometer sized particles, however, the stationary size distribution of nanoparticles is narrower and more symmetric than that predicted by the LSW theory. In general, the growth of nanoparticles in the diffusion-controlled regime results in more narrow final size distributions as compared to those grown in the reaction-controlled regime.

The results of our calculations should provide a deeper insight into the processes occurring during the growth of NPs in colloidal solutions. Of course, the behavior of real NPs in colloidal solutions may differ from our idealized model, e.g. because the Gibbs-Thompson equation was obtained for isotropic spherical particle rather than for “real” nanocrystal having number of facets exposed to solution. Moreover, the simple statistics can be masked by chemical processes which were outside of our consideration. However, the model may allow to optimize synthetic strategies towards monodisperse NP colloids. Two general strategies to improve the size distributions of nanoparticles may be proposed. The first is to grow them in the diffusion controlled regime, for instance by decreasing the diffusion or mass transfer coefficient of the system. The second is to increase the surface tension at the solvent-NP interface, for example by a proper choice of the surfactants.

In the next Chapter we will show that the dynamic distribution of growth rates always accompanying the Ostwald ripening mechanism, probably, causes several other properties to vary within an ensemble of particles.

The approach presented here for colloidal solutions of NPs may be quite universal and can be applied to different processes occurring via the Ostwald ripening mechanism, e.g. growth of ionic salt crystals, ripening of deposits etc. As coarsening processes play an important role in any first-order phase transition [25], the deviations from the classical description shown in this chapter may have to be taken into account for more accurate description of any phase transition in a nanoscale system.

6.8. References

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Chapter 7

Dynamic distribution of growth rates within the ensembles of colloidal II-VI and III-V semiconductor nanocrystals as a factor governing their photoluminescence efficiency

In this Chapter the distribution of properties within ensembles of colloiddally grown II-VI and III-V semiconductor nanocrystals is studied. A drastic difference in the photoluminescence efficiencies of size-selected fractions was observed for both organometallically prepared CdSe and InAs colloids and for CdTe nanocrystals synthesized in aqueous medium, indicating a general character of the phenomenon observed. The difference in the photoluminescence efficiencies is attributed to different averaged surface disorder of the nanocrystals originating from the Ostwald ripening growth mechanism when larger particles in the ensemble grow on the expense of dissolving smaller particles. At any stage of growth, only a fraction of particles within the ensemble of growing colloidal nanocrystals has the most perfect surface and, thus, shows the most efficient photoluminescence. This is explained by a theoretical model developed in Chapter 6 which describes the evolution of an ensemble of nanocrystals in a colloidal solution. In an ensemble of growing nanocrystals, the fraction of particles with the highest photoluminescence corresponds to the particle size having nearly zero average growth rate. The small average growth rate leads to the lowest possible degree of surface disorder at any given reaction conditions.

7.1. Introduction

Several synthetic routes to highly crystalline nearly monodisperse II-VI and III-V semiconductor nanoparticles were developed during the last years [see Chapters 2-4 and references therein]. On the other hand, only a few general aspects of the growth kinetics of nanocrystals in solutions were described [1-3]. In Chapter 6 we presented a model providing a phenomenological description of the evolution of an ensemble of nanocrystals in a colloidal solution. The detailed description of the addition/removal of an unit cell to a nanocrystal was outside the model proposed. In this Chapter we intend to demonstrate how the dynamics of the nanocrystal size evolution can affect the microscopic surface structure and, as a result, governs the macroscopic properties of colloids of nanocrystals.

Since nanocrystals lie in the transition region between molecular species and bulk materials, their growth kinetics can be discussed using either molecular [4] or solid state[5] terminology. The structure of the nanocrystal surface at any given instant of time has to depend, for instance, on the rates at which matter joins the surface or leaves it and on the mobility of the surface atoms. However, the stabilizing shell always present at the surface of colloidal nanocrystals affects all these processes and makes difficult any attempt of direct probing their surface. Moreover, properties of nanocrystals in colloidal solution are always averaged over the whole ensemble and can differ from those of a single particle. As an example, the photoluminescence blinking can be observed only for a single nanocrystal, but never for an ensemble [6].

During Ostwald ripening the particles in an ensemble have different growth rates (see Chapter 6) which has to affect their properties to some extent. Thus, larger particles have positive growth rates while smaller particles show negative ones. In order to investigate the variation of properties with the particle size, we divided the ensemble of nanocrystals into nearly monodisperse fractions by applying the so-called size-selective precipitation procedure [7,8].

To the best of our knowledge, there were no studies on how the properties of nanoparticles vary within particle ensemble in the colloidal solution. In this Chapter, we have investigated the variation of photoluminescence and some other particle properties within ensembles of colloiddally grown CdSe, CdTe and InAs nanocrystals.

7.2. Experimental details to Chapter 7

Synthesis of CdSe, CdTe and InAs nanocrystals. To explore the general behavior of semiconductor nanocrystals, we have tested II-VI and III-V colloids both prepared *via* well established synthetic routes.

CdSe nanocrystals were prepared by a high temperature organometallic synthesis in TOPO-TOP mixtures as described in Chapter 2. The growth of the CdSe nanocrystals occurred at 300°C for different periods of time depending on the desired size.

Aqueous colloids of CdTe nanocrystals capped by thioglycolic acid (TGA) were synthesized as described in Chapter 3. Portions of CdTe nanocrystals of different sizes were taken from the crude solution at different refluxing times. The TGA capping of CdTe nanocrystals makes them air-stable and processable at ambient conditions. Thus, aqueous colloids of CdTe nanocrystals showed no changes in optical properties during months of storage in air.

InAs nanocrystals were synthesized by the dehalosilylation reaction between InCl_3 and tris(trimethylsilyl)arsine (TMS_3As) as described in Chapter 4. To keep the particle size distribution narrow and to prepare InAs particles larger than ~3.5 nm in size, additional injections of precursors were necessary.

Size-selective precipitation of nanocrystals. As the conclusions drawn in this work were based on investigations of size-selectively isolated fractions of nanocrystals, we paid special attention to all procedures involving their post-preparative treatment. First, all manipulations with organometallically prepared CdSe and InAs nanocrystals were performed inside a glovebox under nitrogen atmosphere. Second, we carried out control experiments for all nanocrystals investigated to ensure that no changes of properties were induced by size-selective precipitation.

Size-selective precipitation of aqueous CdTe colloids was carried out as follows. Aliquots of the crude solution were taken at different stages of particle growth, concentrated by a factor of about 3 in a rotary evaporator at 25-40°C and 2-propanol was added dropwise under stirring until the solution become slightly turbid. The precipitate was isolated by centrifugation and re-dissolved in a defined volume of water. The procedure was repeated several times allowing to obtain 6-12 size-selected fractions of CdTe nanocrystals from each portion of the crude solution.

In the case of CdSe and InAs nanocrystals, the TOPO-TOP stabilizing shell is, probably, more labile than the TGA shell on CdTe nanocrystals and can be partially washed out if the concentration of TOP in the solution is low. As a result, a systematic decrease of the PL efficiency of size-selected fractions in comparison with the initial crude solutions was observed. To overcome this problem, we carried out the size-selective precipitation under an inert gas atmosphere and the concentration of TOP was kept at a constant value. Aliquots of the crude solution of either CdSe or InAs nanocrystals were taken from the hot reaction mixture, cooled to room temperature and mixed with a ~10-fold excess of 1-butanol (in the case of CdSe) or toluene (in the case of InAs). Methanol or ethanol was added dropwise until the solutions became turbid and the precipitates were isolated by filtration through 0.2 μm PTFE filters. Subsequently, TOP was added to the supernatant to keep the concentration of TOP at one constant level (5-10 wt.%) at all stages of size-selective precipitation. For optical measurements, the precipitate was re-dissolved in a 10 vol.% solution of TOP in toluene. This procedure was repeated 8-12 times to obtain a series of size-selected fractions of nanocrystals. Unfortunately, toluene has strong absorption bands around 1 eV which disturb the PL spectra of InAs nanocrystals larger than ~3.5 nm. The use of solvents transparent in the near IR, e.g. CCl_4 , did not allow us to prepare InAs colloids stable for long periods of time. Therefore, we worked only with colloids of relatively small InAs nanocrystals emitting above 1 eV. In order to achieve quantitative reproducibility of the optical measurements, the solutions of nanocrystals were removed from the glovebox only in sealed quartz cuvettes preventing any contact of organometallically prepared colloids with air.

7.3. Dynamic distribution of PL efficiencies within ensembles of nanocrystals

7.3.1. Growth of CdSe, CdTe and InAs nanocrystals in crude solutions

The synthesis of nanocrystals involves stages of nucleation and growth which may either take place separately or may partially overlap in time. The former case is realized when so-called “hot injection” technique [7] is applied, where the precursors are rapidly injected into a hot coordinating solvent to achieve very fast nucleation of particles which are subsequently grown at lower temperature for several minutes to several days. During the growth stage, a large number of colloidal particles compete for a finite amount of monomer,

and the total number of particles decreases slowly due to dissolution of the small ones. The strong size-dependence of the optical properties of semiconductor nanocrystals allows to monitor the mean particle size and the size distributions through the temporal evolution of UV-Vis and PL spectra [1,9].

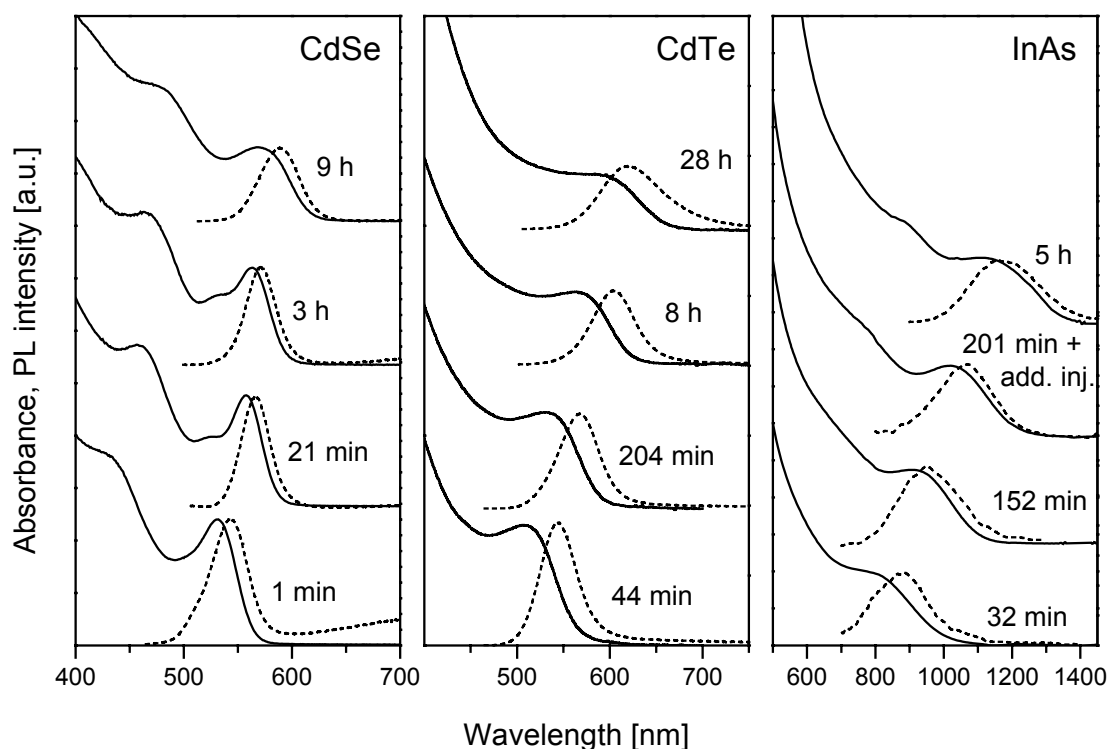


Figure 7.1. Temporal evolution of absorption (solid lines) and PL (dashed lines) spectra of CdSe, CdTe and InAs nanocrystals during their growth in crude solutions. The widths of the PL bands reflect the intrinsic particle size distributions in the crude solution at different stages of growth. In the case of InAs nanocrystals, additional precursor was injected into the reaction mixture to keep size distribution narrow (marked as “add. inj.”).

Figure 7.1 shows absorption and PL spectra of crude CdSe, CdTe and InAs colloidal solutions taken from the reaction flasks at different stages of particle growth. As a consequence of the quantum confinement effect, both, the absorption and the PL spectra of the nanocrystals shifted to longer wavelengths as the particle size increased. The width of the absorption and PL bands reflects the size distributions of the nanocrystals in the crude solutions. In the case of CdSe and InAs nanocrystals grown by the hot injection technique, two regimes of particle growth were observed. During the first ~ 30 min the size distribution

narrowed (focusing), and then started to broaden (defocusing). This behavior first observed by Peng et al. [1] was discussed in Chapter 6. During the focusing stage all nanocrystals grow *via* reaction with the excess of monomer present in the solution after nucleation. During the defocusing stage nanocrystals grow *via* Ostwald ripening accompanied with gradual decrease of the particle concentration. During the growth of CdTe nanocrystals in aqueous solution, no focusing of the particle size distribution was observed. Nevertheless, rather narrow PL spectra of CdTe nanocrystals (FWHM 45-55 nm, corresponding to a standard deviation of the particle size distribution of ~15%) observed at initial stages of the synthesis evidenced that the nucleation and the particle growth stages are rather well separated in time even without applying the hot injection technique.

7.3.2. *Strong non-monotonic difference in PL efficiency of size-selected fractions of CdSe, CdTe and InAs nanocrystals*

Aliquots of the crude solutions of CdSe, CdTe and InAs nanocrystals were taken at different stages of particle growth and divided into several (up to 12) fractions by carefully applying the size-selective precipitation technique. Figure 7.2 shows, as an example, the absorption and PL spectra of 6 size-selected fractions obtained from the crude solution of TOPO-TOP capped CdSe nanocrystals. The size distribution in each fraction was, as expected, narrower than in the initial crude solution leading to better pronounced electronic transitions in the absorption spectra and narrower PL bands (FWHM 30–35 nm). The absorption spectra of the size-selected fractions shifted to shorter wavelengths with decreasing mean particle size and were similar to those previously reported for monodisperse CdSe fractions [1,7]. Noteworthy, the efficiency of the band-edge PL of all size-selected fractions of CdSe nanocrystals shows a clear dependence on the “fraction number”, i.e., on particle size. For instance, the first isolated fraction which contained the largest particles of the aliquot had a lower PL efficiency than the other ones. The increase of the PL intensity from fraction to fraction was non-monotonic: the maximum of the PL was observed in the present case for the fifth fraction with subsequent decrease for the sixth one. The difference between the lowest and the highest PL efficiencies was of about a factor of three (Figure 7.2).

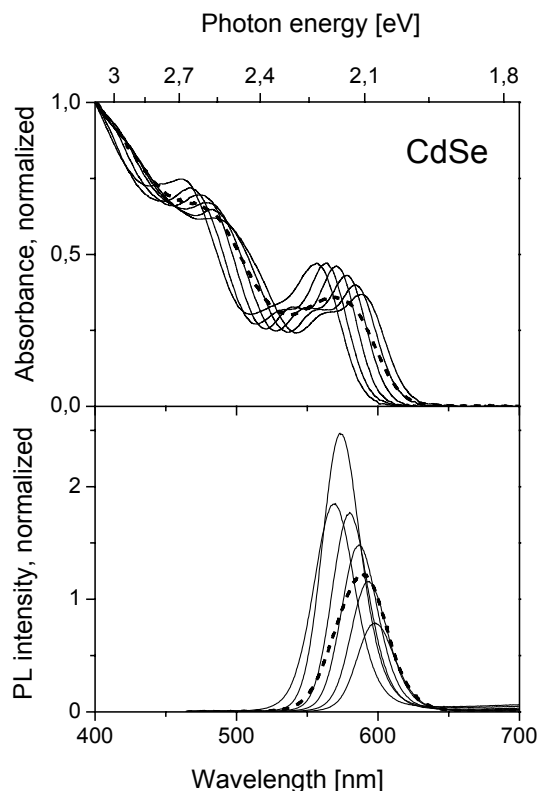


Figure 7.2. Absorption (top) and PL (bottom) spectra of size-selected fractions of CdSe nanocrystals (solid lines). The absorption and PL spectrum of the crude solution (dashed lines) are added for comparison. PL intensities are normalized to identical absorbance at the excitation wavelength (400 nm).

Figure 7.3 shows that similar variations of the PL intensity are observed for size-selected fractions of aliquots taken at earlier stages of growth, i.e., with a smaller average size of the CdSe nanocrystals. In all cases, the fractions in the middle exhibit the highest PL efficiency. Size-selected fractions of TGA-stabilized CdTe nanocrystals and TOP-stabilized InAs nanocrystals showed the same PL dependence (Figure 7.3). Very similar behavior was also observed for the weak band edge emission of TOPO-TOP-capped InP nanocrystals (not shown). These results demonstrate that the phenomenon is common for colloids of different luminescent semiconductor materials.

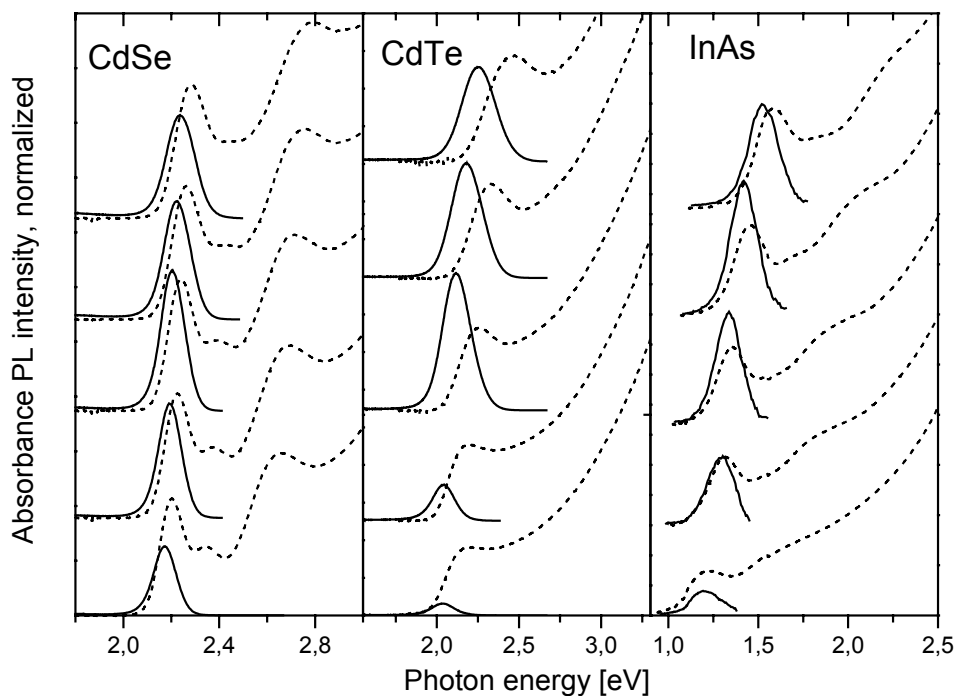


Figure 7.3. Absorption (dashed lines) and PL (solid lines) spectra of size-selected fractions of CdSe, CdTe and InAs nanocrystals. For each material, all fractions were isolated from a single aliquot of the crude solution. All spectra are plotted vs. photon energy for better comparison of relative PL intensities within each series of size-selected fractions.

The PL efficiencies observed for different fractions and materials are summarized in Figure 7.4. The points in this figure present both the absolute value of the PL efficiency (Y-axis) and the position of the PL maximum (X-axis) for each size-selected fraction obtained from three (CdSe), four (CdTe) and two (InAs) crude solutions. The PL spectra of each crude solution is given as solid line; dashed lines present polynomial fits to the experimentally observed “PL efficiency – wavelength” dependencies in each series of fractions. For each series of either CdSe, CdTe or InAs nanocrystals obtained through the size fractionation of the corresponding crude solutions, the “PL efficiency – wavelength” dependence clearly went through a maximum, which in all cases was shifted to shorter wavelengths in comparison to the position of the PL maximum of the corresponding crude solution. The PL efficiency varied systematically and very strongly within each series – up to an order of magnitude for CdTe nanocrystals (synthesized in aqueous solution and capped by thioglycolic acid) and up to ~3-4 times for CdSe and InAs nanocrystals prepared organometallically.

Note, that particles of the same size but obtained from crude solutions of different mean particle size exhibit different PL efficiencies (Figure 7.4). This means that the rather intriguing distribution of PL efficiencies observed within each ensemble of nanocrystals is not simply caused by a variation of the PL efficiency with particle size [10,11].

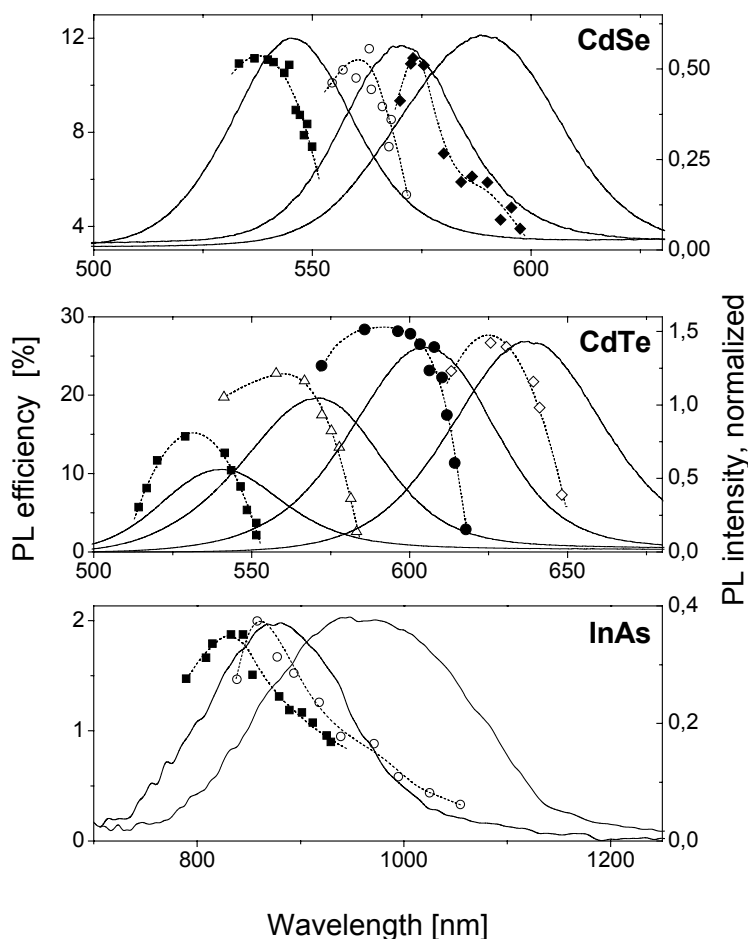


Figure 7.4. *Solid lines:* PL spectra of crude solutions of CdSe, CdTe and InAs nanocrystals measured at different stages of particle growth. *Points:* PL efficiency vs position of the PL maximum of size-selected fractions isolated from each crude solution.

To ensure that the PL behavior observed is not an effect of changes induced by the size-selective precipitation procedure (e.g. partial removal of stabilizing shell), we compared the initial crude solutions with solutions prepared by mixing all size-selectively isolated fractions in the same proportions as they were present in their crude solutions. In Figure 7.5a the absorption and PL spectra of a crude solution of CdTe nanocrystals are compared with those of corresponding re-mixed solution. Nearly quantitative agreement between the UV-Vis

and PL spectra of the crude and the re-mixed solution was observed for all samples investigated. Minor differences in the PL maxima and the PL efficiencies (Figure 7.5b) obviously can not be responsible for a 10 fold variation of the PL efficiency between size-selected fractions. This confirms that the size-selective precipitation and re-dissolution steps did not influence the PL properties of the nanocrystals.

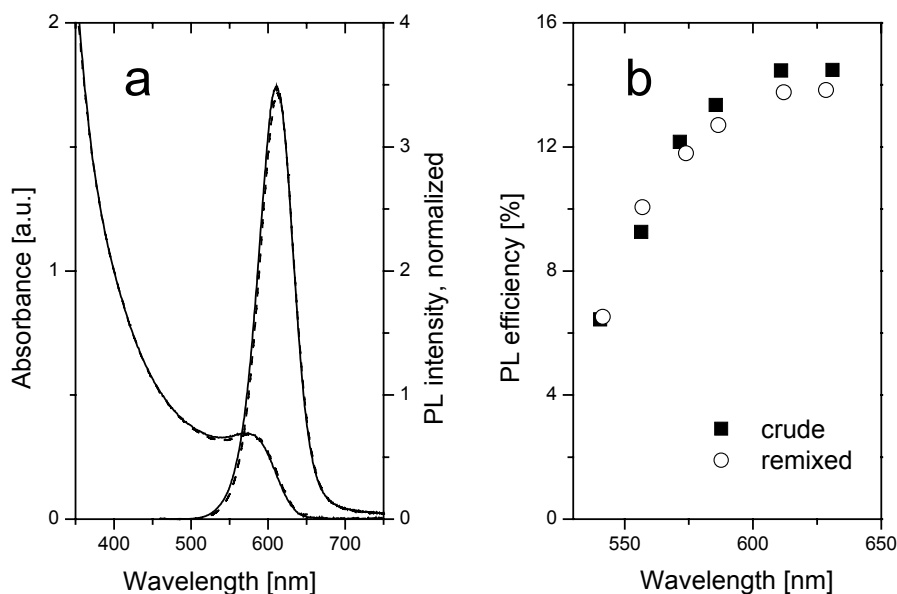


Figure 7.5. (a) Absorption and PL spectra of a crude solution of CdTe nanocrystals (solid line) and of a solution obtained by re-mixing all size-selected fractions isolated from this crude solution (dashed line). (b) PL efficiency vs. position of the PL maximum of crude solutions of CdTe nanocrystals measured at different stages of particle growth (■) and for the corresponding solutions prepared by re-mixing all size-selected fractions (○).

7.3.3. Comparison of the nanocrystal fractions with the lowest and the highest PL efficiency

In the second series of experiments we compared the properties of size-selected nanocrystals belonging to the fraction with the lowest PL efficiency (below referred to as LPL fraction) with those belonging to the fraction showing the highest PL efficiency (HPL fraction).

A direct comparison of HRTEM images of CdSe, CdTe and InAs nanocrystals did not reveal any statistically reliable difference between particles of the HPL and the LPL fractions with respect to average particle crystallinities, shapes, lattice distances, etc. Thus, in the case of CdSe nanocrystals possessing hexagonal (wurtzite) lattice, both the LPL and the HPL fraction consisted of very similar nearly spherical particles (Figure 7.6), so that the difference between LPL and HPL fractions cannot be explained by a difference in the particle shape. The small size of the nanocrystals and the low contrast of the pre-surface lattice planes in the HRTEM images did not allow any comparison of the surface roughness of nanocrystals. No systematic difference between LPL and HPL fractions was observed in the powder XRD patterns as well. Thus, both methods of direct probing the nanocrystal lattices – HRTEM and powder XRD – demonstrated that both LPL and HPL fractions are very similar with respect to the particle crystallinity and shape.

The different behavior of LPL and HPL fractions of size-selected nanocrystals will be further demonstrated in this study on TGA-capped CdTe nanocrystals as they showed the largest difference in the PL efficiencies and were better processable as compared to CdSe and InAs nanocrystals. In the latter cases all manipulations had to be performed inside the glovebox to achieve reproducible results. However, the behavior described below was general and was observed for CdSe and InAs nanocrystals as well.

Figure 7.7 shows the evolution of the PL intensity during further growth of CdTe nanocrystals from the LPL and HPL fractions. Size-selected nanocrystals were placed in solutions of the same composition (i.e., the same concentrations of the nanocrystals, stabilizer, cadmium ions and the same pH) as the initial crude solution the fractions were isolated from, and growth of the nanocrystals was initiated by refluxing. After some time, both samples reached approximately the same size. After growth, both, the LPL fraction and the HPL fraction, showed nearly the same PL efficiencies: they returned to a mean value of ~9%, i.e. the same value as in the initial crude solution of the nanocrystals (PL efficiency $10 \pm 2\%$). After size-selective fractionation, the “PL efficiency – fraction number” dependence of these solutions was almost identical to that observed for the initial crude solution.

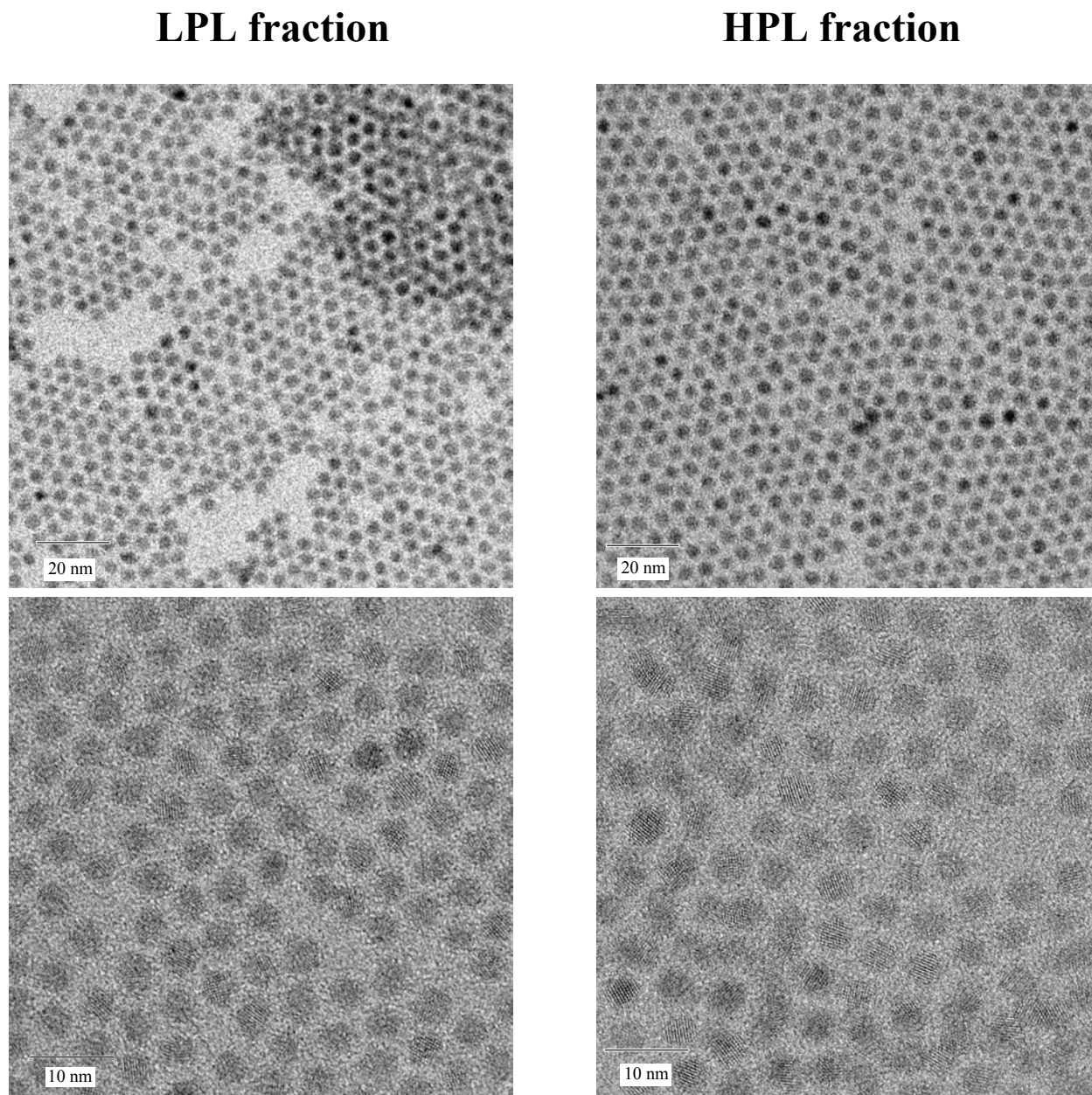


Figure 7.6. *TEM overview (top) and HRTEM (bottom) images of TOPO-TOPSe capped CdSe nanocrystals belonging to the fraction with the lowest PL efficiency (LPL fraction, left) and to the fraction with the highest PL efficiency (HPL fraction, right).*

Further, the LPL and HPL fractions of CdTe nanocrystals evolve very differently under UV-light irradiation (Figure 7.8). To investigate the photostability of nanocrystals, dilute colloidal solutions (either saturated with oxygen or under air-free conditions) were excited at $\lambda_{\text{ex}}=400\pm15$ nm for different intervals of time using a 450 W xenon lamp and a

band pass interference filter. Both in argon- and air-saturated solutions, the nanocrystals from the HPL fraction were remarkably more photostable (Figure 7.8a, c) as evidenced from the temporal evolution of the absorption spectra. We also observed an improvement of the PL efficiencies of both the LPL and HPL fractions at the initial stage of irradiation, which was much more pronounced for the LPL fraction (Figure 7.8b, d).

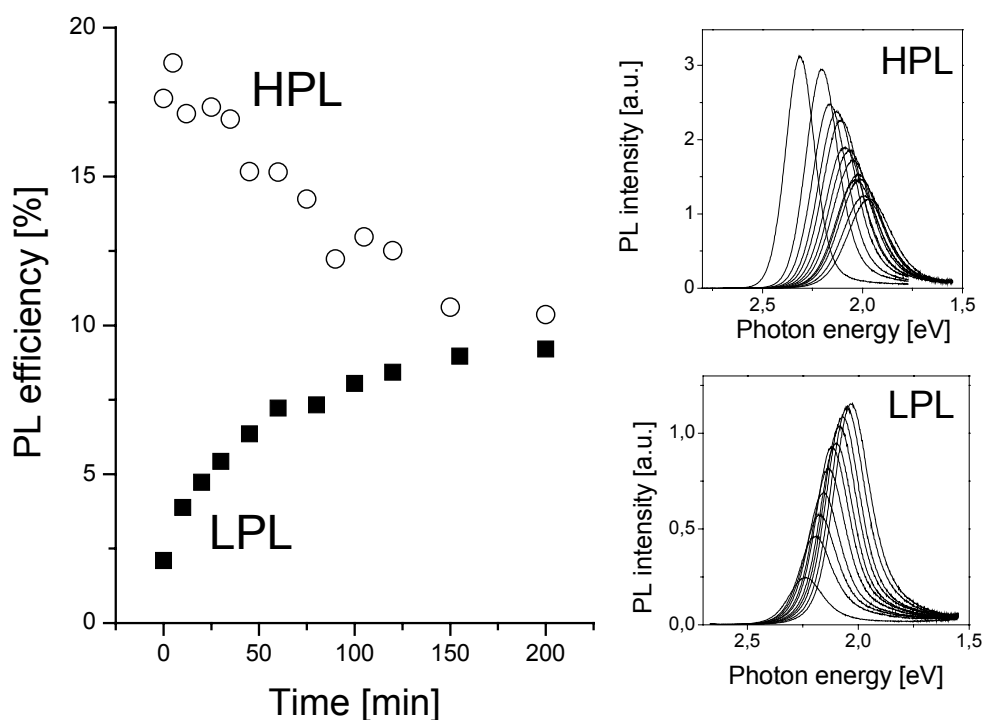


Figure 7.7. (left): Temporal evolution of the PL efficiency of two different size-selected fractions of CdTe nanocrystals upon growth in a solution with composition similar to the crude solution. LPL is the size-selected fraction with the lowest PL efficiency; HPL is the fraction with the highest PL efficiency. (right): Change of the PL spectra of the LPL and HPL fractions during growth in this solution.

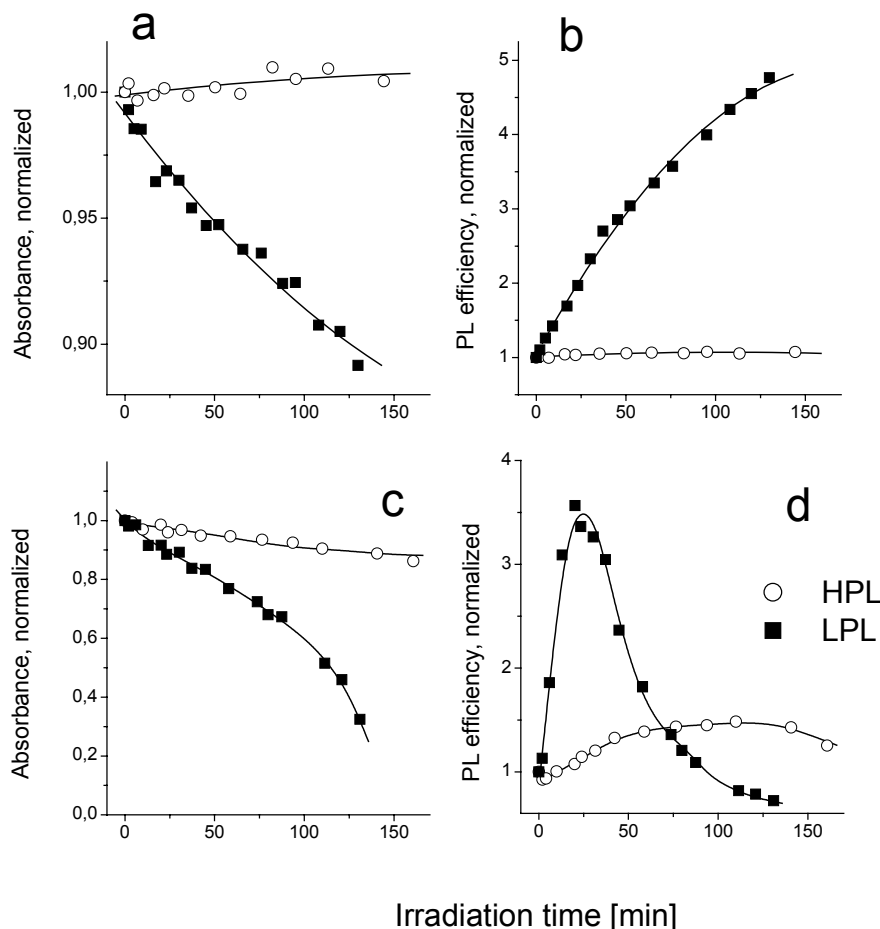


Figure 7.8. Difference in photostability between the LPL (■) and the HPL (○) fractions of CdTe nanocrystals under irradiation with 400 nm light of a 450 W xenon lamp. (a) and (c) show the temporal evolution of the absorption at 400 nm; (b) and (d) show the evolution of the PL efficiency vs. irradiation time. Both absorption and PL efficiency are normalized at their initial values (i.e. before irradiation). (a) and (b) were measured under argon; (c) and (d) – in oxygen-saturated solutions.

7.4. Discussion on the possible origin of the dynamic distribution of the properties within an ensemble of nanocrystals

As was shown in the Section 7.3, the PL efficiency varies strongly within any ensemble of as-prepared semiconductor nanocrystals (Figures 7.2 and 7.3). We observed similar behavior for nanocrystal ensembles prepared *via* different synthetic routes (Figure 7.4). The fact that the PL efficiency distribution keeps nearly constant during all stages of the

ensemble evolution suggests that the growth mechanism itself might be the cause for this variation within each ensemble.

To clarify possible origins of this variation we compared the properties of the fractions with the lowest and the highest PL efficiencies. No distinct difference between LPL and HPL fractions was found by XRD and HRTEM studies. On the other hand, if these size-selected fractions of nanocrystals are allowed to grow further at conditions of Ostwald ripening, their size-distribution and PL efficiency develop towards values typical for the crude solution from which the fractions were isolated (Figure 7.7).

The higher photostability of the nanocrystals of the HPL fraction (Figure 7.8a and c) indicates that their surface quality is much better in terms of a smaller number of surface defects serving as centers of photooxidation. In fact, an enhancement of the PL efficiency under irradiation similar to that observed for the LPL fraction (Figure 7.8b and d) was observed for several kinds of nanocrystals [12,13] and was attributed to processes resulting in the annealing of surface defects acting as traps for photogenerated carriers [12]. Annealing under irradiation should be more pronounced for nanocrystals with higher concentration of defects at the particle surface (i.e., for the LPL fraction). Thus, summarizing the behavior observed for the LPL and HPL fractions we can suggest that the difference between their PL efficiencies originates from the different surface quality (or surface disorder) of nanocrystals – in this paper we use this general term to describe a smooth and defect-free surface (to a smaller or larger extent) being free of traps. The difference in the surface quality of nanocrystals in an ensemble originates from the growth conditions and is not caused by the size-selective precipitation after preparation. The latter is only a tool to isolate fractions of nanocrystals with different surface quality and size.

Why does the surface quality vary in an ensemble of growing nanocrystals systematically with the nanocrystal size? To answer this question we have to consider the parameters governing the surface quality or surface roughness of crystalline solids during their growth. The surface roughness of bulk crystals depends strongly on the growth conditions, mainly on the ratio between the growth temperature and the characteristic temperature (T_R) of the so-called “roughening transition” [14-17]. Below T_R the surface of the growing crystal is microscopically smooth, above it is rough. For most semiconductors, T_R is above 1000°C, being slightly dependent on the crystallographic plane [15]. In principal, for nanocrystalline matter T_R can be much lower, as the melting point depends on the particle size [18]. However, even if we assume that T_R is size-dependent, it would not allow us to explain similar distributions of surface quality within ensembles with different mean particle sizes.

Therefore, it seems more probably that the observed distribution of PL efficiencies can be explained in terms of “kinetic roughening”, the phenomenon well known for the growth of bulk crystalline solids [15,19,20]: when the growth rate of a crystal increases, the critical size of two-dimensional (2D) nucleation sites at the surface becomes so small that the 2D nucleation barrier vanishes. As a result, the crystal surface becomes microscopically rough and macroscopically rounded.

In an ensemble of nanocrystals in colloidal solution the particle growth rate is strongly size-dependent: the main concept of Ostwald ripening implies that larger particles in an ensemble grow by consuming the monomer released by the dissolution of smaller particles. As the Ostwald ripening is a self-similar process with an unique limiting particle size distribution [see Chapter 6 and references therein], the particle growth rate distribution has to be similar at all stages of the particle growth. To explain the influence of the growth mechanism on the distribution of PL efficiency in any ensemble of growing colloidal nanoparticles, we developed a model describing the evolution of a nanocrystal ensemble growing in a solution of monomer.

The growth rate of a single nanocrystal depends strongly on its radius and on the concentration of monomer in solution close to the nanocrystal surface. The size dependencies of the nanocrystal growth rate were calculated in Chapter 6 for different values of S and are presented in Figure 6.10. Note that nanocrystals smaller than a critical radius r_{ZGR} have negative growth rates, i.e. they dissolve. The critical radius corresponding to a net growth rate equal to zero ($dr^*/d\tau = 0$) was calculated in Chapter 6 for different values of the monomer oversaturation (see Eq. (6.7)).

The zero growth rate in terms of a real ensemble of growing nanocrystals implies that the average rate of removal of matter from the nanocrystals is equal to the rate of addition of monomer to the nanocrystal surface. In a real experiment a large number of colloidal particles compete for a finite amount of monomer and the monomer is consumed during nanocrystal growth. As a result, the bulk concentration of monomer as well as the oversaturation S decrease gradually. This results in a shift of r_{ZGR} towards larger sizes and a decrease of the nanocrystal growth rate (Figure 6.10).

A general analytical solution describing all processes occurring during the evolution of the entire ensemble could not be obtained. For this reason, the Monte-Carlo simulation technique was applied to obtain statistical information about the ensemble behavior (see details in the Chapter 6).

The main goal of these simulations was to establish the intrinsic distribution of the particle growth rates within the ensemble at different stages of its evolution. Figure 6.11a presents the temporal evolution of the nanocrystal size distribution during diffusion-controlled Ostwald ripening ($K=0.001$). It is clearly seen that the initially symmetric normal particle radius distribution evolves in time towards an asymmetric negatively skewed one. Figure 6.11b shows a particle size distribution curve of the nanocrystal ensemble grown from a mean particle radius of 1.0 nm to 3.5 nm. The dashed line gives the size dependence of the single particle growth rate as calculated from Eq. (2) for the current value of oversaturation. The particle size corresponding to ZGR is marked by an arrow and is shifted from the maximum of the particle size distribution towards smaller particles. Coming back to Figure 6.11a, one can see that particles with ZGR are situated at the left part of the entire ensemble at all stages of growth.

The monomer preferably leaves the nanocrystals from surface sites having the highest energy (defects, kinks etc.). On the other hand, monomers tend to join the most energetically favorable positions at the surface. The kinetic roughening approach states that the most ideal conditions for annealing of surface defects are realized at small growth rate of the crystal. Consequently, particles with a size close to r_{ZGR} do possess the most smooth and defect-free surfaces of all particles in the ensemble. In fact, comparison of the data presented in Figures 7.2 and 7.4 with the results of our numerical simulations (Figure 6.11) demonstrates, that the size of the particles with the highest PL efficiency (HPL fraction) coincides well with the ZGR size.

According to the simulation, instantaneous increase of the oversaturation of monomer (e.g. by additional injection of precursors) shifts r_{ZGR} to very small values located outside the particle size distribution (Figure 7.9). As a result, all nanocrystals possess positive growth rates and the growth rate increases monotonically with the particle size. To check this statement, we injected additional amount of precursors into the crude solution of growing nanocrystals and measured the PL efficiency distribution within the ensemble before and after the injection. Addition of monomer to the reaction mixture caused rapid growth of the nanocrystals accompanied by focusing of their size distribution and a decrease of the PL intensity (Fig.7.10). Moreover, the “stationary” non-monotonic PL efficiency distribution curve observed before the injection was disturbed after the additional injection as shown in Figure 7.10 for CdSe and CdTe nanocrystals. Size-selected fractions obtained from the crude solutions of both, CdSe and CdTe nanocrystals, showed a monotonic dependence of the PL efficiency on the fraction number. This behavior of the PL efficiency is in agreement with the

numerical simulations (Fig. 7.9), since higher particle growth rates should result in larger surface roughness and, as a result, to a larger concentration of surface defects and lower PL efficiency. The transition from stationary non-monotonic towards monotonic dependence of the PL efficiency on the fraction number occurred quickly after the additional injection of precursors (within ~ 1 min for CdSe and ~ 10 min for CdTe nanocrystals) and did not change during early stages of defocusing of the particle size distribution. Thus, samples of CdSe and CdTe nanocrystals taken in 40 min and 2 h after additional injection, correspondingly, still exhibited monotonic variation of PL efficiency from fraction to fraction. In case of CdTe nanocrystals, long-term (~ 10 h) heating resulted in recovery of the non-monotonic distribution of PL efficiency within the ensemble of nanocrystals. In case of CdSe nanocrystals, the PL efficiency after additional injection continuously decreased in time and became nearly zero after several hours of particle growth at 300°C , so that no reliably data concerning recovery of “stationary” PL efficiency distribution was obtained in this case.

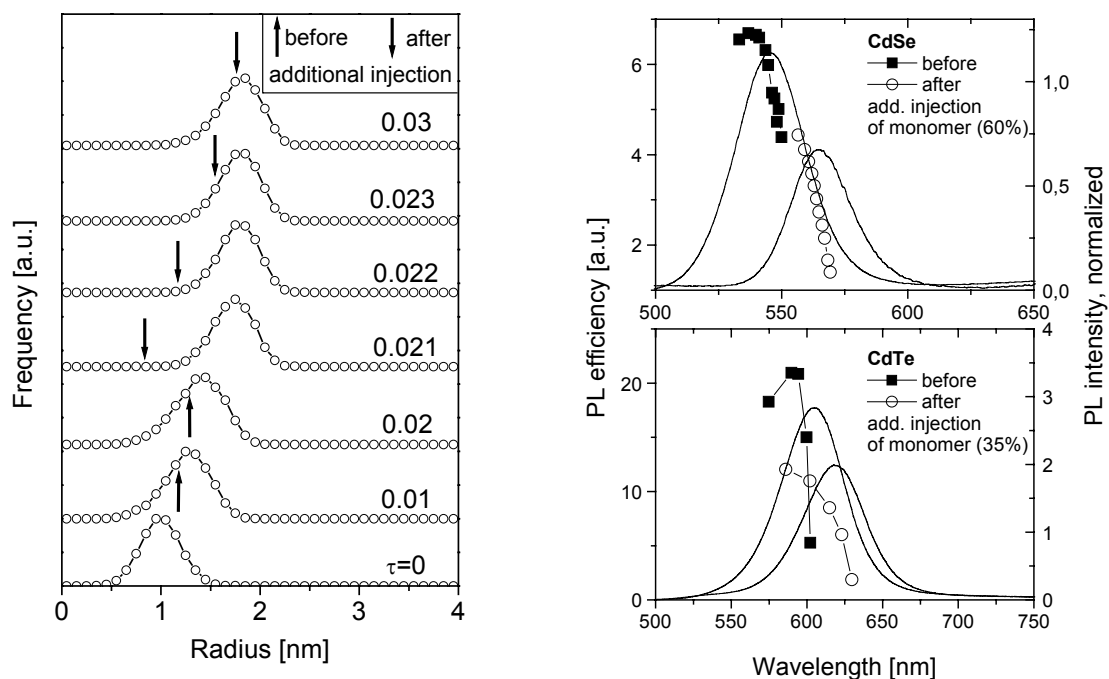


Figure 7.9. (left) Monte Carlo simulations of the particle size with zero growth rate (shown by arrows) within an ensemble of growing nanocrystals before and after additional injection of monomer (80% of the initial amount added) at $\tau = 0.02$. Nanocrystals grow via diffusion-controlled Ostwald ripening ($K=0.001$, $S_0=15$).

Figure 7.10. (right) Changes in the “PL efficiency – wavelength” dependencies of size-selected fractions of CdSe and CdTe nanocrystals caused by additional injections of precursors.

As the numerical simulations show, nanocrystals in the crude solution possess asymmetric negatively skewed particle size distributions (Figure 6.11a). On the other hand, as was emphasized in the literature [11,21], colloidal semiconductor nanocrystals usually exhibit nearly symmetric Gaussian-like PL spectra (see also Figure 7.1). Summarizing the results obtained in this Chapter we suggest that the strongly non-monotonic distribution of PL efficiencies within an ensemble of nanocrystals converts the asymmetric particle size distribution into a symmetric Gaussian-like PL spectrum inherent to crude solutions of nanocrystals.

7.5. Summary

We have found drastic difference in the PL efficiencies of size-selected fractions of CdSe, CdTe and InAs nanocrystals. We suggest that the difference in the PL efficiency originates from the variation of the surface quality within an ensemble of growing nanocrystals. High surface quality refers to a smooth, defect-free, and thus a charge carrier trap free surface. Based on a theoretical model describing the evolution of an ensemble of nanocrystals growing in a solution of monomer, we propose that the nanocrystal fraction with the best surface quality and, thus, with the most efficient PL corresponds to the particle size with the smallest net growth rate within the ensemble. Since annealing of surface defects is most effective at this “zero growth rate”, this condition leads to the highest possible surface quality.

The findings of this work are also important for the use of highly luminescent nanocrystals in optoelectronic, photonic and tagging applications. Thus, simple post-preparative size-selective precipitation of the CdTe nanocrystals described above provides water-soluble, stable, highly processable and surface-functionalized (as almost any type of short-chain thiols can be used as stabilizer) particles with PL efficiencies of up to 20-30%. This value can be enhanced further: as has been shown in Ref. [22] the PL efficiency of TGA-capped CdTe nanocrystals can be considerably increased by forming a shell of cadmium-thiolate complexes at the surface of nanoparticles. The PL quantum efficiency of CdTe nanocrystals from the HPL fraction reached a value of 47% after this treatment.

Moreover, the smooth surface of nanocrystals of the HPL fraction will, probably, result in a better passivation of the nanocrystals by the epitaxial layer of the wide band-gap semiconductor. This is also in accord with a common statement that the best core/shell nanocrystals can be prepared from cores with highest PL efficiencies. Therefore, the use of

HPL fractions for the preparation of core/shell nanocrystals seems to be a general way to further improve the properties (PL efficiency, stability etc.) of luminescent nanocrystals.

Independent of the kind of nanocrystals it is definitely worth to look for the fraction with the highest PL efficiency of a given ensemble if further use of the nanocrystals requires high luminescence efficiency. In any case, coming from an averaged ensemble behavior to any application based on the single particle response (e.g. biolabelling, single particle fluorescence, transistor based on a single nanocrystal) the intrinsic difference between nanocrystals within an ensemble starts to play a dominant role and must be taken into account.

7.6. References

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Chapter 8

Summary

This dissertation focuses on the development of colloidal synthetic approaches for various II-VI and III-V luminescent nanocrystals as well as on the theoretical understanding of processes governing the luminescent properties of semiconductor nanomaterials. Nearly monodisperse series of strongly luminescent **CdSe**, **CdTe**, **InP** and **InAs** nanocrystals as well as **CdSe/CdS**, **CdSe/ZnS** and **InAs/CdSe** core-shell nanocrystals were synthesized *via* various organometallic and aqueous synthetic routes and compared with respect to their luminescent properties and chemical processability. The nanocrystals prepared were characterized by powder XRD, SAXS, HRTEM, XPS, absorption and luminescence spectroscopy.

CdSe nanocrystals were prepared organometallically in a three-component hexadecylamine – trioctylphosphine oxide – trioctylphosphine (HDA-TOPO-TOP) stabilizing mixture. The proposed stabilizing mixture provides exceptionally nice control of the particle size and the size distribution resulting in *in situ* CdSe nanocrystal size distributions as narrow as 4-7%. Generally, introducing of primary amines in the organometallic synthesis of both II-VI and III-V nanocrystals allowed us to considerably improve the existing chemical routes towards high quality semiconductor nanocrystals. Thus, a novel organometallic synthesis of monodisperse primary amine stabilized **CdTe** nanocrystals with size tunable from 2.5 to 7 nm was developed. Colloids of both CdSe and CdTe nanocrystals capped with primary amines exhibit outstanding luminescent properties: sharp colors are tunable by increasing the particle size from blue to red and the room temperature photoluminescence quantum yields are as high as 40-70% for the entire spectral range. Additional passivation of CdSe nanocrystal surface with an inorganic CdS or ZnS shell allowed us to obtain robust luminescent materials with high degree of chemical stability and processability: e.g., highly luminescent **CdSe/ZnS** core-shell nanocrystals can be introduced into polymer matrixes and optoelectronic devices.

Nearly monodisperse and highly crystalline **InP** and **InAs** nanocrystals were prepared *via* Well's dehalosilylation reaction. A novel size-selective photochemical etching technique was proposed for preparation of luminescent colloidal InP nanocrystals with room temperature PL

quantum yields of 25-40%. The PL band of these nanocrystals is tunable from green to near-IR by increasing the particle size. InAs nanocrystals emit in the near-IR spectral region and are of special interest for applications in telecommunication networks. The epitaxial growth of a CdSe shell onto an InAs core allowed us to synthesize colloidal **InAs/CdSe** core-shell nanocrystals with PL quantum yield of 17-20%. By increasing the size of the InAs core the emission band can be tuned from ~800 to 1500 nm.

A new approach to crystallize CdSe nanoparticles in ordered three-dimensional superlattices *via* controlled oversaturation has been developed. The growth technique was based on slow diffusion of a non-solvent (methanol) into a concentrated solution of monodisperse CdSe nanocrystals in toluene, either directly or through a buffer layer of a third component (propanol-2). For the first time, perfectly faceted hexagonal platelets with sizes of about 100 μm have been obtained. In quantum dot solids formed by this way, individual CdSe nanocrystals playing the role of building blocks (artificial atoms in the next level of hierarchy) aligned in a regular fcc-like 3D superlattice as confirmed by TEM.

The growth of nanocrystals in a colloidal solution was studied theoretically by investigating the evolution of ensemble of particles with respect to the average particle growth rate, monodispersity, shape of the particle size distribution, etc. The stationary particle size distribution inherent to the Ostwald ripening process in ensembles of nanoparticles of less than 5 nm in radius is narrower and more symmetric than that predicted by the Lifshitz-Slyozov-Wagner theory for ensembles of larger (> 20 nm in radius) colloidal particles. The growth of nanoparticles in the diffusion-controlled regime results in better final size distributions as compared with those grown in the reaction-controlled regime.

Nanoparticles in ensembles grown *via* Ostwald ripening always show drastic differences in their photoluminescence efficiency. This behavior is very similar for CdSe, CdTe and InAs nanocrystals, indicating a general character of the phenomenon. It was observed for the first time and was attributed to different averaged surface disorder of the nanocrystals originating from the Ostwald ripening growth mechanism. At any stage of growth, only a fraction of particles within the ensemble of growing colloidal nanocrystals has the most perfect surface and, thus, shows the most efficient photoluminescence. In an ensemble of growing nanocrystals, the fraction of particles with the highest photoluminescence corresponds to the particle size having nearly zero average growth rate.

Appendix 1

Experimental Section

A1.1. Chemicals and Apparatus. All chemicals used were of analytical grade or of the highest purity available. Toluene, methanol, n-hexane (all anhydrous, Aldrich), pyridine (anhydrous, Fluka), selenium (99.99%, ChemPur), tellurium (99.999%, ChemPur), dimethylcadmium (99.999%, EpiChem), InCl_3 (anhydrous, Alfa), tris-trimethylsilylphosphide $(\text{TMS})_3\text{P}$ (Alfa), allylamine (Fluka) were used as received. Tri-*n*-octylphosphine oxide (TOPO, 90%, Aldrich) was generally used as received or distilled in vacuum for some control experiments. Tri-*n*-octylphosphine (TOP, Fluka) was purified by distillation. Octylamine, dodecylamine and hexadecylamine (all Merck) were purified and degassed in the reaction vessel by heating under vacuum for several hours at temperatures slightly below their boiling points. Tris-trimethylsilylarsine $(\text{TMS})_3\text{As}$ was synthesized as described in Ref.[1]

UV-Vis-NIR absorption spectra were taken on a Cary 500 (Varian) spectrophotometer. Photoluminescence spectra in the visible (CdSe, CdTe, CdSe/CdS, CdS/ZnS and InP) and near IR (InAs, InAs/CdSe) spectral regions were measured, respectively, with a Fluoromax-2 (Instruments SA) spectrofluorimeter and a custom-made spectrofluorimeter with a nitrogen cooled germanium detector and lock-in amplification. The latter was thoroughly calibrated using the known spectrum of a tungsten-halogen lamp as reported by Cao et al. [2] Powder X-ray diffraction spectra were taken on a Philips X'Pert diffractometer ($\text{Cu K}\alpha$ -radiation). High resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray analysis (EDX) were performed on a Phillips CM 300 UT microscope operating at 300 kV. Small-angle X-ray scattering measurements were carried out with a Kratky camera (Anton Paar). The XPS experiments were performed at the undulator Beamline BW3 ($h\nu = 20\text{--}1800\text{ eV}$) at HASYLAB / DESY. All organometallic syntheses were carried out using standard airless techniques under dry nitrogen. The stock solutions were prepared inside the glovebox and transferred to reaction flasks connected to a Schlenk line under nitrogen flow.

A1.2. Estimation of absolute photoluminescence quantum yields

All PL spectra of colloidal solutions were measured at optical densities at the excitation wavelength between 0.10 and 0.14. The small values of optical density guaranty that no artifacts can arise from different light penetration depths and readsorption of emitted light. The photoluminescence excitation spectra were found to be nearly identical to the absorption spectra in a wide spectral region for all samples studied. The latter indicates no dependence of the emission spectra on the excitation wavelength. If not specially mentioned in text, an excitation wavelengths of 400 nm were used for CdSe, CdTe, CdSe/CdS, CdS/ZnS and InP nanocrystals and of 600 nm for InAs nanocrystals. To compare the PL efficiencies of different samples, we normalized each PL spectrum with respect to the absorbed light intensity at the excitation wavelength and subsequently integrated the PL intensity vs. photon energy over the entire emission spectrum. The absolute values of room temperature PL efficiency of nanocrystals were estimated by comparison with solutions of Rhodamin 6G in ethanol (CdSe), quinine in aqueous 0.5 M H₂SO₄ (CdTe) and IR 125 dye (Lambda Physik) in DMSO (InAs). We used literature values for the room temperature PL efficiencies of these dyes, i.e., 0.95 [3], 0.55 [4], and 0.13 [2], respectively. We did not correct the values of quantum yield for different refractive indexes of the various solvents. The error is, however, smaller than 5% for the solvents used. The measurement error of the PL quantum yield was estimated to be about 10%.

A1.3. Organometallic synthesis of CdSe nanocrystals

One milliliter of 1.26 M solution of tri-*n*-octylphosphine selenide (TOPSe, 1.26 mmol) in TOP, prepared by dissolving Se shot in TOP, was mixed with 0.11 mL of dimethylcadmium (1.47 mmol). This stock solution was transferred to a 50 mL three-neck flask containing a vigorously stirred warm (40°C) mixture of 5 mL of DDA and 5 mL of TOP. The temperature was gradually increased up to 90-140°C depending on the desirable size of the CdSe nanocrystals. The growth was monitored by measuring the absorption spectra of aliquots extracted from the reaction solution. For instance, highly monodisperse CdSe nanocrystals with an average size of ~1.5 nm exhibiting bright blue emission peaked at 460 nm with QE 17% were obtained by heating the reaction mixture at 110°C for three days. Finally, the reaction mixture was cooled to room temperature and 20 mL of toluene was

added under stirring. This method yielded CdSe nanocrystals with sizes ranging from 1.2 to ~2.5 nm and band edge PL (QE ~20%) covering the spectrum from blue to green. When left in crude solution, the smallest CdSe nanocrystals have a tendency to grow slowly even at room temperature and therefore have to be immediately isolated by size-selective precipitation to keep the size distribution narrow. Particles of larger size (up to ~5.0 nm) can be synthesized either by additional injection of stock solution to the CdSe colloids or by using three-component mixtures containing amine, TOPO and TOP as size-regulating solvents. In the latter case, rapid injection of stock solution at 300°C permits to achieve a very narrow particles size distribution, which shows negligible broadening during the particle growth. In a typical synthesis, 1 mmol of TOPSe and 1.35 mmol of dimethylcadmium were dissolved in 5 mL of TOP and rapidly injected into a vigorously stirred mixture of 10 g of TOPO (55 mol%) and 5 g of HDA (45 mol%) heated to 300°C. Injection resulted in an immediate nucleation of nanoparticles displaying a broad adsorption maximum around 450 nm. Further growth occurred at 250-310°C depending on the desirable size. The ratio between TOPO and HDA strongly affected the growth kinetics. The general tendency was, that with increasing HDA content the initial particle size and the growth rate decreased. In mixtures containing more than about 80 mol% of HDA, precipitation of CdSe nanocrystals was observed above 200°C. To prepare CdSe nanocrystals with sizes above 4.5-5.0 nm, additional injections of stock solution were required.

Isolated nanocrystals were stable both under nitrogen and in air over months, retaining their photoluminescence properties.

A1.4. Synthesis of CdSe/ZnS core-shell nanocrystals

In a typical synthesis of CdSe/ZnS core-shell nanocrystals, 2.5 mL of the crude solution of CdSe nanocrystals prepared as described in Section A1.1.1 were mixed with 5 g of TOPO and 2.5 g of HDA and heated to 220°C. The amount of Zn:S stock solution (see below) necessary to obtain the desired shell thickness was calculated from the ratio between the core and shell volumes using bulk lattice parameters of CdSe and ZnS. This amount was then added dropwise to the vigorously stirred solution of CdSe nanocrystals. After addition of ZnS shell precursors, the temperature was decreased to 90°C and heating was continued for 1h. The core-shell nanocrystals can be isolated from the growth solution via the same procedure that was applied to “bare” CdSe nanocrystals (see Section A1.2). A maximum of the photoluminescence quantum efficiency (~70%) was observed for a ~1.6 monolayers thick

ZnS shell and was reproducibly 50% or above for a wide range of shell thicknesses and core sizes.

Composition of the Zn:S stock solution: 0.4 mmol of diethylzinc and 0.51 mmol of bis-trimethylsilylsulfide in 3 mL of TOP

A1.5. Synthesis of CdSe/ZnS nanocrystals – polylaurylmethacrylate composites.

CdSe/ZnS core-shell nanocrystals were synthesized as described in Section A1.3. The synthesized nanocrystals were isolated from the growth solution and then redispersed into laurylmethacrylate monomer with TOP (~5 vol. %). Then, ethyleneglycol dimethacrylate crosslinker was added to the solution of nanocrystals in monomer with 1:4 volume ratio of cross-linker to monomer. After azobisisobutyronitrile (AIBN) radical initiator (<1 wt. %) was added, the final solution was transferred to a glass tube with diameter of 5 mm and polymerized in an oven at 70-75 °C for 2 h. A high-clarity QD-polymer composite rod was then removed from the glass mold.

A1.6. Organometallic Synthesis of amino-stabilized CdTe nanocrystals.

Method A. Five grams of dodecylamine (DDA) were dissolved in 7 ml of tri-*n*-octylphosphine (TOP) at 50°C in a 50 mL two-neck flask with a reflux condenser attached. Subsequently, 0.11 mL (1.47 mmol) of dimethylcadmium and 0.128 g (1 mmol) of tellurium powder were added under stirring and the temperature was slowly increased to 180°C. After 30 min the temperature was raised to 200°C, and growth of the nanocrystals was allowed to proceed at this temperature for 20 hours. Under these conditions tellurium slowly dissolves in the reaction mixture, resulting in a very slow growth of CdTe nanocrystals at sufficiently high temperatures. Finally, toluene was added to the warm solution and the mixture was left for 24 hours at room temperature under stirring.

This method allowed to obtain CdTe nanocrystals in the size range of 4.0 – 6.0 nm emitting from yellow to red with extremely high PL quantum yields exceeding 60%.

Method B. 0.65 g of tellurium were dissolved in 10 mL of TOP by overnight heating at 220°C. After cooling to room temperature, 1.96 mL of the resulting greenish-yellow solution were mixed with 0.11 mL (1.47 mmol) of dimethylcadmium and 3 mL of TOP. This mixture was loaded into a 5 mL syringe and injected into ten grams of DDA vigorously stirred at 150°C in a 50 mL two-neck flask with attached reflux condenser. Directly before injection, the heater from the reaction flask has been removed. The deep-yellow transparent solution

obtained after injection slowly changed its color to bloody-red with time. Heating was resumed after approx. 10-15 min when the temperature of the reaction mixture had reached 90-100°C. This initiated further slow growth of the particles which was monitored by measuring the absorption and photoluminescence spectra of the reaction mixture at regular intervals of time.

The temperature and the duration of growth determine the final size of the particles. Yellow-emitting CdTe nanocrystals with an average size of ca. 3 nm, for instance, were obtained by heating the reaction mixture between 150 and 180°C for a few hours only. The largest particles were prepared by overnight (10-12 hours) heating at 200°C. By this method, CdTe nanocrystals with mean sizes ranging from 2.5 to 5 nm have been obtained. They show strong band-gap emission with quantum yields exceeding 30%. Depending on particle size, emission colors between green and red are observed. CdTe nanocrystals of larger size (up to app. 7.0 nm) were grown by the dropwise addition of mixed Cd and Te precursors (the same amounts as used for the synthesis itself). Before this additional injection, the reaction mixture was cooled to 70°C. After injection, the temperature was raised to 100°C for 3 hours with subsequent annealing at 180°C. After completion of the particle growth and cooling the reaction mixture to ~50°C, 20 mL of toluene was added to the solution and the mixture was left for 24 hours at room temperature under permanent stirring.

Isolation of CdTe nanocrystals. Aliquots of 5 mL were removed from the reaction mixture, cooled to ~ 70-80°C and mixed with 10 mL of anhydrous toluene to prevent DDA from solidification. After byproducts and unreacted tellurium had been removed by passing the mixture through a 0.22 µm membrane filter (Millipore), the standard solvent/nonsolvent size selective precipitation procedure was carried out by adding small volumes of methanol to the mixture and collecting the precipitate by filtration. Isolated fractions of CdTe nanocrystals were readily dispersible in a variety of organic solvents such as toluene, n-hexane, CH₂Cl₂ etc. The luminescence efficiency was stable during the storage of the redispersed CdTe crystallites in a glovebox over months. The storage of the crude colloidal solution of CdTe nanoparticles inside the glovebox for several weeks resulted in a slight enhancement of their band edge PL quantum yield.

A1.7. Aqueous Synthesis of thiol-stabilized CdTe nanocrystals

In a typical synthesis (Figure A1.1) 0.985 g (2.35 mmol) of Cd(ClO₄)₂·6H₂O is dissolved in 125 mL of water, and 5.7 mmol of the thiol stabilizer (Table 3.2 shows mercapto-compounds

used as capping agents) are added under stirring, followed by adjusting the pH to the appropriate values (depending on the stabilizer nature, see Table 3.2) by dropwise addition of 1 M solution of NaOH. Occasionally, the solution can remain slightly turbid at this stage because of the incomplete solubility of Cd thiolate complexes, but this does not influence the further synthesis. The solution is placed in a three-necked flask fitted with a septum, connected to the Schlenk line and is deaerated by N₂ bubbling for ~ 20 min. Under stirring, H₂Te gas (generated by the reaction of 0.2 g (0,46 mmol) of Al₂Te₃ lumps with 15-20 mL of 0.5 M H₂SO₄ under N₂ atmosphere) is passed through the solution together with a slow nitrogen flow for ~ 20 min. CdTe precursors are formed at this stage which is accompanied by a change of the solution color, depending on the thiols used, to yellow (1-thioglycerol (TG), mercaptoethanol (ME)), orange (thioglycolic acid (TGA)) or dark-red (2-mercaptoethylamine (MA), 2-(dimethylamino)ethanethiol). They show an absorption spectrum being unstructured in the visible spectral region with a tail extending to 650-700 nm, and no luminescence. The precursors are converted to CdTe nanocrystals by refluxing the reaction mixture at 100°C (with condenser attached, under open-air conditions). A clearly resolved absorption maximum of the first electronic transition of CdTe QDs appears at ~420 nm corresponding to the smallest CdTe nanocrystals (<2 nm size) which shifts to longer wavelengths as the particles grow in the course of heating. Green (luminescence maximum at ~510 nm) band-edge emission appears when the CdTe nanocrystals reach the size of ~2 nm. Thus, the size of the growing CdTe QDs is controlled by the duration of refluxing and can easily be monitored by absorption and PL spectra. The duration of the heat treatment necessary to reach a certain particle size depends on the nature of the stabilizer. Thus, it takes 2-3 days to grow ~5 nm large CdTe nanocrystals (luminescence maximum at ~ 650 nm) in the presence of thioglycolic acid or mercaptoethylamine and up to 12 days when thioglycerol is used as a stabilizer. To grow larger CdTe nanocrystals with the emission spreading into the near IR (PL maximum up to 730 nm) additional injections of precursors are applied.

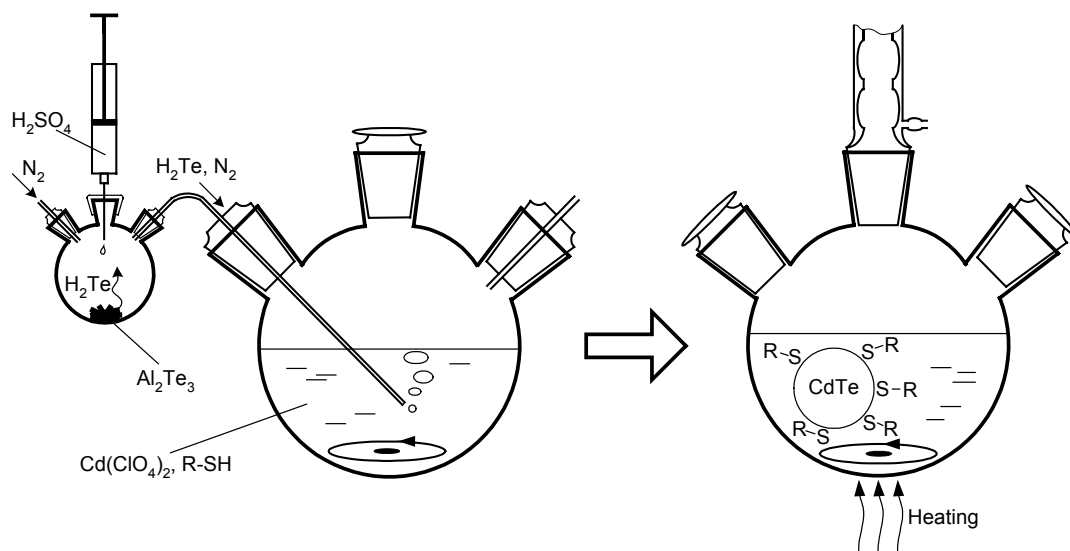


Figure A1.1. Schematic presentation of the synthesis of thiol-capped CdTe QDs.

A1.8. Organometallic synthesis of amino-stabilized InP nanocrystals

A 0.63 M solution of InCl_3 in TOP was prepared by stirring 0.7 g of anhydrous InCl_3 with 5 mL of TOP at 100°C for several hours. This solution was cooled to room temperature, mixed inside the glovebox with 0.78 mL of $(\text{TMS})_3\text{P}$ and injected into a 50 mL three-neck flask containing 10 g of DDA heated to 150°C . The temperature of 150°C was kept for 4 h. Thereafter it was increased to 240°C and the further growth of InP nanoparticles continued at this temperature for 48 h. Aliquots were removed to monitor the growth of nanocrystals in time. In general, heating at 240°C for extended periods of time resulted in a marked improvement of the size distribution and the crystallinity of the nanoparticles. By this method, InP nanocrystals with mean sizes ranging from 1.5 to 4.0 nm have been prepared. They show a relatively weak PL (both band edge and trapped) with $\text{QE} < 1\%$. Colloidal solutions of nanocrystals isolated from crude solutions were stable for months when kept under nitrogen.

A1.9. Etching of InP nanocrystals with fluorine compounds.

The TOPO-TOP stabilized InP nanocrystals were prepared as described in Ref.[1] and subjected to size-selective precipitation to isolate nearly monodisperse nanocrystal fractions. The concentration of InP nanocrystals in each size-selected fraction was estimated from the UV-Vis spectrum using the extinction coefficients known for InP nanocrystals (see details in Chapter 4). An aliquot of InP nanocrystals containing $\sim 1 \cdot 10^{-7}$ mol of particles dispersed in

hexane or toluene was mixed with 25 mL of n-butanol and 0.25 g of TOPO were added. This mixture was loaded into a 50 mL vessel from transparent PFE (Teflon) and 50-200 μ L of HF-containing etching solution were added under stirring. The HF-etching solution was prepared by mixing 0.527 mL of aqueous HF (40 wt. % solution), 0.065 mL of H₂O and 5.0 mL of n-butanol. Immediately after the addition of HF, the reaction mixture was irradiated with light passed through a cut-off filter with the cut-off wavelength depending on the particle size (see details in Chapter 4). A 450 W xenon lamp was used as the light source. The process of etching is finished after approx. 20 h. Highly luminescent HF-etched InP nanocrystals can be isolated from the reaction mixture by the addition of ca. 25 mL of CH₃CN, centrifugation of the suspension of flocculated nanocrystals and subsequent re-dispersing them in hexane. Properly etched InP nanocrystals exhibit strong band edge luminescence with a PL quantum efficiency of about 20-30% and color tunable from green to near-IR with increasing particle size. Isolated nanocrystals were stable both under nitrogen and in air over months, retaining their photoluminescence properties.

A1.10. Organometallic synthesis of InAs nanocrystals.

First, a concentrated solution of InCl₃ in TOP was prepared by dissolving 9 g of InCl₃ in 30 mL of TOP at 260 °C. In a typical synthesis, 0.76 mL of this InCl₃·TOP solution were mixed with 0.24 mL of tris-trimethylsilylarsine and swiftly injected into 4 mL of TOP heated previously to 300°C. Immediately after injection of the stock solution, the reaction mixture was cooled to 260 °C for further growth. The size of the growing InAs nanocrystals was controlled by the duration of heating. Additional injections of precursors were required to prepare nanocrystals larger than ~4 nm. Upon reaching the desired size, the reaction mixture was allowed to cool to room temperature and anhydrous toluene was added. To isolate the nanocrystals from crude solution, the particles were precipitated by adding anhydrous methanol and separated by centrifugation. The precipitate could be easily re-dissolved in hexane or toluene.

A1.11. Synthesis of InAs/CdSe core-shell nanocrystals.

TOP-stabilized InAs nanocrystals were prepared as described in Section A1.9 and subjected to the size selective precipitation procedure to isolate monodisperse fractions of the desired size. All manipulations were performed inside the glovebox. The concentration of

InAs nanocrystals in each size-selected fraction was estimated from the absorption spectrum as described in Chapter 4. An aliquot containing about 10 mg of InAs nanocrystals in hexane was mixed with 6 mL of TOP and the hexane was pumped off. The solution was heated up to 260°C and the desired amount of Cd:Se stock solution was added dropwise to the hot solution. About 5 min after addition of the last portion of stock solution the reaction mixture was cooled to room temperature.

The composition of the Cd:Se stock solution was the same as the one used in synthesis of bare CdSe nanocrystals (see Section A1.2) The amount of stock solution employed was calculated as described in Section A1.2. To separate the nanocrystals from crude solution, they were precipitated by adding anhydrous methanol, centrifugated and the precipitate was re-dissolved in hexane or toluene.

A1.12. Crystallization of CdSe Nanoparticles in Ordered 3D Superlattices.

CdSe nanocrystals have been synthesized either in a TOPO-TOP or in a HDA-TOPO-TOP mixtures as described in Section A1.2. To precipitate TOPO-TOP capped CdSe nanocrystals size-selectively, 40 mL of 1-butanol were added to 4 mL of the crude CdSe solution. The solution was filtrated and methanol was slowly added. The precipitated nanocrystals were isolated by filtration, washed thoroughly with methanol and re-dissolved in toluene. In the case of HDA-TOPO-TOP capped nanocrystals, toluene and ethanol were used as solvent and non-solvent, respectively.

The crystallization of CdSe quantum dots has been carried out in vertically positioned glass tubes of 20 cm in length and 0.8 cm in diameter. They were filled with colloidal solutions of CdSe nanocrystals in toluene (~ 1.1 mg/mL) to a height of ~6 cm and then either with methanol only (6 cm in high) or with propanol-2 (2 cm in high) and methanol (6 cm in high). The tubes were left in darkness for two months.

Reference

1. Haubold, S. PhD thesis “*Synthese und Charakterisierung von III-V Halbleiter-Nanoclustern*” University of Hamburg, Hamburg 2000.
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Appendix 2

Evolution of a single nanoparticle (NP) in a colloidal solution

Consider a model describing the behavior of a single NP of radius r placed in an infinite volume of solution with a constant concentration of monomer, thereafter referred to as the bulk concentration $[M]$. The monomer can react with the surface, thereby adding a new unit to the particle (NP grows) or can leave the surface, thereby removing one unit (NP dissolves). Both processes occur along the reaction path including the activated complex with the chemical potential $^{\ddagger}\mu$ (Figure 6.1). The resulting activation energies for growth and dissolution of the NP are $\Delta^{\ddagger}\mu_g$ and $\Delta^{\ddagger}\mu_d$, respectively. The chemical potential of the solid depends on the curvature of the surface by means of the Kelvin equation [1], and the activation energy $\Delta^{\ddagger}\mu$ is a function of the particle radius:

$$\Delta^{\ddagger}\mu_g(r) = \Delta^{\ddagger}\mu_g^{\infty} + \alpha \frac{2\gamma V_m}{r} \quad (1)$$

$$\Delta^{\ddagger}\mu_d(r) = \Delta^{\ddagger}\mu_d^{\infty} - \beta \frac{2\gamma V_m}{r} \quad (2)$$

where α and β are the transfer coefficients ($\alpha + \beta = 1$); $\Delta^{\ddagger}\mu^{\infty}$ is the activation energy in the case of a flat interface.

In the framework of the theory of the activated complex, the rate constant can be expressed through the height of the activation barrier [1]:

$$k = B \exp(-\Delta^{\ddagger}\mu / RT) \quad (3)$$

where B is a constant with the same dimension as k .

In the case of the polynuclear-layer growth mechanism [2], which seems to be the most probable for NPs in colloidal solution, the flux of monomer J_g^{react} towards the particle surface is described by a first-order surface reaction:

$$J_g^{react} = 4\pi r^2 k_g [M]_r = 4\pi r^2 k_g^{flat} [M]_r \exp\left[-\alpha \frac{2\gamma V_m}{rRT}\right] \quad (4)$$

where $[M]_r$ is the concentration of the monomer near the particle surface and $k_g^{flat} = B_g \exp(-\Delta^{\ddagger}\mu_g^{\infty} / RT)$ is the growth rate constant for growth of a flat ($r=\infty$) surface.

In the simple case when the rate of the dissolution of a solid does not depend on the monomer concentration in solution, the flux of monomer J_d^{react} toward the particle surface can be expressed as follows:

$$J_d^{react} = -4\pi r^2 k_d = -4\pi k_d^{flat} r^2 \exp\left[\beta \frac{2\gamma W_m}{rRT}\right] \quad (5)$$

where $k_d^{flat} = B_d \exp(-\Delta^\ddagger \mu_d^\infty / RT)$ is the dissolution rate constant for a flat ($r=\infty$) interface.

The ratio between k_d^{flat} and k_g^{flat} gives the equilibrium constant for the dissolution of the bulk material $K_{eq} = a_{solute} / a_{solid} \approx C_0^{flat}$ (a is the activity of a component):

$$K_{eq} = k_d^{flat} / k_g^{flat} = C_0^{flat} \quad (6)$$

Diffusion of the monomer from the bulk of solution towards the particle surface is expressed by Fick's first law:

$$J^{diff} = 4\pi x^2 D \left(\frac{d[M]}{dx} \right)_{x \geq r} \quad (7)$$

where D is the diffusion coefficient and x is the distance from the center of the particle.

Integration of $[M]$ from $r+\delta$ to r , where δ is the thickness of the diffusion layer, gives the steady state flux towards an isolated spherical particle [3,4]:

$$J^{diff} = \frac{4\pi D r (r+\delta)}{\delta} ([M]_{bulk} - [M]_r) \quad (8)$$

where $[M]_{bulk}$ is the monomer concentration in the bulk of solution, δ is the thickness of the diffusion layer.

As was mentioned by Peng et al. [5], under real conditions the size of the NP is negligible compared to the thickness of the diffusion layer ($r \ll \delta$) and Eq. (8) can be simplified:

$$J^{diff} = 4\pi D r ([M]_{bulk} - [M]_r) \quad (9)$$

Note, that upon stirring of the solution, the diffusion coefficient has to be replaced by the mass-transfer coefficient which can be calculated or experimentally estimated for any particular case.

Under steady-state conditions the number of monomer units added and removed from the particle surface have to be equal to those diffusing toward the particle from the bulk of the solution. Hence,

$$J_g^{react} + J_d^{react} = J^{diff} \quad (10)$$

Substitution of Eqs. (4), (5) and (9) into Eq. (10) allows expressing the stationary concentration of the monomer near the particle interface:

$$[M]_r = \frac{D[M]_{bulk} + rk_d^{flat} \exp\left[\beta \frac{2\gamma V_m}{rRT}\right]}{rk_g^{flat} \exp\left[-\alpha \frac{2\gamma V_m}{rRT}\right] + D} \quad (11)$$

In the case of purely diffusion-controlled dissolution the stationary concentration estimated from Eq.(11) tends to the equilibrium value described by the Gibbs-Thompson equation.

Substitution of the stationary monomer concentration into Eq.(9) gives the expression for the total flux of monomers toward the particle surface. On the other hand, J^{diff} is related to the particle growth rate dr/dt as [3]:

$$J^{diff} = (4\pi r^2/V_m) \frac{dr}{dt} \quad (12)$$

The resulting expression for the size dependent rate of the particle radius evolution obtained from Eqs. (9), (11) and (12) is:

$$\frac{dr}{dt} = V_m DC_{flat}^0 \left\{ \frac{\frac{[M]_{bulk}}{C_{flat}^0} - \exp\left[\frac{2\gamma V_m}{rRT}\right]}{r + \frac{D}{k_g^{flat}} \exp\left[\alpha \frac{2\gamma V_m}{rRT}\right]} \right\} \quad (13)$$

or

$$\frac{dr^*}{d\tau} = \frac{S - \exp\left[\frac{I}{r^*}\right]}{r^* + K \exp\left[\frac{\alpha}{r^*}\right]} \quad (14)$$

The parameters of Eq. (14) which will be further used in our simulations are:

$$\text{dimensionless radius } r^* = \frac{RT}{2\gamma V_m} r \quad (15)$$

$$\text{dimensionless time } \tau = \frac{R^2 T^2 DC_{flat}^0}{4\gamma^2 V_m} t \quad (16)$$

$$K = \frac{RT}{2\gamma V_m} \frac{D}{k_g^{flat}} \quad (17)$$

$$S = [M]_{bulk} / C_{flat}^0 \quad (18)$$

K is a dimensionless parameter describing the type of the control of the process (the ratio between diffusion and reaction rate constants for a flat interface); S is a dimensionless parameter describing the oversaturation of the monomer in solution.

References

1. Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry*, Oxford University Press, Oxford, **2000**.
2. Nielsen, A. E. *Kinetics of precipitation*. Oxford. New York **1964**.
3. Sugimoto, T. *Adv. Colloid Interfac. Sci.* **1987**, 28, 65.
4. Zener, C. *J. Appl. Phys.* **1949**, 20, 950.
5. Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, 123, 1389.

Appendix 3

Safety precaution information on the used chemicals

Substance	R-phrases	S-phrases	Hazard signs
Acetone	11-36-66-67	9-16-26	[F][Xi]
Al ₂ Te ₃	Not fully examined compound		
Bis-trimethylsilylsulphide	10-36/37/38	16-26-37/39	[Xi]
Butanol	60-20-37/38-41	16-45-53-36/37/39	[F][Xn]
Cd(ClO ₄) ₂ ·6H ₂ O	20/21/22-9-49	17-22-45-53	[T][O]
Diethylzinc	34-20/21/22-14	16-3/7-45-36/37/39	[F][C][Xn]
Dimethylcadmium	17-20/21/22	7/8-16-23-45- 36/37/39	[T+][F][C]
Dodecanethiol	36/37/38	26-28	[F][Xi]
Dodecylamine	22-35	26-28.1-36/37/39-45	[C]
Ethanol	11	7-16	[F]
Hexadecylamine	34	26-36/37/39-45	[C]
Hexane	11-48/20	9-16-24/25-29-51	[F][Xn][N]
InCl ₃	36/37/38	22-26-36/37/	[C][Xi]
Isopropanol	11	7-16	[F][Xi]
Methanol	11-23/25	7-16-24-45	[F][T+]
Na/K-alloy	34-14/15	16-26-27-36/37/39	[F]
Selenium	23/25-33	S 20/21-28-45	[T+][F]
Tellurium	10-25	22-28-36/37/39-45	[T+][F]
Thioglycolic acid	23/24/25-34	25-27-28-45	[T]
Toluene	11-20	16-25-29-33	[F][Xn]
Tri-n-butylphosphine	17-34	16-26-27-36/37/39	[C][Xi]
Trimethylsilylchloride	11-14-34	16-26-29	[F][C]
Trioctylphosphine	36/37/38	26-36	[Xi]
Trioctylphosphine oxide	34-50/53	26-36/37/39-45-60-61	[C][Xi]
Tris-trimethylsilylarsine	17-23/25-36/37/38	16-26-27-28-20/21- 36/37/39	[T+]
Tris-trimethylsilylphosphine	17-36/37/38	16-26-27-28-36/37/39	[T]

A3.2. Risk (R-) and safety precaution (S-) phrases used in the classification, packaging, labelling and provision of information on dangerous substances

Risk phrases (R-Phrases)

- R1: Explosive when dry
- R2: Risk of explosion by shock, friction fire or other sources of ignition
- R3: Extreme risk of explosion by shock friction, fire or other sources of ignition
- R4: Forms very sensitive explosive metallic compounds
- R5: Heating may cause an explosion
- R6: Explosive with or without contact with air
- R7: May cause fire
- R8: Contact with combustible material may cause fire
- R9: Explosive when mixed with combustible material
- R10: Flammable
- R11: Highly flammable
- R12 : Extremely flammable
- R13: Extremely flammable liquefied gas
- R14: Reacts violently with water
- R15: Contact with water liberates highly flammable gases
- R16: Explosive when mixed with oxidising substances
- R17: Spontaneously flammable in air
- R18: In use, may form flammable/explosive vapour-air mixture
- R19: May form explosive peroxides
- R20: Harmful by inhalation
- R21: Harmful in contact with skin
- R22: Harmful if swallowed
- R23: Toxic by inhalation
- R24: Toxic in contact with skin
- R25: Toxic if swallowed
- R26: Very toxic by inhalation
- R27: Very toxic in contact with skin
- R28: Very toxic if swallowed
- R29: Contact with water liberates toxic gas
- R30: Can become highly flammable in use
- R31: Contact with acids liberates toxic gas
- R32: Contact with acids liberates very toxic gas
- R33: Danger of cumulative effects
- R34: Causes burns
- R35: Causes severe burns
- R36: Irritating to eyes
- R37: Irritating to respiratory system
- R38: Irritating to skin
- R39: Danger of very serious irreversible effects
- R40: Possible risk of irreversible effects
- R41: Risk of serious damage to eyes
- R42: May cause sensitisation by inhalation
- R43: May cause sensitisation by skin contact
- R44: Risk of explosion if heated under confinement
- R45: May cause cancer
- R46: May cause heritable genetic damage
- R47: May cause birth defects
- R48: Danger of serious damage to health by prolonged exposure
- R49: May cause cancer by inhalation
- R50: Very toxic to aquatic organisms

R51: Toxic to aquatic organisms
R52: Harmful to aquatic organisms
R53: May cause long-term adverse effects in the aquatic environment
R54: Toxic to flora
R55: Toxic to fauna
R56: Toxic to soil organisms
R57: Toxic to bees
R58: May cause long-term adverse effects in the environment
R59: Dangerous to the ozone layer
R60: May impair fertility
R61: May cause harm to the unborn child
R62: Possible risk of impaired fertility
R63: Possible risk of harm to the unborn child
R64: May cause harm to breastfed babies

Combination of risks

R14/15: Reacts violently with water, liberating highly flammable gases
R15/29: Contact with water liberates toxic, highly flammable gas
R20/21: Harmful by inhalation and in contact with skin
R20/21/22: Harmful by inhalation, in contact with skin and if swallowed
R20/22: Harmful by inhalation and if swallowed
R21/22: Harmful in contact with skin and if swallowed
R23/24: Toxic by inhalation and in contact with skin
R23/24/25: Toxic by inhalation, in contact with skin and if swallowed
R23/25: Toxic by inhalation and if swallowed
R24/25: Toxic in contact with skin and if swallowed
R26/27: Very toxic by inhalation and in contact with skin
R26/27/28: Very toxic by inhalation, in contact with skin and if swallowed
R26/28: Very toxic by inhalation and if swallowed
R27/28: Very toxic in contact with skin and if swallowed
R36/37: Irritating to eyes and respiratory system
R36/37/38: Irritating to eyes, respiratory system and skin
R36/38: Irritating to eyes and skin
R37/38: Irritating to respiratory system and skin
R42/43: May cause sensitisation by inhalation and skin contact.
R48/20: Harmful: danger of serious damage to health by prolonged exposure
R48/20/21: Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with the skin
R48/20/21/22: Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R48/20/22: Harmful: danger of serious damage to health by prolonged exposure through inhalation, and if swallowed
R48/21: Harmful: danger of serious damage to health by prolonged exposure in contact with skin
R48/21/22: Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/22: Harmful: danger of serious damage to health by prolonged exposure if swallowed
R48/23: Toxic: danger of serious damage to health by prolonged exposure through inhalation
R48/23/24: Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin
R48/23/24/25: Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R48/23/25: Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/24: Toxic: danger of serious damage to health by prolonged exposure in contact with skin
R48/24/25: Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed

R48/25: Toxic: danger of serious damage to health by prolonged exposure if swallowed

R50/53: Very toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment

R51/53: Toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment

R52/53: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Safety precaution phrases (S-Phrases)

S1: Keep locked up

S2: Keep out of reach of children

S3: Keep in a cool place

S4: Keep away from living quarters

S5: Keep contents under . . . (appropriate liquid to be specified by the manufacturer)

S6: Keep under . . . (inert gas to be specified by the manufacturer)

S7: Keep container tightly closed

S8: Keep container dry

S9: Keep container in a well ventilated place

S12: Do not keep the container sealed

S13: Keep away from food, drink and animal feeding stuffs

S14: Keep away from . . . (incompatible materials to be indicated by the manufacturer)

S15: Keep away from heat

S16: Keep away from sources of ignition-No Smoking

S17: Keep away from combustible material

S18: Handle and open container with care

S20: When using do not eat or drink

S21: When using do not smoke

S22: Do not breathe dust

S23: Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by manufacturer)

S24: Avoid contact with skin

S25: Avoid contact with eyes

S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

S27: Take off immediately all contaminated clothing

S28: After contact with skin, wash immediately with plenty of . . . (to be specified by the manufacturer)

S29: Do not empty into drains

S30: Never add water to this product

S33: Take precautionary measures against static discharges

S34: Avoid shock and friction

S35: This material and its container must be disposed of in a safe way

S36: Wear suitable protective clothing

S37: Wear suitable gloves

S38: In case of insufficient ventilation, wear suitable respiratory equipment

S39: Wear eye/face protection

S40: To clean the floor and all objects contaminated by this material use (to be specified by the manufacturer)

S41: In case of fire and/or explosion do not breath fumes

S42: During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer)

S43: In case of fire, use ... (indicate in the space the precise type of fire fighting equipment. If water increases the risk, add "never use water")

S44: If you feel unwell, seek medical advice (show the label where possible)

S45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)

S46: If swallowed, seek medical advice immediately and show the container or label

S47: Keep at temperature not exceeding ... °C (to be specified by the manufacturer)

S48: Keep wetted with ... (appropriate material to be specified by the manufacturer)
S49: Keep only in the original container
S50: Do not mix with ... (to be specified by the manufacturer)
S51: Use only in well ventilated areas
S52: Not recommended for interior use on large surface areas
S53: Avoid exposure - obtain special instructions before use
S54: Obtain the consent of pollution control authorities before discharging to waste-water treatment plants
S55: Treat using the best available techniques before discharge into drains or the aquatic environment
S56: Do not discharge into drains or the environment, dispose to an authorised waste collection point
S57: Use appropriate containment to avoid environmental contamination
S58: To be disposed of as hazardous waste
S59: Refer to manufacturer/supplier for information on recovery/recycling
S60: This material and/or its container must be disposed of as hazardous waste
S61: Avoid release to the environment. Refer to special instructions / safety data sheet
S62: If swallowed, do not induce vomiting: seek medical advice immediately and show the container or label

Combined safety phrases

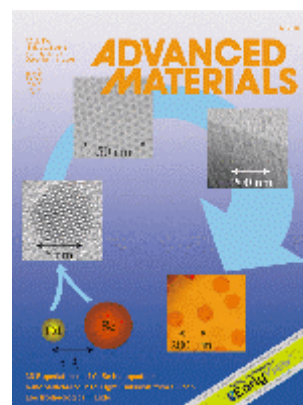
S1/2: Keep locked up and out of reach of children
S3/9: Keep in a cool, well ventilated place
S3/7/9: Keep container tightly closed in a cool, well ventilated place
S3/14: Keep in a cool place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/14: Keep in a cool, well ventilated place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/49: Keep only in the original container in a cool, well ventilated place
S3/9/14/49: Keep only in the original container in a cool, well ventilated place away from (incompatible materials to be indicated by the manufacturer)
S3/9/49: Keep only in the original container in a cool, well ventilated place
S3/14: Keep in a cool place away from...(incompatible materials to be indicated by the manufacturer)
S7/8: Keep container tightly closed and dry
S7/9: Keep container tightly closed and in a well ventilated place
S7/47: Keep container tightly closed and at a temperature not exceeding...°C (to be specified by manufacturer)
S20/21: When using do not eat, drink or smoke
S24/25: Avoid contact with skin and eyes
S29/56: Do not empty into drains, dispose of this material and its container to hazardous or special waste collection point
S36/37: Wear suitable protective clothing and gloves
S36/37/39: Wear suitable protective clothing, gloves and eye/face protection
S36/39: Wear suitable protective clothing, and eye/face protection
S37/39: Wear suitable gloves and eye/face protection
S47/49: Keep only in the original container at temperature not exceeding...°C (to be specified by the manufacturer)

Appendix 4

Publications and Presentations

A4.1 First Author

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A4.3 Conference Oral Presentations

“Organometallic synthesis and characterization of amino-stabilized colloids of the semiconductor nanocrystals.” NATO Advanced Research Workshop on Nanoparticle-Based Nanostructures, Vigo, Spain, October 2000.

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Declaration

The material contained in this thesis is the result of my own work and all sources of information as well as the results obtained in collaboration with other people are pointed out.

This dissertation has not been submitted in whole or in part for the award of a degree at this or any other university.

Hamburg, February 2002

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