

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.