The assembling of semiconductor and metal nanocrystals

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The reported synthesis of strongly luminescent semiconductor nanocrystals is based on the wet-chemical approach. The use of water as the solvent and avoiding of dangerous and unstable precursors make this synthetic approach to be easily up-scaleable. The reaction yields are approaching approx. 1 g of the dried product and are limited solely by the laboratory facilities. They may be further increased by using industrial equipment. The nanocrystals obtained by this route are strongly luminescing and suitable for various assembling procedures allowing the creation of core-shell spherical and thin-film composites that are promising for photonic and optoelectronic applications. New assembly procedures allowing the template-based formation of different types of metal-dielectric and porous metal nanostructures are also presented.

1. INTRODUCTION

Ordered assemblies of nanocrystalline materials receive increasing interest in recent years. Nanoparticles (often referred to as artificial atoms) are used to build up artificial molecules and solids. These arrays and superlattices offer new perspectives for the application of nanoparticles for example in optoelectronic devices. Various approaches towards assembling of nanocrystals are known. Three dimensional superlattices of semiconductor nanoparticles have been built up via self organization and crystallization. Another main route towards ordered structures of nanocrystals is covalent binding with and without special linker molecules. These efforts have a direct correlation to the investigations in the fields of covalent coupling of nanoparticles to biomolecules and surface functionalization of nanocrystals. Here we report on recent advances made in our group in the synthesis of the nanocrystals as well as in the preparation and the characterization of various assemblies of them.

2. RESULTS AND DISCUSSION

2.1. Synthesis of ZnSe, CdTe, HgTe and CdHgTe nanocrystals

In a typical synthesis corresponding metal ions (Zn²⁺, Cd²⁺, Hg²⁺) react under N₂ atmosphere in aqueous solution with the H₂Te or H₂Se gas in the presence of the thiol-stabilizer (1-thioglycerol, 2-mercaptoethanol, thioglycolic acid (TGA), mercaptopropionic acid (MPA), 2-(dimethylamino)ethanethiol), 2-mercaptoethylamine, etc.). The adjusting of the pH to the appropriate values (depending on the stabilizer nature: 5.6-5.9 for amino-thiols and 10-12 for the rest) as well as the proper choice of absolute and relative concentrations of the reaction components allow efficient controlling of the reaction rate, quality of the product and its photoluminescence (PL) quantum efficiency. The nanocrystals (NCs) grow with the time of reflux at 100°C or upon mixing at room temperature in the case of HgTe. The size of the NCs growing can easily be monitored by absorption and PL spectra. For HgTe typically 2 hours of mixing at room temperature is enough to get high-concentrated solutions of strongly near-infrared emitting HgTe NCs of ca. 4 nm size. Moreover, the post-preparative addition of controlled amounts of Hg perchlorate in the colloidal solution of CdTe NCs allows to synthesize alloyed CdHgTe NCs which luminescence cover the intermediate spectral region between 800 and 1300 nm. Fig. 1 shows typical room temperature PL spectra of a size series of CdTe, CdHgTe and HgTe nanocrystals. The spectra were measured on as-prepared colloidal solutions which were taken from the refluxing reaction mixture at different intervals of time. The PL bands are located typically close to the absorption thresholds (so-called band-edge or “excitonic” PL) and are sufficiently narrow (FWHM as low as 35 nm being increased up to 55-60 nm for size fractions of large NCs). The position of the PL maximum of the smallest (~ 2 nm) luminescing CdTe NCs is located at 510 nm (green emission) whereas the largest (~ 6 nm) CdTe nanocrystals obtained emit in the far red with a PL maximum at 800 nm. The whole spectral range between these two wavelengths is covered by the intermediate sizes of CdTe NCs. The PL quantum efficiency (QE) of as-synthesized CdTe nanocrystals depends on the nature of the stabilizing agent. The PL QE lies typically below 10% for thioglycerol, dithioglycerol, and mercaptoethanol stabilized NCs, values of 30-35% for 2-(dimethylamino)ethanethiol stabilized nanocrystals were attained. Recent improvements of the synthetic procedure showed the possibility to get 40-60% PL QE for as prepared CdTe NCs in the presence of thioglycolic or mercaptopropionic acids if the Cd:stabilizer ratio at the beginning of the synthesis was in the range of 1-1.5. The detailed investigation of this phenomenon is currently going on and the results will be published elsewhere. In most cases the PL QE can be sufficiently improved by post-preparative treatments of the NCs (size-selective precipitation, photochemical etching, etc).

The synthetic procedure for ZnSe NCs is very similar to the synthesis of CdTe. The stabilizer of choice is TGA. The synthesis of ZnSe NCs is done at pH 6.5 giving rise to stable colloidal solutions with moderate...
luminescence (PL QE below 1% as prepared). As a further procedure of post-preparative treatment, photochemical etching was applied and was studied in detail. Optimal conditions leading to 25-30% of PL QE were established. The optical spectra as well as powder-XRD and a HRTEM analysis show that the improvement of the PL QE is accompanied by the growth of the NCs and by a phase transfer from the cubic to the hexagonal crystalline structure. The XRD lines also shift to values which are characteristic for ZnSe/ZnS alloys (the sulfur appears as a product of photodecomposition of the TGA in solution). The formation of such a shell from larger band gap material should provide an additional stabilization of core particle and hence better optical properties. Solutions treated in this way show narrow PL bands being almost free from trap-associated emission.

**FIG 1:** Typical photoluminescence spectra (normalized) of CdTe, CdHgTe and HgTe nanocrystals. Top right: water soluble emitting powders (ca. 200 mg) of CdTe NCs of 2 different sizes under day light and under UV-lamp excitation. True color image of different solutions of CdTe and ZnSe NCs under UV-lamp excitation.

As mentioned above, the nature of the thiol influences the particle growth and the PL QE of the NCs. Besides that, each type of stabilizer has its own advantages and disadvantages allowing the use of NCs capped with varying thiols for different purposes. The NCs stabilized by TGA or MPA or by mercaptoethylamine show efficient PL as prepared and possess either negative or positive surface charge because of the surface carboxylic or amino groups, respectively. The possibility to manipulate these NCs, e.g. by the layer-by-layer (LbL) technique, electrostatic assembly or by electrophoresis, as well as the availability of free functional groups of the capping molecules for conjugation makes them especially attractive for the assembling and the fabrication of functional materials.

### 2.2. Assembly of nanocrystals

**Layer-by-layer (LbL) assembly on flat and/or porous surfaces.** Uniform and multicomponent thin films consisting of functional molecules and/or NCs may be formed by applying the so-called LbL technique which was originally introduced for the assembly of polymer electrolytes and which was recently adapted to the deposition of charged NCs both on flat and on curved surfaces. The formation of monolayers of deposited material is based on the electrostatic interaction between the NCs and the surface. Alternation of the sign of the charges of the species to be deposited allows to grow quite thick multilayers while the introduction of new components in one of the layers yields the opportunity of virtually non-limited but controllable variations of LbL-multistructure compositions. The application of the method described to the modification of artificial opals allowed to obtain intrinsically light emitting photonic crystals which were successfully used for investigations on photonic confinement phenomena. The thickness of the LbL film depends linearly on the number of deposited NC/polyelectrolyte “bilayers”. Moreover, a linear dependence of the absorption in the region of the first absorption maximum on the number of bilayers was observed.

**LbL on microbeads.** The LbL assembly of NCs on the surface of polymer (Polystyrene (PS), Polymethylmethacrylate (PMMA), Melaminformaldehyde (MF) etc.) or silica beads opens up an opportunity to create submicronized objects exhibiting the properties of the nanosized components. In this case, the LbL assembly can be done by suspending of the beads in solutions of the corresponding layer component. The contents of the solutions are generally the same as for the procedures described above. Repetitive centrifugation from pure water suspensions are used for washing of the beads and removal of excessive or non-specifically adsorbed reactants. The modified beads retain the PL properties of the NCs used with a slight red shift of the PL maximum due to energy transfer from the smaller to the largest NCs in the assembled surface film. The comparatively large size of the beads allows to manipulate them by optical tweezers or to use them as a tip mounted at the end of an optical fibre. Thus, the beads can be used as sub-wavelength-sized light sources for photonic applications or for the selective amplification of a signal in the scanning near-field optical microscopy (SNOM). The LbL modified
beads of larger sizes (> 2µm) show an efficient coupling of the light emitted by the NCs with the whispering gallery modes (WGM) of the spherical microresonators.\textsuperscript{27,28} The use of beads made from materials which can be dissolved after LbL deposition of the polyelectrolytes (like e.g. MF, MnCO\textsubscript{3}, etc.) allows the formation of hollow polyelectrolyte/NCs shells.\textsuperscript{30-32} The shells are promising as microcapsules for drug delivery systems where the PL of the NCs inserted can be used for the monitoring of the delivery process.\textsuperscript{33}

Solvent-controlled precipitation. Another method of coating microspheres has been established through the controlled precipitation of NCs by means of their aggregation in solution onto latex spheres\textsuperscript{34}. The approach is a variation of heteroaggregation phenomena in a colloidal environment. The aggregation of NCs onto colloidal beads was induced by the solvent-non-solvent pair precipitation technique which is normally successfully used to separate semiconductor nanocrystals by size. Colloidal cores statistically harvest aggregated NCs which consequently leads to the formation of a shell. Moreover, the thickness of the shell can efficiently be controlled through the proper choice of the concentration ratio of the colloidal particles serving as the cores and the precipitated species.

Covalent coupling of NCs. While the covalent coupling between NCs is still in an infant status the carbodiimide chemistry may well be applied to the coupling of NCs to pre-treated surfaces. Accordingly, we used appropriate fractions of CdTe NCs for the conjugation with various substrates like glass, silica or silicon with different shapes of the surfaces.\textsuperscript{35} The method is based on the binding of acid-stabilized NCs to aminated surfaces with the aid of carbodiimide as a mediator and is not limited to bulk substrates but is of more generality as seen by our successful attempts to coat glass spheres of micron size or silica beads by CdTe NCs.\textsuperscript{35} The luminescence from the spheres modified is not altered for at least 3 months.

Template directed electrostatic assembly and chemical plating of metal NCs. A new method of the formation of 3D ordered silica-Au nanocomposites was developed.\textsuperscript{36} The method includes the synthesis of monodisperse silica beads, their modification with surface amino groups, the assembly of the beads into artificial opals, and the electrostatic assembly of small (3 nm) gold nanocrystals in the voids of the opals. Slow chemical deposition of the gold from the solution by utilizing pre-assembled Au-nanoparticles as seeds allows the controllable growth of Au nanocrystals up to 50 nm in diameter (Fig.2). The size of the nanoparticles in the 3D film can easily be controlled by simply adjusting the gold plating time and the 3D ordered structure is still retained. A study of the surface-enhanced Raman scattering (SERS) properties of the structures obtained was performed by using Rhodamine 6G as probe molecules. It is found that the resulting gold-coated 3D ordered colloidal crystal films can be used as SERS substrates and exhibit an excellent enhancement ability which depends on the gold particle size.\textsuperscript{36}

Controllable formation of 3D hollow nanostructures of hierarchical porosity made from Au/Pt alloyed nanocrystals was also demonstrated.\textsuperscript{37} The amino-modified silica colloidal crystals were employed as substrates for the Au particle self assembly and subsequent Pt plating. Etching of the silica template led to hollow metal structures. Controlling of the plating time and the kind of template ordering make possible the formation of various structures, e.g. inverse opals, ordered hollow spheres and semispheres, and disordered macroporous films (Fig. 3). Possible applications of the structures obtained in photonics and in catalysis are currently under investigation.
3. CONCLUSIONS

The synthesis of semiconductor nanocrystals as well as the preparation and the characterization of various assemblies of them were reviewed. Methods allowing the controllable deposition of metal nanocrystals into voids of 3D matrices are demonstrated. The approaches presented are promising for photonic, optoelectronic and catalytic applications.