Synthesis and surface modification of amino-stabilized CdSe, CdTe and InP nanocrystals

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Abstract

CdSe, CdTe and InP nanocrystals were prepared by an organometallic synthesis using mixtures of highly boiling primary amines and trioctylphosphine (TOP) as the coordinating solvent, and were characterized by powder XRD, SAXS, HRTEM, absorption and luminescence spectroscopy. The use of amines allowed us to obtain small crystalline nanoparticles for all materials investigated. In all cases, as-prepared colloids show rather narrow particle size distributions which can be further improved by standard size selective precipitation. Amino-capped II–VI nanocrystals show strong size-dependent band edge photoluminescence (PL). CdSe nanocrystals with the mean particle size in the range of 1.2–3.0 nm exhibit emission from blue to green with room temperature quantum yields of 15–20%. CdTe nanocrystals (2.5–5.0 nm size range) show a PL tunable from green to red with quantum yields up to 65% at room temperature. InP nanocrystals (1.5–4.0 nm size range) possess a weak emission (<1% quantum efficiency (QE)). A simple method is proposed to transfer nanocrystals from organic solvents to water which allows to retain sufficiently strong luminescence of CdTe nanoparticles. CdSe nanocrystals synthesized in trioctylphosphine–trioctylphosphine oxide mixture (TOP–TOPO) show an increased QE of about 70% after subsequent treatment with primary amines. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The chemical synthesis and the size-dependent properties of II–VI and III–V semiconductor nanocrystals are of great interest owing to their potential application in electrical and optoelectronic devices [1–7]. One of the most established non-aqueous synthesis routes to crystalline colloidal II–VI [8] and III–V [9,10] nanoparticles is the decomposition of organometallic precursors in mixtures of the highly boiling coordinating solvents trioctylphosphine and trioctylphosphine oxide (TOP–TOPO). More recently, the syntheses of ZnSe [11] and CdS [12] nanocrystals in aminoalkanes have been reported.
For a number of optoelectronic applications, e.g. light-emitting diodes (LED) [2,3,6], strongly luminescent semiconductor nanocrystals are highly desirable. Due to the large surface-to-volume ratio of nanoparticles, the most common reason for poor luminescence efficiency is non-radiative recombination of light-generated charge carriers at surface traps. Elimination of these traps can be achieved either by proper chemical modification of the particle surface [13,14] or by growing hetero-epitactically an inorganic passivation shell around the semiconductor cores [15–18].

In this paper, we report on the organometallic synthesis of crystalline II–VI and III–V nanocrystals using primary amines as extremely effective capping agents. This allows us to obtain a size series of highly luminescent CdSe and CdTe nanocrystals without passivating their surface with inorganic shells. The method also allows to synthesize CdSe, CdTe and InP nanocrystals of extremely small sizes, not easily obtained by the common TOP–TOPO synthesis. We also propose a simple method to transfer amino-capped II–VI semiconductor nanoparticles from organic solvents to water allowing to retain sufficiently strong luminescence of CdTe nanocrystals. This might be of interest for potential applications such as biolabeling [19,20].

2. Experimental section

2.1. Chemicals and apparatus

Toluene, methanol, n-hexane (all anhydrous, Aldrich), pyridine (anhydrous, Fluka), selenium (99.99%, ChemPur), tellurium (99.999%, ChemPur), dimethylcadmium (EpiChem), InCl₃ (anhydrous, Alfa), tris–trimethylsilylphosphide (TMS)₃P (Alfa), allylamine (Fluka), and N,N-dimethyl-2-mercaptoethylammonium chloride (Merck) were of analytical grade or of the highest purity available and used as received. n-TOPO (90%, Aldrich) was generally used as received or distilled in vacuum for some control experiments. n-TOP (Fluka) was purified by distillation. Octylamine, dodecylamine (DDA) 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.

UV–vis absorption and photoluminescence (PL) spectra were measured at room temperature with a Perkin–Elmer Lambda 40 UV–vis spectrophotometer and a FluoroMax-2 spectrofluorimeter (Instruments SA), respectively. PL spectra were taken on colloidal solutions having optical densities of less than 0.2 at the excitation wavelength λ_{exc} = 400 nm. Rhodamin 6G (laser grade, Lambda Physik) was used as a standard for determining PL quantum efficiencies (QE). Powder X-ray diffraction (P-XRD) spectra were taken on a Philips X’Pert diffractometer (Cu Kα-radiation). High resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray analysis (EDX) were performed on a Philips CM 300 UT microscope operating at 300 kV. Small-angle X-ray scattering measurements were carried out with a Kratky camera (Anton Paar). The size distribution of nanocrystals in solution was calculated from the scattering data by means of indirect Fourier transformation [21,22].

2.2. Organometallic synthesis of semiconductor nanocrystals in the amine medium

All 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.

2.2.1. CdSe nanocrystals

One milliliter of 1.26 M solution of tri-n-octylphosphine selenide (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 3 days. Finally, the reaction mixture was cooled to room temperature and 20 ml of toluene were 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 a size-regulating solvent. In the latter case, rapid injection of stock solution at 300 °C permits to achieve a very narrow particle size distribution, which shows negligible broadening during the particle growth. Isolated nanocrystals were stable both under nitrogen and in air over months, retaining their PL properties.

2.2.2. CdTe nanocrystals

The tellurium precursor was prepared by dissolving 0.65 g of tellurium in 10 ml of TOP by overnight stirring at 220 °C inside a glovebox. About 1.96 ml of the resulting greenish–yellow solution (1 mmol referring to Te) were mixed with 0.1 ml (1.35 mmol) of dimethylcadmium and 3 ml of TOP. This stock solution was mixed with 10 g of DDA at 50 °C in a 50 ml three-neck flask with the reflux condenser attached, and the temperature was increased to 120 °C. The reaction mixture was kept at this temperature for 2 h. The color of the solution slowly changed on this stage from pale yellow to bloody-red, owing to nucleation and growth of CdTe nanoparticles. Further growth was induced by heating at 150–180 °C for several (up to 20) hours and was accompanied by a considerable improvement of nanoparticle crystallinity. The final size of the nanoparticles is also a function of the temperature and the duration of heating. By this method, CdTe nanocrystals with mean sizes ranging from 2.5 to 5.0 nm have been prepared. They show strong band edge PL with QE 30–65% and emission colors between green and red depending on particle size. Even larger CdTe nanocrystals (up to ~7.0 nm) can be prepared by injecting additional cadmium and tellurium precursors into the solution of growing nanoparticles. After completion of particle growth, the reaction mixture was allowed to cool to ~50 °C, and 20 ml of toluene were added. Finally, the mixture was left for 24 h at room temperature under permanent stirring.

2.2.3. InP nanocrystals

A 0.63 M solution of InCl₃ in TOP was prepared by stirring 0.7 g of anhydrous InCl₃ 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 (TMS)₃P 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 period of time resulted to marked improvement of size distribution and 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 QE <1%. Colloidal solutions of nanocrystals isolated from crude solutions were stable for months when kept under nitrogen.

For comparison, CdSe, CdTe and InP nanocrystals have been synthesized according to the TOP–TOPO organometallic routes described in the literature [8,10,23].

2.3. Isolation of the nanocrystal fractions

Aliquots were taken from the reaction mixture, and byproducts were removed by passing the solution through a 0.22 μm membrane filter (Milipore). Standard solvent/nonsolvent size selective precipitation [8] was carried out by adding small volumes of methanol to the supernatant and col-
lecting the precipitate by filtration. Isolated nanocrystal fractions were readily dispersible in a variety of organic solvents such as toluene, n-hexane, chloroform etc.

2.4. Surface exchange

To modify the surface of amino-capped CdSe and CdTe nanocrystals with different organic ligands, we used a procedure similar to that described in [24,25]. Thus, to make nanoparticles soluble in pyridine, 1–2 mg of nanocrystals were isolated from the crude solution inside a glovebox, dispersed in a small volume of pyridine and left under stirring at 50 °C until the solution became optically clear. Subsequently, the nanocrystals were precipitated by addition of hexane and re-dispersed in pyridine. The procedure had to be repeated several times to produce nanocrystals readily dispersible in pyridine and absolutely insoluble in aliphatics. A similar method was employed to modify the particles surface with 3-methylthiophene.

2.5. Transfer of nanocrystals from organic solvents to water

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. About 20–50 mg of freshly prepared CdSe or 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-mercaptethylammonium 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. In the case of CdTe, nanocrystals retained sufficiently strong band edge PL (QE 13–18% depending on the particle sizes) after being transferred in aqueous solution. The PL of CdSe nanocrystals transferred to water was, however, almost quenched.

2.6. Surface modification of TOPO-capped CdSe nanocrystals with amines

Highly monodisperse TOPO-capped CdSe nanocrystals with an average size of ~ 3.7 nm were prepared according to the literature method [8]. The high quality of these particles was confirmed by XRD and HRTEM measurements. To modify the surface of nanoparticles with amines, 1 ml of the crude solution containing ~ 10 mg of CdSe nanocrystals was mixed with 5 ml of DDA or allylamine inside the glovebox and subsequently stirred at 100 °C (DDA) and 50 °C (allylamine) for 24 h. The nanocrystals were precipitated with methanol and re-dispersed in hexane for optical measurements. The surface modification with DDA resulted in an improved PL QE of up to ~ 70% which is about an order of magnitude larger compared with untreated TOPO-capped CdSe nanocrystals. The surface modification with allylamine led to a PL QE of ~ 50%.

3. Results and discussion

3.1. Synthesis and characterization of amino-capped nanocrystals

Fig. 1 shows typical absorption and PL spectra of as-prepared CdSe, CdTe and InP nanocrystals synthesized in DDA–TOP mixtures. In all cases, sufficiently narrow particle size distributions are maintained during the growth of the nanocrystals. Prolonged heating significantly increases the sharpness of transitions in the absorption spectra of nanocrystals presumably owing to ‘focusing’ of the size distribution [26] in combination with annealing of defects. The resulting size distribution of the CdTe nanocrystals in the crude solution was calculated from SAXS data and is presented in Fig. 2. The position of the pronounced maximum in the distribution corresponds to the weight-averaged mean radius of the CdTe nanocrystals. The radius 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 better than that
observed for CdTe nanocrystals prepared by the TOPO–TOP procedure. Subsequent size selective precipitation allows to further narrow down the size distribution.

PL excitation spectra show that the luminescence of as-prepared DDA-capped CdTe nanocrystals is inhomogeneously broadened (Fig. 3). At a resolution of 2 nm of both emission and excitation monochromators, well-structured excitation spectra of CdTe nanocrystals were obtained displaying rather sharp transitions even at room temperature.

The energy of the first maximum in the absorption spectra of CdSe, CdTe and InP nanocrystals can be tuned in the ranges presented in Fig. 4 by properly adjusting the growth conditions. Also shown are the literature values for the TOP–TOPO synthesis. For CdSe, CdTe and InP the use of amines as stabilizing and size-regulating agent generally permits to obtain smaller nanocrystals than is achieved by the conventional TOP–TOPO method (Fig. 4).

In addition, amines provide much better passivation of surface traps participating in the non-radioactive recombination processes. Thus, DDA-capped CdSe and CdTe nanocrystals, including the smallest particles prepared, show room temperature band edge PL QE of 15–20 and 50–60%, respectively, which is markedly higher than TOPO-capped nanocrystals. DDA-capped InP nanocrystals show both the band edge luminescence and a PL band red-shifted from the absorption edge (Fig. 1) which originates from the
recombination of electrons and holes trapped in surface states and is commonly observed for as-prepared InP nanoparticles [9,10]. The overall PL QE, however, does not exceed 1%, although this value is larger than that reported in [10]. We are currently investigating the possibility of improvement of the luminescence efficiency of InP nanocrystals through a suitable surface capping.

Fig. 5 shows P-XRD spectra for size-selected fractions of CdSe, CdTe and InP nanocrystals. All particles are crystalline, and the positions of diffraction peaks at wide angles match those of the bulk phases of cubic CdTe and InP (zincblende phase) modifications. In the case of CdSe, the XRD pattern permits no clear determination between the cubic and the hexagonal phases. As expected, the width of the diffraction peaks is considerably broadened and increases with decreasing the 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 hexagonal dense packing of nearly monodisperse particles, the distance between nearest neighbors has been calculated using the Bragg equation [27]. The calculated values are slightly larger for all samples than the particle sizes obtained from the Scherrer equation.

Overview TEM images (Fig. 6) present 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 the ratios given by the bulk formula. In case of CdSe, extremely narrow distribution of the particle sizes results in packing of the nanocrystals in an ordered array after evaporation of the solvent. High
resolution TEM images of amino-capped CdSe, CdTe and InP nanocrystals show crystalline nanoparticles with clearly resolved lattice fringes (Fig. 6).

A proper choice of the amine is an important point in the synthetic route we have proposed. For instance, octylamine with its relatively low boiling point did not allow to use temperatures higher than 160–170 °C and the particles have the tendency to partially precipitate during heating. The use of secondary amines, e.g. dioctylamine, as a solvent resulted in a very week stabilization and poorly controlled growth of the particles. Among the amine–TOP mixtures investigated, DDA was found to have several advantages over other amines resulting in the most narrow particles size distributions. On the other hand, hexadecylamine provided the best conditions of the CdSe growth when it was used in a three-component mixture together with TOPO and TOP.

3.2. Surface modification of nanocrystals

Further functionalization and modification of amino-capped nanocrystals, in particularly their solubility in a variety of solvents can be realized by surface exchange of the amine capping groups. Thus, surface DDA groups of CdSe and CdTe nanocrystals can be readily substituted by pyridine as described in the Section 2. The surface exchange of DDA can be also successfully carried out with other amines (e.g. octylamine or allylamine) and with sulfur-containing compounds such as 3-methylthiophene.

The possibility to make luminescent semiconductor nanocrystals water-soluble is of special interest due to their potential application as biolabels [19,20,28]. For this purpose, we treated CdSe and CdTe nanocrystals with \( \text{N,N-dimethyl-2-mercaptoethylammonium chloride} \) in order to attach these highly polar surface capping molecules dissociating in aqueous solution to the nanocrystal surface (Scheme 1).

Under the soft conditions applied (room temperature), a complete exchange of stabilizing DDA molecules by thiol molecules is improbable. Nevertheless, it was possible to make both CdSe and CdTe nanocrystals soluble in water and, in the case of CdTe nanoparticles, to retain a sufficiently high PL (QE up to 18%). This value is comparable with those achieved for more complex water-soluble core–shell CdSe/CdS/SiO\(_2\) and CdSe/ZnS nanocrystals used for biolabeling [19,20], and for thiol-capped CdTe nanocrystals synthesized in aqueous solutions [14].

The observed quenching of the PL of CdSe nanocrystals after their transfer to water is in accord with earlier experiments, showing that thiol-capped CdSe nanocrystals synthesized in aqueous solutions do not have any band edge PL [29], while thiol-capped CdTe nanocrystals show band edge PL with QE up to 18% [14,30,31].
These results may be explained by the assumption that bonding of the mercapto-groups lead to appearance of non-radiative traps at the particle surface, which are positioned below and above the valence band in cases of CdTe and CdSe, respectively.

The observed enhanced PL QE of DDA-capped CdSe, CdTe and InP nanocrystals, as well as the ability to produce smaller nanoparticles as compared with the TOP–TOPO synthesis, may be the result of strong bonding of the amines to the nanocrystal surface [18]. Less sterically hindered amines may create larger capping densities, which improves surface capping and, hence, the passivation of traps [11].

If these assumptions are true, it should be possible to improve the PL of TOPO-capped nanocrystals by surface exchange with amines. To prove this, we carried out the surface substitution of TOPO by different amines, using TOPO-capped CdSe nanocrystals synthesized according to literature methods [8,26]. The results exceeded our expectations, after treating the nanocrystals with DDA the band edge PL increases by about an order of magnitude and reaches an extremely high QE of ~70% (Fig. 7). The use of allylamine instead of DDA leads to a similar effect (QE 50%) confirming the role of the amino-group in the surface passivation. Exchange of TOPO by amines at the surface of nanocrystals is accompanied by a slight blue shift of both the absorption spectrum and the maximum of the band edge PL band (Fig. 7). This may be explained by a slight decrease of the size of nanocrystals caused by losing the surface Cd and Se atoms with leaving TOPO molecules [8], or by re-distribution of electronic density in the semiconductor core under the influence of passivating groups.

4. Summary

Highly crystalline CdSe, CdTe and InP nanocrystals are 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 both II–VI and III–V semiconductor nanocrystals with sizes smaller than obtained in the conventional TOP–TOPO method. DDA-capped CdSe and CdTe nanocrystals show a room temperature PL QE of 15–20% and 30–65%, respectively, without passivating the surface of the nanoparticles with an inorganic shell. The PL QE is markedly higher than that of TOPO-capped nanocrystals. Depending on the particle size, the band edge luminescence of CdSe and CdTe nanocrystals covers the whole visible spectral range from blue to red. A simple method is proposed to transfer CdSe and CdTe nanocrystals from organic solvents to water which allows to retain a sufficiently strong luminescence of the CdTe nanoparticles. Treatment of pre-synthesized TOPO-capped CdSe nanocrystals with primary amines allows to reach a QE of the band edge luminescence as high as 70%.
Fig. 7. Room temperature absorption and emission spectra of 3.7 nm CdSe nanocrystals passivated with TOPO (solid) and DDA (dashed).

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