Phosphine-Free Synthesis of CdSe Nanocrystals

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High quality CdSe nanocrystals have been prepared using elemental selenium as the chalcogenide precursor dispersed in 1-octadecene (ODE). The conditions used to prepare the Se precursor were found to be critical for successful nanocrystal synthesis. Systematic titration of the Se precursor solution with tri-*n*-octylphosphine (TOP) allowed the Se reactivity to be tuned and the final particle size to be controlled. Band-edge and surface related emission were observed for samples prepared in the presence and absence of added TOP. In the absence of a selenium passivant, the crystal structure of CdSe nanocrystals could be altered from zinc blende to wurtzite by the addition of bis(2,2,4-trimethylpentyl)phosphinic acid (TMPPA).

Introduction

Many methods currently exist for the preparation of nearly monodisperse semiconductor nanocrystals with tunable sizes.[1−3] Unravelling the different effects of the solvent molecules and the nanocrystal precursors on the growth kinetics and final particle size distribution remains a serious challenge. Thus far, most attention has focused on the role of different metal salts on the rate of particle growth.[4−6] Very few studies have been carried out which directly compare the effects of different chalcogenide reagents. One noteworthy study was reported by Cao et al. who compared two different sulfur sources (tetra-ethylthiuram disulfide and 2,2′-dithiobisbensothiazole) on the yield of CdS nanocrystals.[7] In the case of CdSe nanocrystal synthesis, virtually all nonaqueous synthetic routes have employed tertiary alkylphosphine selenides as the selenium precursor because of their high solubility and reactivity in a range of organic solvents. Hence, it has been difficult to determine the effects of such agents on crystal growth dynamics and photoluminescence properties. Recently, the synthesis of CdSe in the coordinating solvent tri-*n*-octylphosphine oxide (TOPO) has been extended to the less hazardous, more inert solvent 1-octadecene (ODE).[4] The use of this solvent enables systematic investigations to be carried out on the effects of different precursors on the nucleation and growth of nanocrystals. Here, we report for the first time the development of a non-organometallic phosphine-free selenium precursor.[1] This synthetic approach allows us to tune the nucleation and growth of CdSe by altering the reactivity of selenium and to probe more clearly the role of the chalcogenide precursor on CdSe nanocrystal synthesis, as well as the role of an alkylphosphine (TOP) on surface passivation. The precursor solution developed here comprises a homogeneous solution of selenium dissolved in ODE, analogous to the sulfur dispersion reported by Yu et al.[4] Using this simpler and cleaner nanocrystal synthetic route, we demonstrate that TOP does influence the kinetics of CdSe formation, but it does not introduce any additional nonradiative surface states.

Experimental Section

Chemicals. Cadmium oxide (CdO, Aldrich, 99.99%), selenium powder (Aldrich, 99.9%), oleic acid (Aldrich, 90%), trioctylphosphine (TOP, Aldrich, 90%), 1-octadecene (ODE, Aldrich, 90%), and bis(2,2,4-trimethylpentyl)phosphinic acid (TMPPA, Cytec Specialty Chemicals) were used in the preparations described here. Hexane, chloroform, and toluene were all of analytical grade and purchased from Univar. All chemicals and solvents were used without further purification.

Experimental Details

The nanocrystal preparations were adapted from those reported by van Embden et al.[8] A stock solution of the cadmium source was prepared by first degassing CdO (1.2 g, 9.3 mmol) and oleic acid (30 g, 106 mmol) in 120 g of ODE at 100 °C for 30 min and then heating this solution under nitrogen to 300 °C for 6 h. The solution was cooled to 100 °C and degassed for a further 30 min to remove any residual water formed during the reaction. This solution remained heated at 60 °C during the course of the study. The Se stock solution was made by degassing Se (0.744 g, 9.4 mmol) in 80 g of ODE at 100 °C for 20 min and subsequently heating the mixture under nitrogen at 200 °C for 2 h. During this time, the ODE/Se mixture changed from colorless to orange-red and finally to yellow. The resulting transparent yellow solution was then cooled to room temperature where it remained stable for weeks under nitrogen.

For studies concerning the tunability of the Se precursor, the CdSe nanocrystals were prepared by mixing 7.5 g of the Cd stock solution (0.47 mmol) with 6.54 g of ODE and heating the solution to 300 °C under nitrogen. The Se injection solution

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TABLE 1: Reaction Parameters Used for the Injection Solution in the TOP Titration Preparations

reaction	TOP (mmol)	final [TOP] (mM)	ODE (g)	[Cd] (mM)	[Se] (mM)	[TMPPA] (mM)	[OA] (mM)
1	0.00	0.00	1.850	18.4	18.4	80.6	205.5
2	0.02	0.78	1.843	18.4	18.4	80.6	205.5
3	0.04	1.56	1.835	18.4	18.4	80.6	205.5
4	0.055	2.15	1.830	18.4	18.4	80.6	205.5
5	0.12	4.69	1.805	18.4	18.4	80.6	205.5

was prepared by mixing 4 g of the Se stock solution (0.47 mmol of Se) with TMPPA (0.6 g, 2.1 mmol) and a 1.85 g buffer consisting of ODE/TOP in varying ratios to give a final injection mass of 6.45 g. Table 1 shows the different ratios of ODE/TOP needed to achieve the varying TOP/Se mole ratios used in this study. Reaction 1 in Table 1will henceforth be referred to as "TOP-free" CdSe.

For the traditional "TOPSe" based preparations, the cadmium solution is composed of 7.5 g of the Cd stock solution and 6.54 g of ODE. The injection solution was prepared by dissolving Se (0.037 g, 0.47 mmol) in TOP (1.16 g, 3.1 mmol) and then adding TMPPA (0.6 g, 2.1 mmol) and finally 4.7 g of ODE to give a final mass of 6.45 g. Completely phosphorus-free CdSe nanocrystals grown in the absence of both TMPPA and TOP were prepared by heating 7.5 g of Cd stock solution and 14 g of ODE. The injection solution in this case consisted only of 4 g of the ODE/Se solution. These nanocrystals will herein be referred to as "TMPPA−TOP-free" CdSe. In all of these experiments, the Cd and Se molar quantities were fixed at n(Cd) = 0.47 and n(Se) = 0.47 mmol. The temperature of the solutions dropped following injection, and growth of the nascent crystallites occurred at 230 °C. To ensure reproducibility, great care was taken so that each experiment had very similar temperature profiles. Each reaction batch was heated for exactly 20 min following injection.

To monitor the growth dynamics, aliquots were periodically removed from the growth solution and subsequently diluted with a known quantity of hexane or chloroform. Absorbance and photoluminescence spectra were collected with a Cary 5 UV−vis−NIR spectrometer and a Varian Eclipse instrument, respectively. Using published relationships, the concentration and average particle diameter could be determined from the absorbance measurements.[9] No postpreparative size sorting was performed on the samples. All reported sizes and concentrations in this study are based on nanocrystals grown for the maximum time of 20 min.

Results and Discussion

Figure 1 shows the resulting absorbance and normalized photoluminescence (PL) spectra for the aliquots taken at various times after injection for batches of CdSe nanocrystals prepared using the TOPSe (A), TOP-free (B), and TOP−TMPPA-free (C) precursors. Series A is representative of a typical TOPSe based preparation. As expected, the nanocrystals exhibit trap emission during the early stages of growth. The sharp features resolvable in the absorbance spectra and the narrow full width at half-maximum (fwhm) of the emission bands of series B demonstrate that TOP is not necessary for the production of high quality CdSe. The PL band after 10 s of growth displays prominent trap emission, contrary to the findings of Kalyuzhny et al. who suggested that trap emission is caused by TOP complexing surface Se sites.[10] Further removal of TMPPA, as seen in series C, proves that monodisperse CdSe can still be grown using oleic acid as the sole capping agent. The observation of trap emission after 10 s of growth proves that TMPPA
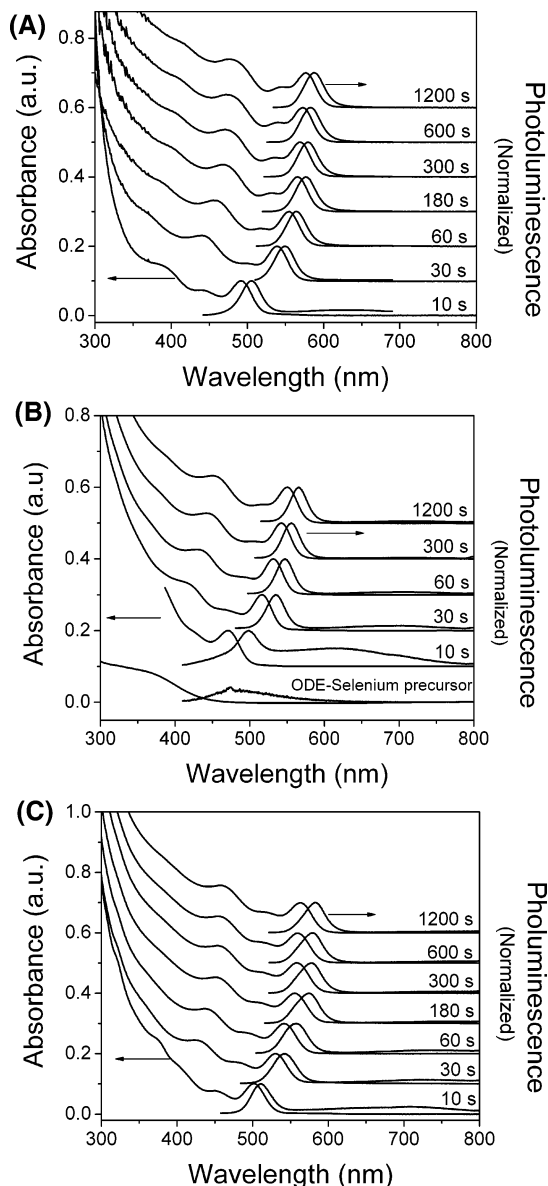

Figure 1. Absorbance and normalized photoluminescence spectra obtained during the growth of (A) TOPSe, (B) TOP-free, and (C) TOP−TMPPA-free CdSe nanocrystals under nitrogen. n(Cd) = n(Se) = 0.47 mmol, temperature = 230 °C.

is not the cause of the trap emission observed in the TOP-free CdSe samples. Typical quantum yields of the as-synthesized quantum dots for all preparations ranged between 5 and 10% as compared with rhodamine 6G.

To elucidate the precise role of TOP during the synthesis of CdSe, varying amounts of TOP were incorporated into the ODE/Se injection solution. Figure 2A shows the absorption spectra taken after 20 min of growth for CdSe batches with [TOP] ranging from 0 to 4.69 mM. As the concentration of TOP is increased throughout this range, a gradual red shift in the first absorption maximum is observed. We note that at [TOP] < 2.2 mM the particle size distribution remains narrow. Higher concentrations of TOP were found to result in a significant broadening of the size distribution. A summary of the effects of [TOP] on both final particle diameter and concentration is shown in Figure 2B. We observe that for the TOP-free synthesis the concentration of CdSe nanocrystals is ∼25 µM. A linear decrease in the particle concentration is observed as [TOP] is increased from 0 to 2.2 mM. A concomitant increase in particle diameter from 3.1 to 3.8 nm is noted within this range, giving
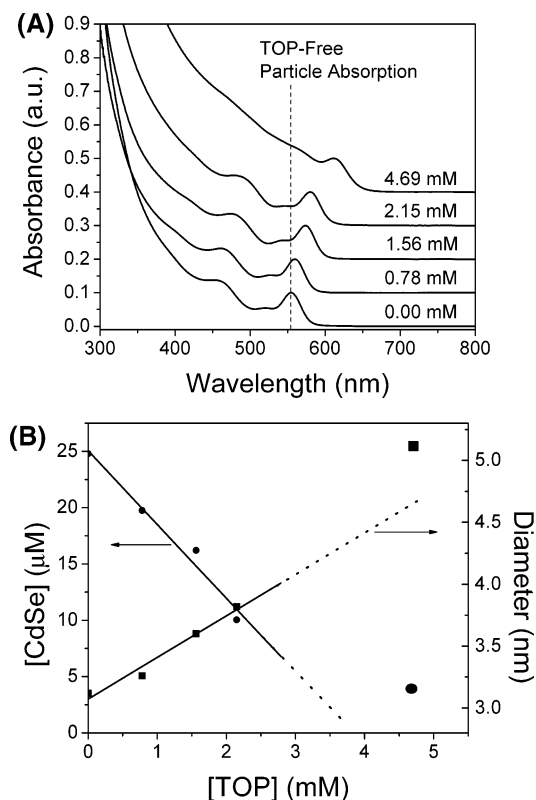
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Figure 2. (A) Absorption profiles of CdSe nanocrystals following 20 min of growth under nitrogen at different TOP concentrations (as included in figure). (B) The effect of [TOP] (mM) on the final nanoparticle concentration (●) and diameter (■). [Cd] = 18.4 mM, [Se] = 18.4 mM, temperature = 230 °C. Included are two lines of best fit for the low [TOP] regime. The dashed lines are intended as guides.
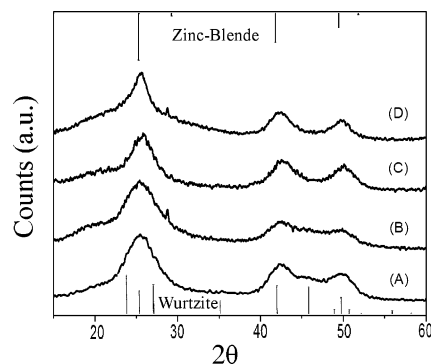

Figure 3. Powder X-ray diffraction patterns obtained from CdSe nanocrystals prepared using (A) TOPSe, (B) TOP-free, and (C) TMPPA−TOP-free conditions and (D) TMPPA−TOP-free conditions with titrated TOP in the injection solution. All XRD diffraction patterns were collected on nanocrystal samples with similar sizes, ∼3−3.5 nm in diameter.

fine spectral tunability between ∼550 and 590 nm.[9] Attempts to grow still larger particles by increasing the TOP concentration above 2.2 mM not only resulted in particles with a broad size distribution, but the linear relationship between [TOP] and [CdSe] was no longer observed.

In the course of this study, it was found that the ODE/Se precursor culminated in poorer nucleation than the conventional precursor (TOPSe) formed by dissolving elemental Se in TOP. Under the otherwise identical conditions used for the synthesis of TOP-free CdSe, nucleation from TOPSe typically resulted in twice as many particles (∼50 μM). This dramatic increase in particle yield indicates that TOPSe facilitates nucleation by providing a more readily available source of selenium than does ODE/Se.

The TOP-free method does however possess one significant advantage over conventional TOPSe preparations. It allows for the study of the nanocrystal surface properties in the absence of a selenium passivant. Several research groups have investigated the role of Cd and Se surface sites in photobrightening and trap emission.[10−13] The conclusions of these studies have nonetheless been complicated by the lack of a clean reference point. The syntheses outlined here provide, for the first time, access to particles with "naked" selenium surface sites, thus enabling in-depth photophysical studies on the passivation of these sites to be investigated.

Due to the novel nature of the ODE/Se precursor, it is worthwhile to consider the complexities involved in its formation. It is well-known that the most common allotrope of sulfur is the cyclic S_8 compound. This particular allotrope undergoes a ring-opening polymerization when heated between tempera-

tures of ∼140 and 170 °C.[14] The polymeric sulfur chain is insoluble in the same solvents and is typically termed "insoluble sulfur".[15] In the case of Se, which exists in analogous forms to sulfur, we believe that the initial 2 h of heating leads to the thermal dissolution of the crystalline selenium powder into its various allotropes. At that point, it was found that the precursor was viable for the nucleation of particles. Prolonged heating at high temperatures (200 °C for more than 4 h) resulted in the deactivation of this precursor. Attempts to nucleate particles from the ODE/Se at this point were found to be unsuccessful, probably due to the polymerization of Se into long, unranked chains. Finally, by comparing the absorbance spectrum of ODE/Se (Figure 1) to colloidal selenium,[16] we can eliminate this species as being present in our precursor solution. At present, it seems that the ODE/Se precursor is polymeric Se, while, in the presence of the complexing agent TOP, it is molecularly dispersed.

The viable form of the ODE/Se precursor provides a highly reproducible route for the preparation of CdSe nanocrystals. As TOP is known to strongly complex Se, it is expected that TOPSe formation will affect both the kinetics and thermodynamics of particle nucleation and growth. In Figure 2B, the decrease in [CdSe] observed with increasing [TOP] is consistent with greater selenium solubility in the growth solution. Given that particles with a broad size distribution are formed above [TOP] = 2.2 mM, we argue that the selenium solubility has become too high for successful nucleation. At very high TOP concentrations, we observe dominant bimodal growth kinetics, which suggests that both TOPSe and ODE/Se are independently competing as precursors for CdSe formation.

The TOPSe, TOP-free, and TOP−TMPPA-free CdSe nanocrystals were characterized using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). It has previously been established that wurtzite quantum dots are obtained in ODE/TOPO/TOP/tetradecylphosphonic acid (TDPA) systems with TOPSe and cadmium oxide.[17] Figure 3A shows that TOPSe based preparations in the presence of TMPPA also lead to wurtzite CdSe. When switching to the ODE/Se precursor in a typical TOP-free preparation, as seen in Figure 3B, it was found that the crystal structure remained hexagonal. However, TMPPA−TOP-free CdSe nanocrystals were found to exhibit the zinc blende structure (Figure 3C). Figure 3D clearly demonstrates that the subsequent incorporation of TOP into the TMPPA−TOP-free system still leads to the zinc blende structure. These results allow us to conclude that TMPPA is responsible for the changes in crystal structure, rather than TOP.
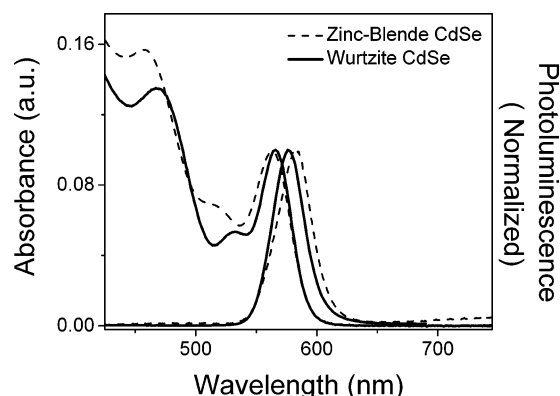
Figure 4. Comparison of the absorption and photoluminescence spectra of zinc blende and wurtzite CdSe nanocrystals in chloroform.

It would seem that when using the ODE/Se precursor the crystal phase is strongly dependent on the nature of the ligand passivating the surface cadmium atoms. A recent study by Mohamed et al. on CdSe grown in ODE/octadecylamine (ODA)/TOP/TDPA showed that depending on whether the TDPA was used during the heating of the cadmium source or as an additive in the selenium injection solution, wurtzite or zinc blende CdSe nanocrystals could be grown, respectively.[18] Here, we definitively show that through the use of TMPPA in the growth solution the nanoparticle crystal structure can also be selected.

Figure 4 shows a comparison between the absorption profiles of wurtzite and zinc blende nanocrystals. It is clear that the second and third excitonic transitions are shifted to higher energies for the zinc blende crystal structure. This observation is in agreement with recent reports.[18] We also observe a stronger Stokes shift in the luminescence from zinc blende CdSe nanocrystals. All particles in this study were found to be spherical in nature as observed through TEM (see Supporting Information).

Conclusions

We have developed a stable Se precursor for the preparation of CdSe nanocrystals. The selenium source consists of selenium dissolved directly in ODE and enables "phosphine-free" particles to be synthesized. This enables the hole scavenging and photophysical effects of these stabilizers to be examined in detail. The new precursor provides a simple alternative to TOPSe, TBPSe, and (TMS)$_2$Se. We have found that through the judicious use of TOP in the reaction mixture fine-tuning of the particle size is achieved. The role of TOP is believed to increase the solubility of the selenium in ODE, leading to

decreased particle yields and increased particle sizes. By comparing TOP-free and TOPSe based preparations, we showed that TOP does not introduce any new surface defects as proposed by Murray and colleagues. Surface trap emission was observed in the presence and absence of TOP, suggesting that this radiative pathway is intrinsic to unpassivated surface states. In this study, we also reported CdSe synthesis of one of the "cleanest" colloidal CdSe systems to date, one with oleic acid as the sole stabilizer. Finally, through the selective use of TMPPA in this oleic acid system, we have demonstrated tht the final crystal structure can be altered from wurtzite to zinc blende. This suggests that in the absence of a selenium passivant the nature of the ligands binding the surface cadmium atoms is directly responsible for the resulting crystal phase.

Supporting Information Available: TEM images of TOPSe, TOP-free, and TMPPA−TOP-free CdSe nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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