A New Class of Capping Ligands for CdSe Nanocrystal Synthesis

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A new method is described for the synthesis of high-quality CdSe nanocrystals (NCs) that eliminates the need for tri-octylphosphine oxide (TOPO). This new method is an adaptation of previously reported methods that use Cd salts as precursors for the CdSe NCs. High-boiling esters and ketones such as hexadecyl hexadecanoate (HH) and benzophenone (BP) appear to be excellent replacements for TOPO in this reaction. Compared with TOPO, HH offers a significant synthetic advantage as it slows the initial growth of the NC nuclei formed after injection of the Se precursor. This allows for superior control over particle size in the initial stages of the reaction, and thus permits facile production of high-quality CdSe NCs with very small diameters (<4 nm). Based upon the results presented here, a possible role is identified for TOPO in the CdSe NC synthesis. Understanding of the role of TOPO and other reaction components is crucial for continued progress in the synthesis of high-quality NCs.

Introduction

The synthesis of colloidal semiconductor nanocrystals is a rapidly maturing research area. A tremendous amount of recent work has been devoted to this field with a particular emphasis on II−VI compound semiconductor systems such as CdSe.[1−5] This work has led to significant improvements in particle size tunability, size homogeneity, reproducibility, and even reduction of environmental hazards and safety problems. Nevertheless, further improvements are still possible and desirable in all of these areas. Further improvements in material quality and monodispersity will yield commensurate improvements in performance of NC-based devices. More importantly, continued research on synthesis of CdSe NCs will yield a more complete understanding of this important model system, and this improved understanding will form the basis for synthetic optimization of a broader range of semiconductor NCs.

A curious feature of the CdSe NC system has been the ubiquitous use of tri-*n*-alkylphosphine oxides such as tri-octylphosphine oxide (TOPO)[6] as coordinating ligands to cap the growing nanocrystals. While many refinements to the original CdSe NC synthesis have been reported over the past 10 years, almost all of these have included TOPO as a component in the reaction mixture. In cases in which TOPO has been omitted, the particle size distribution has suffered to varying degrees.[7,8] A few previous reports have examined in detail the binding of capping ligands at the NC surface;[9,10] however, these studies have not completely differentiated the functional roles of the various capping ligands used in the CdSe synthesis. The inability to explain the precise function of TOPO in the preparation of CdSe NCs and to rationally replace TOPO with a suitable alternative highlights our incomplete understanding of the CdSe NC nucleation and growth processes. Since TOPO represents an environmental hazard of unknown severity, its replacement by other reagents is desirable. In addition, the replacement of TOPO with a suitable [water-soluble] substitute might enable the production of monodisperse CdSe NCs directly in aqueous solution.

In the past few years, Peng and co-workers have improved on the synthetic method originally reported by Murray et al.[1] by replacing the traditional organometallic precursors with inorganic cadmium salts in the presence of fatty acid ligands.[3,7,11−14] This safer, greener approach produces highly monodisperse nanocrystals without a need for postreaction size sorting. A major drawback of the newer method, however, is that the low nucleation yield and rapid growth renders the production of small nanocrystals (<4 nm diameter) impractical since the reaction cannot be quenched quickly and reproducibly enough to isolate small, monodis-

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perse particles. More recently, it has been demonstrated that noncoordinating solvents such as octadecene (ODE) can be used to tune the reactivity and nucleation rate of monomeric precursors by diluting the coordinating ligands present in solution. The ability to tune reactivity with noncoordinating solvents was first demonstrated for CdS nanocrystals[15] and was later extended to InP and InAs nanocrystals.[16] In these systems, it was shown that the usual coordinating solvent, TOPO, could be eliminated completely in favor of an ODE/fatty acid mixture without adverse effects on the particle size distribution. Unfortunately, this simple substitution does not work as well in the CdSe system.[8,17,18] Based on a survey of published accounts, the production of highly monodisperse CdSe nanocrystals requires TOPO, and work in our laboratory has confirmed that the CdSe NC size distribution systems suffers when TOPO is eliminated from the reaction mixture. The TOPO requirement appears to be a unique feature of the CdSe system that does not apply to CdS, InP, or InAs.

We report here our findings regarding the importance of TOPO in the synthesis of CdSe nanocrystals and address the task of eliminating TOPO in the synthesis of CdSe NCs. Suitable, and perhaps even superior, alternative ligands are identified, and an explanation is proposed regarding the role of TOPO in the preparation of CdSe NCs. A simple and complete synthetic protocol for CdSe NCs is described that offers a very narrow size distribution tunable over a broad range of sizes. An unpredicted benefit of the new alternative ligands is that they slow the growth process, facilitating the reproducible production of smaller (<4 nm diameter) NCs, which are typically difficult to produce by preferred methods, as described above.

Experimental Section

All chemicals were used as received without further purification. Selenium powder (99.999%), octadecane (OD) 99%, technical grade tri-octylphosphine oxide (TOPO) 90%, technical grade 1-hexadecylamine (HDA) 90%, benzophenone (BP) 99%, hexadecyl hexadecanoate (HH) 98%, tri-octylphosphine (TOP), and stearic acid 98+% were obtained from Aldrich. Cadmium perchlorate was obtained from Alfa Aesar. Chloroform (A.C.S. reagent grade) was obtained from Spectrum Chemical Mfg. Corp. Methanol (HPLC grade) was obtained from Fisher Scientific. Cadmium stearate was prepared by combining $Cd(ClO_4)_2 \cdot 6H_2O$ with stearic acid in hot deionized water (resistivity $\geq$ 18 MΩ·cm).

The synthetic method reported here is an adaptation of the method previously reported by Peng et al.[7,14,19] The procedure involves the rapid injection of a selenium precursor into a hot solution of cadmium stearate in a mixture of octadecane, with coordinating ligands. A typical synthesis is as follows: Cadmium stearate (0.1 mmol), HH (0.1 g), HDA (1 g), and OD (5 g) were dried and degassed in a reaction flask by heating to 200 °C for 30 min under a stream of argon. (OD serves as a high-boiling, noncoordinating solvent. Other long-chain alkanes and alkenes can be substituted to limit the reaction temperature or to access even higher temperatures than have been used here.) The temperature was then raised quickly to 310 °C under 1 atm Ar, and 1 mmol of Se dissolved in a few milliliters of TOP was injected quickly by syringe into the rapidly stirring solution. Color changes were observed over a period of minutes following injection, progressing from colorless to yellow to orange to red to dark red. Some time after injection of the Se, and judging from the solution color or absorption measurements, the heat source was removed to stop the reaction. The temperature was stabilized and maintained at 150 °C for 3 h for annealing. It has been previously reported that the surface structure/reconstruction of nanocrystals might be improved by annealing in the presence of amines and that such annealing can lead to moderate improvements in PL quantum yield.[20,21] Our experiments have shown similar results. Nanocrystals with a very narrow size distribution were obtained from the foregoing procedure. With adjustment of growth time, reaction temperature, Cd:Se molar ratio, and the amount of noncoordinating solvent, the mean particle size can be tuned over a broad range. For example, samples with mean particle diameter less than 4 nm can be obtained by using a Cd:Se molar ratio of 1:10 and a TOPSe injection temperature in the range of 270−310 °C. Samples with mean particle diameter near 5 nm can be obtained using a Cd:Se molar ratio of 1:5 and an injection temperature of 310−330 °C. Samples with mean particle diameter of about 6 nm can be obtained by using a Cd:Se molar ratio of 1:2 and an injection temperature of 330−340 °C. In general, larger particles were favored by increasing growth times, by elevating the reaction temperature, by raising the Cd:Se molar ratio, and by reducing the amount of noncoordinating solvent.

The importance of TOPO was tested by performing the same reaction while omitting TOPO. In addition, other potential capping ligands were substituted for TOPO in numerous trials. Of particular interest were the cases in which 1 g of BP or 0.1 g of HH was substituted for the 0.25 g of TOPO. Results from these reactions will be discussed in detail in the next section.

After the reaction mixture had cooled to about 60 °C, methanol was added. CdSe NCs were extracted into the OD phase while excess coordinating solvent and unreacted precursors were removed with the methanol phase. This extraction was repeated four times. It was found that the addition of a few milliliters of chloroform improved the separation. Following the methanol extraction, excess acetone was added to precipitate the NCs from the OD phase. The sample was centrifuged to ensure high collection yield. The resulting powder was then redissolved in chloroform for future use.

Size-selective precipitation was not necessary to further narrow the size distribution.

UV−visible absorption measurements were carried out using an Agilent Technologies 8453 diode array spectrophotometer. Photoluminescence (PL) emission measurements were performed using a Photon Technology International C-60 spectrophotometer. A 75 W Xe lamp and monochromator were used to select 500 nm light for excitation. Emitted light was collected at 90° from the excitation and focused into a double monochromator with a photomultiplier tube detector operating in photon counting mode.

For transmission electron microscopy (TEM) measurements, a few microliters of a highly diluted sample were placed onto copper

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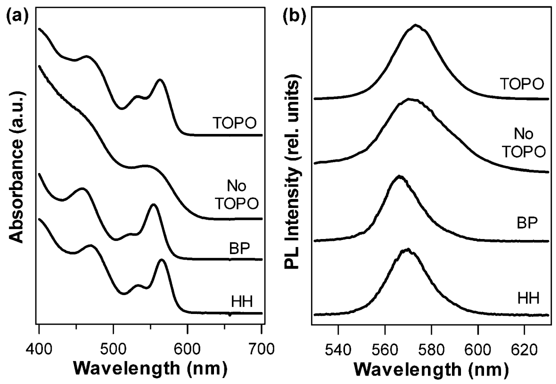

Figure 1. (a) UV−visible absorption spectra and (b) PL spectra of four CdSe NC samples prepared under similar reaction conditions but with different capping ligands employed in place of TOPO. From top to bottom, the samples were prepared with TOPO, without TOPO or any substitute reagent, with 1 g of benzophenone in place of TOPO, and with 0.1 g of hexadecyl hexadecanoate in place of TOPO.

grids coated with an amorphous carbon film and allowed to dry. A JEOL JEM-1010 Electron Microscope was used for imaging. Particle diameters were measured directly on photographic negatives at 120 000× magnification using a 30× magnifying loupe with reticle calibrated to 0.0025 in.

Results and Discussion

Figure 1a shows UV−visible absorption spectra from four CdSe NC samples prepared under similar reaction conditions. The only difference between these four samples was the presence of TOPO or a substitute reagent for TOPO in the reaction mixture. The topmost spectrum is from a sample prepared with 0.25 g of TOPO added into the reaction mixture. Below this are the spectra obtained (in order from top to bottom) without TOPO or any substitute ligand added into the reaction mixture, with 1.0 g of BP substituted for TOPO, and with 0.1 g of HH substituted for TOPO. The width of the first exciton absorption features, near 560 nm, are radically different in these four samples, indicating marked differences in the size heterogeneities of these samples.

A more quantitative comparison of size heterogeneity can be obtained from the PL emission spectra, which are shown in Figure 1b. Since the emission from a single nanocrystal is spectrally narrow, and since emission wavelength depends on particle size, the emission peak width provides a convenient comparative measure of particle size distribution between various samples. To make this comparison, the emission spectra were fit to Gaussian spectral profiles and the intensity observed within a particular wavelength range dλ was assumed to be directly proportional to the number of emitting nanocrystals within the corresponding size range dD. This analysis implicitly assumes that nanocrystals of all sizes within the sample are excited with equal probability and that the excited nanocrystals emit with equal probability. It is known that these assumptions lead to a systematic exaggeration of the size heterogeneity of the sample.[4] For this reason, the size distributions of selected samples were also measured directly from transmission electron micrographs (see Tables 1 and 2). Trends in the direct TEM measurements closely followed the trends observed in the emission peaks widths. In this report, emission peak width is emphasized as a relative measure of size homogeneity because this measurement is entirely unaffected by human biases which might affect the process of selection and measurement of particles from a TEM image field.

The mathematical relationship between emission wavelength and particle diameter was determined from measurements on a series of nearly monodisperse CdSe nanocrystal samples, each with a different mean particle size. In these calibration samples the prevalent particle size (i.e., most probable diameter, D) in a sample was determined from the absorption spectrum using the empirical equation previously reported by Yu et al. that relates D to λ_a, the wavelength in nanometers of the lowest energy excitonic peak in the absorption spectrum:[22]

$$D = (1.6122 \times 10^{-9})\lambda_a^{\ 4} - (2.6575 \times 10^{-6})\lambda_a^{\ 3} + (1.6242 \times 10^{-3})\lambda_a^{\ 2} - (0.4277)\lambda_a + 41.57 \quad (1)$$

Once the prevalent particle size, D, was determined from absorption measurements, emission measurements on these samples were used to determine the relationship between D and the peak emision wavelengths, λ_e, over the size range of interest (2−8.5 nm). The relationship between particle diameter and emission wavelength was found to obey the relationship

$$D = (2.6786 \times 10^{-9})\lambda_e^{\ 4} - (4.9348 \times 10^{-6})\lambda_e^{\ 3} + (3.4222 \times 10^{-3})\lambda_e^{\ 2} - (1.0511)\lambda_e + 121.74 \quad (2)$$

For each sample, the abscissa of the PL spectrum was transformed from λ_e to D using eq 2 and a Gaussian function was fit to this size distribution function in order to determine the estimated standard deviation in the diameter, σ_D. Size statistics determined by this method are presented in Table 1 for the samples depicted in Figure 1. As mentioned above, the relative standard deviation of the size distribution is measurably overestimated by the emission peak width, but this effect is systematic and does not hinder comparisons between samples.

The data in Figure 1 show that HH (a long-chain ester) and BP strongly favor narrow size distributions in CdSe nanocrystals. The size distribution for the sample prepared in the presence of BP and HH were even narrower than that obtained in the presence of TOPO. Although both of these alternative capping ligands performed well compared to TOPO, HH produced more reproducible size distributions than did BP (more consistent in both mean diameter and standard deviation) and required less material for equivalent performance. Based on these observations, further experiments were performed to evaluate the effects of HH on CdSe nanocrystal size distribution.

An important consideration in CdSe nanocrystal synthesis is the ability to vary nanocrystal size reproducibly over a range that allows broad spectral tuning. With slight modifications, the procedure described here has been used to synthesize CdSe nanocrystals with optical band gaps ranging

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Table 1. Spectral Characteristics and Size Statistics of CdSe NCs Prepared in the Presence of Various Coordinating Ligands

coordinating ligand	peak absorption wavelength λ_a (nm)	peak emission wavelength λ_e (nm)	prevalent diameter D (Å)	emission fwhm (nm)	σ_D (%) (PL spectrum)[a]	σ_D (%) (TEM)[b]
none	541	570	29	33	16	n/a
TOPO	563	573	33	23	11	6.2
BP	554	566	31	18	8.3	5.5
HH	565	570	34	20	9.3	5.6

[a] Relative standard deviation as estimated by a Gaussian fit to the emission spectrum (see text for details). This method exaggerates the absolute σ_D value, but is useful for comparison of samples. [b] Relative standard deviation as estimated from measurements on transmission electron micrographs ($N = 100$ particles).

Table 2. Size Tunability of CdSe NCs Prepared in the Presence of Hexadecyl Hexadecanoate (HH)

sample	peak absorption wavelength λ_a (nm)	peak emission wavelength λ_e (nm)	prevalent NC diameter D (Å)	emission fwhm (nm)	σ_D (%) (PL spectrum)[a]	σ_D (%) (TEM)[b]
a	625	632	59	23	11	n/a
b	587	591	41	21	10	5.9
c	580	586	38	22	9.8	5.6
d	566	571	34	21	9.4	5.6
e	555	563	32	20	9.3	n/a
f	522	529	26	21	8.0	n/a

[a] Relative standard deviation as estimated by a Gaussian fit to the emission spectrum (see text for details). This method exaggerates the absolute σ_D value, but is useful for comparison of samples. [b] Relative standard deviation as estimated from measurements on transmission electron micrographs ($N = 100$ particles).

from about 1.8 to 2.5 eV. This range of optical band gaps corresponds roughly to a particle diameter range of 25−60 Å. Figure 2 shows UV−visible absorption spectra and photoluminescence spectra of several samples of CdSe NCs with different particle sizes using HH as a coordinating ligand. This set of data demonstrates the wide tunability of particle size that is possible using HH as a capping ligand. The narrow emission peaks in these samples attest to the nearly monodisperse size distribution within the individual samples. Moreover, the PL spectra are free of any noticeable trap state effects. We have synthesized particles as small as 18−20 Å by the present method, and these particles do exhibit noticeable trap state emission; however, particles with diameters of 2.5 nm or larger that are prepared by this method do not exhibit significant trap state emission. Statistical analyses of size distributions in these samples were performed using the emission peak width method described above. In addition, particle sizes were also directly measured from transmission electron micrographs (100 particles per sample) for some of the samples. Representative TEM images of two of these samples are shown in Figure 3. A listing of particle size statistics for the samples whose spectra are shown in Figure 2 is given in Table 2.

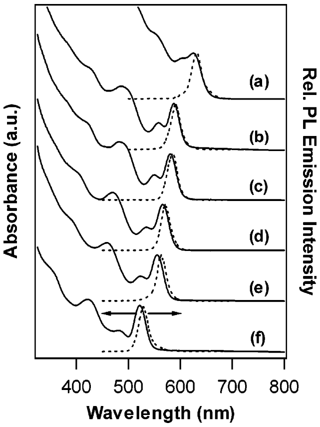

Figure 2. UV−visible absorption and PL emission spectra of differently sized CdSe NCs prepared by the method described here. Complete size statistics for these NCs are given in Table 2.

The method described herein provides four different means to control particle size. First, changes in growth time allow for minor adjustments of particle size with longer times favoring larger particles. Second, the addition of excess noncoordinating solvent favors formation of smaller particles. The reason for this is that a larger number of nuclei are formed during the nucleation phase when the stearate capping ligands are diluted.[15] Third, the nucleation temperature strongly influences particle size. Higher injection temperatures tend to yield larger particles. With control of injection temperature over the range 200−350 °C, particle sizes can be varied from approximately 2 to 6 nm. Finally, the Cd:Se molar ratio also affects the size of the resulting particles. Under conditions typically employed in our laboratory, NCs less than about 4 nm in diameter can be obtained using a Cd:Se molar ratio of 1:10, while NCs of about 5 nm can be

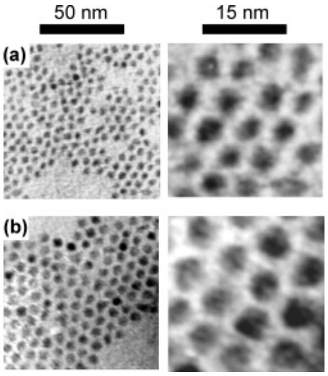

Figure 3. TEM images of CdSe NCs prepared in the presence of HH. Average particle diameters in these samples are (a) 4.7 nm and (b) 5.7 nm. Images on the right are higher magnification images taken from the same samples as those shown on the left.

obtained with a Cd:Se ratio of about 1:5, and NCs of about 6 nm can be obtained with a Cd:Se ratio of 1:2. Further adjustments of the ratio lead to the production of still larger particles.

TOPO appears to play an important role in the preparation of monodisperse CdSe NCs. As the early preparative procedure devised by Murray et al.[1] has been extensively modified over the past decade, almost all of the precursors and solvents used in the original method have been successfully substituted with other reagents without detrimental impact on particle size distribution. The major exception is TOPO. Often, TOPO has been combined with additional coordinating ligands, such as phosphonic acids,[23] alkylamines,[24,25] and carboxylic acids.[7] The affinity of long-chain carboxylic acids and phosphonic acids for Cd^{2+} is sufficiently strong that these ligands can dramatically hinder CdSe nucleation, even at high temperatures.[15] By comparison, TOPO is a weaker ligand; even at high concentration it does not prevent CdSe nucleation. Nevertheless, it has been a required ingredient for preparation of highly monodisperse CdSe nanocrystals even when more strongly coordinating ligands are present.

The ubiquity of TOPO in CdSe synthesis and its relatively weak coordination compared to other ligands which are often present in the same mixture suggests a unique and subtle role for TOPO during nanoparticle growth. Only a small amount of TOPO (3% or less of the reaction mixture) is required to achieve a narrow particle size distribution. Nevertheless, its presence appears to be critical to the production of high-quality CdSe nanocrystals. A comparison of absorption and emission spectra from samples with and without TOPO (top two curves in Figure 1) supports this idea. The absence of TOPO not only broadens the size distribution but also produces a noticeable asymmetry in the distribution, as indicated by the PL spectral line shape.

Since TOPO is unable to inhibit nucleation, it seems most likely that the influence of TOPO on the particle size distribution comes primarily during the growth phase. The growth phase of the nanocrystal synthesis has been discussed previously by Peng et al.[4] in relation to a model previously described in detail by Sugimoto.[26] These authors distinguish between two possible growth regimes: a focusing regime and a defocusing regime, which are characterized respectively by a narrowing and by a broadening of the size distribution. The difference between these two regimes is related to the tendency of nanocrystals to dissolve back into monomeric precursors, which is described by the Gibbs−Thomson equation:

$$C_e = C_B \exp(2\sigma V_m/rRT) \tag{3}$$

In this equation, C_e and C_B are the nanocrystal and bulk solubilities, σ is the surface energy, r is the nanocrystal radius, and V_m is the molar volume. Within certain limits, and in the case of diffusion-controlled growth, this model predicts a size-dependent particle growth rate given by

$$dr/dt = K(1/r + 1/\delta)(1/r^* - 1/r) \tag{4}$$

where K is a scaling factor that depends on the diffusion coefficients of the monomeric species, δ is the thickness of the diffusion layer at the nanocrystal surface, and r^* is a critical radius at which the solubility of the nanocrystal material would exactly equal the concentration of the monomers in solution. Particles larger than r^* grow while those smaller than r^* shrink. If the vast majority of particles in solution are larger than r^*, then size focusing is observed since smaller particles tend to grow faster than larger ones ($1/r$ dependence in the growth rate equation). High surface energy and/or very low monomer concentration promote a large critical radius, which in turn favors defocusing. The reason that a large critical radius favors defocusing is because those particles smaller than the critical radius shrink at a size-dependent rate, with smallest particles shrinking fastest. This process is well-known as Ostwald ripening, and its consequence in this case is a broadening of the size distribution.

Evidently, the presence of TOPO favors the focusing regime in a manner different from fatty acids or many other ligands. Under the model described above, this requires suppression of the critical radius during growth, presumably through a reduction of the specific surface energy, consistent with TOPO's capping function. The fact that TOPO is not required for preparation of monodisperse nanocrystals of other cadmium chalcogenides (CdS or CdTe)[15,22] suggests that the TOPO function specifically involves either Se ions or Se sites at the nanocrystal surface. Previous work has shown that Se ions at the nanocrystal surfaces are predominantly unbonded;[10] however, ^{31}P NMR data have led Kuno et al. to hypothesize that TOPO binds strongly to Se vacancies at the surface.[9] This model involves bridging of two or more Cd sites through the terminal O atom in TOPO. Such a picture is consistent with the observations reported here. TOPO could effectively suppress shrinkage of small particles by specifically binding high-energy Se vacancies that would otherwise be particularly vulnerable to solvent attack. Such anion vacancies may be less prevalent or more stable during growth of CdS nanocrystals, allowing the CdS system to remain in the focusing regime even in the absence of TOPO.

Based on the hypothesis above, several TOPO substitutes have been identified for CdSe NC synthesis. Preliminary successes with these ligands suggest that a variety of other ligands may be used in this capacity. The two primary criteria used in selecting these ligands were that they have a neutral terminal oxygen similar to the phosphine oxide group and that they have a high boiling point in excess of 250 °C. As shown in Figure 1, excellent results have been obtained with both BP (bp = 305 °C) and HH (bp = 360 °C). A high boiling point is an essential feature for a capping agent to be useful in the preparation of CdSe NCs. For this reason, dialkyl esters, with their higher boiling points, appear to be better suited for this application than dialkyl ketones of comparable molecular weight. BP (a di*aryl* ketone) has a high enough boiling point to allow its use in the CdSe NC

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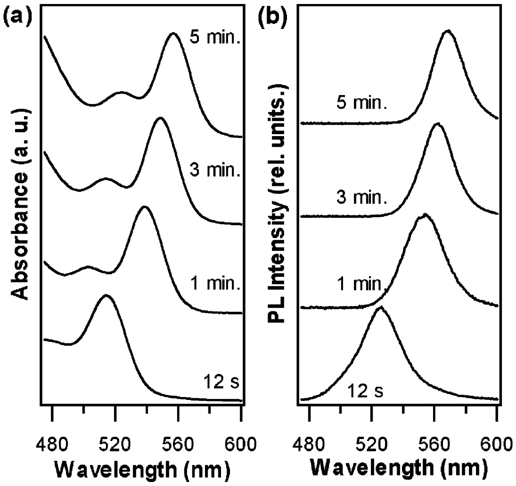

Figure 4. Evolution of (a) UV−visible absorption and (b) PL spectra during synthesis of CdSe nanocrystals at 310 °C with Cd:Se molar ratio of 1:10.

synthesis, although HH permits higher nucleation temperatures. These two molecules differ significantly in their ability to offer steric protection at the nanocrystal surface. This packing efficiency may account for the fact that significantly smaller quantities of HH (about 1/10 as much) were required to obtain comparable particle size distribution.

The results presented above show that both BP and HH represent excellent alternatives to TOPO in the synthesis of CdSe NCs. However, HH has an important synthetic advantage over TOPO when used with this method: particle growth rate at elevated temperature is significantly retarded in the presence of HH. Under the conditions used in this work (precursor concentration, Cd:Se ratio, and nucleation temperature), the CdSe NCs nucleate and grow rapidly in the presence of TOPO, reaching a limiting diameter of 5 nm within approximately 1 min. In the presence of HH, the particle growth rate is nearly 10 times slower. Figure 4 shows the evolution of (a) UV−visible absorption and (b) PL spectra of the CdSe NCs within the first few minutes after injection of the TOPSe precursor at 310 °C. The data show that the NC growth proceeds over a period of minutes, with growth continuing even after 5 min. An additional feature of this process is that the particle size distribution remains narrow over this entire period of growth. This is in contrast to most of the growth processes observed by Peng et al., which showed optimal size distributions after a short period of time, followed by rapid procession to the defocusing regime.[7] In fact, during the period between 12 s and 5 min after injection, the PL peak width narrows from about 35 nm fwhm to less than 24 nm fwhm. The relatively slow particle growth rate described here makes it feasible to stop the reaction quickly enough to produce very small ($<$4 nm) NCs when HH is used as a capping ligand. In contrast, the rapid nanocrystal growth using the fatty acid/TOPO/alkylamine system makes it difficult or impossible to reproducibly and reliably synthesize such very small CdSe NCs.[7,17] Both the growth rate and the narrowing of the size distribution that are shown in Figure 4 are temperature-dependent. At lower temperature, the growth and size focusing processes are slower still.

In summary, this contribution represents progress both in methodology and in understanding of the synthesis of CdSe NCs from ionic Cd^{2+} precursors. A new class of carbonyl-containing capping ligands has been identified to replace phosphine oxides as capping ligands in the reaction medium. This substitution allows for production of high-quality, nearly monodisperse NCs comparable to those previously obtained by Peng et al.[7] This substitution, however, is accompanied by at least two important advantages over previously reported methods. The first advantage is that the elimination of phosphine oxide in the reaction medium is a further step toward development of a green process for CdSe NC synthesis. The second advantage is slower initial growth of the NC nuclei. This slower growth allows for facile, reproducible production of very small (2−4 nm) NCs. The method described here can easily be combined with standard methods[12,24,27,28] for production of insulating CdS, ZnSe, or ZnS shells to reduce the sensitivity of the PL emission to the particle's local environment. In principle, ligand exchange and subsequent extraction of these NCs into other solvents such as water can also be achieved using existing methods.[2]

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