

Synthesis and Surface Composition Study of CdSe Nanoclusters Prepared Using Solvent Systems Containing Primary, Secondary, and Tertiary Amines

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A series of primary, secondary, and tertiary amines have been examined as cosolvents with trioctylphosphine oxide (TOPO) for the synthesis of CdSe nanoclusters. Syntheses were conducted in 66 mol % hexadecylamine (HDA), dodecylamine (DDA), dioctylamine (DOA), or trioctylamine (TOA) in TOPO and the growth rates and size distributions of the resulting products compared with those obtained from the same reaction conducted in pure TOPO. DOA was found to advantageously slow the growth rate of the nanoclusters and produce material with a narrow size distribution and moderate fluorescence quantum yield. Thermal gravimetric analysis (TGA) of the products has been used to quantify the ratio of TOPO to amine on the nanocluster surface and shows that the primary amines attain the highest packing densities. STM imaging of materials synthesized in the presence of HDA or DOA and then self-assembled on nonanedithiol SAMs shows improved surface stability for the DOA synthesized products.

Introduction

The synthesis of II–VI semiconductor quantum dots, in particular CdSe, has become well-established,¹ and interest in these materials has been fueled by the ability to synthetically adjust their size-dependent electronic and optical properties. Recent advances in the synthesis of these materials have included the use of more stable cadmium phosphonic or carboxylic acid complexes as the starting material,² as well as the addition of primary amines to the growth solvent,³ leading to improvements in both the size distribution and the quantum yield (QY) of the isolated products. Indeed, the QY of CdSe core quantum dots has been reported to be as high as 70%⁴ after treatment with primary amines, values once obtainable only through overcoating the CdSe cores with a wider band gap shell material, usually ZnS. While a variety of primary amines have been utilized for surface passivation, little mention has been made of the use of secondary and tertiary amines as a component of the reaction system. The benefits of primary amines over phosphines and phosphine oxides as coordinating species in nanocluster synthesis are believed to be due to higher packing densities,^{3b,4} with the role of the amine–metal bond strength remaining somewhat unclear.⁵ Thus, secondary and tertiary amines must also be examined if a complete picture is to be developed.

Herein we report a comprehensive study of the effect of different primary, secondary, and tertiary amines on the growth of CdSe quantum dots and find that the use of secondary amines can be advantageous under certain conditions.

High-quality CdSe quantum dots have been defined as possessing a narrow size distribution ($\sigma \sim 5\%$), high QY, and crystalline core over a large range of sizes with desirable surface properties.⁶ A variety of procedures have been reported which optimize these first two parameters, thereby producing strongly fluorescent, near-monodisperse material suitable for solution study. Less attention has been focused on the effect of the ligand shell on the physical behavior of the nanoparticles, however, particularly when it does not interfere with optical measurements. For example, in the context of our own work involving the self-assembly of CdSe quantum dots onto conducting substrates, we have found it necessary to also consider the self-assembly behavior of the resulting materials in addition to QY and size distribution. In this situation, a linking agent present on the substrate must either exchange with a nanocluster encapsulating species or coordinate to a vacant site on the nanocluster surface to allow binding. As many as four different coordinating species can be present in these synthetic schemes, and the exact composition of the encapsulating layer in the final product is poorly understood; yet the components of the organic layer encapsulating the CdSe core play a critical role by mediating the interaction of the nanocluster surface with the substrate. It is reasonable to assume that longer organic chain lengths and higher packing densities result in slower exchange. Recent work using oligomeric or dendron coatings on the surface of the quantum dot seems to support this view since

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the resulting materials show increased stability in solution,⁷ although no mention of the exchange behavior is made. Introducing a more exchange-compatible amine or other coordinating group into the system can be difficult, however, since “ligand exchange” procedures on a bare CdSe surface generally result in a reduction in the QY attributed to an increase in surface defects.⁸ Coordination to the nanoclusters during synthesis would seem to be a better route; however, a minimum organic chain length is required to obtain a boiling point compatible with the high CdSe synthesis temperature (>250 °C). In the case of the primary amines, this minimum effectively occurs at a chain length of 12 carbon atoms (dodecylamine, bp = 247–249 °C). One way to address these issues is to use a secondary or tertiary amine in place of the primary amine, where the added molecular mass of additional substituents allows the length of the organic chain to be shortened while still maintaining a compatible boiling point. The footprint of these materials on the nanocluster surface is also larger, with approximate estimated values of 0.25 nm² for primary, 0.5 nm² for secondary, and 0.73 nm² for tertiary amine structures,⁹ potentially reducing the packing density and thereby opening the surface to substitution. These factors must be carefully balanced, however, since a more accessible surface can also decrease the stability of the material.

Detailed surface analysis using XPS and ATR-IR has been conducted for CdSe nanoclusters synthesized in hexadecylamine;¹⁰ however, few studies thus far have examined the use of secondary or tertiary amines as a component of the growth reaction. Qu and Peng¹¹ mention the use of dioctylamine, but only in the presence of hexadecylamine as a solvent for Se/tributylphosphine precursor. Their conclusion is that the dioctylamine has no effect on the reaction. In contrast, Talapin et. al. use dioctylamine for the growth of CdSe and CdTe nanocrystals, but observe a precipitation of the reaction product.^{4,12} One significant difference between these studies is the choice of Cd source, which is CdO in the former and Me₂Cd in the latter. Trioctylamine has also been used as a solvent for the synthesis of CdS nanocrystals using a CdO-based method,¹³ and XPS analysis of the products indicated that oleic acid was the major surface species. To fully explore the effect of these interesting ligands as components of the synthesis, however, it is necessary to compare them in a single consistent reaction system. The experiments reported herein detail the effects of primary, secondary, and tertiary amine addition to the synthesis of

CdSe nanoparticles in TOPO, using a CdO/phosphonic acid precursor. The packing density and surface composition of these materials are determined via analysis of TGA data, and using dithiol SAMs on Au we demonstrate that the successful self-assembly of these nanocluster materials is highly dependent on the amine cosolvent used in the synthesis.

Experimental Section

General Considerations. Where appropriate, standard Schlenk and drybox techniques were used for the manipulation of materials under inert atmosphere conditions. All solvents were obtained from commercial sources and used as received. CdO (99.99%) was purchased from Strem. Tetradecyl phosphonic acid (TDPA) (98%) was purchased from Alfa. Trioctylphosphine oxide (TOPO) (99%), trioctylphosphine (TOP) (90%), hexadecylamine (HDA) (90% and 98%), dodecylamine (DDA) (98%), dioctylamine (DOA) (98%), trioctylamine (TOA) (98%), and Se (99.5+%) were purchased from Aldrich. All reagents were used as received without further purification. UV/vis spectra were recorded in toluene using a ThermoSpectronic Unicam UV 500 spectrophotometer, using 0.5 or 1 cm path length quartz cells. Thermal gravimetric analysis (TGA) was performed under N₂ on a TA instruments Q500 analyzer, using a heating rate of 10 °C/min to a maximum temperature of 600 °C. The mass of the TGA samples ranged from 1 to 5 mg. Photoluminescence (PL) spectra of aliquots taken from reactions were measured using a fiber-coupled CCD (Ocean Optics) with excitation from a hand-held UV lamp (365 nm). Quantum yields (QY) were measured by comparing integrated fluorescence intensity of absorbance matched solutions of quantum dot cores to a reference sample in a calibrated spectrofluorimeter (SPEX Fluorolog). The reference sample was a buffered solution of fluorescein (pH 9.5, Molecular Probes) with solution QY of 95%.¹⁴ ¹H and ³¹P NMR spectra were recorded on a Bruker Avance 300 NMR system operating at 300 and 121.5 MHz, respectively, and referenced to either TMS using the residual proton signal of CDCl₃ at δ 7.24 or to an external phosphoric acid standard set at δ 0.0 in the case of ³¹P spectra. The STM measurements were carried out in an ultrahigh vacuum (UHV) system (base pressure 5 × 10⁻¹¹ Torr). STM was performed in a constant current mode at various substrate biases (V_s) at room temperature. Tungsten STM tips were prepared by electrochemical etching in 0.1 M NaOH solution. After the tips were placed in a vacuum, they were Ar-ion-sputtered (0.5 keV) for 20 min. Powder X-ray diffraction (XRD) data were collected on a Bruker AXS D8 diffractometer using Cu Kα radiation; samples were 10–20 mg and deposited on low background quartz slides using a small amount of hydrocarbon grease.

Synthesis of CdSe Quantum Dots. The CdSe core nanocrystals were prepared using a modification of a previously reported procedure.^{2b} The exact conditions of the reaction strongly influence the properties of the final product; thus, details of a typical reaction are as follows: Solid CdO (0.0707 g; 0.55 mmol), TDPA (0.3162 g; 1.14 mmol), TOPO (3.5678 g; 9.23 mmol), and 90% HDA (4.2970 g; 17.8 mmol) were combined in a flask and warmed to 120 °C under vacuum (<1 Torr), leading to melting of all components except CdO. Heating of the system was accomplished using a mantle connected to a temperature controller, while the temperature input was provided by a thermocouple immersed in an oil-filled dip tube which was inserted through one neck of the flask using a ground-glass thermometer adapter. The mixture was degassed at 120 °C until bubbling had ceased (approximately 20

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min). The system was then backfilled with N₂ and the temperature increased to 310 °C under N₂ flow until formation of the Cd/TDPA complex occurred as indicated by a change from an orange mixture to a clear, colorless solution. While the reaction was heating to temperature, the Se solution was prepared by adding Se powder (0.05 g; 0.6 mmol) to 4.2 mL of TOP in the drybox, sealing the flask with a septum, and then briefly sonicating until no solid Se was visible. This solution was then loaded into a syringe and injected rapidly into the reaction flask, causing an immediate drop in the temperature to approximately 270 °C. The color slowly evolved from yellow to orange to red as nucleation and growth of the nanoclusters occurred, and during this time the temperature was brought back to 310 °C. When the growth had proceeded for the desired amount of time, typically 5–10 min, the heating mantle was removed and the reaction rapidly cooled to ~100 °C by blowing air across the surface of the flask. At this point 10 mL of butanol was added to the crude reaction mixture, forming a clear solution which was subsequently poured into 150 mL of MeOH, causing immediate precipitation. The solid was then collected by centrifugation (4 min at 4500 rpm) and dried under an N₂ stream, and the soluble portion was extracted into 2–4 mL of toluene. This mixture is again centrifuged to separate out the insoluble fraction, which was collected and dried to yield 0.3843 g of solid. Evaporation of the supernatant to dryness produces 2.8129 g of soluble material. Dissolution of this soluble fraction in 2–4 mL of toluene followed by addition to a second 20 mL portion of MeOH results in the precipitation of 0.5641 g of material. The toluene insoluble material isolated after the first precipitation was found to be sparingly soluble in CDCl₃ and was analyzed by NMR. ¹H NMR: δ 0.85 (t), 1.25 (s), 1.60 (bm). ³¹P{¹H} NMR: δ 35.4 (s), 49.1 (s) (see Supporting Information).

When another amine was substituted for HDA, the procedure detailed above was still utilized. The total mmol of TOPO and amine were kept constant for all reactions, including when no amine was used and TOPO was the only solvent. For DOA and TOA, EtOH was found to be a better solvent for the free amine and was substituted for MeOH in those cases. For all reactions examined other than those using HDA, a mass yield of 30–50 mg of soluble material was typically obtained after the second precipitation step.

For experiments where aliquots were removed during the reaction, the procedure was conducted as described above. Following Se/TOP injection, a syringe was used to remove a needle tip amount (10 in. 20-gauge needle, approximately 0.1 mL) of reaction solution, which was immediately added to 1 mL of toluene. The PL and UV/vis spectra of these samples were collected immediately after dilution.

TGA Study of Reaction Precipitates. All samples for TGA analysis were precipitated a total of two times from MeOH as described above for the HDA reaction and vacuum-dried to produce the solid used for the analysis (referred to in the text as the “standard” procedure). In all cases, only the toluene-soluble portion of the material was utilized, and any insoluble material present was removed by centrifuging the sample and decanting off the supernatant prior to its addition to MeOH. For the HDA reaction, this procedure results in the isolation of material which is mostly organic by mass (see Table 1); thus, several different precipitation procedures were utilized in order to improve the purity of the final product. The best results were obtained when, after the first precipitation exactly as described above, approximately one-quarter of the solid isolated was dried and redissolved in ~10 mL of toluene. The product was then precipitated a second time with an approximately equal volume of MeOH, added slowly until reaching the point at which flocculation is first noticed. This solid was then isolated by centrifugation and dried, and 2.5 mg of soluble material

Table 1. Summary of TGA Data for CdSe Synthesis Using Amines

solvent mixture used for synthesis ^a	final wt % ^b	precipitation procedure used ^c
pure TOPO	81.09%	standard
HDA/TOPO	1.22%	standard
HDA/TOPO	71.44%	alternate
DDA/TOPO	80.47%	standard
DOA/TOPO	77.17%	standard
TOA/TOPO	78.93%	standard

^a All amines present at 66 mol %. ^b Only the toluene-soluble product was used for the TGA experiments. ^c See Experimental Section for full details.

was obtained for analysis (referred to as the “alternate” procedure; see Table 1). Other methods examined included addition of the crude reaction mix directly to 125 mL of MeOH without first adding butanol, or dilution of the crude reaction mix with ~15 mL of a 50:50 (v/v) toluene/butanol mix before addition to 125 mL of MeOH. These methods also produced samples that contained a very high percentage of organic material by TGA, similar to the standard procedure.

STM Sample Preparation. Vacuum-evaporated Au films on cleaved Mica substrates were prepared by repeated cycles of Ar ion sputtering (0.5 keV) and annealing (680–720 K) in UHV prior to depositing the self-assembled monolayers (SAMs) of 1,9-nonanedithiol. SAMs were prepared by immersing the annealed Au sample into a ~1 mM solution of 1,9-nonanedithiol in ethanol for 15 min, after which the sample was rinsed in pure ethanol. The SAM-coated gold sample was then transferred to a ~25 nM solution of CdSe quantum dots either in toluene or in chloroform for 15 min. This solution was prepared from successive dilutions of a stock of known concentration, determined from UV/vis measurement of the wavelength of the first excitonic absorption peak and application of the functions provided in ref 15. After removal of the sample from the quantum dot solution, it was rinsed in pure toluene or chloroform, dried under a stream of nitrogen, and immediately inserted into the UHV system for STM measurements.

Results and Discussion

Effects of HDA Addition on CdSe Synthesis. To establish a baseline for comparison of the different reaction conditions studied, initial experiments used HDA cosolvent based on its prevalence in the literature. The results of a typical growth reaction using an approximately 66% HDA in TOPO (mol %) solvent mixture are shown in Figure 1. This ratio was selected since it is near the reported upper limit of 80 mol % for the controlled synthesis of CdSe.^{3b} Absorption and PL spectra recorded of the aliquots taken from the reaction are shown in Figure 1a, while the wavelength maximum of the PL peak is plotted as a function of reaction time in Figure 1b. Since the position of the PL peak predicts the size of the nanoparticles,¹⁶ Figure 1b indirectly charts the growth in size of the particles over the course of the reaction. Two general observations can be made. First, the initial growth in size of the CdSe is rapid but slows as the reaction progresses, effectively “leveling off” at a specific size corresponding to 600 nm emission. Second, the full-width at half-maximum (fwhm) of the PL peaks (Figure 1a) increases as the reaction progresses. Since

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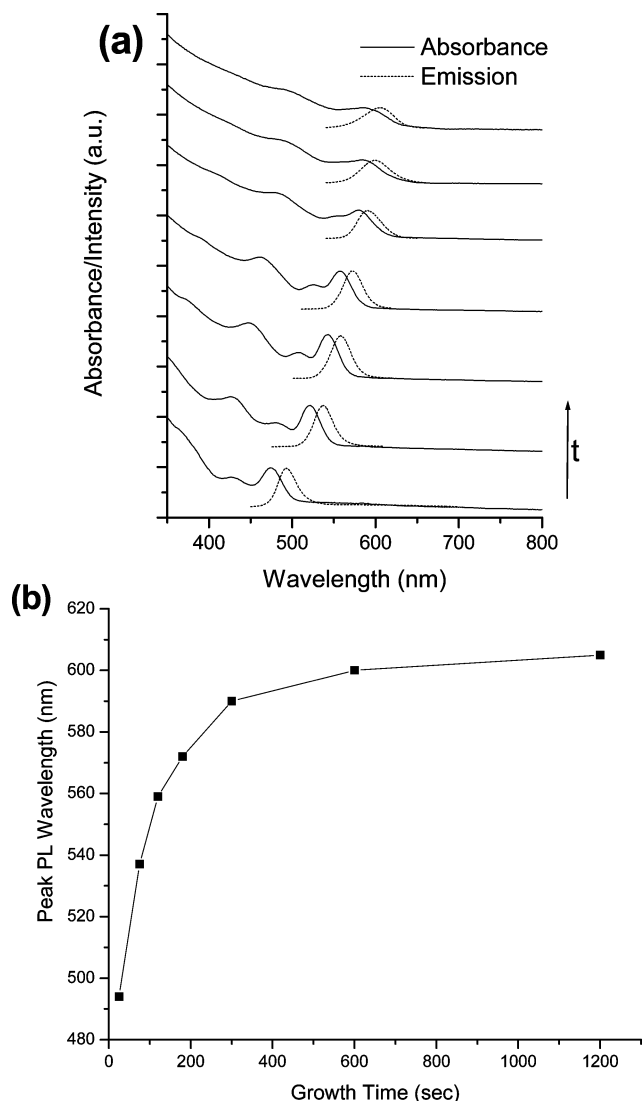


Figure 1. Growth of CdSe nanoclusters in 66 mol % HDA in TOPO showing (a) absorbance and PL spectra of aliquots removed during the reaction and (b) PL peak position as a function of time. Each PL spectra in (a) corresponds to a point in (b).

the fwhm is an indication of the size distribution of the sample,^{11,17} there is clearly an optimal time to isolate product from the reaction, a point after which only minimal growth occurs but the size distribution of the material broadens. The nanoclusters produced using this synthesis exhibit a higher QY and a narrower fwhm than the products of reactions where the amine is excluded, and this is particularly true for material isolated before growth is dramatically slowed (first 500 s of Figure 1b). However, during the workup of the reaction a large amount (approximately 380 mg) of toluene-insoluble material is also generated in addition to the soluble product. This solid exhibits PL, consistent with the CdSe cores, and thus likely contains some desired product from the reaction, yet attempts to extract soluble nanoclusters from this material were unsuccessful. Analysis of this solid by ¹H NMR shows resonances at δ 0.85, 1.25, and 1.6 (see Supporting Information), consistent with the presence of aliphatic hydrocarbon chains. Resonances in this chemical

shift range are seen for HDA, TOPO, TOP, and TDPA; Cd complexes of these species would also be expected to show peaks similar to the free ligands in this region. All of these species are components of the reaction; thus, we are not able to unambiguously identify this material. Similar results are obtained from ³¹P NMR, where a peak at δ 49.1 corresponding to TOPO is the primary feature. Also troubling is the TGA data obtained from the toluene-soluble product dried as a solid, which is presented in Table 1 (HDA/TOPO; standard precipitation). Nearly all of the sample weight is lost during the experiment (final weight percentage = 1.82%), and similar results were obtained using several different workup procedures (see Experimental Section for details). Substitution of 98% purity HDA for 90% HDA in the synthesis reaction also produces material with a low final weight percentage. Based on the assumption that all weight loss is due to organic material, the bulk of the soluble product obtained using this procedure is therefore not core material and still contains a significant fraction of organic impurity, most likely HDA. Previous TGA studies⁸ have reported a final weight percentage of ~77% for CdSe nanoclusters, although the synthesis and purification procedure differ from those utilized here. With use of the alternate precipitation procedure (vide supra) wherein the overall nanocluster concentration is reduced and approximately equal volumes of toluene and MeOH are employed in the second step, a more reasonable final weight percentage of 71% is obtained. An identical synthesis in pure TOPO using the standard two-step workup procedure results in a final weight percent of 81% (Table 1), although a direct comparison of these two values cannot be made since the primary amines would be expected to pack more densely on the nanocluster surface. This topic is addressed in greater detail in a separate section (vide infra). To briefly summarize, however, three important observations can be made from these HDA experiments which will help to put the other reaction systems in context. First, the size distribution is narrow and the QY^{3b,4} high; second, insoluble, luminescent material is generated from the reaction in addition to the desired product; and third, the purification of the resulting product is highly sensitive to the precipitation conditions employed and excess HDA is difficult to fully remove.

Effects of Other Amines on CdSe Synthesis. This same growth reaction was also conducted using a series of different amines (primary, secondary, and tertiary) under identical conditions, and the results are summarized in Figure 2, with the corresponding absorption and emission spectra used to generate the plot shown in Figure 3. For comparison, a reaction conducted using only TOPO is also shown. It is clear that the addition of amines slows the growth rate considerably from pure TOPO solvent, while at the same time reducing the ultimate size of the nanoclusters. The slowed growth rate is an important consideration since the highest quality material is isolated early in the reaction (vide supra), and the smallest sizes of quantum dots can be difficult to isolate from pure TOPO due to the speed of the reaction. The slowed growth rate is particularly noticeable in the early stages of the reaction, where the amine-containing experiments delay the initial nucleation of the particles as judged

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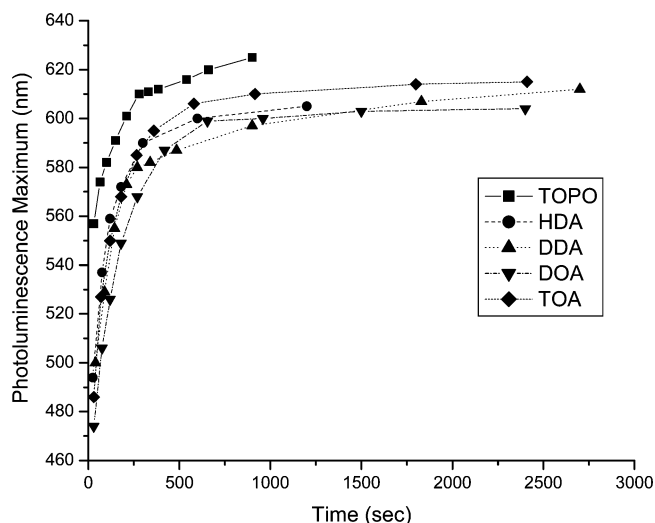


Figure 2. Comparison of the growth of CdSe nanoclusters in primary, secondary, and tertiary amines. All amines are present at 66 mol % in TOPO.

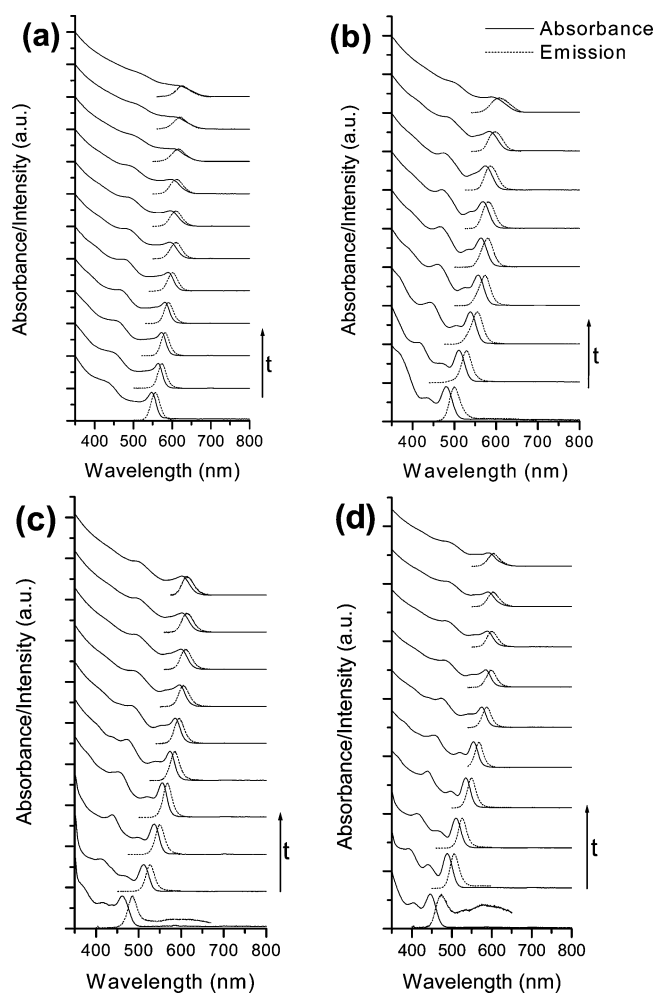


Figure 3. Absorbance and PL spectra of the aliquots taken from reactions conducted in (a) pure TOPO, (b) DDA, (c) TOA, and (d) DOA. All amines are 66 mol % in TOPO, and each PL spectrum corresponds to a point in Figure 2.

by the PL wavelength of the initial aliquot sample. The differences in the aliphatic chain lengths, cone angles, and coordination strengths between the primary, secondary, and tertiary amines are likely responsible for the observed rate differences. It has been shown that changes to either the coordination strength or the steric hindrance of ligands in

Table 2. Average (\pm std. dev.) for PL Measurements of the Aliquots Obtained during CdSe Synthesis

solvent mixture used for synthesis ^a	initial PL maximum (nm) ^b	final PL maximum (nm) ^c
pure TOPO	515 \pm 30	609 \pm 9
HDA	496 \pm 2	599 \pm 6
DDA	497 \pm 3	614 \pm 2
DOA	480 \pm 6	601 \pm 2
TOA	481 \pm 4	603 \pm 10

^a All amines present at 66 mol %. ^b First aliquot removed from the reaction. ^c Final aliquot removed from the reaction.

the reaction can impact the reactivity of the Cd-containing precursor complexes during the nucleation stage of the reaction,¹⁸ and it is likely both of these parameters are changing simultaneously while progressing through the series presented in Figure 2. With regard to the reproducibility of the data, the slowing of the growth rate relative to pure TOPO is always observed when amines are added to the system; however, some variation in the absolute measurement of the PL does occur from reaction to reaction, particularly for the initial aliquots taken shortly after nucleation. This is illustrated in Table 2, where measurements for the PL maxima averaged over multiple runs are reported for both the beginning and end of the reaction. It should be noted that the error in Table 2 corresponds to both variation in the PL from reaction to reaction reproducibility, as well as temporal error in the extraction of aliquots. This latter effect is accentuated for the initial aliquot measurements due to the initial slope of the curves in Figure 2.

To parallel the characterization performed for the HDA study, the TGA data for the products isolated from reactions using these other amines is also shown in Table 1. The DDA, DOA, and TOA systems all produce material with final weight percentages approaching the value obtained for the pure TOPO reaction. Not accounted for in the table is the fact that some insoluble, luminescent material is also present in the DDA reaction product after the initial precipitation, similar to what is observed for the HDA reaction but greatly reduced in quantity. In contrast, the DOA and TOA products are completely soluble following the same workup procedure. It stands to reason that the presence of any organic impurity in a solution would be detrimental to the self-assembly process, particularly if it is able to interact chemically with the dithiol-treated Au surface used in these experiments (vide infra).

Significant differences are also seen in the comparison of fwhm values for the PL between the different reaction systems. Figure 4 gives these values as a function of the PL emission wavelength during the course of the reaction. Interestingly, the pure TOPO reaction system produces product that is very satisfactory by this measure, and the secondary and tertiary amines seem to produce similar results. All three systems perform better than the primary amines, perhaps somewhat surprising since the fwhm of the as-prepared material was noticeably improved when HDA was used with Me₂Cd as the starting material.^{3b} When these trends are considered along with the kinetic data discussed earlier, the picture that begins to emerge is that the DOA

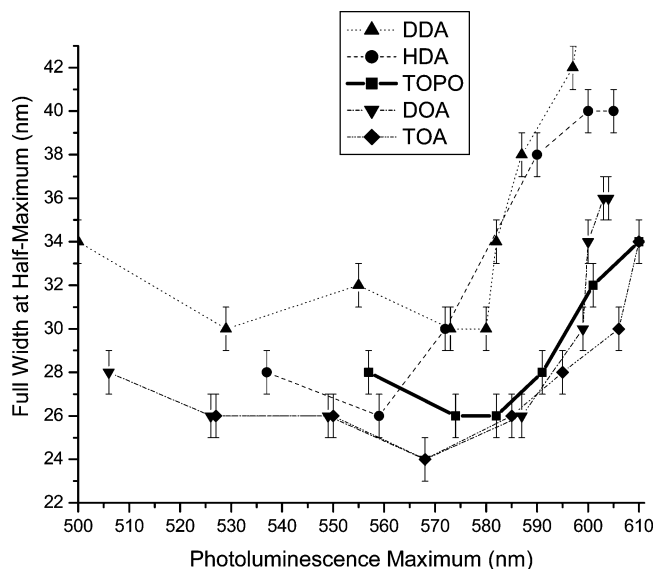


Figure 4. FWHM vs PL maximum for the synthesis of CdSe nanoclusters in primary, secondary, and tertiary amines.

and TOA are excellent choices for the production of small core sizes, while the TOPO only system is more suited to the production of larger core materials. Newer Cd starting materials based on carboxylic acid/CdO complexes are also well-suited for producing high-quality product at even larger sizes (PL max > 600 nm).^{2a,11} Secondary injections of reagents can also be used to increase the range of sizes isolated from a synthesis,¹⁷ though for CdO-based systems this strategy is less common. It is important then to consider the specific application and desired properties of the final product when determining which set of growth conditions should be utilized for a particular experiment.

The data presented in the above discussion demonstrates that secondary and tertiary amines both slow the growth rate of the reaction and narrow the fwhm of the product PL relative to TOPO. The main benefit of primary amine addition, therefore, appears to be its effect on the QY of the final product,¹¹ which can be significantly higher than when using TOPO alone. Our data interpretation suggests that, by this measure, the DOA and TOA have an intermediate effect, with the DOA exhibiting an increase in QY over pure TOPO and the TOA showing essentially no benefit to the QY. The QY of isolated products can vary dramatically based on the emission wavelength of the material as well as a variety of different synthesis parameters which have been examined in detail elsewhere.¹¹ In general, however, we have obtained QY of approximately 8% for reactions containing only TOPO and values of 11–30% for both DOA and DDA. Standard ZnS overcoating procedures have successfully been used to increase these values.¹⁹

Quantification of Surface Organic Coverage Using TGA. As mentioned previously, the weight percentages reported in Table 1 are not directly comparable due to the different packing densities expected for primary, secondary, and tertiary amines on the surface of a CdSe nanocluster.

There are few reports of TGA analysis of CdSe nanoclusters in the literature,⁸ but these studies do not examine material that has been synthesized in an amine cosolvent. The model presented here allows a determination to be made of both the packing density and composition of the nanocluster surface.

Assuming the weight loss during the TGA experiment is due exclusively to organic material and none is retained by the CdSe residue, the final weight percentage can be taken to be representative of the inorganic CdSe core. Kuno et al.⁸ have published a model for determining the number of surface Cd atoms available for binding. With use of this model and the assumption that the surface coordinating species only bind at Cd sites, the mass fraction of organic material can be expressed as follows:

$$X_{\text{org}} = \frac{SM_{\text{org}}\gamma}{SM_{\text{org}}\gamma + M_{\text{core}}} \quad (1)$$

where X_{org} is the mass fraction of organic material, S is the number of surface Cd atoms, M_{org} is the mass of the organic encapsulating groups, M_{core} is the mass of the CdSe core, and γ is the fraction of surface Cd atoms which are bonded to coordinating species. This “packing factor” term has previously been used for a similar TGA model of Au nanocluster cores.^{20,21} Solving (1) for γ gives

$$\gamma = \frac{X_{\text{org}}M_{\text{core}}}{SM_{\text{org}} - X_{\text{org}}SM_{\text{org}}} \quad (2)$$

Furthermore,^{8,22}

$$M_{\text{core}} = \frac{4/3\pi r^3 NMW_{\text{CdSe}}}{VN_A}$$

$$S = \frac{\{4/3\pi r^3 - [4/3\pi(r-d)^3]\}N}{V}$$

Here, r is the radius of the CdSe core, N is the number of CdSe units per unit cell, V is the volume of a unit cell, N_A is Avogadro's Number, MW_{CdSe} is the formula weight of CdSe, and d is the Cd–Se bond length. Therefore, by measuring the weight lost during the TGA experiment and inferring the size of the nanocluster core (by comparison of the UV/vis spectra of the sample with the empirical function provided in ref 15), the packing of the surface-coordinating species can be estimated. This is straightforward if only a single species is present on the nanocluster surface, and using the data presented in Table 1 for the reaction conducted only in TOPO, we calculate a γ of 0.3 which compares quite favorably with the 30% coverage reported previously for material obtained from a different synthetic system,⁸ as well as material from a CdO-based synthesis studied through NMR analysis.²³ The situation becomes more complex for

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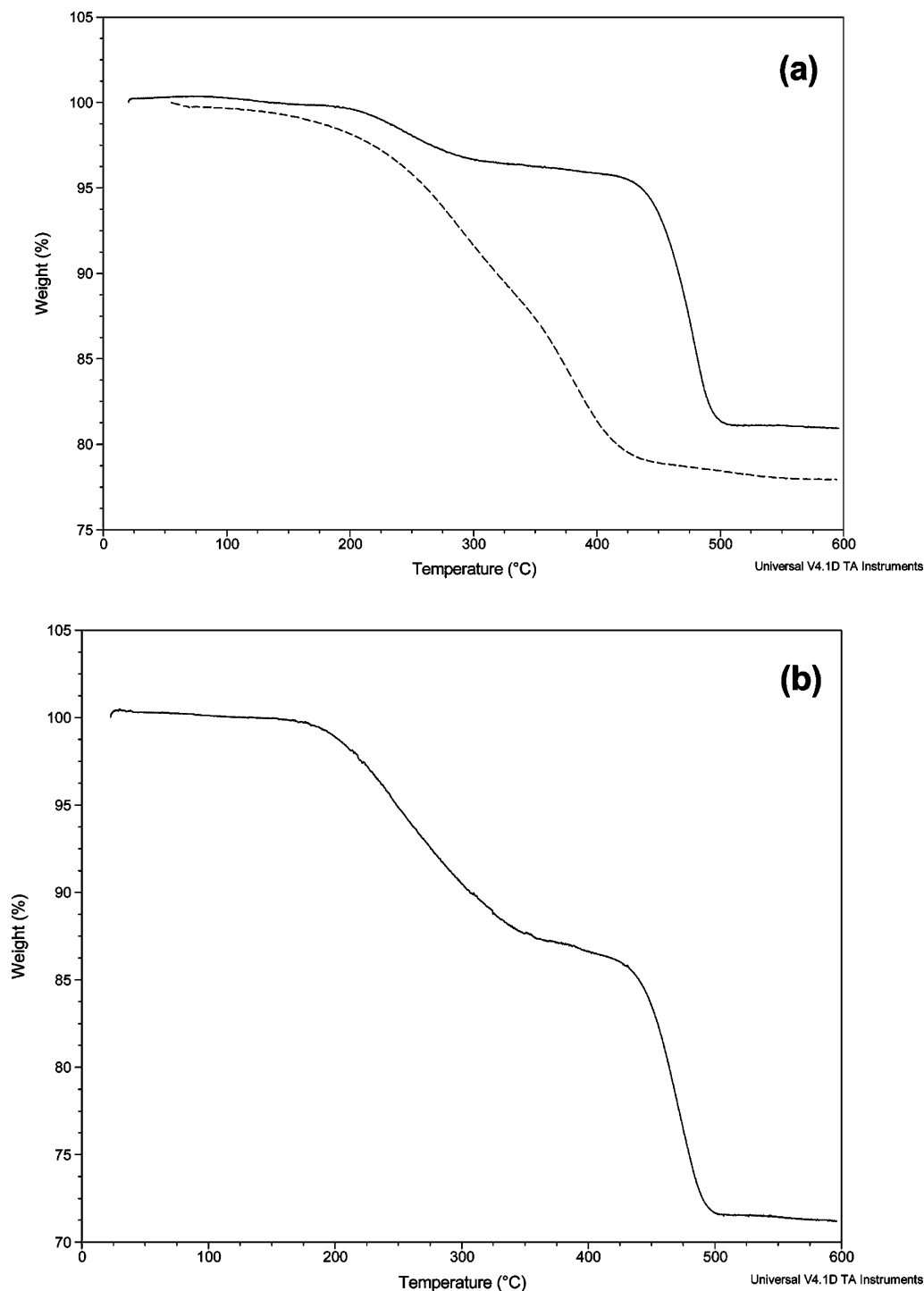


Figure 5. TGA data showing (a) reactions conducted in TOPO only (solid line) and HDA only (dashed line) and (b) 66 mol % HDA in TOPO.

the reactions conducted using an amine cosolvent, however, since a combination of several different species can be present on the surface simultaneously. Fortunately, the TGA experiment also provides insight into this question, as we observe two distinct thermal events in the decomposition profile when amine is present in the synthesis, as shown in Figure 5b. The first occurs at a temperature of approximately 200 °C, and the second occurs at approximately 425 °C. The sample synthesized without amine in TOPO (Figure 5a) shows the bulk of its decomposition beginning at 425 °C; thus, we assign the thermal event in this region to the loss of TOPO, TDPA, TOP, and/or TOPSe from the nanocluster.

It should be noted that a small mass loss ($\sim 3.7\%$) is also observed for this sample at ~ 200 °C, possibly due to the presence of other weakly bound phosphine species. We therefore attribute the lower temperature mass loss observed in the amine-containing samples to weakly binding species, which should predominately be the amine molecules. To verify this assignment, a sample of CdSe nanoclusters was prepared using an alternative method which uses only HDA solvent,²⁴ with no TOPO or TOP present in the synthesis.

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Table 3. CdSe Surface Composition Analysis from TGA Data

solvent mixture used for synthesis	CdSe core radius (r) in nm ^a	amine wt %	phosphine wt %	amine:phosphine molar ratio ^b	calculated γ_{amine}	calculated $\gamma_{\text{phosphine}}$	calculated γ^c
pure TOPO	2.12	0.0	18.9%			0.3	0.3
HDA/TOPO	1.72	13.4%	15.1%	1.4:1	0.3	0.2	0.6
DDA/TOPO	2.08	9.8%	9.7%	2.1:1	0.3	0.2	0.6
DOA/TOPO	1.91	6.8%	16.1%	0.7:1	0.2	0.3	0.5
TOA/TOPO	2.03	1.8%	19.9%	0.1:1	<0.1	0.4	0.4

^a The radius of the nanocluster core was calculated by UV/vis measurement of the wavelength of the first excitonic absorption peak and application of the functions provided in ref 15. ^b This ratio, calculated from the TGA data, is independent of S , the calculated number of surface Cd atoms. ^c Rounding errors account for those γ values that differ from the sum of γ_{amine} and $\gamma_{\text{phosphine}}$.

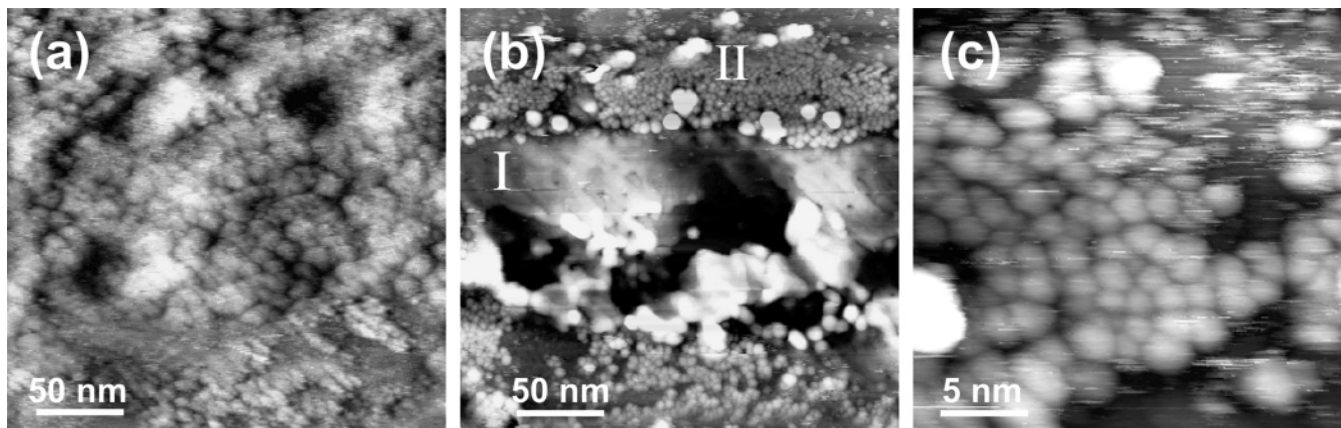


Figure 6. STM images of CdSe nanoclusters grown in (a) HDA [$V_s = -1.7$ V; $I_T = 0.1$ nA] and (b, c) DOA [$V_s = 2.45$ V; $I_T = 0.56$ nA] solvent systems. In (b), regions of bare SAM (I) and areas covered by a monolayer of CdSe nanoclusters (II) are clearly identified. A detailed image of a nanocluster monolayer (c) reveals a tightly packed structure of particles.

TGA of this exclusively amine-stabilized material is shown in Figure 5a and exhibits a broad mass loss beginning at ~ 175 °C and no evidence of the 425 °C event, thus confirming our assignments.

Separation of the mass loss into two regions and broadly identifying them as either “amine” or “phosphine” allow the mass percentage and molar ratio of each to be calculated for the sample, assuming a sequential elimination. In Figure 5b, these percentages were calculated at a temperature of 400 °C. Then, using the molecular mass of each and applying eq 2, the packing density of each species on the nanocluster surface, γ_{amine} and $\gamma_{\text{phosphine}}$, can be calculated. Similarly, by using the total organic weight lost and the ratio of amine to phosphine calculated for the sample, the total packing density γ of all coordinating species can be determined. These results are presented in Table 3. As expected, the primary amine-prepared samples show the highest packing densities and highest mass percentages, followed by the secondary and then tertiary amines. In addition, considering the approximations of this model, the value of $\gamma_{\text{phosphine}}$ remains relatively consistent for all samples, implying that the amines displace little if any of the phosphine species, and instead occupy available binding sites on the nanocluster surface. Primary amines should be better able to penetrate the phosphine encapsulating shell and attach to these sites, and indeed DDA and HDA show the highest values for both γ_{amine} and γ . It is also worth noting that the loss of the amines at lower temperatures during the TGA experiments can be interpreted to suggest that they bind more weakly than the phosphine species, and the observed PL increase due to primary amine addition is solely a packing density effect due to increased

passivation of the nanocluster surface. Further analysis of the surface species composition in these systems is currently underway.

STM Analysis of Self-assembled Structures. Our main interests with respect to these materials are in the area of self-assembly on conducting substrates, in a situation similar to previous work utilizing Au nanoclusters.²⁵ In these previous experiments, the assembly behavior was critically dependent on both the thickness of the cluster encapsulating layer as well as the length of the dithiol tethering the nanocluster to the substrate. Initial experiments with the self-assembly of CdSe relied on the material synthesized using HDA cosolvent and were found to produce surfaces which either were unstable to STM imaging or produced disordered surface structures. These results can be attributed to both the length and packing density of the HDA on the nanocluster surface, as well as to the possible presence of organic contaminants retained from the synthesis. With use of the results presented above as a guide, DOA was selected as the optimum material for preparation of nanoclusters for these experiments since it provides material with a narrow fwhm and good QY, while the surface-coordinating species should be more amenable to self-assembly due to their significantly shorter length. In addition, the DOA molecules have a lower packing density than the primary amines (Table 3), which may allow enhanced attachment through available Cd binding sites. Indeed, when the materials produced from these syntheses are exposed to a nonanedithiol-functionalized Au substrate, the difference in the final self-assembled structure

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is dramatic, as shown in Figure 6. The STM image of a sample surface exposed to HDA-synthesized CdSe nanoclusters shows an amorphous surface layer with very little order. A typical feature size is 15–20 nm, which is significantly larger than the expected core size. Consequently, it is reasonable to attribute the observed features to clusters or multilayers of CdSe nanoclusters, contaminated with excess organic material. In contrast, a quite different surface structure is exhibited by a sample surface exposed to the DOA-synthesized material. Individual nanoclusters with a typical diameter of 3.7 nm are observed to form monolayer-thick rafts on the SAM-covered surface. These monolayers appeared to be reasonably stable, withstanding the STM imaging well; very little change was observed during the capture of multiple image frames over a given area.

Summary. In summary, a comparison of the growth of CdSe nanoclusters in primary, secondary, and tertiary amines using a single consistent synthetic scheme has shown that the main benefit of primary amine addition to the nanocluster synthesis reaction is in the isolation of material with a high QY. Other benefits, such as slower growth rate and narrower size distribution, can also be realized or improved through the use of secondary and tertiary amines. In addition, a

straightforward TGA method can be used to determine the surface packing and composition of these nanoclusters. Taken together, the data provide a picture that one set of growth conditions may not be suitable for all possible applications, and the desired properties of the final material should be balanced when selecting a preparative scheme. This was demonstrated by the self-assembly of CdSe nanoclusters on Au substrates, where the choice of amine was found to strongly influence the quality of the resulting structure. Further studies of these self-assembled films are currently underway.

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Supporting Information Available: Derivations for eqs 1 and 2, ^1H and ^{31}P NMR data for the insoluble material isolated from the HDA reaction, and XRD patterns for the products of all reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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