

Synthesis of CdSe Quantum Dots by Evaporation of Bulk CdSe using SMAD and Digestive Ripening Processes

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Here we report synthesis of CdSe quantum dots (QDs) by evaporation of bulk CdSe using the solvated metal atom dispersion method (SMAD), followed by reflux in toluene and in *t*-butyltoluene (TBT). The as-prepared SMAD product exhibits broad photoluminescence spectra (PL), but upon reflux in toluene or *t*-butyltoluene, interestingly, the PL spectra become narrow with an increase in fluorescence intensity. The temporal evolution of quantum dots was monitored by in situ UV–vis spectroscopy. The XRD data reveal that the formed CdSe QDs retain the wurtzite structure of the starting bulk CdSe material. The merits of this synthesis procedure are the use of bulk CdSe as starting material, possibility of scale up, elimination of high-temperature injection and size-selective precipitation processes.

1. Introduction

Semiconductor quantum dots of groups II–VI have been intensively studied because of their size-tunable optical properties and their applications, primarily involving CdSe NCs in photostable luminescent biomedical labeling,^{1,2} solar cells,^{3,4} and light emitting devices (LEDs).^{5–7} Over the past few years, several synthetic routes have been established to synthesize CdSe NCs, and one such synthetic route is the use of (CH₃)₂Cd as a source of Cd, SeTOP as a source of Se, trioctylphosphine (TOP), and trioctylphosphine oxide (TOPO) as capping agents.⁸ An alternate method was established by Peng et al., where they used CdO with hexylphosphonic acid or tetradecylphosphonic acids and SeTOP to synthesize high-quality CdSe NCs.⁹ A single-source precursor composed of both Cd and Se has also been employed for the synthesis of CdSe NCs.^{10,11} Porous CdSe aerogels have also been synthesized,¹² where thiolated-capped CdSe nanoparticles were transformed into aerogels by CO₂

supercritical drying.^{12,13} In many of these procedures, there is an effect of ligand choice, ligand amount, solvent chosen, and temperature^{14,15} that allows the control of particle size and resultant optical properties. Besides TOP and TOPO, hexadecylamine (HDA) has also been used as a third coordinating ligand for surface passivation,¹⁶ and for aid in particle size adjustment.¹⁷

In the work described herein, bulk CdSe was evaporated under vacuum and co-condensed with tetrahydrofuran (THF). This “SMAD” product was then digestively ripened¹⁸ in toluene and in *t*-butyl toluene in the presence of excess capping ligands to synthesize monodispersed CdSe QDs with increased fluorescence intensity. TOP/HDA and TOPO/HDA in 60:40 molar ratio were used for the surface passivation of CdSe QDs.

2. Experimental Procedures

Preparation of CdSe–THF–TOP–HDA–Toluene As-Prepared SMAD Colloid. A stationary reactor described in detail in ref.¹⁹ was used for the synthesis of CdSe–THF–toluene–TOP–HDA colloid. THF and toluene were purchased from Fisher. These solvents were distilled and degassed four times by the standard freeze–thaw procedure prior to the reaction. TOP and HDA were purchased from Aldrich and used as received. All the glassware was vigorously cleaned before use. **Caution!** Acid and base baths may cause burns and should be handled with care wearing proper protective clothing, gloves, and goggles.

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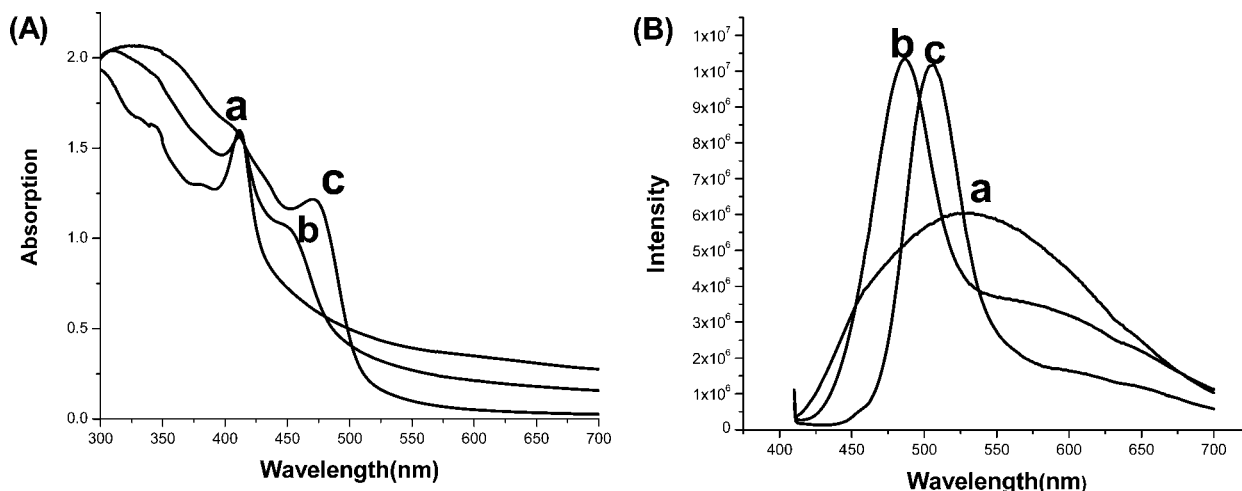


Figure 1. (A) UV-vis absorption spectra of CdSe with TOP and HDA in 60:40 ratio: (a) as-prepared SMAD product, (b) after 1 h of reflux, and (c) after 16 h of reflux in toluene; and (B) corresponding photoluminescence spectra.

Typically, 0.3 g of bulk CdSe powder was evaporated using a C9 boron nitride crucible (R.D. Mathis # C9-BN) resting in a tungsten wire basket (R. D. Mathis # B8B # x. 030 w), which was in turn connected to water-cooled copper electrodes. **Caution!** CdSe is carcinogenic. Protective gloves are necessary when handling this chemical. During the vaporization process, heat transfer from the hot crucible to the walls of the SMAD reactor was minimized by covering the crucible and the basket with a fibrous alumina ceramic insulator (Zircar product, Inc.) A solvent shower head was inserted into the reaction vessel for THF solvent vapor delivery. Coordination ligands (TOP and HDA in 60:40 molar ratios) were dissolved in 60 mL of toluene and placed at the bottom of a 3 L reactor vessel along with a stirring bar. The above crucible connected to electrodes was then vacuum sealed within the reactor vessel using a vacuum line with a liquid nitrogen trap and diffusion pump. The reactor vessel was then surrounded by a liquid nitrogen Dewar and cooled to 77 K. When the vacuum reached 4×10^{-3} torr, 50 mL of THF was initially condensed onto the reactor vessel, and the bulk CdSe was then vaporized by gradually increasing the heating temperature up to ~ 900 °C using the water-cooled electrodes.

During vaporization, 50 mL of THF was allowed to co-condense with the evaporated CdSe. A total sum of 100 mL of THF was used for co-condensation. In this way, the aggregation of evaporated CdSe was restricted. It took ~ 2 h for complete vaporization of CdSe. The frozen matrix had a deep brown color. The liquid N₂ Dewar was removed, and the matrix was warmed with a heat gun. Upon melting, the CdSe-THF matrix was allowed to mix with the coordination ligands in toluene by vigorous stirring for 45 min and the color became yellow-orange with a single phase. The as-prepared SMAD product was then siphoned into a Schlenk tube under argon. **Caution!** Eye protection is necessary when working with a vacuum line.

Preparation of CdSe-TOP-HDA-Toluene Colloid. The Schlenk tube containing the as-prepared SMAD product was connected to a vacuum and the THF was evaporated along with a small amount of toluene. The remaining product, now CdSe-TOP-HDA-Toluene colloid was deep yellow-orange in color.

Digestive Ripening. Digestive ripening involves heating of the CdSe-TOP-HDA-Toluene solution under reflux at the boiling point of toluene (109 °C) under argon.¹⁸ It is the key step for the formation of monodispersed and highly fluorescent QDs. Isolation of CdSe QDs was carried out by precipitation in anhydrous methanol and then washing with acetone and anhydrous methanol. This process was repeated three times to remove excess ligands,

and the product was then redispersed in toluene. Anhydrous methanol and acetone were purchased from Aldrich. No post-preparative size-selective precipitation process was carried out. On the basis of our previous calculations on gold-dodecanthiol SMAD preparation system²⁰ (see ref 17 in that paper), the yield is about 78% based on CdSe.²¹

Preparation of CdSe-TOP-HDA-*t*-Butyltoluene (TBT) Colloid. To achieve a higher temperature for digestive ripening, we used TBT instead of toluene while keeping all other parameters constant. In addition, CdSe with TOPO and HDA was also synthesized (see the Supporting Information for details).

Characterization. UV-Vis Spectroscopy. UV-vis absorption spectra were obtained using an in situ UV-vis optical fiber, assisted by a DH-2000 UV-vis optical spectrophotometer instrument (Ocean Optics Inc.).

Photoluminescence Spectroscopy. Fluorescence spectra were measured by using a Fluoro Max-2 instrument from HORIBA Jobin Yvon Company. These samples were all excited at 400 nm. Photoluminescence quantum yield values (Φ_{em}) of CdSe were measured relative to Rhodamine 6G in methanol, assuming it is PL QYs as 95%, by following the previous procedures^{22,23} and calculated using eq 1.

$$\Phi_{em} = \Phi_S(I/I_S)(A_S/A)(n^2/n_S^2) \quad (1)$$

In eq 1, I (sample) and I_S (standard) are the integrated emission peak areas, up to 480 nm excitation. A (sample) and A_S (standard)

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(21) On the basis of the gold-dodecanthiol system, each QD had Cd₃₀₀₀Se₃₀₀₀, (TOP)₃₂₅, and (HDA)₃₂₅. On this basis, the empirical formula of QD is (CdSe)(TOP)_{0.11}(HDA)_{0.11}; 80% of CdSe (0.3 g) weight is available during QD synthesis. So, CdSe used for QD is 0.24 g. Total number of CdSe molecules present in $0.24 \text{ g} = 0.24 \text{ g} \times (6.023 \times 10^{23} \text{ mol}^{-1}) / (191.36 \text{ g mol}^{-1}) = 7.554 \times 10^{20}$. Total number of TOP in the system = $7.554 \times 10^{20} \times 0.11 = 8.31 \times 10^{19}$. Total number of HDA in the system = $7.554 \times 10^{20} \times 0.11 = 8.31 \times 10^{19}$. Therefore, total number of ligands = 1.662×10^{20} . Converting the number of molecules into weight (grams), weight of CdSe = 0.24 g. Weight of TOP = $(8.31 \times 10^{19}) \times (370.65 \text{ g mol}^{-1}) / (6.023 \times 10^{23} \text{ mol}^{-1}) = 0.0511 \text{ g}$. Weight of HDA = $(8.31 \times 10^{19}) \times (241.46 \text{ g mol}^{-1}) / (6.023 \times 10^{23} \text{ mol}^{-1}) = 0.0333 \text{ g}$. Total weight of QDs (theoretical yield) = $0.24 \text{ g} + 0.0511 \text{ g} + 0.0333 \text{ g} = 0.3244 \text{ g}$. Experimental yield = 0.2547 g. Percentage yield = $(\text{experimental yield}) / (\text{theoretical yield}) \times 100 = (0.2547 \text{ g}) / (0.3244 \text{ g}) \times 100 = 78.5\%$.

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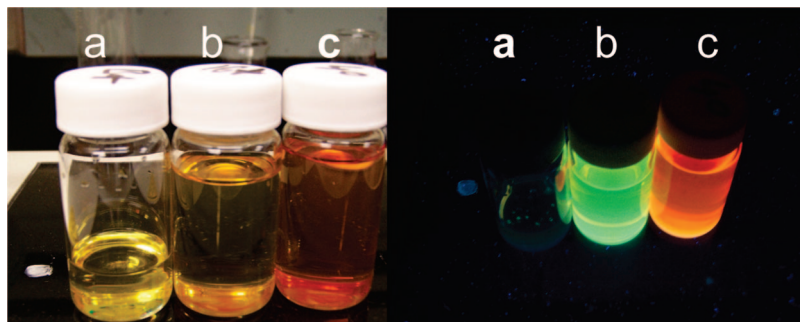


Figure 2. Corresponding samples (a) before reflux, (b) after 1 h of reflux, and (c) after 16 h of reflux in toluene, (left) without UV-vis light on and (right) with UV-vis on.

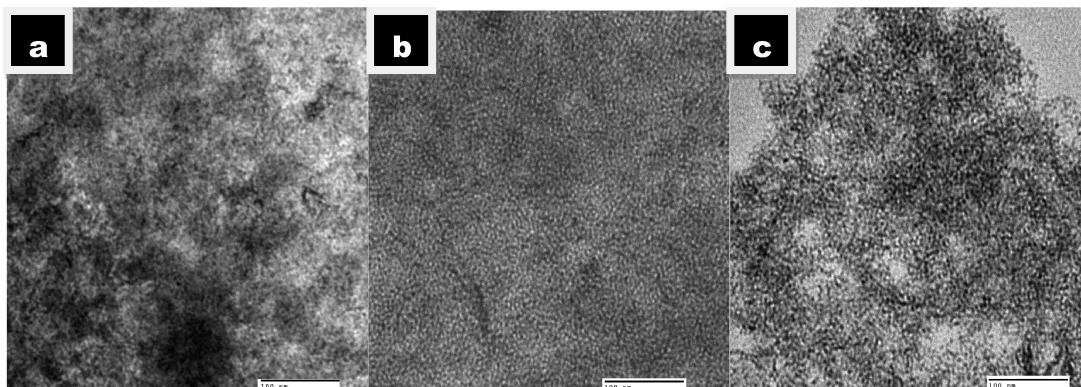


Figure 3. TEM images (a) before reflux, (b) after 1 h of reflux, and (c) after 16 h of reflux in toluene. The scale bar = 100 nm.

are the absorption (<0.1) at 480 nm; n (sample) and n_s (standard) are the refractive indices of the solvents; and Φ_{em} and Φ_s are the PL QYs for the sample and the standard, respectively.

Transmission Electron Microscopy. TEM studies were performed on a Philips CM100 operating at 100kV. The TEM samples were prepared by placing a few microliters of precipitated, washed, and redissolved sample in toluene onto a carbon-coated Formvar copper grid. The grids were allowed to dry under ambient conditions for 4–5 h.

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction patterns were recorded by a Bruker D8 X-ray diffractometer with Cu K α radiation. PXRD samples were prepared by the evaporation of toluene from the CdSe/toluene dispersion loaded on XRD glass plates. The samples were scanned from $20 < 2\theta < 80^\circ$ at increments of $0.02^\circ/\text{min}$, and the total acquisition time period was more than 2 h.

3. Results and Discussion

CdSe–TOP–HDA–Toluene. Initial attempts to synthesize CdSe QDs by adopting our previous bulk material:ligand ratio (1:30)²⁰ were not satisfactory. A higher ligand ratio (1:40) produced particles in different shapes as shown in the Supporting Information, and this procedure lacked reproducibility. Such results were not uncommon, especially when using TOPO.²⁴ HDA as a coordination ligand in addition to TOP or TOPO worked best when the molar ratio was 60:40 for TOP:HDA. It is believed that HDA, being a weaker ligand than TOP/TOPO, helps in growth kinetics.^{15,16} Figure 1A shows the UV-vis absorption spectra of “as-prepared CdSe–TOP–HDA–toluene colloidal SMAD product”, after

Table 1. Comparison of UV-vis Absorption and Emission Spectra of CdSe with TOP and HDA in 60:40 Ratio at Various Temperatures in TBT

6 h of heating and reflux in TBT	UV-vis absorption wavelength λ_{max} (nm)	emission spectra
before reflux	410	broad band
120 °C	446	528 nm
150 °C	488	536 nm
after reflux at 190 °C	518	552 nm

1 h of reflux and 16 h of reflux in toluene and Figure 1B shows the corresponding emission data, all the samples being excited at 400 nm. The as-prepared SMAD product is polydispersed in size and the narrow size distribution of these quantum confined particles was achieved by the digestive ripening. The as-prepared SMAD product has a broad fluorescence band, but upon digestive ripening, the fluorescence narrowed significantly. The UV-vis and PL data indicated a red shift upon prolonged reflux, suggesting particle growth. After 1 h of reflux, these particles gave a green color fluorescence and after prolonged 16 h of reflux the same sample fluoresced at higher wavelength (Figure 2). The TEM (Figure 3) images also support the formation of quasi monodispersed particles, showing narrowing of the size distribution after digestive ripening, even after just 1 h. The measured QY of these samples after reflux are 6–11%.

CdSe–TOP–HDA–*t*-Butyltoluene. In toluene (bp 109 °C), only smaller size particles were synthesized. A possible explanation for the smaller size of CdSe QDs in toluene is that when the boiling point is lower (109 °C), there is lower kinetic motion for CdSe QDs and hence fewer collisions and slower particle size adjustment. So, we used TBT (bp 190 °C) to achieve higher temperature for reflux. Figure 4A

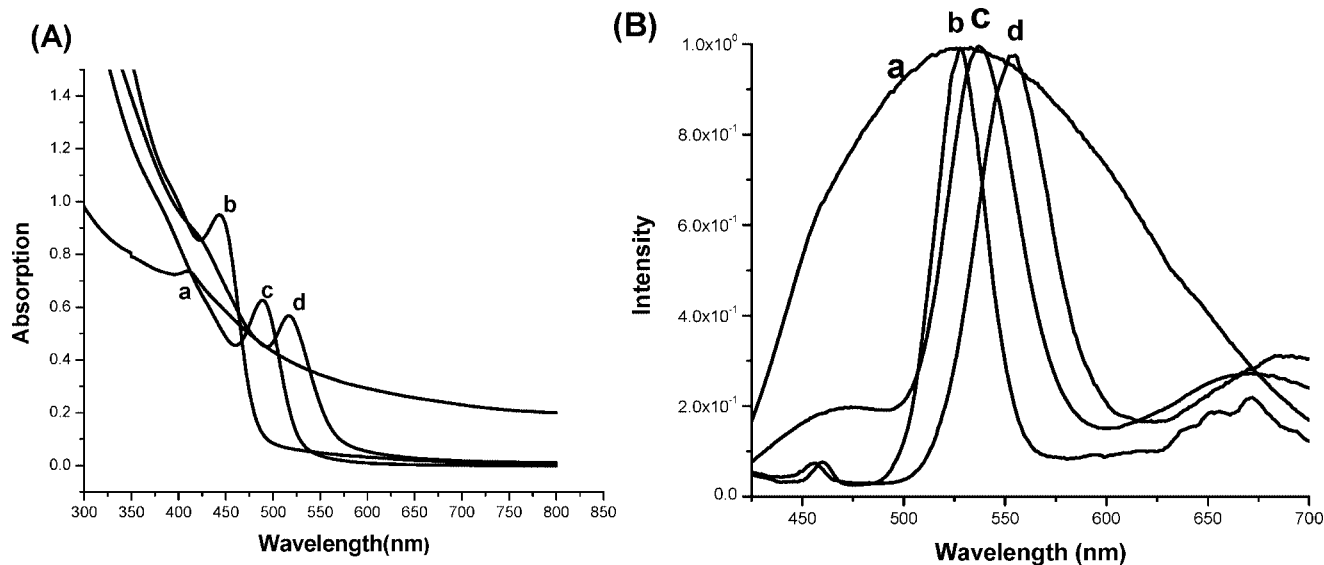


Figure 4. (A) UV-vis absorption spectra of CdSe with TOP and HDA in a 60:40 ratio: (a) as prepared SMAD product, (b) after 6 h at 120 °C, (c) after 6 h at 150 °C, and (d) after 6 h of reflux at 190 °C in TBT. (B) Corresponding photoluminescence spectra.

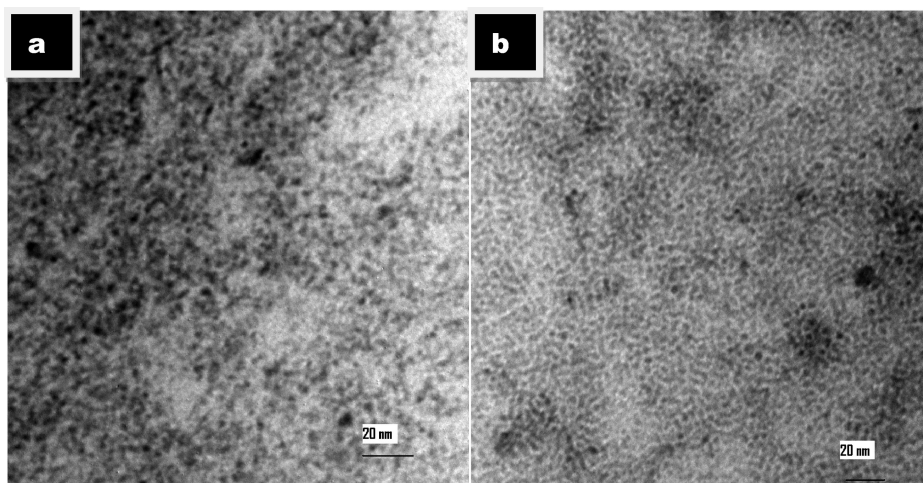


Figure 5. TEM images (a) before reflux and (b) after 6 h of reflux in TBT at 190 °C. The scale bar = 20 nm.

shows the UV-vis and Figure 4B shows the fluorescence spectra of the sample heated at 120 °C for 6 h, heated at 150 °C for 6 h and after 6 h of reflux at 190 °C in TBT. The measured QY of these samples are 16–28%. The increased QY can be attributed to the larger, more monodisperse particles with fewer defects and surface traps than in smaller particles. The broad band from 650 to 700 nm in Figure 4B might be due to the loss of some of the surface ligands during the washing process.²⁵

The TEM images (Figure 5) show a narrowing of the particle size distribution after 6 h of reflux in TBT at 190 °C. It took 16 h to see a considerable increase in fluorescence intensity and to form quasi monodispersed QDs in toluene; in TBT, it took 6 h. UV-vis and PL spectral data in Table 1 show a red shift in absorption as well as in emission with raise in temperature. In separate experiments, CdSe QDs were prepared with TOPO and HDA in a 60:40 ratio, where this shift is less significant, which indicates less particle growth that might be due to strong binding of TOPO to CdSe

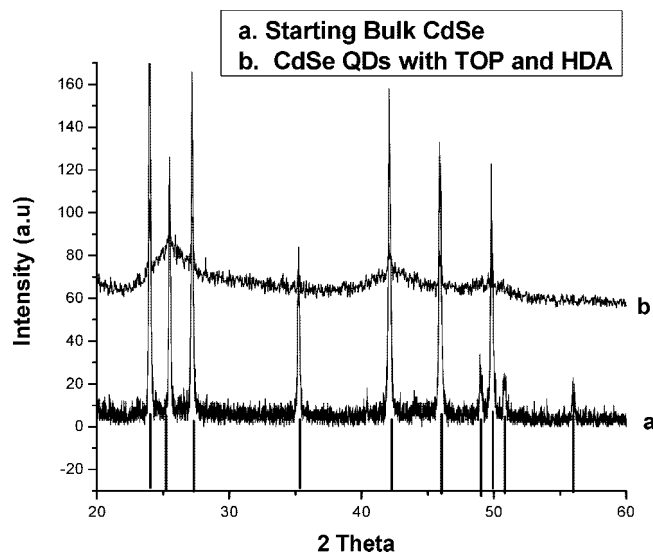


Figure 6. Powder XRD patterns of (a) starting bulk CdSe and (b) CdSe QDs with TOP and HDA after 6 h of reflux at 190 °C in *t*-butyltoluene. Wurtzite lines are shown from ref 26.

QDs compared to TOP (see the Supporting Information for UV-vis, PL, and TEM images).

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The powder XRD data (Figure 6) revealed the wurtzite structure of CdSe QDs, the same as the bulk material. The transformations from narrow peaks (bulk) to broad peaks are indicative of smaller crystallite. Powder XRD data are consistent with the published PXRD data.²⁶ Our further work will focus on application of this procedure for the synthesis of other group II–IV semiconductor nanocrystals and on demonstrating further scale-up.

4. Conclusions

First, the polydispersed CdSe QDs were synthesized by using the SMAD method that involved the vaporization of the bulk CdSe followed by co condensation with THF solvent at liquid N₂ temperature. Second, quasi monodispersed CdSe QDs were obtained after subjecting the SMAD prepared polydispersed CdSe QDs to digestive ripening as a successful postsynthesis treatment.²⁷ The XRD data revealed that these CdSe QDs have the wurtzite structure of bulk CdSe. Moreover, we observed very significant effects of the

solvents (Toluene and TBT) and ligands (TOP, TOPO and HDA) on the narrowing of the particles size distribution, UV–vis, photoluminescence properties, and QY of CdSe QDs. We found TBT as a more preferable solvent for the synthesis of monodispersed CdSe QDs in a shorter digestive ripening time (6 h) compared with toluene (16 h). This is likely due to the higher boiling point of TBT that makes digestive ripening more effective. Likewise, we observed better fluorescence properties of CdSe QDs with an appropriate combination of TOP and HDA ligands compared with TOPO and HDA or just with TOPO.

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Supporting Information Available: TEM images of CdSe QDs obtained with a 1:40 CdSe:TOPO ratio without HDA. Detailed UV–vis absorption spectra of CdSe QDs with TOPO and HDA in a 60:40 ratio of as-prepared SMAD product, heated at 120° for 6 h, heated at 150° for 6 h, heated at 170° for 6 h, and after reflux in *t*-butyltoluene for 6 h and corresponding fluorescence spectra, TEM images and samples without and with UV–vis light (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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