

Alternative Routes toward High Quality CdSe Nanocrystals

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ABSTRACT

Different kinds of safe, common, and low-cost compounds were proven to be good solvents/precursors for the synthesis of high quality CdSe nanocrystals. The size, shape, and crystal structure of CdSe nanocrystals synthesized by these alternative routes can be varied in a controllable manner in a very broad size range, from about 1.5 nm to above 25 nm. Without any size sorting, the size distribution of the wurtzite nanocrystals in the size range smaller than about 15 nm can be readily controlled as narrow as with 5–10% relative standard deviation. The highest photoluminescence quantum efficiency of the nanocrystals was up to 20–30%. Cd(Ac)₂ and fatty acids were found to be the most versatile cadmium precursor and solvent/ligand, respectively. The synthesis of high quality CdSe nanocrystals in the current systems is not feasible when the system contains any anions from a strong acid, either in the form of a cadmium precursor or as an added cadmium ligand. The experimental results indicate that the synthesis of high quality colloidal nanocrystals is far less delicate than it has been thought to be.

Synthesis of high quality semiconductor nanocrystals has been an important topic in the field of materials chemistry in recent years^{1–10} because of the technical and fundamental importance of these novel materials.^{11–15} In the early 90s, high quality CdSe nanocrystals became available by using Cd(CH₃)₂ as the cadmium precursor and technical-grade trioctylphosphine oxide (Tech TOPO) as the reaction solvent.^{9,16} The synthesis of CdSe nanocrystals through this organometallic route has led the synthesis of high quality semiconductor nanocrystals for about 10 years.^{3,5} However, some key chemicals used in this traditional route are extremely toxic, pyrophoric, explosive, and/or expensive. The synthesis is hard to control and is not very reproducible. This motivates us to develop alternative synthetic methods for this well-studied model system. We hope knowledge gained by studying this important model system will help us to eventually develop green chemical approaches for the synthesis of other kinds of high quality nanocrystals.

The results to be described below will demonstrate that the synthesis of high quality CdSe nanocrystals is not as delicate as it has been thought to be. By a one-pot approach, CdSe nanocrystals can be obtained directly in more than 10 different solvent systems, such as fatty acids, amines, phosphine oxides (Tech TOPO or pure TOPO), phosphonic acids (only in the mixture with TOPO), and the mixture of these common chemicals with certain compositions (see examples in Figure 1). Our very recent work¹ described that CdO is a more desirable precursor for the synthesis of high quality CdTe, CdSe, and CdS nanocrystals in comparison

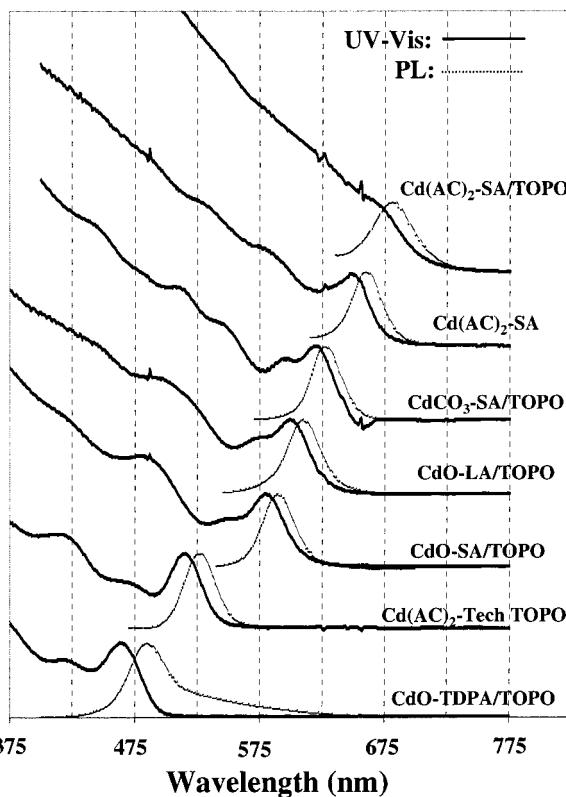


Figure 1. UV-vis and photoluminescence (PL) spectra of different sized wurtzite CdSe nanocrystals (as-prepared). TDPA: tetradecylphosphonic acid.

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to Cd(CH₃)₂. In addition to this discovery, we will demonstrate below that cadmium salts with an anion of a weak

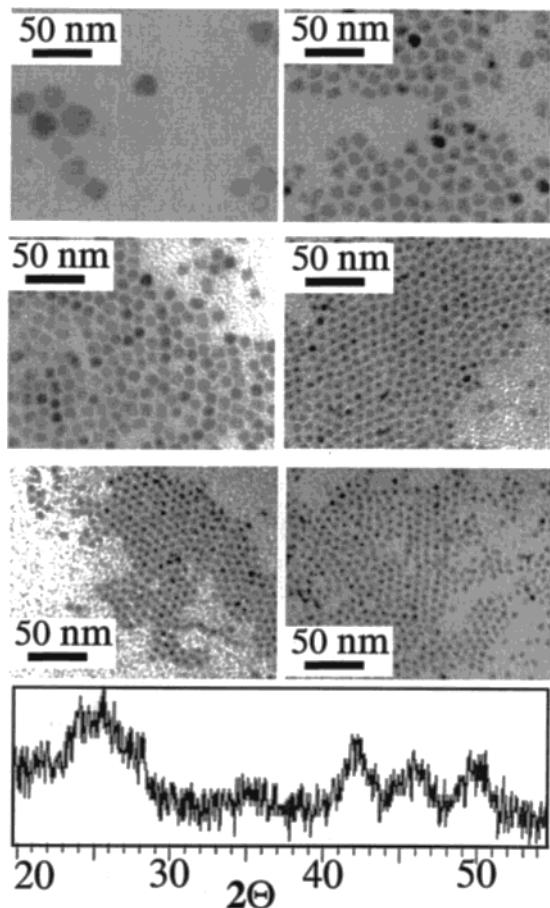


Figure 2. Transmission electron micrographs of different sized wurtzite CdSe nanocrystals (as-prepared) synthesized in the SA related solvents. The powder X-ray diffraction pattern of a sample (about 6 nm in size) demonstrates the highly crystalline feature of these nanocrystals.

acid are all presumably excellent cadmium precursors for the synthesis of high quality CdSe nanocrystals. Among all tested compounds, $\text{Cd}(\text{Ac})_2$ (Figure 3) and fatty acids (Figures 2 and 4) were proven to be the most versatile cadmium precursor and solvent, respectively. The existence of any anion of a strong acid, either in the form of cadmium precursor or as an added cadmium ligand, made it impossible to form high quality CdSe nanocrystals in the current systems. Thiols, which are very strong ligands to cadmium, were found to inhibit the nucleation process. We will demonstrate that, by the methods discussed below, the crystal structure of CdSe nanocrystals can be controllably varied between zinc blende and wurtzite phases. The achievable size range of nearly monodisperse CdSe dots, from about 1.5 nm to above 25 nm, is much broader than that achieved by the original organometallic method.

Experimentally, a chosen solvent and a cadmium precursor were heated to about 250–360 °C under Ar flow and resulted in an optically clear solution. Consequently, a selenium solution (Se powder dissolved in trioctylphosphine or tri-n-butylphosphine) was injected into the reaction vessel. The growth temperature was set between 200 and 320 °C. If amines, such as dodecylamine (DA), are involved, the injection/growth temperatures were typically set at 220/200

°C. The reactions were monitored by recording the UV–vis spectra of the aliquots taken from the reaction vessel. In general, the addition of TOPO as a cosolvent makes taking aliquots much easier because of its relatively slow solidification rate. The initial Cd:Se molar ratio was varied between 2:1 to 1:5. It should be pointed out that the powder X-ray diffraction patterns verified that the crystal structure of CdSe nanocrystals kept unchanged by varying the Cd:Se ratio. The cadmium concentration was varied between 0.015 mol/kg and 0.30 mol/kg. All of the samples for the measurements were as-prepared and without any further sizing. In a typical synthesis using a stearic acid/TOPO/ CdCO_3 system, 0.2 mmol CdCO_3 was mixed with 2 g stearic acid and heated to about 130 °C under Ar flow until all of the mixture became optically clear. The system was allowed to cool to room temperature, and 2 g of 99% TOPO was added. The flask was resealed and reheated up to 360 °C under Ar flow. A selenium solution (2 g) with 0.5 mmol powder selenium and 0.2 g of toluene dissolved in trioctylphosphine was quickly injected into the reaction flask. The temperature of the reaction mixture decreased to 300 °C by the injection and maintained at this temperature for the growth of the nanocrystals. The reaction was monitored by UV–vis by taking aliquots from the flask (see Figure 4). After the reaction was completed, the reaction flask was removed from the heating mantle and allowed to cool to 20–50 °C. Acetone was added to precipitate nanocrystals. The nanocrystals further isolated by centrifugation and decantation. For large sized nanocrystals, it is advisable to store at a muddy state instead of a dry powder form. The as-prepared nanocrystals were soluble in typical nonpolar solvents, such as chloroform and toluene.

Among all the systems tested, fatty acids were determined as the most versatile ligand/solvent for the synthesis of wurtzite CdSe nanocrystals. Using stearic acid (SA) as an example, without any secondary injection, this solvent system yields CdSe nanocrystals in a very broad size range without any secondary injection, from about 2 nm to over 25 nm (all samples shown in Figure 2). This solvent system is ideal for synthesizing large-sized CdSe nanocrystals with a diameter above about 4 nm. The shape of CdSe nanocrystals with a diameter up to above 25 nm can be purposely controlled to dot-shape (Figure 2). On contrast, large-sized CdSe nanocrystals synthesized by the traditional dimethyl cadmium/TOPO method using multiple injections were generally limited to around 11 nm and often with a significant aspect ratio (see more details below).^{3,5,9,16} The very big nanocrystals may be used for studying mechanical properties of nanocrystals, although they are too big to exhibit quantum-confinement effects.¹⁵ The size distribution of CdSe dots in the size range smaller than 12 nm can be reproducibly controlled, with 5–10% relative standard deviation (Figure 2). For very large nanocrystals, the size distribution is somewhat broader (Figure 2). For the entire size range, nanocrystals synthesized in this solvent system luminesce quite well, with a quantum efficiency from a few percent to 20–30%. The photoluminescence quantum efficiency showed a tendency to drop with the increase of the particle size.

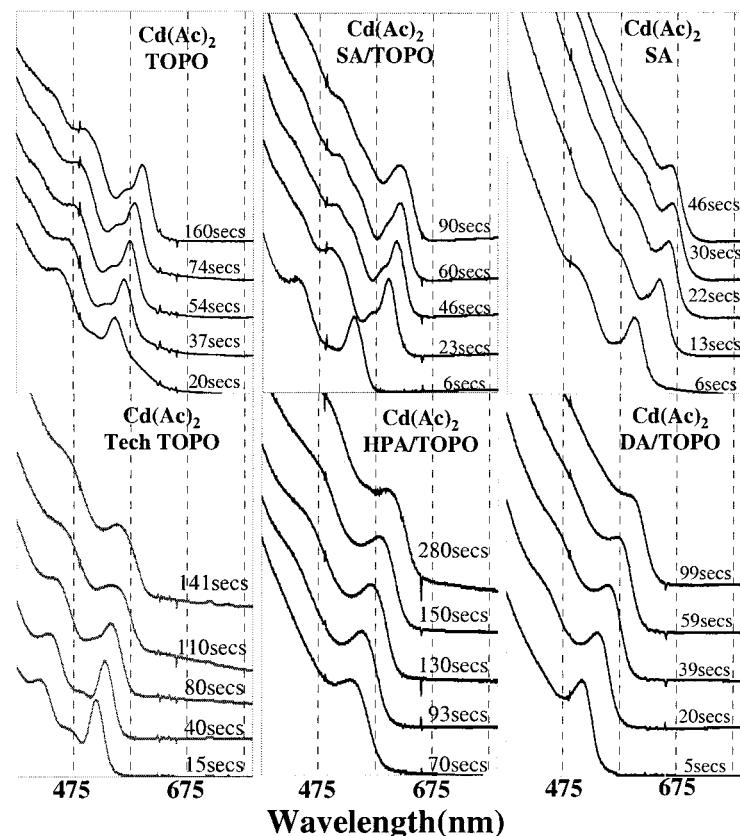


Figure 3. Growth kinetics of CdSe nanocrystals in different solvent systems. All of the reactions were performed under the same reaction conditions, except that the injection/growth temperatures in DA/TOPO were lower (see the Experimental Section). The initial cadmium concentration was 0.33 mol/kg. The Cd:Se molar ratio was 1:5. For the reactions that took place in a bicomponent solvent, the ratio between the two components was 1:1, except in the HPA/TOPO case. For the HPA/TOPO system, HPA was set at 0.66 mol/kg.

Although all resulting nanocrystals emit, the control over luminescence quantum yield was not as reproducible as was the control of the nanocrystal sizes.

In general, the temporal evolution of the size and size distribution of CdSe nanocrystals in fatty acid systems were quite reproducible, although the reaction rates were fast. We consider this is to be due probably to the more controllable nucleation step initiated by cadmium carboxylates instead of the extremely active $\text{Cd}(\text{CH}_3)_2$ used in the traditional organometallic approach. This phenomenon implies that the control of the nucleation process may be the key step toward a fully controllable synthesis. In practice, the fatty acid systems are not recommended to synthesize small nanocrystals because of the fast growth rates of the nanocrystals.

The fatty acid solvent system is compatible with all of the cadmium precursors tested (see examples in Figure 4). Growth of nanocrystals in fatty acids with different chain lengths, such as lauric acid (LA), speeds up as the chain length of the fatty acid decreases. With high cadmium concentrations, above about 0.1 mol/kg, the fatty acid systems may show some degree of decomposition at high temperatures. The color of the mixture before the injections may change to yellowish to brownish. The shorter the chain was, the more pronounced was the decomposition that occurred. For instance, the $\text{Cd}(\text{Ac})_2/\text{TOPO}$ system with high concentrations would not stabilize at temperatures over about 300 °C. Up to present, no influence over the growth of

nanocrystals was observed as long as no precipitation was formed in the system before injections.

Compared to phosphonic acids, which were the essential ligands added in pure TOPO for the previously reported CdO scheme,¹ fatty acids are much less expensive and more environmentally friendly.

Encouraged by the outstanding synthetic success for CdSe nanocrystals using $\text{Cd}(\text{CH}_3)_2$ as the precursor,^{9,16} the traditional TOPO solvent system composed of either Tech TOPO or pure TOPO plus the related impurities in the technical grade reagent has been the most popular choice for the synthetic development of a variety of colloidal nanocrystals in nonaqueous solutions in the past 10 years,^{1,3,4,7,17–19} although the final results may have revealed that it did not work at all.^{6,20} For the synthesis of CdSe nanocrystals using the new precursors, this traditional solvent system worked well in the strong quantum-confinement size regime (roughly speaking, with the first exciton absorption peak below 600 nm and a diameter smaller than about 4.5 nm). The synthesis in the relatively large size regime often resulted in elongated nanocrystals (not very uniformly), with little or no photoluminescence.

We observed that, using $\text{Cd}(\text{Ac})_2$ as the precursor, pure TOPO actually worked well for synthesizing nearly mono-disperse CdSe nanocrystals with a size up to about 6–8 nm (Figure 3), although the emission of the nanocrystals was weaker than that of those nanocrystals synthesized in fatty

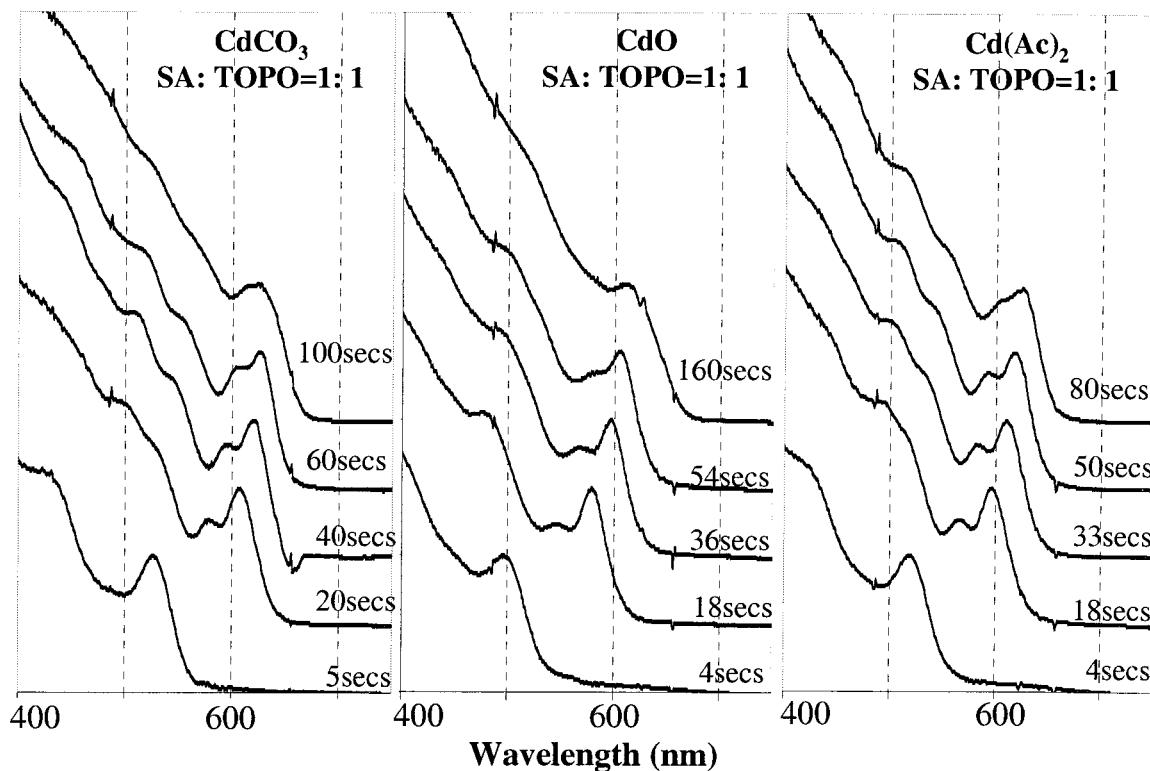


Figure 4. Growth kinetics of CdSe nanocrystals using different cadmium precursors under the same reaction conditions (see the Experimental Section).

acids. The Cd(Ac)₂/pure-TOPO system was much more reproducible than the Cd(CH₃)₂/pure-TOPO system.²¹ It should be pointed out that, based on the present results, it was impossible to judge the role of acetate ions for the growth of nanocrystals in the Cd(Ac)₂/TOPO system. Likely, both TOPO and acetate ions may have played a significant role to stabilize the nanocrystals.

Using Cd(Ac)₂ as the cadmium precursor, highly crystalline CdSe nanocrystals were synthesized in amines (Figure 3), although the size distribution of those nanocrystals was only moderately good. This is probably because of the relatively low injection/growth temperatures (170–220 °C). The system tested could not withstand high temperatures because Cd(Ac)₂ decomposed rapidly in the presence of amines at higher temperatures. Interestingly, under the same reaction conditions, the nanocrystals formed in amines seemed to be zinc blende crystals, instead of the common wurtzite structure formed in the other solvent systems (Figure 2). This phenomenon is under active investigation and details will be reported later.

Alcohols could not be used as the solvent for the formation of high quality CdSe nanocrystals under the tested conditions, because all tested precursors were insoluble in alcohols at elevated temperatures. The synthesis using sulfonic acid as ligands resulted in insoluble large crystals. Similarly, nanocrystals with controlled sizes were difficult to form in thiols under the reaction conditions tested.

Cd(Ac)₂ (Figure 3) and other types of cadmium carboxylate were found to be very versatile cadmium precursors. Both CdCO₃ and CdO worked only in the presence of either fatty acids or phosphonic acids. The growth kinetics of CdSe

nanocrystals using different precursors did show some variation (Figure 4). At this moment, we do not know why. Although the solubility of CdCl₂ or CdSO₄ in tested solvents was usually good, the related one-pot synthesis generated only bulk-sized CdSe. This is probably a result of the relatively high stability under acidic conditions of the salt formed by cadmium and a strong acid in comparison to that of CdSe.¹ We noticed that some types of cadmium salts with strong acids were used for water-based synthesis of cadmium chalcogenides nanocrystals.⁸ In aqueous solution, these salts exist more or less in the form of ions instead of very stable compounds in the present systems.

In conclusion, many safe, low cost, and common compounds were proven to be good precursors/solvents/ligands for reproducibly synthesizing high quality CdSe nanocrystals in a very broad size range. The results reported here provide a starting point to establish a precursor/solvent/ligand database for designing optimized green-chemical synthetic approaches for high quality nanocrystals. Among all of the solvent systems tested, fatty acids are excellent candidates for synthesizing relatively large-sized CdSe nanocrystals (4–25 nm), although the formation of CdSe nanocrystals between 2 and 4 nm was also observed. In comparison, phosphonic acids/TOPO, Tech TOPO, or pure TOPO are good solvents for synthesizing CdSe nanocrystals in the strong confinement size regime. Preliminary results suggested that CdSe nanocrystals with zinc blende structure may be prepared. All anions of strong acids and thiolates should be avoided in the synthesis of high quality CdSe nanocrystals in nonaqueous solutions because the related cadmium salts/

complexes are too stable to properly initiate the nucleation process.

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