

## Formation of High-Quality CdTe, CdSe, and CdS Nanocrystals Using CdO as Precursor

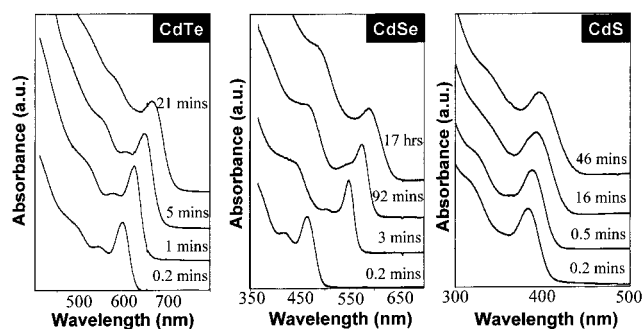
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High-quality colloidal semiconductor nanocrystals are nanometer-sized, single crystalline fragments of the corresponding bulk crystals, which have well-controlled size and size distribution and are dispersible in desired solvents/media. Recently, semiconductor nanocrystals are of great interest for both fundamental research and technical applications,<sup>1–8</sup> due to their strong size dependent properties and excellent chemical processibility. Synthesis of high-quality semiconductor nanocrystals has been playing a critical role in this very active field.<sup>1,9–15</sup> As the most developed system in terms of synthesis,<sup>1,9,10,15</sup> high-quality CdSe nanocrystals with nearly monodisperse size and shape are in active industrial development for biological labeling reagents.<sup>5,6</sup> Since Murray et al.<sup>15</sup> reported the synthesis of high quality cadmium chalcogenides nanocrystals using dimethyl cadmium ( $\text{Cd}(\text{CH}_3)_2$ ) as the cadmium precursor, the synthesis of CdSe nanocrystals using this precursor has been well developed.<sup>1,9,10</sup> In comparison, the synthesis of CdTe and CdS<sup>15,16</sup> are not as advanced. For instance, there is no method to controllably vary the shape of CdTe and CdS nanocrystals.  $\text{Cd}(\text{CH}_3)_2$  is extremely toxic, pyrophoric, expensive, unstable at room temperature, and explosive at elevated temperatures by releasing large amount of gas. Due to these reasons, the  $\text{Cd}(\text{CH}_3)_2$ -related schemes require very restricted equipments and conditions and are not suited for large-scale synthesis. In this paper, we will prove that  $\text{Cd}(\text{CH}_3)_2$  can be replaced by CdO. Surprisingly, this new synthetic scheme works significantly better than the  $\text{Cd}(\text{CH}_3)_2$ -related ones. Without any size-sorting, the quality of quantum-confined dots and rods (quantum dots and quantum rods) of all cadmium chalcogenides formed by the new method is comparable to that of the best CdSe nanocrystals reported in the literature. The new scheme is reproducible and simple and thus can be readily scaled up for industrial production.

Recently, we identified that  $\text{Cd}(\text{CH}_3)_2$  decomposes in hot trioctylphosphine oxide (TOPO) and generates insoluble metallic precipitate.<sup>9</sup> With a strong ligand, either hexylphosphonic acid



**Figure 1.** Temporal evolution of size and size distribution of CdTe, CdSe, and CdS nanocrystals studied by UV–vis.

(HPA) or tetradecylphosphonic acid (TDPA),  $\text{Cd}(\text{CH}_3)_2$  is immediately converted into cadmium HPA/TDPA complex ( $\text{Cd-HPA/Cd-TDPA}$ ) if the cadmium to HPA/TDPA ratio is lower than 1. After the formation of the complex, an injection of Se dissolved in tributylphosphine (TBP) generates high-quality CdSe nanocrystals. This result implies that  $\text{Cd}(\text{CH}_3)_2$  may not be necessary, if we can generate the complex by other means. We first synthesized and purified  $\text{Cd-HPA}$  from  $\text{CdCl}_2$  or  $\text{Cd}(\text{CH}_3)_2$ . High-quality CdSe nanocrystals were indeed yielded from this complex. This success encouraged us to develop a one-pot synthesis which does not require separated preparation of cadmium complex. We failed to make high-quality CdSe nanocrystals using  $\text{CdCl}_2$  by the one-pot approach although  $\text{CdCl}_2$  can be dissolved in the reaction mixture at elevated temperatures. In contrast, CdO works very well for the one-pot approach. We think this is due to the low stability of CdO relative to phosphonic acids, compared to that of  $\text{CdCl}_2$ .

Experimentally, CdO, TOPO, and HPA/TDPA were loaded in a three-neck flask. At about 300 °C, reddish CdO powder was dissolved and generated a colorless homogeneous solution. Introducing tellurium, selenium, and sulfur stock solutions yields high quality nanocrystals.<sup>17</sup> The samples for all of the measurements shown in this paper are directly from synthesis without any size separation.

The growth kinetics of nanocrystals grown by the new approach possesses a pattern similar to that of the best CdSe nanocrystals formed by the  $\text{Cd}(\text{CH}_3)_2$  approach (Figure 1).<sup>10</sup> Figure 1 and Figure 2 further reveal that the size of all three kinds of nanocrystals can be close to monodisperse, represented by the sharp absorption peaks if the growth stops in the “focusing of size distribution” regime.<sup>10</sup> Transmission electron microscopy (TEM) measurements indicate that these nanocrystals have very narrow distribution. The relative standard deviation of the size of the nanocrystals shown in Figure 3 (top) is about 10%. The high crystallinity of these wurtzite nanocrystals was confirmed by X-ray powder diffraction.

For this CdO approach, the size of relatively monodisperse CdSe nanocrystals can be continuously tuned down to the sizes with the first absorption peak at 440 nm (see the first absorption spectrum in Figure 1). Relatively monodisperse CdSe nanocrystals with the first exciton absorption peak below 480 nm are difficult to synthesize directly with the existing  $\text{Cd}(\text{CH}_3)_2$ -related approach.<sup>10,18</sup>

(17) A typical synthesis for CdTe nanocrystals: 0.0514 g of CdO, 0.2232 g of TDPA and 3.7768 g of TOPO were loaded into a 25 mL flask. The mixture was heated to 300–320 °C under Ar flow, and CdO was dissolved in TDPA and TOPO. The temperature of the solution was cooled to 270 °C, tellurium stock solution (0.0664 g of tellurium powder dissolved in 2 g of TOP) was injected. After injection, nanocrystals grew at 250 °C to reach desired size.

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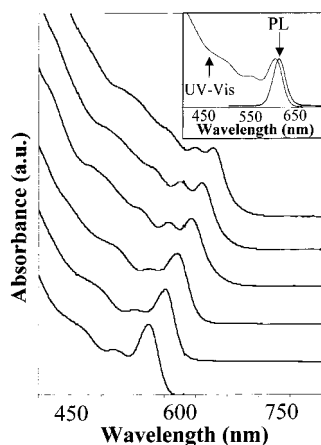
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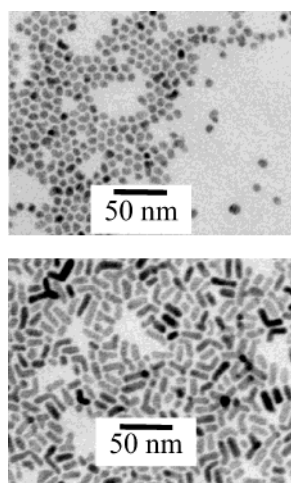
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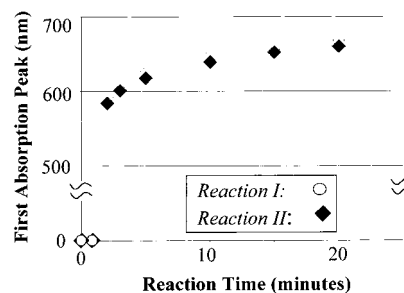
**Figure 2.** Absorption spectra of different-sized CdTe nanocrystals in the size range from 2 to 8 nm. Inset: photoluminescence (PL) and absorption of a CdTe nanocrystal sample.



**Figure 3.** TEM pictures of shape-controlled CdTe nanocrystals synthesized by the CdO approach.

Apart from high-quality quantum dots for all three cadmium chalcogenides, the CdO one-pot approach can further generate high-quality quantum rods (Figure 3, bottom) by using higher initial monomer concentrations.

The initial nucleation of this new approach can be tuned tens of seconds later after the injection (Figure 4). We believe the slow initial nucleation is because of the relatively high stability of Cd-HPA/Cd-TDPA. In the Cd(CH<sub>3</sub>)<sub>2</sub> approach, the instant initial nucleation is due to the extremely high reactivity of Cd(CH<sub>3</sub>)<sub>2</sub>. The slow initial nucleation rate bears three important advantages in practice. One, the injection temperature does not need to be 340–360 °C. Instead, 250–300 °C is fine. Two, both nucleation and growth of nanocrystals are barely related to the injection. As a result, the synthesis is very reproducible (Figure 4). Three, this time delay of initial nucleation implies that the initial injection can take as long as tens of seconds. A large quantity of stock solution can be added into the reaction vessel, provided the non-pyrophoric and nonexplosive reactants used for the new scheme. In a 100 mL flask, a synthesis with adding 15–



**Figure 4.** Example showing the reproducibility of the CdO approach. Two reactions of CdTe nanocrystals synthesis gave identical results within the experimental error.

20 mL of stock solution was tested and yielded about 700 mg high-quality CdTe nanocrystals. We expect that, industrial-scale synthesis should be very possible with this new approach. It should be mentioned that, with the Cd(CH<sub>3</sub>)<sub>2</sub> scheme developed by Peng et al.,<sup>10</sup> the explosive stock solution containing Cd(CH<sub>3</sub>)<sub>2</sub> and Se dissolved in TBP should be initially injected within sub-seconds at 340–360 °C to take the advantage of the “focusing of size distribution”<sup>10</sup> and the “1D-growth”.<sup>1,9</sup> Therefore, an injection volume close to 5–6 mL requires special caution and is very dangerous. This explosive nature is a combination of the gas released from Cd(CH<sub>3</sub>)<sub>2</sub> and the rapid boiling of TBP.<sup>18</sup>

Currently, CdTe and CdSe nanocrystals are of great industrial interest for developing photoluminescence-based biomedical labeling reagents.<sup>5,6</sup> The photoluminescence properties of the nanocrystals synthesized by this CdO approach are compatible to the nanocrystals synthesized by existing Cd(CH<sub>3</sub>)<sub>2</sub>-related methods. Figure 2 (inset) illustrates the absorption and emission spectra of one CdTe sample. In general, the quantum efficiency of CdTe nanocrystals synthesized by the new scheme is the highest, which can be well above 20%.

The CdO approach is well suited for studying growth mechanisms of colloidal nanocrystals, especially for nucleation. First of all, different from the Cd(CH<sub>3</sub>)<sub>2</sub> related approach, the cadmium precursor in the entire nucleation and growth period is one species Cd-HPA/Cd-TDPA. Second, the initial nucleation is slow, which makes it possible to access the nucleation process. Also, due to the slow nucleation and growth rate, time-resolved, in situ study of crystallization is possible. Currently, we are actively developing methods for such in situ studies.

In conclusion, a reproducible one-pot synthesis of high-quality quantum rods and dots of CdTe, CdSe, and CdS was developed using CdO as cadmium precursor. The resulting nanocrystals can be close to monodisperse without any size separation. The reaction conditions are mild and simple. In principle, a large-scale synthesis without using a glovebox is possible. We consider this one-pot synthetic scheme as a major step toward a green-chemistry approach for synthesizing high-quality semiconductor nanocrystals. This new approach may also be used for time-resolved, in situ study of crystallization. Furthermore, this new scheme implies that, with appropriate knowledge, spontaneous formation of shape-controlled high-quality colloidal nanocrystals under mild conditions is possible.

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