Colloidal CdSe Nanocrystals Synthesized in Noncoordinating Solvents with the Addition of a Secondary Ligand: Exceptional Growth Kinetics

Quanqin Dai, Dongmei Li, Haiyong Chen, Shihai Kan,* Hongdong Li, Shiyong Gao, Yuanyuan Hou, Bingbing Liu, and Guangtian Zou

National Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China

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The addition of a secondary ligand, trioctylphosphine oxide, in the synthesis of cadmium selenide nanocrystals performed in a system with oleic acid as the primary ligand and octadecene as the noncoordinating solvent gives rise to the improvement of nanocrystal size distribution. This phenomenon, which is more significant in the nucleation process than in the growth process, demonstrates that the existence of trioctylphosphine oxide allows for superior nucleation control and permits the facile and reproducible production of extremely small CdSe nanocrystals with narrow size distribution. A systematic study of the nanocrystal formation processes shows that the well-established colloidal nanocrystal growth mechanism, in which nucleation is followed by focusing of size distribution and ended with defocusing of size distribution, cannot be applied to our reactions. Instead, we observed an exceptional type of growth mechanism in which, after nucleation, clear defocusing instead of focusing follows; then slight focusing occurs.

1. Introduction

In the studies of semiconductor nanocrystals, an ultimate goal is to develop the ability to manipulate the size and the shape.[1–3] In such a fashion the unique optical, electrical, and magnetic properties of semiconductor nanocrystals, found in neither their corresponding single molecules nor bulk crystals, can be utilized for industrial applications, such as biomedical tags,[4,5] light-emitting diodes,[6,7] lasers,[8,9] and solar cells.[10,11] Evidently, such applications have been speeded up greatly since 1993, when highly monodisperse and crystalline CdE (E = S, Se, Te) nanocrystals with particle size tunability were synthesized by Murray et al., using an organometallic compound $Cd(CH_3)_2$ as the cadmium precursor in a coordinating solvent trioctylphosphine oxide (TOPO);[12] and then II–VI semiconductor nanocrystals with monodisperse size and shape were reproducibly and controllably synthesized using the same or modified approaches.

The method of Murray and co-workers[12] was considered to be an inspiring one and was widely used to synthesize high-quality CdSe quantum dots/rods in the 1990s.[1,2] $Cd(CH_3)_2$, however, is extremely toxic, pyrophoric, explosive, and expensive; and worse, its extremely high reactivity caused the initial nucleation and even subsequent growth to be out of control, which led to the replacement of the $Cd(CH_3)_2$-related synthetic approach by the CdO-related one.[13] Using the subsequent approach, high-quality quantum dots/rods of all cadmium chalcogenides, such as CdTe, CdSe, and CdS, could be prepared under mild conditions.[13–15] The quality of these as-prepared semiconductor nanocrystals could be compared to that of the best CdSe nanocrystals prepared with the $Cd(CH_3)_2$-related synthetic approaches. Therefore, the CdO-related approaches, considered environmentally benign and user-friendly,[15] have been extensively employed to synthesize high-quality cadmium-related semiconductor nanocrystals in recent years.[14–17] Almost all of these relatively successful synthetic approaches, including those that are $Cd(CH_3)_2$-related and the CdO-related, were carried out in the coordinating solvent TOPO.[1,2,12–16] It seemed that TOPO was required for the synthesis of highly monodisperse II–VI semiconductor nanocrystals. Recently, Yu and Peng reported that TOPO could be completely replaced with a noncoordinating solvent octadecene (ODE) without deteriorating the nanocrystal monodispersity.[18] This approach was used to synthesize monodisperse CdS nanocrystals first, followed by CdTe and even InP and InAs nanocrystals.[18–20] This replacement makes the synthetic procedure and chemicals used for the synthesis of these high-quality semiconductor nanocrystals less expensive, safer, and greener in comparison to those reported previously.[1,2,12–17] However, this relatively simple approach does not work as well in the synthesis of CdSe nanocrystals.[21,22] The size distribution of CdSe nanocrystals synthesized in ODE suffered to varying degrees, compared with that synthesized in TOPO.[13,21] Therefore, more effort should be given to study the reaction system of CdSe nanocrystals performed in ODE.

As described above, the synthesis of highly monodisperse CdSe nanocrystals requires TOPO. Unfortunately, TOPO may generate unknown pollutants.[15,20,22] For the sake of the environment, the reduced use of TOPO is desirable. In this report, we show that, by introducing a small amount of TOPO, the size distribution of CdSe nanocrystals grown in ODE can be improved greatly. Also, the addition of TOPO offers an unpredicted control of the nucleation process, which is difficult or even impossible using the previously reported approaches.[1,2,12,14,17] Moreover, a novel growth mechanism, which is different from the well-established model,[23] is observed and provides further understanding of the nanocrystal formation processes in noncoordinating solvents.

2. Experimental Section

2.1. Materials. CdO, Se powder, oleic acid (OA), trioctylphosphine (TOP), octadecene (ODE), and trioctylphosphine oxide (TOPO) were purchased from Aldrich. Toluene, acetone, and methanol were ordered from Sangon.

* Corresponding author. E-mail: connectdai@yahoo.com.cn; kansh@jlu.edu.cn.

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2.2. Syntheses in Noncoordinating Solvents with the Addition of a Secondary Ligand. TOPO, used the most in the synthesis of cadmium-related semiconductor nanocrystals in the 1990s, was used as a secondary ligand in the noncoordinating solvent ODE. Typically, 0.0154 g (0.12 mmol) of CdO, 0.339 g (1.2 mmol) of OA, 2.7177 g of ODE, and 0.928 g (2.4 mmol) of TOPO were loaded into a three-neck flask as the growth solution and heated to 300 °C under Ar flow. At this temperature, a Se solution containing 0.019 g (0.24 mmol) of Se, 0.3558 g (0.96 mmol) of TOP, and 1.6253 g of ODE prepared in a glovebox was swiftly injected into the vigorously stirred growth solution. After the injection, the temperature was dropped to ∼260 °C for the growth of CdSe nanocrystals. At different reaction moments, aliquots were taken from the flask; and then each aliquot was immediately cooled to room temperature to quench the reaction by mixing it with about 1.5 mL of cold toluene. In the above reaction, the initial TOPO/OA molar ratio is 2. Reactions with other TOPO/OA molar ratios (from 0.3 to 6) were carried out as well.

2.3. Typical Synthesis in Noncoordinating Solvents without TOPO. The only difference between this synthesis and the one described above is that 0.928 g of ODE was used in place of 0.928 g of TOPO. Such synthesis could produce CdSe nanocrystals capped by OA.

2.4. Characterization. The nucleation and growth processes of the CdSe nanocrystals were monitored by a Shimadzu UV-3150 spectrometer. Photoluminescence (PL) spectra were recorded by a Shimadzu RF-5301PC spectrophotometer using an excitation wavelength of 360 nm and a Renishaw 1000 Raman spectrometer using 514.5-nm argon ion laser as the excitation source. For UV−vis and PL measurements, nanocrystals were dispersed in toluene without size sorting. Fourier transform infrared (FTIR) spectra, which were used to characterize the surface capping state of the purified CdSe nanocrystals, were taken by a Nicolet Avatar 360 FTIR spectrometer. FTIR samples were dispersed in KBr. A Hitachi H-8100IV transmission electron microscope was used to take transmission electron microscopy (TEM) images. TEM samples were prepared by evaporating two drops of the dilute aliquot solution onto the carbon-coated copper grid.

3. Results and Discussion

Figure 1 shows the evolution of the CdSe nanocrystal absorption spectra for reactions carried out in ODE under identical conditions, except for the TOPO/OA molar ratio. A characteristic red-shift of the spectra, which corresponds to the growth of the nanocrystals with increased reaction time, can be seen in all the reactions. In Figure 1a, which represents the reaction with no addition of TOPO, the absorption peaks are broad, which reflects broad nanocrystal size distribution. When TOPO was added in the reaction, the absorption peaks are narrower (Figure 1, parts b−e), which indicates that the size distribution of the resulting nanocrystals is narrow.

To characterize the size distribution of the nanocrystals formed under different conditions, two important parameters of semiconductor nanocrystals, HWHM (half width at half-maximum to the long wavelength side of the first absorption peak) and fwhm (full width at half-maximum of the PL spectrum), are used. A smaller HWHM or fwhm corresponds to a narrower size distribution.[24] The HWHM values shown in Figure 2a (deduced from the absorption spectra in Figure 1, parts b−e), which belong to the nanocrystals synthesized with the addition of TOPO, are smaller than the ones shown in Figure 2b (deduced from the absorption spectra in Figure 1a), which

are for the nanocrystals grown without the addition of TOPO. Therefore, the size distributions of the nanocrystals formed with the existence of TOPO are narrower than the ones of the nanocrystals obtained without the addition of TOPO. This confirms that TOPO is necessary for synthesizing highly monodisperse CdSe nanocrystals. For the synthesis of other highly monodisperse cadmium-related nanocrystals, such as CdS and CdTe,[18,19] TOPO is not required, which implies that at the surface of CdSe nanocrystals TOPO strongly binds to Se vacancies, and two or more Cd sites are bridged through the terminal O atom in TOPO. Such implication has been hypothesized by Kuno et al.,[25] and later confirmed by Wu et al.,[22] who discussed the function of TOPO in the synthesis of highly monodisperse CdSe nanocrystals and proposed that the presence of TOPO favored the focusing regime of CdSe nanocrystals because TOPO could effectively prevent the small particles from shrinking by specifically binding the high-energy Se vacancies that would otherwise be particularly vulnerable to solvent attack. However, in the case of CdS and CdTe, such anion vacancies may be less prevalent or more stable during the nanocrystal growth, which allows the focusing regime to remain even in the absence of TOPO. This explained why TOPO can be replaced by ODE in the synthesis of highly monodisperse CdS and CdTe nanocrystals, without degrading the size distribution.

An unpredicted benefit from the addition of TOPO as the secondary ligand is that we are able to synthesize extremely small nanocrystals (<2.3-nm diameter) with a narrow size distribution (∼6%) if the reaction is stopped shortly after injection. As shown in Figure 1, parts b−e, with the increase of the TOPO/OA molar ratio, smaller and smaller monodisperse CdSe nanocrystals can be obtained. For example, the narrow absorption peak at 449 nm, corresponding to an average size of 1.7 nm and a size distribution of as small as 5% (estimated from the comparison of ref 14), was obtained (Figure 1e). Small nanocrystals with similar size distributions can be easily and reproducibly synthesized under different TOPO/OA molar ratios, as indicated in Figure 3. Thus it can be seen that the nucleation process in the reaction with the addition of TOPO can be better controlled. In contrast, the previously reported approaches have a major drawback that the undesired nucleation control and rapid growth make the synthesis of small nanocrystals (<4-nm diameter) impractical because their corresponding reactions cannot be quenched quickly and reproducibly enough to obtain small nanocrystals.[14,15,17,26,27]

Surprisingly, in our reaction system, the nanocrystal growth kinetics is different from the one discussed by Peng et al.,[23] in which after injection the reaction started with a nucleation stage where the size distribution of the nanocrystals was relatively broad; when the nanocrystals in the reaction solution were all slightly larger than the critical size, at which the solubility of the existing nanocrystals was identical to the monomer concentration, focusing of size distributions occurred due to a faster growth rate of the smaller nanocrystals and would last for some time; when the monomer concentration was depleted due to focusing, the critical size became larger than the average size of the nanocrystals, which caused some smaller nanocrystals to shrink and eventually disappear while larger ones kept growing; and thus the size distribution began to broaden, which was referred to as defocusing of size distributions or Ostwald ripening. In short, the kinetics discussed by Peng et al.[23] is, after injection, nucleation took place rapidly; clear focusing followed; finally defocusing occurred. However, the growth kinetics presented in our reactions is a different one: after injection and nucleation nanocrystals with narrow size distribu-
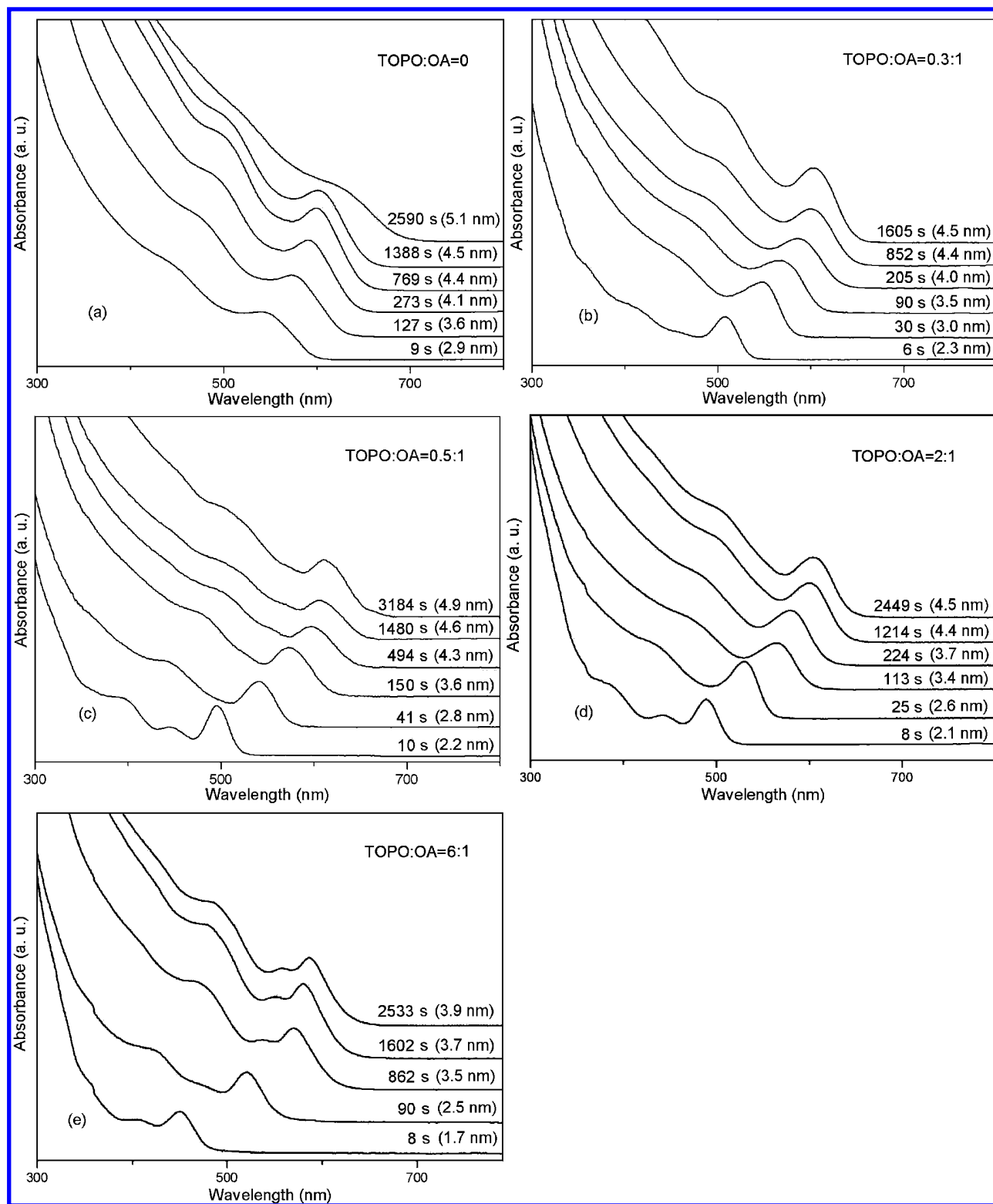
Figure 1. Temporal evolution of UV−vis spectra of the CdSe nanocrystals grown in ODE with different TOPO/OA molar ratios. The numbers in the parentheses are the diameters of the corresponding nanocrystals.

tion form in a short time, followed by clear defocusing, instead of focusing; then slight focusing occurs. Such growth kinetics is clearly demonstrated in Figure 2a, where the size distribution variation follows a trend opposite to the one reported by Peng et al.[23] (Figure 2b).

The growth kinetics discussed by Peng et al.[23] is relatively universal.[13,14,17−22] It can be observed not only for the reactions performed in coordinating solvents but also for the ones in non-

coordinating solvents. However, the observation presented in this work shows that the Peng et al.'s growth kinetics cannot be used to explain the reactions that happened in noncoordinating solvents with the addition of a secondary ligand TOPO. To verify our exceptional growth kinetics, the reactions conducted with the addition of TOPO were repeated, and all the results support the evolution of size distributions shown in Figure 2a. Additionally, this exceptional growth kinetics is also
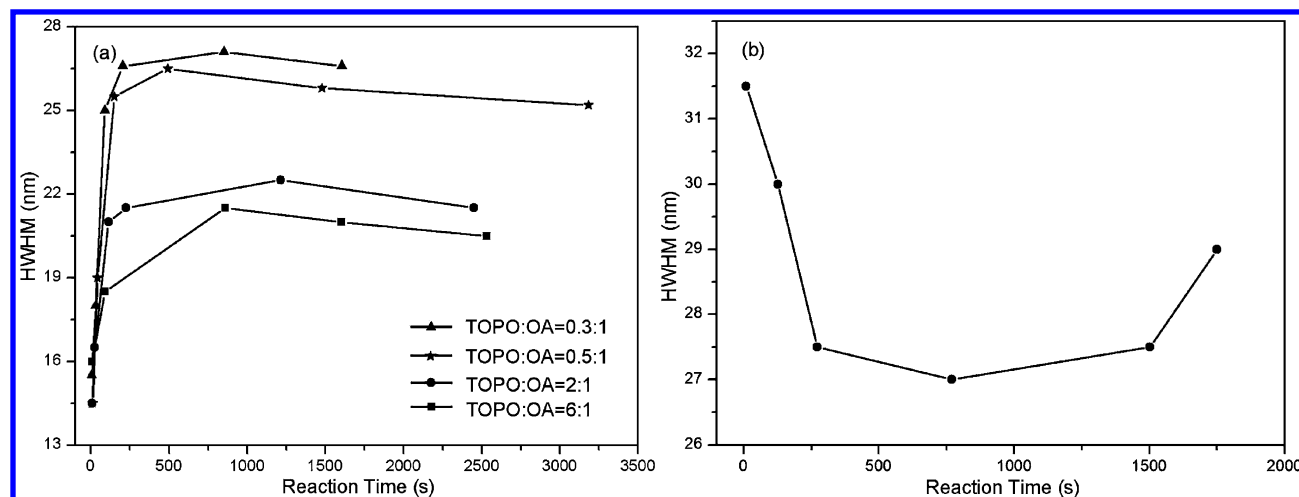
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Figure 2. (a) Temporal evolution of HWHM-indicated size distributions of the CdSe nanocrystals prepared in ODE with different TOPO/OA molar ratios. (b) Evolution of HWHM-indicated size distributions of the CdSe nanocrystals synthesized in pure ODE.
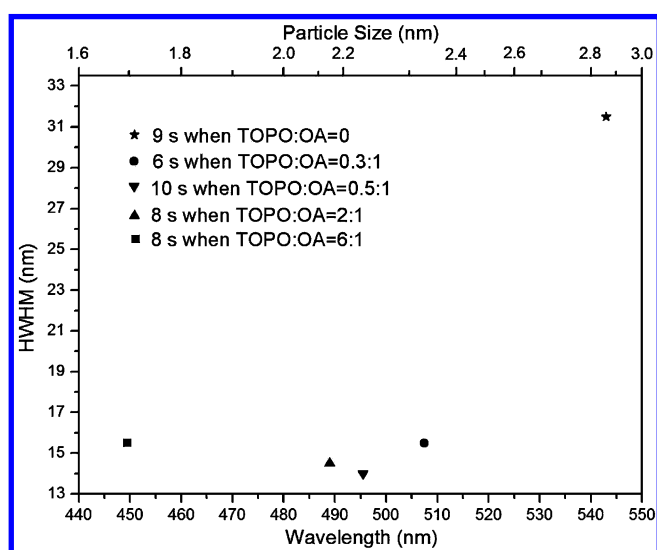

Figure 3. Particle size and HWHM-indicated size distribution of the CdSe nanocrystals formed within 10 s after injection.

demonstrated by the evolution of PL spectra (Figure 4a and Figure S1 of the Supporting Information).

Figure 4b shows a typical room-temperature absorption and PL spectra of a CdSe nanocrystals sample synthesized via our strategy. The shape of the intensive PL peak and the reasonable Stokes shift value indicate that the emission is purely band-gap, devoid of significant trap-state emission. A representative TEM image shows that the resulting nanocrystals appear dotlike with a high shape uniformity (Figure 5).

The growth kinetics proposed in this work may be the results of TOPO-induced transformation in small CdSe nanocrystals. Previous works suggested that surface ligands play a much more important role on the stability of the small CdSe nanocrystals than that of the larger ones because small nanocrystals are primarily composed of surface atoms.[28,29] Recently, an example of secondary ligand-induced change of particle size and size distribution of small nanocrystals was demonstrated by Landes et al.,[30] who observed a remarkable blue-shift and narrowing of the band gap absorption peak of small CdSe nanocrystals by the adsorption of an alkylamine as a strong hole acceptor. The relatively broad and weak absorption peak centered at 445 nm was transformed to a much narrower and stronger peak centered at 414 nm when butylamine, isobutylamine, or benzylamine was introduced into a colloidal suspension of 1.6-nm CdSe nano-crystals. It was suggested that the dramatic changes of absorption
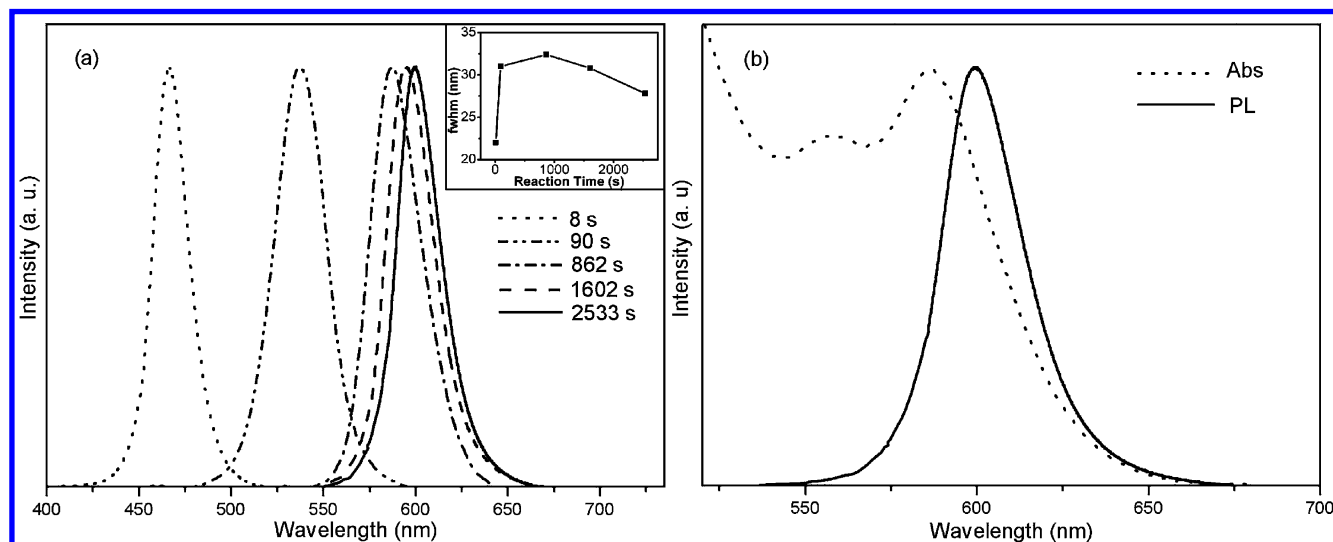

Figure 4. (a) Temporal evolution of room-temperature PL spectra obtained from a representative reaction performed in ODE with the TOPO/OA molar ratio of 6:1. Inset: The fhmw-indicated size distribution evolution. (b) Room-temperature absorption and PL spectra of a sample taken from this representative reaction.
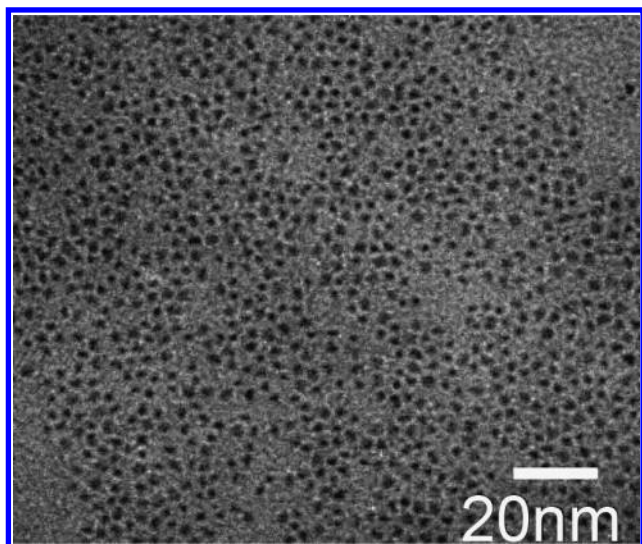
Figure 5. Representative TEM image of the CdSe nanocrystals synthesized in ODE with the addition of TOPO.

spectra were due to electron and hole transitions in CdSe nanocrystals that had been transformed to smaller ones with narrower size distribution, and not due to electronic transition in a CdSe−amine complex with the original nanocrystals. Alkylamines such as butylamine, isobutylamine, and benzylamine were considered to have higher surface-bonding ability, so that they could penetrate through the bulky TOPO/TOP capping layer and their free electron pair could be employed to provide a stronger binding with the nanocrystal surface atoms, which induced the transformation of particle size and size distribution observed in absorption spectra. Such transformation is believed to exist in our reaction systems as well when TOPO is introduced, because TOPO can penetrate the OA capping layer of small CdSe nanocrystals, bind with the nanocrystal surface atoms (Figure S2 of the Supporting Information), and finally result in a transformation involving a blue-shift of the absorption or emission peak and a narrowing of the size distribution. However, the transformation depends on the particle size and happens only in small nanocrystals, as demonstrated by a comparison between the previous study on 3.2-nm CdSe nanocrystals (where the above-reported transformation did not occur when butylamine was added into the suspension of these nanocrystals)[31] and the report on 1.6-nm ones.[30] This size-dependent transformation was also supported by the theoretical modeling[32] and experimental study,[33] which showed that the stability of CdSe nanocrystals needed certain electronic and geometric combinations of atoms, and the discontinuity of such stability appeared when the nanocrystal size was below 2 nm or so.

On the basis of the above discussions, we suppose a growth kinetics of the nanocrystals in our reaction systems with TOPO as a secondary ligand. After the nucleation, extremely small CdSe nanocrystals with broad size distribution form, as also observed by Peng et al.[23] With the attack of TOPO, these small nanocrystals are transformed to even smaller crystals, and thus the original absorption or emission peak exhibits a blue-shift; meanwhile, the transformation involves a narrowing of size distribution. This explains the facile and reproducible production of very small CdSe nanocrystals with narrow size distribution. Nanocrystals continue to grow, and when they reach a critical size (about 2 nm), the above transformation stops, which makes it clear that the subsequent size distribution appears broader than the initial one with relatively small particle size. Due to no transformation, the subsequent growth is dominated by the growth kinetics reported by Peng et al.,[23] and thus focusing of

size distribution will gradually occur. Evidently, the monomer concentration has been almost depleted during the past growth stage, and as a result the size distribution can only be narrowed slightly.

4. Conclusions

In this report, we have showed that addition of a small amount of coordinating solvent as the secondary ligand in the synthesis of CdSe nanocrystals carried out in noncoordinating solvents and fatty acids allow us to synthesize extremely small nanocrystals and greatly improve the size distribution of the as-synthesized nanocrystals. This study is accompanied by the methodology and the understanding of growth kinetics, and it will be helpful in improving the syntheses of other semiconductor nanocrystals such as those of the III−V and IV−VI groups.

Supporting Information Available: PL spectra of the CdSe nanocrystals grown in ODE with TOPO/OA molar ratios varying from 0.3:1 to 2:1 (Figure S1). FTIR spectra of TOPO and the purified CdSe nanocrystals (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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