A New Two-Phase Route to High-Quality CdS Nanocrystals

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Abstract: A new two-phase route has been developed to synthesize high-quality CdS nanocrystals with a narrow size distribution and a high photoluminescence (PL) quantum yield (QY). In the two-phase system, toluene and water were used as separate solvents for cadmium myristate (CdM_2) and thiourea, which served as cadmium source and sulfur source, respectively, and oleic acid (OA) was used as a ligand for stabilizing the nanocrystals. The reactions were completed in the heated autoclaves. The initial Cd/S molar ratio of the precursors and the reaction temperature were found to be factors that affected the growth of nanocrystals. Furthermore, a seeding-growth technique was developed to synthesize CdS nanocrystals of different sizes, which exhibit PL peaks with quite similar full width at half-maximum (FWHM) values compared to those of the initial nanocrystal seeds in all cases.

Keywords: cadmium sulfide · nanotechnology · seeding-growth technique · semiconductors

Introduction

Owing to the quantum confinement effect, semiconductor nanocrystals, especially the II–VI semiconductor nanocrystals, exhibit remarkable size-dependent optical properties,[1] which have attracted a great deal of attention in recent years for both fundamental research and technical applications such as light-emitting diodes (LED),[2–4] solar cells,[5,6] lasers[7] and biological markers.[8–10] In the past two decades, considerable effort has been made to synthesize high-quality semiconductor nanocrystals. Among the methods employed for synthesizing dot-shaped semiconductor nanocrystals, the organometallic approach[11–13] and its variations[14–17] have proved the most popular, although other methods have also been very successful.[10,18–20]

For any applications based on the optical properties of nanocrystals, it is essential to use high-quality nanocrystals. In principle, high-quality nanocrystals should possess at least two characteristics, high emission color purity and high photoluminescence quantum yield (PL QY). The color purity of the emission is strongly dependent on the size distribution of the nanocrystals. The narrower the size distribution, the purer the color of the emission light, which can be reflected by the narrow PL emission bandwidth and/or the narrow UV/Vis band-edge absorption bandwidth.[10–22] The PL QY is very sensitive to the surface environment of the nanocrystals, and can be dramatically reduced by surface trap states.[22] These surface trap states result from the dangling bonds and/or stacking faults of some of the surface atoms.[10,22,23] Surface passivation with suitable organic or inorganic materials and an increase of the crystallinity can effectively remove the surface trap states, and lead to a significant increase in the quantum yield.

Among the II–VI semiconductor nanocrystals, CdSe nanocrystals have been most extensively investigated, and their size and size distribution can be controlled, whereas relatively little work has been done on CdS nanocrystals. Recently, high-quality CdS nanocrystals with a controllable size and a narrow size distribution were prepared successfully in a noncoordinating solvent.[16] It was believed that maintaining a good balance between nucleation and growth by tuning the activities of the precursors was the key to this success. Very recently, Pan et al. developed a two-phase approach to successfully synthesize highly luminescent and nearly monodisperse CdS nanocrystals.[24] The reaction was carried out under mild conditions (at below 100 °C) with less

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toxic reagents than employed traditionally. The possible mechanism was based on slow nucleation and slow growth; it is definitely different from a mechanism based on fast nucleation and slow growth as reported previously. In fact, the two-phase approach, in which the reaction occurs at the interface of two liquid phases, was first applied to the synthesis of gold nanocrystals by Brust et al.[25] in 1994. Based on the work by Pan et al., we developed a new two-phase approach to synthesize high-quality CdS nanocrysals in an autoclave. Compared with the earlier results, the CdS nanocrystals obtained by the new approach exhibit a narrower size distribution and a higher PL QY. Moreover, through a seeding-growth technique, tunable size CdS nanocrystals were obtained with PL peaks with a quite similar full width at half-maximum (FWHM = 18–22 nm) to those of the initial nanocrystal seeds throughout the whole controllable size range. In this study, cadmium myristate (CdM_2) and thiourea were used as cadmium source and sulfur source, respectively, and oleic acid (OA) was used as a ligand for stabilizing the nanocrystals. It was found that the resulting nanocrystals, without any size sorting, appeared to be comparable with the CdS nanocrystals reported previously.

Results and Discussion

Figure 1 shows the temporal evolution of the UV/Vis and PL spectra (a–d) and the corresponding PL peak positions (e) and FWHM (f), respectively, of the CdS nanocrystals prepared at 180 °C from precursors of four different initial Cd/S ratios. In these reactions, the amount of the initial cadmium precursor was kept constant (0.1134 g, 0.2 mmol), while that of the sulfur precursor was varied from 0.24 to 1.0 mmol. The other experimental conditions were also kept constant. It is found that the initial Cd/S ratio of the precursors affects the growth of the CdS nanocrystals. For the same reaction time, a larger proportion of sulfur precursor results in a faster growth of nanocrystals, accompanied by a red shift of the PL peak. For example, when the Cd/S ratio was 1:5 and the reaction time was 0.5 h, the band-edge PL peak of the nanocrystals was near 409 nm, whereas under the same reaction conditions except for a Cd/S ratio of 1:1.2, the band-edge PL peak position of the nanocrystals was near 390 nm, and the peak near 310 nm ascribed to the "magic size" nanoclusters, which are those clusters with no more than one unit cell of the bulk crystal and close-shell structures in the size range between 1 and 2 nm,[14b] was still very strong, which implies the existence of a high monomer concentration in the system after the reaction had occurred for 0.5 h when less sulfur precursor was used.[26] This is a kinetics-driven result.

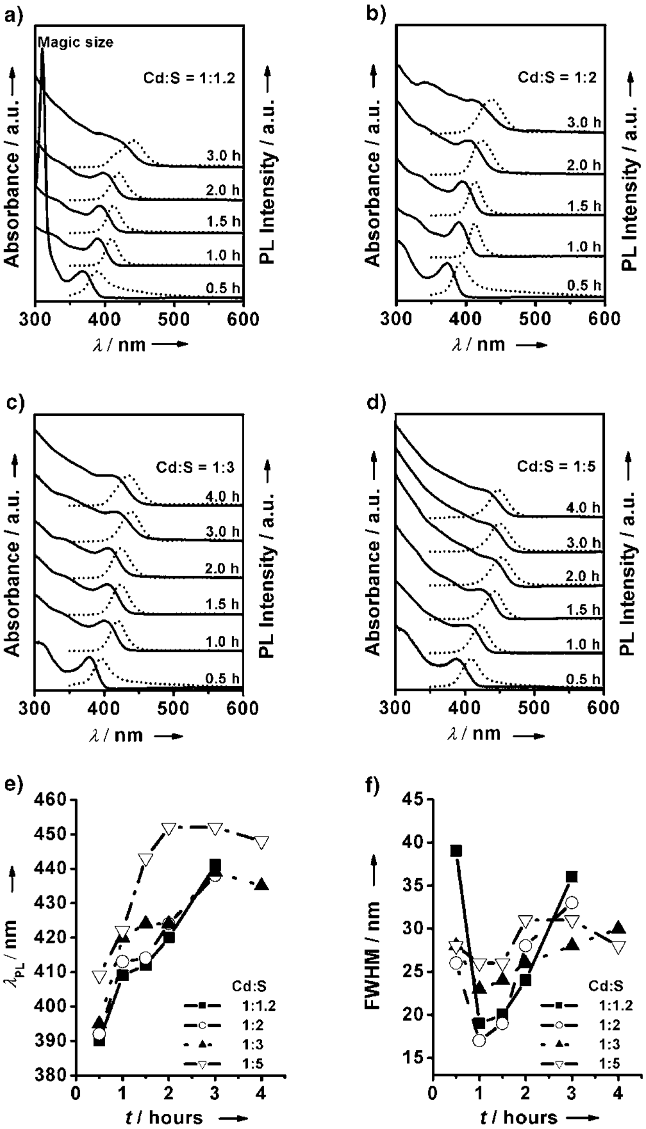

Figure 1. Temporal evolution of the UV/Vis (——) and PL (•••••) spectra (a–d) and the corresponding PL peak positions (e) and FWHM (f), respectively, of CdS nanocrystals prepared at 180 °C from precursors of different initial Cd/S ratios.

In addition, at a reaction time between 1.0 and 1.5 h, the samples exhibit a relatively narrow PL FWHM, implying a narrow size distribution; a lower sulfur monomer concentration favors a narrower size distribution. For example, a sample with a PL FWHM of 17 nm was obtained when the Cd/S ratio was 1:2 and the reaction time was 1 h. When the reaction time exceeds 1.5 h, the PL FWHM of samples increases for all the reactions, and this increase is more dramatic for the samples prepared at low sulfur monomer concentrations. Such results suggest that Ostwald ripening starts for the reactions up to 1.5 h owing to the decrease of monomer concentration to a critical threshold.[12] During Ostwald ripening, the large nanocrystals continuously grow, while the small ones shrink and eventually disappear, inevitably leading to a wide size distribution of nanocrystals. In the two-phase system, the surface of the nanocrystals is usually covered by oleic acid (OA), which facilitates the dispersion of the nanocrystals in the oil phase. However, it is observed that when the reaction time is further extended, larger orange particles are formed due to Ostwald ripening and those drop into the water phase due to the loss of surface ligands, while the smaller ones are left in the oil phase, which are used as the samples for measuring UV/Vis and PL spectra. This is the reason why the wavelength and/or FWHM of some of the PL peaks for the nanocrystals obtained after a longer reaction time become smaller (see Figure 1 c, d).

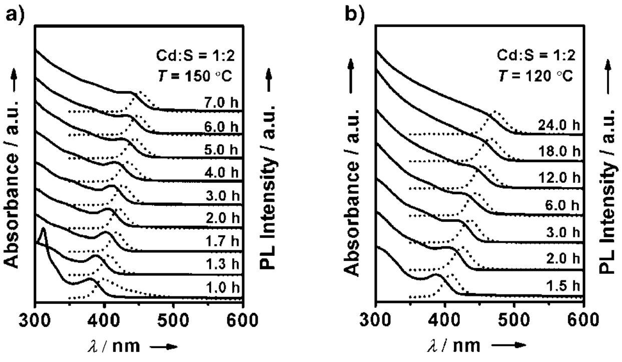

Figure 2. Temporal evolution of the UV/Vis (——) and PL (•••••) spectra of CdS nanocrystals grown at 150 °C (a) and 120 °C (b), respectively.

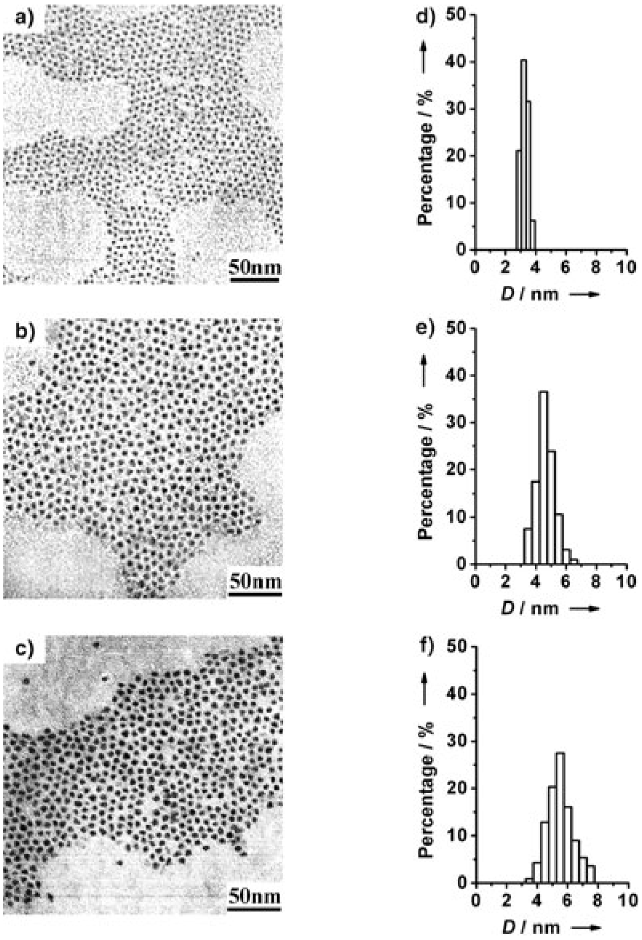

Figure 3. TEM images of CdS nanocrystals prepared at 180 °C (a), 150 °C (b), and 120 °C (c), and their corresponding size distribution histograms (d–f), respectively.

The effect of the reaction temperature on the growth of nanocrystals is also significant. Figure 2a and b show a temporal evolution of the UV/Vis and PL spectra of CdS nanocrystals grown at 150 and 120 °C, respectively. In these two cases the reaction conditions were the same as those for the growth of the nanocrystals shown in Figure 1b except for the reaction temperature. The nanocrystals obtained at lower reaction temperature tend to show a wider PL peak. For example, the smallest PL FWHM we obtained for the nanocrystals grown at 150 and 120 °C was 20 nm and 24 nm, respectively. This suggests that use of a low temperature is a disadvantage for the synthesis of the nanocrystals with a narrow size distribution. This is further supported by the transmission electron microscope (TEM) images (Figure 3 a–c) and the corresponding size distribution histograms (Figure 3 d–f) of the nanocrystals obtained under different temperatures. The reason may be that lower temperatures result in a worse mixing of the two phases. Thus, there are always some of the small particles unable to grow into large ones due to a lower probability of their arrival at the interface from the oil phase. This is responsible for the broadening of the size distribution at lower temperatures. On the other hand, a lower reaction temperature can postpone the occurrence of Ostwald ripening, and the range of tunable size can be widened. Compared with the samples obtained at 180 and 150 °C, the nanocrystals prepared at 120 °C can grow for up to 24 h, and the PL peak can shift to 473 nm without a significant widening of the FWHM. In fact, the decomposition rate of thiourea is temperature-dependent; a higher temperature can accelerate the decomposition of thiourea, which gives rise to a rapid formation of more nuclei at the oil/water interface, so the reaction monomers are depleted faster due to the growth of nuclei into nanocrystals. As a result, Ostwald ripening occurs faster at high temperature. Unlike single-phase systems, in which nucleation and growth occur separately at two different temperatures, and thus lead to nanocrystals with a narrow size distribution,[11–17] in a two-phase system, nucleation and growth are rather complicated, and their separation is likely to be dependent on the concentrations of the remaining monomers in both phases. In fact, during the nucleation stage, nucleation and growth in the two-phase system take place simultaneously, although the former is dominant. This is supported by the formation of a broad PL peak and the coexistence of a first excitonic absorption peak near 368 nm and a strong absorption peak near 310 nm attributable to "magic size" nanoclusters, a kind of stable nuclei, at short reaction times (see Figure 1a). A similar phenomenon was observed in the work by Pan et al., where the absorption peak due to magic size nanoclusters was maintained for over 30 min.[24] However, when the concentration of the remaining monomers drops to a critical threshold, the growth of the nuclei becomes predominant. Owing to their higher energy and lower stability, smaller particles always grow faster than larger ones before Ostwald ripening occurs. As long as the monomers needed for the growth of the smaller particles can be provided adequately at the oil/water interface, the focusing of the size distribution can be realized.[12]

Of particular interest is that a high-temperature process generates CdS nanocrystals that exhibit a high PL QY. For example, as the reaction temperature increases from 120 to 150 and 180 °C, the maxima of the PL QYs of the resulting nanocrystals gradually increase from 34 to 48 and 57 %, respectively. The reason for this may be that at a higher temperature the molecular species on the nanocrystal surface are more likely to readjust their position to reach an optimal surface structure, and therefore decrease stacking faults and surface disorder.[22]

The above study shows that a high reaction temperature favors the synthesis of CdS nanocrystals with a narrow size distribution, but their tunable size range is narrow before Ostwald ripening occurs. On the other hand, at a low reaction temperature, a wide-range size control can be realized, but a narrow size distribution is difficult to achieve. Therefore, it is a challenge to synthesize nanocrystals with both a narrow size distribution and a wide tunable size range. Here, a seeding-growth technique has been developed to achieve this goal. Similar to the procedure mentioned above, an initial Cd/S ratio of 1:2 (0.2 mmol of CdM_2 and 0.4 mmol of thiourea) and a reaction temperature of 180 °C and a reaction time of one hour were selected for the synthesis of small-size nanocrystals as initial “nanocrystal seeds”, which are denoted as “a”. A fresh mixture of the precursors was mixed with the original oil phase containing the nanocrystal seeds “a” for the completion of the first growth reaction, and the resulting nanocrystals were denoted as “b” and used as seeds for the next growth reaction. The reaction time used here for the growth reactions is 1.5 h. This growth cycle was repeated by using nanocrystals from the previous cycle as seeds, and the resulting nanocrystals were denoted respectively as “c, d···” in sequence (see Experimental Section for details). The as-prepared CdS nanocrystal colloidal solution was used after dilution with toluene for the measurement of the optical properties without any other post-treatment, and the temporal evolution of their UV/Vis and PL spectra is shown in Figure 4. It is found that all the PL peaks have rather narrow FWHM values (18–22 nm), suggesting that our approach is very effective in synthesizing nearly monodisperse nanocrystals with different sizes. This is further demonstrated by the TEM images shown in Figure 5. In addition, the high-resolution transmission electron microscopy (HRTEM) image shown in the inset of Figure 5 confirms the highly crystalline nature of the nanocrystals, which are free from stacking faults. The PL QYs of a solution of these nanocrystals in toluene were also assessed at room temperature by using 9,10-diphenylanthracence (PL QY 90 % in cyclohexane) as a reference.[27] A monotonic decrease is observed with the decrease of the nanocrystal size (see the inset of Figure 4). Moreover, the average sizes of the nanocrystals were estimated according to the literature,[16,28] and found to range from 3.2 nm to 6.0 nm. Figure 6 shows the wide-angle X-ray diffraction (WAXD) patterns of the CdS nanocrystals pre-

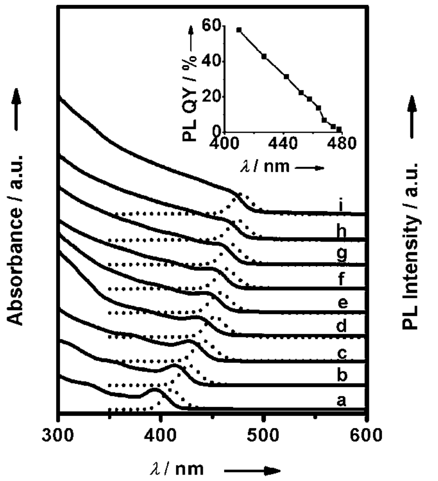

Figure 4. UV/Vis (——) and PL (•••••) spectra of CdS nanocrystals obtained by the seeding-growth technique at 180 °C. The average sizes of nanocrystals are 3.2 nm (a), 3.8 nm (b), 4.3 nm (c), 4.6 nm (d), 4.9 nm (e), 5.3 nm (f), 5.5 nm (g), 5.8 nm (h) and 6.0 nm (i), respectively. Inset: PL QY of different-sized CdS nanocrystals versus their emission peak positions relative to 9,10-diphenylanthracence.

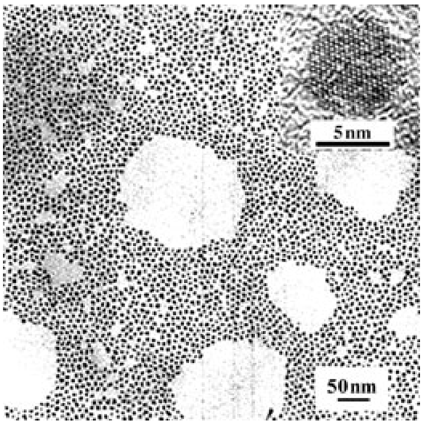

Figure 5. TEM and HRTEM images of CdS nanocrystals synthesized by the seeding-growth technique at 180 °C.

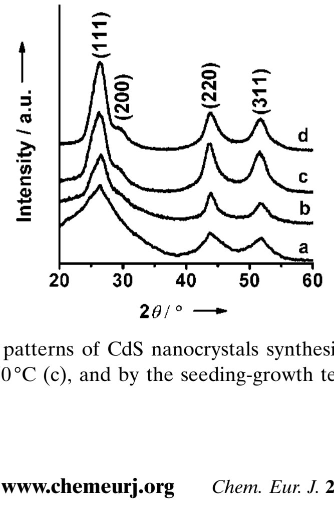

Figure 6. WAXD patterns of CdS nanocrystals synthesized at 180 °C (a), 120 °C (b) and 150 °C (c), and by the seeding-growth technique at 180 °C (d).

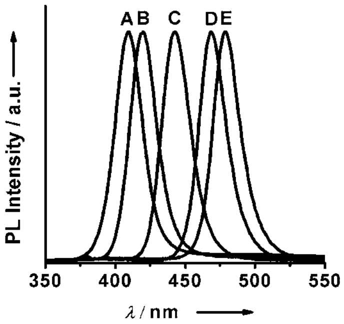

Figure 7. PL spectra of CdS nanocrystals grown under different experimental conditions by the seeding-growth technique at 180 °C.[29]

pared at different temperatures, confirming that all the samples obtained belong to the cubic zinc blende structure.

It is also noted in Figure 4 that the degree of red shift for the PL emission in each growth cycle is uneven, and the shifts in the first three cycles are larger than those in the other cylces, although the new reaction monomers in terms of mass are identical in each of the seeding-growth reactions (see Experimental Section for details). When we set the reaction time to 1 h instead of 1.5 h for every growth reaction, similar results were obtained to that described in Figure 4, except that the degree of red-shift of the PL peaks in the first three cycles was smaller. Therefore, it is necessary to adjust simultaneously the amount of new monomers and reaction time to obtain nanocrystals with the desired wavelength of PL emission[29] (Figure 7). In contrast, in the growth reactions, either excessively increasing the amount of new monomers or excessively reducing the amount of added nanocrystal seeds, or using a too short reaction time is likely to generate new nuclei, resulting in two emission peaks in the PL spectra of the nanocrystals. Too long a growth reaction time can easily lead to a broadening of the nanocrystal size distribution, which is not desirable.

Conclusion

In conclusion, a new two-phase approach has been developed for synthesizing high-quality CdS nanocrystals with a relatively narrow size distribution and a high PL QY up to 57 %. By using a seeding-growth technique, a relatively wide controllable size range of nanocrystals can be achieved and a focusing of the size distribution can be maintained throughout the whole size range. Compared with the traditional route, the approach can be performed at relatively low temperature without the need for stirring and hot-injection. In addition, the approach may be applied to the synthesis of other semiconductor nanocrystals; in particular, the seeding-growth technique also provides a novel and feasible approach for the synthesis of high-quality nanocrystals with core/shell structure, work on which is currently underway.

Experimental Section

Materials: Cadmium oxide (CdO) (99.5 %), myristic acid (MA) (99.5 %), oleic acid (OA) (technical grade, 90 %), and thiourea were purchased from Aldrich. 9, 10-Diphenylanthracene was obtained from Acros, and methanol and toluene from the Beijing chemical company in China. Cadmium myristate (CdM_2) was prepared according to following method: CdO (1.926 g, 15 mmol) and MA (7.5 g, 33 mmol) were loaded into a reaction flask and heated at 220 °C for 10 min to produce an optically clear solution. The CdM_2 was obtained. The crude product was re-crystallized twice from toluene for use in further reactions.

Synthesis: Typically, a mixture of CdM_2 (0.1134 g, 0.2 mmol), oleic acid (1 mL), and toluene (10 mL) was first loaded into the Teflon liner of a 30-mL stainless steel autoclave, and then heated at 80–100 °C to produce an optically clear solution. After the heating had been turned off and the solution was allowed to cool to room temperature, an aqueous solution of thiourea (10 mL; 0.0183–0.0761 g, 0.24 ~1.0 mmol for different Cd/S molar ratio) was added to the organic solution to form a two-phase reaction system. The Teflon liner containing the mixture was then sealed in the stainless steel autoclave and maintained at the desired temperature (e.g. 180, 150, or 120 °C) for a fixed reaction time. The autoclave was cooled naturally to ambient temperature after a given reaction time.

In the reactions using the seeding-growth technique, an initial Cd/S ratio of 1:2 (0.2 mmol of CdM_2 and 0.4 mmol of thiourea), a reaction temperature of 180 °C, and a reaction time of one hour were selected to synthesize small-size nanocrystals as initial "nanocrystal seeds". Then, a fresh mixture of CdM_2 (0.0113 g, 0.02 mmol), OA (0.5 mL), and toluene (1 mL) was placed into the Teflon liner of another stainless steel autoclave and heated at 80–100 °C to produce an optically clear solution, to which 9 mL of the original oil phase containing the above-mentioned nanocrystal seeds was added, and the mixture was cooled to ambient temperature before 10 mL of a new aqueous solution of thiourea (0.0183 g, 0.24 mmol) was injected into the Teflon liner. Finally, the Teflon-lined stainless steel autoclave containing the two-phase mixture was sealed and maintained at 180 °C for 1 or 1.5 h without any stirring for the completion of the first growth reaction, and the resulting nanocrystals were used as seeds for the next one. The following growth reactions were carried out analogously to the first one, and the nanocrystals obtained from the last growth reaction were always used as seeds for the next growth reaction. The as-prepared CdS nanocrystal colloidal solution was diluted with toluene and then the optical properties were investigated without any other post-preparative treatment.

Characterization: UV/Vis absorptions were recorded on a Shimadzu UV-2450 spectrometer. The photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301 PC fluorometer with an excitation wavelength of 340 nm. Room-temperature photoluminescence quantum yields (PL QY) were calculated according to Eaton et al.,[27] whereby 9,10-diphenylanthracene in cyclohexane as was used as the reference (QY = 90 %). The absorbance of the sample and the reference at the excitation wavelength (340 nm) are similar and smaller than 0.1, thus avoiding self-absorbance. The full width at half-maximum (FWHM) of PL peaks was obtained by applying the program "Fit Gaussian" in the software "Origin 7.0". The nanocrystals were precipitated with ethanol and then isolated by centrifugation and decantation. The purified nanocrystals were used for TEM and wide-angle X-ray diffraction (WAXD) analyses. The WAXD patterns were recorded on a Japan Rigaku D/max-2500 X-ray diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). The low-resolution TEM images were recorded on a JEM-2000FX transmission electron microscope with an accelerating voltage of 160 kV. High-resolution TEM (HRTEM) images were recorded by using a JEM-2010 microscope with an accelerating voltage of 200 kV. The size distribution histograms were obtained by measuring more than 300 individual CdS nanocrystals on enlarged photographs.

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[29] The preparation procedure of samples A–E is described here. Sample A (initial nanocrystal seeds): CdM_2 (0.1134 g, 0.2 mmol) in toluene (10 mL), thiourea (0.0304 g, 0.4 mmol) in deionized water (10 mL), and oleic acid (1 mL) were mixed together and heated for 1 h. Sample B: CdM_2 (0.1134 g, 0.2 mmol) in toluene (1 mL), thiourea (0.0076 g, 0.1 mmol) in deionized water (10 mL), oleic acid (0.5 mL), 9 mL of the original oil phase containing sample A as seeds, were mixed together and heated for 1 h. Sample C: CdM_2 (0.0340 g, 0.06 mmol) in toluene (1 mL), thiourea (0.0457 g, 0.6 mmol) in deionized water (10 mL), oleic acid (0.5 mL), 9 mL of the original oil phase containing sample B as seeds, were mixed together and heated for 1.5 h. Sample D: CdM_2 (0.0567 g, 0.1 mmol) in toluene (1 mL), thiourea (0.076 g, 1 mmol) in deionized water (10 mL), oleic acid (0.5 mL), 9 mL of the original oil phase containing sample C as seeds, were mixed together and heated for 1.5 h. Sample E: CdM_2 (0.0454 g, 0.08 mmol) in toluene (1 mL), thiourea (0.0609 g, 0.8 mmol) in deionized water (10 mL), oleic acid (0.5 mL), 9 mL of the original oil phase containing sample D as seeds, were mixed together and heated for 1.5 h.

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