Noninjection Synthesis of CdS and Alloyed CdS_{x}Se_{1−x} Nanocrystals Without Nucleation Initiators

Yu Zou · Dongsheng Li · Deren Yang

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Abstract CdS and alloyed CdS_{x}Se_{1−x} nanocrystals were prepared by a simple noninjection method without nucleation initiators. Oleic acid (OA) was used to stabilize the growth of the CdS nanocrystals. The size of the CdS nanocrystals can be tuned by changing the OA/Cd molar ratios. On the basis of the successful synthesis of CdS nanocrystals, alloyed CdS_{x}Se_{1−x} nanocrystals can also be prepared by simply replacing certain amount of S precursor with equal amount of Se precursor, verified by TEM, XRD, EDX as well as UV–Vis absorption analysis. The optical properties of the alloyed CdS_{x}Se_{1−x} nanocrystals can be tuned by adjusting the S/Se feed molar ratios. This synthetic approach developed is highly reproducible and can be readily scaled up for potential industrial production.

Keywords Nanocrystals · CdS · CdS_{x}Se_{1−x} · Noninjection synthesis · Oleic acid

Introduction

Colloidal semiconductor nanocrystals have been intensively studied due to their unique physical properties. They exhibit quantum confinement effect such as size-dependent optical and electric properties for applications in optoelectronic devices [1–3] and biological fluorescence labeling [4, 5]. CdS, with a bulk band gap of ~2.42 eV (~512 nm) and exciton Bohr radius of ~3 nm, is a candidate for quantum-dot blue light-emitting diodes [6] and can be used in photovoltaic devices [7]. In order to tune the optical properties of CdS quantum dots for specific applications, two schemes have been put forward. One is to change the size of the quantum dots for specific applications, two schemes have been put forward. One is to change the size of the quantum dots, based on the quantum confinement effect. The other is to alloy CdS with other materials, such as CdSe, to form alloyed quantum dots whose band gap energy can vary with composition without changing size. In the past decades, significant advancement has been made in the synthesis of CdS [8–10] and CdS_{x}Se_{1−x} [11–13] quantum dots based on the classic hot-injection method developed by Bawendi’s group [14], the key part of which is the injection of room-temperature organometallic precursors into well-stirred hot organic solvents. However, these injection-based methods are not suitable for large-scale industrial preparation due to the difficulty of large mass transfer in the process of the injection.

In 2004, Cao et al. [15] reported a novel synthetic method for producing high-quality CdS quantum dots by simply heating the reaction mixture containing Cadmium myristate, Sulfur (S) and 1-octadecene without injection. They added two nucleation initiators (tetraethylthiuram and 2,2′-dithiobisbenzothiazole) into the reaction medium to increase the reactivity of S and found that the nucleation initiators were the key to successfully prepare the high-quality quantum dots. Ouyang et al. [16] extended this noninjection method to synthesize alloyed CdS_{x}Se_{1−x} quantum dots. Nucleation initiator 2,2′-dithiobisbenzothiazole is still applied in their work. Moreover, CdSe quantum dots have been prepared without precursor injection and nucleation initiators simultaneously by Cao’s group [17]. Oleic acid, a natural surfactant, was chosen to stabilize the growth of the quantum dots. From this viewpoint, CdS and alloyed CdS_{x}Se_{1−x} quantum dots may be synthesized without nucleation initiators if oleic acid is...
added into the reaction mixture, which could make the synthesis greener. Recently, Li et al. [18] have prepared CdS magic-sized nanocrystals using OA as stabilizer and highly reactive bis(trimethylsilyl)sulfide as S source at low temperatures (90–140°C).

Herein, we report the successful synthesis of CdS and alloyed CdSₓSₓ⁻¹ nanocrystals without injection and nucleation initiators by simply heating the reaction medium. All the source chemicals used including cadmium acetate, sulfur, selenium, oleic acid and 1-octadecene are air-stable and inexpensive relatively. The optical properties of the obtained quantum dots can be tuned by changing the OA/Cd or the S/Se feed molar ratio. The former and latter changing of feed molar ratio results in the change of the size and the composition, respectively. This synthetic approach developed is very simple and highly reproducible and thus suitable for large-scale preparation of CdS and CdSₓSₓ⁻¹ nanocrystals.

Experiment

Materials

All of the chemicals are commercially available and were used as received. Cadmium acetate dihydrate (Cd(OAc)₂·2H₂O, 99.5%), sulfur (S, 99.5%) and Selenium (Se, 99.95%) were purchased from Shanghai Chemical Reagent Ltd.. Oleic acid (OA, tech. 90%) and 1-octadecene (ODE, tech. 90%) were purchased from Aldrich.

Synthesis

In a typical synthesis of CdS nanocrystals, a 100-ml three-neck flask containing 1 mmol Cd(OAc)₂, 6 mmol OA and 15 ml ODE was heated to 120°C and was degassed under vacuum for 30 min. The flask then was filled with argon gas, and its temperature was lowered to about 30°C. A total of 0.5 mmol S was added into the flask, and then the mixture was heated to 240°C at a rate of ~20°C/min and reacted at this temperature for 60 min under a flow of argon gas. To monitor the growth of nanocrystals, small aliquots (~0.1 ml) of the reaction mixture were taken out from the flask and quenched in cold hexane (25°C) in order to stop further growth. The time was counted as 0 when the temperature reached to 240°C. At last, the quantum dots were isolated by precipitation with ethanol, then centrifuged and the resulted nanocrystals were redispersed in hexane. This process was repeated several times to wash the samples. To investigate the effect of OA, only the amount of OA was changed. For the synthesis of CdSₓSₓ⁻¹ nanocrystals, certain amount of S was replaced with equal amount of Se while the amount of OA was fixed at 6 mmol. The other experimental conditions were the same as those to the preparation and purification of CdS nanocrystals.

Characterization

Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) images were collected using a Philips CM200 transmission electron microscope operating at 160 kV. A sample for TEM analysis was prepared by drying a drop of nanocrystal hexane solution on a carbon-coated copper grid and letting it dry in air. X-ray powder diffraction (XRD) was conducted on a Rigaku D/max-ga X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). Energy-dispersive X-ray (EDX) analysis was performed using an EDAX X-ray detector attached to a Hitachi S-4800 scanning electron microscope. Ultraviolet–Visible absorption spectra were recorded on a U-4100 UV–Vis spectrophotometer. Photoluminescence (PL) spectra were taken with a He–Cd laser as the excitation source and an excitation wavelength of 325 nm.

Results and Discussions

Figure 1 shows the temporal evolution of absorption and PL spectra of the CdS nanocrystals prepared with the OA/Cd molar ratio of 6. It can be seen that small nanocrystals did appear when the reaction temperature reached 220°C, indicated by the appearance of the absorption and PL peak. The nanocrystals grown fast, and the size distribution decreased evidently with the temperature increasing to 240°C, confirmed by the narrowing of the PL peaks. After the temperature reached 240°C, the growth was slow relatively, and no additional nucleation occurred. The narrow size distribution was maintained in the first 10 min and increased slightly after a 60-min growth. The PL spectra of the CdS quantum dots contain a higher energy and narrow peak assigned to band gap emission, and a low-energy and wide peak assigned to trap emission, which is the same as the PL of the as-prepared CdS nanocrystals obtained in the presence of nucleation initiators [15]. In general, the growth kinetics is similar to that in the presence of nucleation initiators, and the quality of the CdS nanocrystals is comparable, indicating the noninjection synthesis of CdS nanocrystals without nucleation initiators in the presence of OA is feasible undoubtedly.

Compared with the synthesis in the presence of nucleation initiators, OA must play an important role here. To investigate the effect of OA, we changed the molar ratio of OA to Cd in the reaction mixture (the amount of Cd precursors is fixed at 1 mmol). Figure 2a–c show the TEM
Highly monodispersed nanocrystals with narrow size distribution are obtained for all molar ratios of OA to Cd, and these nanocrystals can readily form array even superlattice on the carbon films. The HRTEM image shown in Fig. 2d confirms the obtained nanocrystals are crystalline. The mean size of the CdS nanocrystals increases with the increase in the molar ratio of OA to Cd, which are 2.5, 3.6 and 4 nm, respectively, when the molar ratio is 2, 6 and 10. The change in size is attributed to the tunable reactivity of Cd monomers in the reaction medium [8, 19]. The reactivity of Cd monomers decreases with the increasing of the ratio of OA to Cd, leading to the decrease in the number of nuclei formed in the nucleation stage and the increase in the monomer concentration remained in the reaction medium for further growth. As a result, nanocrystals with larger size are obtained when the molar ratio of OA to Cd is higher. The absorption and PL spectra of the CdS nanocrystals prepared with different OA/Cd feed molar ratios presented in Fig. 3 also confirm that the more OA added, the larger CdS nanocrystals obtained, indicated by the systematic red-shift of the spectra with the increase in the amount of OA added. The distinct absorption peaks of
each spectrum suggest that the high-quality CdS nanocrystals could be obtained for all the OA/Cd molar ratios. Therefore, we can conclude that it is not the OA/Cd molar ratio but the OA itself that results in the successful synthesis of high-quality CdS nanocrystals in the absence of nucleation initiators.

OA has been noticed as a special ligand due to its unique configuration of hydrocarbon chains. OA is more bending than saturated fatty acid, such as myristic acid, due to the existence of a cis-double bond in the middle of the hydrocarbon chains, which makes the Cd–Oleate complex more reactive [19]. Therefore, OA should play two roles here. First, OA accelerates the nucleation just as the nucleation initiators do. In contrast to the nucleation initiators that increase the reactivity of S [15], OA increases the reactivity of Cd precursors relative to myristic acid. Secondly, OA stabilizes the further growth as myristic acid does. As a result, the presence of OA separates and balances the nucleation and growth of CdS nanocrystals, leading to the successful synthesis of high-quality CdS nanocrystals without nucleation initiators.

On the basis of the synthesis of the CdS nanocrystals, we extended this simple scheme to prepare alloyed CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals. By substituting certain amount (25, 50 and 75\%) of S with equal amount of Se, we obtained CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals. EDX analysis was used to determine the composition of the obtained nanocrystals, which are, CdS\textsubscript{0.78}Se\textsubscript{0.22}, CdS\textsubscript{0.44}Se\textsubscript{0.56} and CdS\textsubscript{0.28}Se\textsubscript{0.72}, close to the feed molar ratios. Although the EDX results are not very accurate, they confirm the increase in Se content in the nanocrystals with the increase in Se/S feed molar ratio qualitatively at least. Figure 4a–c shows the TEM images of the CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals after 60-min growth while the OA/Cd feed molar ratio is fixed at 6. Highly monodispersed nanocrystals with narrow size distribution are obtained for all the molar ratios of S to Se. The mean size of the CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals is quite similar to that of the CdS nanocrystals prepared under the same experiment conditions, i.e. 3.6 nm. Fig. 4d shows a typical HRTEM image of CdS\textsubscript{0.44}Se\textsubscript{0.56}, which indicates the obtained nanocrystals are crystalline. UV–Vis absorption spectra of the CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals are shown in Fig. 5. The spectra shift to large wavelength with the increase in Se/S molar ratio, suggesting the nanocrystals are alloyed, because the size of the nanocrystals with different Se/S molar ratio is quite close and the change of the band gap energy attributed to the quantum confinement effect should be small. The result is consistent with that from the injection approach [12] or the noninjection approach in the presence of nucleation initiators [16]. However, the optical bowing effect is not observed distinctly in this work, and the band gap energy of the CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals shifts almost linearly with composition. Compared with CdSe\textsubscript{0.78}Te\textsubscript{0.22}, CdS\textsubscript{0.44}Se\textsubscript{0.56} and CdS\textsubscript{0.28}Se\textsubscript{0.72} nanocrystals [20, 21], the optical bowing effect observed in CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals is minor [12]. The bowing constant of CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals is only 0.3, while that of CdSe\textsubscript{0.78}Te\textsubscript{0.22} and CdS\textsubscript{0.28}Te\textsubscript{0.72} nanocrystals is 1.19 and 3.17, respectively. The error of the composition of CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals obtained by EDX analysis may also influence the observation of the bowing effect. Regardless of the optical bowing effect, the results confirm that the optical properties of the nanocrystals can be tuned by adjusting the composition without changing the size.

The XRD patterns of the CdS and CdS\textsubscript{x}Se\textsubscript{1−x} nanocrystals as shown in Fig. 6 confirm a cubic structure (zinc-blende) throughout the range of compositions, as indicated by the absence of the characteristic diffraction peaks of
(102) and (103) planes of the hexagonal structure. Moreover, the spectra shift to smaller $2\theta$ with the increase in Se/S molar ratio, indicating a linear increase in lattice spacing due to the increase in Se content in the nanocrystals, which is another proof of formation of alloy nanocrystals [12, 16].
Conclusions

We report the successful synthesis of CdS and CdSSe nanocrystals without injection and nucleation initiators. Highly monodispersed nanocrystals with narrow size distribution are obtained by simply heating a mixture containing Cd(OAc)$_2$, S, Se, OA and ODE. This method is very economical and suitable for industrial production. OA plays an important role in the reaction, which increases the reactivity of Cd precursors and stabilizes the growth of nanocrystals. The effects of the OA/Cd or Se/S feed molar ratios on the optical properties of the nanocrystals have been studied. High OA/Cd molar ratios and high Se/S feed molar ratios lead to nanocrystals with small band gap.

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