

Synthesis of CdS, ZnS, and CdS/ZnS Core/Shell Nanocrystals Using Dodecanethiol

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We report a new route to synthesize high quality zinc blende CdS and ZnS nanocrystals in noncoordinating solvent 1-octadecene, using dodecanethiol (DDT) molecules as both the sulfur source and surface capping ligands. Different reaction temperatures and Cd(Zn)/DDT molar ratios were tested to optimize the synthesis conditions. Absorption photoluminescence (PL) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) pattern, and transmission electron microscopy (TEM) were used to characterize as-synthesized nanocrystals. The narrow half width at the half-maximum on the long wavelength side of the first-excitonic absorption peak and TEM images demonstrated nearly monodisperse size distributions of as-prepared CdS, ZnS, and CdS/ZnS core/shell nanocrystals. Only trap emissions of the nanocrystals were detected when the amount of DDT was excessive, this came from the strong quenching effect of thiol groups on the nanocrystal surfaces. After overcoating with ZnS shells, band-gap emissions of CdS nanocrystals were partially recovered.

Key Words : CdS, ZnS, Nanocrystals, Dodecanethiol

Introduction

Since the concept of “size quantization effect” was introduced in 1980s by Brus,¹ semiconductor nanocrystals have attracted great attention in scientific circles because of their unique optical and electronic properties. In 1993, Bawendi's group introduced the organometallic method to synthesize uniform sized CdE (E=S, Se, Te) nanocrystals.² In 2000s, Peng introduced CdO as the new Cd source to replace the dangerous dimethyl cadmium ($\text{Cd}(\text{CH}_3)_2$),³ and noncoordinating solvent was used to replace traditional coordinating solvents.⁴ The syntheses of semiconductor nanocrystals are investigated world widely,²⁻¹² especially for II-VI semiconductor nanocrystals such as CdSe, CdS, ZnSe, ZnS, *etc.*²⁻⁹ However, new synthesis methods are still needed for fundamental understanding of the synthetic chemistry of nanocrystals and to explore their applications.

In this paper, we report a new route to synthesize high quality zinc blende CdS and ZnS nanocrystals. In our experiments, CdO and ZnO reacted with oleic acid (OA) to form Cd-OA and Zn-OA complexes as the Cd and Zn precursors, respectively. Dodecanethiol (DDT) was used as both the sulfur (S) source and surface capping ligands for the growth of nanocrystals. The synthesis conditions were optimized by testing different reaction temperatures and precursor molar ratios, and CdS and ZnS nanocrystals with narrow size distributions were prepared successfully. As a strong ligand to nanocrystals, DDT will quench the band-gap emissions of CdS and ZnS nanocrystals. After the overgrowth of the ZnS shells, band-gap emissions of CdS nanocrystals could be observed.

Experimental

Chemicals. Cadmium oxide (CdO, 99.99%), oleic acid (OA, 90%), dodecanethiol (DDT, 90%), 1-octadecene (ODE, 90%), zinc oxide (ZnO, 99.99%), sulfur (S, 99.98%), and octadecylamine (ODA) were purchased from Aldrich. Hexanes (analytical grade) and methanol (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China. All reagents were used as received without further experimental purification.

Cd, Zn, and S Precursors. Cd precursor: A mixture of CdO (0.0128 g, 0.10 mmol), oleic acid (0.0846 g, 0.30 mmol), and ODE (4 g) was loaded in a 25 mL three-neck reaction flask and heated to 240 °C under nitrogen flow to obtain a clear colorless solution as the Cd precursor.

Zn precursor: A mixture of ZnO (0.0163 g, 0.20 mmol), oleic acid (0.1692 g, 0.60 mmol), and ODE (4 g) was loaded in a 25 mL three-neck reaction flask and heated to 260 °C under nitrogen flow to get a clear colorless solution as the Zn precursor.

S precursor: DDT was diluted in ODE to serve as the S precursor for the reactions, and the concentration of DDT stock solution was 0.5 M.

Synthesis of CdS and ZnS Nanocrystals. In a typical synthesis of CdS nanocrystals, the Cd precursor was heated to 260 °C in the reaction flask under nitrogen flow, 0.4 mL of DDT precursor solution was swiftly injected into the reaction solution. In the process of the growth of CdS nanocrystals, the temperature was maintained at 260 °C. The color of the reaction solution turned from clear colorless to light yellow in a short time at the early stage and finally

became bright yellow. Aliquots were taken at different time intervals via syringe and quenched into hexanes for UV-vis and PL spectra characterizations.

The way to synthesize ZnS nanocrystals was the same as that to synthesize CdS nanocrystals, but the amounts of Zn and S reagents added were doubled because of the low yields of ZnS nanocrystals.

Stock Solutions for Shell Growth. The Zn and S precursors used in these experiments were prepared by methods below: 0.2441 g (3 mmol) ZnO powder, 8.46 g (30 mmol) OA, and 20.5 mL of ODE were put into a three-neck flask and the mixture was heated to 310 °C for about 30 minutes to get a clear colorless solution, then the solution was cooled down to room temperature for further use. The molar concentration of as-prepared Zn precursor was 0.1 M. The S precursor was prepared by mixing 0.048 g (1.5 mmol) S powder and 15 mL of ODE in a three-neck flask and then heated it to 150 °C for a few minutes, the solution was cooled down to room temperature for further use.

All the above stock solutions were prepared under nitrogen flow.

Synthesis of CdS/ZnS Core/shell Nanocrystals. For the growth of the ZnS shells, as-prepared CdS nanocrystals were purified with methanol/hexanes for several times and redissolved in ODE, and then this solution was heated to 240 °C for shell growth. The growth of ZnS shells on CdS core nanocrystals was conducted by the standard successive ions layer adsorption and reaction (SILAR) method reported by Jack Li *et al.*¹²

Characterization. UV-vis absorption spectra were taken on PerkinElmer lambda-35 UV-vis spectrometer. PL and PL excitation (PLE) spectra were taken using SPEX F212 photometer. Fourier transform infrared (FTIR) spectra in the region of 500–4000 cm⁻¹ were recorded on Nicolet, AVATAR 360. X-ray diffraction (XRD) studies of nanocrystals were carried out with a Philips X' Pert Pro X-ray diffractometer using Cu K α radiation with wavelength at 1.54 Å. Drop casted films of nanocrystals were deposited on glass substrates for XRD characterization. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) studies were performed on Jeol JEM-100CX II microscope and Jeol JEM-2010 microscope. TEM samples were prepared by placing a drop of diluted hexanes solution of the nanocrystals onto a 400 mesh carbon covered copper grid.

Results and Discussion

In our experiments, CdS nanocrystals were synthesized using a hot-injection method. CdO powder was used as the Cd source and DDT molecules were used as both the sulfur source and surface ligands. At elevated temperature, CdO reacted with OA molecules to form the Cd-OA complexes in ODE, and this reaction solution was colorless transparent. After injecting the DDT precursor into above reaction solution, the solution color became light yellow, indicated the formation of CdS nanocrystals, and the XRD results in

the following text demonstrated this. According to previous report,¹³ with the addition of DDT, at first DDT took the place of OA to bond to Cd species because of the stronger complexation of thiol groups to Cd ions than the OA molecules, then DDT undergoes cleavage of the C-S bonds, and CdS nanocrystals were formed, so the color changed to yellow finally.

Different CdO:DDT molar ratios and reaction/growth temperatures were tested to optimize the synthesis conditions. It was found that the precursor ratios had less effect on the synthesis of CdS nanocrystals, which can be synthesized with CdO:DDT molar ratios of 5:1, 2:1, 1:1, 1:2, 1:5, *etc.* The growth speed was lower with smaller CdO:DDT molar ratios, which may due to that high DDT concentration created a closely packed ligand layer on the nanocrystal surfaces to hinder monomer diffusion to the nanocrystal surfaces for the subsequent growth. To get high quality CdS nanocrystals, the reasonable molar ratio of CdO:DDT was set of 1:2.

We also investigated the effects of reaction temperatures on the synthesis of nanocrystals and found that the injection/growth temperature of 260 °C/260 °C was suitable for a reasonable growth speed of nanocrystals. Traditionally, for the synthesis of high quality nanocrystals, the growth temperature was usually set lower than the injection temperature in order to get a balanced speed for both nucleation and growth of nanocrystals.⁴ But for DDT molecules which served as the S source here, equal injection and growth temperatures were needed for the growth of high quality CdS nanocrystals considering the difference of the activation energy of DDT and sulfur. It was also found that when the reaction temperature was below 230 °C, CdS nanocrystals can hardly be synthesized.

Figure 1 shows the temporal evolution of the absorption spectra of CdS nanocrystals which were synthesized with CdO:DDT molar ratio of 1:2 and grew at 260 °C. In 32 minutes, the first-excitonic absorption peak of CdS nanocrystals red shifted from about 360 nm to 435 nm, shows an obvious size dependent property. Using DDT as the sulfur source here, the growth speed was very low compared with previous report.⁴ 2 minutes after the injection of precursors, the first-excitonic absorption peak appeared at about 360 nm in our experiments, while for previous report, the absorption peaks appeared early before 20 seconds after the injection of precursors. This slow growth favors the size control of CdS nanocrystals. There are obvious excitonic absorption features in each of the absorption spectrum in Figure 1. The narrow half width at the half-maximum (HWHM) on the long wavelength side of the first-excitonic absorption peak is about 16 nm, indicates the narrow size distributions of as-synthesized CdS nanocrystals.

There were no band-gap emission of CdS nanocrystals could be detected when the molar ratio of CdO:DDT was smaller than 1:1. However, band-gap emissions of CdS nanocrystals with narrow full width at half-maximum (FWHM) were detected when the molar ratio of CdO:DDT was larger than 1:1 though the emissions are weak. This reagent molar

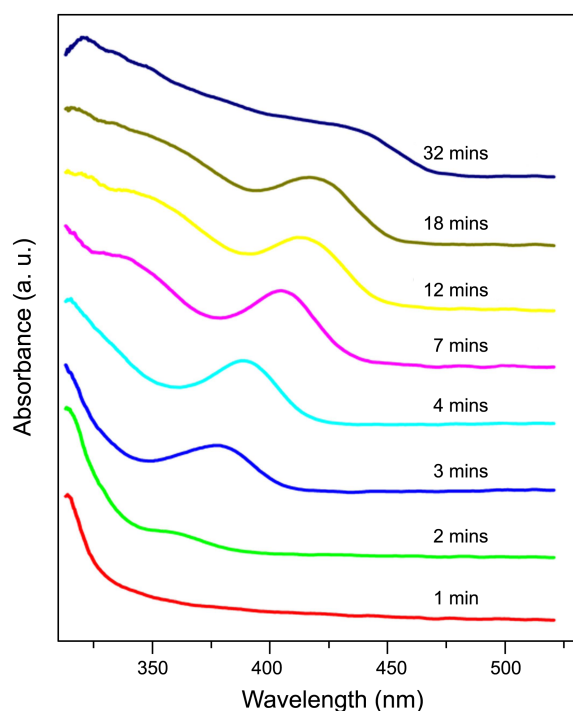


Figure 1. Temporal evolution of the UV-vis absorption spectra of CdS nanocrystals synthesized with the molar ratio of CdO:DDT at 1:2 and the $T_{\text{inject}}/T_{\text{growth}}$ of 260/260 °C.

ratio dependent property must come from the quenching effect of DDT molecules. It was found that when the amount of DDT molecules added in was more than the stoichiometric sulfur needed for the formation of CdS, the unreacted DDT molecules would replace the OA molecules to perform as capping ligands. As an effective hole acceptor, the thiol group in DDT would strongly quench the band-gap emissions of CdS nanocrystals,¹⁴ so the band-gap emission could not be detected. This quenching effect had been demonstrated in phase transfer experiments before,¹⁵ where with the mercaptopropionic acid (MPA) as the new surface ligands to replace the original OA ligands, the PL quantum yields (QYs) reduced dramatically. The -SH groups in MPA molecules were considered to bind to the surfaces of nanocrystals and quenched the PL. On the other hand, this quenching effect favors the transport of photogenerated electrons/holes, and will increase the conversion efficiencies of optoelectronic devices.¹⁶ In our experiments, when the molar ratios of CdO:DDT were higher than 1:1, almost all the DDT molecules served as the sulfur source to form the CdS nanocrystals, few DDT molecules were remained to replace OA molecules to act as the surface ligands for CdS nanocrystals. It has been demonstrated that OA molecules are good ligands for semiconductor nanocrystals and will not affect the surface crystallinity of CdS,¹⁷ so the band-gap emissions of CdS could be detected.

To recover the band-gap emission of CdS nanocrystals, CdS/ZnS core/shell nanocrystals were synthesized. Shown in Figure 2 are the absorption spectra, PL spectra, PLE spectra of typical CdS nanocrystals and corresponding CdS/

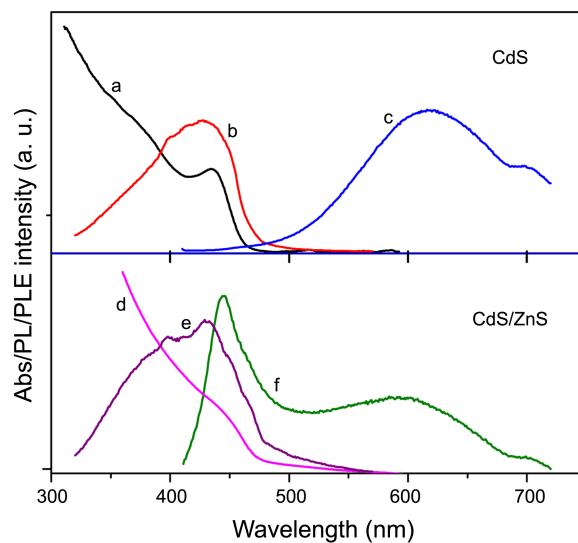


Figure 2. Absorption (a), PLE (b, monitored at 620 nm), PL (c, excited at 380 nm) spectra of as-synthesized CdS nanocrystals; Absorption (d), PLE (e, monitored at 620 nm), PL (f, excited at 380 nm) spectra of CdS/ZnS nanocrystals.

ZnS core/shell nanocrystals. Obviously, bare CdS nanocrystals have no band-gap emission when the molar ratio of Cd:DDT is 1:2, only trap emissions centered at about 620 nm were detected with excitation wavelength of 380 nm. After the overgrowth of ZnS shells, the band-gap emission of CdS nanocrystals with a sharp PL peak at 444 nm appeared with excitation wavelength of 380 nm. This is because the ZnS shells eliminated the surface defects of CdS core nanocrystals, and photogenerated excitons were located in the CdS cores, so the quenching effect of DDT molecules was reduced and the band-gap emission of CdS could be detected. Similar to the magic sized CdSe nanocrystals,¹⁸ the combination of the CdS band gap emission and the wide surface trap emission result in a white light emission. Additionally, the synthesis of our CdS nanocrystals was easy to control, so the CdS/ZnS core/shell nanocrystals synthesized here may act as a candidate for white light emitting materials in the future.

The FTIR spectra in Figure 3 demonstrated the composition of the surface ligands. The CdS and CdS/ZnS nanocrystals used for FTIR characterizations were totally purified using methanol and hexanes to get nanocrystal powders. The FTIR spectra of CdS and CdS/ZnS nanocrystals are largely different from that of OA molecules, indicate the major surface ligands of nanocrystals were not OA molecules. It was found that the FTIR spectra of DDT molecules, CdS nanocrystals, and CdS/ZnS core/shell nanocrystals all have sharp bands at 2922 and 2852 cm^{-1} , which can be assigned to the asymmetric methyl stretching and asymmetric/symmetric methylene stretching modes respectively, and indicate the surface ligands of both CdS and CdS/ZnS nanocrystals were DDT molecules. For the CdS nanocrystals with DDT ligands, no band-gap emission was detected in Figure 2. However, after the overgrowth of ZnS shells, though the surface ligands of CdS/ZnS nanocrystals were also DDT

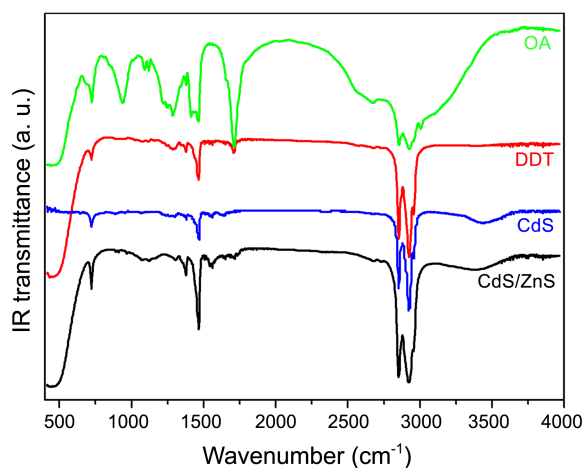


Figure 3. FTIR spectra of OA, DDT, CdS and subsequent CdS/ZnS nanocrystal powders.

molecules, the band-gap emission of CdS nanocrystals appeared. This indicated that the existence of ZnS shells prohibited the direct contact of CdS and DDT, so the photo-generated excitons were localized in CdS nanocrystals, the holes were difficult to tunnel through the ZnS shells to reach DDT molecules, and the quenching effect of DDT was partially decreased, so the band-gap emission of CdS nanocrystals was partially recovered.

Using DDT as the S source, CdS nanocrystals with small sizes could be obtained facily. With the injection/growth temperature of 240 °C/240 °C, the CdS nanocrystals had a very slow growth speed and small sized CdS nanocrystals with first excitonic absorption peak at 360 nm were easily synthesized. This may because DDT molecules were not easy to decompose under lower temperatures, so not enough S could react with Cd species to form CdS. And the stronger complexation of DDT with Cd species would impede the growth of CdS nanocrystals, so the growth speed was low and small sized CdS nanocrystals were easily synthesized.

The synthesis of ZnS nanocrystals using DDT as sulfur source was similar to the synthesis of CdS nanocrystals described above. Figure 4(c) demonstrated the formation of zinc blende structured ZnS nanocrystals with the ZnO:DDT molar ratio of 1:2.

Figure 4 shows the XRD patterns of as-synthesized CdS, CdS/ZnS, and ZnS nanocrystals. The diffraction peaks of CdS and ZnS nanocrystals (Figure 4(a) and 4(c)) match well with the diffraction lines of bulk CdS and ZnS with zinc blende structures. With the overgrowth of ZnS shells on the CdS core nanocrystals, the diffraction peaks of nanocrystals shift from a zinc blende CdS-like diffraction pattern to a zinc blende ZnS-like diffraction pattern (Figure 4(b)), the peak positions are located in the middle of pure CdS and pure ZnS's diffraction positions. According to previous reports,^{12,19-21} this shift phenomenon of the diffraction peaks from a CdS-like pattern to a ZnS-like pattern after the overgrowth of ZnS indicates the formation of CdS/ZnS core/shell nanocrystals. All the diffraction peaks are broadened because of the finite size of the nanocrystals, the mean crystal domain sizes of

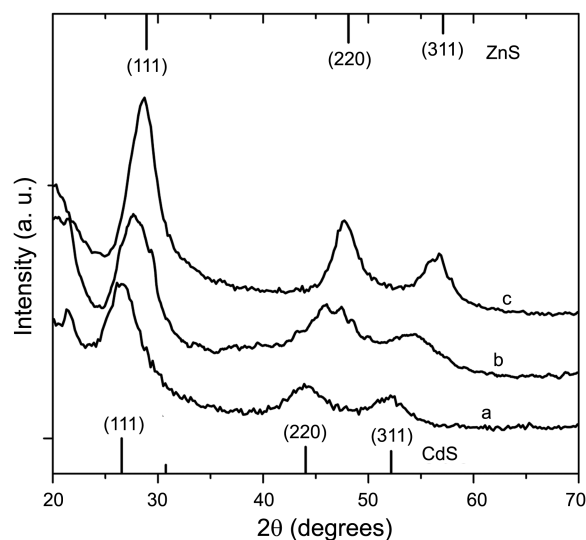


Figure 4. Powder X-ray diffraction patterns of CdS (a), CdS/ZnS core/shell (b), and ZnS (c) nanocrystals.

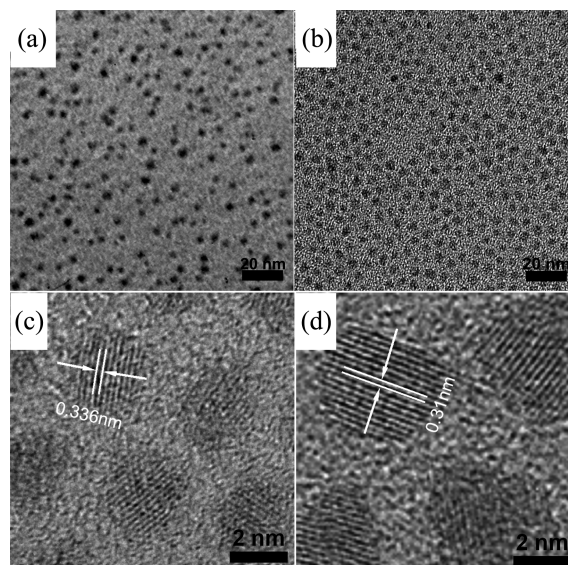


Figure 5. TEM images of CdS (a) and subsequent CdS/ZnS core/shell nanocrystals (b). (c) and (d) are the corresponding HRTEM images of (a) and (b), respectively.

CdS and CdS/ZnS nanocrystals are estimated to be 2.8 nm and 5.0 nm respectively by applying the Scherrer equation from the strongest (111) diffraction peaks. These values are a little smaller than the sizes from the TEM images in Figure 5 (2.9 nm and 5.2 nm, respectively) because the crystalline domain sizes (calculated from the XRD data) are smaller than the grain sizes measured by TEM images.

TEM and HRTEM images of CdS nanocrystals and subsequent CdS/ZnS core/shell nanocrystals are shown in Figure 5. Both samples are of narrow size-distributions from the TEM images. After the growth of ZnS shells, the average size increased from about 2.9 nm (Figure 5(a)) to 5.2 nm (Figure 5(b)). The HRTEM image of CdS nanocrystals shows a d-spacing of 0.336 nm, which is in accordance with the (111) planes of zinc blende structured CdS. While, after

the overgrowth of ZnS shells, the d-spacing changed to 0.31 nm, corresponding to the (111) planes of zinc blende structured ZnS. The crystal constant change from CdS to ZnS demonstrated the formation of CdS/ZnS core/shell structures after the overgrowth of ZnS shells, which was also in accordance with the size increase from 2.9 nm to 5.2 nm.²²⁻²⁶ Both the two HRTEM images show clear lattice fringes though out the entire particles, demonstrated their high crystallinity.

Conclusions

Here we report a facile way to synthesize zinc blende structured CdS and ZnS nanocrystals using DDT as both the sulfur source and surface ligands. The dot size was easily controlled by the growth temperatures and Cd(Zn)/DDT molar ratios. These as-prepared CdS(ZnS) nanocrystals have narrow size distributions from the absorption spectra and TEM characterizations. As an effective hole acceptor, DDT molecules quenched the band-gap emissions of CdS nanocrystals. After the overgrowth of ZnS shells, the band-gap emission of CdS nanocrystals was partially recovered with sharp emission peak.

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References

1. Brus, L. *J. Phys. Chem.* **1986**, 90, 2555.
2. Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, 115, 8706.
3. Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, 123, 183.
4. Yu, W. W.; Peng, X. *Angew. Chem. Int. Ed.* **2002**, 41, 2368.
5. Tong, H.; Zhu, Y. J. *Nanotechnology* **2006**, 17, 845.
6. Lee, M.; Han, S.; Jeon, Y. J. *Bull. Korean Chem. Soc.* **2010**, 31, 3818.
7. Li, L. S.; Pradhan, N.; Wang, Y. J.; Peng, X. G. *Nano Lett.* **2004**, 4, 2261.
8. Panda, A. B.; Acharya, S.; Efrima, S.; Golan, Y. *Langmuir* **2007**, 23, 765.
9. Wang, Y.; Yang, H.; Xia, Z.; Tong, Z.; Zhou, L. *Bull. Korean Chem. Soc.* **2011**, 32, 2316.
10. Lee, S. S.; Seo, K. W.; Yoon, S. H.; Shim, I. W.; Byun, K. T.; Kwak, H. Y. *Bull. Korean Chem. Soc.* **2005**, 26, 1579.
11. Neo, M. S.; Venkatram, N.; Li, G. S.; Chin, W. S.; Ji, W. J. *Phys. Chem. C* **2010**, 114, 18037.
12. Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johanson, M. B.; Peng, X. *J. Am. Chem. Soc.* **2003**, 125, 12567.
13. Chen, L.; Chen, Y. B.; Wu, L. M. *J. Am. Chem. Soc.* **2004**, 126, 16334.
14. Jasieniak, J.; Mulvaney, P. J. *J. Am. Chem. Soc.* **2007**, 129, 2841.
15. Smith, A. M.; Duan, H.; Rhyner, M. N.; Ruan, G.; Nie, S. *Phys. Chem. Chem. Phys.* **2006**, 8, 3895.
16. Liu, I. S.; Lo, H. H.; Chien, C. T.; Lin, Y. Y.; Chen, C. W.; Chen, Y. F.; Su, W. F.; Liou, S. C. *J. Mater. Chem.* **2008**, 18, 675.
17. Yu, W. W.; Wang, Y. A.; Peng, X. *Chem. Mater.* **2003**, 15, 4300.
18. Bowers, M. J.; McBride, J. R.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2005**, 127, 15378.
19. Lim, S. J.; Chon, B.; Joo, T.; Shin, S. K. *J. Phys. Chem. C* **2008**, 112, 1744.
20. Talapin, D. V.; Mekis, I.; Götzinger, S.; Kornowski, A.; Benson, O.; Weller, H. *J. Phys. Chem. B* **2004**, 108, 18826.
21. Li, X.; Shen, H.; Li, S.; Niu, J. Z.; Wang, H.; Li, L. S. *J. Mater. Chem.* **2010**, 20, 923.
22. Chen, Y.; Vela, J.; Htoon, H.; Casson, J. L.; Werder, D. J.; Bussian, D. A.; Klimov, V. I.; Hollingsworth, J. A. *J. Am. Chem. Soc.* **2008**, 130, 5026.
23. Steckel, J. S.; Zimmer, J. P.; Coe-Sullivan, S.; Stott, N. E.; Bulovic, V.; Bawendi, M. G. *Angew. Chem. Int. Ed.* **2004**, 43, 2154.
24. Wang, J.; Long, Y.; Zhang, Y.; Zhong, X.; Zhu, L. *Chem. Phys. Chem.* **2009**, 10, 680.
25. Lim, J.; Jun, S.; Jang, E.; Baik, H.; Kim, H.; Cho, J. *Adv. Mater.* **2007**, 19, 1927.
26. Protiere, M.; Reiss, P. *Small* **2007**, 3, 399.