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SYNTHESIS AND CHARACTERIZATION OF CdSe/ZnO CORE/SHELL NANOCRYSTALS

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Highly luminescent monodispersed CdSe nanocrystals were prepared from CdO and Se powder in a three-component hexadecylamine-trioctylphosphine oxide-trioctylphosphine (HAD-TOPO-TOP) mixture under high temperature and nitrogen protection. CdSe/ZnO core/shell nanocrystals were produced by adding $Zn(Ac)_2$ and LiOH into CdSe nanocrystals solution under ultrasonic at low temperature. ZnO shell grows heterogeneously on the CdSe substrate. The structure and fluorescence have been characterized by TEM (transmission electron micrograph), XRD (X-ray diffraction), UV-Vis and PL spectra. It can be found that after the surface passivation with ZnO shell, electrons were confined in the CdSe core due to the wide band-gap effect of ZnO, which resulted in the obvious increasing of the fluorescent intensity.

Keywords: CdSe/ZnO; nanocrystals; fluorescent efficiency; heterogeneous growth; PL.

1. Introduction

Semiconductor nanocrystals were so-called "Quantum Dots" or "QD", which were extensively investigated due to their high quantum yield and quantum confinement effect.[1,2] Various applications of semiconductor nanocrystals include display photovoltaic devices,[3] lasers,[4] light-emitting diodes,[5–7] solar cells[8] and biological tagging materials.[9,10] Recently CdSe nanocrystals are still the most extensively investigated for their successful preparation methods in controlling size, shape and monodispersity.[11–17] But, the surface of nanocrystal there is the defects unless passivated.[18] To remove these defects, inorganic passivation has been explored in the core/shell systems such as CdSe/ZnSe,[19] CdSe/ZnS[20] and CdSe/CdS and shown to improve luminescence quantum yields, increase stability.[21–23] In this paper, ZnO was firstly used to coat CdSe nanocrystals at low temperature in ethanol solution. CdSe/ZnO core/shell nanocrystals were synthesized. The band-edge emission increased due to electrons and holes were sufficiently confined. To choose ZnO as shell material based on the follows. First, the lattice mismatch between CdSe and ZnO is fairly lower (6.9%). Second, band gap energy of ZnO is compared with CdSe, ZnO is high. Thirdly, ZnO has high stability. Temperature of ZnO nucleation was lower than the temperature of CdSe growth and the synthesis was environmentally friendly.

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2. Experimental Section

2.1. *Chemicals and instruments*

Trioctylphosphine oxide (TOPO, technical grade, 90%), trioctylphosphine (TOP, technical grade, 90%), selenium powder (99.999%), hexadecylamine (HDA, 90%), cadmium oxide (99.9%) were purchased from Aldrich Corp. $Li(OH)\cdot H_2O$ (ACROS); Stearic acid (95%), $Zn(Ac)_2\cdot 2H_2O$, methanol, hexane, absolute ethanol chloroform and acetone were analytical grade purchased from Beijing Chemical Cop. All chemicals except absolute ethanol were used directly without further purification. The UV-Vis absorption spectra were measured by Cary-100 UV-Vis Spectrophotometer (Varian, USA). PL spectra were measured with FS920 steady state fluorescence spectrometer (Edinburgh Instruments, UK). Powder X-ray diffraction (XRD) measurement was performed on Rigaku D/max-rA X-ray diffractometer. Images of transmission electron microscopy were taken with Hitachi H-8100IV Transmission Electron Microscope (TEM).

2.2. *Synthesis of CdSe nanocrystals*

All synthetic routes were carried out under nitrogen protection.[24] The reaction flask was dried and degassed before using. Typically, 0.0127 g (0.1 mmol) CdO and 0.114 g (0.4 mmol) stearic acid were added into 50 ml three-neck flask and were heated to 150°C for 30 min, and then Cadmium stearate formed. After cooling the system to room-temperature, 1.94 g TOPO and 1.94 g ODA were added into this flask. Then, the Cd precursor solution was heated to 310°C. Simultaneously, 0.08 g Se powder was mixed with 2 ml TOP and quickly injected into the solution under vigorous stirring, resulting in nucleation of CdSe. The reaction was stopped immediately by quickly reduce the temperature to 190°C, and then continue heating and stiring at 180–200°C for nanocrystals riping for an hour. The mixture was allowed to cool to room temperature, and methanol was added to precipitate the nanocrystals. The vessel was protected from light and left standing for more than one hour to allow the nanocrystals to settle. The precipitate was centrifuged to remove remaining solvent, and then was dried and stored in a vacuum dry box in dark.

2.3. *Stock solution for ZnO precursor*

Absolute ethanol was obtained from distillation of a reaction of ethanol and magnesium strip. 1.10 g (5 mmol) $Zn(Ac)_2\cdot 2H_2O$ was dissolved in 50 ml absolute ethanol at 60°C and then was heated for fully dissolution. After approximate 20 ml distillation including water and some ethanol was vaporized, 15 ml absolute ethanol was added. At last the solution was cooled to room temperature or below, clear anhydrous 42 ml $Zn(Ac)_2$ ethanol solution as ZnO precursor was obtained,[25] with concentration of 0.12 mol/ml.

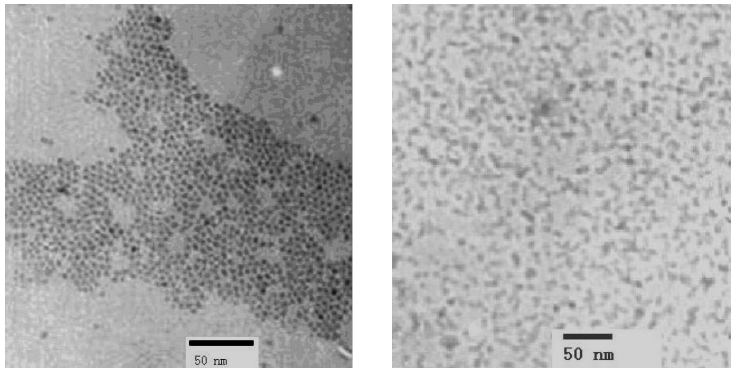
2.4. *Growth of ZnO on CdSe nanocrystal surface*

The ligands on CdSe surface will be destructed under ultrasonic in ethanol,[26] therefore it is easy that the heterogeneous growth of ZnO on CdSe surface. 1.3 mg CdSe powder was dissolved in 5 ml ethanol in a cuvette as standard solution, which was signed as "*A*". Similarly, 1.3 mg CdSe powder and 1 ml $Zn(Ac)_2$ were added into another cuvette with 3 ml ethanol, which was signed as "*B*". 5.72 mg LiOH was dissolved in 1 ml ethanol, and then was added rapidly into "*B*" cuvette under ultrasonic at low temperature for 10 min. By this time "*B*" is brighter than "*A*" by eye. In fact, "*A*" is equal to "*B*" in concentration of CdSe. This opinion is demonstrated by optical density in the following text.

3. Results and Discussion

3.1. *TEM*

Figure 1 shows two TEM images of CdSe plain core nanocrystals and the corresponding CdSe/ZnO core/shell nanocrystals. Both bars are 50 nm. The nearly monodispersed CdSe nanocrystals (Fig. 1(a)) formed good, well-ordered. The CdSe nanocrystals were dots with an average diameter of 4.7 nm. Figure 1(b) showed most spherical CdSe/ZnO nanocrystals with diameters from 5.2 to 7.2 nm and a few CdSe/ZnO nanorods. An increase of nanocrystal size came from the injection of $Zn(Ac)_2$ and formed CdSe/ZnO nanocrystals. Furthermore, the CdSe/ZnO nanorods came from conglomeration of two or three nanoparticles. We come to the conclusion that, CdSe nanocrystals were dispersered in solution and that the lattice mismatch between CdSe and ZnO is fairly low, therefore ZnO easily grows on the CdSe surface. Firstly, it is considered that core/shell structure had formed due to the increase in size. Secondly, the overcoating was not complete on some CdSe surface, in this case, CdSe/ZnO surface without ZnO coating occurred assembling by hydrophobic effect of ligands. Figure 2 showed the shape evolution of the



(a) (b)

Fig. 1. (a) TEM images of CdSe nanocrystals and (b) CdSe/ZnO core/sell nanocrystals.

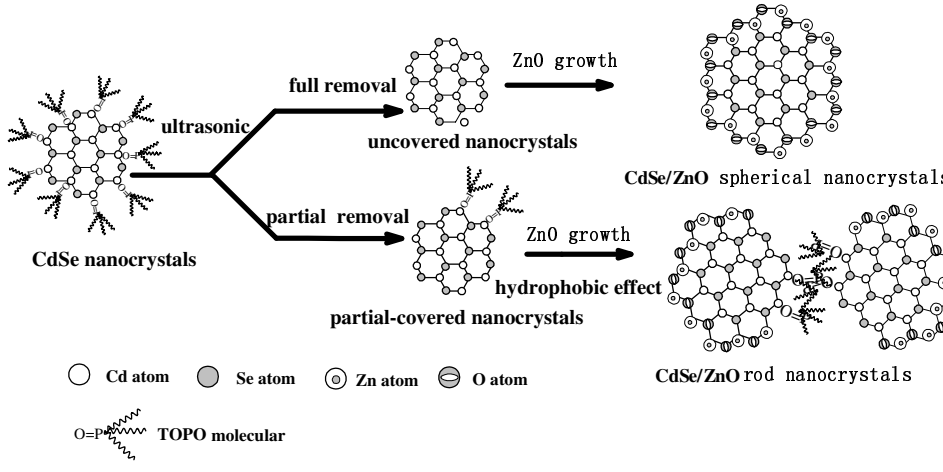


Fig. 2. The evolution of ZnO nanocrystals growth on the surface of CdSe nanocrystals.

dot-shaped and rod-shaped CdSe/ZnO nanocrystals. CdSe nanocrystals modified by organic ligands passed ultrasonic, the ligands removed from surface for ethanol attack to ligands. A part of CdSe became complete-naked Quantum Dot for its ligands were damaged totally, but another came to half-naked for partly. It should be pointed out that CdSe nanocrystals have a wurtzite structure like ZnO and the lattice mismatch between CdSe and ZnO is fairly low (6.9%). ZnO was able to grow rapidly and heterogeneously on naked surface of CdSe results in CdSe/ZnO core/shell spherical nanocrystals. Partial-covered nanocrystals have some ligands, which occurred assembling by hydrophobic effect, so obtained CdSe/ZnO rod-shaped nanocrystals as Fig. 2.

3.2. *XRD*

Figure 3 showed a series XRD patterns of CdSe core, CdSe/ZnO core/shell and ZnO. We are sure that CdSe and ZnO nanocrystals have a wurtzite structure from the XRD pattern analysis. In CdSe nanocrystals, the diffraction peaks at 23.02, 24.31, 25.61, 33.49, 39.80, 43.53 and 47.26 degrees correspond to the diffraction of (100), (002), (101), (102), (110), (103) and (112) faces, respectively. In ZnO nanocrystals, the peaks at 31.90, 34.75, 35.95, 47.55, 56.55, 62.70 and 67.95 degrees correspond to the diffraction of (100), (002), (101), (102), (110), (103) and (112) faces, respectively. In CdSe/ZnO core/shell nanocrystals the peaks at 33.22, 35.12, 36.1 and 47.75 degrees correspond to the diffraction of (100), (002), (101) and (102) faces of ZnO. Compared with ZnO, diffraction intensity at (100) face increased correspondingly, which indicates that preferential growth orientation occurred on (100) face. In conclusion, XRD of CdSe/ZnO core-shell nanocrystals showed characteristic diffraction peaks of ZnO as a result of ZnO grew heterogeneously on naked surface of CdSe. We supposed that ZnO did not heterogeneously grew on CdSe surface, but they are the only compound, in that case

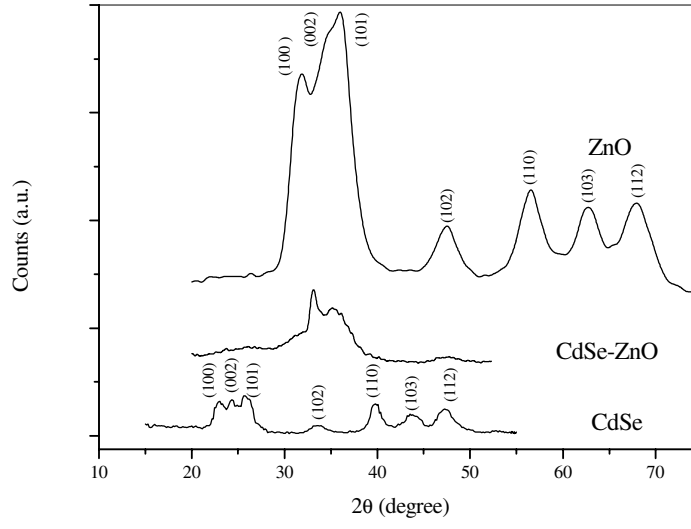


Fig. 3. The XRD patterns of ZnO (top), CdSe/ZnO core/shell (middle) and CdSe (bottom) nanocrystals.

CdSe/ZnO XRD pattern should have characteristic diffraction peak of CdSe and that not transfer of preferential growth orientation. As has been noted, we are sure that ZnO grew on CdSe surface results in core-shell structure nanocrystals and similar core-shell structure, which is partly-coated.

3.3. *UV-Vis spectrum*

Figure 4 showed a series UV-Visible spectra of CdSe core, CdSe/ZnO core/shell and ZnO. As shown in Fig. 4, in CdSe spectrum there are three exciton peaks at 558, 521 and 461 nm that is a character of nearly monodisperse nanocrystals. In comparison with CdSe, after ZnO growth no change of shape was detected in CdSe/ZnO spectrum, but only smaller shifts. The band-edge absorption of these core/shell nanocrystals showed a red shift from 558 to 562 nm for the ZnO growth proceeded. This phenomenon can be explained with the electronic confinement effect, which occurred in core/shell and host/guest-type materials. CdSe/ZnO core/shell nanostructures can be treated as CdSe nanoparticles confined in a ZnO host nanocavity. When the CdSe nanoparticle is confined in ZnO nanocavity, the corresponding Fermi level increases while the band gap decreases. Coherency strain will also lead to a red shift. [27] Because ZnO has a lager bulk band-gap energy (3.2 eV) than CdSe (1.7 eV), the absorption of CdSe/ZnO has not ZnO absorbance in range from 800 to 350 nm. Using information only from UV-Visible absorption spectra cannot verify whether there are separate ZnO formed in solution instead of on the surface of the CdSe core.

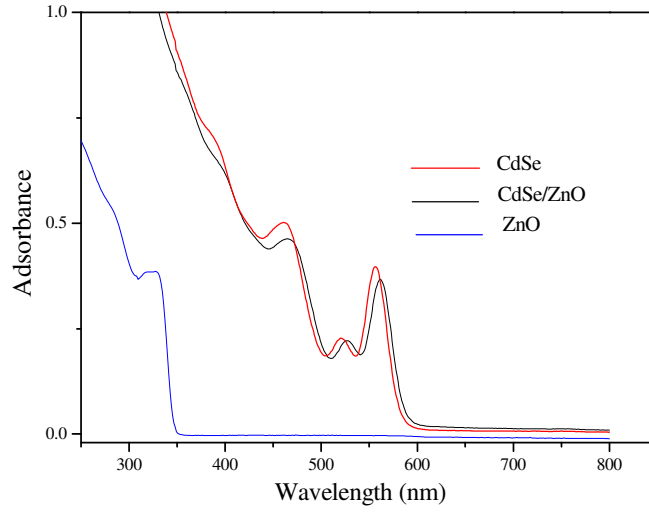


Fig. 4. The UV-Visible spectra of CdSe, ZnO, and CdSe/ZnO core/shell nanocrystals.

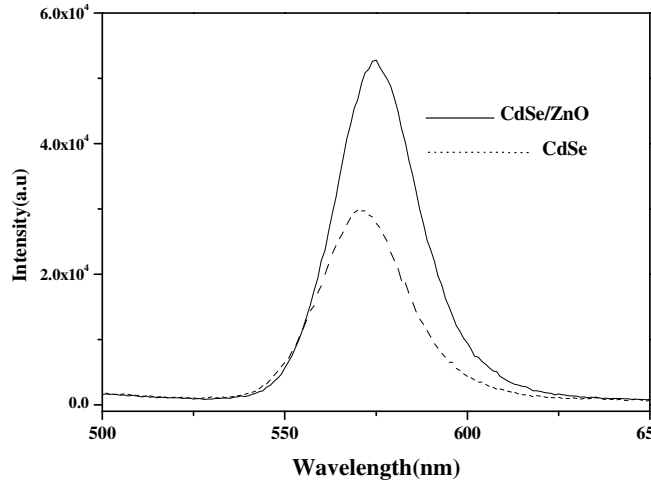


Fig. 5. The PL spectra of CdSe nanocrystals and CdSe/ZnO composited nanocrystals (λ_{ex} = 400 nm).

3.4. *Photoluminescence spectrum*

PL spectra of CdSe/ZnO core/shell nanocrystals and CdSe nanocrystals are showed in Fig. 5. Both of the samples have an optical density at excited wavelength (400 nm). The CdSe and CdSe/ZnO core/shell nanocrystals have good optical quality. The FWHM of these spectra were about 28 nm. The PL yield of CdSe increased obviously after

passivated with ZnO. We also observed a small shift in the PL. CdSe surface atoms are usually unsaturated and have dangling bonds, inorganic epitaxial growth can eliminate both anionic and cationic surface dangling bonds and generate a new core-shell structure compare to organic passivation,[28] which suppressed deep trap emission and brings a high PL quantum yield and stability.

4. Conclusions

To summarize, for the first time CdSe/ZnO core/shell nanocrystals were produced by adding $Zn(Ac)_2$ and LiOH into CdSe nanocrystal solution under ultrasonic at low temperature. ZnO heterogeneously grew on CdSe surface results in core-shell structure nanocrystals and similar core-shell structure, which is partly-coated. Because ZnO passivating reduced dangling bonds and leakage of exciton, PL quantum yield increased simultaneously. PL and absorption spectra shifted to red.

Acknowledgments

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References

1. M. Han, X. Gao, J. Z. Su and S. Nie, *Nature Biotechnol*. **19**, 631 (2001).
2. H. Xia *et al.*, *Chem. J. Chinese Univ.* **23**, 255 (2002).
3. V. L. Colvin, M. C. Schlamp and A. P. Alivisatos, *Nature* **370**, 354 (1994).
4. W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Nature* **295**, 2425 (2002).
5. V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale and M. G. Bawendi, *Science* **290**, 314 (2000).
6. M. C. Schlamp, X. G. Peng and A. P. Alivisatos, *J. Appl. Phys.* **82**, 5837 (1997).
7. H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, E. L. Thomas, M. G. Bawendi and M. F. Rubner, *J. Appl. Phys.* **83**, 7965 (1998).
8. N. Tesster, V. Medvedev, M. Kazes, S. Kan and U. Banin, *Science* **295**, 1506 (2002).
9. N. C. Greenham, X. G. Peng and A. P. Alivisatos, *Phys. Rev. B* **54**, 17628 (1996).
10. M. Bruchez, M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science* **281**, 2013 (1998).
11. X. G. Peng *et al.*, *Nature* **404**, 59 (2000).
12. L. H. Qu, Z. A. Peng and X. G. Peng, *Nano Lett.* **1**, 333 (2001).
13. C. Warren, W. Chan and S. Nie, *Science* **281**, 2016 (1998).
14. X. G. Peng *et al.*, *J. Am. Chem. Soc.* **119**, 7019 (1997).
15. B. O. Babbousi *et al.*, *Phys. Chem.* **101**, 9463 (1997).
16. Y. A. Wang, J. Li and J. Peng, *J. Am. Chem. Soc.* **124**, 2293 (2002).
17. J. Aldana, Y. A. Wang and X. G. Peng, *J. Am. Chem. Soc.* **123**, 8844 (2001).
18. L. Spanhel, M. Haase, H. Weller and A. Henglein, *J. Am. Chem. Soc*. **109**, 5649 (1987).
19. P. Reiss, J. Bleuse and A. Pron, *Nano Lett*. **2**, 781 (2002).
20. W. G. J. H. M. Van Sark *et al.*, *J. Phys. Chem. B* **105**, 8281 (2001).
21. J. J. Li *et al.*, *J. Am. Chem. Soc*. **125**, 12567 (2003).

22. W. Guo, J. J. Li, Y. A. Wang and X. Peng, *J. Am. Chem. Soc*. **125**, 3901 (2003).
23. I. Mekis, D. V. Talapin, A. Kornowski, M. Haase and H. Weller, *J. Phys. Chem. B* **107**, 7454 (2003).
24. L. H. Qu and X. G. Peng, *J. Am. Chem. Soc*. **124**, 2049 (2002).
25. X. T. Zhang *et al.*, *Chem. J. Chinese Univ.* **20**, 1945 (1999).
26. L. Feng, H. Zheng and J. Su, *Chinese J. Inorg. Chem.* **17**, 315 (2001).
27. X. B. Chen, Y. B. Lou, A .C. Samia and C. Burda, *Nano Lett.* **3**, 799 (2003).
28. B. O. Dabbousi, J. Rodriguez–Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen and M. G. Bawendi, *J. Phys. Chem. B* **101**, 9463 (1997).