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Preparation of mercaptoacetic acid-capped ZnSe core–shell nanocrystals by hydrothermal method

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Abstract

Mercaptoacetic acid (MMA)-capped ZnSe (ZnSe–MMA) core–shell nanocrystals have been prepared by two-step hydrothermal method using Se and $Zn(NO_3)_2$ aqueous solution as precursor. The as-prepared ZnSe are zincblende structure with grain size of 4 nm. The MMA-capped ZnSe nanocrystals are more stable and can be preserved long time without oxidation in the air. The ZnSe–MMA core–shell nanocrystals show good absorption for the ultraviolet light.

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Keywords: A. Powders: chemical preparation; C. Optical properties; Core–shell nanocrystals; ZnSe

1. Introduction

The low-dimension structure and quantum size effects of nanomaterials result in various interesting physical phenomena and widely practical applications. During the past decades, core–shell nanocrystals (CSNs) have been received much attention for their excellent optical, electrical, thermal, mechanical, electro-optical, magnetic and catalytical properties [1–7]. Due to the different functional components in core and shell materials, CSNs display interesting properties. ZnSe is a very important wide band gap II–VI semiconductor and has excellent optical properties. It can be used in the fields of blue-green diode lasers, photoelectric diodes, infrared image, laser window materials, solar cells, biologic label and so on [8–10]. In this paper, ZnSe was used as template cores and mercaptoacetic acid (MMA) was utilized as shells to synthesize ZnSe polymer CSNs.

2. Experimental procedure

Se powders, $Zn(NO_3)_2\cdot 6H_2O$ were used as source materials. $Zn(NO_3)_2\cdot 6H_2O$ was dissolved in deionized water, and then MMA was added into the resultant solution under magnetic stirring. Se powders were added into KBH_4 aqueous solution soaked at 60 °C water bath with Ar protection. Then, the Zn and Se solutions were mixed together and a milk-yellow suspension was obtained. After reacting for 5 min, NaOH aqueous solution was added into the suspension. The as-prepared precursor was transferred into a Teflon-lined autoclave up to 70% (49 ml) of its total capacity. The autoclave was heated to 95–150 °C in an oven with heating rate of 3 °C/min. After soaking for 6 h, the autoclave was cooled down naturally. The samples were ultrasonically dispersed and were rinsed by deionized water and ethanol, respectively. Finally, the samples were collected by centrifugation sedimentation and were dried in vacuum oven at 60 °C. The whole synthesis process is schematically shown in Fig. 1.

Phase composition of the samples was identified by a Rigaku D/max-2400 X-ray diffractometer (XRD) using Cu Kα radiation. The microstructure of the samples was studied by a JEOL JEM-3010 transmission electron microscopy (TEM) operating at 300 kV and corresponding selected area electron diffraction (SAED). Linear optical absorption spectra were measured by JASCO V-570 UV–Vis spectrometer at room temperature.

3. Results and discussion

The XRD patterns of the ZnSe–MMA CSNs samples are displayed in Fig. 2. The diffraction peaks can be

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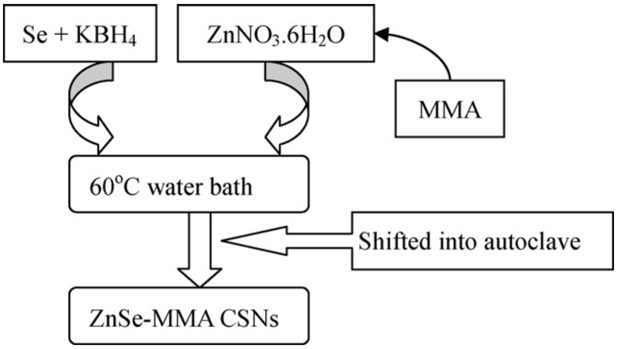


Fig. 1. The experimental processes.

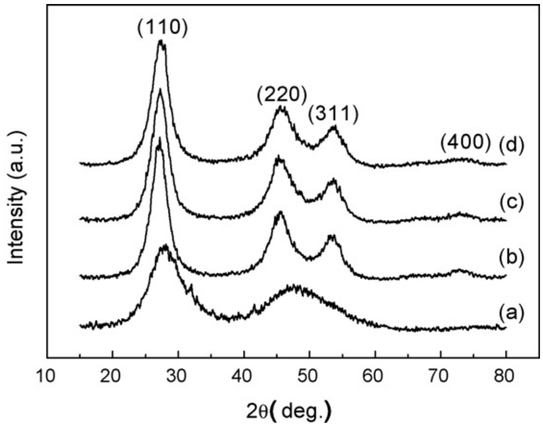


Fig. 2. XRD patterns of the ZnSe–MMA CSNs synthesized by (a) 60 °C water bath, and hydrothermal treated at (b) 95 °C, (c) 125 °C and (d) 150 °C for 6 h.

indexed by zincblende structure of ZnSe (JCPDS: 37–1463). For the sample prepared by 60 °C water bath, the peaks are broadened and only (1 1 0) and (2 2 0) diffraction peaks are detected (Fig. 2a), which indicates that as-prepared ZnSe–MMA CSNs are too small and not well-crystallized. Using Scherrer formula calculation, the grain size of the ZnSe crystals is about 3 nm. After hydrothermal treatment at 95 °C for 6 h, diffraction peaks of (3 1 1) and (4 0 0) are detected (Fig. 2b). With the increasing hydrothermal temperature from 95 to 150 °C, the XRD patterns are similar and the diffraction intensity and the peak width do not change too much (Fig. 2b–d). The grain size calculated by Scherrer formula is about 5 nm. The MMA is capped on the surface of the ZnSe nanocrystals and acts as a capsule shell to confine the growth of the ZnSe nanocrystals cores. Therefore, the grain size of the ZnSe–MMA CSNs is much smaller than that of ZnSe synthesized without MMA [11,12].

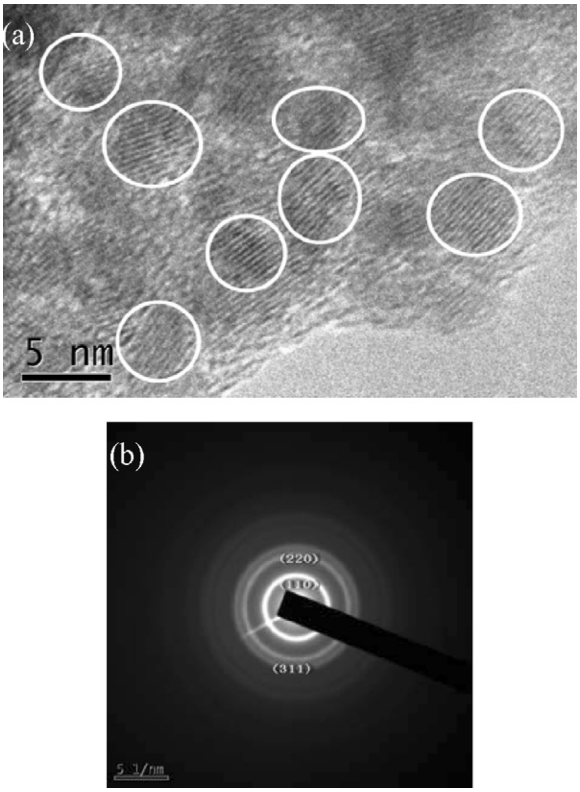


Fig. 3. (a) TEM image and (b) SAED patterns of ZnSe–MMA CSNs synthesized at 150 °C for 6 h.

Fig. 3 shows the TEM images of the ZnSe–MMA CSNs prepared at 150 °C for 6 h. The ZnSe cores are ~4 nm in diameter and are capped with a very thin layer of MMA (Fig. 3a). The crystal size measured by TEM observation is accordance to that calculated from XRD. Due to MMA capping, the ZnSe–MMA CSNs are quasi-monodisperse without obviously aggregating. The inserted selected area electron diffraction (SAED) patterns also confirm the zincblende ZnSe structure of the ZnSe–MMA CSNs (Fig. 3b).

Our previous works showed that the color of ZnSe samples prepared under the same condition without adding MMA would change from bright yellow to dull red due to oxidation of ZnSe nanocrystals when they were exposed in air. However, ZnSe–MMA CSNs can be preserved for a longer time in the air without obvious oxidation even their grains size down to 4 nm. This is directly correlated with the growth mechanism of ZnSe–MMA CSNs. The reactions in the hydrothermal solution can be formulated as the following:

$$\mathrm{KBH_4 + Se + H_2O \rightarrow KHSe + H_3BO_3} \qquad (1)$$

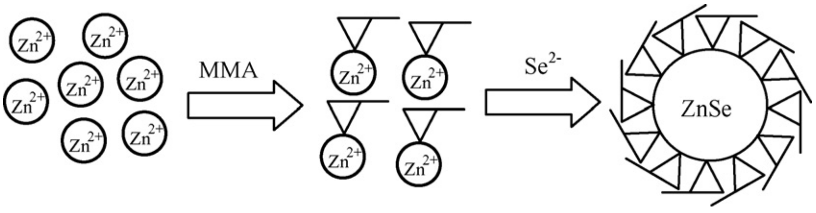


Fig. 4. The illustration on formation of ZnSe–MMA core/shell structure.

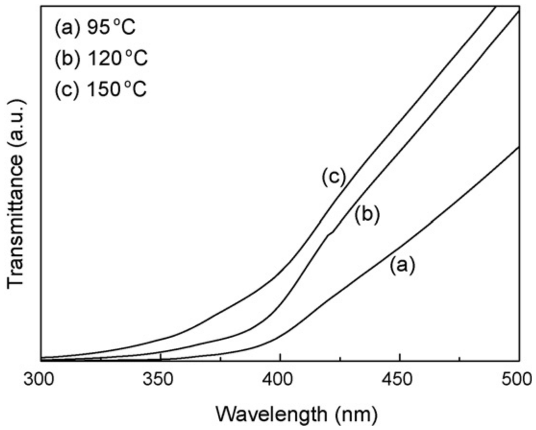
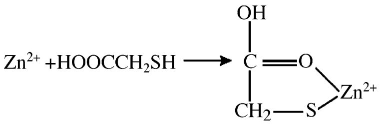
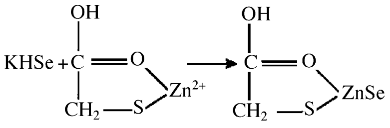


Fig. 5. Optical properties of ZnSe–MMA CSNs synthesized at (a) 95 °C, (b) 125 °C and (c) 150 °C for 6 h.



(2)



(3)

When Se powders are added into KBH_4 aqueous solution, Se is reduced to Se^{2-} in Reaction (1). Zn^{2+}–MMA complexs are formed when MMA is mixed with Zn^{2+} aqueous solution in reaction (2). In reaction (3), Zn–MMA reacts with Se^{2-} to form ZnSe–MMA core–shell structures. The formation of the ZnSe–MMA core–shell structures is schematically showed in Fig. 4.

Fig. 5 shows the optical absorption properties of ZnSe–MMA CSNs synthesized at different hydrothermal temperature of 95–150 °C. The samples show good absorption for the ultraviolet light with the wavelength less than 390 nm, which is much shorter than 467.3 nm derived from ZnSe microspheres [11]. The hydrothermal temperature seems not to affect the optical properties of the samples too much because the phase and grain size do change little with the elevated hydrothermal temperature according to XRD results (Fig. 2).

4. Conclusions

ZnSe–MMA CSNs have been synthesized with a two-step hydrothermal method. The as-synthesized ZnSe nanocrystals are zincblende structure with uniform crystal size of 4 nm. As the ZnSe cores were capped with MMA shell, the growth of the ZnSe was confined and the hydrothermal temperature shows little effect on the phase and grain size of the ZnSe–MMA CSNs. The ZnSe–MMA CSNs were stable in air and show good absorption for the ultraviolet light with the wavelength less than 390 nm.

Acknowledgements

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References

[1] M.A. Hines, P. Guyot-Sionnest, Synthesis and characterization of strongly luminescing ZnS capped CdSe nanocrystals, J. Phys. Chem. 100 (1996) 468–471.

[2] W. Schärtl, Crosslinked sphereical nanoparticles with core–shell topolpgy, Adv. Mater. 12 (2000) 1899–1902.

[3] S.L. Cumberland, K.M. Hanif, A. Javier, Inorganic clusters as single source precursors for preparation of CdSe, ZnSe, and CdSe/ZnS nanomaterials, Chem. Mater. 14 (2002) 1576–1584.

[4] Y. Zhang, Y.D. Li, Synthesis and characterization of monodisperse doped ZnS nanospheres with enhanced thermal stability, J. Phys. Chem. B 108 (2004) 17805–17811.

[5] K. Zhang, L.L. Zheng, X.H. Zhang, X. Chen, Y. Bai, Silica-PMMA core–shell and hollow nanospheres, Colloids Surf. A: Physicochem. Eng. Aspects 277 (2006) 145–150.

[6] F.T. Kong, M.Q. Wang, Y.P. Wang, X. Yao, Enhancement of the stability of ZnSe nanocrystals doped in silica by a new method, Chem. J. Chin. Univ. 26 (1) (2005) 155–157.

[7] J. Xu, J.P. Ge, Y.D. Li, Solvthermal synthesis of monodisperse PbSe nanocrystals, J. Phys. Chem. B 110 (2006) 2497–2501.

[8] Y. Cai, S.K. Chan, I.K. Sou, Y.F. Chan, D.S. Su, N. Wang, The size-dependent growth direction of ZnSe nanowires, Adv. Mater. 18 (2006) 109–114.

[9] T. Kosanovic, M. Bouroushian, N. Spyrellis, Soft growth of the ZnSe compound from alkaline selenosulfite solutions, Mater. Chem. Phys. 90 (2005) 148–154.

[10] X. Wang, J. Zhuang, Q. Peng, Y.D. Li, A general strategy for nanocrystals synthesis, Nature 437 (4055) (2005) 121–124.

[11] H. Gong, H. Huang, M.Q. Wang, K.P. Liu, Characterization and growth mechanism of ZnSe microspheres prepared by hydrothermal synthesis, Ceram. Int. 33 (7) (2007) 1381–1384.

[12] H. Gong, H. Huang, M.Q. Wang, K.P. Liu, Characterization and optical properties of ZnSe prepared by hydrothermal method, J. Cryst. Growth 288 (1) (2006) 96–99.