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Synthesis and characterization of ZnSe/ZnS core/shell nanocrystals by aqueous reflux route

Zhonghai Lin[a,b], Minqiang Wang[a,b,*], Lizhuo Wei[a,b], Xiaohui Song[a,b], Yaohui Xue[a,b], Xi Yao[a,b]

[a] *Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, PR China*
[b] *International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, PR China*

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ABSTRACT

ZnSe/ZnS core/shell nanocrystals (NCs) with strong photoluminescence (PL) intensity and improved photochemical stability are synthesized through a simple water bath reflux route. Diffraction peaks can be indexed by zinc blend structure of ZnSe and ZnS. Transmission electron microscope (TEM) images reveal that each ZnSe NC (27 nm) is coated by a ZnS epitaxial shell. The ZnS shells are constitutive of crystalline and amorphous ZnS NC film with average thickness of 5 nm thick. The photoluminescence of ZnSe/ZnS core/shell NCs is also remarkably improved, which can be approved by the PL spectrum and laser-scanning confocal microscope test.

1. Introduction

Nanocrystals (NCs) are nanometer sized semiconductor crystals, which exhibit unique properties compared to the respective bulk semiconductor materials. Capping NCs with heterogeneously organic or inorganic shells is an efficient strategy to optimize robust photochemical stability, surface functionality, and their photoluminescence (PL) quantum yields (QYs), which are the prerequisites for applications in bio-imaging [1,2], light-emitting devices [3,4], photoeletrochemical and optoelectronic devices [5–8].

In recent years, main efforts have been devoted to prepare various core/shell NCs, such as CdSe/CdS [9], CdSe/ZnS [10], CdSe/ZnSe [11], CdTe/CdSe [12], CdTe/CdS [13], PbSe/PbS [14], and to investigate the influence of different shell materials on the emission properties of these NCs. The prevalent viewpoint is that a lattice matching between shell and core materials is necessary to achieve a better passivation and minimize the structure defects [15]. The optical parameters can be improved by the deposition of a passivating "shell" including larger gap semiconductor depositing on the surface of a "bare" NC. Nonetheless, almost all core/shell NCs are synthesized by organometallic precursors in organic media, while the aqueous synthesis of core/shell NCs is less reported. Comparing with organic ones, the aqueous synthesis of NCs is more reproducible, cheaper, and less toxic. ZnSe/ZnS core/shell NCs have attracted more researchers' attention because of their application in optoelectronic devices in the blue spectral region, such as blue-light emitting diodes and blue injection lasers [16]. In this work, a simple water bath reflux synthesis route to prepare ZnSe and ZnSe/ZnS NCs is acquired. The synthesis route is simple, fast, low-cost and mass-productive. ZnSe/ZnS core/shell NCs are stable against photochemical effect in the air for a long time. The photoluminescence of ZnSe/ZnS core/shell NCs is also remarkably improved.

2. Experimental details

2.1. Synthesis of ZnSe NCs

ZnSe NCs are prepared by a two-step method [17]. Typically, freshly prepared KHSe solution is injected into the solution of $Zn(NO_3)_2$ after degassing with Argon for 20 min at 60 °C, then NaOH solution with high concentration (15 mol/L) is added. The crude solution is transferred into a Teflon-lined autoclave and kept at 150 °C for 6 h to obtain yellow ZnSe NCs.

2.2. Synthesis of ZnSe/ZnS NCs

ZnSe/ZnS core/shell NCs are prepared by water bath reflux at 80 °C for 4 h. Typically, 30 mL of a aqueous solution containing freshly prepared OH-capped ZnSe NC cores was mixed with 0.002 mol of $Zn(NO_3)_2$ in a three-neck flask. After ultrasonic dispersion for 20 min, an amount of thiourea solution was injected. Immediately, the suspension is refluxed with vigorously stirring at 80 °C for 4 h. Finally, the color of the solution changed to light-yellow, it indicates the formation of ZnS shells.

2.3. Phase composition of the samples was identified by a Rigaku D/max-2400 X-ray diffraction (XRD) using Cu Kα radiation

The microstructure of the samples was studied by a JEOL JEM-3010 transmission electron microscope (TEM) operating at 300 kV and corresponding selected area

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* Corresponding author at: Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, PR China. Tel.: +86 29 82668679; fax: +86 29 82668794.
E-mail address: mqwang@mail.xjtu.edu.cn (M. Wang).

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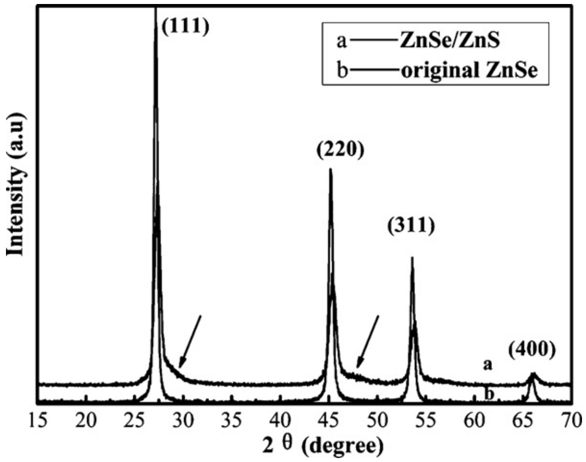

Fig. 1. XRD patterns of original ZnSe and ZnSe/ZnS NCs.

electron diffraction (SAED). Linear optical absorption spectra were measured by JASCO V-570 UV–vis-NIR spectrometer at room temperature. Photoluminescence experiments were performed with fluoroSENS 9000 system and Leica TCS sp5 laser-scanning confocal microscope.

3. Results and discussion

The crystalline structures of ZnSe and ZnSe/ZnS NCs were characterized by XRD analysis. As shown in Fig. 1, the original ZnSe NCs show a cubic zinc blend structure (JCPDS 37-1463). However, the diffraction peaks of ZnSe/ZnS core/shell NCs move towards large angles, which locate between the diffraction peaks of original ZnSe and the cubic zinc blend ZnS phase. It means ZnSe/ZnS NCs are the intermediate substance between these two original compounds. No separate diffraction peak of ZnS is observed and similar XRD results have been reported by Yang et al.'s work [18]. In order to clarify these diffraction peaks, the suspension was sealed in a Teflon-lined autoclave and heated at 100 °C for 6 h. The main diffraction peaks and weak diffraction peaks indicate cubic zinc blend structure of ZnSe and ZnS NCs (JCPDS 05-0566) in Fig. 2, respectively. Separate ZnS peaks are more clearly observed than before (Fig. 1) because ZnS has good crystallization through the hydrothermal treatment.

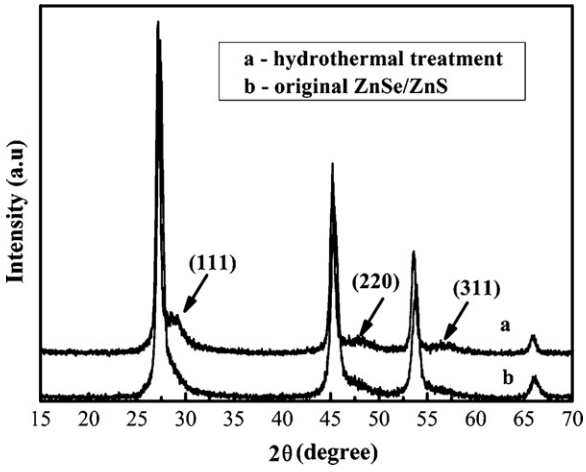

Fig. 2. XRD patterns of ZnSe/ZnS core/shell NCs treated by hydrothermal method at 100 °C for 6 h.

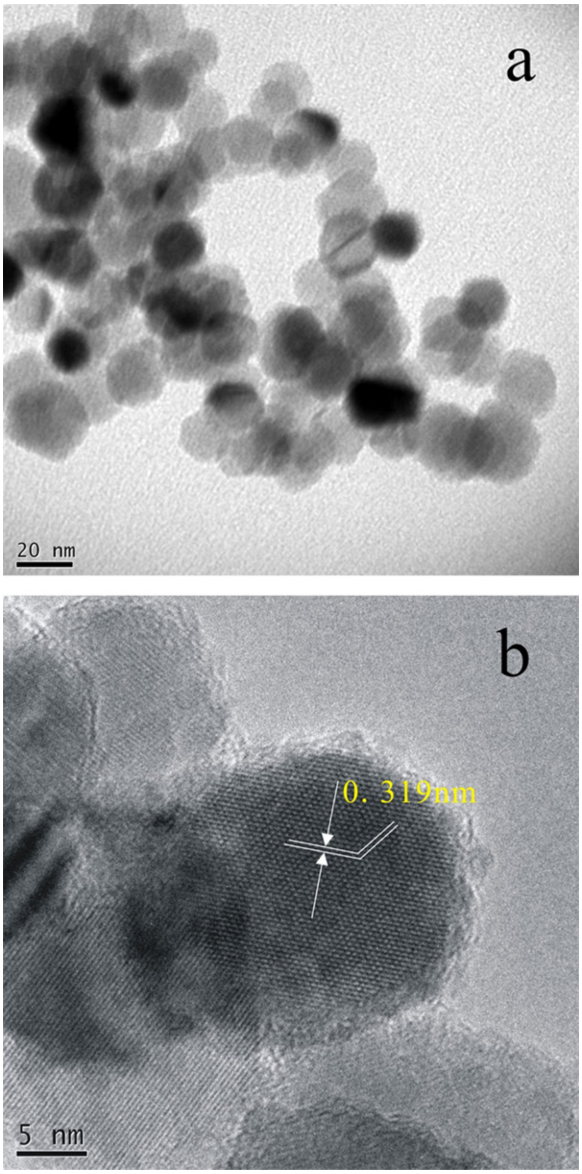

Fig. 3. (a) TEM and (b) HRTEM images of ZnSe NCs synthesized by hydrothermal method at 150 °C for 6 h.

Figs. 3 and 4 show TEM and HRTEM images of ZnSe and ZnSe/ZnS core/shell NCs synthesized by hydrothermal method at 150 °C for 6 h and water bath reflux at 80 °C for 4 h. The images further reveal the difference between ZnSe and ZnSe/ZnS NCs. The grain size of ZnSe NCs growing at 150 °C for 6 h is about 25 nm, which is close to 27 nm calculated by Scherrer formula (Fig. 1). The interfacial spacing is 3.2 Å, corresponding to (1 1 1) crystalline face of the ZnSe NCs and being in accordance with the lattice parameter of 3.272 Å which is obtained from XRD card. As for ZnSe/ZnS NCs, the size of ZnSe core is about 25 nm, which is consistent with the original ZnSe NCs in Fig. 4. Some spherical ZnS NCs (~5 nm) are distinctly observed on the surface of ZnSe core. The ZnS shells are constitutive of crystalline and amorphous ZnS NC film with average thickness of 5 nm thick.

Fig. 5 presents the typical UV–vis absorption of the original ZnSe NCs and ZnSe/ZnS core/shell NCs. The optical absorption of ZnSe NCs has a feature at 450 nm, while ZnSe/ZnS core/shell NCs has one at 460 nm. Compare with ZnSe NCs, ZnSe/ZnS core/shell NCs demonstrate a red shift (10 nm) in absorption. This phenomenon is caused by extensive delocalization of the electron into the surrounding shell and has been previously observed during CdSe/CdS preparations [19].

Fig. 6 shows the room-temperature PL spectrum of ZnSe and ZnSe/ZnS core/shell NCs ($\lambda_{ex} = 419$ nm). The band-edge emission

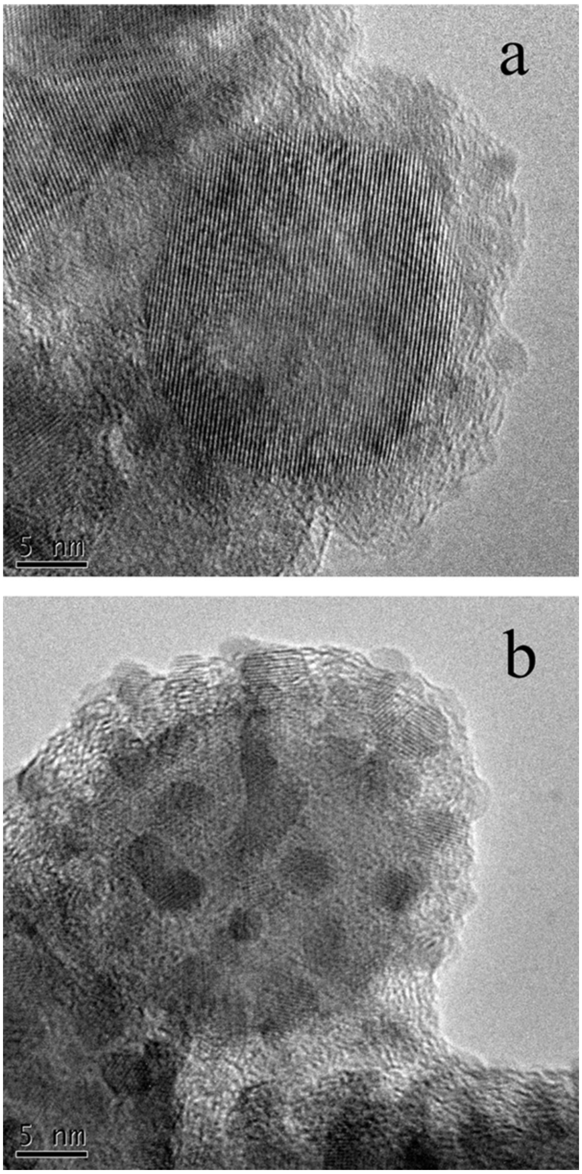

Fig. 4. (a and b) HRTEM images of different ZnSe/ZnS core/shell NCs by water bath reflux at 80 °C for 4 h.

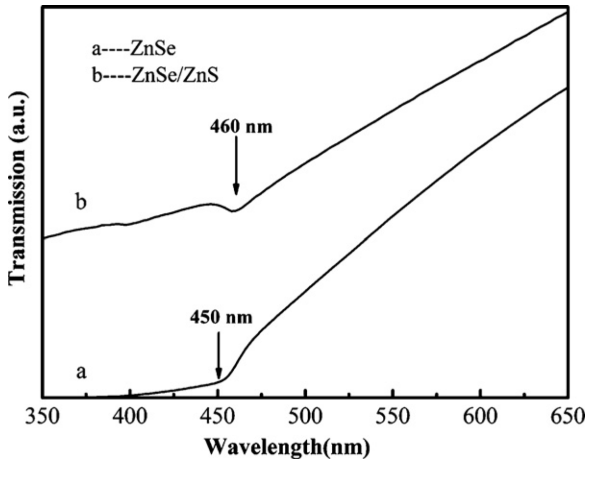

Fig. 5. Absorption spectra of ZnSe and ZnSe/ZnS core/shell NCs by (a) hydrothermal method at 150 °C for 6 h and (b) water bath reflux at 80 °C for 4 h.

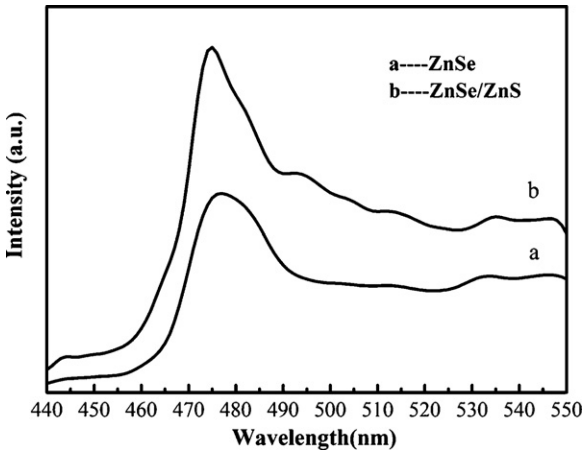

Fig. 6. The room-temperature PL spectra of ZnSe and ZnSe/ZnS core/shell NCs by (a) hydrothermal method at 150 °C for 6 h and (b) water bath reflux at 80 °C for 4 h.

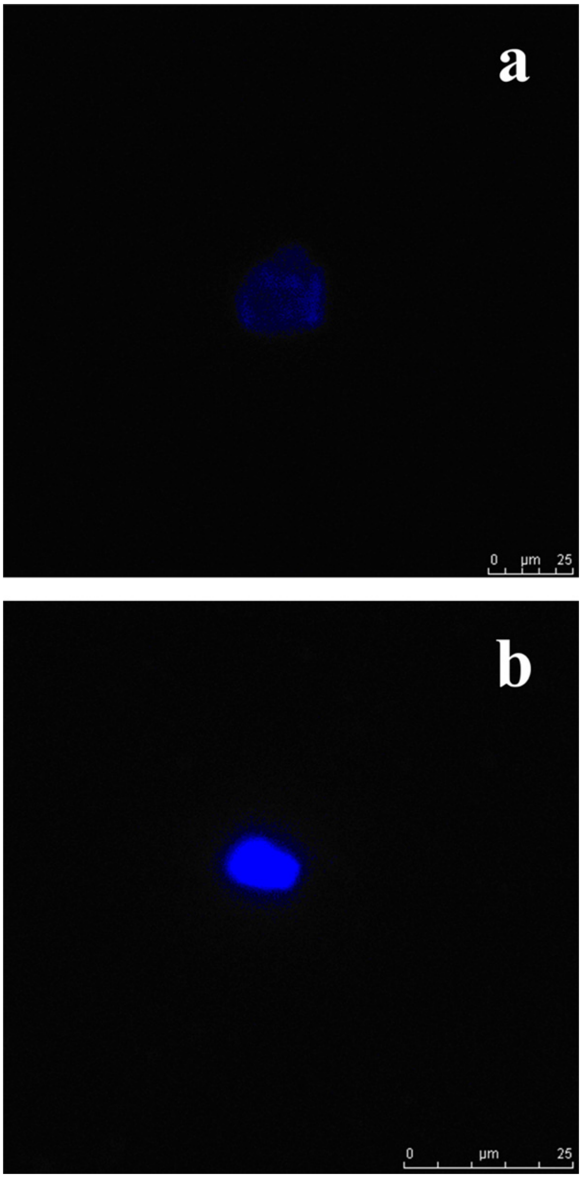

Fig. 7. The room-temperature laser-scanning confocal images of (a) ZnSe and (b) ZnSe/ZnS core/shell NCs.

is centered at 476 nm. The low-emission is most probably associated with the vacancies of Zn in ZnSe, or impurities [20]. The ZnSe/ZnS core/shell NCs emission intensity increases dramatically, owing to the better-passivated NCs surface and localization of the holes in the core region [21]. Furthermore, the increase in emission intensity also confirms the formation of ZnS shell and electronic passivation of ZnSe NCs surface.

In order to investigate the PL character of ZnSe and ZnSe/ZnS core/shell NCs further, the laser-scanning confocal microscope was used to obtain the room-temperature PL images ($\lambda_{ex} = 425$ nm), which is showed in Fig. 7. The ZnSe NCs radiate faint blue light (Fig. 7a), while ZnSe/ZnS core/shell NCs radiate brighter blue light. It is indicated that the intensity of ZnSe/ZnS core/shell NCs emission feature increases dramatically, which corresponds with PL spectrum (Fig. 6).

4. Conclusions

Cubic blend ZnSe nanocrystals (NCs) were prepared through by two steps method. In addition, ZnSe/ZnS NCs have been synthesized using a simple water bath reflux route. The diameter of ZnSe NCs is about 25 nm. The average thickness of ZnS shell is 5 nm. The phase of ZnS shell is constitutive of crystalline and amorphous structure. Due to the better-passivated NCs surface and the localization of holes in the core region, the intensity of emission feature increases significantly for ZnSe/ZnS core/shell NCs.

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