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Short communication

Characterization and growth mechanism of ZnSe microspheres prepared by hydrothermal synthesis

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Abstract

ZnSe microspheres have been prepared in NaOH aqueous solution at 150 °C for 24 h by hydrothermal synthesis using Zn and Se as source materials. Effect of Zn/Se on the morphologies of ZnSe was studied. High ratio of Zn/Se was critical to prepare ZnSe microspheres and only tiny ZnSe grains were derived when Zn/Se was less than 2. The ZnSe microspheres were formed by the attached growth of ZnSe nuclei on the surface of Zn cores while the ZnSe grains were synthesized by the free growth of the nuclei in hydrothermal solution without sustainment.

Keywords: A. Powders: C. Optical properties; D. ZnSe; Chemical preparations

1. Introduction

ZnSe is one of the important II–VI semiconductor luminescence materials with a room temperature band gap of 2.67 eV. ZnSe has long been a candidate for blue light-emitting diodes and laser diodes [1]. In recent years, considerable efforts have been made to prepare ZnSe nanocrystals by wet-chemical method [2–9]. Recently, silica spheres and polymer microspheres have been used as fundamental building blocks in optical applications and carrier materials for drug and catalysis [10–12]. In this paper, ZnSe microspheres have been prepared in NaOH aqueous solution by hydrothermal synthesis using Zn and Se as source materials. The formation mechanism of ZnSe microspheres was proposed.

2. Experimental

Zn and Se powders (99.9% purity) were directly used as source materials and were added into a Teflon-lined autoclave of 70 ml. Then 3.5 mol/L NaOH aqueous solution was poured into the Teflon liner up to 70% (49 ml) of its total capacity. The suspension solution was sealed in the autoclave and was heated in an oven with a heating rate of 3 °C/min. After soaking at 150 °C for 24 h, the autoclave was cooled down to room temperature naturally. The products were collected by centrifugal sedimentation, and washed by ionized water and absolute alcohol repeatedly. Finally, the samples were dried at 80 °C for 2 h. The as-prepared powders were light yellow-greenish.

Phase composition of the samples was identified by a Rigaku D/max-2400 X-ray diffractometer (XRD) using Cu Kα radiation. Morphologies of the ZnSe were observed by a Philips XL20 scanning electron microscopy (SEM). The microstructure of the ZnSe was studied by a JEOL JEM-2010 transmission electron microscopy (TEM) and corresponding selected area electron diffraction (SAED). The composition of the ZnSe samples was detected by energy-dispersive analysis of X-ray (EDAX). The grain size of the ZnSe was measured by a Brook Havern BI20 laser particle size analyzer. The optical properties of the ZnSe were characterized by a JASCO V-570 UV–VIS spectrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples prepared by various ratio of Zn/Se. All the main peaks can be indexed by cubic zinc blende ZnSe. EDAX was further used to analyze the composition of the ZnSe samples prepared with different ratio of Zn/Se. No impurities such as Na are found in the samples.

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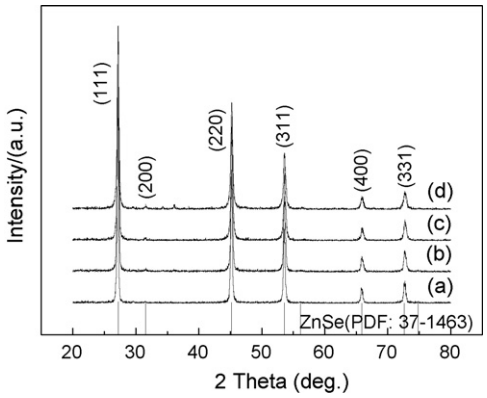

Fig. 1. XRD patterns of the samples prepared with: (a) Zn/Se = 1, (b) Zn/Se = 1.5, (c) Zn/Se = 2 and (d) Zn/Se = 2.5.

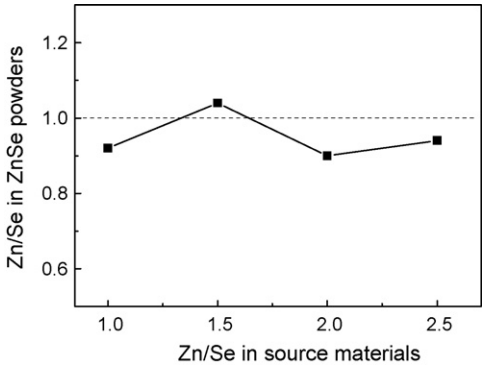

Fig. 2. The ratio of Zn/Se in ZnSe powders vs. Zn/Se in source materials.

The ratio of Zn/Se calculated from EDAX analysis is ranged from 0.90 to 1.04 (as shown in Fig. 2). Zn/Se in the products is less than 1 in most cases and Se is excessive. The excessive Se in the products is believed to be resulted from the oxidation of residual Se^{2-} to Se during the collection of powders, which is absorbed on the surface of the ZnSe powders and is difficult to remove by washing.

Fig. 3 shows the SEM morphologies of the ZnSe prepared with different Zn/Se. The ZnSe grains prepared with Zn/Se = 1 are uniform and the grain size is about 120 nm (Fig. 3a). The ZnSe grains prepared with Zn/Se = 1.5 are congregated into larger particles in several microns (Fig. 3b). With the increasing of the Zn/Se to 2 and 2.5, some ZnSe microspheres with diameter of ~5.7 μm are observed (Fig. 3c and d). The ZnSe microspheres are hollow and some broken spherical shells are observed. The SEM observations indicate that the ratio of Zn/Se has notable effect on the morphologies of ZnSe. The ZnSe crystals in the shell were further observed by TEM (as shown in Fig. 4). It shows that the ZnSe are single crystals and the crystal facets are well developed.

Fig. 5 shows the grain size distribution of ZnSe. The grain size distribution of ZnSe prepared with Zn/Se = 1 is narrow and agrees well with unimodal normal distribution. However, due to the ZnSe microspheres, the grain size distribution of the ZnSe prepared with Zn/Se = 2 is bimodal and it covers a broad range. The grain size distributions coincide with SEM observations (Fig. 3).

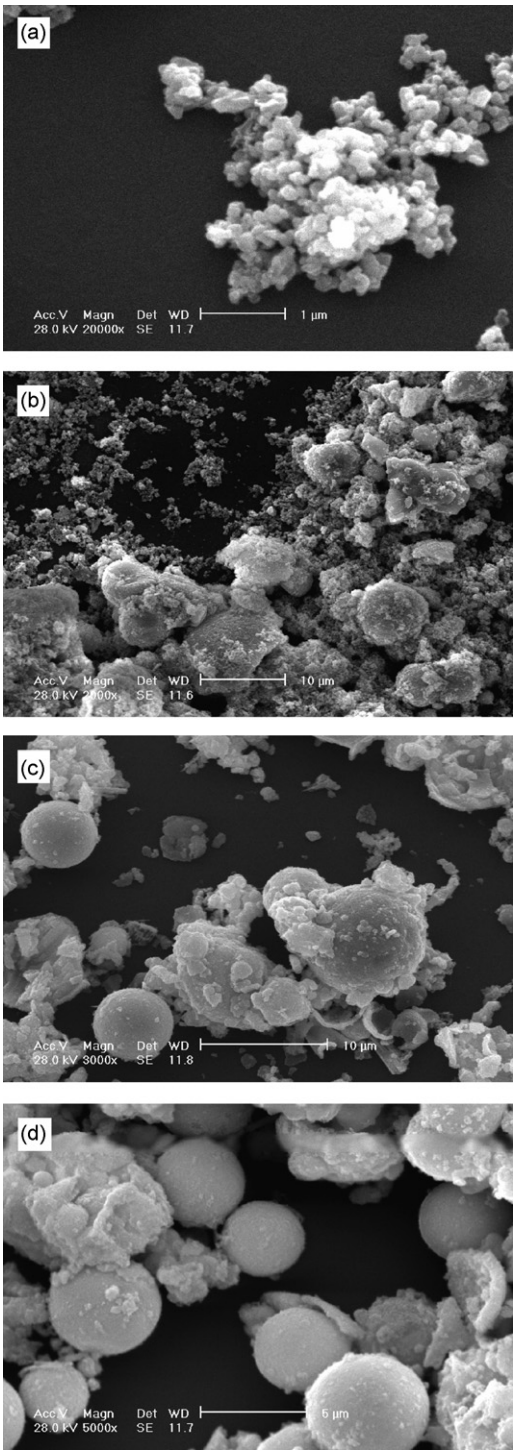

Fig. 3. SEM micrographs of the ZnSe prepared with: (a) Zn/Se = 1, (b) Zn/Se = 1.5, (c) Zn/Se = 2 and (d) Zn/Se = 2.5.

Fig. 6 shows the optical absorption properties of ZnSe prepared with different Zn/Se. The samples show ideal absorption for the ultraviolet light with the wavelength less than 467.3 nm. From the slope curve derived from the absorption curve, the slope peaks of the ZnSe microspheres samples are sharper and it indicates a steep absorption compared to the granular ZnSe sample prepared with Zn/Se = 1.

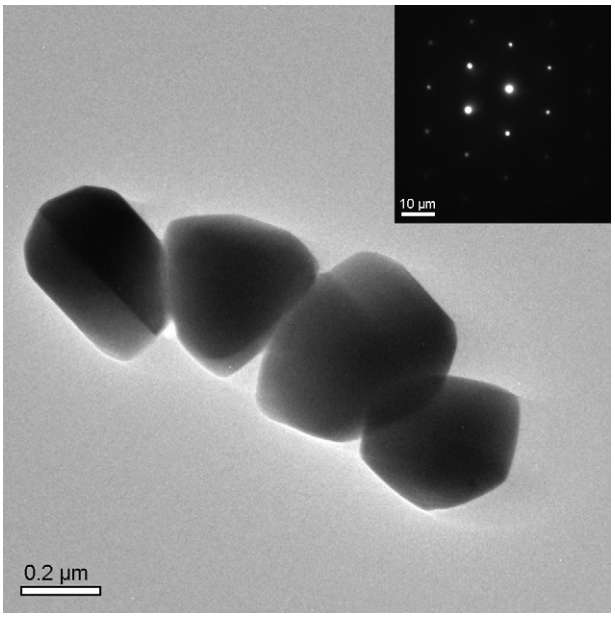

Fig. 4. TEM image of the ZnSe crystals prepared with Zn/Se = 2.

4. Growth mechanism of ZnSe microspheres by hydrothermal synthesis

Based on the SEM and TEM observations, a growth mechanism of the ZnSe microspheres is proposed. In the preparation of ZnSe by hydrothermal synthesis using elemental

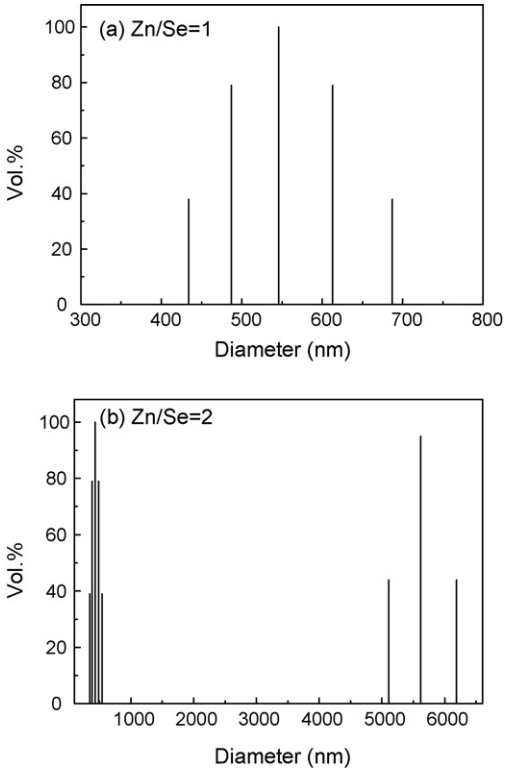

Fig. 5. Grain size distribution of the ZnSe prepared with: (a) Zn/Se = 1 and (b) Zn/Se = 2.

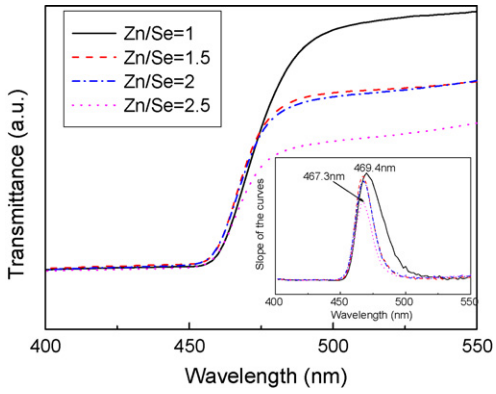

Fig. 6. Optical absorption properties of ZnSe samples prepared with different Zn/Se.

Zn and Se as source materials and NaOH as hydrothermal medium, the reactions in the hydrothermal solution can be formulated as the following:

$$Zn + 2H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-} + H_2\uparrow \quad (1)$$

$$3Se + 6OH^- \rightarrow 2Se^{2-} + SeO_3{}^{2-} + 3H_2O \quad (2)$$

$$3H_2 + SeO_3{}^{2-} \rightarrow Se^{2-} + 3H_2O \quad (3)$$

$$[Zn(OH)_4]^{2-} + Se^{2-} \rightarrow ZnSe\downarrow + 4OH^- \quad (4)$$

Zn and Se react with NaOH respectively and are dissolved in the hydrothermal solution. Then $SeO_3{}^{2-}$ is reduced to Se^{2-} by H_2 generated in reaction (1). Therefore, in order to completely reduce $SeO_3{}^{2-}$ to Se^{2-}, excessive Zn powders are used to generate enough H_2 and maintain sufficient reducing ambient in the hydrothermal system. It is known that reaction (2) is much faster than reaction (1). Se is dissolved completely when NaOH solution is added in while Zn powders are dissolved very slowly. The generation speed of ZnSe is dominated by Zn dissolving speed. Fig. 7 schematically illustrates the growth mechanism of the ZnSe microspheres prepared by hydrothermal synthesis. At first, ZnSe heterogeneously nucleates on the surface of Zn powders (Fig. 7b). The ZnSe nuclei grow up and form a thin ZnSe shells on the surface of the Zn powders (Fig. 7c). The ZnSe shell isolates Zn from hydrothermal solution and it decreases the dissolving speed of Zn cores. With the dissolving of Zn cores continuously, the ZnSe shell becomes thicker and denser (Fig. 7d). After soaking for long time, the Zn cores dissolve completely and hollow ZnSe microspheres are formed (Fig. 7e). However, when fewer Zn powers are added, the reaction between Zn and OH^- is faster and the Zn powers

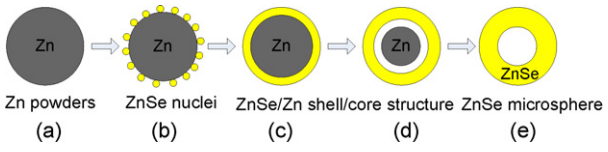

Fig. 7. Schematic illustration of growth mechanism of ZnSe microspheres prepared by hydrothermal synthesis.

will be dissolved completely soon. The ZnSe nuclei formed on the surface of Zn powers will be desorbed and grow up in the hydrothermal solution without sustainment. Therefore, only small granular ZnSe were observed in the sample prepared with Zn/Se = 1 (Fig. 3a) and the grain size distribution was narrow (Fig. 5a). Actually, even the ratio of Zn/Se is very high, considerable amount of ZnSe nuclei are desorbed from Zn surface and grow up in the hydrothermal solution. Thus, both ZnSe microspheres and tiny grains were synthesized (Fig. 3c and d) and the polarized grain size distribution was observed (Fig. 5b).

5. Conclusions

Hollow ZnSe microspheres have been prepared by hydrothermal synthesis using Zn and Se as source materials. The ratio of Zn/Se has great effect on the nucleation and growth of ZnSe. High ratio of Zn/Se is critical to prepare ZnSe microspheres and granular ZnSe is derived when Zn/Se is less than 2. The large ZnSe microspheres are formed by the attached growth of ZnSe nuclei on the surface of Zn cores while the tiny granular ZnSe is synthesized by the free growth of the nuclei in hydrothermal solution without sustainment.

Acknowledgements

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