研究简报

硫化锌纳米空心球:合成及光学性质研究

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ZnS Hollow Nanospheres: Synthesis and Optical Properties

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Abstract: Cubic ZnS hollow nanospheres have been prepared by a simple and template-free solvothermal method. The reaction was accomplished between Zn powder and the *in-situ* prepared S_8. The results of X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) show that the ZnS hollow spheres are composed of ultrafine nanoparticles. The average diameters of the hollow nanospheres are about 100 nm. Their photoluminescence (PL) spectra indicate that they have excellent optical properties.

Key words: ZnS; hollow nanosphere; chemical synthesis; optical property

As an important direct wide-bandgap semiconductor material with the highest Eg among all Ⅱ-Ⅵ compounds[1], ZnS has aroused great interests in material research fields due to its special optical and electronic properties, and it has been applied in infrared windows, sensors, flat-panel displays, cathode-ray tubes, fuel cells, catalysts and so on[2-6]. Synthesis of nanomaterials with different morphologies is expected to meet the needs of more advanced applications. Among them, hollow structures such as hollow nanospheres have been paid much attention because of their large capacity and solubility for potential applications in nanoscale encapsulation, high H_2 storage and drug delivery[7].

ZnS hollow nanospheres have mainly been prepared with silica, polystyrene sphere or surfactant as templates[8]. Peng et al.[9] synthesized a series of hollow nanospheres including ZnS hollow nanospheres by using a convenient chemical conversion way from ZnSe hollow nanospheres. Wolosiuk et al.[10] presented a "double direct templating" approach to obtain hollow ZnS nanospheres perforated with a periodic array of uniform pores. Yan et al.[11] fabricated hollow ZnS and ZnO architectures by employing $Zn_5(CO_3)_2(OH)_6$ nanospheres as the sacrificial template. And template-free route has also attracted much interest[12]. Liu et al.[13] prepared ZnS hollow nanospheres in a simple aqueous system via a template-free hydrothermal route at 140 ℃. Gu et al.[14] synthesized hollow and solid ZnS nanospheres with tunable size in a large scale by a facile chemical solution route. Zhang et al.[7] got ZnS hollow

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nanospheres through solvothermal methods with the mixture of tetrahydrofuran and water as the solvent.

ZnS hollow nanospheres have been prepared in this work by a simple and template-free solvothermal method using the mixture of ethanol and water as the solvent. The reaction is accomplished between Zn powder and the *in-situ* prepared S_8. The hollow nanospheres obtained are composed of ultrafine nanoparticles. The formation mechanism of the hollow structures is also discussed.

1 Experimental

All the reagents used were analytical grade without further purification. The typical procedure can be described as follows: 5 mL of 0.6 mol·L^{-1} $Na_2S·9H_2O$ (0.72 g) together with 15 mL of H_2O and 25 mL of ethanol was poured into teflon-lined autoclave of 50 mL capacity, and then 0.05 g of Zn powder followed by 0.81 g of $K_2S_2O_8$ was also put in the autoclave. A bright yellow precipitation appeared firstly in the solution and then it became white at ambient temperature and pressure. After being sealed, the autoclave was heated to 140 ℃, maintained for 24 h in an oven and then cooled to room temperature by tap water. The obtained product was treated in a hot (60~90 ℃) NaOH solution (10 mol·L^{-1}) for several hours to remove the excessive yellow sulphur and unreacted zinc powder. At last, it was washed with distilled water and absolute alcohol several times, respectively, and dried at 60 ℃ for 4 h.

X-ray diffraction (XRD) was carried out on a Rigaku D/max-rB X-ray diffractometer operated at 40 kV and 80 mA with Cu $K\alpha$ radiation (λ=0.154 18 nm). Field-emission scanning electron microscopy (FESEM) was taken with a field-emission microscope (JEOL 7500B) operated at an acceleration voltage of 10 kV. A thin film of gold was sputtered on the sample surface to prevent charging. Transmission electron microscopic (TEM) images and electron diffraction (ED) patterns were taken with a Hitachi H-800 transmission electron microscope performed at an accelerating voltage of 200 kV. The photoluminescence (PL) measurements were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature (λ_{ex}=290 nm, Ex slit=2.5 nm, Em slit=2.5 nm).

2 Results and discussion

Fig.1 shows the XRD pattern of the typical sample prepared in the mixed solvent of alcohol and water at 140 ℃ for 24 h by the solvothermal method. All of the diffraction peaks could be indexed to cubic ZnS (PDF 77-2100) with lattice constant a=0.539 nm. The low intensity peak marked with SF may be due to stacking faults, and the similar phenomenon was also observed for β-SiC[15]. According to Scherrer′s equation, the average crystallite diameter is about 2.3 nm. The FESEM image (Fig.2a) indicates that the sample is mainly composed of nanospheres. Some broken nanospheres can be observed, giving strong support for the hollow spheres structure. The structure of the spheres was further examined by TEM. Fig.2b indicates that the nanospheres have hollow interiors with the average diameter of about 100 nm. The ED pattern (Fig.2c), taken randomly from a hollow sphere, exhibits three rings which can be indexed to (311), (220) and (111) planes of cubic ZnS, respectively. The result indicates that the shell of ZnS hollow sphere is composed of ultrafine nanoparticles.

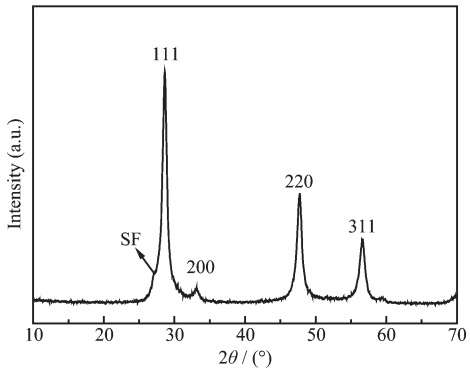


Fig.1 XRD pattern of as-prepared ZnS hollow spheres

In order to investigate the mechanism of the ZnS hollow spheres, a comparison experiment without zinc powder as the reagent was made. It is observed that Na_2S reacts with $K_2S_2O_8$ very quickly to produce yellow precipitates, accompanied by a large amount of gas bubbles. The corresponding XRD pattern (Fig.3a) of the yellow precipitates can be indexed to element S (in the form of S_8, PDF 85-0799), and the FESEM image shows that the intermediate is composed of irregular particles (Fig.3b).

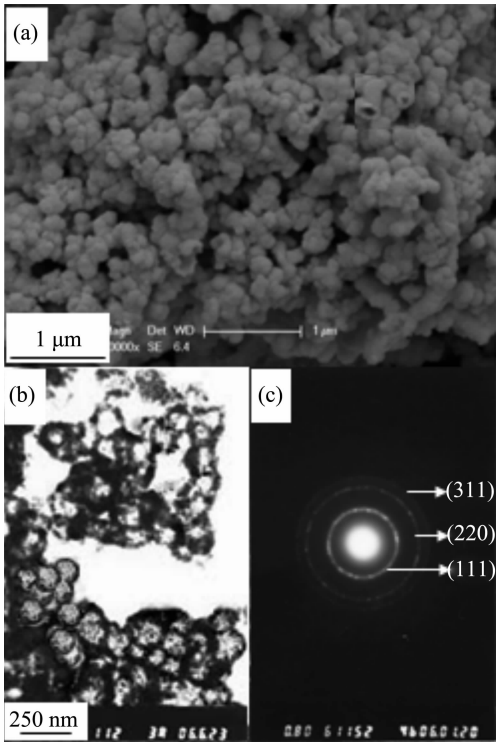


Fig.2　FESEM (a), TEM (b) images and ED Pattern (c) of ZnS hollow spheres prepared in the mixed solvent at 140 ℃ for 24 h

Based on the above observation and analysis of the reactions at ambient temperature and pressure, the solvothermal reaction equations for preparing ZnS hollow nanospheres could be suggested as follows:

$$3S^{2-} + S_2O_8^{2-} \rightarrow S\downarrow + O_2\uparrow + 2S_2O_3^{2-} \quad (\mathbf{1})$$

$$S + Zn \rightarrow ZnS \quad (\mathbf{2})$$

During the reaction process, large quantity of O_2 gas is produced according to equation (**1**). The produced O_2 gas exists in bubbles serving as a soft template for the formation of ZnS hollow spheres. To confirm this mechanism further, the experiment of commercial S powders reacting with Zn powders is done with other reaction conditions unchanged. In this case, no ZnS hollow spheres are observed in the TEM test and only solid nanospheres are obtained. So the O_2 gas plays an important role in the formation of ZnS hollow spheres. The whole growth process of ZnS hollow spheres could be described as Scheme 1.

The solvent is also an important factor to the formation of hollow ZnS structure. When only water is used as the solvent, only ZnS nanoparticles can be obtained. While the solvent is ethanol without water, the reactants can hardly dissolve in it and the reaction can not go on. The results indicate that the mixed solvent of ethanol and water is essential to the formation of hollow nanospheres. In fact, a proper ethanol addition into the solution will increase the lifetime of foam by reducing the surface tension of the solution [16]. That is to say, the mixed solvent of ethanol and water can make the formed oxygen bubbles stable enough to serve as soft templates for the assembly of ZnS nanoparticles to form hollow nanospheres. The importance of the mixed solvent for the formation of ZnS hollow nanospheres is also report-

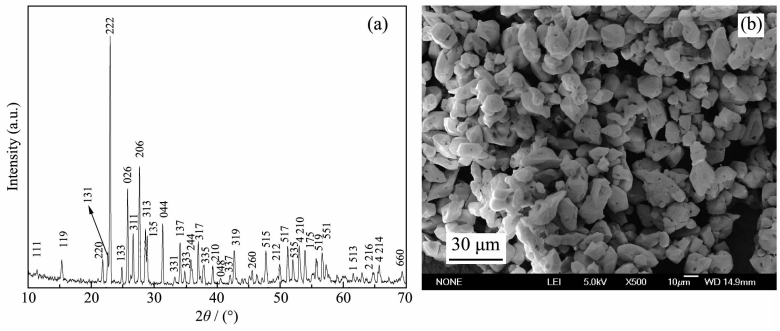
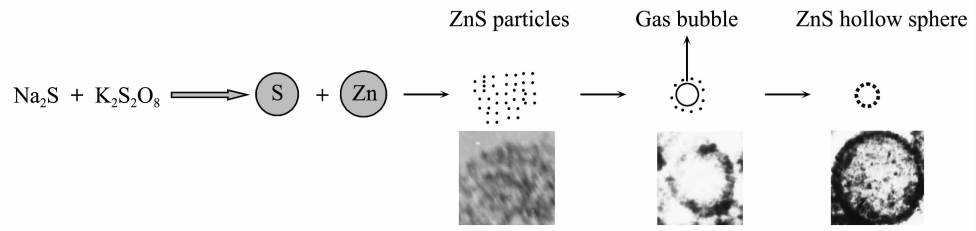


Fig.3　XRD pattern (a) and FESEM image (b) of S_8 obtained by the reaction of Na_2S and $K_2S_2O_8$ without zinc powder



Scheme 1　Growth mechanism of ZnS hollow nanospheres

ed by Zhang et al. and other groups[7,17].

Fig.4 shows the room-temperature photoluminescence spectrum (λ_{ex}=290 nm) of ZnS hollow nanospheres. The spectrum shows a strong peak at about 406 nm, which could be attributed to the bandgap emission of ZnS[9]. The shoulder peak of 454 nm may arise from trapped surface emission[18], while the peak of 470 nm can be caused by zinc vacancies emission[19]. The result is consistent with that reported by Li group[9], who also used the same facility (Hitachi F-4500) to characterize the photoluminescence property.

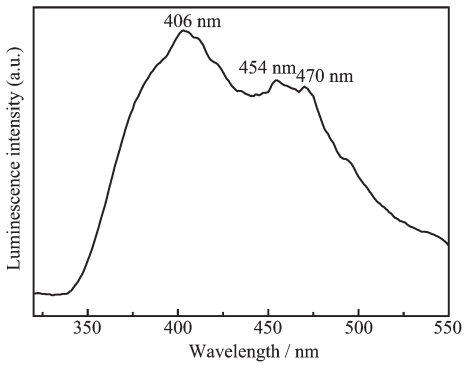


Fig.4 Room-temperature PL spectrum of ZnS hollow spheres

3 Conclusion

In summary, cubic ZnS hollow nanospheres can be synthesized by a simple solvothermal method. The as-prepared hollow nanospheres are obtained by the assembly of ultrafine nanoparticles and these nanospheres have an excellent optical property. It has a strong peak at about 406 nm in the PL spectrum, impling their potential applications in optical devices.

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