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RESEARCH ARTICLE

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Synthesis of ZnS hollow nanospheres with holes using different amine templates

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Abstract ZnS hollow nanospheres with holes were prepared by reacting $ZnSO_4$ with H_2S, the sulfide source formed in the reaction of CS_2 with ethylenediamine, 1,3-propylenediamine, butylamine or 2-(2-aminoethylamino) ethanol, which also acted as a template agent, at 50°C under agitation. The shape, particle size of about 100–850 nm and hole size of about 150–600 nm of ZnS hollow nanospheres with holes were shown by SEM and TEM images. These ZnS nanospheres with β cubic ZnS phase and composed of 2–5 nm nanocrystals were characterized by XRD and HRTEM. The blue shift of maximum absorption in UV-vis displayed the effect of quantum size. The two amino groups of amine templates reacted favorably with Zn^{2+} to form uniform and relatively smooth ZnS nanospheres with holes, while hydroxyethyl played a disadvantageous role. A reasonable mechanism of hole formation by H_2S rushing out is suggested.

Keywords zinc sulphide, amine template, synthesis, hollow nanosphere

1 Introduction

Hollow spheres with sizes from nanometers to micrometers show special structure, optical and surface properties. Their wide potential applications in transportation systems of carriers, photonic crystals, filling agents, catalysts, microreactors and fuel cells are causing increasing interest [1–5]. Some preparations of hollow spheres have been reported, including the templating method using silicon dioxide [6] or polystyrene spheres [7], inducing with triblock copolymers [8], preparing in emulsion/microemulsion [10,11], and solvothermal methods. Despite these successful examples, disadvantages such as troublesome preparation removal of the spherical templates [6], difficulty in recycling the templates in emulsion/microemulsion [10,11], long reaction time under ultrasonic by inducing with triblock copolymers [8], and high temperature in autoclave for solvothermal method [12] still need to be overcome. Thus, the control synthesis of inorganic materials with specific size and shape is still difficult to achieve and remains a great challenge for the future.

As a semiconducting material of group II-VI, ZnS hollow spheres receive much attention in a wide range of potentially useful applications such as the carriers for the controlled release of medicines, highly effective catalysts, fuel cells and confined reactors [8,10]. Despite this promising future, it continues to be a popular field of scientific research to synthesize ZnS hollow spheres with a simple method.

In this paper, the ZnS hollow nanospheres with holes of different shape and size were prepared by a simple method using ethylenediamine, 1,3-propylenediamine, butylamine or 2-(2-aminoethylamino) ethanol as templates. The nanospheres were characterized by XRD, SEM, TEM and UV-vis absorption. These ZnS nanospheres were composed of 2–5 nm nanocrystals. The effects of amine template structure on the shape of ZnS particles are discussed. A reasonable explanation of shape formation is proposed.

2 Experimental

2.1 Synthesis

All chemicals were defined/characterized by analytical purity and used without further purification. All

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solutions were prepared with double distilled water. In a typical synthesis, 0.37 mL of CS_2 was added into 40 mL of 0.15 mol/L aqueous ethylenediamine solution in a flask at room temperature. After mixing completely, 20 mL of 0.1 mol/L $ZnSO_4$ aqueous solution was added. The mixture was heated to 50°C and kept at this temperature for 20 min. The clear solution turned turbid white. The mixture was then cooled and allowed to stand for 48 h at room temperature. The white precipitate was centrifuged (4000 $r \cdot min^{-1}$) and washed with water and ethanol for three times, respectively. The final powder product was dried at 60°C in a vacuum oven for 6 h. Yields of ZnS are all above 90% based on Zn^{2+}.

2.2 Characterization

The products were subjected to characterization by X-ray diffraction (XRD, MSAL XD-2 powder X-ray diffractometer using Cu Ka radiation of wavelength 1.5406 A° at 40 kV and 20 mA), scanning electron microscopy (SEM, JEOL JSM-T300), transmission electron microscopy (TEM, Philips, Tecnai-10, 100 kV), and UV-visible adsorption spectroscopy (UV-vis, type TU-191, Beijing).

3 Results and discussion

3.1 Effect of aging time on the size of ZnS nanospheres with holes

Figure 1 presents the SEM and TEM images of ZnS hollow nanospheres with holes prepared using different amine templates. The holes in ZnS hollow nanospheres can be seen clearly in these images. In Fig. 1(a), ZnS spheres obtained with ethylenediamine have a smooth surface, with uniform size about 700–750 nm, and hole size about 250 nm. Hollow structure with an outer shell thickness of about 50 nm is shown from corresponding TEM. In Fig. 1(b), ZnS spheres obtained with 1,3-propylenediamine had a relatively smooth surface, with uniform size of about 800–850 nm and hole size of about 600 nm. Hollow structure with a thickness of about 50 nm for the outer shell is shown from corresponding

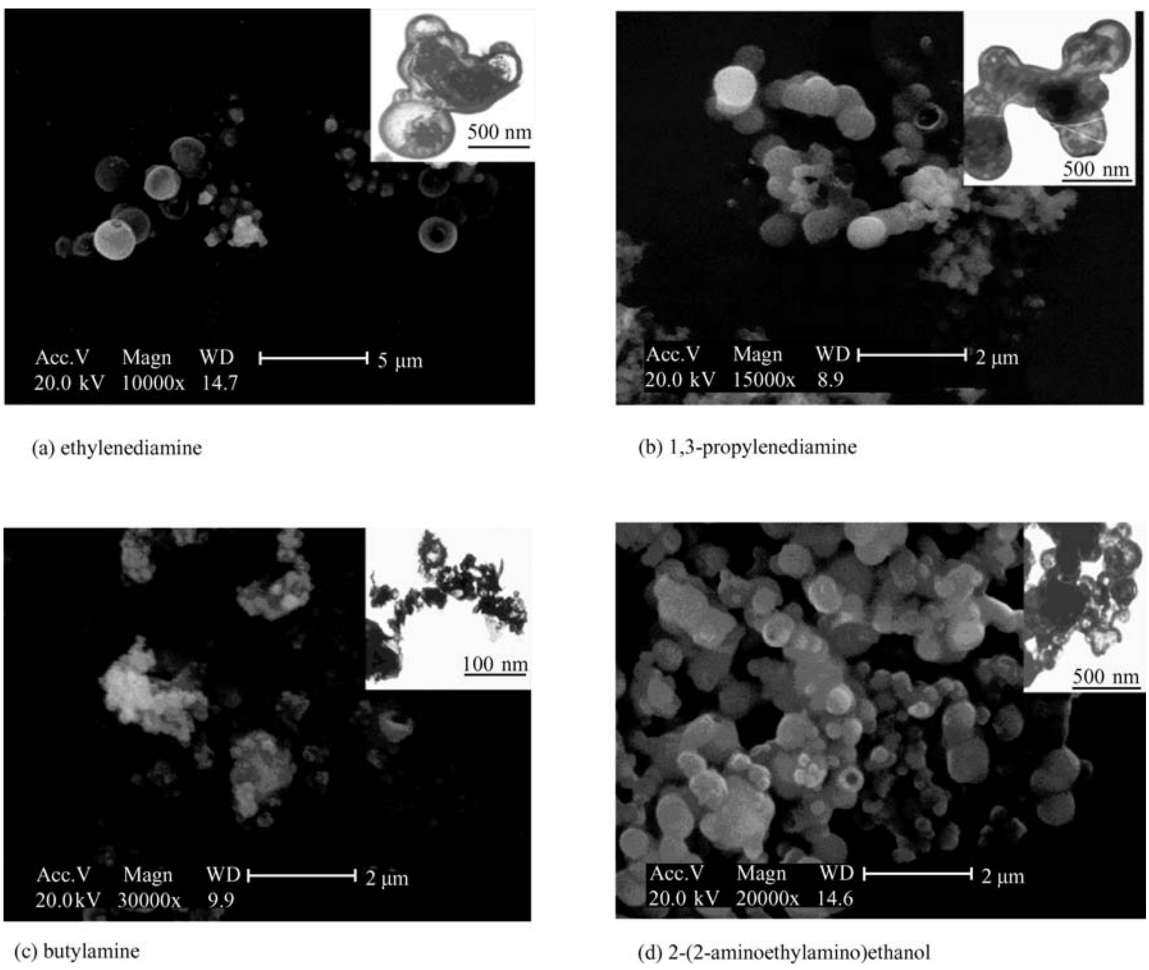


Fig. 1 SEM and TEM (insets) images of ZnS hollow nanospheres obtained with different amine templates

TEM. In Fig. 1(c), ZnS spheres obtained with butylamine had a size of about 400–450 nm and hole size of about 150 nm. Some of these particles aggregate together. The corresponding TEM image indicates that ZnS nanospheres are hollow spheres with a coarse surface attached with particles of about 50 nm. In Fig. 1(d), the seriously aggregated non-uniform ZnS hollow spheres obtained with 2-(2-aminoethylamino) ethanol show a great diversity in size from 100 nm to 800 nm and hole size of about 600 nm, which are further proved by the corresponding TEM image.

The ZnS hollow nanospheres with holes obtained with different amine templates exhibit similar X-ray diffraction in Fig. 2. The three characteristic diffraction peaks appear at about 28.5°, 47.5°and 56.3°, corresponding to the (111), (220), and (311) planes. It can be found that these ZnS nanospheres are of β type and in the cubic ZnS phase by comparing Fig. 2 with standard diffraction (PDF card 5-566). The diffraction peak corresponding to the (111) is sharp for the 1,3-propylenediamine template and is slightly broad for the other three templates. The average crystalline size is estimated to be about 3 nm for the 1,3-propylenediamine template. The size is about 2 nm for the other three amine templates according to line width analysis of the (111) diffraction peak based on the Scherrer formula [13], suggesting that the ZnS hollow nanospheres with holes could consist of primary nanoparticles. This could be further proved by the ED pattern and HRTEM image in Fig. 3.

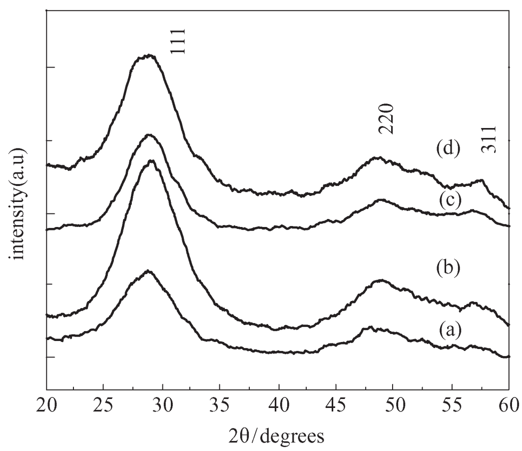
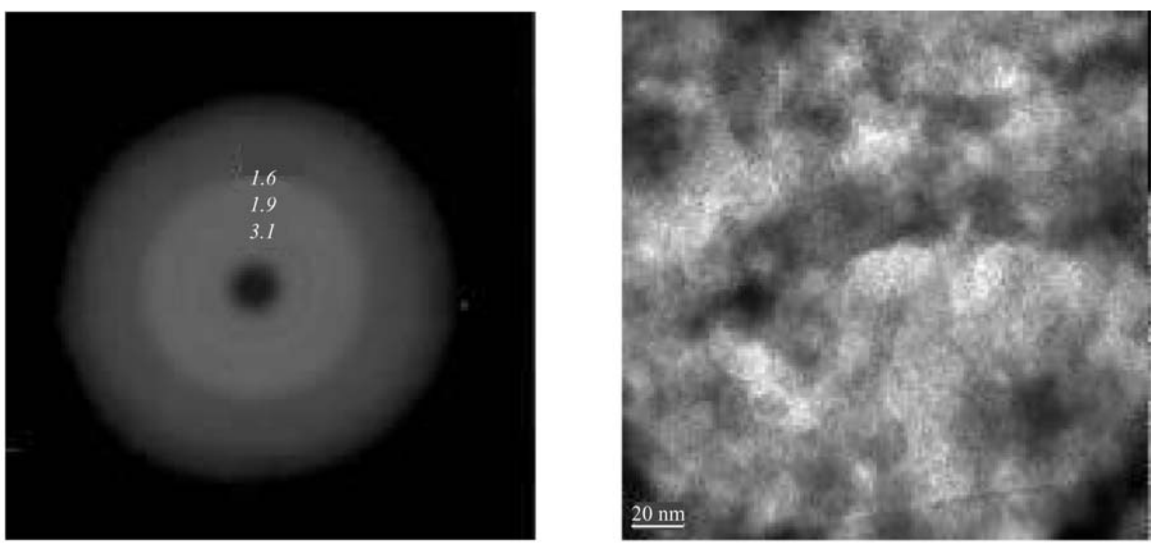


Fig. 2 The XRD diffractions of ZnS hollow nanospheres: (a) ethylenediamine (b) 1,3-propylenediamne, (c) butylamine, (d) 2-(2-aminoethylamino)ethanol

The distances between crystal faces of three rings ($d = 3.1$, 1.9, and 1.6 Å) appearing in electron diffraction (ED) pattern (Fig. 3a) correspond to the (111), (220), and (311) planes of the β type ZnS, further proving the cubic ZnS phase. The HRTEM in (Fig. 3b) shows the coarse surface of ZnS nanospheres obtained with the ethylenediamine template and indicate that the ZnS nanospheres are composed of the nanocrystallite about 2–5 nm. The ZnS nanospheres obtained with other amine templates show similar results.

Figure 4 presents the UV-Vis absorption spectra of different ZnS nanospheres. For templates ethylenediamine(a), butylamine(b) and 2-(2-aminoethylamino) ethanol, the maximum absorptions are all at about 240 nm. For 1,3-propylenediamine, the maximum absorption is at 294 nm. All these absorptions show obvious blue-shifts from 340 nm for bulk zinc blende ZnS due to quantum size effects.



(a) ED pattern (b) HRTEM image

Fig. 3 The ED pattern and HRTEM image of ZnS hollow nanospheres with holes prepared using ethylenediamine

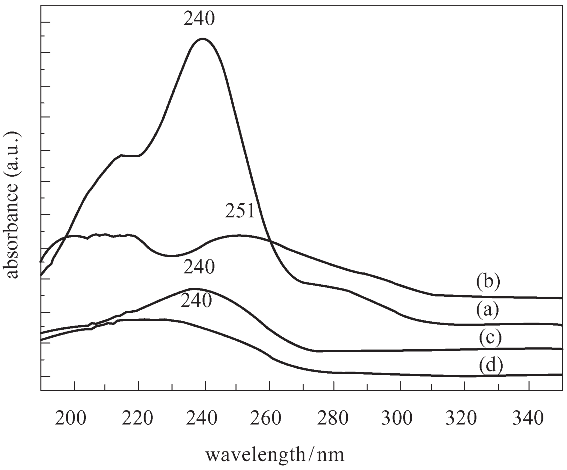


Fig. 4 UV-Vis absorption spectra of ZnS hollow nanospheres with holes (a) ethylenediamine, (b) 1,3-propylenediamne, (c) butylamine, (d) 2-(2-aminoethylamino)ethanol

The hollow structure with holes cannot be obtained at the molar ratio of amine to CS_2 smaller than 1:1 and was practically maintained at the molar ratio of amine to CS_2 bigger than 1 : 1. Thus, the ratio of 1 : 1 was applied. The proper aging time at room temperature is 48 h. The sphere could not be formed over a shorter aging time and became too small to have the hollow structure after a longer aging time. In the solvothermal method, the mechanism that ethylenediamine induced Cd^{2+} at the interface of CS_2 microsphere to react with H_2S - the product of ethylenediamine with CS_2 - to form CdS spheres. Finally, the hollow structure was left after the volatilization of CS_2 in the CdS spheres, as suggested by Qian [14]. This study showed that a similar interaction between Zn^{2+} and ethylenediamine could happen, and thus hollow ZnS nanospheres were prepared. However, the open holes of ZnS nanospheres in this paper are different from the reported results [14]. According to the formation mechanism of ZnS hollow nanospheres, CS_2 was wrapped in the core of the sphere. In this research, H_2S could be produced by the continuous reaction of CS_2 with ethylenediamine in the process of aging. Increasing H_2S gas could rush out to form an open hole such as that in Fig. 1 when the inner pressure reaches a higher level than the outer.

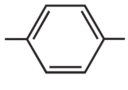
Except ethylenediamine, the other amines can also have the following reactions with CS_2 to give H_2S, and then the H_2S forms ZnS with Zn^{2+}.

$$RNH_2\,(R'_2NH) + CS_2 \longrightarrow RNH{-}CS{-}SH\,(R'_2N{-}CS{-}SH) \quad (1)$$

$$RNH_2\,(R'_2NH) + RNH{-}CS{-}SH\,(R'_2N{-}CS{-}SH) \longrightarrow$$

$$RNH{-}CS{-}NHR\,(R'_2N{-}CS{-}NR'_2) + H_2S \quad (2)$$

$R = {-}CH_2CH_2NH_2$, ${-}CH_2CH_2CH_2NH_2$, ${-}CH_2CH_2CH_2CH_3$, ${-}CH_2CH_2OH$


NH_2, ${-}CH_2CH_2NHCH_2CH_2OH$

$R' = {-}CH_2CH_2OH$

However, the structure of amine templates shows obvious effects on the shape and size of ZnS. The ZnS nanospheres with holes can be obtained by using ethylenediamine, 1,3-propylenediamine, butylamine or 2-(2-aminoethylamino)ethanol as templates. For ethylenediamine and 1,3-propylenediamine, the ZnS spheres are surface smooth spheres with uniform size. Compared with ethylenediamine, the increased one CH_2 of 1,3-propylenediamine results in a large particle size and an open hole. 1,4-phenyldiamine could not form a hollow ZnS sphere probably because of molecular rigidity on the template. For 2-(2-aminoethylamino)ethanol, one of the hydrogen atoms on the amino group of ethylenediamine is replaced by hydroxyethyl. The structure of hollow spheres with holes is maintained, but the ZnS particles become non-uniform, and the surface is rough and easy to aggregate. For butylamine - the one amino template - the ZnS particles become small and form a rough surface. A ZnS nanosphere cannott be obtained for ethanolamine and diethanolamine templates having both amino and hydroxyethyl. From these results, in the structure of amine template the two amino groups are advantageous, whereas hydroxyethyl is disadvantageous to as a template in the preparation of ZnS nanospheres with holes.

4 Conclusions

The ZnS hollow nanospheres with holes were simply prepared by reacting $ZnSO_4$ with H_2S, the sulfide source from the reaction of CS_2 with the templates ethylenediamine, 1,3-propylenediamine, butylamine or 2-(2-aminoethylamino) ethanol at 50°C, and characterized by XRD, SEM, TEM and UV-vis absorption. The effects of different amine structures on the shape of ZnS are investigated. A reasonable formation mechanism is proposed.

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