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Controllable synthesis of ZnS holely microspheres in solution containing ethylenediamine and CS_2

Li Lingang · Tang Yu

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Abstract ZnS holey microspheres (HMSs) were prepared by reacting $ZnSO_4$ with sulfide source from CS_2 and ethylenediamine at 50 °C, then aging at room temperature. The synthesized HMSs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV–visible absorption measurement. The results showed that the holes were formed by gas of H_2S, and the small ZnS HMSs were formed by particles reaggregating with the aid of ethylenediamine. In addition, the size- and shape-controlled synthesis of ZnS HMSs was achieved by varying the process parameters, such as the aging time of the final solution, the molar ratio of CS_2 and ethylenediamine, and so on. A gas obtruding mechanism was proposed.

Introduction

Transition metal sulfides, because of their variable and special optical and electrical properties, have attracted much attention and some of them are used for the fabrication of devices [1]. As an important group II–VI semiconductor with a wide band-gap energy of 3.7 eV at 300 k, ZnS is well known for its widely applications in photocatalysis [2], photoluminescence and electroluminescence [3–5]. In the past few decade, different size and shape of ZnS nanomaterials such as nanoparticles [6–8], nanowires [9–12], nanorods [13,14], nanotubes [15], nanosheets [16, 17], nanobelt [18, 19], spindle-like hollow nanostructures [20], plate-like nanostructures [21] were synthesized via many routes such as ultraviolet emission, ultrasonic waves, hydrothermal, physical evaporation, colloidal, reversed micelles templates, microemulsions, and so on.

Furthermore, hollow spheres with nanometer-to-micrometer dimensions having tailored structural, optical, and surface properties represent an important class of materials that are potentially useful for a wide range of applications such as delivery vehicle systems, photonic crystals, fillers, and catalysts [22], many efforts have been devoted to the synthesis of ZnS hollow spheres. For example, ZnS hollow spheres have been synthesized by templating the pluronic amphiphilic triblock copolymer P123 [22], emulsifier-free emulsion route with the aid of ultrasonic [23], using silica [24], polystyrene [25] and poly (styrene- methyl methacrylate-acrylic acid) (PSMA) latex spheres [26] as sacrificial templates. Generally, the templates often used mainly consist of two types: one is the hard template, including silica spheres, polystyrene latex spheres, etc., the preparation and subsequent elimination of which are often proved to be inconvenient; the other is the soft template, for instance, the droplets of emulsion or microemulsion, which could be removed easily; however, the recycle of the emulsifiers used is a complicated process, the size and shape cannot be controlled easily and the reaction condition are not mild. Therefore, it is of much importance to search for appropriate route to control synthesis of hollow microspheres.

In this work, a facile way to control synthesis of ZnS HMSs by reacting $ZnSO_4$ with sulfide source from CS_2 and

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L. Lingang (✉)
Department of Chemistry and Life Science, West Anhui University, Luan 237012, P.R. China
e-mail: llg041@163.com

L. Lingang · T. Yu
Department of Chemistry, Jinan University, Guangzhou 510632, P.R. China

ethylenediamine at 50 °C is reported, which has many advantages in comparison with other methods. The resultant products appear a hollow microspheres morphology with open holes, without requiring any soft or hard template. And the reaction does not need ultrasonic, high temperature or other harsh condition (Comparision with the work mentioned upward [22–26]). The control of particle size and shape was achieved by varying the aging time of the final solution and the molar ratio of CS_2 and ethylenediamine.

Experiments section

Materials

$ZnSO_4$ (>99.99%), ethylenediamine ($C_2H_8N_2$ purity ≥ 99%), carbon disulfide (CS_2, extra pure) used in the present study were purchased from Tianjin Chemical Reagent Ltd. Co. of china. All chemicals were used directly without any further purification. All solutions were prepared with double distilled water.

Synthesis

ZnS HMSs were synthsized by a facial way at low temperature. In a typical synthesis, certain of CS_2 were added into 40 mL of 0.15 mol/L ethylenediamine aqueous solution in a flask under constant magnetic stirring. Then 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. Then, the mixture was maintained under a static condition for a definite time at room temperature. The white precipitate was centrifuged 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.

Characterization

The transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were captured with a microscope (JEOL, 3010) at an acceleration voltage of 200 kV. The TEM samples were achieved by drying a drop of the sample suspended in anhydrous ethanol on a copper grid. The phase composition and nature of the obtained product were determined by X-ray diffraction (XRD) patterns, using a MSAL XD-2 powder X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-Kα radiation(λ = 1.54178 Å). The optical absorption spectra were measured with a UV–vis spectrophotometer (TU-1901, Beijing). The morphology and structure were characterized by scanning electron microscopy (SEM, JEOL JSM-T300).

Results and discussion

Morphology of ZnS HMSs

Figure 1(a) presents a typical TEM image of ZnS HMSs obtained after aging for 3 days, which showed strong contrast between the dark edge and the pale center of the spherical particles evidencing their hollow nature [27], the diameter of the hollow spheres is about 280–330 nm, and the wall thickness is about 20 nm. From the SEM image (Fig. 1b), it can be clearly seen the open holes in the ZnS hollow microspheres. The wall of hollow ZnS sphere can be seen from the higher magnification TEM image (Fig. 1c), which showed that the wall is very coarse and there are many monodispered black ultrafine particles with an average diameter of 4 nm, suggested it is consisted of primary ZnS nanoparticles [28]. The selected area electron diffraction (SAED) pattern (Fig. 1d) showed principally three rings with *d* spacings 3.1, 1.9, and 1.6 Å, which corresponded to the (111), (220), and (311) planes of zinc blende, the cubic ZnS phase, respectively.

The XRD pattern of ZnS HMSs is shown in Fig. 2. The broad peaks compared to those of bulk ZnS indicate the nanocrystalline nature of the sample. These diffraction features appearing at 28.5°, 47.5°and 56.3° correspond to the (111), (220), and (311) planes of the zinc blende structure. An average crystallite size of the samples estimated from the Debye-Scherrer formula [29] based on the full width at half-maximum of (111) zinc blende reflection is ~4 nm, which is of good agreement with the higher magnification TEM observation. Figure 3 prensents the UV–vis absorption spectrum of the ZnS HMSs, which were recorded after the dried product was dispersed in ethanol. It shows a wide absorbance peak at about 294 nm, which is obviously blue-shifted from 340 nm for bulk zinc blende ZnS because of quantum size effects. It has been documented that the optical absorption of the ZnS nanocrystals with a size of 3.5 nm exhibits an excitonic peak at 288 nm [30]. The similar result suggests that the ZnS hollow microspheres is constituted by a lot of nanocrystals with a size of ~4 nm, which is good consistent with the XRD results and higher magnification TEM image.

Growth mechanism of ZnS HMSs

In this report, a chemical route to synthesize well-crystallized ZnS HMSs in homogeneous solution under easily controlled and mild conditions has been presented. The synthetic design was motivated by the known reactions between CS_2 and ethylenediamine, as described by the following equations [31]:

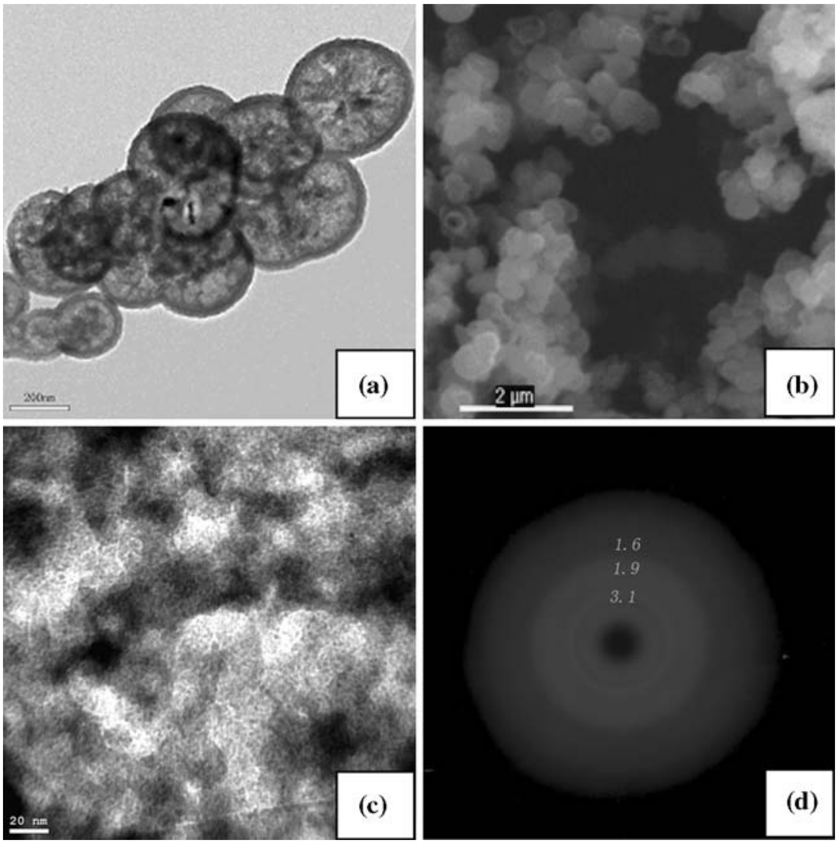

Fig. 1 (**a**) Low magnification TEM image of ZnS HSMSs after aging for 3 days, (**b**) SEM image of ZnS HSMSs after aging for 3 days, (**c**) higher magnification image of the wall of ZnS HSMSs after aging for 3 days, and (**d**) The SAED

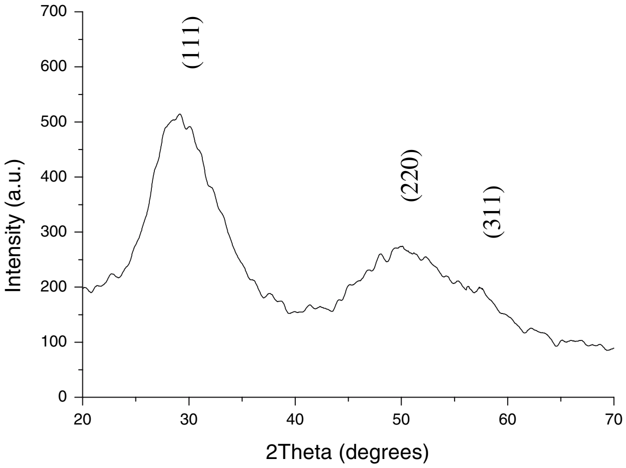

Fig. 2 X-ray diffraction pattern of ZnS hollow microspheres

$$H_2N - CH_2 - CH_2 - NH_2 + CS_2 \rightarrow H_2N - CH_2 - CH_2 - NH - CS - SH \quad (1)$$

$$n(H_2N - CH_2 - CH_2 - NH - CS - SH) \rightarrow (- HN - CH_2 - CH_2 - NH - CS -)_n + H_2S \quad (2)$$

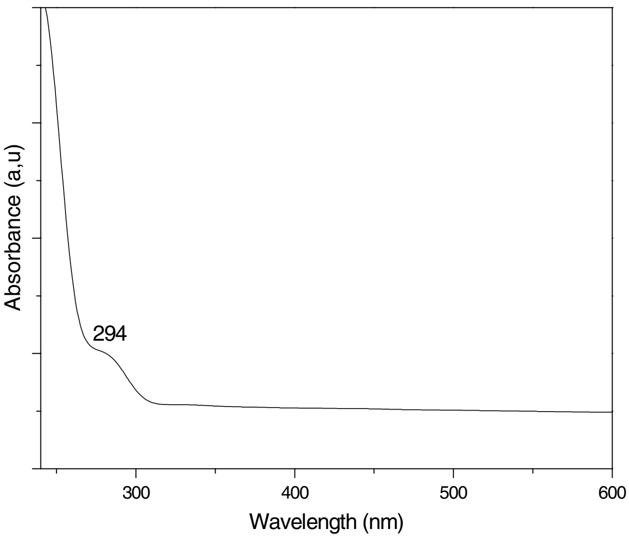

Fig. 3 UV–vis absorption spectrum of ZnS hollow microspheres

It is well known that ethylenediamine is a bidentate ligand and it can react with metal ions to form relatively stable complexes, which may serve as molecular templates in control of the crystal growth [32]. It was pointed out that after Cd^{2+} ions were introduced into the solution, they would be chelated by ethylenediamine, and then, carried from water to the CS_2-water interface where they might react with the released H_2S to form CdS nanocrystals [33]. Here, the situation is same for Zn^{2+} and ZnS. Ethylenediamine have been employed to form complex precursor (ZnS·*x*en) of ZnS and probably acts as connecting molecular bridges between neighboring ZnS chains or layers [34]. In the synthesis of binary transition metal sulfides nanocrystallites MS (M = Zn, Cd, Co, Ni) with hydrothermal method, ethylenediamine is the key factor to the purity and morphology of the products [35]. The controlled fabrication of wurtzite ZnS nanorods is due to a mediated generation of the lamellar phase, ZnS·0.5en, a covalent organic-inorganic network based on ZnS slabs, and to its subsequent thermolysis in aqueous solution [36]. Thus, ethylenediamine can react not only with Zn^{2+} ions but also with ZnS molecules. In our experiments, the concentration of ZnS is high at the CS_2-water interface in the process of early reaction, so the nanocrystals of ZnS may aggregate to form big spheres. By the effect of ethylenediamine, such as the stability action with others on the nanocrystals of ZnS, the nanocrystals of which the ZnS HMSs are composed may aggregate again from the bigger one in the aging time, and form the smaller particles. Ethylenediamine and CS_2 can be enwrapped in the spheres in the process of ZnS nanocrystals aggregating. The H_2S gas is released slowly as the reaction of ethylenediamine with CS_2 proceeding slowly. Thus the reaction of releasing gas may proceed in ZnS spheres, and the holes may be formed by gas obtruding. The more detailed studies about the effect of the coordination agent ethylenediamine and the mechanism of the reaction are in progress.

Control synthesis of ZnS HMSs

Size control of ZnS HMSs

Figure 4 is the typical SEM images of ZnS HMSs obtained at different aging time. Obvious holes can be seen from Fig. 1(a, b). For Fig. 1(c, d), no hole can be seen because the particle is too small. But the hole can be seen from its corresponding TEM image. The morphology of ZnS HMSs is different from the hollow ZnS particles to the best of our knowledge. From the Fig. 4, it can be seen that the obtained ZnS spherical particles are uniform, and the diameter of ZnS HMSs is about 700–750 nm (Fig. 4a), 280–330 nm (Fig. 4b), 150–200 nm (Fig. 4c) and 80–120 nm (Fig. 4d) when aged for 2, 3, 5 and 10 days, respectively. Obviously, ZnS particle becomes smaller and smaller as aging time increased. This is very interesting and unusual. This maybe because as the aging time increasing, the releasing gas become less and less when most reactants have been reacted, the initial nanocrystals linked more and more compactly and the size of ZnS hollow spheres become smaller and smaller. However, some samples such as ZnS aging for ten days exhibit that they can easily aggregate due to their small dimensions and high surface energy.

Shape control of ZnS HMSs

In order to test the mechanism of ZnS HMSs, we investigated to change the molar ratio of CS_2 and thylenediamine. In the initial experiment the molar ratio of CS_2 and thy-

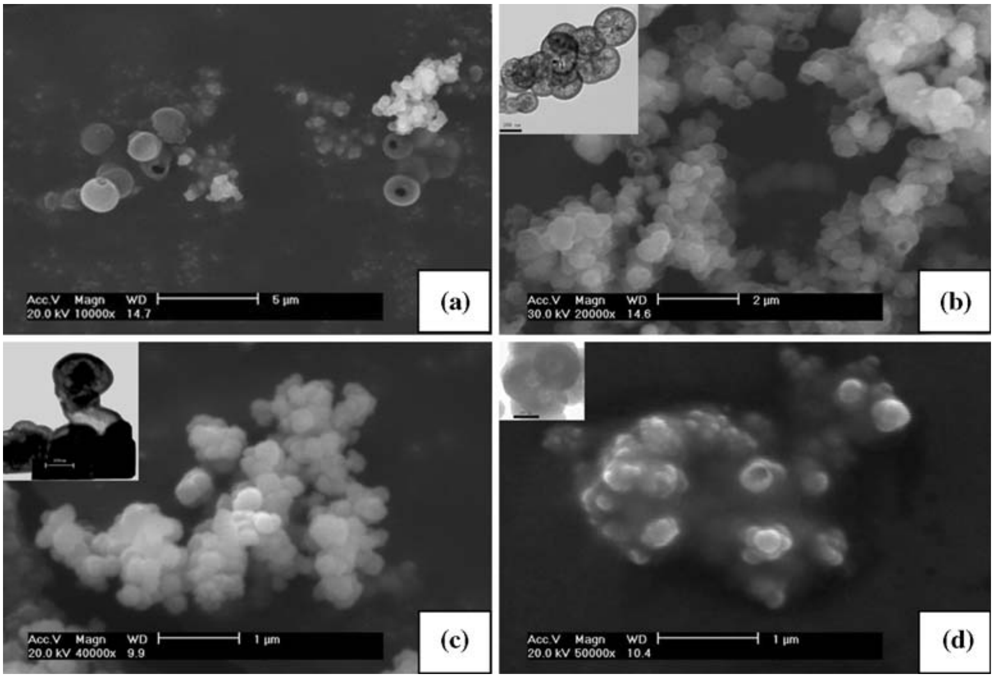

Fig. 4 SEM images of ZnS HSMSs after aging for (**a**) 2 days, (**b**) 3 days, (**c**) 5 days (**d**) 10 days; (**b–d**) inside corresponding TEM images, scale bars: (**b**) 200 nm, (**c**) 100 nm, (**d**) 100 nm

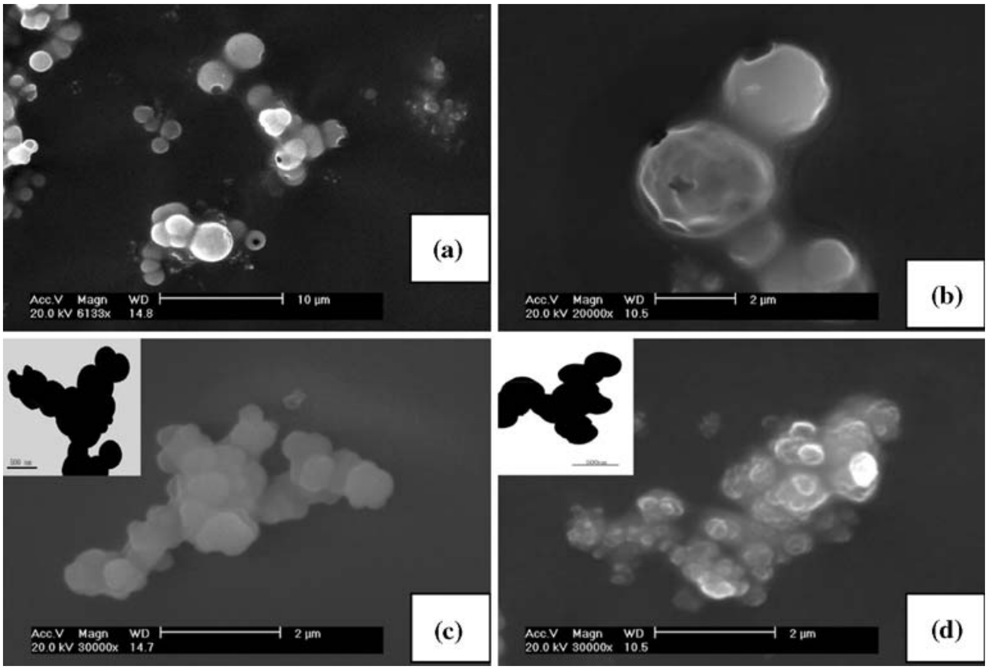

Fig. 5 SEM images of ZnS HSMSs with different moral ratio of CS_2 and thylenediamine after aging for 2 days: (**a**) 3:1, (**b**) 5:1, (**c**) 1:3, (**d**) 1:5; (**c**, **d**) inside corresponding TEM images, Scale bars: 500 nm

lenediamine was $R = 1:1$, $R = [CS_2]/[en]$. After aged for two days, the size of ZnS microspheres is about 700–750 nm, and the hole is single (Fig. 4a); when R was increased to 3:1 and 5:1 (Fig. 5a, b), the size of ZnS holey spheres comes up to about 2 μm and 1.2 μm, furthermore, the number of hole increased, too, two or more holes can be found in a single particles. The reason may be that when the amount of CS_2 is increased, more and more excessive CS_2 will react with Ethylenediamine slowly and release more gas of H_2S in the spheres of the process of ZnS nanocrystals aggregating. And then the spheres will be expanded bigger. When the pressure in the spheres is high enough, the gas will obtrude quickly from the inner of spheres and the holes appeared.

While keeping the amount of CS_2 unchanged, increasing the amount of thylenediamine, the size of ZnS microspheres is changed from about 300 nm ($R = 1:3$, Fig. 5c) to 200 nm ($R = 1:5$, Fig. 5d), but no hole produced, and the corresponding TEM images show that the microspheres are solid. The reason maybe lie on that when the amount of thylenediamine is larger than CS_2, a part of thylenediamine will react with CS_2 in the step (1); the remained thylenediamine may act as dispersant and impede $H_2N–CH_2–CH_2–NH–CS–SH$ to polymerize to $n(H_2N–CH_2–CH_2–NH–CS–SH)$, so the reaction in step (2) become difficult, and the amount of H_2S become much less. No excessive gas in the spheres of the process of ZnS nanocrystals aggregating. As a result, the ZnS microspheres turn to be solid and the size become smaller and smaller.

Conclusions

ZnS HMSs were prepared via a facile route. The particle size and shape can be controlled by varying the process variables, such as the aging time of the final solution, the molar ratio of CS_2 and ethylenediamine. A gas obtruding mechanism was proposed.

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