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Tunable synthesis of multi-shaped PbS via L-cysteine assisted solvothermal method

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ABSTRACT

Lead sulfide (PbS) with multi-morphologies were synthesized via solvothermal route under the assistance of L-cysteine. Reaction conditions such as concentration of L-cysteine, reacting temperature, reacting time and solvents have been systemically investigated in order to obtain shape-controlled PbS micro-crystals. A series of morphologies, such as cubic, Dendritic Hierarchical, Octagonal Hierarchical flowerlike and Vertebration shapes were obtained successfully. Self-assembly and a hypothesis based on Boltzmann distribution were introduced for illustration of morphology evolution obtained under different reacting temperatures, and the effect of the solvents and the role of L-cysteine were also discussed in detail. To testify the effects of different morphologies on the optical properties of PbS, the absorption spectra of some samples were measured. These results demonstrated that our work offers an effective way to develop the tunable synthesis of multi-shaped PbS for various applications.

1. Introduction

Properties of semiconducting materials are closely related to their microstructures, such as crystal size, shape, surface morphology, and self-assembly process [1–5]. Therefore, preparation of semiconducting materials with controllable morphologies is the essential for the application of these materials. PbS is an important IV–VI semiconductor, it possesses a strong absorption cross-section, strong quantum confinement of both electrons and holes, a near-infrared direct narrow bandgap (0.37 eV) and a large exciton Bohr radius (18 nm) [6]. Therefore, it has become a promising material for near-infrared communication [7], photon switch [8], photo-electric devices [9,10], and bio-images [11]. Recently, PbS quantum dots have also been prepared for photoelectric applications [12,13]. Study on the shape-controlled synthesis of PbS materials should be a fundamental and significant work for their applications.

Until now, PbS nanocrystals with various kinds of morphologies have been reported, including cubes [14,15], tubes [16], spheres [17], rod-like shapes [18], wires [19,20], truncated multipods [21], octahedrons [22], flowerlike shapes [23], Dendritic [24], and star-shaped structures [14,22]. Meanwhile, different synthesizing methods including microwave analysis [25], colloidial solutions [26], surfactant-assisted [27], self-assembly [18], and solvothermal method [28] were also developed. Among all the above-mentioned methods, solvothermal method has been widely adopted due to its simplicity, low cost and excellent repeatability. On the other hand, biomolecules assisted synthesis including L-cysteine, has been proven to be an environment-friendly and promising method for the preparation of various materials owing to its convenience and important role in morphology control [29]. Qian and co-workers have reported the preparation of PbS with of Dendritic Hierarchical Structures under the assistance of L-methionine and L-cysteine [3]; Xie's group has synthesized Pagoda-like PbS [30], flowerlike Bi_2S_3 [31], porous spongy-like Ni_3S_2 [32], and network-like MnS nanostructures under the assistance of L-cysteine [33].

Diverse morphologies of PbS make its shape-controlled synthesis still a significant and tough work. Thus further and comprehensive investigations are greatly needed. Herein, the effect of reaction conditions including concentration of L-cysteine, reacting temperature, reacting time gradient, and reacting solvents (including pure and mixed solvents) were investigated in order to obtain shape-controlled PbS nanocrystallines. A series of morphologies, such as cubes, Dendritic Hierarchical, Octagonal Hierarchical flowerlike and Vertebration shapes were obtained successfully. Further, some novel structures which are uncommon in literature were also synthesized. Meanwhile, the mechanism for the growth process of PbS under the assistance of L-cysteine and the self-assembly process were also discussed. As PbS materials possess a relatively narrow band gap and often applied as function materials with near-infrared properties, the viable-IR absorption spectra of

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some samples were finally measured and compared. These results would be useful to develop the tunable synthesis of multi-shaped PbS for various applications.

2. Experimental section

All chemical reagents (analytical grade) were directly used without further purification. $Pb(AC)_2 \cdot 2.5H_2O$ was used as Pb source, and H_2NCSH_2N was used as S source in this study. $Pb(AC)_2 \cdot 2.5H_2O$ and H_2NCSH_2N were put into a 50 mL stainless steel Teflon-lined autoclave with a molar ratio of 1:1. Then different amount of L-cysteine were added into this system. Different solvents, including ethanediamine (en), water, ethanol (EtOH), ethylene glycol (EG) and their mixtures (40 mL) were used, respectively. The system then was stirred for 10 min. Finally, this autoclave was sealed and heated at different temperatures for different time. When the autoclave was cooled to room temperature naturally, black precipitates were collected by centrifugation and washed with distilled water and ethanol for several times. Then the final products were dried in vacuum at 60 °C for 4 h.

The crystal structures of the products were examined by X-ray diffraction (XRD) using a Bruker D8-Advance X-ray diffractometer with graphite monochromated CuKα radiation (λ=0.15406 nm). The surface and fractured surface morphology images were observed using a Hitachi S-4800 field emission scanning electron microscope (FESEM, 10 kV) equipped with an X-ray energy dispersive spectroscope (EDS) at an accelerating voltage of 20 kV. A JEOL 2010 transmission electron microscope (TEM) was used to analyze the morphology. High-resolution TEM (HRTEM) image was performed with a JEOL-2010 TEM at an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Influence of L-cysteine concentration on the microstructure of PbS

Fig. 1 shows the X-ray diffraction (XRD) patterns of the products obtained in en reacted for 6 h with the reacting temperature of 180 °C assisted by L-cysteine with different concentrations. Sharp and strong diffraction patterns indicate the fine crystallinity of all the obtained samples. The reflection peaks of the different products can be indexed as face-centered cubic (fcc) structured PbS, in good accordance with the literature values (JCPDS Card No. 05-592, a=5.936 Å). No peaks of impurities were detected, indicating the high purity of the synthesized products. Furthermore, no obvious changes were found for PbS prepared using different concentration of L-cysteine.

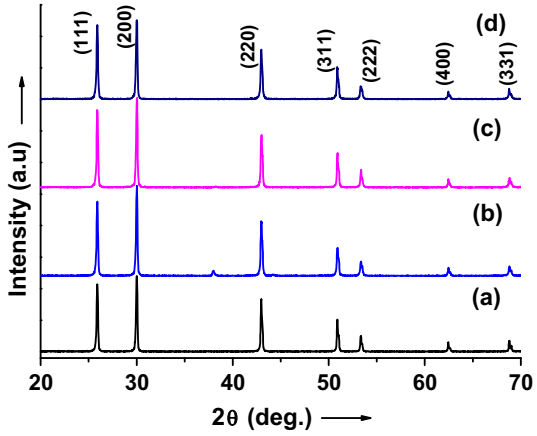

Fig. 1. XRD spectra of the products in en with reaction time of 6 h and reaction temperature of 180 °C assisted by L-cysteine of different concentration, (a) 0 mmol; (b) 0.01 mmol; (c) 0.02 mmol; (d) 0.05 mmol.

To further consider the influence of L-cysteine on the microstructure of PbS, FESEM images were performed, as shown in Fig. 2. It can be seen that PbS exhibited different morphologies when use different amounts of L-cysteine during synthesis. In Fig. 2a, morphologies of PbS were regular hexahedron structures consisting eight regularly stacked cubic modules when no L-cysteine were used. Small grooves were observed at six surface centers in part of PbS micro-crystals when small amount of L-cysteine were added during synthesis. These small grooves gradually enlarged to cross-centered notches with the increase of the concentration of L-cysteine. For instance, when 0.01 mmol of L-cysteine was introduced, most part of the surface was concaved and transformed to shape of quadrihedron (Fig. 2b). When the concentration of L-cysteine was gradually increased, the cube splayed to Octagonal Hierarchical structure (Fig. 2c and d). These differences could be attributed to the expansion of the crystal surface, caused by the introducing of L-cysteine.

HRTEM images and EDS spectrum were obtained for clear characterization of micro-shapes and composition of PbS micro-crystals (Fig. 3). HRTEM images further confirm the regular hexahedron structures.

Fig. 3a shows a typical low- magnification TEM image of a single PbS cubic module with the edge length of about 500 nm and regular hexahedron structure with the edge length of about 1 μm. Fig. 3b gives the details of Fig. 3a, and the fringe spacing of 0.34 nm observed in this image is close to the spacing of (2 0 0) lattice plane of PbS, indicating that the regular hexahedron structure grows preferentially along [1 0 0] direction. The growth pattern is consistent with the results reported in Refs. [34–36]. Peaks of the elements Pb and S were presented in the EDS spectrum in Fig. 2(f) and the atomic ratios were calculated. The results showed that the PbS micro-crystal is composed of 51.57% Pb and 48.43% S, which is close to 1:1 stoichiometry. It indicated that the products possessed a pure phase, which result is consistent with the above XRD results.

3.2. Influence of reacting temperature and reacting time on the microstructures and morphologies of PbS

Reacting temperature is another significant parameter that would strongly the growth of micro-crystal. Thus, growth of PbS between a large temperature range (80–180 °C) were investigated and results are displayed in Fig. 4.

With the increase of the reacting temperature, initial regular hexahedron structures with cross-centered grooves on their surfaces (Fig. 4a and b) gradually spread, and finally Octagonal Hierarchical flowerlike structures (Fig. 4c–f) were formed. Fig. 4a and b possess similar shape, and this is because the low temperature could not offer sufficient energy to trigger the formation of Octagonal Hierarchical structure. Fig. 4c–f shows that the micro-crystal begins to spread above 100 °C, and with increasing temperature, these flower-like structures become stable. Based on these observations, all products exhibit obvious Hierarchical structures, indicating that self-assembly were involved in formation of these morphologies.

In order to understand the growing mechanism of PbS nano-crystal, the microstructures of PbS with different reacting time under two typical reacting temperatures were studied, and the results were shown in Fig. 5. By prolonging the reacting time from 6 h to 12 h, the micro-structure of PbS underwent minor changes. All the PbS micro-crystals formed under 80 °C exhibit regular hexahedron structures with cross-centered grooves (Fig. 5a–d), while those obtained under 180 °C show Octagonal Hierarchical flowerlike structures (Fig. 5e–h). The differences are that fractures