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Star-shaped PbS crystals fabricated by a novel hydrothermal method

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Abstract

Star-shaped PbS crystals have been prepared by a novel thioglycolic acid (TGA) assisted hydrothermal method. X-ray diffraction reveals that the PbS crystals are well crystallized, with the cubic rock-salt structure. Transmission electron microscopy and scanning electron microscopy observations show that the PbS crystals are of star-shaped morphology. Furthermore, the mechanism and the critical factors for the TGA-assisted hydrothermal synthesis of star-shaped PbS crystals are preliminary presented.

1. Introduction

As an important IV–VI semiconductor, PbS has attracted considerable attention due to its special small direct band-gap energy (0.41 eV) [1]. Also, owing to their exceptional third-order nonlinear optical properties, PbS materials have a potential application in high-speed switching [2]. Moreover, PbS is also potentially useful for making devices that require small band-gap semiconductors with optical absorption and emission in the red and near-infrared region of the spectrum. Therefore, lots of effort has been employed to research PbS materials.

Various methods have been used for the preparation of PbS crystals, including sol–gel [3], micelles [4], and Langmuir–Blodgett [5]. Among them, the hydrothermal method provides a more promising way for the synthesis of crystals due to its low cost, high efficiency and potential for large-scale production. Qian *et al* reported a solvothermal synthesis of PbS crystals with several morphologies such as cubic [6], rod-like [7] and frame-film structures [8] in the presence of organic solvent. However, it is inevitable to use toxic, dangerous and expensive solvents in the solvothermal process. Very recently, our groups have employed a novel thioglycolic acid (TGA) assisted hydrothermal process to prepare CdS nanorods [9] and Bi_2S_3 nanowires [10]. As we know, materials with different morphologies exhibit dissimilar properties [11]. Addressing the above issue, we have used the TGA assisted hydrothermal process to successfully synthesize star-shaped PbS crystals, which may have wide potential applications in the future.

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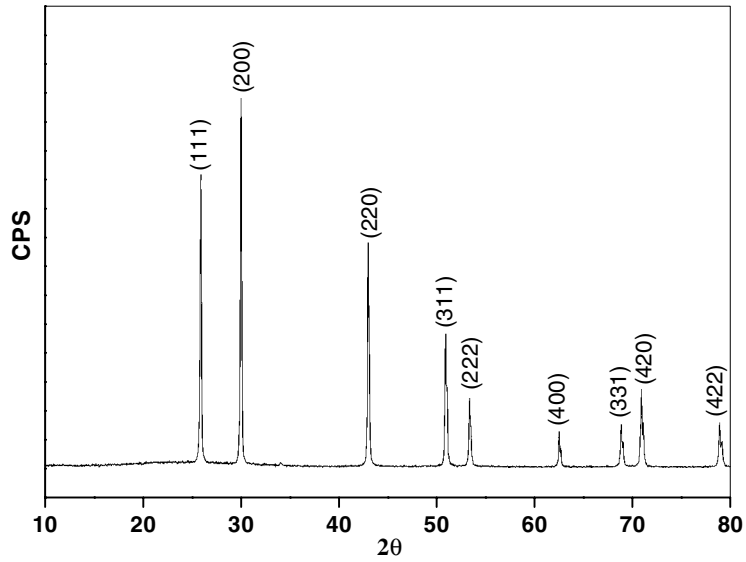

Figure 1. XRD pattern of star-shaped PbS crystals prepared by the TGA-assisted hydrothermal method.

2. Experimental details

All chemicals were analytical grade without further purification. First, 50 ml of $Pb(Ac)_2$ with a concentration of 0.01 M, 50 μl TGA, and 50 ml of thiourea with a concentration of 0.05 M were placed into a beaker. Then, NaOH with a concentration of 0.1 M was added into the beaker until the pH value was about 10. After stirring, the reactants were put into a Teflon-lined autoclave of 150 ml capacity, which was filled with deionized water up to 80% of the total volume. Next, the autoclave was maintained at 200 °C for 20 h, then cooled to room temperature naturally. The mixture turned black due to the formation of PbS precipitates. The products were filtered out, washed with alcohol and deionized water several times, and then dried at 60 °C for 30 min.

An x-ray diffraction (XRD) pattern was obtained on a Rigaku D/max-ga x-ray diffractometer with graphite monochromatized Cu Ka radiation ($\lambda = 1.541\,78$ Å) operating at 40 kV and 30 mA. TEM observation and energy dispersive x-ray (EDX) analysis were performed on a Philips CM200 high-solution transmission electron microscope (TEM) with an accelerating voltage of 200 kV. To prepare the TEM samples, the PbS powder was dispersed in alcohol with ultrasonic stirring; then a small drop of the solution was placed on a Cu grid covered with a carbon film. The SEM images were obtained on a JEOL JSM-T20 scanning electron microscope operating at 20 kV and a working distance (WD) 10 mm.

3. Results and discussion

All the peaks in the XRD pattern shown in figure 1 can be indexed to a cubic rock-salt structure of PbS with lattice constant $a = 5.936$ Å, in good agreement with JCPDS No 05-0592. By means of the XRD analysis, it was found that no impurities were detected. The strong and sharp diffraction peaks suggest that the products are well crystallized. Compared to the standard card, the strong (200) peak reveals the [100] oriented growth of the star-shaped PbS crystals.

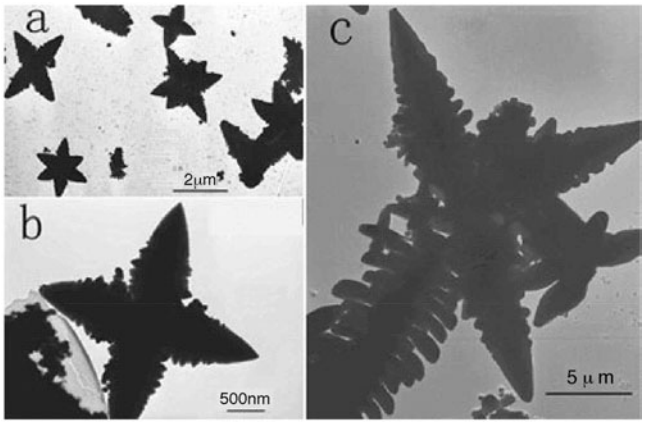

Figure 2. TEM images of star-shaped PbS crystals: (a) multi star-shaped PbS crystals; (b) individual star-shaped PbS crystals; (c) fishbone-like PbS crystals.

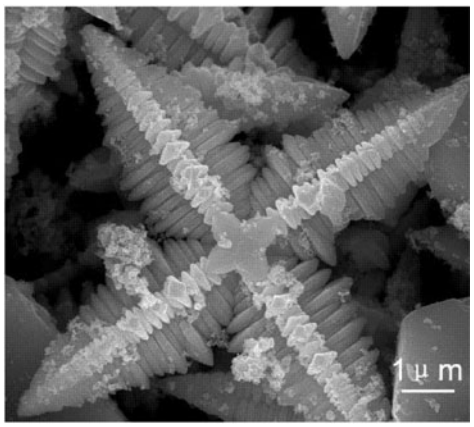

Figure 3. SEM image of star-shaped PbS crystals.

Typical TEM images of as-prepared samples are shown in figure 2. This clearly reveals the star-shaped with multi-rod morphology of PbS crystals, whose size ranges from several micrometres to about twenty micrometres. In addition, fishbone-like structures were also observed (figure 2(c)). Further morphology characterization of the star-shaped PbS crystals was carried out using SEM. Figure 3 shows a typical SEM image of the star-shaped PbS crystals.

The EDX spectrum of the PbS crystals is shown in figure 4. The very strong peaks for Pb and S are found in the spectrum, and no impurity was detected through the EDX spectrum. The C and Cu peaks came from the copper grid used to support the samples.

Previously, TGA was widely used as the stability agent preventing the nanocrystal from aggregating [12, 13]. In our synthetic route, TGA is critical for the formation of the star-shaped structure. The detailed mechanism can be expressed as follows.

$$Pb^{2+} + HSCH_2COOH \Leftrightarrow PbHS^+ + CH_2COOH^+ \quad (1)$$

$$PbHS^+ \Leftrightarrow PbS\downarrow + H^+ \quad (2)$$

$$mPbS + kHSCH_2COONa + kPb^{2+} + kOH^- \Leftrightarrow (PbS)_m(PbSCH_2COONa)_k^{k+} + kH_2O \quad (3)$$

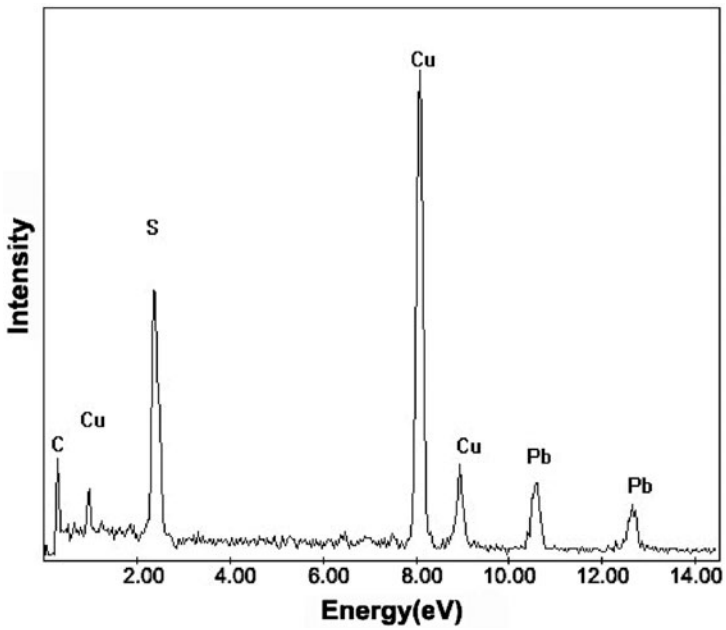

Figure 4. EDX spectrum of the individual star-shaped PbS crystal shown in figure 2.

$$(PbS)_m(PbSCH_2COONa)_k^{k+} \rightarrow (PbS)_m(Pb^{2+})_k + kSCH_2COONa^- \quad (4)$$

$$SC(NH_2)_2 + 2OH^- \Leftrightarrow S^{2-} + CH_2N_2 + 2H_2O \quad (5)$$

$$(PbS)_m(Pb^{2+})_k + kS^{2-} \rightarrow (m+k)PbS. \quad (6)$$

Prior to the hydrothermal process, the formation of PbS nuclei was carried out via reactions (1) and (2). Compared to the conventional hydrothermal process, in the TGA-assisted hydrothermal process, the major difference is the formation of $(PbS)_m(PbSCH_2COONa)_k^{k+}$ complex clusters in the solution via reaction (3). Reaction (4) represents the dissociation of SCH_2COONa^- from the complexed PbS clusters, and the dissociation of S^{2-} was controlled via reaction (5). Furthermore, we believe that the dissociation of SCH_2COONa^- occurs at a local region of the complexed PbS clusters, where the Pb^{2+} is exposed to the S^{2-} existing in the solution. Therefore, during the hydrothermal process, the formation of PbS proceeds along specific directions.

The formation of star-shaped PbS crystals indicates that the nucleation and growth of PbS crystals are well controlled by using thiourea as the source of sulfur. To verify this point, Na_2S was also used as the sulfur source while keeping other conditions unchanged. In this case, only cubic-shaped PbS nanocrystals could be obtained. Typical TEM images of the cubic-shaped PbS nanocrystals are shown in figure 5. As shown in figure 6, compared to the thiourea, Na_2S releases many more S^{2-} ions, which resulted in faster growth on the {111} faces and the formation of the cube-shaped PbS nanocrystals [14]. Moreover, in our work, it was found that the irregular PbS nanoparticles were formed by non-TGA-assisted hydrothermal method or a pH value less than 10 in the TGA-assisted hydrothermal method.

Therefore, TGA, thiourea and pH are three key factors for the hydrothermal formation of star-shaped PbS crystals. The exact mechanism for the formation of star-shaped PbS crystals in TGA-assisted hydrothermal process is still under investigation.

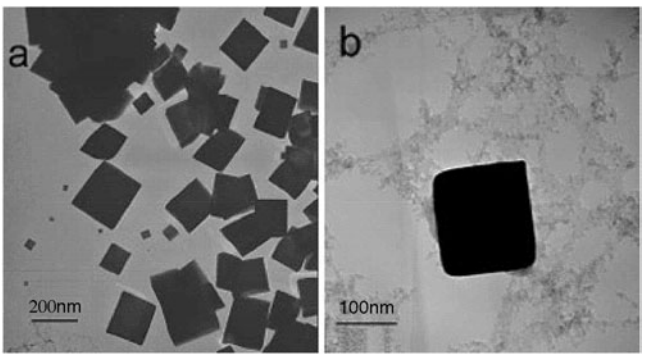

Figure 5. (a), (b) TEM images of cubic-shaped PbS crystals.

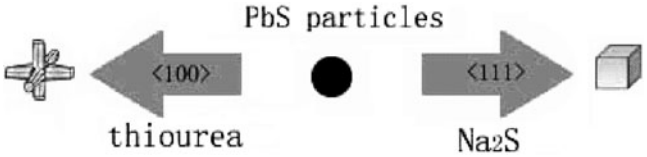

Figure 6. Schematic illustration of the formation of the PbS nanostructures.

4. Conclusion

Star-shaped PbS crystals have been successfully prepared by a TGA-assisted hydrothermal method. The growth mechanism of the star-shaped PbS crystals was discussed and the effects of TGA, thiourea and pH were proposed. Furthermore, it is reasonable to believe that the TGA-assisted hydrothermal process offers a great opportunity for the scaled-up preparation of other morphology chalcogenides.

Acknowledgments

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