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Hierarchical construction of PbS architectures based on the adsorption and sustained release of H_2S by TBAB

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ABSTRACT

Multi-arm PbS architectures were successfully synthesized in high yield by a facile hydrothermal process at 90 °C for 48 h, employing lead nitrate ($Pb(NO_3)_2$) and thioacetamide (TAA) as precursors. A new surfactant: tetrabutyl ammonium bromide (TBAB), was used in this process. The as-prepared PbS products are characterized by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and Fourier transform infrared (FT-IR) spectroscopy. The results showed that the concentration of TBAB, as well as the molar ratio of $Pb(NO_3)_2$ to TAA are crucial factors on the morphologies and sizes of the hierarchical PbS microcrystals. A reasonable possible new formation mechanism of hierarchical PbS structures based on the adsorption and sustained release of H_2S by TBAB has been presented.

1. Introduction

Recently, the three-dimensional (3D) hierarchical structures are of great interest to chemists and materials scientists due to their novel optical, electric, magnetic, and thermal properties, as well as their unique functions in the development of nanoscale electronic and optoelectronic devices [1]. As a result, there has been an increasing number of excellent studies on the fabrication of inorganic materials with various shape, which including surface tension, capillary effects, electric forces, alkaline etching and hydrophobic interactions [2–6]. To date, Co_2P nanostructures constructed by nanorods [7], PbTe symmetric hierarchical superstructures [8], arrays of submicron ZnO structures [9], monodisperse spherical polycrystalline CdS particles [10], and hierarchically structured nanowires made of In_2O_3, CeO_2, SnO, and V_2O_5/TiO_2 [11–14] have been successfully synthesized via different routes.

Lead sulfide (PbS), as an important IV-VI semiconductor with a small bulk band gap of 0.41 eV at 300 K and a large excitation Bohr radius of 18 nm [15], shows great promising application in many fields, such as thermoelectric and optical switching applications, solar electroluminescence, photoluminescence, mode-locking in lasers, and infrared (IR) photoelectric devices. Various methods, such as electrochemical deposition, sonochemistry, alkaline etching, chemical vapor transport, and the solvothermal method, have been used to control the generation of different structures, including star-shaped PbS macrostructures, hierarchical PbS nanowires, PbS nanobars, nanotubes, and PbS nanocrystals capped with 4-fluorothiophenol [16–20]. Huang and co-workers [21] prepared symmetrical hierarchical hollow PbS structures using a facile solvothermal process in the presence of ethylenediamine. They found that these PbS structures were constructed of nanowalls with a thickness of about 80 nm, and the near-infrared absorption spectrum showing a blue shift compared to bulk PbS. Yan and Shen [22] successfully synthesized well-aligned nanoporous PbS nanowire architectures, the resultant homogeneous individual nanowires in the architecture are straight, smooth and well-aligned. A simple, efficient and environmentally benign route has been developed.

This paper reports the synthesis and characterization of multi-arm PbS crystals via a facile hydrothermal route at low temperature by using a new surfactant, TBAB. The effects of reaction time, Pb^{2+}/TAA molar ratio, and the concentrations of TBAB on the morphologies of the final PbS crystals were investigated. A possible formation mechanism based on the adsorption and sustained release of H_2S by TBAB has been proposed.

2. Experimental

Synthetic Route: In a typical procedure, 7.5 mL of 0.05 M TBAB was added to 45 mL of distilled water under sonication. After 30 min of sonication, 3 mL of 0.5 M $Pb(NO_3)_2$, 6 mL of 1 M $C_4H_6O_6$ were added into the above solutions. At last, 3 mL of 0.5 M TAA was added dropwise. The mixture was stirred vigorously for 30 min and then sealed in the Teflon-lined stainless-steel autoclave. The tank was heated and maintained at 90 °C for 48 h. The system was then cooled to room temperature

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naturally. The final products were collected by centrifugation, washed with distilled water and absolute ethanol several times, and then dried under vacuum at 50 °C for 8 h.

The X-ray diffraction (XRD) patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu *Ka* radiation (λ = 1.5406 Å). Surface morphology was examined by a JEOL JSM-7001F field scanning electron microscope. TEM micrographs were obtained by a Japan JEM-100CX transmission electron microscope operated at 200 kV. Fourier transform infrared spectra were taken on a Nexus 470 FTIR spectrometer (Nicolet, USA).

3. Results and discussion

3.1. Sample characterization

XRD patterns of as-prepared products are shown in Fig. 1. All of the diffraction peaks can be clearly indexed as face-centered cubic (*fcc*) rock-salt-structured PbS, which is in good agreement with the standard JCPDS Card (05-592). No impurity phase was detected, indicating that products are pure. Similar phenomena can be obtained in other experiments. The intensity ratio of the (1 1 1) to (2 0 0) peak in our result is 1.72, obviously larger than the standard value (0.85). Such a variation indicates that the crystal has special anisotropic growth along these planes during the nanostructures' growing process. The sharp shape and narrow line widths of the diffraction peaks indicate that the PbS material is highly crystalline.

SEM images of well-defined, star-like PbS crystals synthesized by the controlled release of sulfide ions from TAA are shown in Fig. 2a. Almost all of the products are six-armed star-shaped macrostructures. Typical SEM images of the individual star-shaped crystals viewed from different angles display their three-dimensional (3-D) characteristic (see Fig. 2b and c). The stars have six symmetrical arms extending radially from the center. The length of these arms is about 9 μm, and each arm is composed of small dendritic structures that are parallel to each other and perpendicular to the arm. The TEM image in Fig. 2d proves the six-armed structure. Many nanoparticles were observed in the magnified TEM image, as shown in Fig. 2e, these nanoparticles appear to have cubic morphologies with an average length about 12 nm. To further confirm this nanostructure, HRTEM image of an individual nanocube is displayed in Fig. 2f. One can see clearly the good lattice fringes, which indicating that these PbS cubes are composed of single crystals. The lattice distance is determined to be about 0.30 nm, which is close to the (2 0 0) lattice spacing of the *fcc* PbS crystal, indicating that the growth direction of the PbS nanocubes is preferential along the ⟨1 0 0⟩ direction. The reason for the existing of nanocubes is the electron beam inducing effects in the TEM characterization course. In this process, a local thermal field will form in the surface of the PbS products under the electron beam irradiation. The temperature in the central part of the thermal filed is higher than that of the peripheral part and gradient thermal filed is formed. This will make the Pb and S atoms in the PbS surface diffuse into the peripheral part and tiny nuclei formed in cooling process. These tiny nuclei will grow with the continue diffusion. This can be further certified by the fact that there more nanocubes in the TEM image (Fig. 2e) than in the SEM image (Fig. 2a).

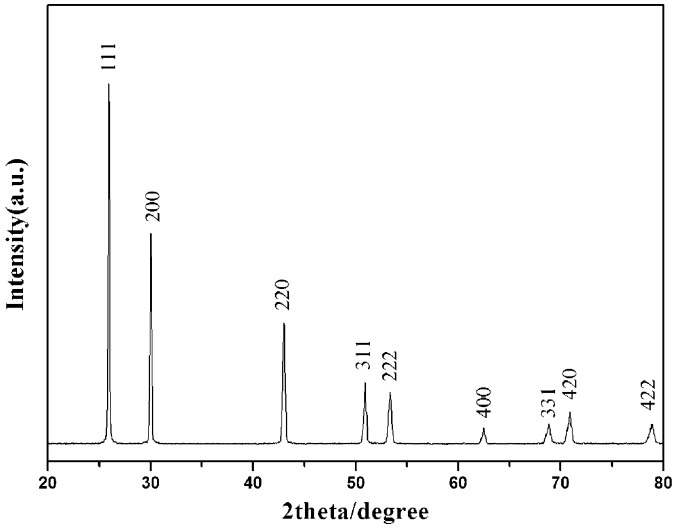

Fig. 1. XRD pattern of PbS formed at [TBAB] = 0.05 M for 48 h.

3.2. Effects of TBAB

TBAB, which has a chemical structure similar to cetyltrimethyl ammonium bromide (CTAB), is rarely studied in the synthesis of macro/nanostructures. Thus, the role of TBAB is carefully explored in our experiment. When other experimental parameters are kept constant (90 °C for 48 h) but the amount of TBAB is varied, the morphology of the resulting products experiences tremendous changes. When no TBAB was added, only submicrobars with diameters ranging from 60 to 100 μm were obtained, which is different from the morphology of the before mentioned products in Fig. 3a. A magnified SEM image of the product (Fig. 3b) reveals that these submicrobars are cuboid in shape with width and length diameters in the ranges of measures 10–15 and 40–80 μm, respectively. The formation of many smaller particles can be observed when the concentration of TBAB was increased to 0.02 M (Fig. 3c), while the proportion of submicrobars decreased. A magnified SEM image of the product (Fig. 3d) shows that the surface of the bars is loose and rough. With the increase of TBAB concentration, more small particles formed and the proportion of submicrobars decreases (Fig. 3e and f). Well-defined hierarchical PbS crystals can be obtained when the TBAB concentration was increased to 0.05 M (see Fig. 2a). When 0.1 M TBAB was used, 3-D PbS structures with six symmetric arms are obtained (see Fig. 3g). A magnified SEM image of the product (see Fig. 3h) indicates that the arms are smooth and have spindle-like shapes, while four rows of prominent parts symmetrically grow on the surface of the trunk along the long axis of the arm. When the concentration of TBAB was increased to further 0.15 M, we surprisingly found that the products consist mainly two types of morphology: octahedral and arm-like structures. Most octahedral products possess perfect morphology with sharp corners and well-defined edges, as shown in Fig. 3i. The octahedral edge lengths range from 5 to 8 μm. Some dendritic structures are also seen in the products. While the arm-like structures are composed of one trunk with a diameter of about 8 μm and several branches. These branches are parallel to each other, are in the same plane, and are perpendicular to the trunk (Fig. 3j).

In order to further understand the effects of TBAB, the X-ray diffraction (XRD) patterns and energy-dispersive X-ray spectra (EDS) of the products prepared with different concentrations of TBAB were recorded. The XRD patterns reveal that the submicrobars prepared without TBAB are well crystallized (Fig. 4a), but are not PbS. Their EDS spectra indicate that the chemical composition of these bars includes Pb, O, and C. While S, an element in PbS, is not observed (see Fig. S1a). With increasing TBAB concentrations, the characteristic peaks of PbS are intensified, while those of the bars are weakened before finally disappearing when the concentration of TBAB was increased to 0.02 M (Fig. 4b–d). The EDS spectra of the products show that the chemical composition of these bars is still Pb, O, and C (see Fig. S1b and d). However, the formation of smaller particles composed of Pb and S is also observed (see Fig. S1c and e). Moreover, according to the quantitative analysis from EDS, the molar ratio of Pb to S is 1:1.04, which is almost consistent with stoichiometric PbS. To the best of our knowledge, this is the first time that the preparation of two dif-