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Shape controllable preparation and characterization of hierarchical PbS submicron cubes via a solvothermal method

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Abstract The controlled synthesis of PbS nanostructures with crystal morphology of hierarchical submicron cubes has been realized by chemical synthesis between lead acetate trihydrate and sulfur via a solvothermal route. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy were used to characterize the products. It was shown that well-dispersed and hierarchical PbS submicron cubes were formed at low temperature. Experiments demonstrated that the morphologies of PbS crystals were significantly influenced by treatment temperature, reaction time, and sulfur sources. A growth model was proposed for the selective formation of hierarchical PbS submicron cubes. Our work demonstrated the growth of hierarchical PbS architectures through a one-step, surfactant-free and solution-phase chemical route under controlled conditions.

Introduction

The architectural control of nano- and micro-crystals with well-defined shapes is an important goal of modern materials chemistry because of the importance of the shape and texture of materials in determining their widely varying properties [1–3]. Specifically, many recent efforts have been devoted to the morphological control and spatial patterning of semiconductor nanocrystals of metal sulfides [4–6].

As an important IV–VI group semiconductor, PbS has attracted considerable attention owing to its especially small direct band gap (0.41 eV at 300 K) and a larger excitation Bohr radius of 18 nm [7]. It has been widely studied in many applied fields such as IR photodetectors, photovoltaics, solar absorbers, electroluminescence, thermal and biological images, and mode-locking in lasers [8–14]. Moreover, an exceptional third-order nonlinear optical property of PbS nanoparticles has been found, which makes PbS nanocrystals a promising candidate for photonic and optical switching device applications [15]. Consequently, obtaining PbS nanocrystals with different morphologies is potentially meaningful in finding novel applications.

Until now, different morphologies of PbS have been observed including nanotubes [16], hollow nanospheres [17], star and dendritic structures [18], nanowires [19], etc. The routes for the synthesis of PbS also involves hydrothermal [18, 20], solvothermal [21, 22], template-assisted [23], microwave irradiation [24], thermal decomposition [25], etc. Among these methods, hydrothermal and solvothermal routes in the presence of surfactants or with the help of hard templates are especially intriguing because of their simplicity and low cost. However, it is known that the use of surfactants or hard templates will inevitably increase the reaction complexity, cause impurity in the products, and is disadvantageous from the viewpoint of green chemistry. Thus, the development of a facile, effective, and surfactant-free approach for the controlled preparation of PbS crystals is highly desirable for the detailed

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investigation of its growth behavior and the potential large-scale production.

In this paper, we reported the fabrication and characterization of hierarchical PbS submicron cubes by a facile solvothermal reaction between lead acetate trihydrate and sulfur in ethylenediamine (en), none of surfactants nor other templates were used in the reaction system. To the best of our knowledge, preparing PbS crystals in en system by using element sulfur as the sulfur source has not been reported to date. Furthermore, this kind of hierarchical submicron cubes has not been reported previously for PbS nanomaterials. The effects of temperature, reaction time, and sulfur sources on the morphologies of the final PbS crystal were investigated. The formation mechanism of such novel hierarchical architectures was discussed. These hierarchical PbS architectures may have great potential application in the fundamental study of nanostructures as well as fabricating nanodevices based on these architectures.

Experimental

All chemicals (Shanghai Chemicals Co. Ltd.) used in this work were of analytical reagent grade and used as received without further purification.

Synthesis

Solvothermal reaction

For a typical synthesis, the precursor solid **1** (1 mmol lead acetate trihydrate) was dissolved in 40 mL ethylenediamine (en), and then the precursor solid **2** (2 mmol element sulfur) was added into the solution under vigorous stirring for 30 min. The autoclave was then placed in an oven at the desired temperature and time. The obtained product was centrifuged and washed several times with distilled water and ethanol and dried under vacuum at 50 °C for 4 h. The reaction conditions were varied to explore the effect of different reaction parameters on the size and morphology of the product.

Effect of reaction temperature

The typical procedure was followed for constant reaction time of 24 h but with varying the temperature from 90 to 120 °C, and 150 °C.

Effect of reaction time

The above procedure was followed at constant reaction temperature of 90 °C, but the reaction time was varied at 1, 5, 12, 18, and 24 h.

Effect of sulfur sources

In this procedure, element sulfur, Na_2S, thioacetamide (TAA, H_3CCSNH_2), and thiourea ($SC(NH_2)_2$) were used with constant molar ratio of Pb:S (1:2), constant reaction time (24 h), and constant reaction temperature (90 °C).

Instruments and characterization

The identity and the phase of the products were verified by the X-ray powder diffraction using a Dmax-3β diffractometer with nickel-filtered Cu K_α radiation ($\lambda = 1.5417$ Å). The surface morphology and the distribution of the product were analyzed using the JEOL JSM-6700F field emission scanning electron microscopy (FESEM). The size, morphology, and selected area electron diffraction (SAED) pattern of the products were determined from a Tecnai F20 transmission electron microscope (TEM).

Results and discussion

In our experiments, by varying the experimental conditions such as the reaction temperature, treatment time, and sulfur sources, PbS crystals with controllable morphologies were conveniently obtained using our proposed method.

Influence of reaction temperature

Figure 1a, b, and c shows typical XRD patterns of the as-prepared products collected after 24 h at the temperature of 90, 120, and 150 °C, respectively. The diffraction patterns distinctly indicate the fine crystallinity of the obtained samples. All diffraction peaks can be assigned to the crystalline PbS in a cubic structure with a lattice constant of $a = 5.936$ Å, which is in good agreement with the literature values (JCPDS Card No. 05-592). No peaks of impurities are detected, indicating that phase-pure PbS can be readily synthesized at low temperature via the solvothermal route.

The SEM images shown in Fig. 2 provide direct information about the size and typical morphologies of the as-synthesized PbS products grown at different temperatures. SEM image in Fig. 2a reveals that PbS products prepared at 90 °C are well dispersed and exhibit a cube-like morphology. The magnified SEM image (Fig. 2b) clearly shows that the PbS samples are hierarchical submicron cubes with the unique size in the range of 400 to 500 nm. The hierarchical submicron cubes are stacked layer by layer. Figure 2c, d shows general morphologies of the PbS samples synthesized at 120 °C. Different from the PbS products prepared at 90 °C, the PbS samples synthesized at 120 °C have two sorts of morphologies, including hierarchical cubes and

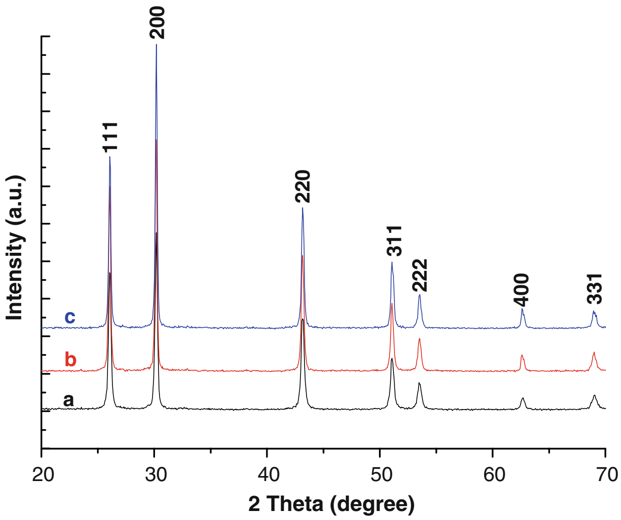

Fig. 1 XRD patterns of PbS crystals obtained at different temperatures: (*a*) 90 °C, (*b*) 120 °C, and (*c*) 150 °C, with reaction for 24 h using element sulfur

irregular aggregates. The hierarchical cubes prepared at 120 °C with a mean size of 1 μm are larger than those synthesized at 90 °C. The irregular aggregates are composed of numerous nanocubes with the size in the range of 50 to 100 nm. With a further increase in temperature up to 150 °C, the morphology and size of the PbS products is similar to those prepared at 120 °C, which can be seen in Fig. 2e, f.

TEM imaging was employed to further investigate the morphologies and crystallographic features of the PbS products. TEM image and SAED pattern for the PbS crystals synthesized at 90 °C are illustrated in Fig. 3. Hierarchical submicron cubes with a unique size from 400 to 500 nm can be clearly observed, which confirms the results in Fig. 2. Figure 3b is the SAED pattern of the hierarchical submicron cube, implying its poly-crystalline nature.

Time-dependent experiments

The formation of the hierarchical submicron cubes can be rationalized on the basis of the above investigations on varying the reaction time. All the diffraction peaks for the PbS products synthesized at 90 °C for different periods of time (see Figure S1 in the Supporting Information) can be indexed to cubic PbS crystallites (JCPDS file No. 05-592) and no other peaks (impurity) are apparent. The XRD patterns indicate that the reaction rate in the solution is rather rapid and pure PbS products have been fabricated after 1 h. With the extension of growth time, the degree of crystallization is higher and higher.

The SEM images of the products obtained by varying the reaction time reveal that it forms irregular aggregates composed of nanocubes with the size less than 100 nm (see Figure S2 in the Supporting Information) in 1 h and on increasing the reaction time to 5 and 12 h, the growth and self-assembly results in the formation of larger nanocubes with the size ranging from 200 to 300 nm (see Figures S3 and S4 in the Supporting Information). With a further reaction time increase to 18 h, more and more nanocubes interlace together to form hierarchical structures (see Figure S5 in the Supporting Information). Finally, when the reaction duration was increased to 24 h, almost all PbS were hierarchical submicron cubes, which can be seen in Fig. 2a, b.

Effect of sulfur sources

To explore the influence of sulfur sources on the morphologies of final PbS products under otherwise same reaction conditions, Na_2S, thiourea, and TAA were used as sulfur sources instead of sulfur powder. When Na_2S was adopted, large amounts of PbS nanoparticles were present and the mean size of the nanoparticles was about several tens of nanometer (see Figure S6 in the Supporting Information). Numerous PbS nanocubes in the range of several tens of nanometers to 100 nm were obtained by employing TAA as the sulfur source (see Figure S7 in the Supporting Information). However, different shapes of PbS crystals were observed when thiourea was used as the sulfur source (see Figure S8 in the Supporting Information), including concaved microcubes and dendrite-like nanostructures. The microcubes with the size of 1–2 μm were concaved from the center of the six facets. Among these concaved microcubes, some concavities were relatively shallow, and eight small submicron cubes were formed on the eight vertexes of a microcube; other concavities were deep, and collapses further happened on the eight small submicron cubes, resulting in the hierarchical architectures on the vertexes of a microcube. The average length of the dendrite-like nanostructures with many small branches was about 2 μm. The branches were about 400 nm in length and 100 nm in width with an aspect ratio of 4. Above results demonstrated the strong dependence of final PbS morphology on the kinds of sulfur sources.

Growth mechanism

The formation of PbS crystals with various shapes is determined by the nucleation and the subsequent growth stages. The growth process develops according to the crystal habit and to the branching process. In our synthetic route, en solvent plays a major role in the reaction. En solvent might not only act as a coordination agent [25], but also play an important role in generating S^{2-} ions in the system [26], which are both significant for the growth of

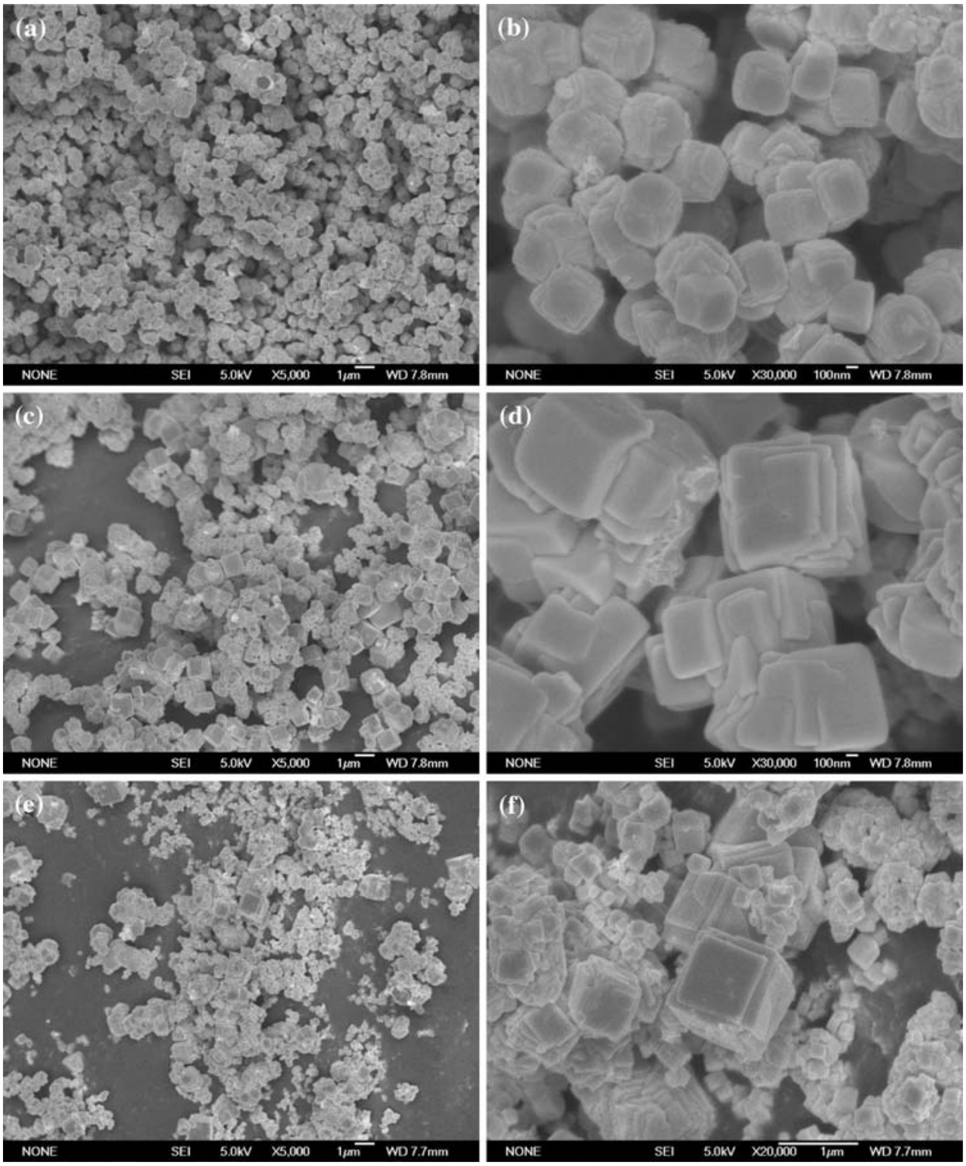

Fig. 2 SEM images of PbS crystals prepared at different temperatures: **a**, **b** 90 °C; **c**, **d** 120 °C; and **e**, **f** 150 °C, with reaction for 24 h using element sulfur

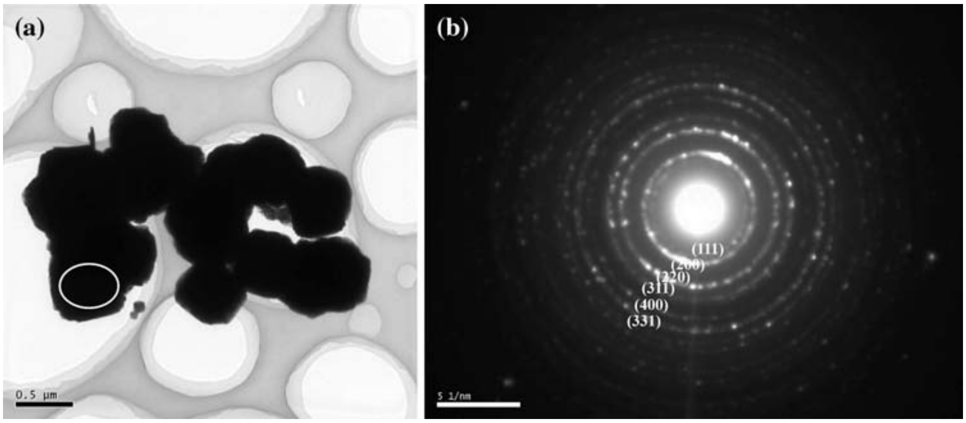

Fig. 3 **a** TEM image of PbS crystals at the temperature of 90 °C with reaction for 24 h using element sulfur. **b** SAED pattern of the submicron cube marked in (**a**)

PbS crystals. First, en acted as nucleophilic agent, attacking Pb^{2+} ions to form an intermediate organometallic complex $Pb(en)_2^{2+}$. After sulfur was dissolved in en, S^{2-} ions generated and reacted with $Pb(en)_2^{2+}$. Therefore, the formation procedure of PbS crystals can be formulated as follows:

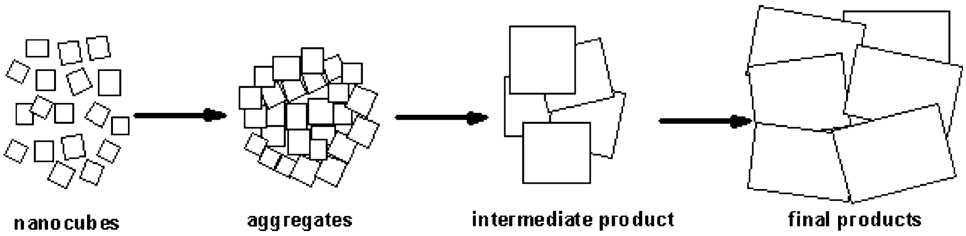

Fig. 4 Illustration for the growth process of hierarchical PbS submicron cubes using element sulfur

$$Pb^{2+} + 2en \rightarrow \left[Pb(en)_2\right]^{2+} \quad (1)$$

$$S_N + 2NH_2CH_2CH_2NH_2 \rightarrow \left[NH_2CH_2CH_2NH - S_{N-1} - NHCH_2CH_2NH_2\right]^{2+} + H_2S \quad (2)$$

$$\left[Pb(en)_2\right]^{2+} + S^{2-} \rightarrow PbS \quad (3)$$

On the basis of the above analyses and the experiment results, we propose the following growth mechanism for the hierarchical architectures at 90 °C. At the initial stage of the reaction (1 h), PbS nuclei were formed and grown into PbS nanocubes. These nanocubes were not stable because of their high surface energy and assembled into aggregates. The principles for assembling the nanocubes were to face the same type of faces, such as {100} to {100}, and align them in the same orientation to enhance the packing density [27]. In the subsequent steps (5, 12, and 18 h), PbS nanocubes with the size less than 100 nm were grown into larger cubes through combining with adjacent nanocubes. The large cubes interlaced with each other. Finally, with a further extension of reaction duration (24 h), hierarchical submicron cubes were formed. On the whole, the growth model of the hierarchical PbS submicron cubes is schematically illustrated in Fig. 4.

The reaction temperature is an important factor influencing the growth of PbS crystals, which is proved by temperature-dependent experiments. When the reaction was preceded at 120 or 150 °C, larger hierarchical PbS cubes and irregular aggregates composed of small nanocubes were formed. It was possible that the comparative high temperature disturbed the equilibrium of the solution. Accordingly, some hierarchical PbS submicron cubes were grown into larger hierarchical PbS microcubes.

It is also worth mentioning here that sulfur sources have great effects on the final morphologies of PbS crystals. As we know, different sulfur sources have different release rate of S^{2-} ions. Once Na_2S was introduced into the en solution, it dissociated into Na^+ and S^{2-} immediately, and therefore the formation of PbS nuclei occurred rapidly. As a result, PbS nuclei grew in an explosive way to form PbS nanoparticles because of the high concentration of S^{2-}. TAA released S^{2-} at room temperature, but the concentration of S^{2-} was a little lower than S^{2-} released from Na_2S. PbS nuclei had the trend toward nanocubes when TAA was introduced into the reaction system. For sulfur powder and thiourea as sulfur sources, the release of S^{2-} only occurred when the reaction temperature reached a certain value to make sulfur sources to produce S^{2-}, and thus the nucleation and growth of PbS crystals were mainly completed at relatively high temperatures. In sulfur-en system, the release rate of S^{2-} was rather slow, resulting in sufficient growth of PbS nuclei to form PbS submicron cubes. The submicron cubes then interacted with each other to produce the hierarchical PbS submicron cubes. In thiourea-en system, the release rate of S^{2-} was also slow, but the PbS crystals were concaved microcubes and dendrite-like nanostructures. When thiourea was introduced into Pb^{2+} solution, the strong complex action between Pb^{2+} and thiourea led to the formation of Pb–thiourea complexes [28].As a consequence, the Pb–thiourea complexes and above-mentioned $Pb(en)_2^{2+}$ complexes vied each other. The two complexes underwent decomposition processes to release Pb^{2+} under the solvothermal conditions. The growth process of PbS crystals was not only manipulated by the release rate of S^{2-}, but also was controlled by the release of Pb^{2+} from Pb–thiourea and Pb–en complexes. It was these factors that resulted in the strange morphology of PbS crystals.

Conclusions

In summary, hierarchical PbS submicron cubes have been prepared by employing lead acetate trihydrate and sulfur as precursors via a facile, template-free, low-temperature solvothermal synthesis. The advantages of our method for the synthesis of hierarchical architectures lie in the low temperature and mild reaction conditions, which permits large-scale production at low cost. The hierarchical PbS submicron cubes may have great potential applications in the fundamental study of nanotechnologies. In addition, this approach is expected to be employed for the control-shaped synthesis of other semiconductor nano- and microstructures.

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