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A Highly Regular Hexapod Structure of Lead Sulfide: Solution Synthesis and Raman Spectroscopy

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Abstract: A highly regular hexapod-like structure of PbS with six symmetric arms has been synthesized by a simple and mild chemical solution route. The hexapod-like PbS structure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). The results show that each arm is perpendicular to the other four, and opposite to the last one. The arms are about 0.3–0.6 μm long, which have about 40–60 nm tips and 150–200 nm base. And the arm shows an icicle-like structure and some clear steps, and grows along ⟨100⟩ directions. The most possible growth mechanism discussed herein is based on the characterization results. The Raman spectra of the hexapod-like PbS structure were investigated. The results show that our products are sensitive to the laser and can be photodegraded easily.

Keywords: crystal growth · hexapod structure · lead sulfide · Raman spectroscopy

Introduction

In recent years nanosemiconductors have attracted the attention of researchers due to their electronic and optical properties and extensively potential applications in various devices, such as light-emitting diodes,[1] single electron transistors[2] and field-effect thin-film transistors.[3] The properties of semiconductor materials can be tuned by varying their shapes and sizes;[4] thus the architectural control of nano- and microcrystalline materials with well-defined shapes and sizes is an important goal in modern materials chemistry. As an important Group IV–VI semiconductor, PbS is an attractive sulfide semiconductor with narrow band gap energy of 0.41 eV and has been widely used in many fields such as a Pb^{2+} ion-selective sensor,[5] in photography,[6] as a IR detector,[7] and solar absorber.[8]

Many different morphologies of lead sulfide nanomaterials have been synthesized by several routes including quantum dots,[9–14] nanorods and nanowires,[15,16] nanotubes,[17] clover-like structure,[18] star-shaped PbS crystals,[19–22] and dendritic structures.[22–24] For example, PbS whiskers were synthesized by heating PbS at 800 °C in a vacuum chamber in the early 1970s.[25] Other PbS structures can be obtained by reaction of sulfur and lead in liquid ammonia at room temperature.[26] Uniform cube-shaped PbS nanocrystals (<10 nm) were produced by mixing metal–oleylamine complexes with sulfur at 220 °C. Larger particles (≈50 nm) were prepared by sintering the precursor in aerosols.[27] Star-shaped PbS nanocrystals have been synthesized in aqueous solutions of mixed cationic/anionic surfactants.[21] Other unique star-shaped PbS nanocrystals with six symmetric arms along the ⟨100⟩ direction[19] and eight symmetric arms along the ⟨111⟩ direction[20] were synthesized by chemical methods. Hexpod-like PbSe nanomaterials have been synthesized by Murray and co-workers.[28]

In this paper, a highly regular hexapod-like nanostructure of lead sulfide (PbS) with six symmetric arms has been synthesized by a simple and mild chemical solution route. Each arm shows an icicle-like structure with apparent steps.

It is well known that lead ions can be reduced by hydrazine monohydrate. Using Pb as precursors, we present in this paper the synthesis of lead sulfides by a reaction between lead and hydrogen sulfide, which was obtained by decomposition of thiourea. The Pb precursors was obtained by

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the reduction of $PbCl_2$ with hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) in the presence of polyvinylpyrrolidone (PVP, M_w 40000) at the constant temperature, then thiourea as the sulfide source was added into the Pb precursors solvents. A hexapod-like lead sulfides nanostructure was finally obtained from the reaction between lead and hydrogen sulfide.

Generally the whole growth process of hexapod-like PbS crystals can be separated into two steps. First, the Pb metal precursor is synthesized via deoxidizing Pb^{2+} ions with $N_2H_4{\cdot}H_2O$. The formation of the precursor is likely to involve the following chemical reactions:

$$Pb^{2+} + N_2H_4 \rightarrow \ldots \rightarrow Pb\downarrow + 4\,NH_3\uparrow + 2\,N_2\uparrow + H_2\uparrow + 2\,H^+ \tag{1}$$

Second, PbS was formed through reaction between Pb and H_2S which decomposed from thiourea. The reaction process can be expressed as follows:

$$NH_2CSNH_2 + 2\,H_2O \rightarrow 2\,NH_3\uparrow + H_2S\uparrow + CO_2\uparrow \tag{2}$$

$$Pb + H_2S \rightarrow PbS + H_2\uparrow \tag{3}$$

In first step, $N_2H_4{\cdot}H_2O$ serves a reducing agent during the reaction and the PVP molecules probably act as soft templates. With regard to the second step, we can assume the temperature of the thiourea in ethylene glycol plays an important role. Due to the boiling point of ethylene glycol of 197 °C, thiourea will slowly decompose at the reaction temperature of 154 °C according to the reaction kinetics. In our other works, the mixed solution was heated close to the boiling point (195 °C) or heated under reflux, though thiourea decomposed so quickly, that we only obtained irregular nanostructures.

Results and Discussion

Characterization of the hexapod-like PbS: Figure 1 shows the X-ray diffraction (XRD) pattern of a typical PbS sample. The strong diffraction peaks excluding the weak peaks marked with star can be indexed to the face-center cubic structure of PbS with lattice constant $a = 5.923$ Å, which is in good agreement with the literature value (JCPDS No. 78-1899). The star-marked peak can be assigned to (111) (200) (220) lattice planes of the precursor metal lead (JCPDS No. 01-0972). And the strong and sharp peaks indicate that the as-synthesized PbS are well crystallized. It is worth noting that the ratio between the intensities of the (200) and (111) diffraction peaks is higher than the conventional value (1.33 versus 1.06), indicating that our product is abundant in {100} facets, and thus lead to relatively greater accelerated growth along the ⟨100⟩ directions.

The morphology of the hexapod-like PbS was visualized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

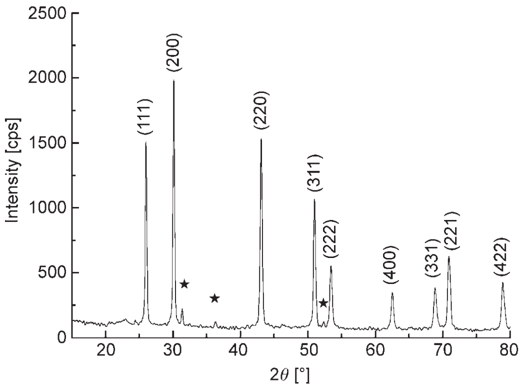

Figure 1. XRD pattern of the as-synthesized lead sulfide.

Figure 2 depicts typical SEM and TEM images of the products, clearly showing that PbS crystals possess a simple and uniform hexapod-like structure. It can be seen that almost every PbS grain has six symmetric arms and each arm shows an icicle-like structure with occasional steps on them. Each arm is perpendicular to the other four and opposite to the last one. The arms are about 0.3–0.6 μm long, which have about 40–60 nm tips and 150–200 nm diameter at the base of the arm. High-resolution TEM (HRTEM) images (Figure 3) provide further insight into the nanostructures of the PbS crystal.

Figure 3a shows a typical HRTEM image of one individual PbS crystal showing well crystallized structure. Figure 3b and c gives the details of the tip and side of one arm. The fringe spacing is determined to be 0.34 nm, which is closed

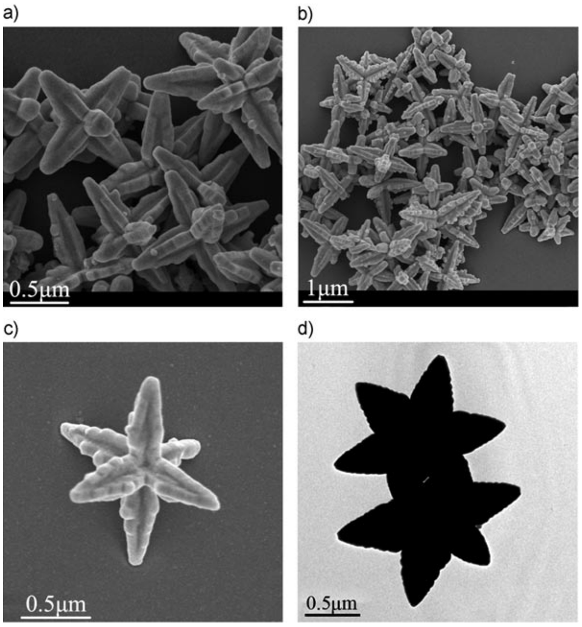

Figure 2. SEM and TEM images of the as-prepared PbS showing hexapod-like morphologies. a),b) Arms of the PbS grain with clear steps. c) PbS grain which only shows bulges on it's arms. d) PbS grain without steps.

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to the (111) lattice spacing of the bulk PbS, indicating that the six arms of the hexapod-like PbS crystals are parallel to the ⟨100⟩ directions. It revealed that the our PbS crystalloid grows along the ⟨100⟩ directions. Another arm was investigated in Figure 3d which plumbs to the arm showing in Figure 3b, and the corner of two arms was shown in Figure 3e, which are orthogonal to each other. The fringe spacing in Figure 3d, e corresponds to (220) planes of PbS lattice. In the details of the corner of two arms shows in Figure 3e, no grain boundary was detected. So, from all the details of PbS crystals (Figure 3b–e), it can de concluded that the individual PbS crystalloid is a single crystal.

Growth mechanism of the hexapod-like PbS: Several studies associated with the growth mechanisms of PbS crystals have been investigated. HRTEM analyses of a series of dendritic[23,24,29] and star-shaped[19] structures have shown that the formation of the cross-like structure occurs through preferential growth of the truncated octahedron-shaped PbS seed ⟨100⟩ directions. In this paper, our products show a more intuitive phenomenon of the cross-like structure growing along ⟨100⟩ directions.

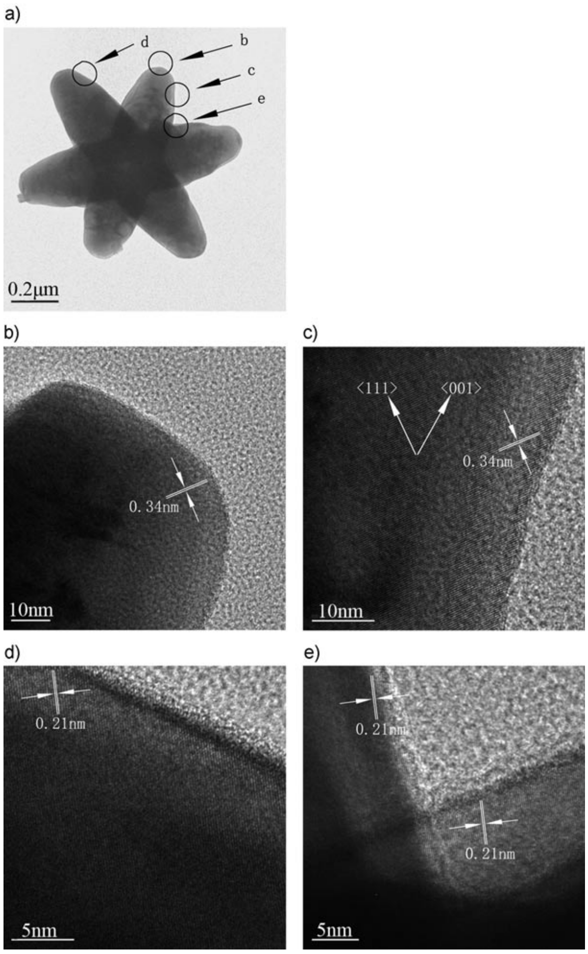

Figure 3. HRTEM images of one of the individual PbS crystal showing well crystallized structure. a) Bright field TEM image of one individual hexapod-like PbS crystal. b), c) HRTEM image of one arm, the tip of the arm with 50 nm width shows in b) and the side of the arm shows in c). d) HRTEM image of another arm which plumbs to the arm showing in b). e) HRTEM image of the corner of two arms.

Regarding the mechanism for the growth of hexapod-like PbS crystals which grows along ⟨100⟩ directions, we believe that both the temperature and PVP (see below) play important roles. As reported by Lee,[19] at low-temperature conditions (140–180°C), the growth on the (100) faces is favored for the PbS grain which may result in star-shaped nanocrystals. Thus, it is reasonable that our products grow along ⟨100⟩ directions at the temperature of 154°C.

Furthermore, in our system, PVP was introduced. It has been shown that a strong interaction exists between the surfaces of nanoparticles and PVP through coordination bonding with the O and N atoms of the pyrrollidone ring.[30,31] We believe that PVP as capping molecules can selectively stabilize the {111} faces since it can strongly interacts with the charged {111} faces containing Pb or S only rather than the uncharged {100} faces which contain mixed Pb/S[32] through coordination bonding, which is similar to the interaction reported by Qi.[21] So the surface energy of the {111} faces decrease largely leading to further greater accelerated growth on the {100} faces relative to the {111} faces. Therefore our products present a greater accelerated growth along the ⟨100⟩ directions, which is in excellent agreement with the XRD result presented above.

To investigate the growth process of the hexapod-like PbS, a few aliquots which contain the PbS materials were taken out at different times after the thiourea was added and the reaction mixture rapidly cooled down to room temperature.

The TEM images of the PbS materials obtained at different heating times are shown in Figure 4. After 5 min upon the addition of thiourea, a PbS nucleus with about 1–2 nm diameter was formed (Figure 4a). Further 15 min into the reaction the hexapod-like PbS with six arms (about 50 nm length) was observed (Figure 4b), along with a PbS crystal with four arms which grew partly was also founded from Figure 4b. The arm length is obviously smaller than the final products. Figure 4c depicts the hexapod-like PbS arms after 30 min grown to about 0.2 μm, which were near the final products length.

Figure 5 shows the schematic representation of the most possible mode of formation of the hexapod-like PbS. First, the cubic PbS nucleus is formed, then preferential growth along the six ⟨100⟩ directions leads to the formation of hexapod-like PbS (Figure 5a). The arms of the PbS grains may present a subordinate growth along the four ⟨100⟩ directions which are perpendicular to the arm's growth direction (Figure 5b). Thus we can observe some clear steps on arms of some PbS grains.

Raman scattering of the hexapod-like PbS: Since the hexapod-like PbS crystals (with six arms, each arm about 0.3–0.6 μm long and 40–60 nm tips) are considerably larger than the exciton Bohr radius (18 nm), quantum-confinement effects are not expected, though the optical properties of

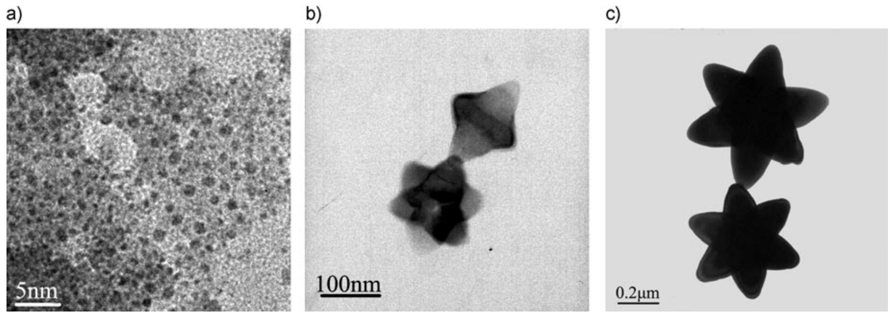

Figure 4. TEM images of the PbS crystals formed after the thiourea was added into the synthesis system: a) 5 min, b) 15 min, c) 30 min.

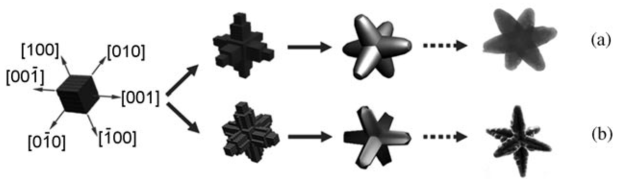

Figure 5. Schematic representation of the growth mode of the hexapod-like PbS. a) Preferential growth along the six ⟨100⟩ directions. b) Further subordinate growth along the four ⟨100⟩ directions which are perpendicular to the arm's growth direction.

nanocrystals are generally impacted by many factors, such as the size, shape, defects and size distribution of the crystals. So it is still worth measuring the optical properties to reveal any possible shape (or defects)-dependent effects.

Raman spectra of the samples were collected by using confocal Raman spectroscopy. The sample was globally illuminated by a He/Ne laser operating at 632.8 nm. The laser radiation was focused on the sample by means of a high-power ×100 microscope objective after passing through a narrow band-pass filter (BPF). The PbS samples were deposited on a conducting glass substrate. The signal integration time was 100 s. In our experiments, the maximal laser power delivered to the sample was 15 mW and could be monitored by a filter wheel with optical densities of 0.3, 1 and 2, which were abbreviated as D0.3, D1, D2, respectively.

A typical Raman spectrum of the hexapod-like PbS with 50 μW (monitored by D2, which means the laser power delivered to the sample after monitored by D2 was 0.15 mW, but only about 50 μW reached the sample) laser power is shown in Figure 6. The strong peaks at 210 and 451 cm^{-1} were clearly observed from Figure 6 which are attributed a one-LO (longitudinal optic) phonon mode and a two-LO phonon mode (the first overtones of the LO phonon mode), respectively. According to earlier reports,[16,34–36] for the PbS quantum dots materials, Raman peaks at 210, 271, 451 cm^{-1} should be observed due to a one-LO phonon mode, a two-phonon process, and a two-LO phonon mode, respectively. But in our result the peak at 210 cm^{-1} was so intense that the peak at 271 cm^{-1} was difficult to characterize.

However, according to Batonneau's work,[33] a peak at 966 cm^{-1} will appear due to the photodegradation of PbS when the laser power was increased to 15 mW. It should be a characteristic peak for the oxidation products $PbSO_4$, $PbO{\cdot}PbSO_4$, $3PbO{\cdot}PbSO_4$, and $4PbO{\cdot}PbSO_4$.

Thus, additional Raman spectra were measured with higher laser powers to investigate the photodegradation activity of our product; the spectra of the sample are shown in Figure 7. The results show that when the laser power was increased to 0.5 mW (monitored by a filter D1, which means the laser power delivered to the sample was 1.5 mW, but only 0.5 mW reached the sample), the peak at 966 cm^{-1} was clearly observed (Figure 7a); when the laser power was increased to 5 mw finally, the peaks at 431, 602 and 966 cm^{-1} were clearly observed (Figure 7c), which fit well with the result reported by Batonneau,[33] indicating that our product is sensitive to the laser, and can be photodegraded at lower laser power.

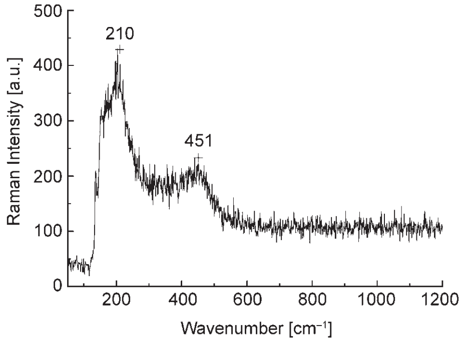

Figure 6. Raman spectra of hexapod-like PbS with 50 μW (monitored by a filter D2) laser power.

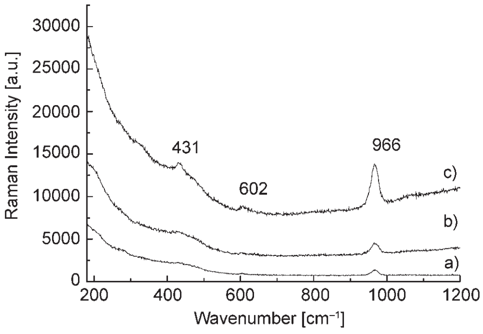

Figure 7. Raman spectra of hexapod-like PbS with different laser powers: a) 0.5 mW (monitored by a filter D1). b) 2.16 mW (monitored by a filter D0.3). c) 5 mW (no filter, which means the laser power delivered to the sample was 15 mW, but only 5 mW reached the sample).

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This effect may be caused by the shape of the PbS crystals. Indeed, the reasons for the surprising result are still far from understood, and still need further investigations.

Conclusion

In summary, a highly regular hexapod-like PbS nanostructure with six symmetric arms has been synthesized by a simple and mild chemical solution route. The arms are about 0.3–0.6 μm long, which have about 40–60 nm tips and 150–200 nm bases. Each arm shows an icicle-like structure and some clear steps on it, and grows along ⟨100⟩ directions. The Raman spectra of the hexapod-like PbS nanostructure were investigated. The results show that our products are sensitive to the laser and can be photodegraded easily, which appears to be a promising feature.

Experimental Section

Synthesis: In a typical procedure for the preparation of hexapod-like lead sulfides, 0.75 mmol $PbCl_2$ and 1.5 g PVP were dissolved in ethylene glycol (EG, 45 mL), then hydrazine monohydrate (80 %, 4 mL) diluted by EG (6 mL was added dropwise with simultaneous vigorous agitation at room temperature. After a given time of vigorous stirring in room temperature, the solution was heated at 154 °C with stirring for 1 h. Then thiourea (0.114 g) dissolved in EG (15 mL) was added to the mixture with stirring at 154 °C. After 1 h of mild stirring and heating at 154 °C, the final black precipitates were formed. The resulting metal sulfide was filtered and washed by absolute ethanol several times, and then dried in vacuum at 60 °C for 2 h.

Characterization: X-ray powder diffraction patterns were obtained on a Rigaku Dmax2200 Advance X-ray diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å). The morphology of the as-prepared hexapod-like PbS was visualized by using a Hitachi Model H-800 transmission electron microscope, a Tecnai F30 high-resolution transmission electron microscope, and a JSM-5800 scanning electron microscope. Raman spectra were recorded with an HR800 (Jobin Yvon company) microscopic confocal Raman spectrometer, which had a helium/neon laser operating at 632.8 nm.

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