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2011 Nanotechnology 22 125602
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Synthesis of single-crystal PbS nanorods via a simple hydrothermal process using PEO–PPO–PEO triblock copolymer as a structure-directing agent

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Received 10 October 2010, in final form 9 December 2010
Published 14 February 2011
Online at stacks.iop.org/Nano/22/125602

Abstract
Single-crystal PbS nanorods were successfully synthesized through a simple hydrothermal route using PEO–PPO–PEO triblock copolymer (P123) as a structure-directing agent. The XRD pattern indicates that the crystal structure of the nanorods is face-centre-cubic rocksalt. A SEM image shows that the nanorods have a diameter of 40–70 nm and a length of 200–600 nm, and both tips exhibit taper-like structures. HRTEM and SAED images reveal the single-crystalline nature of the nanorods with the growth along the ⟨111⟩ direction. The experimental results indicated that the P123 concentration and reaction temperature played important roles in controlling the morphology of the PbS nanostructures. The optical property of PbS nanorods was investigated by UV–Vis absorption spectroscopy and the band structure was calculated by the B3LYP hybrid density functional theory.

1. Introduction
The architectural control of nanocrystals with well-defined shapes is an exciting research focus in modern materials chemistry because of their varying novel size-dependent properties [1–3]. In recent decades, many research efforts have been devoted to the morphology control and spatial patterning of the semiconductor nanocrystals of metal sulfide [4–9]. Among these materials, PbS, as an important IV–VI semiconductor, is an attractive sulfide semiconductor with a special narrow direct band gap of 0.41 eV and a large excitation Bohr radius of 18 nm, which permits size-quantum confinement effects to be clearly visible even for the large particles [10]. With novel and excellent optical and electronic properties, nanoscaled PbS has been widely used for IR detectors [11], solar cells [12] and electroluminescent devices [13].

It is well known that PbS is a cubic rock salt structure, which is three-dimensionally (3D) isotropic. Up to now, a variety of symmetric morphologies of PbS nanocrystals, including spheres [14–16], cubes [4, 15, 17–21], truncated cubes [4, 21], octahedrons [4, 19], star-shaped [4, 22, 23] and dendritic structures [19–21, 24] have been achieved by different methods. In contrast to the synthesis of the above isotropic systems, the preparation of anisotropic PbS nanocrystals, such as one-dimensional (1D) nanostructures including nanorods, nanowires, and nanotubes, remains a major challenge. As the properties of 1D PbS are substantially different from 3D systems due to the change in the degree of charge carriers [9, 25–27], the synthesis of 1D PbS has attracted much interest. So far, PbS nanorods have been prepared in an aqueous solution through the hydrothermal process [28–30], the sonochemical method [31], the solvothermal route [32, 33] and the microemulsion route [34]. However, almost all PbS nanorods obtained by various methods were grown along the ⟨100⟩ direction with a few examples along the ⟨110⟩ direction [9, 32]. PbS nanorods grown along directions other than the ⟨100⟩ and
(110) directions have not been reported yet. Herein, we report the synthesis of PbS nanorods with the growth direction of (111) for the first time.

P123, one type of nonionic polymer, consists of the water-soluble amphiphilic triblock copolymer of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) (designated as PEO–PPO–PEO or EO

\[
\begin{align*}
\text{PO}_4\text{N}_2 \text{H}_3 \text{PO}_4 \text{O}_{13} \text{Ce}^{3+}
\end{align*}
\]

It can be used as a soft template to generate nanostructures, even 1D nanostructures. For example, Xu et al [35] reported the synthesis of lanthanide phosphate \((\text{LnPO}_4)\) microspheres composed of single-crystal \(\text{CePO}_4\) and \(\text{CePO}_4\cdot\text{Tb}\) nanorods by a hydrothermal process using P123, \(\text{H}_3\text{P}_2\text{O}_{13}\) and \(\text{Ce}^{3+}\) composite as a template; Ye et al [36] used mixtures of P123 and tween-60 as the mediated template to generate nanostructures, even 1D nanostructures. As a consequence, P123 could be a good directing agent for the growth of PbS into 1D nanostructure. In this paper, we report the finding of the triblock copolymer P123 as a 1D structure-directing agent to synthesize single-crystal PbS nanorods via a simple hydrothermal process. Electron microscopic measurements reveal the single-crystalline nature of PbS nanorods and the growth direction along (111). Furthermore, the effect of copolymer P123 on the 1D growth of PbS is discussed.

2. Experimental details

The PEO–PPO–PEO triblock copolymer P123 (\(\text{EO}_{20}–\text{PO}_{70}–\text{EO}_{20}\), \(M_n = 5800 \text{ g mol}^{-1}\)) was purchased from Aldrich. Lead nitrate and thiourea were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All reagents were analytic grade purity and directly used without any further purification. In a typical synthesis, 1.45 g P123 was dissolved in 20 ml distilled water to form a homogeneous aqueous solution (0.0125 M), then 0.2 g \(\text{Pb(NO}_3\text{)}_2\) (0.025 M) and 0.1 g thiourea (0.075 M) were added into the solution in turn. After stirring vigorously for 40 min, the mixture solution was transferred into a Teflon-lined stainless steel autoclave of 30 ml capacity. The hydrothermal process was conducted at 100\(\degree\)C for 24 h and then the autoclave was cooled to room temperature naturally. The resulting solution was centrifuged at 6000 rpm for 10 min to remove the unwanted molecule byproducts. The obtained black products were washed with distilled water and absolute ethanol several times, and then dried in air at 60\(\degree\)C for 6 h for further characterizations.

The phase purity and structure of the as-prepared products were characterized by x-ray diffraction (XRD), using a Philips X’pert x-ray diffractometer, at 40 kV/30 mA, equipped with graphite monochromatized Cu \(\text{K}\alpha\) radiation (\(\lambda = 1.541 781 \text{ Å}\)) at a scanning rate of 0.0167\(\text{°} \text{s}^{-1}\) for 2\(\theta\) ranging from 10\(\degree\) to 80\(\degree\). Scanning electron microscopy (SEM) images were taken with a Hitachi S4800 SEM. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and a selected-area electron diffraction (SAED) pattern were obtained on a JEM-2100TEM performing at an accelerating voltage of 200 kV. The composition and chemical state were determined on an x-ray photoelectron spectroscope (XPS, VG, Physical Electrons Quantum 2000 Scanning Esca Microprobe, Al \(\text{K}\alpha\) radiation). The UV–Vis diffuse reflectance spectrum (DRS) of the PbS nanorods was recorded using a Varian Cary-5000 spectrophotometer. The band structure for the PbS primitive cell was predicted by the B3LYP hybrid density functional theory (DFT) without spin polarization using the Vienna \textit{ab initio} simulation package (VASP).

3. Results and discussion

Figure 1 shows the XRD pattern of the as-synthesized products. All ten diffraction peaks can be indexed to the (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) crystal planes of face-centre-cubic rocksalt structured PbS (JCPDS No. 005-0592), respectively. The strong and sharp peaks indicate that the products are well crystallized and no diffraction peak from any other impurities can be detected, revealing the high purity of the as-synthesized products.

The morphology of the obtained PbS products was investigated by using SEM, TEM and HRTEM. Figure 2(a) shows a large-scale SEM image of the product synthesized at 100\(\degree\)C, which displays a rod-like structure and good uniformity. The diameter of the nanorods ranges from about 40 to 70 nm, and the length is about 200–600 nm. And the obtained nanorods are well dispersed. The crystal structure of PbS nanorods was further investigated by using TEM. Figure 2(b) shows the TEM image of an individual PbS nanorod. The diameter and length of this nanorod are about 50 and 260 nm, respectively, and both tips exhibit taper-like structures. The corresponding HRTEM image taken from the tip area is shown in figure 2(c). The clear lattice fringes confirm the high crystallinity of the nanorods. The lattice spacing of 0.348 nm between each adjacent plane is in accordance with the spacing of the (111) crystal planes of the cubic PbS, suggesting that the PbS nanorod crystal grows along the (111) direction. The SAED pattern of the PbS nanorods shown in figure 2(d) further confirms that the growth direction is along...
the $\langle 111 \rangle$ direction, and indicates that the nanorod is in a single-crystalline state.

XPS analysis was employed to detect the chemical states of different atoms in the samples. Figures 3(a) and (b) show the high-resolution XPS spectra of the Pb and S regions of the as-synthesized PbS nanorods. The peaks at 138.2 and 143.1 eV in figure 3(a) correspond to the binding energies of Pb $4f_{7/2}$ and Pb $4f_{5/2}$ core levels, demonstrating that only one chemical phase is detected. As shown in figure 3(b), the binding energy of S $2p_{1/2}$ is observed at 161.2 eV. This range of estimated values supports the presence of a well-defined PbS phase. Moreover, the energy position of the peaks obtained in this work is consistent with those reported for the binding energy of PbS samples [19–21].

In this work, P123 was used as a structure-directing agent to prepare PbS nanorods in an aqueous solution. In order to understand the formation mechanism, the effect of P123 on the morphology of the products was examined first. In an aqueous solution, block copolymer micelles tend to form a core–shell structure by the segregation of insoluble blocks into the core and hydrophilic blocks into the shell [39–41]. Their surface activity which dominates the self-assembly behaviour in solution mainly depends on the concentration and temperature [42]. Accordingly, the concentration- and temperature-dependent experiments were completed. Figure 4 shows the SEM images of the products synthesized in aqueous solution with various P123 concentrations. When the P123 concentration was lower than 0.0005 M (including the case without P123), the products were big block-like PbS crystals (figure 4(a)). By increasing the P123 concentration to 0.005 M, some short nanorods produced besides of block-like PbS crystals can be obtained (figure 4(b)), indicating that P123 could confine and direct the growth of PbS crystals. When the P123 concentration was increased to 0.0125 M, almost all products were the rod-like PbS nanocrystals (figure 4(c)). However, when the P123 concentration was up to 0.05 M, the size of the nanorods decreased a little (figure 4(d)). Therefore, the optimal P123 concentration obtained for the PbS nanorods was 0.0125 M, in which the uniform PbS nanorods can be formed. Figure 5 shows the SEM images of the products obtained at various reaction temperatures. The products were the block-like PbS crystals with a big size difference and no nanorods can be observed at the reaction temperature of 90 °C (figure 5(a)), while the block-like PbS crystals covered by small nanorods were produced at the reaction temperature of 110 °C (figure 5(b)). Only when the reaction was carried out at 100 °C, could the uniform PbS nanorods be obtained (figure 2(a)).

To further understand the growth process of the PbS nanorods, we followed the morphology of the products obtained at various reaction times at 100 °C, which are shown in figure 6. It was found that short nanorods formed after 6 h. When the reaction time was prolonged, the length of the nanorods increased with increasing reaction time from 6 to 24 h while the diameter showed no detectable increase. Further
The possible reactions can be described as follows:

\[
\text{NH}_2\text{CSNH}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{H}_2\text{S} + \text{CO}_2
\]

\[
\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+(1)
\]

\[
\text{HS}^- \rightarrow \text{H}^+ + \text{S}^{2-}(2)
\]

\[
\text{Pb}^{2+} + \text{S}^{2-} \rightarrow \text{PbS}; (3)
\]

Increasing the reaction time, the size of the nanorods remained unchanged.

From the experimental results mentioned above, it can be seen that the P123 concentration and reaction temperature are the key parameters to synthesize PbS nanorods.

In the synthesis process, the possible reactions can be described as follows:

\[
\text{NH}_2\text{CSNH}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{H}_2\text{S} + \text{CO}_2
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\[
\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+(1)
\]

\[
\text{HS}^- \rightarrow \text{H}^+ + \text{S}^{2-}(2)
\]

\[
\text{Pb}^{2+} + \text{S}^{2-} \rightarrow \text{PbS}; (3)
\]

In an aqueous solution, the hydrolysis of thiourea occurred and produced \(\text{H}_2\text{S}\). At a certain temperature, \(\text{Pb}^{2+}\) reacted with \(\text{S}^{2-}\) hydrolyzed from \(\text{H}_2\text{S}\) to form the PbS nuclei. When the P123 concentration in an aqueous solution was very low (including the absence of P123), the PbS nuclei grew along the three-dimensionally to form block-like PbS crystals, showing its cubic symmetry. When the polymer concentration exceeds the critical micelle concentration in an aqueous solution, the P123 in the solution aggregates into micelles with a PPO core and PEO corona. The PEO corona may interact with hydrated protons \([\text{H}_2\text{O}]^+\) under acidic conditions or bind with metal cations [43–46]. When \(\text{Pb(NO}_3)_2\) was added to the P123 solution, the surface of the PEO corona had a strong affinity for \(\text{Pb}^{2+}\) cations. After the addition of thiourea, \(\text{S}^{2-}\) was released from \(\text{H}_2\text{S}\) obtained by the hydrolysis of thiourea. In the hydrothermal process, \(\text{Pb}^{2+}\) cations bound with the surface of PEO reacted with \(\text{S}^{2-}\) to form PbS nuclei. With the reaction proceeding, the PbS nuclei grew into one-dimensional rods in the guidance of P123.

For the growth of crystallites, their exposed surfaces directly relate to the surface energies (\(\gamma\)) of the crystal facets. Facets with lower surface energies usually dominate the morphology as growth is slower along these directions. PbS belongs to a sodium chloride-type structure, and its surface energies (\(\gamma\)) of \{100\} and \{111\} facets are in the sequence \(\gamma_{100} < \gamma_{111}\) [47–49]. Owing to \(\gamma_{100} < \gamma_{111}\), the growth rate of the \{111\} direction is faster than that of the \{100\} direction. Therefore, the PbS nuclei usually grow rapidly along the \{111\} direction and finally form cubes with exposed \{100\} facets. In the present case, when the P123 concentration was low, it would not greatly affect the growth of the PbS crystallites and cube-like PbS products were mainly obtained. When the P123 concentration was increased to 0.0125 M, they could aggregate into micelles and almost all the products were rod-like PbS nanocrystals due to the spatial confinement between the P123 micelles. As the \{111\} direction was the fast growth direction, the longitudinal direction was \{111\}. It should be pointed out that the longitudinal direction of the as-prepared PbS nanorods is different from previously reported ones. In the previous studies, where PbS nanorods with the \{100\} growth orientation were obtained, the surfactants used mainly included polyglycol [28, 31], sodium dodecyl sulfate (SDS) [29], \(N\)-cetyl-\(N,N,N\)-trimethyl-amonium bromide (CTAB) [30], and sodium dioctyl sulfo succinate (AOT) [33]. In the polyglycol system [28] and AOT system [33], PbS nanorods formed through a bridging linked mechanism; in the SDS system [29], PbS nanorods were synthesized via the oriented self-assembly growth of PbS nanorods along surfactant chains; and in the CATB system [30], CTAB may preferentially adsorbed on the faces parallel to the \{100\} axis direction of PbS nanoparticles, leading to preferential growth along the \{100\} direction.

To obtain information about the optical properties of PbS nanorods, a UV–Vis absorption spectrum was performed at room temperature. Figure 7 shows the UV–Vis diffuse reflectance spectrum of PbS nanorods shown in figure 2(a). Although an absorption drop around 750 nm is obviously observed, the actual threshold of the absorption of PbS nanorods is about 2800 nm. Therefore, the optical band gap of PbS nanorods should be 0.443 eV (corresponding to 2800 nm), which shows a little increment compared with that of bulk PbS (0.41 eV) [50–52]. The absorption around 750 nm, which was considered as a blue shift due to the nano-effect by other groups [28, 34], could be due to the excitation of electrons from the top of the valence band to the second empty band. This hypothesis can be supported by the theoretical calculation of the band structures of PbS based on the B3LYP hybrid function without spin polarization using the VASP software, as shown in figure 8. In figure 8, the abscissa axis is composed of geometric
points in the reciprocal space, and the reciprocal space of the PbS primitive cell is a tetrakaidecahedron containing eight hexagons and six tetragons. These high symmetry points G, X, W, and L represent the origin, the central point of the tetragon, the intersection point of two hexagons and one tetragon, and the centre point of the hexagon, respectively. It can be found that both of the top of the valence band and the bottom of the conduction band locate at the high symmetry point L, showing that the PbS material is a direct gap semiconductor. The predicted direct band gap is 0.69 eV (1797 nm), slightly higher than the experimental value of 0.443 eV (2800 nm). The difference may be attributed to the approximation of methodology and the use of computational models. In addition, the gap between the top of the valence band and the second and third conduction bands in the L high symmetry point is 2.13 eV (582 nm), where the second and the third conduction

Figure 4. SEM images of the products obtained in various P123 concentrations. (a) 0.0005 M; (b) 0.005 M; (c) 0.0125 M; (d) 0.05 M.

Figure 5. SEM images of the products obtained at various temperatures. (a) 90°C and (b) 110°C.

Figure 6. SEM images of the products prepared at various times. (a) 6 h and (b) 12 h.
bands in the L high symmetry point are degenerate. The transition process from the top of the valence band to the bottom of the second and third conduction bands in the L high symmetry is also a direct transition. As PbS is a direct band gap semiconductor, the experimental value (750 nm) may correspond to the direct transition from the top of the valence band to the second and third conduction bands in the process of intrinsic absorption, considering the calculated band gap is larger than the actual one.

4. Conclusion

In summary, the single-crystalline PbS nanorods with a diameter of about 40–70 nm and a length of about 200–600 nm were successfully synthesized by a conventional hydrothermal process using a triblock copolymer P123 as the structure-directing agent. XRD and HRTEM studies confirmed a highly crystalline phase and a preferential growth along the \( \langle 111 \rangle \) direction. The as-prepared PbS nanorods were uniform and both tips showed taper-like structures. The P123 concentration and reaction temperature play important roles in controlling the morphology of the products. The UV–Vis absorption spectrum of the PbS nanorods showed a little blue shift in the band gap energy compared to bulk PbS crystals. The potential applications of these PbS nanorods in fundamental studies of nanostructure as well as for integration into opto-electronic devices based on these structures will be further explored. The synthesis method may provide a useful guide for the future fabrication of other inorganic 1D nanostructured materials in P123 aqueous solution.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21021002 and 51072170).

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