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ScienceDirect
Materials Chemistry and Physics 101 (2007) 379–382
MATERIALS CHEMISTRY AND PHYSICS
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# Morphology control of lead sulfide particles in mixed systems of poly-(styrene-alt-maleic acid) and cetyltrimethylammonium bromide

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Received 1 September 2005; received in revised form 1 April 2006; accepted 4 July 2006

**Abstract**

The novel starlike PbS particles were successfully synthesized for the first time in a mixed system of poly-(styrene-alt-maleic acid) (PSMA) and cetyltrimethylammonium bromide (CTAB). The as-prepared hierarchically starlike PbS particles have six symmetric perpendicular arms or arm groups, each of which consists of parallel rods or ellipsoids that are perpendicular to the arm. Moreover, spherical and cubic-shaped PbS particles were facilely produced via varying the concentration of CTAB in the mixed system. The presence of CTAB in the mixed system played a key role in the formation of unusual PbS stars. The faster growth rate in six ⟨1 0 0⟩ directions of PbS crystals induced by the organic additives were thought to be responsible for the formation of such novel starlike PbS particles.


*Keywords:* Morphology control; Lead sulfide; Star; Sphere; Cube; Poly-(styrene-alt-maleic acid); Cetyltrimethylammonium bromide

## 1. Introduction

Morphology control of semiconductor materials has attracted a considerable attention due to the importance of shape, size and texture of the materials in determining their optical and electric properties [1–3]. Lead sulfide (PbS), as an important binary IV–VI semiconductor materials with rather small band gap (0.41 eV at 300 K) and relatively large excitation Bohn radius (18 nm) [4], has been widely used in many fields such as photography [5], IR detectors [6], $Pb^{2+}$ ion-selective sensors [7], and solar absorption [8].

The syntheses of PbS particles with a variety of morphologies have been achieved so far. For example, spherical PbS nanocrystals have been obtained in random copolymer ionomers [9]. Cubic-shaped microcrystals and nanocrystals have been produced by decomposition of thioacetamide [10] and a single source precursor [11], respectively. Rodlike PbS nanocrystals have been produced using a combination of polymer and surfactant as the template [12]. PbS nanowires and nanosheets have been synthesized via a polymer-assisted solvthermal route [13,14]. Recently, novel PbS dendrites consisting of nanorods have been prepared via hydrothermal or solvothermal process [15,16], and clover-like PbS crystals have also been produced by microwave technique [17].

In the present work, we explored the morphology control of PbS particles in the mixed systems of poly-(styrene-alt-maleic-acid) (PSMA) and cetyltrimethylammonium bromide (CTAB). It was found that the presence of PSMA and CTAB had significant influence on the morphology of PbS particles. Unique starlike PbS particles with six perpendicular arms or arm groups, as well as spherical and cubic PbS particles were successfully synthesized via varying CTAB concentration in the mixed PSMA–CTAB systems. The results are important for further understanding the kinetic control on the morphology of PbS crystals and other semiconductor materials.

## 2. Experimental procedure

The copolymer, poly-(styrene-alt-maleic acid) (sodium salt, 30 wt.% aqueous solution, average molecular weight 120,000), was purchased from Aldrich, and used without further purification treatment. The cationic surfactant, cetyltrimethylammonium bromide, and other chemicals used in the experiments were of analytical grade.

The syntheses of PbS particles were carried out by the thermal decomposition of thioacetamide (TAA) in the mixed aqueous solutions of lead nitrate ($Pb(NO_3)_2$), PSMA and CTAB at 80 °C. Aqueous solutions of $Pb(NO_3)_2$ (0.5 M) and TAA (0.5 M) were first prepared as stock solutions. In the synthesis of star-

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0254-0584/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.matchemphys.2006.07.001

shaped PbS particles, 5 mL of TAA solution (0.5 M) was added into 90 mL of the mixed solution of PSMA and CTAB. Then, equal volume (5 mL) of $Pb(NO_3)_2$ solution (0.5 M) was add to the above solution. The starting pH was adjusted to 2 by using 2 M $HNO_3$ and NaOH solution. The total volume of the working solution was 100 mL, and the concentrations of PSMA, CTAB, $Pb(NO_3)_2$ and TAA in the mixed solution were 0.5 g $L^{-1}$, 0.5 mM, 0.025 M and 0.025 M, respectively. The mixed solution was stirred by sonication for 5 min, then was kept at 80 °C for 24 h under static condition, resulting in the production of a black solid precipitates. The precipitates were washed with water and ethanol for four times, respectively, and dried at 60 °C in air. In the other related experiments, the concentration of CTAB was varied, and other conditions were kept the same.

Scanning electron microscopy (SEM) measurements were performed with a JSM-5610LV microscope at 20 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were carried out with a JEM2010 microscope at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on an HZG41B-PC X-ray diffractometer using Cu Kα radiation at a scan rate of 0.05°2θ $S^{-1}$.

## 3. Results and discussion

XRD was used to characterize the crystal structure of the products. Fig. 1 shows the XRD patterns of the products obtained in the mixed system of PSMA and CTAB. All the peaks in Fig. 1 can be readily indexed to a pure face-center-cubic crystalline phase of PbS with calculated lattice content $a = 0.594$ nm, which is in good agreement with the literature values (JCPDS No. 5-592).

Fig. 2 presents the SEM images of the PbS particles obtained in the mixed system of 0.5 g $L^{-1}$ PSMA and 0.5 mM CTAB. It can be seen from Fig. 2(a) that well-defined starlike PbS particles are the predominant products. Further observation shows that these starlike PbS particles appear a hierarchical character (as shown in Fig. 2(b) and (c)). The stars have six symmetric perpendicular arms (Fig. 2(b)) or arm groups (Fig. 2(c)) consisting of parallel small arms growing radially from the center. Each arm contains many smaller rods or ellipsoids that are perpendicular to the arm. This novel hierarchical, six-arm or six-arm-group and

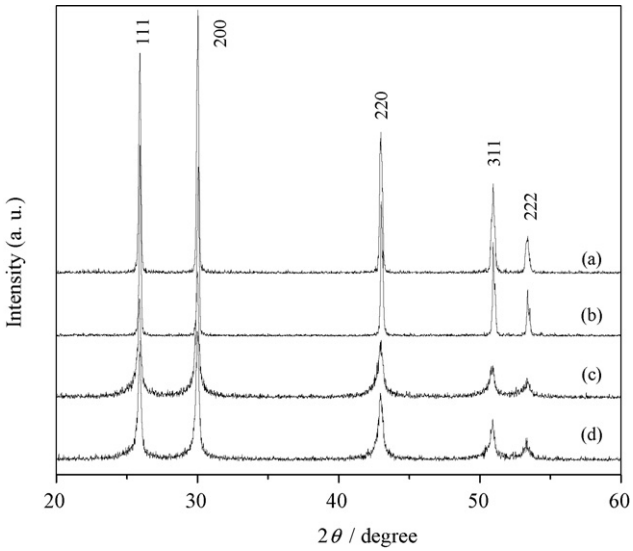


Fig. 1. XRD patterns of PbS particles obtained in the mixed systems of 0.5 g $L^{-1}$ PSMA and CTAB: (a) [CTAB] = 0.5 mM, (b) [CTAB] = 0 mM, (c) [CTAB] = 1.0 mM, and (d) [CTAB] = 1.5 mM.

star-shaped PbS crystals is obviously different from the eight-arm and star-shaped PbS crystals obtained via a simple solution route [18,19], and is also different from the two-dimensional, six-petal and flower-shaped PbS crystals obtained by microwave irradiation technique [17]. To the best of our knowledge, this is the first report on synthesis of such micrometer-sized three-dimensional (3D) starlike PbS particles with six perpendicular arms or arm groups via a polymer-surfactant-assisted route. The XRD results (as shown in Fig. 1(a)) indicated that the as-prepared PbS particles are well crystallized due to strong sharp diffraction peaks.

The presence of CTAB played the key role in the formation of such novel starlike PbS crystals. Fig. 3 depicts the SEM images of the PbS product obtained in the presence of pure PMAA

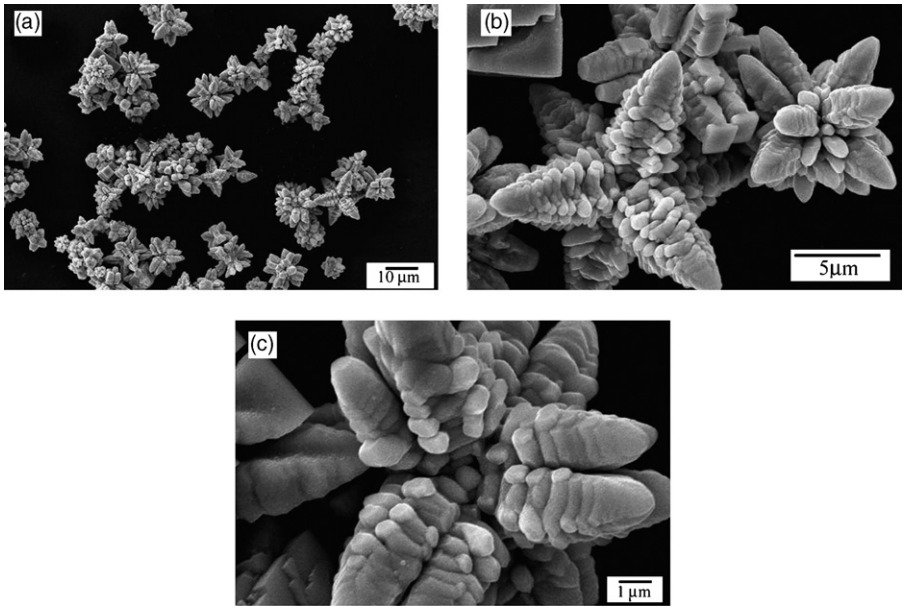


Fig. 2. SEM images of the PbS particles obtained in the mixed systems of 0.5 g $L^{-1}$ PSMA and 0.5 mM CTAB.