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Aminocaproic acid mixed methanolic lead–thiourea complex precursor and its thermal decomposition to star-shaped lead sulfide crystals

Jayesh D. Patel [a,b], Frej Mighri [a,b,*], Abdellah Ajji [a,c]

[a] Center for Applied Research on Polymers and Composites, CREPEC, Canada
[b] Chemical Engineering Department, University of Laval, Quebec, QC, Canada G1K 7P4
[c] Chemical Engineering Department, Ecole Polytechnique, C.P. 6079, Succ. Centre-Ville Montreal, QC, Canada H3C 3A7

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ABSTRACT

In this work, we present for the first time a simple synthetic route to fabricate a controlled lead sulfide (PbS) structure using amino acid mixed precursor. High yield star-shaped PbS crystals were developed by solvothermal synthesis technique using an environment friendly aminocaproic acid (ACA) mixed methanolic Pb–TU complex precursor at 170 °C for 20 h. The mechanism leading to these star-shaped PbS crystals was discussed. The as-synthesized PbS crystals were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Fourier transform infrared (FTIR). The obtained results show that the synthesized star-shaped PbS crystals were exempt of impurities and were crystalline with cubic phase. Finally, the FTIR study indicates that molecules were bounded on the surface of PbS crystal via nitrogen lone pair of the amino head groups.

1. Introduction

The development of inorganic crystals with controlled morphology is becoming a highly exciting research area because the special physiochemical properties of these inorganic materials are tunable through the control of their size and shape [1]. Properties of semiconducting materials highly depend on their surface area. Rod, dendrite, star shaped or hexapod like structures show better semiconducting properties as their surface area increases. Sun et al. [2] mentioned that, due to their higher surface area, branched CdSe tetrapods dispersed in MDMO-PPV showed better electron transport capacity compared to linear CdSe nanorods dispersed in the same matrix. They were able to develop solar cell prototypes with an efficiency varying between 2.4 and 2.8% [2]. PbS is considered as one of the most important semiconductors that can be synthesized with well-controlled morphologies leading to well quantization effect. The combination of such properties makes PbS suitable for efficient electroluminescent devices such as inorganic–organic bulk hybrid solar cells [3], tunable near-infrared detectors [4], and solid state lasers [5]. During the last few years, various PbS structures have been synthesized via solution phase methods. These structures include nanotubes, nanowires, cubes, octahedrons, flower structures, sheet-like shape, dendrite and macrostar-like hierarchical structures [6–11]. Their synthesis techniques generally include hydrothermal, solvothermal, chemical or thermal decomposition routes with suitable surfactants or capping molecules. Recently, biomolecule-assisted chemical route has become highly promising due to its novelty and its environmentally friendly character for a large variety of nanomaterials and also for its strong utility in morphology control [12]. Moreover, PbS nanostructures are also synthesized using amino acids as bio-capping molecules [13,14]. Among the various amino acids, aminocaproic acid (ACA) is very useful to produce size and shape controlled particles including their organized self-assembled nanostructures [15].

To the best of our knowledge, the synthesis of PbS nanoparticles or nanostructures using ACA as a biomolecule is not reported in the literature. In this work, we propose a simple environment friendly solvothermal route for the synthesis of star-shaped PbS crystals with high yield using ACA biomolecule/methanolic lead–thiourea (Pb–TU) complex precursor.

2. Experimental

All chemicals were purchased from Sigma-Aldrich, Canada, and were used as received without further purification. ACA biomolecule mixed methanolic Pb–TU complex precursor was prepared as follows: first, lead acetate trihydrate (0.05 mmol, 1.89 g) and thiourea (0.05 mmol, 0.380 g) were dissolved in 100 mL of methanol to obtain a clear methanolic Pb–TU complex solution. Further, ACA (0.1 mmol, 1.31 g) was added to this solution under magnetic stirring at room temperature to obtain a final clear precursor solution. After 1 h of stirring, this precursor solution was transferred to a Teflonlined stainless steel autoclave (capacity of 1 L), which was filled with distilled water up to 80% of the total volume and treated at 170 °C for 20 h then cooled naturally to room temperature. The obtained product was

* Corresponding author at: Chemical Engineering Department, University of Laval, Quebec, QC, Canada G1K 7P4. Tel.: +1 418 656 2241; fax: +1 418 656 5993.
E-mail address: Frej.Mighri@gch.ulaval.ca (F. Mighri).

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filtered out, washed several times by ethanol and distilled water, and then dried at 50 °C for 1 h.

Powder XRD data of the sample was recorded on a Siemens D5000 X-ray diffractometer, using Cu-Kα radiation (λ = 1.54059 Å). SEM and EDS were recorded using a Jeol JSM-6360/LV scanning electron microscope. The sample was dispersed sonochemically in methanol and a drop of methanolic dispersion placed on SEM stud (covered with carbon tape) and immediately evaporated at ambient temperature. FTIR of ACA and PbS crystals were obtained using a Nicolet (Thermo Fisher) Model 380 FTIR with an attenuated total reflectance sampling device, model Smart Performer with a ZnSe crystal. The infrared spectra were collected within the range of 650 to 4000 cm^{-1} with 10 scans per spectrum.

3. Results and discussion

It's well known that methanolic Pb–TU complex is metastable and is slowly decomposed into nanostructured PbS particles at room temperature [16]. Controlled decomposition of Pb–TU complex is highly beneficial to regulate the size and morphology of the PbS particles. ACA biomolecule used in this study is composed of an alkyl chain and two head ends of $–NH_2$ and –COOH groups, which have strong abilities for coordination with the metal ions. At the initial stage of the synthesis, the thermal decomposition of Pb–TU complex may release Pb^{+2} cations and S^{-2} anions, which could form a highly active ACA bound PbS nuclei. In the primary formation stage of the nuclei, the decomposition rate of the Pb–TU complex is slow and crystals grow in the low Pb^{+2} concentration. Further, increasing Pb^{+2} concentrations promotes the two-dimensional nucleation and increases the growth rates along the four <100> directions. Finally, at the end of the synthesis, four <100> directions growth leads to star-shaped PbS crystals, as shown in Scheme 1.

It is well known that crystallinity of good perfection degree of semiconducting crystals enables them to have a good mobility of the charges, i.e., good electronic conductivity compared to their polycrystalline or nanocrystalline form. Powder XRD was performed to identify the composition and phase structure of the synthesized star-shaped PbS crystals. The corresponding results are shown in Fig. 1. The sharp and intense diffraction patterns are a good indication of the high crystallinity of the developed PbS crystals. All the observed peaks, indexed on the basis of JCPDS standards, correspond to face-centered cubic PbS (JCPDS Card No.05-0592) and are due to

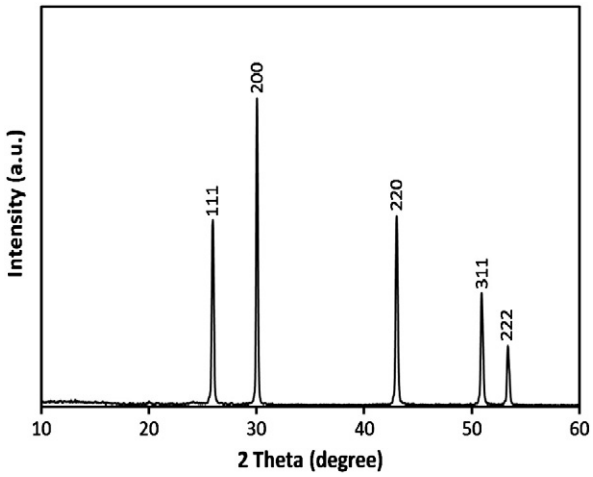
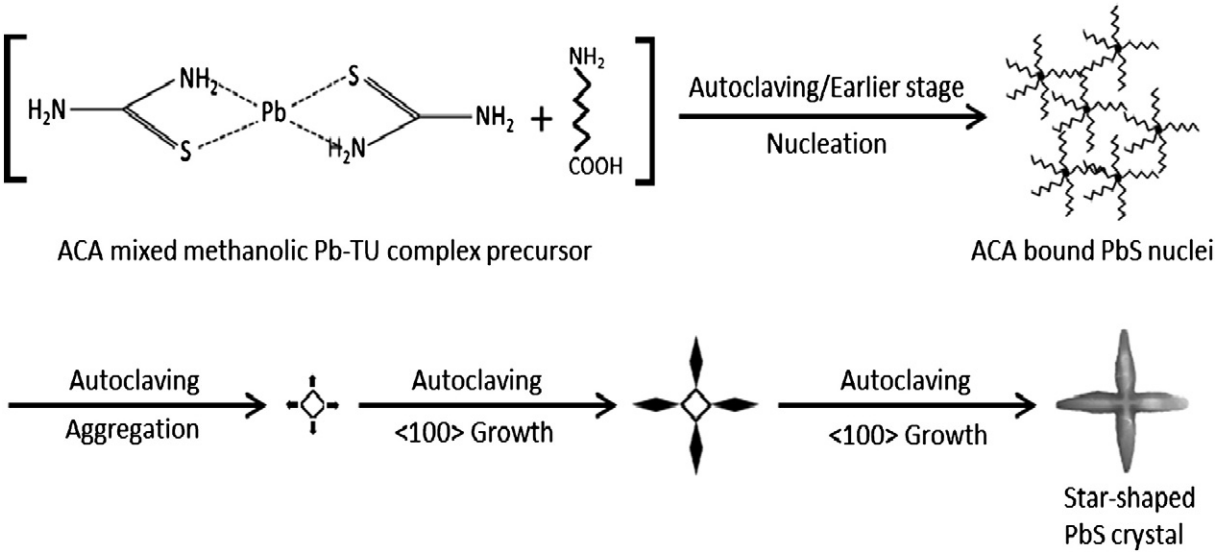


Fig. 1. Powder XRD patterns of star-shaped PbS crystals.

the reflections from (111), (200), (220), (311) and (222) planes. From Fig. 1, the calculated ratio between the intensities of the (200) and (111) diffraction peaks is 1.65, which is higher than the standard ratio of 1.049 (according to JCPDS) indicating that PbS crystals abound in {100} facets, and grow along the <100> directions.

The morphology of the synthesized PbS crystals was examined by SEM. Fig. 2(a) and (b)shows typical SEM images of PbS crystals. From the low magnification SEM image (Fig. 2(a)), it is clearly seen that PbS crystals exhibit star-shaped morphology with crystal size varying between 4 and 8 μm. Higher magnification of the individual PbS crystal (Fig. 2(b)) not only shows a star-shaped morphology, but also reveals that the star-shaped PbS crystals are composed by single rod-like star morphology. This is completely different from previously reported results showing star-shaped PbS crystals with multi-rod or multi-armed like morphologies [17,18]. As observed in SEM images of Fig. 2, this could be due to the sonication treatment, which destroyed their morphology during the dispersion of the sample. In order to characterize the composition of the star-shaped PbS crystals, their EDS spectrum was obtained (Fig. 2(c)). This spectrum reveals that the sample contains elements of Pb and S. The other peaks corresponding to C, Au and Pd are due to the stud and sample metallization before SEM examination.



Scheme 1. The possible mechanism for the <100> directions growth process of star-shaped PbS crystals.