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Biomolecule and surfactant-assisted hydrothermal synthesis of PbS crystals

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Abstract

PbS crystals were hydrothermally synthesized using $Pb(NO_3)_2$, L-cysteine, and *N*-cetyl pyridinium chloride in solutions with different pH values at 140 °C. Flower-like, granular and truncated cubic PbS crystals composing of Pb and S were detected using an X-ray diffractometer (XRD), a scanning electron microscope (SEM), a transmission electron microscope (TEM), a selected area electron diffraction (SAED) technique and an energy dispersive X-ray (EDX) analyzer. In addition, a Raman spectrometer revealed the presence of the first and second overtone modes at 436 and 602 cm^{-1}, respectively. Emission spectra of the products were detected at 412 nm using a photoluminescence (PL) spectrometer.

Keywords: Hydrothermal synthesis; L-Cysteine; *N*-Cetyl pyridinium chloride; PbS crystals

1. Introduction

It is generally known that luminescence of materials are influenced by their different shapes and sizes [1]. Therefore, the synthesis of nano- and micro-crystals has become increasingly attractive. One of the materials is PbS which has a small band gap (0.41 eV) and a large exciton Bohr radius (18 nm) [2–4]. It has novel semiconducting and optical properties [5], which are very sensitive to the quantum-size effect [2,3]. There are a variety of shapes and sizes that play a role in determining their properties. Among them are cross shaped [6], star-like [3,7], fish bone-like [3], flower-like [3,8], nano-cubic [7], nano-rod [9], nano-belt [9], and nano-dendrite [9]. Biomolecules were used as a sulfur source and complexing agent for the synthetic processes [10,11]. A surfactant was used as the directing molecule to control the shapes and sizes of the crystals [1,4,9]. Currently, there are no reports on the use of both bio- and surfactant-molecules in a reaction process. For the present research, nano- and micro-crystalline PbS was hydrothermally synthesized using L-cysteine and *N*-cetyl pyridinium chloride at different pH values and at prolonged times. The final products were then analyzed for further discussion.

2. Experiment

Different shapes and sizes of PbS crystals were synthesized in home-made stainless steel autoclaves using 0.003 mol $Pb(NO_3)_2$, 0.003 mol L-cysteine ($C_3H_7NO_2S$) and 0.0005 mol *N*-cetyl pyridinium chloride ($C_{21}H_{38}NCl$) in 40 ml deionized water at 140 °C. After washing with water and 95% ethanol, and drying at 80 °C for 24 h, the final products were analyzed using an X-ray diffractometer (XRD) operated at 20 kV, 15 mA and using Cu Kα radiation in the 2θ angular range of 15–60°, transmission electron microscope (TEM) as well as the use of the selected area electron diffraction (SAED) technique operated at 200 kV, a scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) analyzer operated at 15 kV, a Raman spectrometer using 50 mW Ar Laser with $\lambda = 514.5$ nm, and a luminescence spectrometer using 250 nm exciting wavelength.

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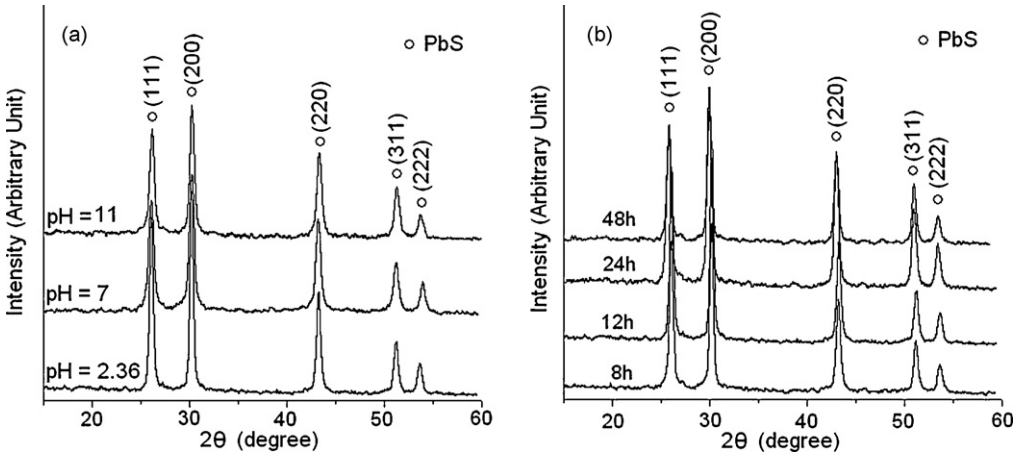

Fig. 1. XRD spectra of the products synthesized in (a) the solutions with different pH values for 12 h and (b) the solutions with the pH of 2.36 for different hydrothermal times.

3. Results and discussion

XRD spectra (Fig. 1) were indexed using Bragg's law for X-ray diffraction and compared with those of the JCPDS software (reference code: 05-0592) [12]. They were specified as cubic PbS with Fm-3m space group. The spectra are very sharp showing that well-crystallized PbS was successfully synthesized [13–15]. The products compose of a number of atoms aligning in a periodic lattice. The strongest intensity is at $2\theta = 30.08^\circ$ and diffracted from (2 0 0) plane of the crystalline products. For the present analysis, no characteristic peaks of impurities were detected showing that the products are pure phase.

Morphologies of the products were analyzed using SEM. Their images (Fig. 2) show that the products were successfully synthesized in a variety of shapes and sizes which were influenced by the pH values, cationic surfactant and hydrothermal times. At a pH of 7 and 11 for 12 h hydrothermal reaction, the products compose of a number of nano-sized granules. At a pH of 2.36 and 8–48 h prolonged times, the products become micro-sized flowers. At 8 h hydrothermal reaction, the flower-like product is made up of three to four petals and is not complete. At 12 h reaction, the product is made up of several petals. A distance between two apices of the two petals across the center of the flower is approximately fourteen microns long. Each of the petals is composed of a number of small plates arranged in systematic order. The products are more complete and contain a greater number of petals when the hydrothermal times were prolonged. There are ten petals at 48 h reaction. The products are very beautiful and attractive. They have never been synthesized using the biomolecule and surfactant in the hydrothermal reaction.

In addition to these, TEM images and SAED patterns (Fig. 3) are used to specify the morphologies and phases of the products. At a pH of 7 and 12 h, the product is composed of a number of <10 nm particles in nano-sized clusters. SAED

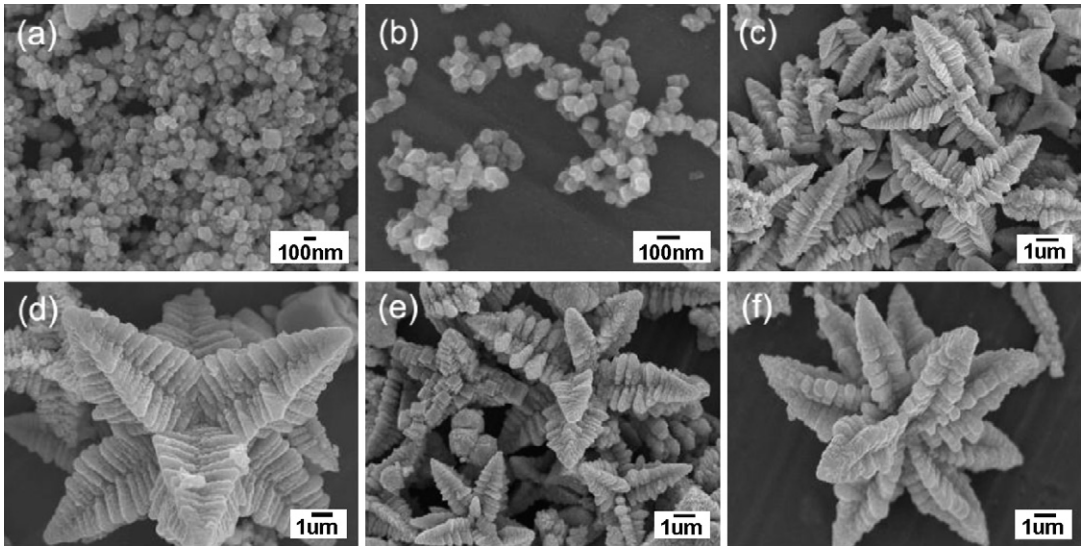

Fig. 2. SEM images of the products synthesized in (a and b) the solutions with the pH of 7 and 11 for 12 h and (c–f) the solutions with the pH of 2.36 for 8, 12, 24 and 48 h, respectively.

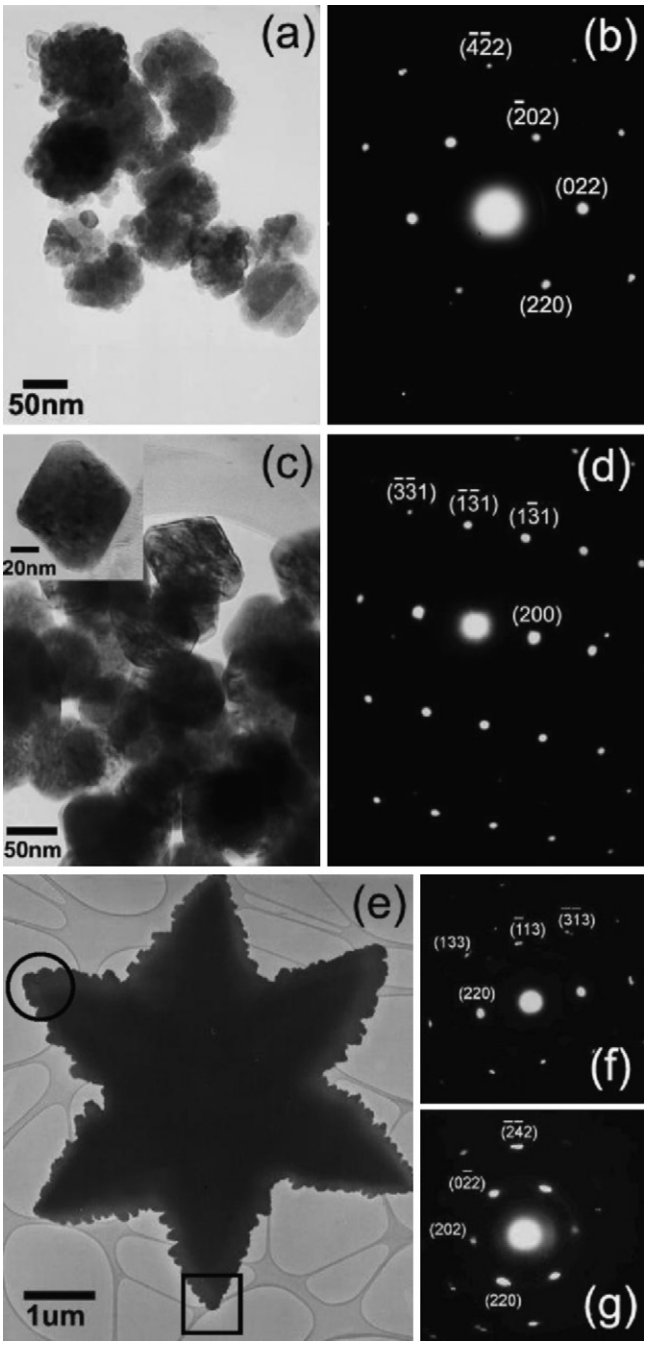

Fig. 3. TEM images and SAED patterns of the products synthesized at different pH values and hydrothermal times. (a and b) pH 7 and 12 h; (c and d) pH 11 and 12 h, and (e, f and g) pH 2.36 and 48 h. [(f and g) were analyzed on the (e)-product marked with a circle and square, respectively].

pattern of the product appears as systematic array of bright spots showing that a number of atoms are aligned in their normal lattice. The pattern was interpreted [16,17], and specified as cubic PbS crystal [12]. For the present analysis, the calculated electron beam [17] is in the $[\bar{1}\,1\,\bar{1}]$ direction. It is the direction that a beam of electrons was sent to the face of a crystal. When the pH was increased to 11, the product was composed of 75 nm truncated cubes. At lower magnification shown in the SEM image, it appears as granular. The SAED pattern was analyzed using an electron beam in the [0 1 3]

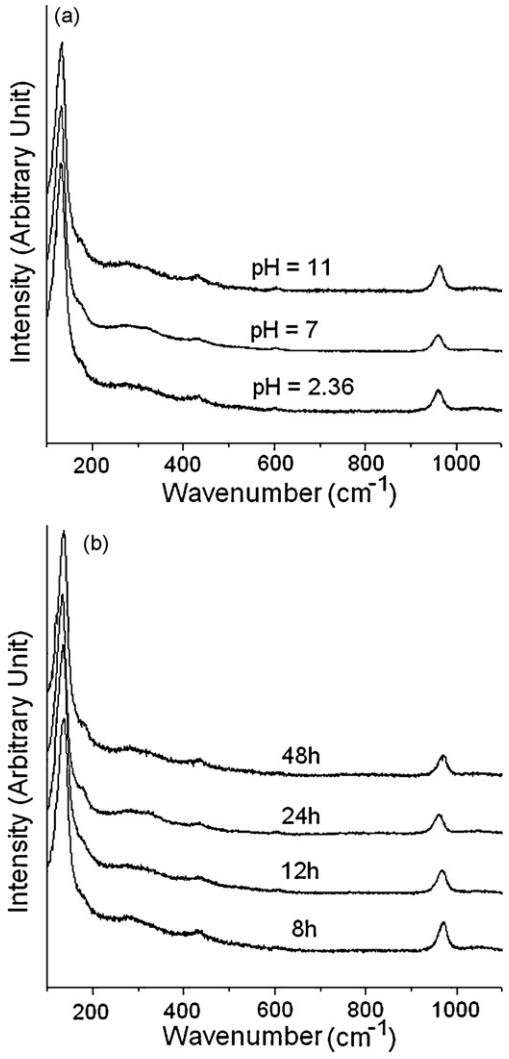

Fig. 4. Raman spectra of the products synthesized in (a) the solutions with different pH values for 12 h, and (b) the solutions with the pH of 2.36 for different hydrothermal times.

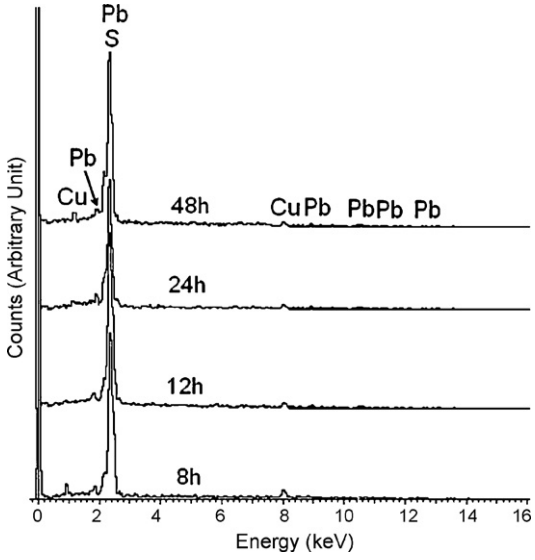

Fig. 5. EDX spectra of the products synthesized in the solutions with the pH of 2.36 for different hydrothermal times.

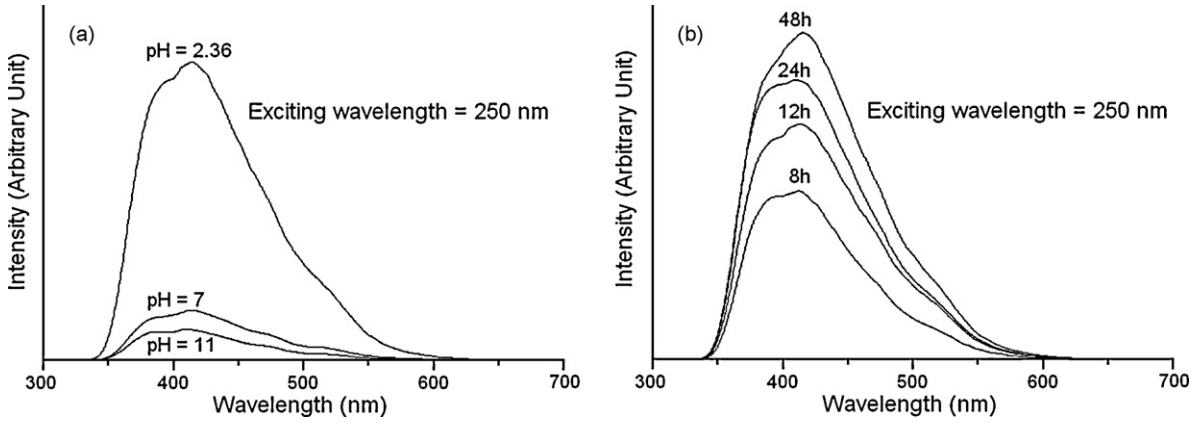

Fig. 6. PL emission of the products synthesized in (a) the solutions with different pH values for 12 h, and (b) the solutions with the pH of 2.36 for different hydrothermal times.

direction and specified as cubic PbS as well. At a pH of 2.36 and 48 h, the product is flower-like and specified as cubic PbS phase. Calculated electron beams used for the product analysis at a circle and square of the corresponding TEM image are in $[3\,\bar{3}\,2]$ and $[1\,\bar{1}\,\bar{1}]$ directions, respectively.

For the present research, *N*-cetyl pyridinium chloride was used as a cationic surfactant. L-Cysteine, a neutral and genetically coded amino acid, was used as a sulfur source and complexing agent. When $Pb(NO_3)_2$ reacted with L-cysteine to form a complex followed by the production of PbS nuclei (very fine particles) in the solution with the pH of 2.36, the surfactant was selectively adsorbed onto their surfaces. Therefore, the crystals were modeled to grow into small plates which compose the petals of micro-sized flowers. At a pH of 7 and 11, the solutions contain a greater number of OH^- ions than the acidic solution does. The cationic surfactant became less efficient in adsorbing onto PbS nuclei, which were capable of growing into the nano-sized particles in clusters and truncated cubes at the pH of 7 and 11, respectively.

A definite existence of the products was analyzed using a Raman spectrometer. The spectra (Fig. 4) contain prominent bands at the same wavenumbers although the products were synthesized using different conditions. Among the different spectra, their peaks are at 135, 278, 436, 602 and 970 cm^{-1}. The peak below 150 cm^{-1} is tentatively attributable to the so-called plasma line of the excitation laser [5,18]. The 278 cm^{-1} peak corresponds to two phonon process [5]. Those at 436 and 602 cm^{-1} are specified as the first and second overtone modes, respectively [18]. The peak above 960 cm^{-1} is attributable to oxy-sulfates [5,18]. Their constituents were characterized using EDX. The spectra (Fig. 5) reveal the presence of Pb and S. Cu of a copper stub was also detected. The detection of Pb and S using the EDX is in accord with the detection of PbS using the XRD and SAED.

Photoluminescence (PL) property of the products was characterized using a 250 nm exciting wavelength. Their PL spectra are shown in Fig. 6. The maximum intensities were detected at the same wavelength of 412 nm although their intensities are different. The intensities are sensitive to the morphologies. They increased with the increase in the acidities and hydrothermal times. At a constant hydrothermal time and different pH values, the PL intensity of the flower-like particles (pH 2.36, 12 h) is higher than those of the granules (pH 7, 12 h), and truncated cubes (pH 11, 12 h). At a constant pH value of 2.36, the flowers became the most complete at 48 h. At the present stage, the PL intensity was the highest. In general, the intensities are very sensitive to the number of electronic transfers and defects in the products as well [19].

4. Conclusions

Different shapes and sizes of PbS crystals were hydrothermally synthesized using biomolecule (L-cysteine) and surfactant (*N*-cetyl pyridinium chloride) at 140 °C. The detection of PbS phase, Pb and S constituents, and the first and second overtone modes are in good accord. These shapes are truncated cubes, granules and flower-like particles at a pH of 11, 7 and 2.36, respectively. At a pH of 2.36 and 48 h, the flowers were composed of ten petals. Their emission wavelengths were detected at the same value of 412 nm.

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