

## SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF LEAD SULFIDE NANOPARTICLES

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Large-scale PbS nanoparticles were successfully synthesized by a sonochemical method using  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and  $\text{CH}_3\text{CSNH}_2$  as lead and sulfur sources in ethylene glycol as solvent. The structure, morphology and phase of the PbS nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy and photoluminescence (PL) spectroscopy. They were found that the as-synthesized products were cubic structured PbS nanoparticles. By using 254 nm excitation wavelength, the nanoparticles show an emission peak at 390 nm. The formation mechanism of these PbS nanocrystals was also proposed in this report.

(Received June 14, 2012; Accepted September 14, 2012)

*Keywords:* Sonochemical method; PbS nanoparticles; Luminescence

### 1. Introduction

At present, nanostructured semiconducting materials are very interesting for materials scientists and engineers because of their novel properties, comparing to their corresponding bulks [1]. Among them, PbS is a very attractive sulfide material with narrow band gap of 0.41 eV at 300 K and large exciton Bohr radius of 18 nm [1-3]. It has non-linear optical properties and it shows a number of potential applications in optical switches and photography as IR detectors, solar cells, electroluminescent and photoluminescent material, including mode-locking for lasers [1, 3, 4].

Sonochemical is a novel and simple method, and has been proven to be a useful technique for the synthesis of nanomaterials such as ZnO,  $\text{MMoO}_4$  (M = Ca, Sr and Ba), and CdS [5-7]. The method arises from acoustic cavitation phenomenon, due to the formation, growth and implosive collapse of bubbles in a liquid medium, creating localized hot spots of high temperature and pressure (5000 °C and 20 MPa), including the heating and cooling rates above 1010 K/s by acoustic cavitation [1, 3, 4, 8, 9].

In this paper, highly uniform lead sulfide (PbS) nanoparticles were synthesized by a simple and mild sonochemical method. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray (EDX) spectroscopy and photoluminescence (PL) spectroscopy.

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## 2. Experiment

To synthesize PbS nanoparticles, each 0.005 mol of  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and  $\text{CH}_3\text{CSNH}_2$  was dissolved in 25 ml ethylene glycol (EG) under 30 min stirring at room temperature. The mixture was put in an ultrasonic bath and sonicated by 35 kHz ultrasonic wave for 1-5 h. Finally, gray-black precipitates were synthesized, collected, washed with de-ionized water and ethanol, and dried at 80 °C for 24 h, for further characterization.

The products were characterized by a SIEMENS D500 X-ray powder diffractometer (XRD) with a  $\text{Cu-K}_\alpha$  line of 1.542 Å wavelength, operating at 45 kV and 35 mA, including a JEOL JEM-2010 transmission electron microscope (TEM) and selected area electron diffractometer (SAED) equipped with an energy dispersive X-ray (EDX) analyzer (Oxford instruments, INCA) operating at 200 kV. The photoluminescence (PL) spectrum was collected by a PerkinElmer LS50B spectrometer over the 200-700 nm wavelength range at room temperature.

## 3. Results and discussion

XRD patterns of the as-synthesized PbS samples are shown in Fig. 1. In this research, the intensities of all diffraction peaks were increased with an increase in the prolonged ultrasonic reaction time. For the 5 h ultrasonic reaction time, the diffraction pattern was the highest intensity and the sharpest diffraction peaks, implying that this product contained the most ordered atomic arrangement with the highest crystalline degree. These patterns were indexed to be cubic rock-salt PbS structure, corresponding to the JCPDS database no. 05-0592 [10]. The average crystallite size was calculated by Scherrer formula

$$D = k\lambda / \beta \cos\theta \quad (1)$$

where  $D$  is the average crystallite size,  $k$  a constant equal to 0.89,  $\lambda$  the wavelength of the X-rays (0.1542 nm), and  $\beta$  the corrected half-width of the (111) plane [11, 12]. The calculated average crystallite size of PbS nanocrystallites were 20, 38 and 75 nm for 1, 3 and 5 h, became enlarged by the increasing in the lengths of the sonochemical processing time.

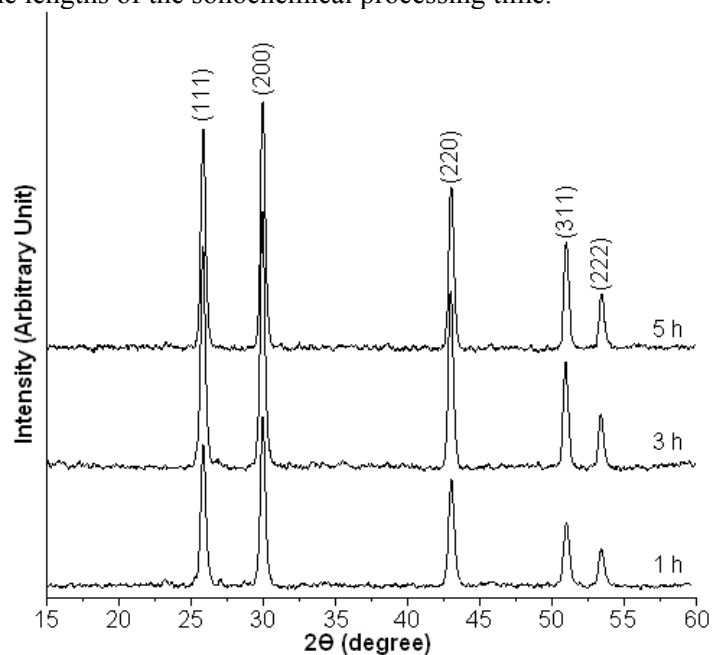


Fig. 1. XRD patterns of the products synthesized by sonochemical method for 1, 3 and 5 h.

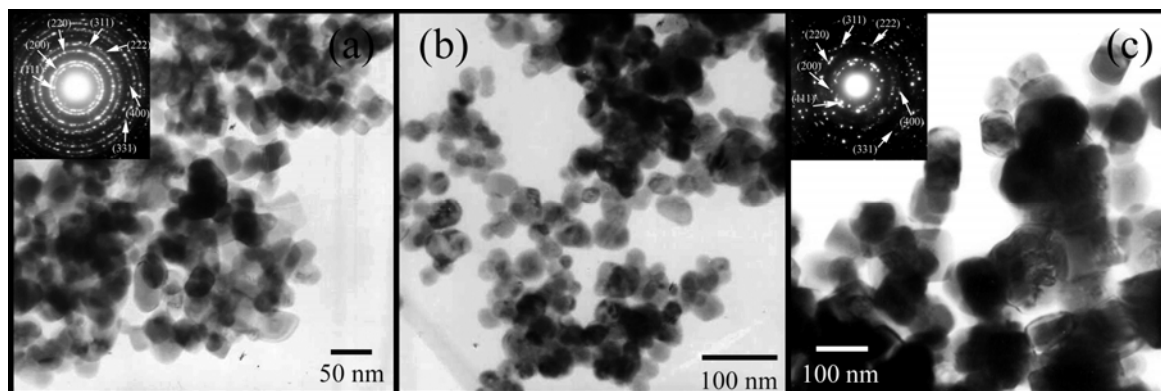


Fig. 2. TEM images and SAED patterns of PbS nanoparticles synthesized by sonochemical method for (a-c) 1, 3 and 5 h, respectively.

The effect of reaction time on the morphologies of PbS nanocrystals was investigated by TEM (Fig. 2). They were found that the PbS nanoparticles were formed by ultrasonic irradiation for 1 h. They were increased in size for the prolonging reaction time. For 5 h sonochemical reaction time, the product still retained their shape as spherical nanoparticles. By using TEM analysis, PbS samples were spherical nanoparticles with different size range, depending on the length of reaction time. Their average particle sizes were  $20.77 \pm 7.77$ ,  $29.39 \pm 5.76$  and  $82.86 \pm 20.96$  nm for 1, 3 and 5 h, respectively. The longer the sonochemical processing time was used, the larger the crystallite size was achieved. For 5 h sonochemical processing time, the facets and angles of the nanoparticles became more obvious. Particle size of the products was synthesized in all size with very narrow distribution, implying that their sizes were rather uniform – in favor with the luminescent property. The SAED patterns show a number of continuously bright spots diffracted from randomly nanoparticles. The patterns are so close that they formed fully concentric rings with the same centers. These indicate that the products were consisted of a number of nanocrystals oriented in different directions. The SAED patterns were indexed to correspond with the (111), (200), (220), (311), (222), (400) and (331) planes, in accordance with the cubic PbS rock-salt structure [10]. The quantitative and qualitative characterization of the PbS nanoparticles by energy dispersive X-ray (EDX) spectroscopy is shown in Fig. 3. They show the EDX spectra taken from an assembly of PbS nanoparticles synthesized by sonochemical method for 1 and 5 h. Peaks of EDX spectra associated with Pb and S were clearly detected and provided strong evidence of the PbS nanocrystals, including the atomic ratio of Pb:S of 1:1. However, the peaks associated with copper and carbon in the EDX spectra were caused by the electronic transition of carbon coated copper grids used as substrates during the analysis.

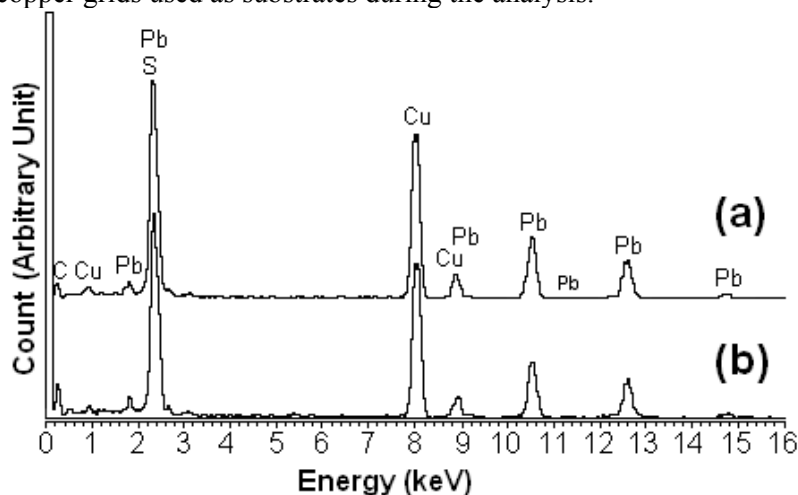


Fig. 3. EDX spectra of the as-synthesized PbS nanoparticles synthesized by sonochemical method for (a) 1 h and (b) 5 h.

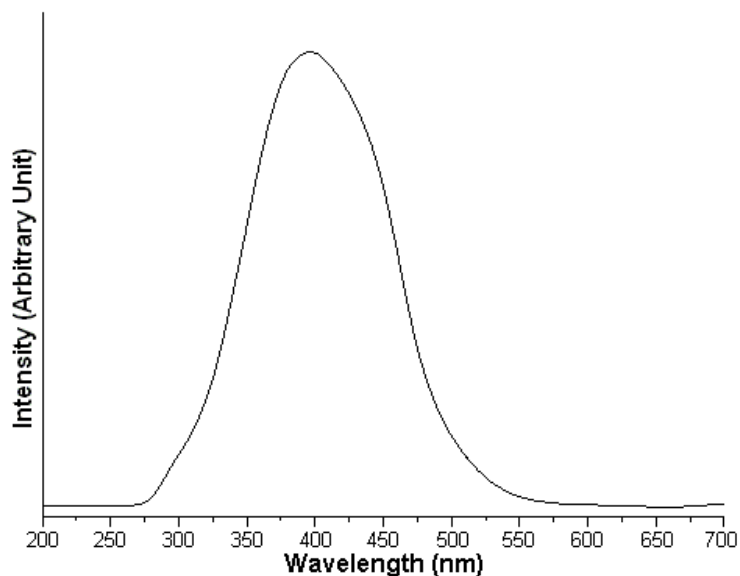
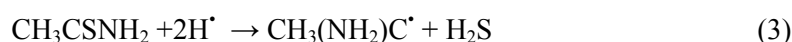


Fig. 4. PL spectrum of the as-synthesized PbS nanoparticles synthesized by sonochemical method for 5 h.

A possible formation mechanism of PbS nanoparticles was explained as shown below [2, 4, 13].



During sonochemical processing, the primary  $\text{H}^\bullet$  radicals formed by the ultrasonic vibration, which induced by the dissociation of water within the collapsing gas bubbles. In the solution,  $\text{H}^\bullet$  is a strong reducing radical. Rapidly,  $\text{CH}_3(\text{NH}_2)\text{C}^\bullet$  formed with the evolution of  $\text{H}_2\text{S}$ . Subsequently,  $\text{H}_2\text{S}$  reacted with  $\text{Pb}^{2+}$  ions to synthesize PbS molecules, which nucleated to form nuclei. These freshly born nuclei in the solution were able to grow into larger PbS grains to achieve the PbS nanoparticles with different orientations.

Fig. 4 shows photoluminescence (PL) spectrum of PbS nanoparticles excited by 254 nm wavelength at room temperature. It shows a strong and broad emission band centered at 390 nm, due to the transition of electrons from the conduction band edge to combine with holes trapped in the  $\text{Pb}^{2+}$  interstitial sites [13]. The as-synthesized PbS nanoparticles exhibit a blue-shift in the PL spectrum comparing to its bulk material, caused by the quantum size effect [14, 15].

#### 4. Conclusions

A simple sonochemical method was used to synthesize PbS nanoparticles in the presence of EG. XRD patterns were specified as only pure phase of cubic PbS structure, with an emission peak at 390 nm due to the recombination of electrons from the conduction band edge to holes trapped at the  $\text{Pb}^{2+}$  interstitial sites.

#### Acknowledgement

We wish to thank the Thailand's Office of the Higher Education Commission for providing financial support through the National Research University (NRU) Project for Chiang Mai University.

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