Properties of PbS Nanocrystals Synthesized by Sonochemical and Sonoelectrochemical Methods*

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Lead sulfide nanocrystals have been synthesized via sonochemical and sonoelectrochemical methods from precursors such as lead acetate ($\text{Pb}(\text{Ac})_2$: $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$), thioacetamide (TAA: CH_3CSNH_2) and cetyltrimethyl ammonium bromide (CTAB: $\text{C}_{19}\text{H}_{42}\text{BrN}$). The samples were characterized by X-ray diffraction, high resolution transmission electron microscopy, selected area electron diffraction and ultraviolet-visible absorption spectroscopy. The results showed that the samples prepared by sonoelectrochemical technique have a cluster-like form composed of the small nanocrystals with the size of 6-10 nm, while the samples prepared by sonochemical technique constituted of the nanoparticles with the size of about 20 nm, mixed with the nanorods of 20 nm in width and 80 nm in length. All the PbS nanocrystals have a face-centered cubic crystal structure. The optical absorption spectra exhibit a strong blue-shift due to the quantum size effect. [DOI: 10.1380/ejsnt.2011.494]

Keywords: Nanocrystals; Lead sulfide; Sonochemical; Sonoelectrochemical methods

I. INTRODUCTION

Lead sulfide (PbS) is an important IV-VI semiconductor compound. Bulk PbS has a cubic (rock salt) crystal structure and a narrow direct band gap (0.4 eV) at the L point of the Brillouin zone [1]. PbS is used for fabricating infrared detectors, Pb^{2+} ion-selective sensors. In the past decades, there has been much interest in synthesis and characterization of nanoscale PbS because of its large exciton Bohr radius (~ 18 nm). Indeed, it is relatively easy to prepare particles of ~ 18 nm size and it could be expected that these PbS nanoparticles will exhibit a strong quantum confinement effect. It was reported that the band gap of PbS can be widened to the visible region by forming nanoparticles [2–6]. PbS nanoparticles are hence promising materials in electroluminescent devices such as light-emitting diodes and luminescent display devices. PbS nanostructures with different morphologies have been prepared including particles [3–5], wires [7], rods [6, 8], tubes [9], and hollow spheres [10] by different methods such as wet chemistry [4, 6, 7], solvothermal [11], thermal decomposition [12], microwave irradiation [5], electrodeposition [13], sonochemical [5, 9, 10], and photochemical using UV- or γ - irradiation [3, 14].

Sonochemistry is the application of ultrasound to chemical reactions and processes. In the past decades, sonochemistry was applied in materials science as a very useful synthetic method. It was discovered as early as 1934 that the application of ultrasonic energy could increase the rate of electrolytic water cleavage. The effects of ultrasonic radiation on chemical reactions are due to the very high temperatures (~ 5000 K) and pressures (~ 1800 atm), which develop in and around the collapsing bubble [15, 16]. However, only recently the potential benefit of combining sonochemistry with electrochemistry has been increasingly studied. Some of these beneficial effects

include acceleration of mass transport, cleaning and degassing of the electrode surface, and an increased reaction rate [17, 18].

In this paper we report the synthesis of PbS nanocrystals by both sonochemical and sonoelectrochemical methods. X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analyses showed that the prepared PbS samples possess a cubic rock salt crystal structure. Ultraviolet-visible (UV-vis) absorption spectra indicated a strong blue-shift in the PbS nanocrystals due to the quantum confinement effect.

II. EXPERIMENTAL

A. Synthesis of PbS nanocrystals

In our experiment, all reagents were of analytical grade and were used without any further purification. Preparation of precursor solutions was as follows: Solution of 0.2 M lead acetate ($\text{Pb}(\text{Ac})_2$: $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) and solution of 0.2 M thioacetamide (TAA: CH_3CSNH_2) were mixed in a certain mole ratio. An appropriate amount of 0.2 M cetyltrimethylammonium bromide (CTAB: $\text{C}_{19}\text{H}_{42}\text{BrN}$) solution was added to the mixture. The solution mixture was sonicated for 5 min. The as-prepared mixture was transferred to a glass vessel for executing sonochemical or sonoelectrochemical process. The sonochemical or sonoelectrochemical process was carried out at room temperature for 60 min under flowing nitrogen gas to remove oxygen. When the reaction finished, a black precipitate occurred. The precipitate was separated by centrifugation at the rate of 15000 rpm, washed repeatedly with distilled water and absolute ethanol to remove the residue of organic solvents. The final products were dried in air at 60°C for 6 h.

B. Instruments

The schematics of the experimental setup assembled for sonochemical and sonoelectrochemical experiments are

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FIG. 1: Experimental setup for (a) sonochemical and (b) sonoelectrochemical experiments, (c) Schematic representation of (above) the current and (below) the ultrasonic pulse forms.

shown in Fig. 1. A VCX 750 ultrasonic generator (Ti-horn 20 kHz, 1.3 cm diameter and 15 cm long) worked as the ultrasound source. Ti-horn was immersed by 1.5 cm in the reaction solution. In the sonochemical experiment, the ultrasonic pulse had the duration of 5 s and the repetition period of 10 s.

In the case of sonoelectrochemistry, two platinum plates (1 cm × 1 cm × 0.05 cm) were used as electrodes. The current pulse possessed the duration $t_e \sim 0.3$ s and the repetition period $T \sim 1.3$ s. The ultrasonic pulse had the length $t_s \sim 0.2$ s and was on right at the moment the current pulse was off (see Fig. 1(c)).

C. Characterization of the samples

The crystal structure of the PbS samples was analyzed by using an x-ray diffractometer (SIEMENS D5005, Bruker, Germany) with Cu-K α_1 ($\lambda = 0.154056$ nm) irradiation. The morphology of the samples was characterized by using a high resolution transmission electron microscope (FEI Tecnai TF20 FEG TEM). The composition of the samples was determined by an energy dispersive X-ray (EDX) spectrometer (EDS, OXFORD ISIS 300) attached to the JEOL-JSM 5410 LV scanning electron microscope. UV-vis absorption spectra of the nanoparticle containing solutions were collected with a Shimadzu UV 2450 PC spectrometer. Diffuse reflection spectroscopy measurements of the PbS powders were carried out on an UV-VIS-NIR Cary 5G spectrophotometer. Spectra were recorded at room temperature. Absorption spectra of the samples were obtained from the diffuse reflectance values by using the Kubelka-Munk function [19]: $F(R) = (1 - R)^2/2R = K/S$ where R , K and S are the reflection, the absorption and the scattering coefficient, respectively.

III. RESULTS AND DISCUSSION

A. The PbS samples prepared by sonoelectrochemical method

XRD pattern of the PbS nanoparticles is shown in Fig. 2(a). Diffraction peaks at 25.7° , 29.8° , 42.7° , and 50.6° correspond to the (111), (200), (220), and (311) lattice planes of the PbS face-centered cubic structure. Lattice

FIG. 2: (a) XRD pattern and (b) energy dispersive x-ray spectrum of the PbS samples prepared by sonoelectrochemical method.

constant determined from XRD pattern is $a = 5.933$ Å in good agreement with the value of 5.936 Å in JCPDS-ICDD 1993, No.5-592. The crystal size of about 6 nm has been obtained from the following Debye - Scherrer relations [20]:

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

where β is the full width at half maximum (FWHM) in radians of the diffraction peaks, θ is the Bragg's diffraction angle and λ is the wavelength for the K α_1 component of the employed copper radiation (1.54056 Å). The EDX spectrum showed in Fig. 2(b) indicated that there are only elements Pb and S in the prepared PbS samples.

FIG. 3: (a) TEM image, (b) HRTEM image, and (c) SAED image of the PbS nanocrystals prepared by sonoelectrochemical method. The inset in Fig. 3(a) is a low magnified image of the PbS samples. The inset in Fig. 3(b) is the fast Fourier transform pattern of the (111) planes.

FIG. 4: UV-vis absorption spectrum of the PbS nanocrystals dispersed in water. The inset is the plot of $(\alpha h\nu)^2$ as a function of photon energy $h\nu$.

FIG. 5: Typical XRD pattern of the PbS nanocrystals prepared by sonochemical method.

Typical TEM, HRTEM images and SAED pattern of the PbS samples are shown in Fig. 3. It can be seen from Fig. 3(a) and the inset in it, the nanoparticles agglomerate, forming nanoclusters with the size of about 50 nm. Figure 3(b) represents the magnified HRTEM image of the PbS nanoparticles with the lattice fringes of the (111) planes. The spacing of the adjacent (111) lattice planes in the HRTEM image is found to be 3.35 Å, which is in agreement with the value of 3.45 Å obtained

from the XRD analysis. The fast Fourier transform (FFT) pattern of the HRTEM image shown in the inset of Fig. 3(b) also confirmed a face-centered cubic structure. The SAED image depicted in Fig. 3(c) consisted of diffraction rings, which indicates that the PbS nanocrystals arrange in random manner without priority direction. In particular, one can observe more diffraction rings in the SAED pattern than these in XRD pattern. To measure UV-vis absorption, the PbS nanocrystals were dispersed in water. A typical UV-vis absorption spectrum of the PbS nanocrystals is presented in Fig. 4.

The PbS nanocrystals start strong absorption from the wavelength of 600 nm, in agreement with previous work [14]. The relation between the absorption coefficients (α) and the incident photon energy ($h\nu$) for the case of allowed direct transition is written as [21]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where A is a constant and is the bandgap of the material. The plot of the $(\alpha h\nu)^2$ versus $h\nu$ for the PbS nanocrystals is represented in the inset of Fig. 4. By extrapolating the straight portion of the graph on $h\nu$ axis at $\alpha = 0$, we found the bandgap of the PbS to be 2.79 eV, which is much larger than that of bulk PbS. This indicates that the PbS nanocrystals exhibit the quantum confinement effect due to the decrease of the crystal size.

B. The PbS samples prepared by sonochemical method

XRD pattern depicted in Fig. 5 points out that the PbS nanocrystals prepared by sonochemical method also possess face-centered cubic structure. Diffraction peaks correspond to the (111), (200), (220), (311), (222), (400), and (331) lattice planes. Lattice constant calculated from XRD pattern is $a = 5.962$ Å. The size of PbS nanocrystals determined according to Debye-Scherrer formula is about 10 nm.

Representative TEM, HRTEM images and SAED pattern of the PbS samples are shown in Fig. 6. As can be seen from Fig. 6(a), the nanoparticles are clearly separated each from other, (some of them have a cubic form with the size of 10 nm), and mixed with PbS nanorods

FIG. 6: (a) TEM image, (b) HRTEM image, and (c) SAED image of the PbS nanocrystals prepared by sonochemical method. The inset in Fig. 6(b) is the fast Fourier transform pattern of the (111) planes.

FIG. 7: (a) UV-vis absorption spectrum of the PbS nanocrystals dispersed in water, (b) UV-vis absorption spectrum of the PbS nanopowders obtained from the data of diffuse reflection measurement. The insets are the plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$.

with the width approximate to the size of particles and fairly long length. Aspect ratio (length-to-width ratio) has the values from 4 to 5. The distance between the adjacent (111) lattice planes in the HRTEM image (see Fig. 6(b)) is found to be 3.45 Å, which is in good agreement with the value of 3.45 Å obtained from the XRD analysis. The SAED image presented in Fig. 6(c) consisted of diffraction rings, which indicates that the PbS nanocrystals arrange in random manner.

Figure 7(a) shows the UV-vis absorption spectrum at room temperature of the PbS nanoparticles dispersed in

water. From the plot of the $(\alpha h\nu)^2$ as a function of $h\nu$, one found the value of the bandgap to be 3.22 eV, which is lower than the value of 3.49 eV obtained by previous paper [5]. To verify the blue-shift of the absorption edge, we measure diffuse reflection spectra of the PbS nanopowders. Absorption spectra of the samples were obtained from the diffuse reflectance values by using the Kubelka-Munk function. Typical spectrum is presented in Fig. 7(b). The spectrum exhibits a sharp absorption edge and an onset of absorption at the wavelength of 365 nm. From the plot of the $(\alpha h\nu)^2$ as a function of $h\nu$, one found the value of the bandgap to be 3.26 eV, which is in good agreement with the results in the case of the PbS nanoparticles dispersed in water.

IV. CONCLUSION

PbS nanocrystals have been synthesized via sonochemical and sonoelectrochemical methods from precursors such as lead acetate ($\text{Pb}(\text{Ac})_2$: $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$), thioacetamide (TAA: CH_3CSNH_2) and cetyltrimethyl ammonium bromide (CTAB: $\text{C}_{19}\text{H}_{42}\text{BrN}$). The results of XRD, HRTEM, and SAED analysis indicated that all the PbS nanocrystals possess a face-centered cubic structure. The samples prepared by sonoelectrochemical technique are the nanoclusters with the size of ~ 50 nm and composed of the small nanocrystals with the size of 6 - 10 nm, while the samples prepared by sonochemical technique constituted of the nanoparticles with the size of about 20 nm, mixed with the nanorods of 20 nm in width and 80 nm in length. The UV-vis optical absorption spectra exhibit a strong blue-shift due to the quantum size effect. The bandgap of the samples prepared by sonoelectrochemical and sonochemical methods are determined to be 2.79 eV and 3.26 eV, respectively.

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- [1] Landolt-Bornstein, Group III Condensed Matter, Volume 41C, *Non-Tetrahedrally Bonded Elements and Binary Compounds I* (Springer-Verlag, 1998), p. 1.
 - [2] Y. Wang, A. Suna, W. Mahler, and R. J. Kasowski, J. Chem. Phys. **87**, 7315 (1987).
 - [3] N. B. Egorov, L. P. Eremin, V. F. Usov, and A. M. Larionov, High Energy Chem. **41**, 251 (2007).
 - [4] J. H. Warner, E. Thomsen, A. RWatt, N. R. Heckenberg, and H. Rubinsztein-Dunlop, Nanotechnology **16**, 175 (2005).
 - [5] Y. Zhao, X. H. Liao, J. M. Hong, and J. J. Zhu, Mater. Chem. Phys. **87**, 149 (2004).
 - [6] W. P. Lim, H. Y. Low, and W. S. Chin, J. Phys. Chem. B **108**, 13093 (2004).
 - [7] D. Yu, D. Wang, Z. Meng, J. Lu, and Y. J. Qian, J. Mater. Chem. **12**, 403 (2002).
 - [8] S. Wang, and S. Yang, Langmuir **16**, 389 (2000).
 - [9] S. F. Wang, F. Gu, M. K. Lu, G. J. Zhou, and A. Y. Zhang, J. Cryst. Growth **289**, 621 (2006).
 - [10] S. F. Wang, F. Gu, and M. K. Lu, Langmuir **22**, 398 (2006).
 - [11] L. Xu, W. Q. Zhang, Y. W. Ding, W. C. Yu, J. Y. Xing, F. Q. Li, and Y. T. Qian, J. Cryst. Growth **273**, 213 (2004).
 - [12] S. M. Lee, Y. W. Jun, S. N. Cho, and J. W. Cheon, J. Am. Chem. Soc. **124**, 11244 (2002).
 - [13] M. Sharon, K. S. Ramaiah, M. I. Kumar, M. Neumann-Spallart, and C. Levy-Clement, J. Electroanal. Chem. **436**, 49 (1997).
 - [14] X. Changqi, Z. Zhicheng, W. Hailong, and Y. Qiang, Mater. Sci. Engin. B **104**, 5 (2003).
 - [15] E. B. Flint and K. S. Suslick, Science **253**, 1397 (1991).
 - [16] K. S. Suslick, S. B. Choe, A. A. Cichowlas, and M. W. Grinstaff, Nature **353**, 414 (1991).
 - [17] T. J. Mason, J. P. Walton, and D. J. Lorimer, Ultrasonics **28**, 333 (1990).
 - [18] F. Marken and R. Compton, Ultrasonics Sonochem. **3**, S131 (1996).
 - [19] N. N. Yamashita, J. Phys. Soc. Jpn. **35**, 1089 (1973).
 - [20] B. E. Warren, *X-ray Diffraction* (Dover publications, Inc., New York, 1990), p. 253.
 - [21] J. I. Pankove, *Optical Processes in Semiconductors* (Prentice-Hall Inc., 1971), p. 36.