

Sonochemically prepared PbS nanostructures and investigation of their optical and structural properties

Z. HOSSEINI^a, Y. AZIZIAN-KALANDARAGH^b, A. KHODAYARI^c, B. NEDAEI-SHAKARAB^d

^aIslamic Azad University Maragheh Branch Maragheh Iran

^bDepartment of Physics, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran

^cDepartment of Chemistry, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran

^dIslamic Azad University- Ardabil Branch, Ardabil-Iran

A facile and room temperature route for the production of very small, nearly monodispersed nanocrystalline lead sulfide (PbS) by ultrasonic irradiation in aqueous solution are presented. In this process, 3-mercaptopropionic acid (3-MPA) was used as a capping agent. The X-ray diffraction (XRD) studies display that the products are well crystallized in the form of cubic structure. The morphology of as-prepared nanoparticles was characterized by scanning electron microscopy (SEM). The optical absorption studies also show the band gap of PbS material was blue shifted due to quantum confinement of charge carriers in quantum sized volume. A possible formation mechanism for the production of nanostructures in the aqueous solution of the product with the aid of ultrasonic irradiation is proposed.

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1. Introduction

In recent years, there has been considerable interest in semiconductors nanostructures due to the quantum size effect they exhibit [1-4]. Lead sulfide has important optical and structural properties it is therefore, and an important extensively used such as in Pb²⁺ ion-selective sensors [5], IR detectors [6] photography [7], and solar absorbers [8]. Many methods have been developed for synthesis of lead sulfides including liquid phase synthesis [9], gas phase synthesis [10], solvothermal [11], Chemical vapor deposition [12], electrodeposition [13], polymer films route [14], epitaxially growth [15] microwave [16] and sonochemical method [17].

Generally, these reactions require high temperature (500°C), complicated and long reaction time and consumption of toxic and highly sensitive compounds. The utilization of ultrasonic irradiation for production of nanomaterials has been a research topic of great interest due to simplicity of sonochemical method, inexpensive price of equipment and approvingly material is obtained in the crystalline phase. The chemical effects of ultrasound come from non-linear acoustic phenomena, primarily acoustic cavitation. The extreme conditions attained during ultrasonic irradiation have been exploited to generate metal sulfides [18,19]. Ultrasound-assisted method has been accepted as a new green chemical method for preparation of different types of nanomaterials [20-23].

In this paper we report the synthesis of PbS nanostructures in aqueous solution in the presence of 3-MPA acting as a stabilizing agent, which have been grown via an ultrasound-assisted process.

2. Experimental details

Lead (II) acetate (Pb(C₂H₃O₂)₂·3H₂O extra pure), sodium sulfide (Na₂S), 3-mercaptopropionic acid (3-MPA) and ethanol were obtained from Merck, and employed without further purification. At room temperature, 5.7g lead acetate and 1.2g of sodium sulfide were added to 3 ml of the aqueous solution of 10% 3-MPA in a flask and imposed to ultrasonic irradiation for 60 min. The dark black precipitates were separated by centrifugation, washed at least four times with deionized water and ethanol. Production yield of the sample imposed to ultrasonic irradiation is considerably higher.

The obtained products were characterized by X-ray diffraction (XRD, Philips Xpert, Cu K α radiation $\lambda = 0.15406$ nm), scanning electron microscope (SEM, LEO 1430VP), energy dispersive analysis of X-rays (EDX, JEOL 2000FX) and Optical absorption measurement (UV-Visible spectrophotometer model Carry 5, Varian).

3. Results and discussion

The XRD pattern of the as-prepared PbS nanoparticles is depicted in Fig. 1. The diffraction peaks reveal that all products have same crystal structure and correspond to planes of (111), (200), (220), (311), (222), (400) and (311) for the cubic type PbS nanocrystal system. The lower weak diffraction curve is due to selecting weaker recording parameters, such as current and voltage in XRD instrument.

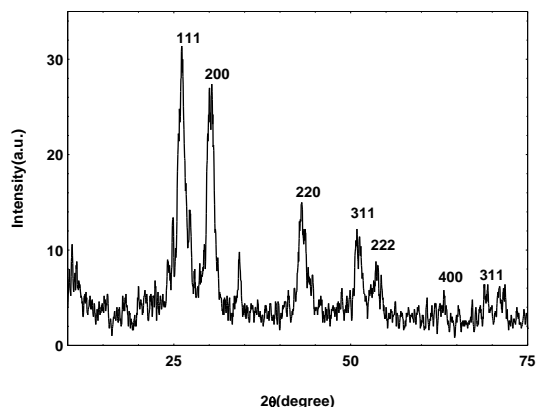


Fig. 1. XRD pattern of as-prepared PbS nanostructures prepared using ultrasound-assisted method.

The average diameter of the nanoparticles, D , was also determined using Scherrer's equation [23]

$$D = \lambda / (B \cos \theta_B) \quad (1)$$

where B is the FWHM in diffraction pattern (at $2\theta_B$) and λ is the applied wavelength (0.15406 nm). The particle size obtained accordingly is 10.2 nm for (111) plane.

The SEM records are exhibited in Fig. 2(a,b). From Fig. 2 (a,b) the distribution of the particles produced in water as solvent, is nearly monodispersed nanoparticles with average sizes between 10-50nm which aggregated in the form of polydispersive nanoclusters with average cluster sizes between 50-100nm.

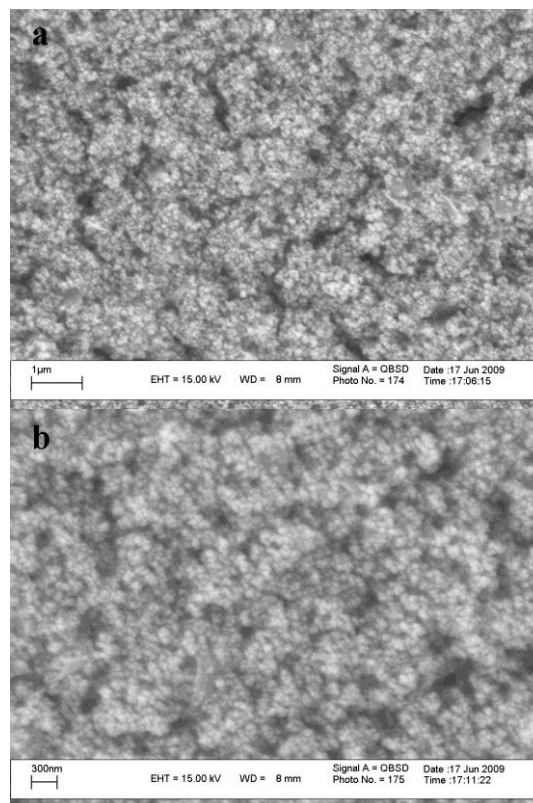


Fig. 2 .(a and b). The SEM image of the as-prepared PbS nanostructures at 30kx and 50kx magnifications.

The EDX pattern is displayed in Fig. 3. The curve reveals the presence of Pb and S peaks with nearly stoichiometric ratio (Pb: 46%, and S: 54%). Other peaks in this figure correspond to copper which are due to sputter coating and were not considered for elemental analysis of Pb and S.

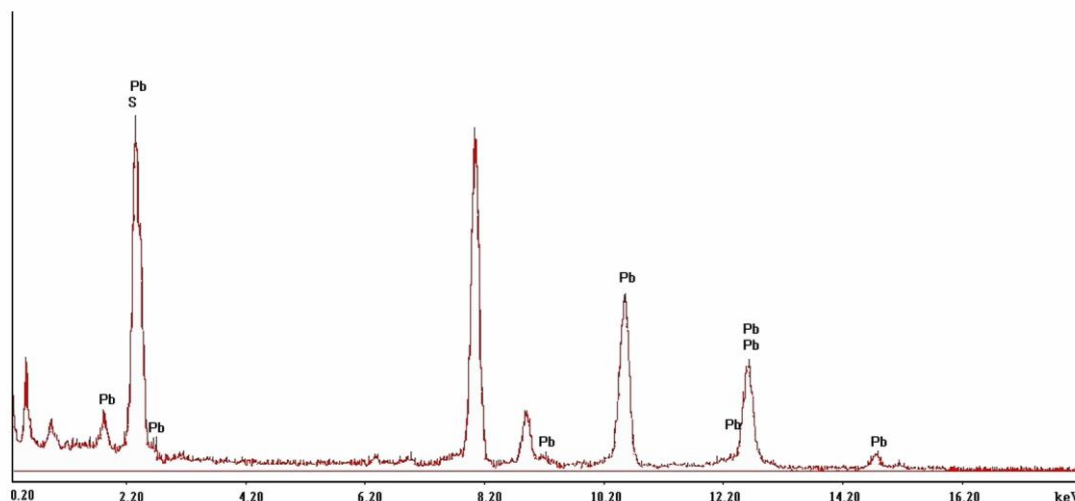
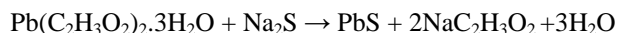


Fig. 3. The EDX pattern of the as-prepared PbS nanostructures prepared by ultrasound- assisted method.

A possible formation mechanism of PbS nanoclusters in aqueous solutions using ultrasound-assisted method is presented.



Reaction of the metal cations with the sulfide anions lead to metal chalcogenide. Thus PbS particles can

preferably grow on these active sites and finally lead to PbS nanostructures.

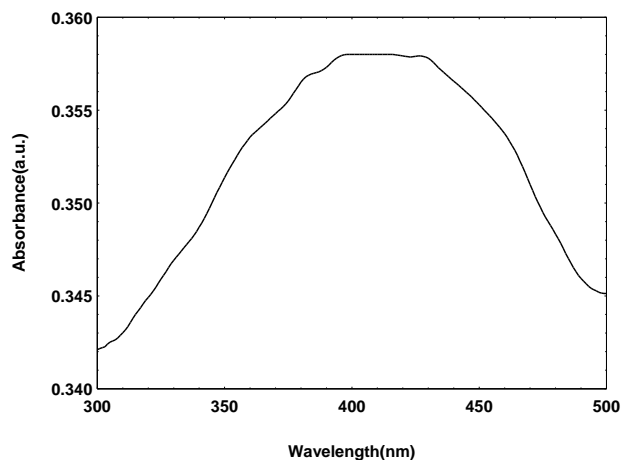


Fig. 4. *Uv-Visible absorptions spectra of PbS nanostructures prepared by ultrasound-assisted method.*

Fig. 4 illustrates of UV-Vis spectra of PbS nanocrystals prepared by an ultrasound-assisted technique. It is evident from this figure that sample exhibit an absorption peak at wavelength correspond to 3eV energy gap, suggesting blue shift of about 2.6eV in comparison with its bulk crystals of semiconductor PbS of about 0.4eV [24], indicating the nanoparticles are small and the blue shift corresponds to the confinement of electrons and holes in an extremely small volume of space.

4. Conclusions

Ultrasound-assisted method was proposed for preparation of pure crystalline PbS nanostructures. This room-temperature and environmentally benign green method is fast which remarkably shortens synthesis time and avoids the complicated synthetic procedures. Huge shift in band gap of PbS nanostructures was observed due to confinement of electrons and holes in a very small region.

References

- [1] L. Manna, E. C. Scher, A. P. Alivisatos, *J. Am. Chem. Soc.* **122**(12) 700 (2000).
- [2] S. Kolahi, S. Farjami-Shayesteh, Y. Azizian-Kalandaragh, *Materials Science in Semiconductor Processing* **14**, 294 (2011).
- [3] A. R. Loukanov, C. D. Dushkin, *Colloid. Surf. A* **245**, 9 (2004).
- [4] A. P. Alivisatos, W. Cu, C. Larabell, *Annu. Rev. Biomed. Eng.* **7**, 55 (2005).
- [5] H. Hirata, K. Higashiyama, *Bull. Chem. Soc. Japan* **44**, 2420 (1971).
- [6] P. Gadenne, Y. Yagil, G. Deutscher, *J. Appl. Phys.* **66**, 3019 (1989).
- [7] P. K. Nair, O. Gomezdaza, M. T. S. Nair, *Adv. Mater. Opt. Electron.* **1**, 139 (1992).
- [8] T. K. Chaudhuri, S. Chatterjes, *Proc. Int. Conf. Thermoelectr.* **11**, 40 (1992).
- [9] T. Trindade, P. O. Brien, X. Zhang, M. Motevalli, *J. Mater. Chem.* **7**, 1011 (1997).
- [10] C. Kaito, Y. Saito, K. Fujita, *Jpn. J. Appl. Phys.* **26**, 1973 (1987).
- [11] C. Zhang, Z. Kang, E. Shen, E. Wang, L. Gao, F. Luo, C. Tian, C. Wang, Y. Lan, *J. Phys. Chem.* **B110**, 184 (2006).
- [12] J. P. Ge, J. Wang, H. X. Zhang, X. Wang, Q. Peng, Y. D. Li, *Chem. Eur. J.* **11**, 1889 (2005).
- [13] K. K. Nanda, S. N. Sahu, *Adv. Mater.* **13**, 280 (2001).
- [14] S. H. Wang, S. H. Yang, *Langmuir* **16**, 389 (2000).
- [15] J. P. Yang, J. H. Fendler, *J. Phys. Chem.* **99**, 5505 (1995).
- [16] A. S. Obaid, M. A. Mahdi, Y. Yusof, M. Bououdina, Z. Hassan, *Materials Science in Semiconductor Processing*, **16**(3), 971 (2013).
- [17] A. Phuruangrat, S. Thongtem, T. Thongtem, B. Kuntalue, *Digest Journal of Nanomaterials and Biostructures*, **7**(4), 1413 (2012).
- [18] Y. Azizian-Kalandaragh, A. Khodayari, *Phys. Status Solidi A* **207**(9), 2144 (2010).
- [19] Y. A. Kalandaragh, M. B. Muradov, R. K. Mamedov, M. Behboudnia, A. Khodayari, *Optoelectron. Adv. Mater. - Rapid Comm.* **2**(1), 42 (2008).
- [20] Y. Azizian-Kalandaragh, *Optoelectron. Adv. Mater. - Rapid Comm.* **4**(2), 174 (2010).
- [21] Y. Azizian-Kalandaragh, *Optoelectron. Adv. Mater. - Rapid Comm.* **4**(11), 1655 (2010).
- [22] J. Hassanzadeh, Y. Azizian-Kalandaragh, A. Khodayari, *J. Optoelectron. Adv. Mater.* **14**(5-6), 473 (2012).
- [23] B. D. Cullity, *Elements of X-ray diffraction*, 2nd ed, London: Addison Wesley, 1978.
- [24] Yonghong Ni, Hongjiang Liu, Fei Wang, Yongye Liang, Jianming Hong, Xiang Ma, Zheng Xu, *Cryst. Res. Technol.* **39**(3), 200 (2004).

*Corresponding author: azizian@uma.ac.ir
yashar.a.k@gmail.com