Facile and Room Temperature Preparation and Characterization of PbS Nanoparticles in Aqueous [EMIM][EtSO₄] Ionic Liquid Using Ultrasonic Irradiation

M. Behboudnia,[†,*] A. Habibi-Yangjeh, Y. Jafari-Tarzanag, and A. Khodayari

Department of Chemistry, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran
[†]Department of Physics, Urmia University of Technology, P.O. Box 57155-419, Urmia, Iran
[*]E-mail: mbehboudnia@yahoo.com
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At room-temperature, a facile, seedless, and environmentally benign green route for the synthesis of star like PbS nanoclusters at 7 min in aqueous solution of 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIM] [EtSO₄], room-temperature ionic liquid (RTIL), *via* ultrasonic irradiation is proposed. The X-ray diffraction studies display that the products are excellently crystallized in the form of cubic structure. An energy dispersive X-ray spectroscopy (EDX) investigation reveals the products are extremely pure. The absorption spectra of the product exhibit band gap energy of about 4.27 eV which shows an enormous blue shift of 3.86 eV that can be attributed to very small size of PbS nanoparticles produced and quantum confinement effect. A possible formation mechanism of the PbS nanoparticles using ultrasonic irradiation in aqueous solution of the RTIL is presented.

Key Word : Room-temperature ionic liquid, Ultrasonic irradiation, PbS, Nanoclusters

Introduction

Semiconductor nanomaterials have attained extensive attention because of their special optical, catalytic and electronic properties arising from quantum confinement of electrons and large surface area. PbS is an important semiconductor material with a narrow band gap (0.41 eV) and large exciton Bohr radius (18 nm).[1] The strong quantum confinement effect exhibited by PbS nanoparticles has led to their potential application as IR detector.[2] Lead sulfide nanoparticles have also been used in optical devices such as optical switches due to their non-linear optical properties.[3] Because of its unique optical and emission properties, infrared emitters and solar control coatings are some of the recent applications of PbS.[4,5] Up to now, numerous chemical methods such as micelles, polymers, sol-gel technique, hydrothermal technique and microwave irradiation[6] have been developed to fabricate PbS nanomaterials. However, high temperature or long reaction time was usually involved in these methods. Also, most of the methods involved environmentally malignant chemicals and organic solvents, which are toxic and not easily degraded in the environment.

The utilization of ultrasonic irradiation (USI) for production of nanomaterials has been a research topic of great interest. This is in consequence of the simplicity of sonochemical method, the inexpensive price of the equipment and that in many cases the as-prepared 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 USI (transient temperature of ~ 5000 K, pressure of 1800 atm and cooling rates in excess of 10^{10} K/S)[7] has been exploited to generate metal sulfides.[8-10]

Room-temperature ionic liquids have shown tremendous promise as replacements for the toxic and volatile organic solvents used in many applications. Ionic liquids have been widely studied as a new kind of reaction media owing to their unique properties such as extremely low volatility, wide liquid temperature range, good thermal stability, designable structure, high ionic conductivity, air and water stability, low toxicity, nonflammability, and wide electrothermal windows, etc.[20-27] Furthermore, they readily dissolve many organic, inorganic and organometalic compounds. Room temperature ionic liquids (RTILs) have attracted increasing attention as the green, high-tech reaction media of the future.[28] RTILs have recently received a great deal of attention as potential new media for nanomaterials synthesis.[19-25]

The most commonly used RTILs have PF_6^- and BF_4^- ions.[26] RTILs with these ions are known to decompose in the presence of water and as a result toxic and corrosive species such as hydrofluoric and phosphoric acids are formed.[28,29] The RTILs with alkyl sulfate anions are halogenfree and relatively hydrolysis-stable compounds and they could be an interesting alternative for industrial application due to the fact that they avoid the liberation of toxic and corrosive materials into the environment.[30] One of the largest barriers to the application of RTILs in various fields arises from their high cost relative to conventional solvents.[26] In order to overcome this problem, also better tune and tailor the physicochemical properties of the RTIL of interest in a favorable fashion, researchers have started to focus on RTIL-based mixed green molecular solvent systems.[31]

In continuing our investigations about nanomaterials preparations and RTILs,[8-10,12-14] ultrasonic-assisted aqueous room temperature ionic liquid (UARTIL) method was applied for the preparation of lead sulfide nanoparticles. For above mentioned reasons, halide-free and low cost RTIL, 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]), was used in this work.[32,33]

Experimental Details

Materials. Lead acetate (Pb(CH₃COO)₂·3H₂O purity: 99.999%) received from Aldrich, thioacetamide (TAA,

CH₃CSNH₂ GR for analysis) and absolute ethanol were obtained from Merck, and employed without further purification. The ionic liquid was 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIM][EtSO₄], and simply synthesized according to the literature.[33]

Instruments. Surface morphology and distribution of particles were studied via LEO 1430VP scanning electron microscope (SEM), using an accelerating voltage of 15 kV. The purity and elemental analysis of the products were obtained by energy dispersive analysis of X-rays (EDX) on the same LEO 1430VP instrument with the accelerating voltage of 20 kV. The sample used for SEM and EDX observations was prepared by transferring the particles, which at first was dispersed in the ethanol to glass substrate attached to the SEM stage. After allowing the evaporation of ethanol from the substrate, the particles on the stage were coated with a thin layer of gold and palladium. The X-ray diffraction (XRD) pattern was recorded on Philips Xpert X-ray diffractometer with Cu Kα radiation λ= 0.15406 nm), employing scanning rate of 0.02°/s in 2θ range from 15° to 75°. UV-visible absorption spectrum of the sample was recorded employing a double beam, Shimadzu, 1650 spectrometer, Japan, applying quartz cuvettes of optical path length 1cm. The ultrasound radiation was performed using dr. heilscher high intensity ultrasound processor UP200H Germany (0.7 cm diameter Ti horn, 140W, 23 kHz).

Preparation of PbS nanomaterials. At room temperature, 0.151 g lead acetate (Pb(CH₃COO)₂·3H₂O) and 0.03 g of TAA (CH₃CSNH₂) were added to 5 ml of the ionic liquid, [EMIM] [EtSO₄], and 15 ml of double distilled water in a 50 ml beaker imposed to ultrasonic irradiation for 7 min. The titanium tip of the horn was immersed directly in the reaction solution. The formed dark brown color suspension was centrifuged to get the precipitate out and washed two times with double distilled water and ethanol respectively to remove the unreacted reagents. To investigate the effect of ultrasound on the properties of the products, one more comparative sample was prepared, keeping the reaction parameters constant except that the product is prepared at continuous stirring for 24 h without the aid of ultrasonic irradiation. Therefore, synthesis procedure was similar to the typical process described above, except for elimination of ultrasound irradiation.

Results and Discussion

The XRD pattern of the as-prepared PbS nanomaterials arranged in two different ways, is depicted in Figure 1. The diffraction peaks correspond to (111), (200), (220), (311), (222), (400), (331) and (420) planes of cubic PbS crystal system (ICSD reference code: 78-1056). It is clear from the figure that all products have the same cubic crystal structure and the peak broadening in the pattern indicates the PbS nanoclusters formed are very small in size. The average particle size, *D*, was determined using Scherrer's equation.[34]

$$D = K\lambda (B\cos\theta) \qquad (1)$$

where λ is the wavelength of X-ray radiation (0.15406 nm), *K* the Scherrer constant ($K = 0.9$), θ the characteristic X-ray radiation ($\theta = 26.8°$) and *B* is the full-width-at-half-maximum of the (222) plane (in radians). The particle size obtained accordingly is 22.8 nm.

The morphology of the PbS nanoclusters prepared in the two different ways was investigated by scanning electron microscope (SEM) which their records at magnification of 50k are shown in Figures 2(a) and 2(b). The sample prepared in ionic liquid and water without USI is somehow mono-
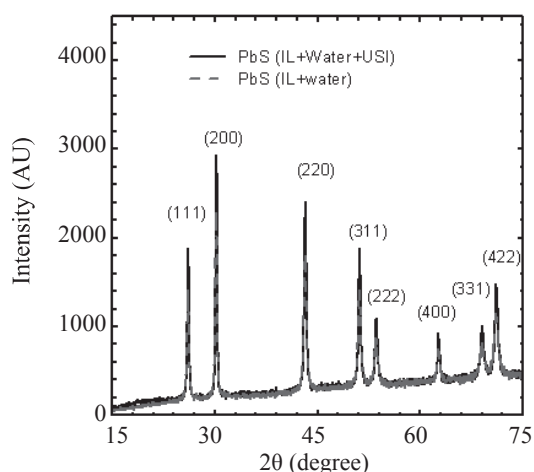

Figure 1. The powder XRD pattern of as-prepared PbS nanoclusters prepared in ionic liquid and water (1:1 in volume) with and without the aid of USI.
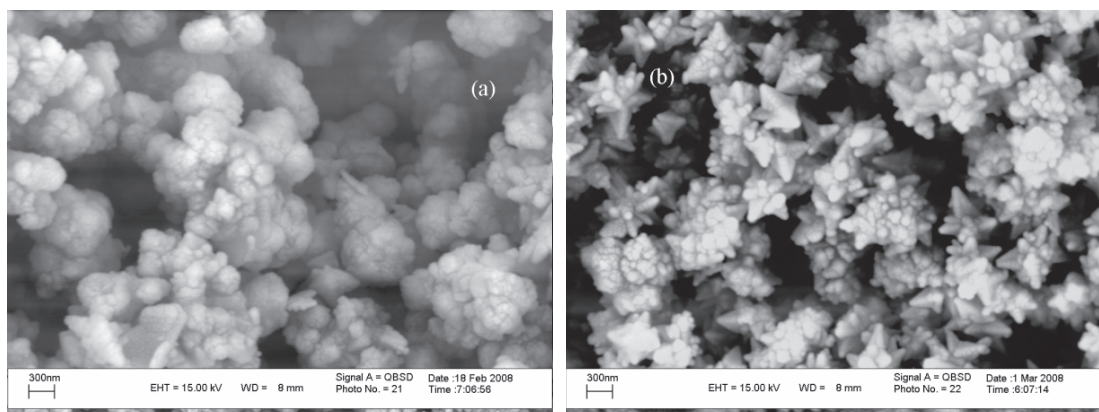

Figure 2. The SEM image of the as-prepared PbS nanoclusters prepared in ionic liquid and water (a) without USI, (b) with USI at magnification of 50K.

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dispersive nanoclusters possessing approximately regular spherical shape, Fig. 2(a). In comparison the PbS nanocrystallites formed in aqueous solution of the ionic liquid with the aid of USI is highly monodispersive of star-like nanoclusters of smaller dimension. Although they agglomerate in different shapes however in both cases the boundaries between single crystallites are clearly observable, having spherical shape with diameter of approximately 30 nm and agrees well with the results obtained by Scherrer's equation.

The purity and composition of the products was studied by energy dispersive X-ray spectroscopy (EDX) and is displayed in Figure 3. The curve reveals the presence of Pb and S peaks and the average atomic percentage ratio of Pb:S are about 65:35 and 59:41 for the structures prepared in ionic liquid plus water with and without the aid of USI respectively. Other peaks in this figure correspond to gold, palladium and silicate which are due to sputter coating of glass substrate
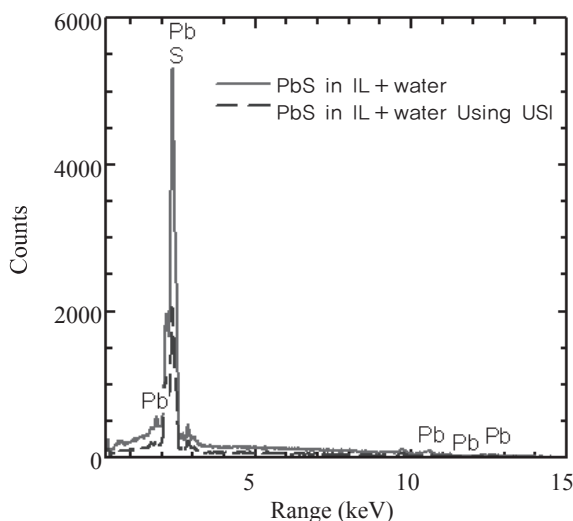

Figure 3. The EDX pattern of the as-prepared PbS nanoclusters prepared in two different conditions.
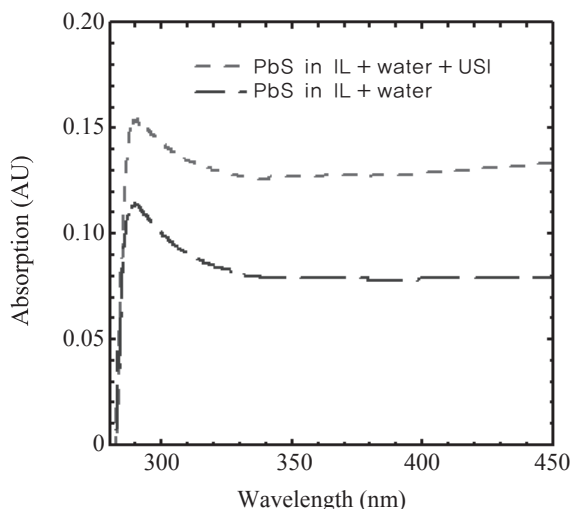

Figure 4. UV-visible absorption spectra of as-prepared PbS nanoclusters prepared in ionic liquid and water (1:1 in volume) with and without the aid of USI.

on the EDX stage and were not considered for elemental analysis of Pb and S.

Figure 4, exhibits the UV-visible absorption spectra of as-prepared PbS nanoparticles, dispersed in ethanol, prepared in two different ways. An absorption peak at about 290 nm (4.27 eV) was observed for both samples. It is clear that these spectra almost coincide, indicating the samples contain the same components. The band gap energy is increased compared to that (0.41 eV) of bulk PbS shows an enormous blue shift of 3.86 eV and can be attributed to very small size of PbS nanoparticles produced and quantum confinement effect. The correlation between absorption edge value and PbS nanoparticle diameter was made by Moffitt and Eisenberg[35] using a theoretical model developed by Wang *et al.*:[36]
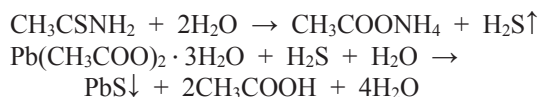
$$2R = \exp(0.9587 + 0.09468\lambda^{1/2}) \tag{2}$$

where R is the radius of particle and λ is the absorption wavelength. The diameter of the PbS nanoparticles determined by this relation from absorption maximum ($\lambda_m = 290$ nm) and absorption edge ($\lambda_e = 341$ nm) are about 1.31 and 1.49 nm, respectively. A useful measure of polydispersity of the samples is obtained by determining the half-width of size distribution, $d_{1/2}$. The $d_{1/2}$ (i.e. number of particles *vs.* particle diameter) is,

$$d_{1/2} = 2R(\lambda_e) - 2R(\lambda_m) \tag{3}$$

where $R(\lambda_e)$ and $R(\lambda_m)$ are radius of PbS nanoparticles from absorption edge and absorption maximum, respec- tively. It has been shown that the smaller the $d_{1/2}$ value, the closer to monodisperse the particles are.[37] The determined $d_{1/2}$ value is 0.18 nm; indicating a narrow size distribution of PbS nanoparticles.

Based on the experimental results, a possible formation mechanism of the PbS nanoparticles in aqueous solutions of the ionic liquid using ultrasonic irradiation is presented. TAA has a strong coordination ability to combine with transition metal ions; metal complex consequently forms and then dissociates to form metal chalcogenide. The possible formation of PbS nanoparticles may be expressed by the following equations:

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3COONH_4 + H_2S\uparrow$$
$$Pb(CH_3COO)_2 \cdot 3H_2O + H_2S + H_2O \rightarrow$$
$$PbS\downarrow + 2CH_3COOH + 4H_2O$$

The formation of PbS nanoparticles may be obtained from the reaction between lead acetate and H_2S released from the TAA. As the Gibbs free energy of the surface is usually very high due to the large surface/volume ratio and the existence of dangling bonds, freshly formed nanostructures have a tendency to randomly aggregate until they become stable. When aqueous solutions of an ionic liquid is used as a reaction medium, the solute is solvated by ions, thus, the reaction proceeds in an environmentally different from that when water or ordinary organic solvents are used. RTILs form extended hydrogen-bond systems in liquid state and are therefore highly structured.[38] The RTIL, [EMIM][EtSO4], consists of [EMIM]⁺ cations and [EtSO4]⁻ anions. The imida-

zolum ring is an electron-withdrawing group and it can attract the electron pair shared by hydrogen and carbon of position 2 of imidazolum ring,[12] thus the hydrogen-bonding between the RTIL and sulfide moieties of PbS nuclei is strong.[39] Also, [EMIM]$^+$ cations can combine with sulfide moieties of PbS nuclei through electrostatic attraction.[39] In aqueous solutions of the ionic liquid medium, dissociation of the lead acetate gives rise to solvated metal cations, along with the acetate anions. Reaction of the metal cations with the sulfide anions gives rise to metal chalcogenide. As soon as the metal chalcogenide nuclei are formed, they get coated by the RTIL, thereby producing a control on the growth. Meanwhile, the activities of freshly generated PbS surface will be greatly inhibited by [EMIM]$^+$ions, so the anisotropic growth of the PbS crystals will markedly be modified. When the experiments are performed in the presence of ultrasound, some active sites can be uniformly produced on PbS nanoparticles surrounded by [EMIM]$^+$ ions to enhanced mobility triggered by the irradiation of ultrasound.[40] Thus PbS particles can preferably grow on these active sites and finally lead to PbS nanoparticles. Then, hydrogen-bonding interactions formed between the hydrogen atoms at position-2 of the imidazolium ring and the sulfide ions of PbS crystal cores and electrostatic interactions between them, may act as an effective bridge to connect the produced nuclei of lead sulfide and cations of the ionic liquid, playing a decisive role for the PbS nanoparticles growing.

Conclusions

Ultrasonic-assisted aqueous room temperature ionic liquid (UARTIL) method was proposed for preparation of PbS nanoparticles. This room-temperature and environmentally benign green method is fast and template-free which remarkably shortens synthesis time and avoids the complicated synthetic procedures. The as-prepared nanoclusters show an enormous blue shift of 3.86 eV that can be attributed to very small size of particles and quantum confinement effect. The strategy presented in this work is expected to prepare other transition metal sulfide nanomaterials. In this method aqueous solution of the RTIL can act as solvent for reactants and morphology templates for the products at the same time, which enable the synthesis of inorganic materials with novel and improved properties.

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