

ULTRASONIC PREPARATION OF STIBNITE NANOSTRUCTURES USING ALIPHATIC PHOSPHONIUM IONIC LIQUID

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Sb₂S₃ nanorods were successfully synthesized by the ionic liquid assisted sonochemical method (ILASM). The starting reagents were Sb₂Cl₃, Thioacetamide, absolute ethanol (ETA) and the new ionic liquid used was isobutyl-3 hexyl-phosphonium tetrafluoroborate ([iBH₃P][BF₄]). The synthesized materials were subjected to 120°C annealing temperature under controlled vacuum conditions. X ray powder diffraction analysis showed that the ionic liquid played a key role in the crystallinity of Sb₂S₃. Scanning electron microscopy displayed single-crystalline Sb₂S₃ nanorods that could be prepared in the presence of [iBH₃P][BF₄]. Energy-dispersive X-ray spectroscopy confirmed the formation of Sb₂S₃. The optical properties (band gap) were similar to that reported for bulk Sb₂S₃.

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1. Introduction

Ionic liquids (ILs) have shown tremendous promise as replacements for volatile organic solvents. Those compounds 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, wide electrothermal window, etc. [1]. The preparation of nanostructures using ILs is an environment friendly process and was initially reported by Dupont [2] and nowadays is a vigorous growing field [3]. In most cases, Imidazolium-based ILs has been the preferred solvent media with very few exceptions as pyrrolidiniums [4], ammoniums [5], tetrazolium [6] and guanidinium [7].

Chalcogenide semiconductor materials are interesting due to their properties and potential applications in the manufacture of electronic and optoelectronic devices. Sb₂S₃ is as a potential material for photovoltaic [8], photocatalytic [9] and thermoelectric [10] applications. There is a wide variety of prepared Sb₂S₃ 1D structures as nanoribbons [11], nanowires [12], nanorods [13] and nanotubes [14] or thin films [15] using different processes as hydrothermal [16], sonochemical [17], solvothermal [18], chemical bath deposition [19], SILAR [20] or microwave [21].

Ultrasound waves radiate through the solution causing alternating high and low pressures in the liquid medium. Millions of microscopic bubbles form and grow in the low-pressure stage, and subsequently collapse violently in the high-pressure stage. These collapses generate microjets and shockwaves that lead to pressures reaching hundreds of atmospheres. The energy released from this process, known as acoustic cavitation can lead to enhanced chemical reactivities [22]. Ultrasound radiation synthesis of nanostructures has been developed over recent years [23].

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Phosphonium ionic liquids (PILs) have been recently used as solvent media for the synthesis of nanostructures. For instance, CdS quantum dots [24], CdS nanostructures [25], CdSe nanoparticles [26] as well as ZnS, PbS and MnS np's had been achieved [27]. Silver halide [28] and Eu_3F [29] fosfor nanostructures have also been prepared using PIL as base solvent in addition to n-ZnO preparation [30] under microwave irradiation. Also, metallic nanocrystals as Pd [31], Ru [32] and Au [33] had been prepared in the absence of any organic solvents. Also, CdS thin films were electrodeposited by reduction of thiosulfate in the presence of Cd(II) ions using alkyl PIL [34] as solvent. Furthermore, a suitable PIL was used during pulsed electrodeposition resulting in the incorporation of CdS nanoparticles inside a layered conductive PEDOT scaffold [35].

The IL assisted sonochemical technique was first introduced by Wu for the preparation of ZnS nanocrystals [36]. This technique aims to combine an environmental friendly solvent with ultrasonic irradiation. A wide variety of metallic nanoparticles as Au [37], Fe [38], and Ag [39] as well as metal oxides as SnO_2 [40] and TiO_2 [41] and chalcogenides as PbS [42], CuS [43] and CdS [44] has been prepared using ILs under ultrasound. Recently, 1-D nanostructures as Pb(OH)Br [45], CuO [46], ZnO [47], MoO_3 [48] and Sb_2S_3 [17]. In all cases only imidazolium ILs has been used. It has been stated [13] that imidazolium ILs can form extended hydrogen bonded systems in the liquid state; particularly the hydrogen bond π - π stack mechanism is useful to explain the influence of ILs on the morphologic control of crystal growth. Therefore it becomes interesting to test alternative ILs as solvent media using ultrasonic irradiation to observe structure formation. In this work we report for the first time the preparation of Sb_2S_3 nanostructures using aliphatic phosphonium ionic liquids using ultrasonic irradiation.

2. Experimental

Antimony trichloride (SbCl_3), and thioacetamide were adquired from Fluka, absolute ethanol and acetone from CTR Scientific and isobutyl-tri-hexyl-phosphonium tetrafluoroborate ($[\text{iBH}_3\text{P}][\text{BF}_4]$) was synthesized according to previous report [49]. For the synthesis of antimony trisulfide (Sb_2S_3) we used 0.40g of SbCl_3 and 0.45g of thioacetamide and both were dissolved in variable amounts of absolute ethanol and $[\text{iBH}_3\text{P}][\text{BF}_4]$ in a 100mL two neck round bottom flask which was immersed in an ultrasound bath Branson1510 (70W, 42kHz) where 60°C was reached during reaction time (24 hr). The collected precipitate was washed with distilled water and absolute alcohol for several times and annealed under vacuum at 60 - 120°C for 1 h. To corroborate the ultrasonic and ionic liquid effect on the formation of nanostructures, separate experiments was performed at 60°C without the use of ultrasonic irradiation and with and without the addition of PIL under vigorous stirring. The summary of performed experiments is presented at Table 1.

XRD analysis was performed using a Rigaku Miniflex Desktop X-ray diffractometer ($\text{CuK}\alpha 1$, Ni, 1.540562nm , 30kV , 15mA , step size 0.02° , step time 2s). XPS analyses were performed in a Riber LDM-32 system. Morphology of the synthesized products was analyzed using a SEM Jeol JSM-6490LV. Elemental analysis was made by EDAX (JEOL-JFC 1600) on samples previously prepared with a thin layer of gold deposited by cathode sputtering using a Pelco-7 sputter machine. Optical properties were analyzed using a Perkin Elmer Paragon Lambda 12 UV-Vis spectrometer on diffuse reflectance mode.

Table 1. Experimental conditions of Sb_2S_3 preparation

Sample	Ultrasonic irradiation	Reaction Temperature (°C)	Ethanol (mL)	[iBH ₃ P][BF ₄] (mL)	Annealing Temperature (°C)	Crystalline	Morphology	Band gap (eV)
A	yes	60	10	0	60	no	Irregular Nps	2.25
B	yes	60	10	0	120	no	Regular Nps	2.20
C	yes	60	6	4	120	yes	Nanorods	1.80
D	no	60	10	0	120	no	Irregular Nps	1.72
E	no	60	6	4	N.A.	N.A	No powder observed	N.A.

3. Results and discussion

On table 1 we describe experimental results of as-prepared powders under UI/IL assistant along one hour of thermal annealing under vacuum at 60-120°C. Sample A and sample B were prepared under UI without the assistant of IL to test the annealing temperature effect and we obtained non-crystalline NPs. Sample D and experiment E were run to test the presence of PIL without ultrasonic irradiation and we observe non crystalline irregular NP formation with ethanol as the sole solvent (sample D). Our phosphonium IL seems to hinder nanoparticle formation since no powder was collected under those experimental conditions (experiment E). This is a discrepancy when imidazolium-based IL was used under similar conditions and noncrystalline irregular NPs were obtained [Error! Bookmark not defined.]. On the other hand, when ultrasonic irradiation was applied (sample C) we obtained, after annealing; a rather crystalline material was obtained (nanorods by SEM observation, discussed later). See Figure 1, at the bottom, we plotted JCPDS 06-0474 data as a reference. The principal stibnite peaks of sample C were fully evolved and we observe more than 3000 counts at the highest peak. All diffraction peaks can be indexed to a pure orthorhombic phase of Sb_2S_3 . On the other hand, it is noticeable that $\langle 200 \rangle$, $\langle 220 \rangle$ and $\langle 130 \rangle$ planes have relatively high intensity suggesting a crystal growth preferably along the (001) direction, in agreement with 1D growth [50].

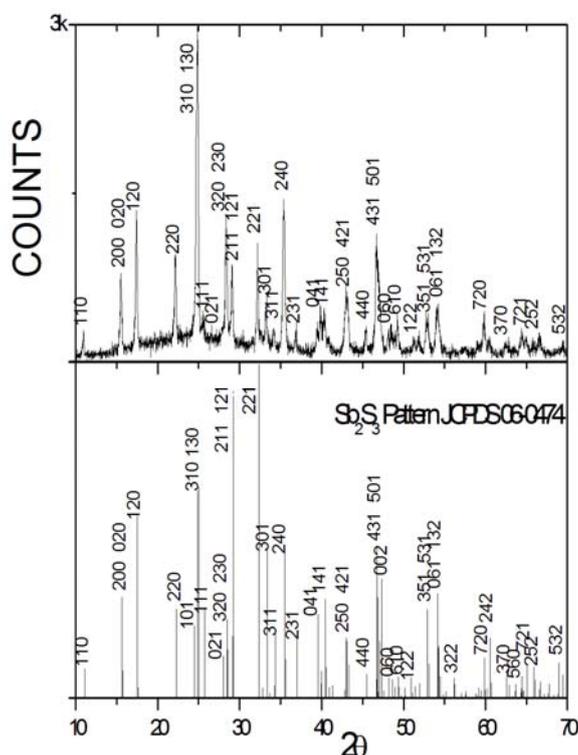


Fig. 1. XRD powder diffraction of prepared Sb_2S_3 (sample C).

The size of nanoparticles using XRD pattern can be estimated from the Scherrer equation:

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta_{hkl}} \quad (1)$$

where D_{hkl} is the average crystalline size perpendicular to the normal line of the $\langle hkl \rangle$ plane, λ is the wavelength of X-ray (Cu $K\alpha$, 0.15406 nm), k is a constant (approximately equal to 0.9), β_{hkl} is the full width at half maximum (FWHM) of the $\langle hkl \rangle$ diffraction peak and θ_{hkl} is the Bragg's angle of $\langle hkl \rangle$ peak. The mean size of Sb_2S_3 NPs was calculated using Eq. (1). The mean particle sizes for the crystallographic planes $\langle 130 \rangle$, $\langle 120 \rangle$, and $\langle 230 \rangle$ were 47.8, 65.8, and 53.1 nm, respectively. There are no peaks attributing to antimony oxide hence the sample prepared is considered relatively pure.

Scanning electron microscopy was performed to elucidate the morphology of the Sb_2S_3 obtained under several annealing temperatures on Sample C (all performed during 1 hour). At 120°C, (see figure 2a) we observe rod-like morphology with partial agglomeration; further heating (155°C, figure 2b) develops densification. Heating at 200°C demonstrates intensive agglomeration as expected (Fig 2c). EDAX analysis is shown on Sample C (see figure 2d) was performed and we detect antimony and sulfur ratio close to 2:3 Sb:S. These morphologies can be explained by the assistance of ionic liquid. The already formed Sb_2S_3 get coated by IL because of electrostatic phenomena between the cations of IL and nuclei of Sb_2S_3 , anisotropic nanostructures such as nanorods are possible because of the fact that IL aliphatic chains work as templates for sulphur ions turning into this particular morphology.

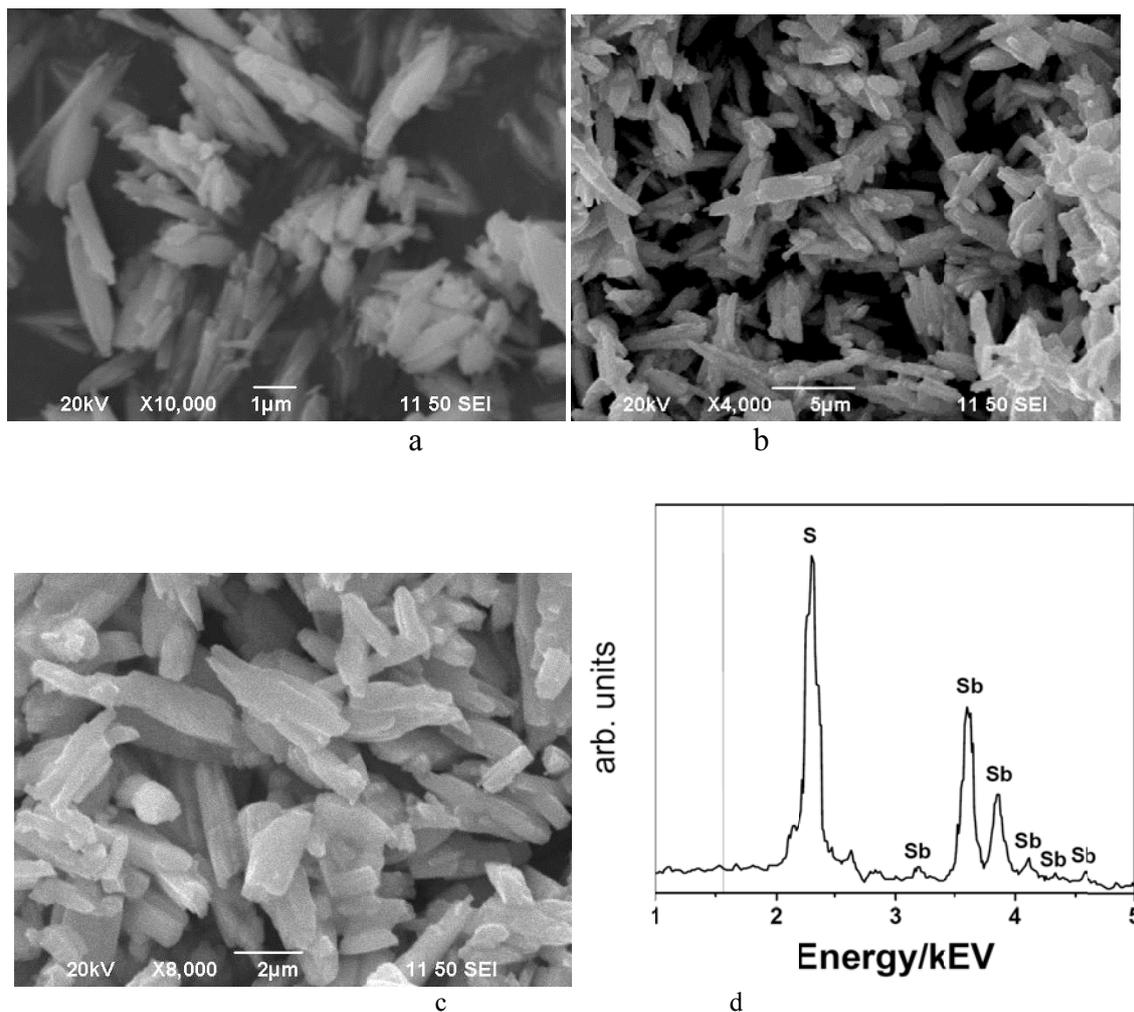


Fig. 2. Vacuum thermal treatment of sample C.

To characterize the chemical state of the product, X-ray photoelectron spectroscopy was carried out and a typical full XPS spectrum of Sb_2S_3 is displayed on Figure 3 where C 1s was used as the reference at 284.6 eV and no impurities were detected. An amplification of the XPS for antimony 3d is shown on right insert in Figure 3. The Sb $3d^{5/2}$ and Sb $3d^{3/2}$ doublet-peaks associated with the Sb–S bonding were observed around 529.6 and 538.6 eV, respectively. Both peaks are characteristic of Sb^{3+} oxidation state rather than Sb^{5+} . A magnification of the XPS for sulfur 2p is shown on left insert in Figure 2 where the S2p peak is observed at 161.6 eV. Peak positions for both Sb and S are closed to those reported on literature [17]. Also, the ratio of Sb to S is found to be very close to 2:3, corresponding to Sb_2S_3 . On the basis of the above characterizations of the XRD pattern and XPS, the as synthesized products are pure-phase Sb_2S_3 .

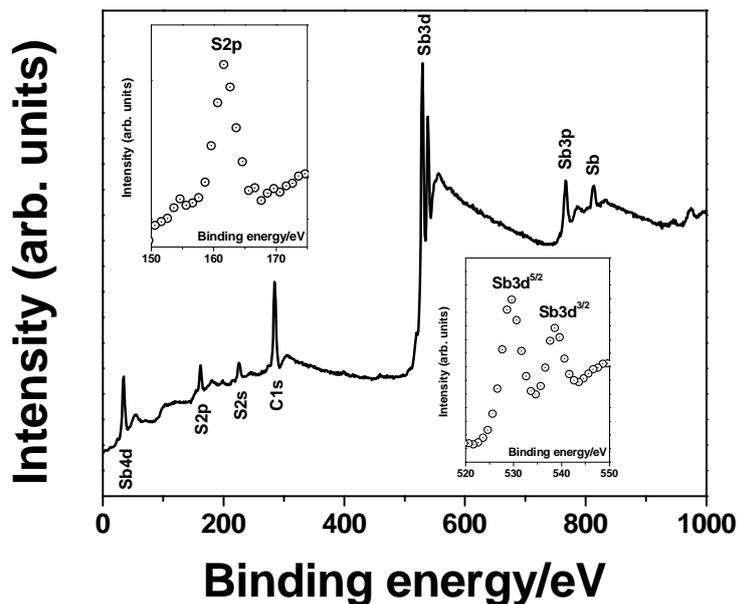


Fig. 3. XPS of prepared Sb_2S_3 , sample C.

To determine the Sb_2S_3 band gap, tauc plots were obtained from UV-vis spectroscopy analysis in the diffuse reflectance mode and the use of the Kubelka-Munk theory. The Kubelka-Munk (K-M) theory relates the determined diffuse reflectance of a sample to scattering and absorption coefficients. The K-M equation was used for a direct transition semiconductor with a coefficient of $1/2$, so it was not necessary to calculate the phonon energy for the exciton transition from the valence band to the conduction band given the linear relationship between energy input and absorption. Figure 4 displays an energy (E_g) vs absorption plot of powders synthesized with IL assistance under ultrasound irradiation and several thermal annealing treatments (1 h for each temperature) under controlled vacuum conditions. It is remarkable that when amorphous Sb_2S_3 (no thermal treatment) was converted into crystalline powders (according to XRD analysis), the absorption edge shifted and band gap decreased. Here, the band gap is around 1.80 eV for 120, 155 and 200°C. This band gap shift is explained on the variation of crystallinity on Sb_2S_3 structure evolution under thermal annealing.

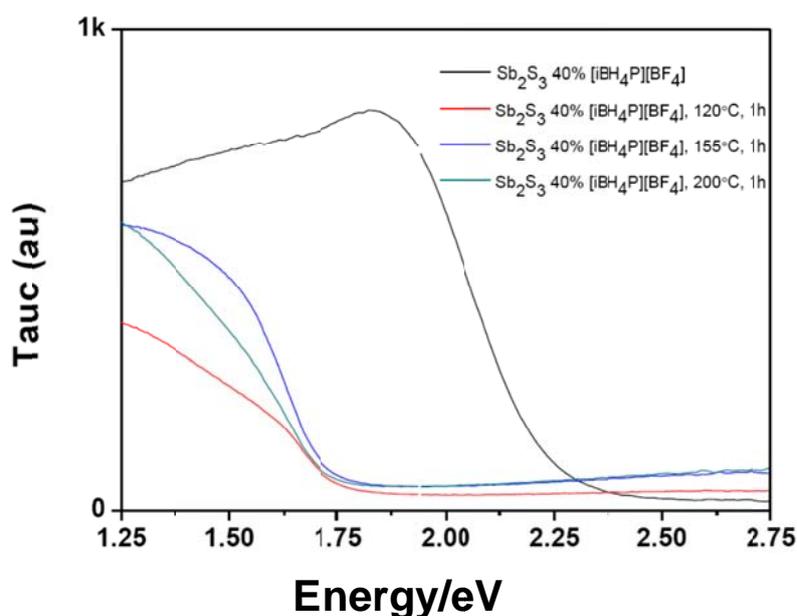


Fig. 4 Sb_2S_3 band gap measurements.

Organic molecules containing thiols [51] are known for their ability to coat nanostructures, the functional density theory [52] allows us to predict that long tri-n-hexyl chains which are coplanar, are electrically bonded to the phosphorous ion to $[BF_4]^-$ and sulphur ions bond to the aliphatic chains that work as templates and that yields the anisotropic growth of Sb_2S_3 nanostructures. This kind of behavior is homologous to the one observed by several researchers such as She et al., [53], Lu et al. [54], Wang [55] et. al., among others in the preparation of one-dimensional nanostructures where surfactants were used to produce these 1D morphologies

4. Conclusions

The addition of $[iBH_3P][BF_4]$ ionic liquid into the ultrasonic synthesis of Sb_2S_3 comprises a favorable route for the formation of 1-D nanostructures (nanorods), furthermore, it evidently helped to achieve a high crystallization degree even at a moderate annealing temperature of $120^\circ C$. XPS analysis confirmed the formation of Sb_2S_3 . Band Gap determination for the synthesized materials showed a value of $1.80 eV$ as expected given the very high crystallization degree that was reached as could be seen in the XRD analysis.

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