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SONOCHEMICALLY SYNTHESIZED β-In_2S_3 NANOPARTICLES USING DIVERSE INDIUM SALTS

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This paper compares β-In_2S_3 nanoparticles synthesized via sonochemical method, using diverse indium salts and thioacetamide as a sulfur source in aqueous media. A direct immersion ultrasonic probe was used as an ultrasound source. It was found that the indium precursor plays an important role in the formation of In-S bond. X-ray diffraction, transmission electron microscopy and UV-vis spectroscopy were used to characterize the products. The choice of indium precursor was also found to be the important factor for the product rate of aggregation.

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1. Introduction

Researches in the area of nano-scale metal chalcogenides with 2:3 molar ratio of metal to chalcogenide in their unit cells are increasing due to their specific properties and therefore many potential technological applications. One of many important metal chalcogenides is indium sulfide (In_2S_3), a member of III-VI group. It has three polymorphic phases at atmospheric pressure: α-, β- and γ-In_2S_3 [1, 2]. The most promising phase is the room temperature stable tetragonal β-phase with a defect spinel structure and stability up to 1027 K. β-In_2S_3 is a mid-band gap (2.0-2.3 eV) *n*-type semiconductor with special optical, electronic, optoelectronic and photoluminescence properties [3, 4]. Particular characteristics of materials are the cause for many technological applications, for example, in dry cells and solar cells, preparation of green and red phosphorus in the manufacture of picture tubes for colour televisions, in lithium ion rechargeable battery, etc. [5-8]. Indium sulfide nanoparticles bioconjugates have also been employed in the medical area for cancer diagnosis [9].

Unique properties of material are highly dependent on their size and shape. Therefore, many different techniques were used for the synthesis of β-In_2S_3 nanoparticles, like organothermal synthesis [10], chemical bath deposition [11], hydrothermal synthesis [12, 13], solvothermal synthesis [14], ion-exchange and sulfurization method [15], in situ oxidization-sulfurization growth routh [16] and sonochemical synthesis [17-20].

In the presented work, β-In_2S_3 nanoparticles obtained by sonochemical method using diverse indium precursors and thioacetamide in aqueous medium are compared. The sonochemical method with the phenomenon of acoustic cavitation provides unique reaction conditions in liquid medium [21] so the products are generally nanosized. To the best of our knowledge, there have not yet been done a comparison between sonochemically synthesized β-In_2S_3 nanoparticles with

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diverse indium precursors. In addition, there seem to be no reports about using indium nitrate as In-precursor in sonochemical preparation of β-In_2S_3. X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet-visible spectroscopy (UV-vis) were used to characterize the obtained products.

2. Experimental

Indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$), indium trichloride ($InCl_3$), indium sulfate ($In_2(SO_4)_3$) and indium acetate ($In(CH_3COO)_3$) were used as indium precursors and thioacetamide (C_2H_5NS) as sulfur source, respectively. All reagents were analytical graded, and used without further purification. In a typical synthesis process an equimolar ratio of indium salt and thioacetamide was dissolved in aqueous medium. Firstly, 2.5 mmol of indium salt was dissolved in 25 mL of distilled water. In another baker the 25 mL aqueous solution of 2.5 mmol of thioacetamide (= 0.188 g) was prepared and added to the previously prepared solution of indium salt. The mixture was stirred until a homogeneous solution was obtained. The as-prepared samples were sonicated with high-intensity ultrasonic probe (Sonics & Materials, VCX 750, 20 kHz, 70 % amplitude, Ti direct immersion horn) for 1h at atmospheric conditions. During ultrasonic irradiation, the temperature of the sample rose to around 360 K. After being cooled down to room temperature by natural cooling, the obtained precipitation was centrifuged at 5000 RPM, washed twice with distilled water and once with absolute ethanol, and dried in air. In the case of using indium salts of strong acids, the formed precipitates are orange-colored, while a gray product was obtained when using indium acetate.

The as-obtained samples were characterized with X-ray powder diffraction (XRD; AXS Bruker/Siemens, D5005) using CuK_α radiation at 293 K. The XRD patterns were registered in the 10 - 70° range in steps of 0,036°. The morphology and particle size of the products were investigated by transmission electron microscopy (TEM; JEOL 2100, Cu –grid, 200 kV). The crystalline size was also calculated using Scherrer equation. UV-vis absorption spectra of β-In_2S_3 nanoparticles dispersed in ethanol were measured on a Varian Cary 50 UV/Vis spectrophotometer.

3. Results and discussion

Fig. 1a shows the XRD patterns for the samples prepared from diverse indium salts of strong acids and thioacetamide via sonication for 1h. There are visible differences among the diffraction peaks in the patterns. The peak at $2\theta = 43.5^o$ (1015) is clearly visible in the sample synthesized with $In(NO_3)_3$, indicated in the sample were $InCl_3$ was used as In-source, while essentially unobservable in the sample synthesized using $In_2(SO_4)_3$. Peaks (103) and (116) are visible only in the diffraction pattern (a). Nevertheless, all prominent diffraction peaks correspond to the standard body centered tetragonal form of β-In_2S_3 (JCPDS card No. 25-0390) and no obvious peaks for other impurities such as In_2O_3 and S were observed.

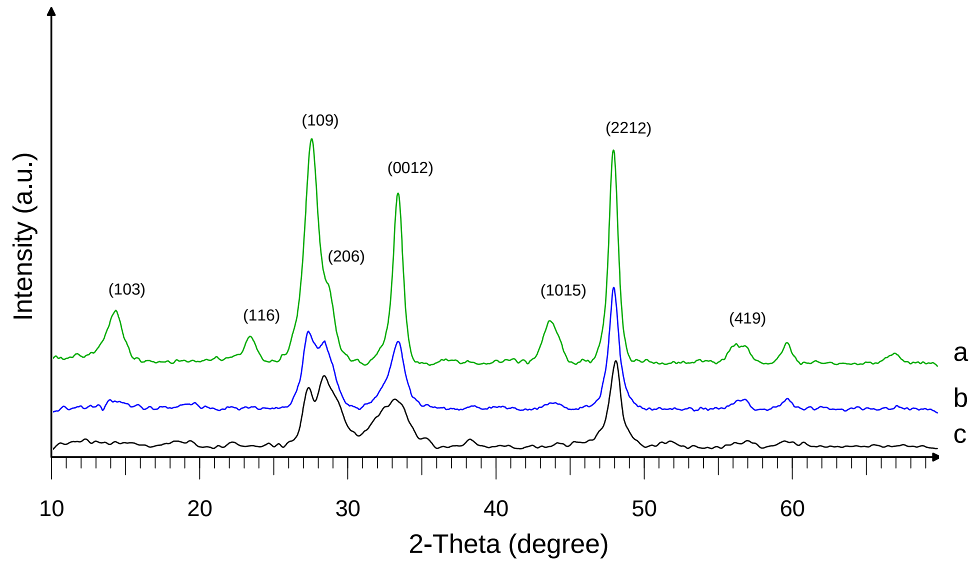

Fig. 1a. XRD patterns of the products prepared with (a) $In(NO_3)_3 \cdot xH_2O$, (b) $InCl_3$ and (c) $In_2(SO_4)_3$

The possible reason for the differences in the existence and the intensity of diffraction peaks between samples is the time of ultrasonic irradiation of the particles, i.e. ultrasonic irradiation between the beginning of the particles formation (visible in the change of colour of the sample) and the finishing time of sonication. For the sample where $In(NO_3)_3$ was used as In-source, this time was approx. 45 min, while it was only 25 min for the sample with $In_2(SO_4)_3$.

The crystallite sizes of the samples were calculated from the peaks at $2\theta = 33.2°$ and $47.7°$ using Scherrer equation $D = 0.94\lambda/\beta cos\theta$, where D is a diameter of the crystallites, λ is x-ray wavelength (1.542 Å), β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle. The crystallite size of the samples varies between 12 and 14 nm. The smallest crystallite size was estimated for nanoparticles synthesized using $InCl_3$ as indium source.

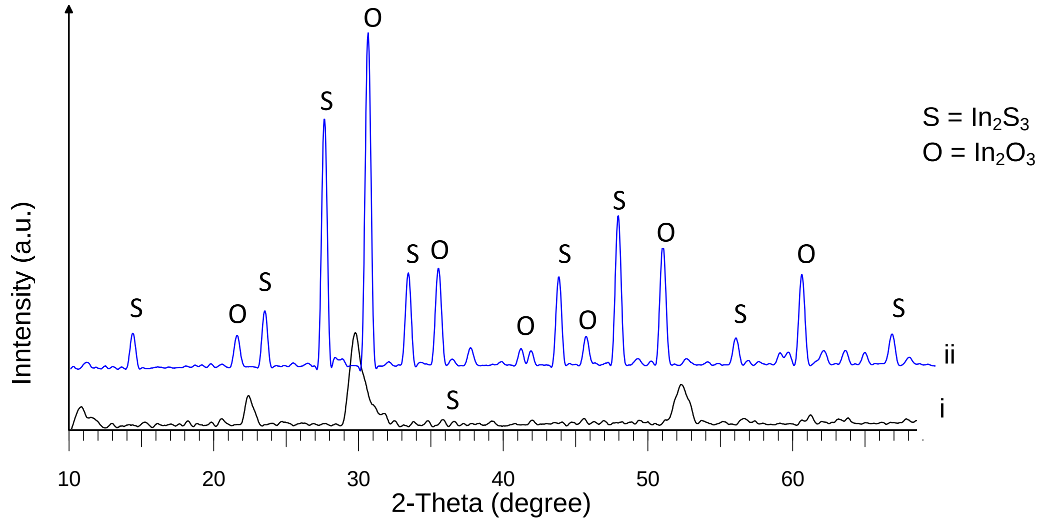

Fig. 1b. XRD patterns of the product prepared with $In(CH_3COO)_3$ before (i) and after (ii) heating to 773 K

The diffraction pattern (i) in Fig. 1b for the product derived from indium acetate and thioacetamide revealed a product which was hard to characterize. Therefore, the sample was heated up to 773 K in nitrogen with a heating rate of 10 K/min. From the diffraction pattern (ii) in Fig. 1b it can be seen that the product after heating consists of the cubic form of β-In_2S_3 (JCPDS card No. 32-0456) and the cubic form of In_2O_3 (JCPDS card No. 06-0416). To obtain pure β-In_2S_3 nanoparticles from sonochemical reaction between indium acetate and thioacetamide the control of other parameters of the synthesis (e.g. pH, molar ratio and reaction time) seems to be required. Only samples where the tetragonal form of β-In_2S_3 nanoparticles was formed were used for further characterization and comparison.

Fig. 2 shows the TEM images of β-In_2S_3 nanoparticles formed from three different indium salts of strong acids at the same conditions and the example of primary nanoparticles.

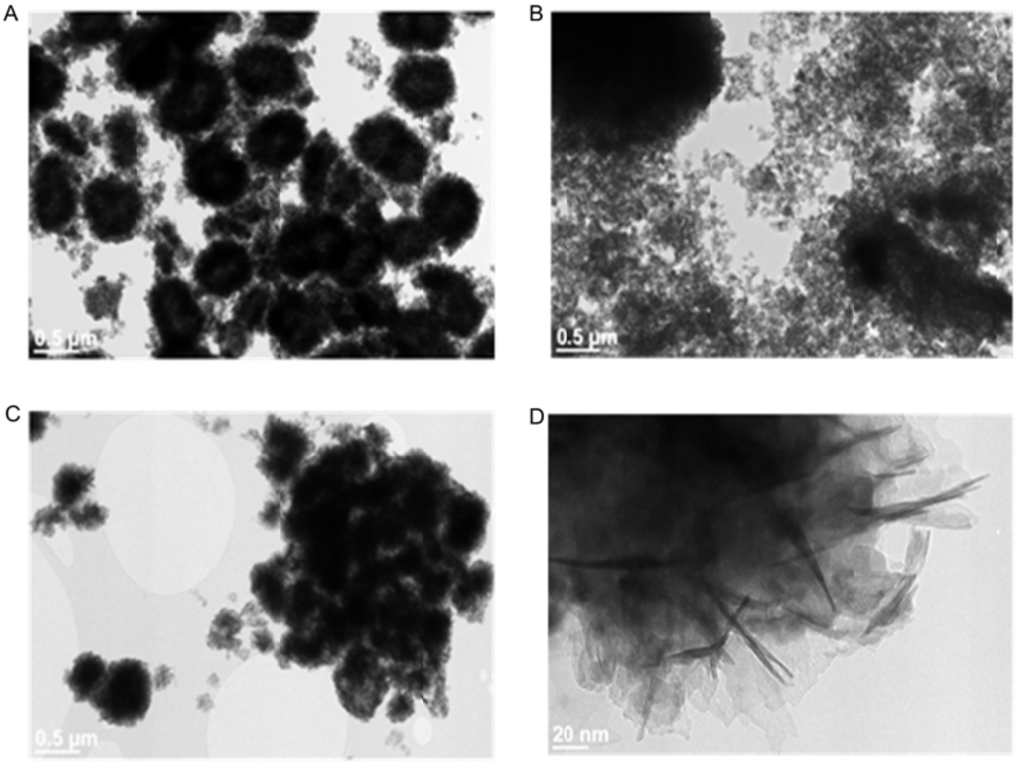

Fig. 2. TEM images of β-In_2S_3 nanoparticles obtained with diverse indium source: (A) $In(NO_3)_3 \cdot xH_2O$, (B) $InCl_3$ and (C) $In_2(SO_4)_3$, and (D) primary nanoparticles

β-In_2S_3 nanoparticles synthesized using $In(NO_3)_3 \cdot xH_2O$ as indium precursor are in the form of aggregated ~ 0.5 μm spheres (fig. 2A), consisting of primary, flat nanoflakes with a thickness of 5 nm and a width between 10 and 60 nm (fig. 2D). The EDXS spectrum of this sample showed traces of nitrogen and oxygen next to indium and sulfur. Particles of β-In_2S_3 produced from $In_2(SO_4)_3$ as indium precursor (fig. 2C) are similar but smaller when compared to those produced from $In(NO_3)_3 \cdot xH_2O$. This can be attributed to the longer ultrasonic irradiation relative to the origin of particle formation. When $In_2(SO_4)_3$ was used as indium source the particles formation begin approximately 35 minutes after the sonication starts, which is almost half slower than when using $In(NO_3)_3 \cdot xH_2O$ as indium precursor. These results are consistent with a discussion by Abbasi and Morsali [22]. In the product, synthesized using $InCl_3$ as indium source (Fig. 2B), primary nanoparticles are not aggregated into spheres, but are in the form of major and minor agglomerates. Although the ultrasonic irradiation time from the beginning of the particles formation until the end of the sonification is very similar in the case of using $In(NO_3)_3$ and $InCl_3$, there is a difference regarding aggregation rate. The aggregation rate of as-prepared β-In_2S_3 nanoparticles it seems to be anion dependent: $Cl^- < NO_3^- < SO_4^{2-}$.

Fig. 3 presents the UV-vis absorption spectra of the as-prepared β-In_2S_3 nanoparticles, showing a moderate blue shift when compared to bulk In_2S_3. Samples (A) and (C) show similar behaviour at lower wavelengths, with very broad absorptions at 525 nm (2.4 eV) and 445 nm (2.8 eV), respectively. The band gap value for sample (B) calculated from the absorption edge using the extrapolation method is 2.5 eV. The band gap values reported in literature for bulk In_2S_3 vary between 2.0 and 2.2 eV [23-25], suggesting that although the size of as-prepared samples is significantly above the Bohr radius of the exciton for In_2S_3, which is about 34 nm [26], quantum confinement takes place inside the primary nanoflakes with a thickness of 5 nm.

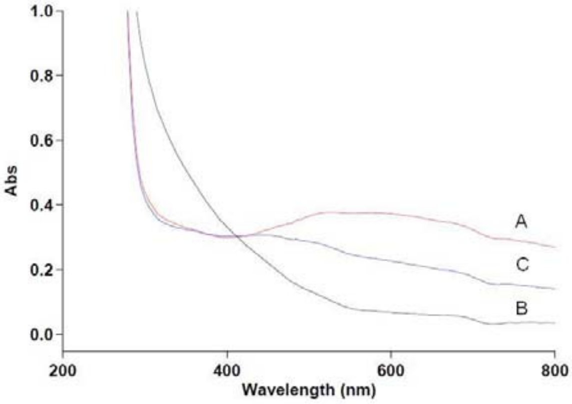

Fig. 3. UV - Vis spectra of β-In_2S_3 *nanoparticles prepared from (A)* $In(NO_3)_3 \cdot xH_2O$, *(B)* $InCl_3$ *and (C)* $In_2(SO_4)_3$

4. Conclusions

β-In_2S_3 nanoparticles were successfully sonochemically synthesized in aqueous medium using diverse indium salts of strong acids. The sonochemical method is simple, fast, economical and environmentally benign. In our case, the particles size and shape of as-synthesized products at the same conditions do not differ significantly, while they differ according to the rate of aggregation. This finding is important for further research, particularly in terms of stabilizing and further processing of particles.

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