Morphology control in microwave synthesized bismuth sulfide by using different bismuth salts

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ABSTRACT

Bismuth sulfide (Bi_2S_3) is a promising semiconductor for optoelectronic applications. In this work we show that different morphologies of Bi_2S_3 such as nanofibers, nanorods or nano-hedgehogs, can be obtained by microwave assisted solution synthesis. The morphology of the products largely depends on the bismuth salt sources that manifest different dissociation kinetics. Nanofibers of highly crystalline Bi_2S_3 are formed with the slowly dissociated $BiCl_3$, whereas the morphology of "urchin" type is obtained with highly ionic $Bi(NO_3)_3$. On the other hand, the size of those nanostructures is mostly determined by the thermodynamic parameters of the synthesis, such as the type of solvents, the solution pH, the reaction temperature and the solution concentration. Total diffuse reflectance spectra of the Bi_2S_3 products suggest a direct band-gap of 1.3 eV with absorption coefficients as a function of the synthesis process. It demonstrates that the morphology of semiconductor nanostructures of Bi_2S_3 can be modified by controlling the reaction kinetics during the nucleation process in microwave synthesis.

1. Introduction

The semiconductors of Group V-VI have been extensively studied due to their excellent photoconductivity, photosensitivity and thermoelectric properties, which make them promising candidates as active materials in sensors, infrared spectroscopy, and photovoltaic converters [1–4]. Particularly, low energy band gap bismuth sulfide (1.3 eV) [5–10] has received intense attention for its possible application in photovoltaics [11], energy storage [12], and thermoelectric cooling technologies [9]. Depending on the purpose of the application, the morphology of the semiconductor products is an important factor to be considered. For example, spheres of Bi_2S_3 have large specific surface areas that make them good candidates for hydrogen storage [12] or in the DNA detection analysis [10]. On the other hand, nanowires of Bi_2S_3 could be well interconnected to form a Bi_2S_3 network that provides high electrical conductivity and a good photovoltaic performance in hybrid solar cells [13].

Nanostructured Bi_2S_3 can be synthesized by thermal decomposition [14–17], high-temperature evaporation method [18], spray pyrolysis [19], microwave heating [20,21], hydrothermal/solvothermal process [22,23], or chemical deposition [24,25]. Many of them use surfactants such as PVP [9,26,27], EDTA [24], SDS [8], CTAB [8], or SUDEI [10], to control the morphology of the products. The use of surfactants originates undesirable impurities in the final Bi_2S_3 products [10]. Among the above mentioned synthesis methods, microwave synthesis is capable to produce nanowires or spheres of Bi_2S_3 without the use of any surfactant. Moreover, it is a fast, effective, economical and environmentally friendly method [28].

Without surfactant, the control of the morphology of metal sulfides is an important issue to deal with. During the process of crystal growth, the initial formation of the crystalline seeds (nucleation) depends largely on the reaction kinetics of the metal and sulfur salts in different solvents. The subsequent crystal growth of those seeds determines the final morphology of the products. In this work we demonstrate that the morphology of microwave synthesized surfactant-free Bi_2S_3 products can be controlled by using different bismuth salts, and we propose possible mechanisms of the formation of nanofibers or "urchins" in those Bi_2S_3 products. Other parameters such as the type of solvent, reaction temperature and solution concentration are also considered as factors that influence the size and amount but not the morphology of the products. Similarly, the reaction time affects the final amount but not the morphology of Bi_2S_3 products synthesized by microwave

heating [29]. Similar results are obtained in our laboratory, and complementary, the stoichiometry and purity of the products can be improved with an optimized reaction time (20 min of reaction time for all our Bi_2S_3 synthesis).

It is important to mention that the type of sulfide sources is another parameter that affects the nucleation process of crystal growth. The use of thioacetamide (TA) as the sulfide source produces agglomerated small spheres with undefined microstructure in the microwave synthesized Bi_2S_3 products. It can be attributed to rapid dissociation of TA in comparison with other sulfide sources such as thiourea (TU). This hypothesis is in accordance with the study about the effect of sulfide sources on the morphology of CdS [30]. Considering reported works on the synthesis of Bi_2S_3 with different sulfide sources [9,20,29], we choose TU as the sulfide source and study the influence of bismuth sources on the morphology and purity of microwave synthesized Bi_2S_3 products.

2. Experimental

All reagents were used as received without further purification. Bismuth nitrate pentahydrate (Bi $(NO_3)_3 \cdot 5H_2O$, Sigma Aldrich) or bismuth chloride ($BiCl_3$, Sigma Aldrich) were used as the sources of bismuth, and thiourea (NH_2CSNH_2, Fermont) as the source of sulfur. Ethylene glycol (EG), distilled water or dimethyl formamide (DMF) were used as solvents. The solvent volume in all cases was of 50 mL, unless otherwise is mentioned. For Bi_2S_3 synthesis with $Bi(NO_3)_3$, the concentration of bismuth salt was 0.05 M, and that of thiourea (TU), 0.25 M. In the case of Bi_2S_3 synthesis with $BiCl_3$, the concentration of $BiCl_3$ was 0.01 M, and the corresponding TU solution, 0.05 M. When water was used as solvent, the dissolution of the bismuth and sulfur salts gave an acidic solution (pH1). By adding a small amount of 1 M KOH into that solution, it became alkaline with pH13. Both of them were used for synthesis of Bi_2S_3. All the reaction solutions were set under ultrasound shaking at room temperature for 10 min or until the salts were dissolved completely. Subsequently, the solutions were sealed in Teflon tubes (reactor) of 100 mL, and placed inside the microwave oven (CEM MARS-6) under high speed stirring. The temperature of the oven was set at a point between 100 °C and 170 °C, and the power of the oven at 600 W. The reaction and ramp time remained constant: 20 and 10 min, respectively. After the reaction, black Bi_2S_3 products were centrifuged, washed several times with ethanol and dried at room temperature.

The crystalline phases in the Bi_2S_3 products were analyzed using an X-ray diffractometer (Rigaku DMAX-2200) with Cu-K$_\alpha$ ($\lambda = 1.54$ Å) radiation in the 2θ range from 5 to 70°. Scherrer equation was used for the calculation of crystal sizes from XRD patterns, by choosing the Full Width at Half Maximum (FWHM) of the second most intense peak at 2θ $\approx 28.6°$, which corresponds to the crystalline plane of (130) and is relatively isolated from the nearby diffraction peaks. The morphology and elemental analysis (EDS) of the products were obtained with a Hitachi S-5500 scanning electron microscope (SEM), transmission electron microscopy (TEM) using JEOL JEM-1010 and Images of high resolution transmission electron microscopy (HRTEM) were obtained with a JEOL 2010 FEG operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was made using a Thermo Fisher Scientific 250Xi with Al-Kα radiation. Diffused reflectance spectra of Bi_2S_3 powder samples were collected on a UV–VIS–NIR spectrometer Shimadzu UV-3101PC at wavelength range of 250–2500 nm with the scanning rate of 20 nm s^{-1}.

3. Results and discussion

3.1. Nanofibers from $BiCl_3$ salt

When Bi_2S_3 is synthesized with $BiCl_3$ salt in ethylene glycol (EG), SEM images in Fig. 1 show the formation of nanofibers for all temperatures. The effect of the reaction temperature is observed on the size of the fibers: the sample synthesized at 100 °C (Fig. 1a) shows diameters between 46 and 78 nm and lengths from 1.2 to 2.0 μm, the one synthesized at 140 °C (Fig. 1b) had diameters between 40 and 105 nm and lengths from 1.2 to 4.4 μm, and the sample obtained at 170 °C (Fig. 1c) exhibited fibers of diameters between 30 nm and 430 nm and the lengths from 1.4 to 5.9 μm. The TEM image of the 170 °C sample shown in Fig. 1d confirms the nanofiber morphology of those Bi_2S_3 products. Fig. 1e displays a HRTEM image of the end of an individual Bi_2S_3 nanofiber. Its magnification in Fig. 1f shows the fringe of 0.245 nm, which assigns well with the spacing of (231) lattice plane of Bi_2S_3 orthorhombic phase. The diffraction spots of the corresponding SAED pattern of (Inset in Fig. 1f) can be indexed as the (231) lattice plane of Bi_2S_3, and the angle of 36.7° between (231) plane and [001] direction matches well with theoretical value.

X-ray diffractograms of the above three samples (Fig. 2) indicate that the main crystalline phase is the orthorhombic Bi_2S_3 (bismuthinite, JCPDS file 17-0320). The sample prepared at 100 °C has a crystal size of 18.6 nm, and contains bismuth oxychloride (BiOCl) as an additional impurity. This is in agreement with what had been observed in Ref. [31], probably due to the incompleteness of the reaction at such low temperature. EDS analysis of the three Bi_2S_3 products (Table 1) confirms that effectively larger amount of elemental oxygen and chloride are found in the 100 °C sample in comparison to the 140 and 170 °C ones. Additionally, the crystal size increases with the reaction temperature (Table 1): from 33.9 nm at 140 °C to 38.3 nm at 170 °C. The crystal size in the last two cases approaches the lower limit of fiber diameters, which indicates that some parts of the fibers are formed by single crystals, as suggested by HRTEM images in Fig. 1. The same is also observed for Bi_2S_3 nanowires obtained by hydrothermal methods [13]. Our research results show that nanofibers of Bi_2S_3 can be achieved with the microwave method, which is faster and more efficient than the hydrothermal one.

The solvent is a dielectric medium that not only dissolves the salts, but also absorbs the microwave radiation and generates heat in the reactors. The parameter that describes the heating capacity of the solvent in a microwave reaction is the loss tangent. The loss tangent of a dielectric material (water, EG or DMF) is defined as $tan\delta = \varepsilon''/\varepsilon'$, where ε'' is the imaginary permittivity and ε', the real permittivity (dielectric constant) of the material. According to its value, a dielectric material can be classified as a high ($tan\delta > 0.5$), medium ($0.1 < tan\delta < 0.5$), or low ($tan\delta < 0.1$) microwave absorbent material [32–34]. EG has a high $tan\delta$ value (1.350) and DMF, medium (0.161) [32]. Under the same synthesis conditions DMF absorbs less microwave radiation and generates less heat (or originates lower local temperature) inside the reactor than EG.

Therefore, if we change the type of solvent, the morphology of the final product is slightly modified by using the same sources of bismuth and sulfur. It is observed that the reaction kinetics of $BiCl_3$ in DMF is slower than in EG, probably due to larger tangent loss of EG (1.35) than that of DMF (0.16) [32]. With DMF as solvent, no precipitate is formed at 100 °C. As the reaction temperature increases to 140 °C, a very small amount of suspended particles are appeared to enable only the analysis of SEM (Fig. 3). In this case, thicker and shorter bars are observed in comparison with the same product obtained in EG, between 70 and 200 nm in diameter and from 0.7 to 2.0 μm in length.

When water is used as solvent, both at pH1 and pH13, no product was formed at 100 °C by using $BiCl_3$ as the bismuth source. As the synthesis temperatures is set at 140 °C, the EDS analysis reveals a large amount of oxygen and chloride and an extremely low Bi:S ratios in the final products, 1:0.06 or 1:0.13 (Table 1), suggesting that there is no bismuth sulfide formed in them. Apparently, Bi^{3+} cations reacted predominantly with oxygen (and chloride) than with the sulfide ions, impeding the formation of Bi_2S_3 in aqueous solutions. Also, the products prepared at higher temperatures show morphology of leaflets instead of fibers or rods.