Low temperature quaternary microemulsion synthesis of Bi_2S_3 nanospheres and nanorods

D. J. JOVANOVIĆ*, I. Lj.VALIDŽIĆ, I. A. JANKOVIĆ, J. M. NEDELJKOVIĆ
Vinča Institute of Nuclear Sciences, P.O. Box 522, University of Belgrade, 11001 Belgrade, Serbia

Two different morphologies of bismuth sulphide (Bi_2S_3), nanospheres and nanorods, were obtained in W/O microemulsions (cyclohexane / Triton X-100 / n-pentanol / water) as a reaction medium. The structural characterization of the Bi_2S_3 nanoparticulates was performed using transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. The difference in morphology was achieved by adjusting reactant concentrations. The Bi_2S_3 nanospheres have bimodal size distribution with sizes in the range 2-5 nm and 20-40 nm while the diameter of nanorods is in between 5 and 20 nm and their length is in the range from 150 to 400 nm. Both kinds of nanostructures are well-crystalline although they were prepared at 60 ^{0}C without any further thermal treatment. Based on optical measurements the band gaps were estimated to be 1.5 and 1.57 eV for nanospheres and nanorods, respectively. These values are larger compared to the bulk material as a consequence of reduced dimensionality of the Bi_2S_3 nanostructures.

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1. Introduction

In the past years, the family of nanocrystalline semiconductor chalcogenides $A_2^VB_3^{VI}$ (A = Sb, Bi, As; B = S, Se, Te) have been a subject of investigation by many research groups. These compounds have been studied because of their excellent properties (photoconductivity, photosensitivity and thermoelectric effect) and possible applications in television cameras, thermoelectric, electronic and optoelectronic devices, as well as infrared spectroscopy [1-3]. In particular, much attention has been focused on bismuth sulphide (Bi_2S_3) which can be used in photovoltaic cells, photodiode cells, sensors and thermoelectronic cooling technologies [4]. Recently, the Bi_2S_3 nanoparticles found new application as imaging agent in X-ray computed tomography [5].

Complex morphological forms of Bi_2S_3 such as nanowhiskers, nanoflowers and snowflakes have been prepared in ionic liquid solutions by employing the soft templates (polymers or biomolecules) [6-8]. Nanorods and/or nanowires of Bi_2S_3 with different diameters and aspect ratios have been synthesized by simple polyol solution process [9], colloidal solution methods [10], reflux process [11], solventless arrested precipitation [12], hydrothermal [13-16], solvothermal [17-19] and microwave solvothermal techniques [20]. It should be noted that a number of authors have prepared nanorods with diameter in the range from 5 to 30 nm but all syntheses were performed at elevated temperatures (120-225 ^{0}C) [9-10, 12, 14, 16-20].

Recently, Liu et al. [21] and Zhu et al. [22] obtained nanorods of Bi_2S_3 with diameters between 10 and 20 nm at lower temperatures, 95 and 74 ^{0}C, respectively. Also, Yu et al. [23] have presented a novel chemical route for synthesis of Bi_2S_3 nanowires under milder experimental conditions (60 ^{0}C). These authors synthesized single-crystalline Bi_2S_3 nanowires with diameters in the range 80-200 nm and lengths up to tens of micrometers through surfactant micelle - template inducing reaction.

In the present work, quaternary W/O microemulsion (cyclohexane /Triton X-100 / n-pentanol / water) was used as reaction media and two different morphologies of Bi_2S_3 (nanospheres and nanorods) were obtained under mild experimental conditions. The difference in morphology was achieved by adjusting reactant concentrations. The obtained nanorods were well-crystalline with diameter in the nanosize regime (5-20 nm). The structural and optical properties of the Bi_2S_3 nanostructures were studied in details using transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-Vis spectroscopy.

2. Experimental

All chemical reagents in this work (bismuth nitrate pentahydrate ($Bi_2(NO_3)_3$ x $5H_2O$) (≥98.5%), sodium sulphide (Na_2S x $9H_2O$) (≥98.0%), cyclohexane (99.5%), Triton X-100 (99.5 %), n-pentanol (>98 %), hydrochloric acid (35%), methanol (99.8%), n-hexane (99%)) were used without further purification. Each microemulsion contained 0.46 g of n-pentanol, 3.37 g of Triton X-100, 7.64 g of cyclohexane and 1g of water, and consequently the molar ratio between water and surfactant was ω = $[H_2O]$/[Triton X-100] = 11 in all experiments. Molar ratio between sulphide and bismuth ions was also constant ($[S^{2-}]/[Bi^{3+}] = 5$), while concentrations of bismuth ions were either 0.1 M for synthesis of nanospheres or 0.5 M for synthesis of Bi_2S_3 nanorods. Due to hydrolysis of $Bi(NO_3)_3$ and consequent formation of milky solution, prepared aqueous solution was treated with hydrochloric acid till the white precipitate was dissolved completely.

In a typical synthesis, two separated microemulsions containing the same amounts of Triton X-100, cyclohexane, n-pentanol and aqueous solution of either Bi^{3+} or S^{2-} were mixed in a flask after mechanical agitation for about 15 min. After mixing, the flask was heated from room temperature up to 60 ^{0}C in oil bath, kept at this temperature for 48 hours and then cooled down to room temperature. All the time the mixture was vigorously stirred. Microemulsions containing Bi_2S_3 nanospheres or nanorods were destabilized by adding methanol, solid being separated by centrifugation and washed with methanol. This procedure was repeated three times. The precipitate was then washed with n-hexane three times and collected black precipitate dried in air for 24 hours was used for characterizations.

Microstructural characterization of Bi_2S_3 nanostructures was performed by transmission electron microscopy (TEM) using Philips EM 400 microscope operated at 120 kV. The samples for TEM measurements were prepared by dissolving one droplet of microemulsion in 2 ml of ethanol. The obtained samples were placed on C-coated Cu grids.

The powder X-ray diffraction (XRD) measurements were carried out on a BRUKER D8 ADVANCE diffractometer in theta/theta reflection geometry. Diffraction data for structure analysis were collected in 2θ range from 10 to 110 ^{0} with step 0.02 ^{0} and 10 s counting time per step.

Absorption spectra of Bi_2S_3 nanostructures dispersed in methanol were measured using a Perkin Elmer Lambda 5 UV-Vis Spectrophotometer.

3. Results and discussion

The quaternary W/O microemulsion (cyclohexane / Triton X -100 / n-pentanol / water) was used as reaction media for synthesis of two morphologically different forms of Bi_2S_3 particles. The morphology of the synthesized Bi_2S_3 nanostructures was revealed by TEM. Typical TEM images of the synthesized Bi_2S_3 nanostructures are shown in Figure 1. Synthesis with lower concentration of reactants (0.1 M Bi^{3+} and 0.5 M S^{2-}) yielded Bi_2S_3 particles in the nanometer size domain with bimodal size distribution, as shown in Figure 1a. The agglomerated Bi_2S_3 particles in the size range from 20 to 40 nm can be noticed, and also significantly smaller particles in the size range from 2 to 5 nm. It should be mentioned that some of the 20-40 nm Bi_2S_3 particles are non-spherical with two dimensional images close to hexagon. Similar shape was observed in the case of ZnS particles prepared in the same manner [24].

Rod-like particles were synthesized using higher concentrations of reactants (0.5 M Bi^{3+} and 2.5 M S^{2-}). Typically, diameters were in between 5 and 20 nm, while lengths were in the range from 150 to 400 nm, as can be seen in Figure 1b. It should be noticed that a number of authors have prepared the Bi_2S_3 nanorods with diameter in the similar size range (5-30 nm) but using different techniques based on high temperature treatment [9-10, 12, 14, 16-22].

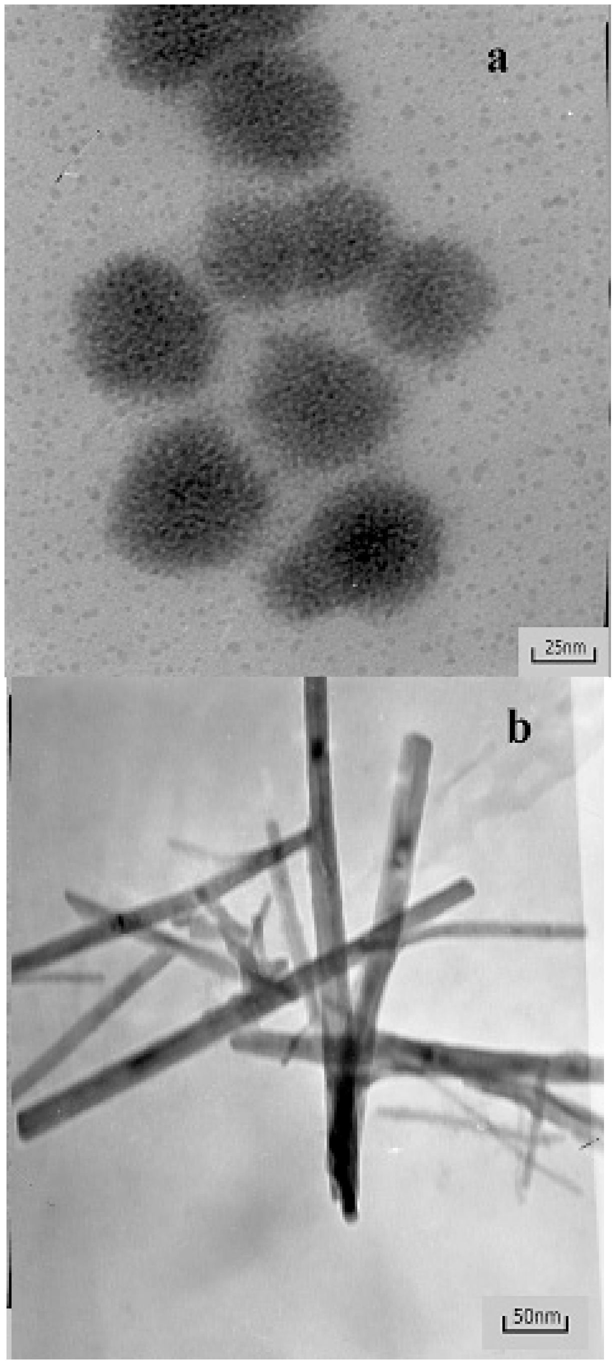

Fig. 1. Typical TEM images of the Bi_2S_3 nanostructures prepared in W/O microemulsions: a) nanosphere, and b) nanorods.

To the best of our knowledge, there is only one similar study on Bi_2S_3 nanowires in literature reported by Yu et al. [23]. These authors reported formation of the Bi_2S_3 nanowires in W/O microemusions with diameter in the size range from 80 to 200 nm and length of several microns. Different experimental conditions used in this study compared to above mentioned work (lower reactant concentration, introduction of cosurfactant and longer reaction time) led to the formation of the Bi_2S_3 nanorods with significantly reduced size.

The formation of the rod-like morphology of Bi_2S_3 has been ascribed in literature to several factors. First, the crystal structure of Bi_2S_3 should be responsible for one dimensional growth. It is known that Bi_2S_3 crystallizes with a lamellar structure with linked Bi_2S_3 units forming infinite chains, which in turn are connected via much weaker van der Waals interactions. The stronger covalent bond in chains facilitates higher growth rate along the chain axis causing the preferential growth of the particles, thus forming one dimensional nanostructures [12, 17, 25]. Second, it is well known that the surfactant molecules spontaneously organize into rod-shaped micelles or inverses micelles when their concentrations reach certain value. These structures can be used as soft templates to promote the formation of one dimensional nanostructured materials [26]. Additional study is necessary to clarify why at lower reactant concentrations Bi_2S_3 nanospheres were obtained instead of nanorods under identical experimental conditions.

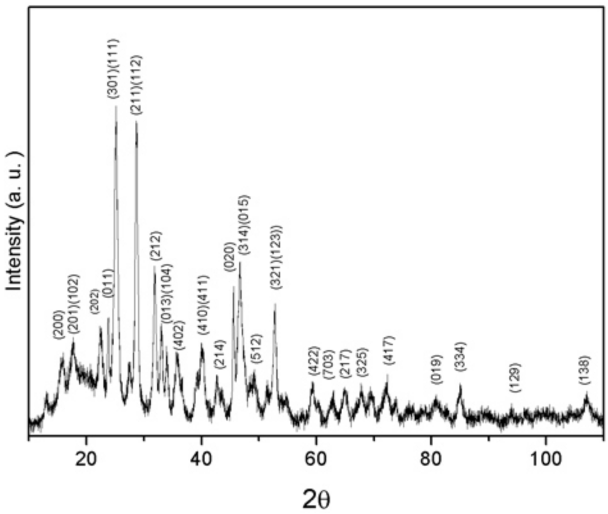

Fig. 2. The XRD pattern of the Bi_2S_3 nanospheres.

The XRD pattern of the Bi_2S_3 nanospheres is shown in Figure 2. The identical XRD pattern of the Bi_2S_3 nanorods was observed and it is not shown for the sake of clarity. All diffraction peaks are labeled and can be indexed to a pure orthorhombic phase of bismuth sulphide (bismuthinite) with Pnma space group. The derived lattice constants (a = 11.2983 Å, b = 3.9854 Å and c = 11.1447 Å) are in a good agreement with the literature values for Bi_2S_3 [27]. It is important to point out that there are no additional peaks from any impurity. The average crystalline domain size was estimated using the Debye - Scherrer diffraction formula. The grain size was found to be around 25 nm for both morphologies of Bi_2S_3. It should be noticed that the crystalline domain size is very close to the microscopically estimated average size of larger fraction of Bi_2S_3 nanospheres. Also, the crystalline domain size of the nanorods is close to their average diameter.

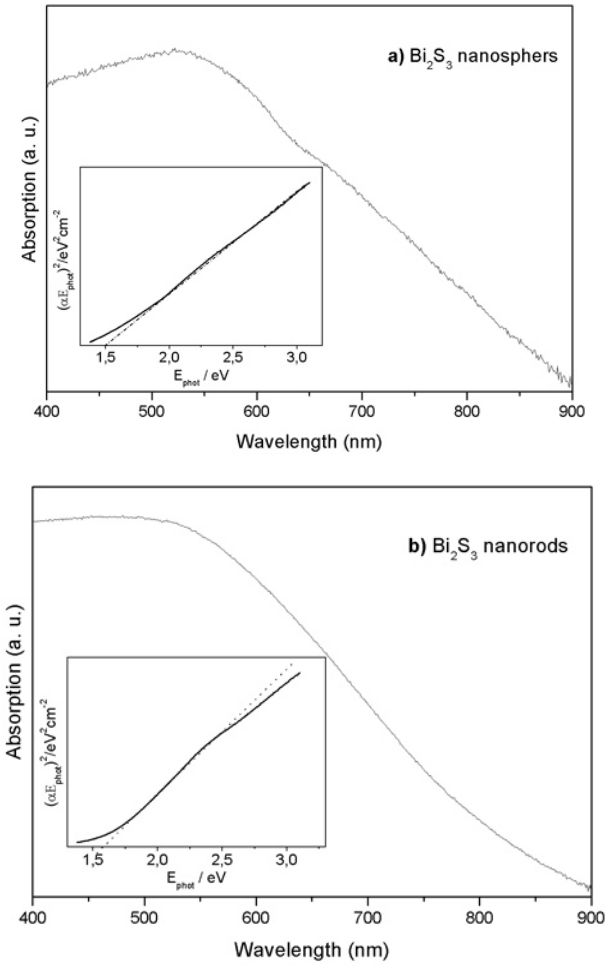

Fig. 3. Absorption spectra of the Bi_2S_3 nanostructures: a) nanospheres and b) nanorods. Insets show the $(\alpha\ E_{ph})^2$ versus E_{ph} plot.

Absorption spectra of Bi_2S_3 nanospheres and nanorods dispersed in methanol are presented in Figures 3a and 3b, respectively. Bismuth sulphide is a semiconductor with a direct optical band gap of 1.3 eV at room temperature. Tauc's plots, $(\alpha\ E_{ph})^2$ versus E_{ph}, were used for estimation of band gap energies of both kinds of Bi_2S_3 nanoparticulates, and they are presented as insets to Figure 3. Both estimated values (1.5 and 1.57 eV for Bi_2S_3 nanospheres and nanorods, respectively) are larger compared to the band gap energy of bulk material (1.3 eV). The observed effect is the consequence of quantum confinement due to reduced dimensionality, and this result is in agreement with reported band gap values by other authors for Bi_2S_3 nanoparticles obtained using different preparative route [20, 25, 28-29].

In summary, two different morphological forms of Bi_2S_3 (nanospheres and nanorods) were synthesized using quaternary W/O microemulsion (cyclohexane / Triton X-100 / n-pentanol / water) as a reaction medium. Well-crystalline particles were obtained at the temperature as low as 60 ^{0}C without any further thermal treatment. The synthesized Bi_2S_3 nanoparticulates exhibit quantum size effects due to reduced dimensionality.

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*Corresponding author: draganaj@vinca.rs