

# Investigation of optical and structural properties of sonochemically prepared 3-mercaptopropionic acid capped bismuth sulfide nanostructures

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3-mercaptopropionic acid(3-MPA) capped bismuth sulfide nanostructures have been synthesized using an ultrasound-assisted method in an aqueous medium and some of their optical and structural properties have been characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) and UV-Visible spectroscopy. Reference experiments have also been performed in the absence of capping agent to clearly illustrate the effect of capping mechanism. XRD results show broadening of peaks, suggesting formation of the nanometer sized materials and more smaller sizes in the presence of 3-MPA. UV-Vis absorption spectroscopy results show shifting toward lower wavelength, also confirming the formation of nanostructures with smaller dimension. Surface morphology of the prepared material shows the formation of nearly spherical aggregates of nanoclusters.

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## 1. Introduction

Nanocrystalline chalcogenides of the transition metals have attracted a great deal of attention because of their novel electronic and optical properties for the construction of advanced functional nanodevices [1, 2]. The synthesis of nanostructured materials with controlled structures and novel properties has been widely studied for their novel physical and chemical properties. The shape and size of nanostructures are two critical factors for determining their properties [3, 4]. One of the most interesting effects of low-dimensional semiconductor structures is the size-dependent band gap. Semiconductors, which have changed properties resulting from quantum confinement, have drawn considerable interest and are currently being investigated [5-6].

Among the numerous metallic sulfides, bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) is one of the most important V-VI semiconductors, and has attracted great attention for its technological applications [5]. The most recent value of the band gap is reported to be in the range of about 1.3 to 1.7 eV [7]. It has a number of potential applications such as photovoltaic and optoelectronic, thermoelectric cooling systems, IR devices; X-ray computed tomography, photocatalysis for hydrogen evolution, and electrochemical hydrogen storage [7-10]. In recent years,  $\text{Bi}_2\text{S}_3$  has been synthesized through various solution-based synthetic schemes such as, template growth [11], molten salt solvent method [1], chemical drop method [8], spray pyrolysis [12], chemical bath deposition [5], sol-gel [13] and ultrasound-assisted[14] methods.

However, among them, ultrasound-assisted method is very simple and has evident advantages due to good compositional control, low equipment cost and lower crystallization temperature. In the present work, we report the ultrasound-assisted method for preparation of  $\text{Bi}_2\text{S}_3$  nanostructures. The ultrasound-assisted methods involve ultrasound irradiation of the precursor during synthesis. Ultrasound irradiation has been used extensively to produce novel materials with interesting properties. Because of the immense physical and chemical effects of ultrasonic waves in solutions, by using this method we can produce materials with novel properties. The ultrasound irradiation method has advantages such as rapid reaction rate, controllable reaction, uniform shape, narrow size distribution and high purity. The chemical effects of ultrasound arise from the phenomenon called acoustic cavitation, i.e., the formation, growth and implosive collapse of bubbles in an ultrasonically irradiated liquid. The unique reaction conditions, temperatures of 5000 K, pressures of about 500 bar and rapid cooling rates greater than  $10^9$  K/s, enable the synthesis of metastable phases that are difficult to prepare in other ways [14].

In this paper, we describe a simple ultrasound-assisted method to produce  $\text{Bi}_2\text{S}_3$  nanostructures using 3-mercaptopropionic acid (3-MPA) as the capping molecule. The structural and optical properties of the nanostructures samples are investigated precisely.

## 2. Experimental

To synthesize bismuth sulfide nanostructures the chemicals used were bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), 3-mercaptopropionic acid (3-MPA) and sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ). In a typical procedure, aqueous stock solutions of (0.2M) 1.94g of  $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , were dissolved in 20 ml doubled distilled water, in another baker and 0.94 g sodium sulfide were dissolved in 20 ml of distilled water, respectively. The bismuth nitrate solution was then added to the sodium sulfide solution. Then cooled to room temperature, the solution with black precipitate is appeared. Ultrasonic irradiation was achieved using Dr. Heilscher high-intensity ultrasound processor, UP200H, Germany. After sonication the solution was centrifuged several times. The precipitation were washed repeatedly with distilled water and then dried at vacuum pump. The reactions take place as followed:

$$\text{Bi}(\text{NO}_3)_3 + \text{Na}_2\text{S} \rightarrow \text{Bi}_2\text{S}_3 + \text{NaNO}_3$$

### 2.1 Instrument

The X-ray diffraction (XRD) patterns of products were recorded on a Philips X'pert X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) employing a scanning step of  $0.025^\circ$ , in  $2\theta$  range from  $20^\circ$  to  $80^\circ$ . Surface morphologies were studied using the LEO1430 VP scanning electron microscope (SEM) with 15 and 18 kV accelerating voltages. UV-Vis absorption spectra of the samples were obtained using a Shimadzu spectrophotometer (Japan, model 1650).

## 3. Results and discussion

Fig. 1(a) and 1(b) shows the XRD patterns of uncapped and 3-MPA-capped  $\text{Bi}_2\text{S}_3$  nanostructures. The broadening of the diffraction peaks indicates the nanocrystalline nature of the sample. All diffraction peaks can be readily indexed to cubic  $\text{Bi}_2\text{S}_3$  nanoparticles, no other peaks were observed such as Bi or S, which indicating the high purity of the samples. The diffraction peaks are markedly broadened with increasing in the capping agent, which indicates that the crystalline sizes of samples are very small.

The average crystallite size is calculated from the full width at half maximum (FWHM) of the diffraction peaks using Debye-Scherrer formula  $D = 0.94\lambda/\beta\cos\theta$  where D is the mean grain size,  $\lambda$  is the X-ray wavelength,  $\beta$  is the FWHM of diffraction peak and  $\theta$  is the diffraction angle [15]. The average grain size of the uncapped and 3-MPA-capped  $\text{Bi}_2\text{S}_3$  particles calculated from the peaks is 30 and 26 nm respectively. The size of nanocrystals of the sample is thus in the strong confinement effect.

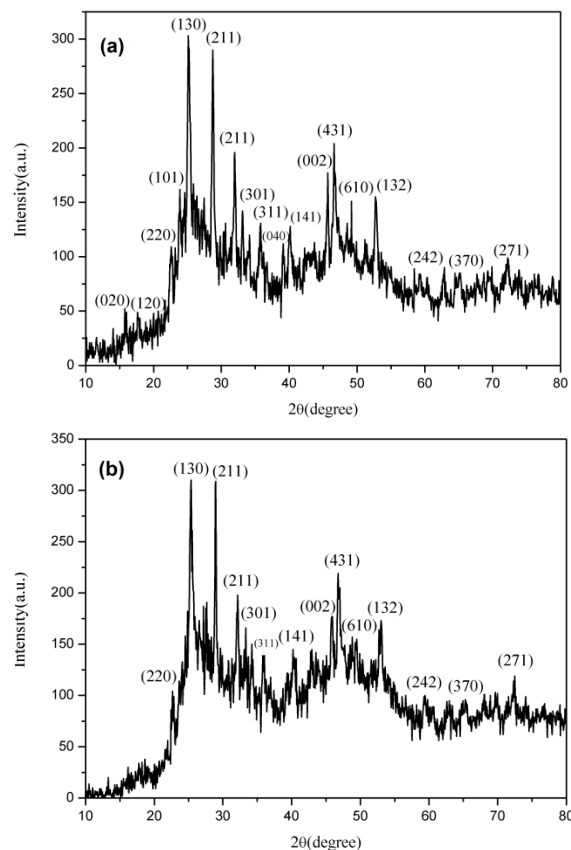


Fig. 1. (a) and (b) XRD pattern of uncapped and capped (3-MPA)  $\text{Bi}_2\text{S}_3$  nanostructures

Fig. 2 shows the UV-Vis absorbance spectra as prepared samples. The variation of the excitation peak position indicates, change of the particles size or influence of the surfactant in prepared solution. These absorption edges of capped  $\text{Bi}_2\text{S}_3$  nanostructures were at shorter wavelength than for bulk. The shifting of absorption edges to shorter wavelength could be explained by the quantum confinement of  $\text{Bi}_2\text{S}_3$  nanostructures.

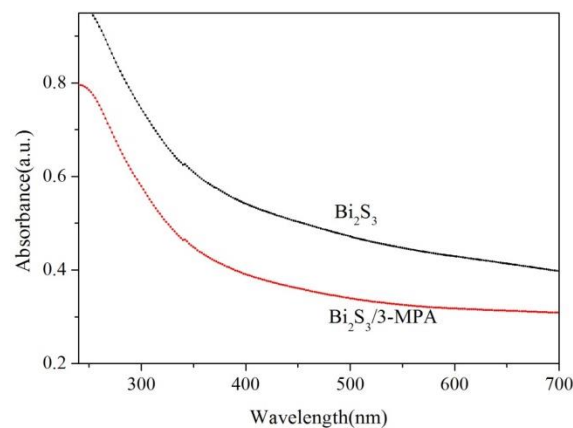


Fig. 2. UV-Vis spectra of uncapped and capped (3-MPA)  $\text{Bi}_2\text{S}_3$  nanostructures

For crystallite semiconductor, the optical absorption near the band edge follows the equation  $\alpha h\nu = A(h\nu - E_g)^{1/2}$ , where  $\alpha$ ,  $\nu$ ,  $E_g$  and  $A$  are the absorption coefficient, the light frequency, the band gap and a constant respectively [16]. Figs. 3(a) and 3(b) shows the Tauc plot of the as-prepared samples due uncapped and capped (3-MPA)  $\text{Bi}_2\text{S}_3$  nanostructures respectively.

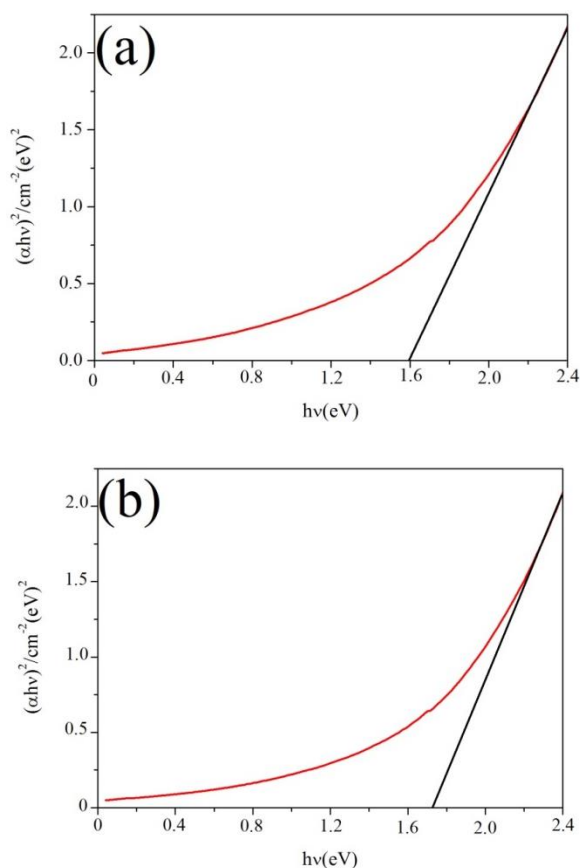


Fig. 3. Tauc plot of (a) uncapped sample. (b) 3-MPA-capped sample of  $\text{Bi}_2\text{S}_3$  nanostructures

The corresponding band gap energy  $\text{Bi}_2\text{S}_3$  samples to be calculated 1.59 and 1.67eV. The increasing trends of the band gap energy upon the decreasing particle size are well presented for the as-prepared samples. The clearly observed the blue shift occurred when the capping agent added to sample.

The nanostructures of obtained bismuth sulfide were studied by scanning electron microscopy (SEM). Fig. 4(a and b) and (c and d) shows the SEM images of uncapped and capped (3-MPA)  $\text{Bi}_2\text{S}_3$  nanostructures respectively.

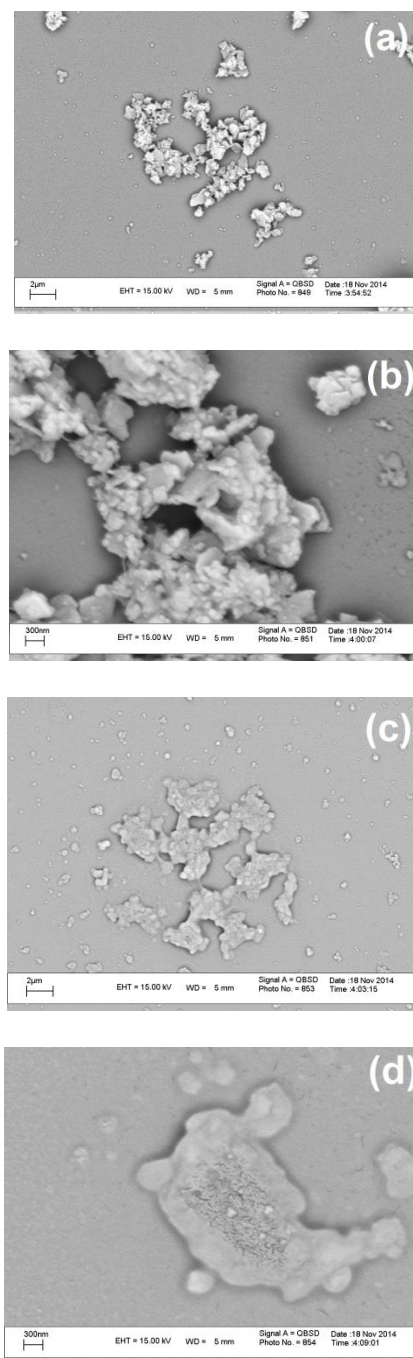


Fig. 4. SEM images of (a and b) uncapped sample and (c and d) 3-MPA capped sample of  $\text{Bi}_2\text{S}_3$  nanostructures

From the images it is observed that the distributions of grains are not uniform. In the uncapped sample the nanoparticles have been agglomerated in the form of polydisperse small size in the nanoscale. In 3-MPA capped sample, the particle size has been smaller size and different distribution.

#### 4. Conclusion

Bismuth sulfide nanostructures were synthesized through simple ultrasound-assisted method with 3-MPA

capping agent. XRD results confirmed the decrement of crystallite size with the increase of capping agent. Morphological studies by SEM showed the formation of spherical nanoparticles and changed in nanostructures size distribution. The UV-Vis spectra are found to be shifted towards the blue shift with the increase of capping agent, indicating the decrease in the particle size.

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