Preparation and Characterization of Bismuth Sulfide (Bi_2S_3) Nanostructures by Ultrasonic Method

M. Ranjbar[1], M. A. Taher[2], Peyman Rajaei[3]

Abstract

In the present work, Bi2S3 nanostructures have been synthesized with the aid of thioglycollic acid (TGA) a solvent, capping agent, and sulfide source in the presence of ultrasonic method. The as-synthesized products were characterized by X-ray diffraction (XRD), Energy Dispersive X-ray spectroscopy (EDS), scanning electron microscope (SEM), and photoluminescence (PL) spectroscopy. The band gap of nanoparticles calculated 2.37 eV that shows a blue shift compare Bi_2S_3 bulk. The effects of reaction time and ultrasonic power on the morphology and particle size of product were studied.

Keywords: Nanostructures; Bi_2S_3; Ultrasonic; Electron microscopy; TGA

1. Introduction

Semiconductor nanocrystals (NCs) have attracted great attention on their synthesis and characterization because of the unique size- and shape-dependent properties and could be widely used in photocatalyst, solar cell, lasers, biomedical probes, light emitting diodes, photoluminescence and optoelectronic devices, etc. [1-3]. Among these materials bismuth sulfide (Bi_2S_3) is of great interest because of its uniqueoptical and electronic properties [4-6]. It has a direct band gap of around 1.3eV [7], and can be used in various fields such as thermoelectric devices [8], photovoltaics [9], nonlinear absorption [10], biomolecule detection [11], photovoltaic material, photodiode array and infrared spectroscopy [12, 13]. Up to now,various morphologies of Bi_2S_3 such asnanorods [14], nanowires and nanoflowers [15],nanoparticles [16], have been synthesized by using a variety of methods such as hydrothermal route [15], precipitation [16], and microwave irradiation [17]. In this paper we report a simple, novel, and rapid procedure for preparation of Bi2S3 nanostructures via an ultrasonic method by employing thioglycollic acid (TGA) as a solvent, capping agent, and sulfide source. The effects of reaction time and ultrasonic power on the morphology and particle size of product were studied.

2. Experimental

2.1 Synthesis of Bi2S3 nanostructures

All the chemicals used in this method were of analytical grad and used as received without further purification. 0.4 mmol of $Bi(NO_3)_3$ was dissolved in 40 mL of TGA. The mixture was loaded into a microwave Teflon container, and the reaction was performed in an ultrasonic digestion system under various conditions (Table 1). The black obtained precipitates were centrifuged, washed with ethanol and distilled

Table 1. Reaction conditions for preparation of Bi_2S_3 nanostructures from $Bi(NO_3)_3$and TGA

Sample No.	Time (min)	Power (W)
1	–	–
2	30	30
3	30	50
4	30	70
5	20	50
6	40	50
7	60	50
8	80	50

1- Young Researchers and Elite Club, Kerman Branch, Islamic Azad University, Kerman, Iran.
2- Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran.
3- Faculty of Science, Kerman Branch, Islamic Azad University Kerman, Iran.

Corresponding author: M. Ranjbar, Young Researchers and Elites Club, Kerman Branch, Islamic Azad University, Kerman, Iran.
Email: Mehdi.Ranjbar@outlook.com

water several times and dried at 70 °C at vacuum oven for 8h**.**

2.2 Materials and physical measurements

All chemical reagents in this experiment were of analytical grade and used without further purification. The XRD patterns were collected from a diffract meter of Philips Company with X'pert promonochromatized Cu Kα radiation (λ = 1.54 Å). Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. EDS spectrum was recorded on a XL30, Philips. Room temperature photoluminescence (PL) properties of product were studied on a Perkin-Elmer (LS 55) fluorescence spectrophotometer.

3. Result and Discussion

XRD pattern of the as-synthesized powders at 50 W for 30 min (sample 3) is shown in Fig. 1. The XRD pattern of the as-synthesized Bi_2S_3 (sample 3) indicated the formation of orthorhombic phase Bi_2S_3 (JCPDS No. 75-1306). Extremely broad reflection peaks were observed in Fig. 1, which indicated the fine particle nature of the obtained Bi_2S_3 nanostructures. No other crystalline phases were detected in the product. From XRD data, the crystallite diameter (Dc) of Bi_2S_3 nanoparticles obtained from sample 3 was calculated to be 23 nm using the Scherer equation (1):

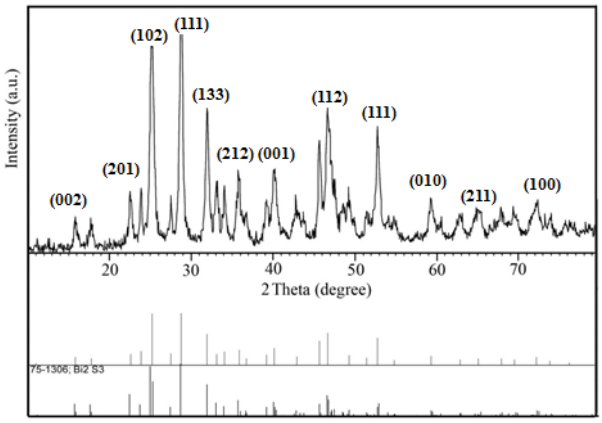

Fig. 1. XRD pattern of as synthesized Bi_2S_3nanorods at 50 W for 30 min (sample 3).

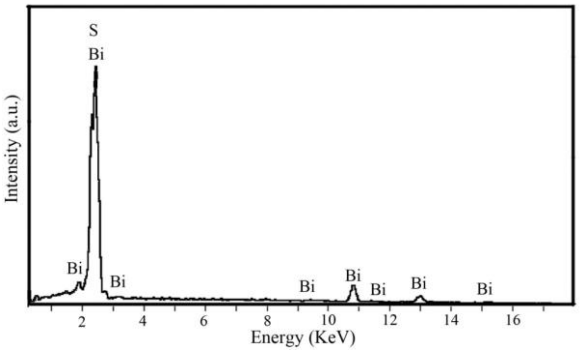

Fig. 2. EDS spectrum of the as synthesized Bi_2S_3nanorods at 50 W for 30 min (sample 3).

$$Dc=K\lambda/\beta\cos\theta \quad (1)$$

where β is the breadth of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. EDS analysis was employed to investigate the chemical composition and purity of the as-synthesized Bi_2S_3 nanostructures. EDS spectrum of Bi_2S_3 (sample 3, Fig. 2) revealed the presence of Bi and S elements in the as-prepared Bi_2S_3 nanostructures. The EDS results gave a rough atomic ratio of Bi:S as nearly 2:3, revealed that pure Bi_2S_3 were successfully synthesized via the present synthetic route (Table 2). To understand the influence of ultrasonic power and reaction time on the size and morphology of Bi_2S_3 nanostructures, several experiments were carried out, and the products obtained at different stages were investigated using SEM techniques. SEM image of Bi_2S_3 (sample 1) prepared in the absence of ultrasonic irradiation is shown in Fig. 3a. The product is mainly composed of a large amount of micro particle and nanorod, which with regular shapes were easily aggregated together. SEM

Table 2. Table of chemical composition of EDS analysis

Element	Series	Wt. %	At. %
Bismuth	K series	49.80	52.40
Sulfide	K series	50.20	47.60

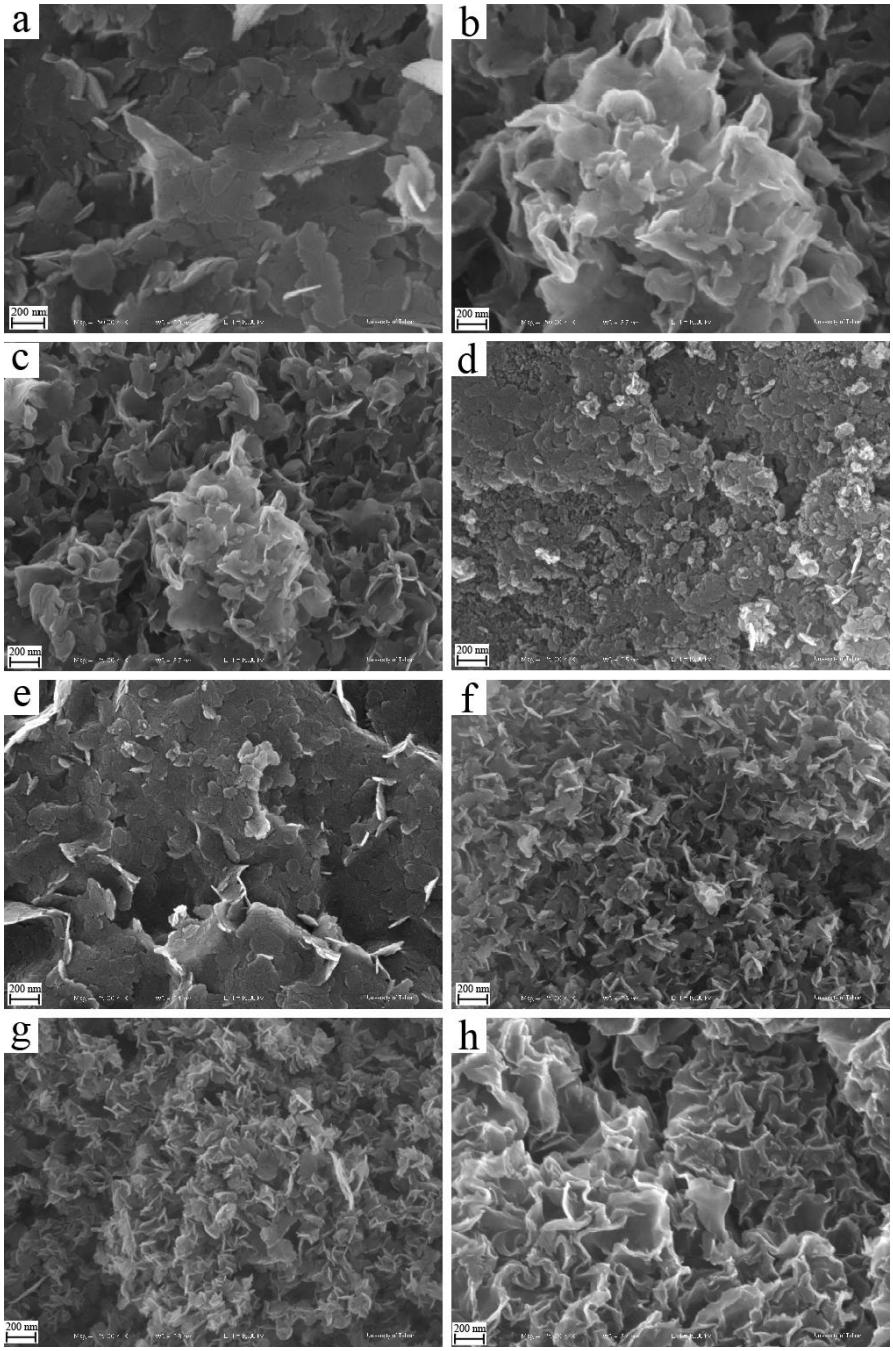

Fig. 3. SEM images of the products (a) sample 1 (b) sample 2 (c) sample 3 (d) sample 4 (e) sample 5 (f) sample 6 (g) sample 7 (h) sample 8

images of samples 2-4 prepared at 30, 50, and 70 W are shown in Fig. 3b and 3c, and 3d, respectively. According to the Fig. 3b (sample 2), product composed of large amount of nanorods. Increase power to 50 W results in decrease nanorods size (Fig. 3c). When power increased to 70 W (sample 4) agglomeration occurs due to the formation of unstable and ultra-fine nuclei that have a strong tendency to be stable by agglomeration occurred (Fig.3d). Thus, the optimum power for synthesis of Bi_2S_3 nanostructure is 50 W. To investigation the effect of reaction time, synthesis Bi2S3 performed in different time 20, 40, 60, and 80 min, respectively (Figs. 3e-h). Decrease reaction time from 30 to 20 mine cause the agglomeration of nanorods, as shown in Fig. 3e (sample 5). Increasing reaction time from 20 to 40 min while ultrasonic power constant at 50W (sample 6), product composed of rod-like nanostructures with diameters of 10-20 nm and lengths of 100-200 nm obtained (Fig. 3f).

Further elevating of reaction time to 60 and 80 min led to increase size of product and create flower-like nanostructures (Fig. 3g and h). So with prolonged reaction condition under ultrasonication, smaller particles cannot be obtained. Increasing of particle's size may be due to two processes which were discussed by Morsali et al. [18] for AgI nanoparticles. One of these processes is diffusion process of the reactants at the surface of the growing crystallite and the other ones is reaction at these surfaces to incorporate the reactant as a part of the growth process. All of these processes will lead to increase in particle's size. The optical properties of Bi_2S_3 (sample 2, 3, and 8) were characterized by PL spectrum. The PL spectra of the Bi_2S_3 were recorded in ethanol solution and in solid state as shown in Figs. 4a, b, and c in which the scan rate is 1500 nm/min, respectively. The PL spectra were consisted of strong peaks at 590, 523, and 565 nm (excitation at 435.5 nm) for sample 2, 3, and 8, respectively. The PL spectra show a blue shift (2.1, 2.37, and 2.2 eV) compared to that of the bulk Bi2S3 (1.3 eV). According to the SEM images and PL data increase in particles size result in decrease in band gap of Bi_2S_3 nanostructure.

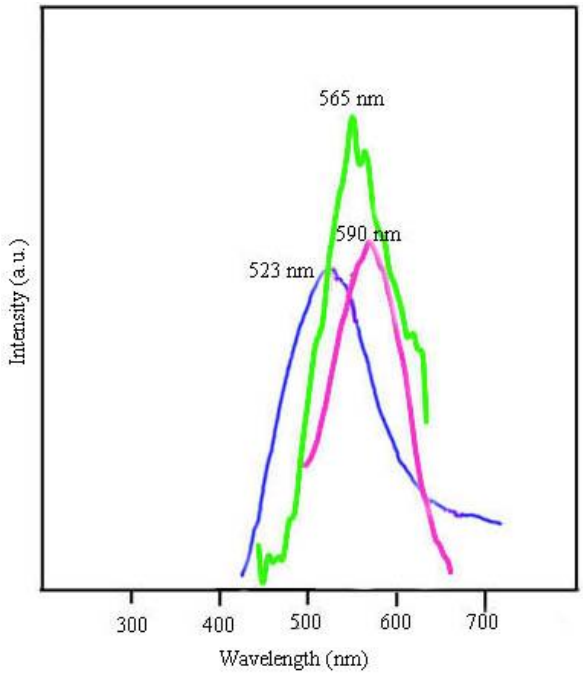

Fig. 4. PL spectrum of the as synthesized Bi_2S_3 nanorods (a) sample 2 (b) sample 3 (c) sample 8.

4. Conclusions

In summary, Bi_2S_3 nanostructures with different morphologies have been successfully synthesized via an ultrasonic method by employing TGA as a solvent, capping agent, and sulfide source. The reaction time, power, and ultrasonic irradiation have an important effect on the size and morphology of the products. It was found out that the size, morphology, and properties of the products were greatly influenced by these parameters. From XRD data the average diameter of the Bi_2S_3 nanostructures was 23 nm. By comparing this method and other works, it was found that the present method is simple, novel, low cost, and fast. Furthermore, The XRD, EDS, SEM, and PL were used to characterize the products.

Acknowledgements

The authors are grateful to Shahid Bahounar University and Kerman Branch Islamic Azad University for supporting this work.

References

1. R. C. Somers, M. G. Bawendi, D. G. Nocera, *Chem. Soc. Rev*. 36 (2007) 579–591.
2. C. L. Feng, X. Zhong, M. Steinhart, A. M. Caminade, J. P. Majoral, W. Knoll, *Adv. Mater*. 19 (2007) 1933–1936.
3. N. Tessler, V. Medvedev, M. Kazes, S. H. Kan, U. Banin, *Science.* 295 (2002) 1506–1508.
4. D. Arivuoli, F.D. Gnanam, P. Ramasamy, J. *Mater. Sci. Lett.* 7 (1998) 711–713.
5. D.D. Miller, A. Heller, *Nature* 262 (1976) 280–87.
6. P. Boudjouk,M.P. Remngton Jr., D.G. Grier, B.R. Jarabek, G.J. McCarthy, *Inorg. Chem*. 37 (1998) 3538–3541.
7. M. Salavati-Niasari, D. Ghanbari, M. R. Loghman-Estarki, *Polyhedron*., 35 (2012) 149-153.
8. M. Yousefi, M. Salavati-Niasari, F. Gholamian, D. Ghanbari, A. Aminifazl, *Inorg. ChimActa*., 371 (2011) 1-5.
9. H.F. Cheng, B.B. Huang, X.Y. Qin, X.Y. Zhang, Y. Dai, *Chem. Commun*. 48 (2012) 97–99.
10. X.Y. Yang, W.D. Xiang, H.J. Zhao, H.T. Liu, X.Y. Zhang, X.J. Liang, *J. Alloys Compd*. 509 (2011) 7283–7289.

11. L. Cademartiri, F. Scotognella, P.G. O'Brien, B.V. Lotsch, J. Thomson, S. Petrov,N.P. Kherani, G.A. Ozin, *Nano Lett*. 9 (2009) 1482–1486.
12. S.H. Pawar, P.N. Bhosale, M.D. Uplane, S. Tanhankar, *Thin Solid Films* 110 (1983) 165–170.
13. J. Grigas, E. Talik, V. Lazauskas, *Phys. Status Solid B.* 232 (2002) 220–230.
14. Z. Liu, J. Fang, W. Xu, X. Xu, S. Wu, X. Zhu, *Mater. Lett.* 88 (2012) 82–85.
15. C.J. Tang, G.Z. Wang, H.Q. Wang, Y.X. Zhang, G.H. Li, *Mater. Lett.* 62 (2008) 3663–3665.
16. L. Shi, D. Gu,W. Li, L. Han, H. Wei, B. Tu, RenchaoChe, *J Alloys Compd*. 509 (2011) 9382–9386.
17. Y. Jiang, Y.J. Zhu, Z.L. Xu, *Mater. Lett*. 60 (2006) 2294–2298.
18. A.R. Abbasi, A. Morsali, *Ultrason.Sonochem*. 17 (2010) 572–578.