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Hydrothermal Synthesis of Bi$_2$S$_3$ Nanostructures and ABS-Based Polymeric Nanocomposite

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Abstract

Bismuth sulfide nano-rods and nano-flowers were synthesized via a hydrothermal reaction at a relatively low temperature. Thioglycolic acid is used as sulfur source and capping agent simultaneously. Bi$_2$S$_3$ nanostructures were then added to acrylonitrile-butadiene-styrene (ABS) copolymer. The thermal stability behavior of ABS filled with bismuth sulfide nano-rods were investigated by thermogravimetric analysis (TGA). Nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The flame retardancy behavior of ABS-Bi$_2$S$_3$ was studied by UL-94 analysis.

1. Introduction

Hydrothermal is a unique method for fabricating nanostructures with specific and controlled morphologies. While predominant morphology in other methods like sol-gel, sonochemical and etc is nanoparticle. Hydrothermal method provides preferred orientation morphology. In hydrothermal method because of some particular conditions (high temperature and pressure) the nanoparticles grow in situ and form nanostructure shape. Nanoparticles have gained much attention in composite industries due to the fact that adding of a small amount of nanostructure to a composite can lead to a great improvement in physical and chemical properties of the composite. The key advantages of polymeric nanocomposites over many metallic alloys are low density, corrosion resistance and thermal insulation. However the polymeric compounds suffer from high flammability. Thus improving the thermal stability and flame retardancy of polymers is a major challenge for extending their applications. The most famous flame retardant (FR) additives for polymeric matrixes are halogen-containing, metal hydroxides, phosphorus-based compounds and layered silicates [1-4]. The higher level of flame retardancy of nanoparticles is due to their bigger surface to volume fractions which let them to

disperse into the polymeric matrix homogeneously, and hence leads to formation of a compact char during the combustion. ABS is widely used as an important engineering thermoplastic because of its desirable properties, which include suitable mechanical properties, chemical resistance and appropriate processing characteristics. ABS is composed of a styrene-acrylonitrile copolymer matrix phase, with grafted polybutadiene particles whose composition, it has a good balance among various physical properties such as processability of styrene, toughness and chemical resistance of acrylonitrile and impact resistance of butadiene [5–10]. However, this copolymer is flammable and is known as one of the most difficult polymers to flame retard. Nanocomposites are very attractive due to the fact that small amount of nanostructure can lead to great improvement in many properties, such as mechanical and thermal property [11-15]. We were interested in the synthesis of metal sulfide nanostructures using thioglycolic acid via hydrothermal method for a few years [16-18].

It is revealed that thioglycolic acid acts as the oriented growth reactant during above process. This synthesis is a mild, simple, practical, and environmental hydrothermal method.

V–VI compound semiconductor materials have drawn much attention because of their excellent properties such as photoconductivity, photosensitivity, infrared spectroscopy and thermoelectric [1]. Bi_2S_3, owing to its high figure of merit value, is widely used as a thermoelectronic-cooling material. It has a direct band gap material with Eg lying between 1.3 and 1.7 eV, which makes it useful in photodiode array and photovoltaic converters. It also has application in television cameras, optoelectronic devices and IR spectroscopy [1].

In this work we have used the thioglycolic acid assisted hydrothermal process to successfully synthesize Bi_2S_3 nanoparticles. Bi_2S_3 nanoparticles were then added to acrylonitrile-butadiene-styrene copolymer. The thermal stability and flame retardancy behavior of ABS filled with bismuth sulfide nano-rods were investigated by thermogravimetric analysis and UL-94 respectively.

2. Experimental
2.1. Materials and characterization
$Bi(NO_3)_3$ $5H_2O$ and thioglycolic acid (Tga) were purchased from Merck Company. All the chemicals were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered CuK_α radiation. A multi-wave ultrasonic generator (Bandeline MS 73) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. Scanning electron microscopy (SEM) images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation. In UL-94 a bar shape specimen of plastic $130 \times 13 \times 1.6$ mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each).

2.2. Synthesis of Bi_2S_3 nano-rods-nano-flower
In a typical synthesis, 0.001 mol of $Bi(NO_3)_3 \cdot 5H_2O$ powder is dissolved in 100 ml distilled water. 100 ml of 0.03M thioglycolic acid was added to the solution under stirring. After stirring, the reactants were put into a 250 ml capacity Teflon-lined

autoclave. The autoclave was maintained at 110-160 °C for 6 h and then cooled down to room temperature naturally. The product was centrifuged, washed with alcohol and distilled water for several times, and dried in oven at 50 ∘C for 10 h. A schematic diagram for experimental setup used for this hydrothermal reaction is given in Fig. 1.
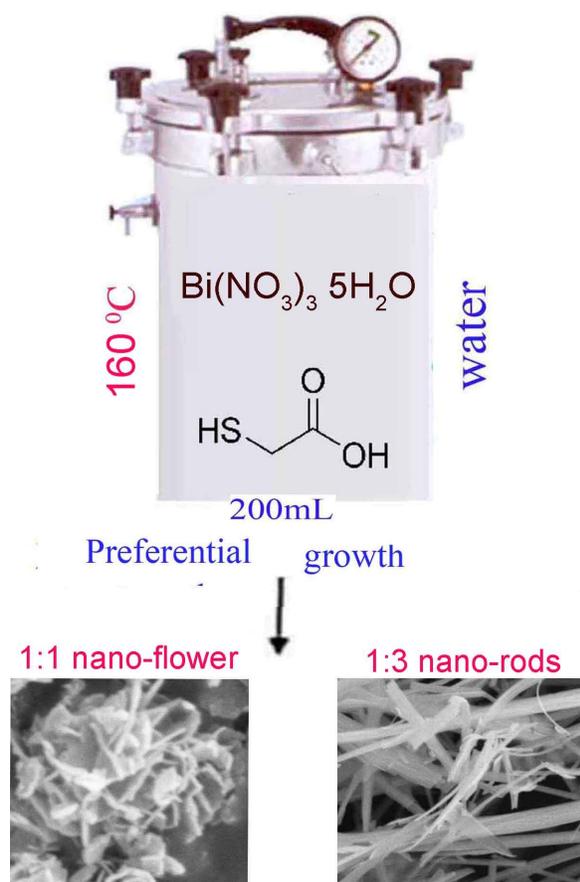
Fig. 1. Schematic diagram of Bi_2S_3 nanostructures preparation

2.3. Synthesis of ABS-Bi_2S_3 nanocomposite

4 g of ABS is dissolved in 15 ml dichloromethane solution. 1 g of Bi_2S_3 is dispersed in 10 ml dichloromethane solution with ultrasonic waves (30 min, 60W). The Bi_2S_3 dispersion is then slowly added to the polymer solution. The new solution is then mixed and stirred for 6 hours. In order to evaporate the solvent, the product is casted on a

piece of glass template and it is left for 24 hours (Fig 2).
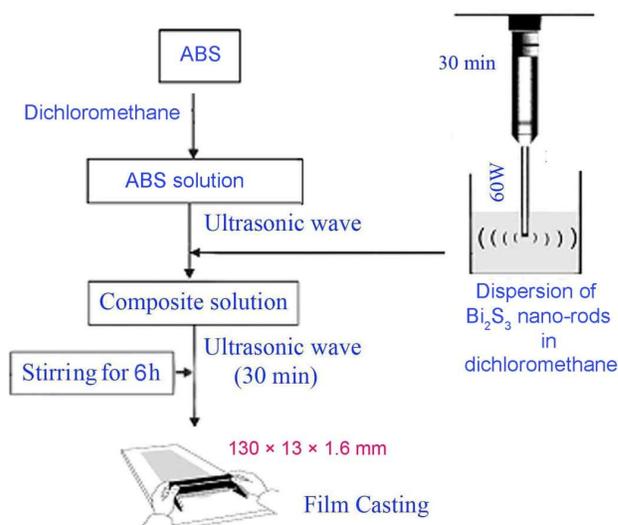
Fig. 2. Preparation of ABS-Bi_2S_3 nanocomposite

3. Results and discussion

The XRD pattern of nano-rods is shown in Fig. 3 and is indexed as a pure orthorhombic phase (space group: Pbnm). The experimental values are very close to the literature (JCPDS No. 17-0320). The crystallite size measurements were carried out using the Scherrer equation, $Dc=0.9\lambda/\beta\cos\theta$, (1); β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (CuK$_\alpha$ radiation, 0.154 nm). The estimated crystallite size is about 35 nm. Pattern of nanocomposite also confirms existence of Bi_2S_3 in the ABS matrix. Synthesis at 110 °C and ratio 1:3 was chosen as a basic reaction in our work, in this condition nano-rod was observed.

The effect of molar ratio of Bi^{3+} to thioglycolic acid (Tga) on shape and particle size is shown in Fig 4. At ratio Bi^{3+}:TGA (1:1) flower-like nanostructures were obtained that diameter of plates of flowers is lower than 30 nm.

The trick in hydrothermal synthesis of nano-rod or flower-like Bi_2S_3 nanocrystal presented here is the application of thioglycolic acid as a sulfur source and stability agents. Temperature effect was investigated by SEM image in Fig. 5.
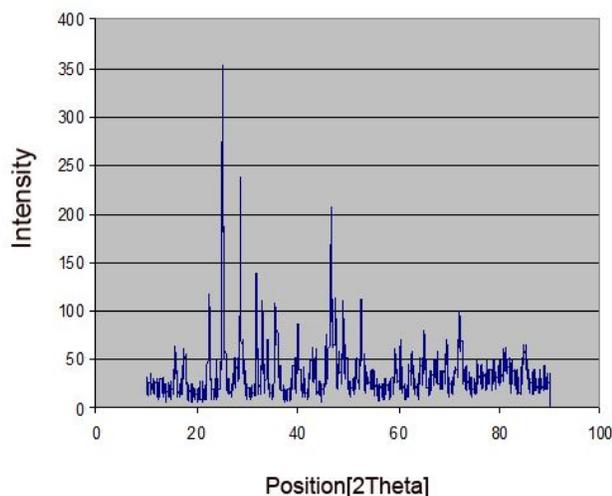
Fig. 3. XRD pattern of Bi_2S_3 nano-rods prepared at 160°C

At ratio Bi^{3+}:TGA 1:3 in 160° C nano-rods with average diameter less than 70 nm were synthesized. The influence of time on the morphology of the product is shown in Fig. 6 in two different magnifications. It seems by increasing time from 6h to 18 h growth stage overcome to nucleation stage and rods with bigger diameters were obtained and also length of nano-rods was decreased.

SEM image of surface of ABS-Bi_2S_3 nanocomposite is shown in Fig.7 that confirms presence and dispersion of nano-rods in the copolymer matrix. Pure polymer shows a flat surface under SEM images.

Topographic AFM plots of ABS and ABS-Bi_2S_3 are depicted in Fig. 8. Pure polymer shows smooth surfaces (Fig. 8a). Roughness in the surface of the nanocomposite approves the presence of the nano-rods in the copolymer (Fig. 8b).
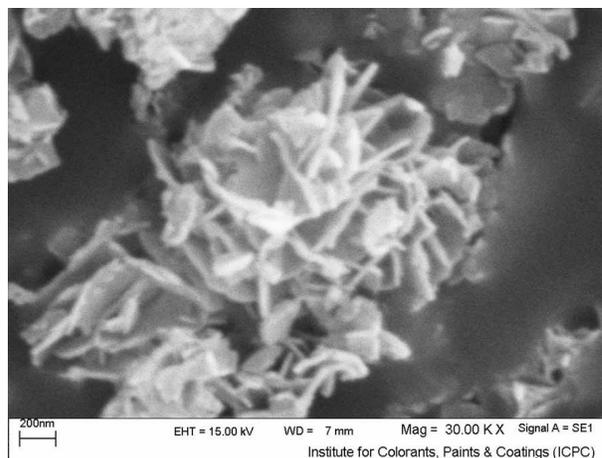
Fig. 4. SEM image of Bi_2S_3 nano-flower obtained at 110 $^\circ$C (ratio 1:1)
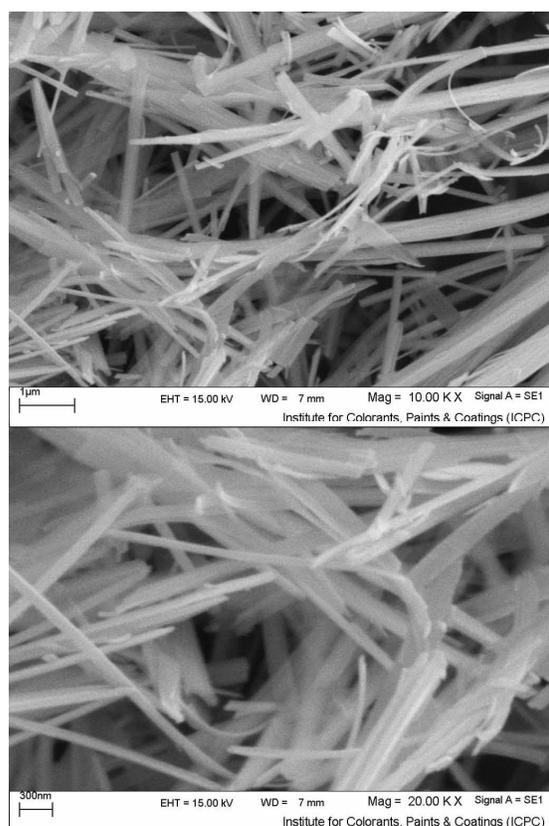
Fig. 5. SEM images of Bi_2S_3 nano-rods at 160 $^\circ$C (ratio:1:3)

Thermal gravimetric graphs of pure ABS and ABS-Bi_2S_3 nanocomposite are illustrated in Fig.9a and 9b respectively. Despite initial temperature of thermal decomposition (T_{onset}) of the ABS-Bi_2S_3 is decreased

but after 400°C, degradation of nanocomposite shifts towards higher temperature in the presence of Bi_2S_3 nanostructures.
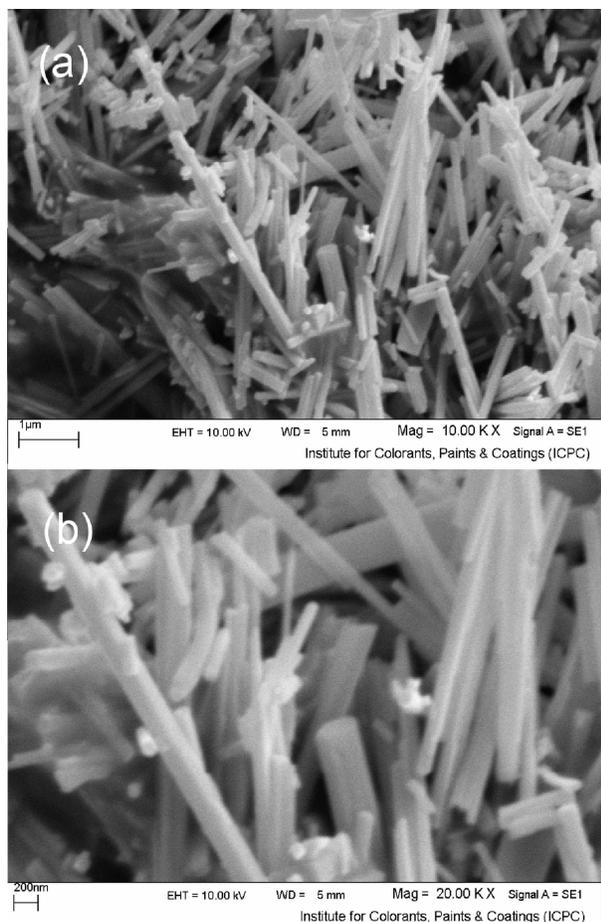
Fig. 6. SEM images of Bi_2S_3 nano-rods at 110°C (18h)
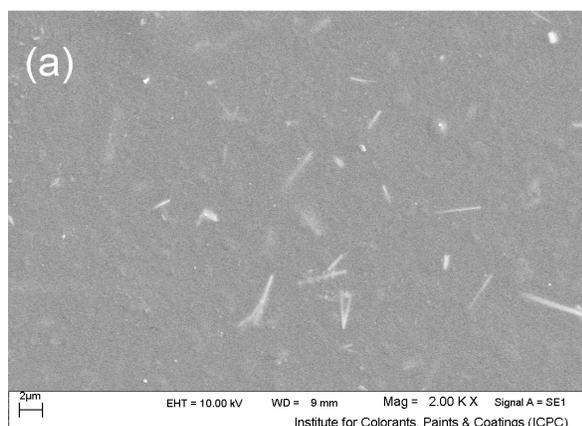
Fig. 7. SEM image of ABS-Bi_2S_3 nanocomposite

Bi_2S_3 has barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. So residual amount of nanocomposites is higher than pure polymer. It can be used as a char that prevent propagation of flame.
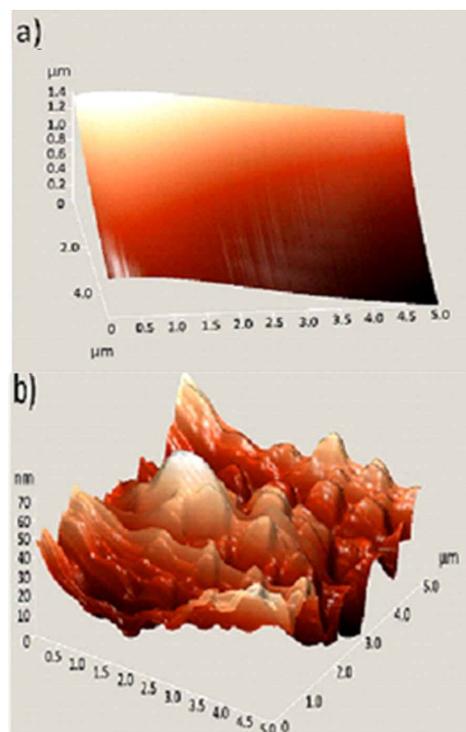
Fig. 8 AFM images of (a) pure ABS (b) ABS-Bi_2S_3 nanocomposite

The effect of Bi_2S_3 nanostructure on the flame retardant properties has been considered using UL-94 test. A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles are allowed as long as they are not inflamed. A V-1 classification is received by a sample with maximum combustion time lower than 30 s, drips of particles are allowed as long as they are not inflamed The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming d-
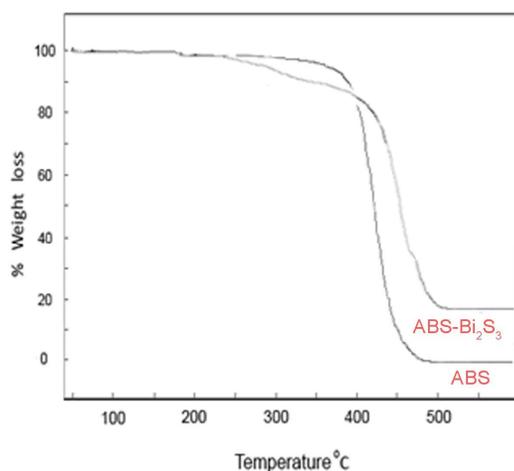
Fig. 9. TGA graphs of (a) pure ABS (b) ABS-Bi$_2$S$_3$ nanocomposite

rips are allowed [15]. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The results of UL-94 test for both ABS and ABS-Bi$_2$S$_3$ nanocomposites is N.C. The results show (according this test) that the Bi$_2$S$_3$ nanostructures cannot suitably enhance the flame retardant property of the ABS matrix.

4. Conclusion

Bismuth sulfide nanostructures were synthesized via a hydrothermal reaction between Bi(NO$_3$)$_3$.5H$_2$O and thioglycolic acid. The trick in hydrothermal synthesis of nano-rod or flower-like Bi$_2$S$_3$ nanocrystal presented here is the application of thioglycolic acid as a sulfur source and stability agents. Nano-rods were then appropriately were dispersed in ABS matrix. The influence of the inorganic phase on the thermal stability properties and flame retardancy of ABS matrix was studied.

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