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The effect of agitation states on hydrothermal synthesis of Bi_2S_3 nanorods

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Abstract

The effect of agitation states on the synthesis of Bi_2S_3 was discussed via stirred-assisted, oscillated-assisted and static hydrothermal preparation methods. Results showed that agitation influences the crystallinity and size of Bi_2S_3 nanorods. It is of interest that Bi_2S_3 nanorods with a high degree of crystallinity are obtained via stirred-assisted hydrothermal method at the temperature as low as 95°C.

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1. Introduction

Nanocrystalline materials display the unique properties when compared to the corresponding bulk phase. Group V–VI compounds have widely been studied because of their excellent properties like photoconductivity, photosensitivity, infra-red (IR) spectroscopy and thermoelectric effect [1–5]. Bi_2S_3, with a band gap Eg of 1.3 eV, is a direct band gap material [6,7] useful for photodiode arrays or photovoltaics [8–10].

Preparation method for Bi_2S_3 include: direct reaction of bismuth and sulfur vapor in a quartz vessel at high temperature [2,11]; thermal degradation of metal complexes with sulfur-containing ligands needing to be processed in a stream of H_2S or H_2/H_2S at high temperature [7,12–14]; single-source method using expansive precursor [15], solvothermal method needing organic solvent [16] and so on.

Hydrothermal synthesis methods are of particular interest for the preparation of nanocrystalline materials. This promising solution chemical method requires no organometallic or toxic precursors, and reactions may be carried out at comparatively low temperatures.

To our knowledge, many hydrothermal reactors are static. Lack of agitation may result in a narrower crystallization field [17], various structures [17–19], large colloid size distribution [17], different morphology of particles [20,21], and low crystallization rate and worse crystallization conditions [17,22]. Therefore, liquid solution syntheses

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of Bi_2S_3 often yield products that are mostly amorphous, poorly crystallized, or consisting of colloidal particles [23–25]. These shortcomings may be overcome by raising temperature [26]. In this study, agitation's effect on hydrothermal synthesis of Bi_2S_3 nanorods at lower temperature is examined and discussed.

2. Experimental procedure

Experiment details were as follows: 0.01 mol of analytically pure $BiCl_3$ (0.005 mol EDTA was added to prevent $BiCl_3$ from hydrolysis) and 0.015 mol Na_2S were dissolved in distilled water, respectively. Then solutions were mixed while stirring. The mixture was filled in a Teflon-lined autoclave of 50 ml capacity to 90% of the total volume.

There were three kinds of agitation conditions under which the hydrothermal process was operated: (a) using a motor-driven magnetic agitator (1 revolution per second); (b) using a horizontal oscillator (1 Hz, 25 mm Amplitude); (c) static state.

The autoclaves were maintained at 95°C for 12 h and then allowed to cool to room temperature. The precipitates were washed with distilled water. The products were dried in vacuum at 60°C for 1 h.

3. Results and discussion

Products were characterized by powder X-ray diffraction (XRD) patterns at a scanning rate of $0.02^\circ\,s^{-1}$ in the 2θ range from 10° to 70°, using a Rigaku (Japan) D/Max-γA X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54178$ Å).

The XRD patterns of three samples are shown in Fig. 1. All the intense peaks can be indexed to an orthorhombic lattice with cell constants $a = 11.15 \pm 0.01$ Å, $b = 11.32 \pm 0.01$ Å, and $c = 3.99 \pm 0.004$ Å, which are in agreement with the reported values $a = 11.149$ Å, $b = 11.304$ Å, $c = 3.981$ Å (JCPDS 17-320).

TEM images and ED patterns were taken with a Hitachi Model H-800 transmission electron microscope.

The TEM image, shown in Fig. 2a, shows nanorods obtained from the stirred-assisted hydrothermal method. Particles were uniform size with an average diameter of 43 nm. The ED pattern, shown in Fig. 3a, reveals that the nanorods obtained were single-crystalline.

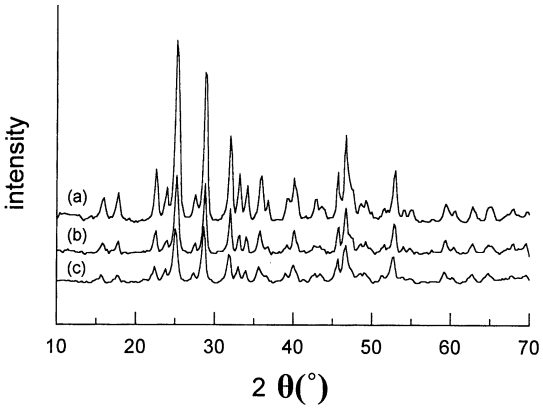

Fig. 1. XRD patterns of: (a) stirred-assisted hydrothermal method; (b) oscillated-assisted hydrothermal method; (c) static hydrothermal method.

The TEM image (Fig. 2b) and ED pattern (Fig. 3b) are of particles from the oscillated-assisted hydrothermal method. The nanorods, with average diameter of 28 nm, were not as uniform nor well crystallized as those from the stirred-assisted one. Some Bi_2S_3 nanocrystallites were fusiform.

There was a little coacervation in the sample produced using the static hydrothermal method. The average diameter was 25 nm according to the TEM image (Fig. 2c). The nanorods were polycrystalline according to the ED pattern (Fig. 3c).

The agitator in stirred-assisted method was installed inside, which supplied the system with more uniform distributions of temperature and concentrations than oscillated-assisted method did. And this is favorable for the formation of single-crystalline Bi_2S_3 nanorods.

4. Conclusion

In summary, we discussed the effect of agitation on hydrothermal synthesis of Bi_2S_3 nanorods via stirred-assisted, oscillated-assisted and static methods. The stirred-assisted method provided better condition for crystallization; the oscillated-assisted

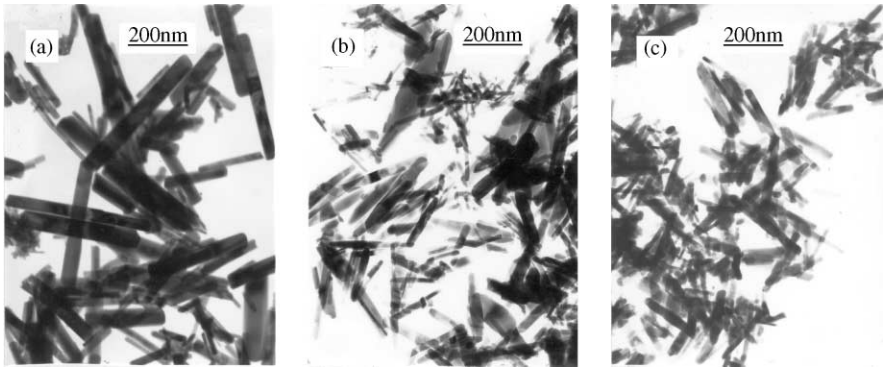

Fig. 2. TEM images of: (a) stirred-assisted hydrothermal method; (b) oscillated-assisted hydrothermal method; (c) static hydrothermal method.

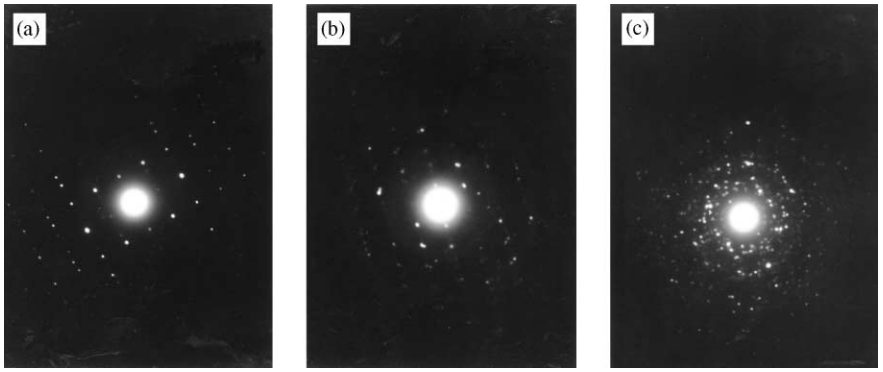

Fig. 3. ED patterns of: (a) stirred-assisted hydrothermal method; (b) oscillated-assisted hydrothermal method; (c) static hydrothermal method.

and static methods are inferior. Agitation had large effects on the size, and especially crystallinity of the resulting particles. The quality of the Bi_2S_3 nanorods could be controlled by the agitation condition during synthesis.

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