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Characterization of $AgBiS_2$ nanostructured flowers produced by solvothermal reaction

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ABSTRACT

$AgBiS_2$ nanostructured flowers were produced from CH_3COOAg, $Bi(NO_3)_3.5H_2O$ and thiosemicarbazide ($NH_2CSNHNH_2$) using different solvents [ethylene glycol (EG), water (H_2O), polyethylene glycol with molecular weight of 200 (PEG200), and propylene glycol (PG)] in Teflon-lined stainless steel autoclaves. The phase and purity were detected using X-ray diffraction (XRD), controlled by the solvents. The product was purified $AgBiS_2$ produced by the 200 °C and 24 h reaction in EG, corresponding to selected area electron diffraction (SAED) and simulation patterns. Scanning and transmission electron microscopies (SEM and TEM) revealed the formation of nanostructured flowers — enlarged by the increase in the lengths of time and temperature. Their photoluminescence (PL) emissions were detected at the same wavelength of 382 nm (3.24 eV), although they were produced under different conditions.

1. Introduction

Presently, energy saving is one of the top policies of humans in all parts of the world. Thus a number of scientists and engineers pay much attention on different processes for large scale productions. Solvothermal and hydrothermal reactions are very appropriate for such of these; especially, for materials with nanostructured flowers. $AgBiS_2$, one of the semiconducting ternary sulfides, has been very attractive, due to its linear and non-linear properties [1,2]. It has high potential to use as optoelectronic and thermoelectric devices, including optical recording media [1,2]. To the best of our knowledge, there are not many reports on the synthesis of $AgBiS_2$ with different morphologies. Among them are dendrites by microwave synthesis [1], nanorods and coral-shaped crystals by a polyol route [2,3], and flowers and hexapods by cyclic microwave-assisted synthesis [4]. For the present research, production of purified $AgBiS_2$ nanostructured flowers using the solvothermal process was studied and reported.

2. Experiment

To produce nanostructured $AgBiS_2$, 0.003 mol CH_3COOAg, 0.003 mol $Bi(NO_3)_3.5H_2O$ and 0.006 mol thiosemicarbazide ($NH_2CSNHNH_2$) were separately dissolved in different solvents [ethylene glycol (EG), water (H_2O), polyethylene glycol with molecular weight of 200 (PEG200), and propylene glycol (PG)]. The Ag^+ and Bi^{3+} solutions were mixed to form a mixture, to which the thiosemicarbazide solution was subsequently added. Volumes of each mixture were adjusted to be 50 ml, with 10 min stirring. The chemical reactions proceeded at 140–200 °C for 24–72 h, in tightly closed stainless steel autoclaves lined with Teflon. Finally, black precipitates were produced, separated by filtration, washed with de-ionized water and absolute ethanol, and dried at 70 °C for 24 h. The products were characterized to determine their phase(s), purity, morphologies and emissions.

3. Results and discussion

Fig. 1 shows XRD spectra of the products produced in the autoclaves under different conditions. At 200 °C for 24 h in different solvents (Fig. 1a), the products were specified as cubic $AgBiS_2$ (JCPDS no. 04-0699) [5] with some Bi_2S_3 (JCPDS no. 17-0320) [5] as the impurity — excluding that produced in EG. To save energy consumption, the solvothermal temperature was reduced in a series of steps from 200 °C to 140 °C. It was found that the XRD peaks (Fig. 1b) for the production in EG became broadened — the crystalline degrees of these pure products became lower. These products were no longer pure, when the temperature was lower than 180 °C — some Bi_2S_3 impurity was also detected. At 200 °C and longer time in EG, XRD spectra (Fig. 1c) of the products were very sharp. They are independent of the length of time. These imply that both the purity and degree of crystallinity remain unchanged.

SEM and TEM images (Figs. 2a–c, 3a and e) show nanostructured flowers of $AgBiS_2$ produced at different temperatures and lengths of time. They are totally different from the previous report [4]. Increasing in the temperatures and lengths of time has the influence to enlarge

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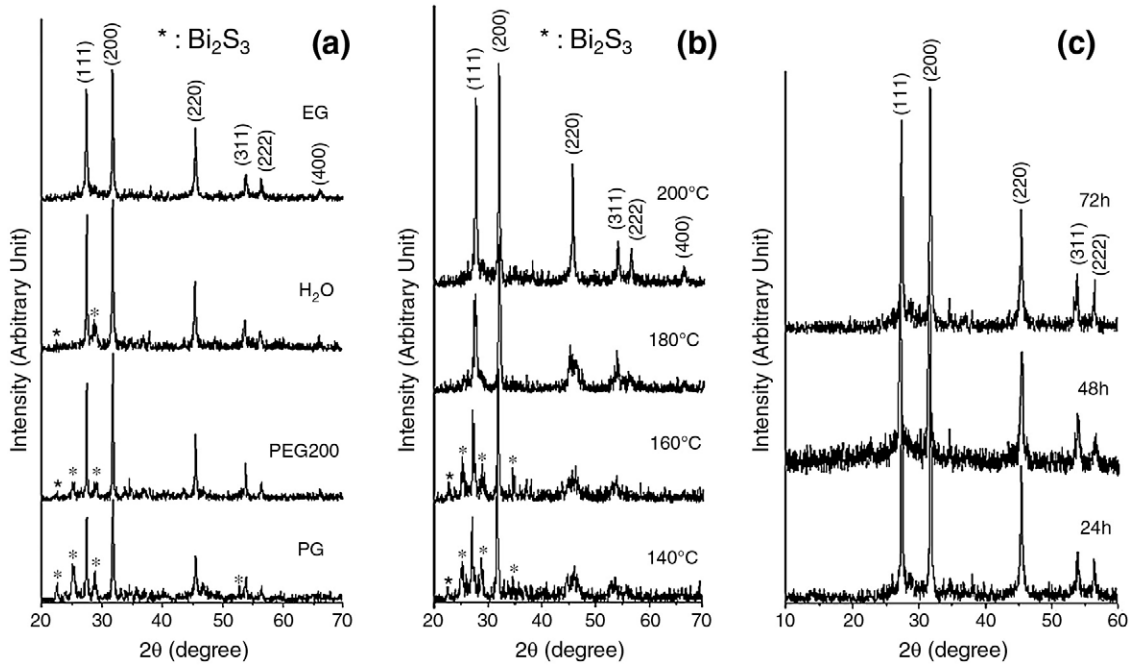

Fig. 1. XRD spectra of the products produced at (a) 200 °C for 24 h in different solvents, (b) different temperatures for 24 h in EG, and (c) 200 °C for different lengths of time in EG.

their sizes. Some petals not only became longer and larger, but also have branches. High magnification TEM image (Fig. 3c) of a petal produced at 200 °C for 24 h shows a number of parallel lattice planes with 3.19 Å apart, corresponding to the (111) crystallographic plane of the product. A SAED pattern (Fig. 3b) of the product with 200 °C and 24 h reaction composed of a number of bright spots, arranged in concentric circles. These circles are diffuse and hollow, implying that the product is poly-nanocrystals. Another SAED pattern (Fig. 3d), which is in good accordance with that of the simulation [6] — systematic and symmetric array of dark spots (Fig. 3f), appears as light spots of diffraction electrons from a single crystal with the [−112] direction as zone axis. They (Fig. 3b and d) were indexed [7] and specified as cubic $AgBiS_2$ (JCPDS no. 04-0699) [5].

To produce $AgBiS_2$, CH_3COOAg and $Bi(NO_3)_3.5H_2O$ in ethylene glycol (EG) were mixed to form a mixture, to which thiosemicarbazide ($NH_2CSNHNH_2$) in EG was subsequently added. At this stage, Ag^+

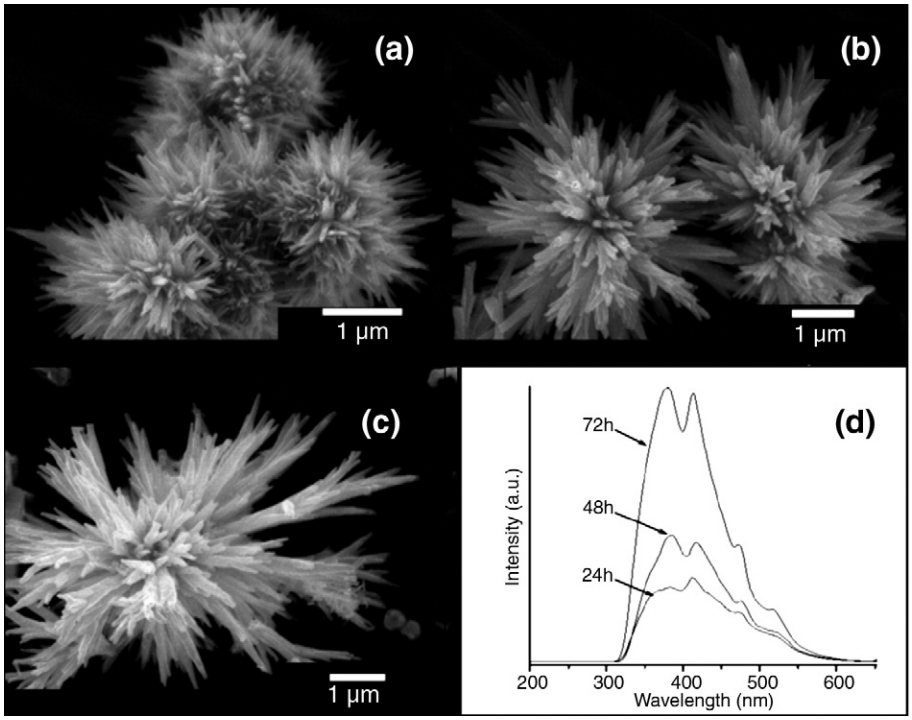

Fig. 2. SEM images of $AgBiS_2$ produced in EG at (a) 180 °C for 24 h, (b) 200 °C for 24 h, and (c) 200 °C for 48 h. (d) PL emissions of $AgBiS_2$ produced in EG at 200 °C for 24 h, 48 h and 72 h.