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Transformation of cubic $AgBiS_2$ from nanoparticles to nanostructured flowers by a microwave-refluxing method

Narongrit Tipcompor[a], Somchai Thongtem[b,c], Titipun Thongtem[a,c,*]

[a]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[b]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[c]Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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Abstract

Cubic $AgBiS_2$ nanoparticles and flower-like clusters were successfully synthesized by microwave refluxing of CH_3COOAg, $Bi(NO_3)_3 \cdot 5H_2O$ and thiosemicarbazide ($NH_2NHCSNH_2$) in ethylene glycol. The phase was detected by X-ray diffraction (XRD) and selected area electron diffraction (SAED). The SAED pattern was also in accordance with that of the simulation. Scanning and transmission electron microscopy (SEM and TEM) revealed the gradual transformation of nanoparticles into flower-like clusters by increasing microwave power. Their UV–visible absorption and photoluminescence (PL) emission were detected by spectrometry. Possible formation mechanism of nanoparticles and nanostructured flowers was also proposed according to the experimental results.

Keywords: B. Electron microscopy; B. Spectroscopy; B. X-ray methods; E. Functional applications

1. Introduction

At present, I–V–VI ternary chalcogenides are very attractive materials, especially silver bismuth sulfide ($AgBiS_2$). It is a promising candidate for use as novel semiconductors [1] and has high potential for use as optoelectric and thermoelectric devices including optical recording media [2].

Microwave refluxing is a distillation process by microwave radiation involving the condensation of vapors and the return of the condensate (liquid produced by condensation of steam) to the original system. This process is very simple, fast, effective and environmentally benign. It can solve the problems of temperature and concentration gradients, and provides uniform growth media. It has been developed and widely used in industrial and laboratory distillations [3].

The motivation of doing this research is to synthesize $AgBiS_2$ crystals the shape and size of nanoparticles and flower-like clusters by a microwave-assisted refluxing method. The success in this synthesis may lead to different applications in the near future.

2. Experiment

In this research, 1 mmol CH_3COOAg, 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 2 mmol thiosemicarbazide ($NH_2NHCSNH_2$) with 1:1:2 M ratio Ag:Bi:S were dissolved in 50 ml of different solvents—ethylene glycol (EG), propylene glycol (PG), ethylene diamine (ED) and water. Each 50 ml solution was refluxed by 100, 300, 600 and 800 W microwave radiation for 20, 40 and 60 min. Finally, black precipitates were synthesized, separated by filtration, washed with de-ionized water and ethanol, and dried at 70 °C for 12 h.

The products were then characterized by different methods: X-ray diffractometer (XRD, SIEMENS D500, Germany) operating at 20 kV, 15 mA, and using Cu-K_α line in combination with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) [4]; scanning electron microscope (SEM, JEOL JSM-6335F, Japan) operating at 15 kV; transmission electron microscope (TEM, JEOL JEM-2010, Japan) and selected area electron diffractometer (SAED) operating at 200 kV; UV–visible spectrometer (Lambda 25

*Corresponding author at: Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel.: +66 0 53 943344; fax: +66 0 53 892277.
E-mail address: ttpthongtem@yahoo.com (T. Thongtem).

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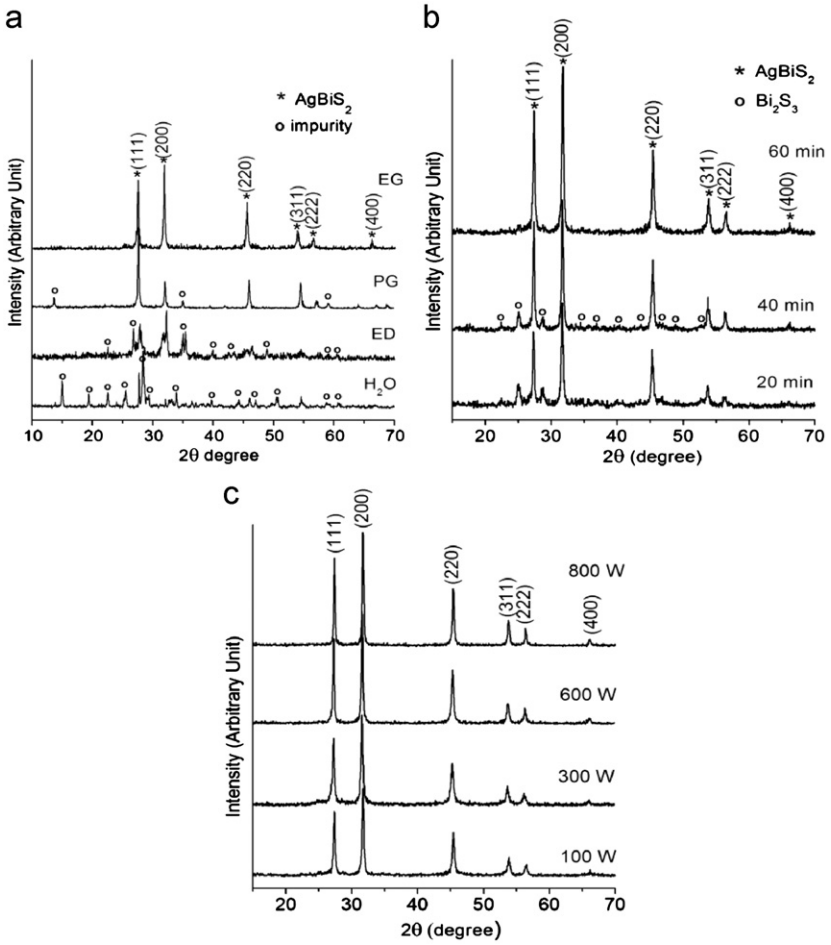

Fig. 1. XRD patterns of $AgBiS_2$ synthesized by a microwave-assisted refluxing method in (a) different solvents at 800 W microwave for 60 min, (b) EG at 800 W microwave for different lengths of time and (c) EG at different heating powers for 60 min.

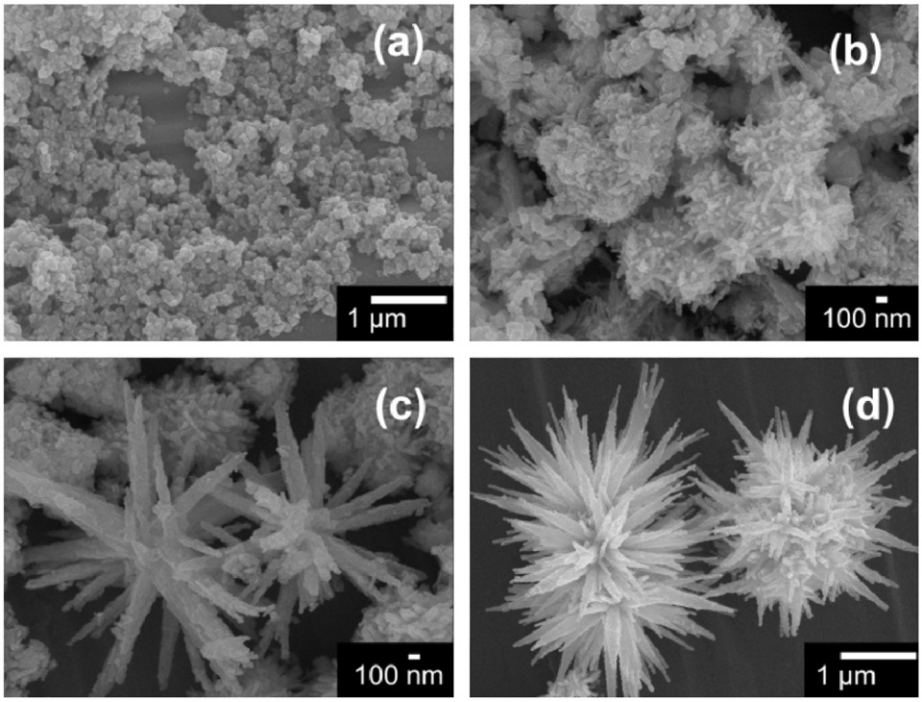

Fig. 2. SEM images of $AgBiS_2$ synthesized by (a–d) 100, 300, 600 and 800 W microwave refluxing method in EG for 60 min, respectively.

PerkinElmer, U.S.A.) using a UV lamp with the resolution of 1 nm; and photoluminescence (PL) spectrometer (LS 50B PerkinElmer, U.S.A.) using a 300 nm excitation wavelength at room temperature.

3. Results and discussion

3.1. XRD

XRD patterns (Fig. 1a) of the products synthesized by 800 W microwave refluxing of the starting agents dissolved in different solvents for 60 min. They were indexed and specified as cubic $AgBiS_2$ (JCPDS no. 04-0699) [4] without impurity detection only in the EG. Upon reducing the lengths of microwave refluxing time from 60 min to 40 and 20 min (Fig. 1b), the chemical reaction became incomplete and some Bi_2S_3 (JCPDS no. 06-0333) [4] residue was also detected.

To save the consumption of energy, the refluxing power of microwave was gradually reduced step by step from 800 W to 600, 300 and 100 W (Fig. 1c). The product was the still pure $AgBiS_2$ phase but the crystalline degree was lessened.

3.2. Electron microscopy

The as-synthesized products with different morphologies were characterized by SEM and TEM. At 100 W (Figs. 2a and 3a), the product was composed of a number of nanoparticles oriented in different directions. They are crystals with facets and angles. Their size distribution (Fig. 3c) is in the 30–100 nm range, with the average of 58.14 ± 11.87 nm. By increasing the refluxing power of the microwave, the products (Figs. 2b–d and 4a and b) gradually transformed into flower-like clusters at 800 W. SAED patterns of nanoparticles (Fig. 3b) and a petal of the flower-like cluster (Fig. 4c) were both indexed to correspond with polycrystalline and single crystalline $AgBiS_2$ [5], respectively. The interpreted pattern was also in accordance with that obtained by simulation (Fig. 4d).

3.3. Proposed mechanism

To synthesize $AgBiS_2$ by a microwave-assisted refluxing method, CH_3COOAg, $Bi(NO_3)_3 \cdot 5H_2O$ and thiosemicarbazide (TS) were dissolved in ethylene glycol (EG). Ag^+ and Bi^{3+} ions formed complexes with thiosemicarbazide during stirring. At this stage, free ions of Ag^+, Bi^{3+} and S^{2-} were very low. Thus, Ag_2S and Bi_2S_3 formations were prohibited.

During the microwave refluxing, the complexes were decomposed to synthesize $(AgBiS_2)_n$ nuclei. The decomposition proceeded with rather slow rates. Their concentration was lower than that obtained by the direct ion-exchange

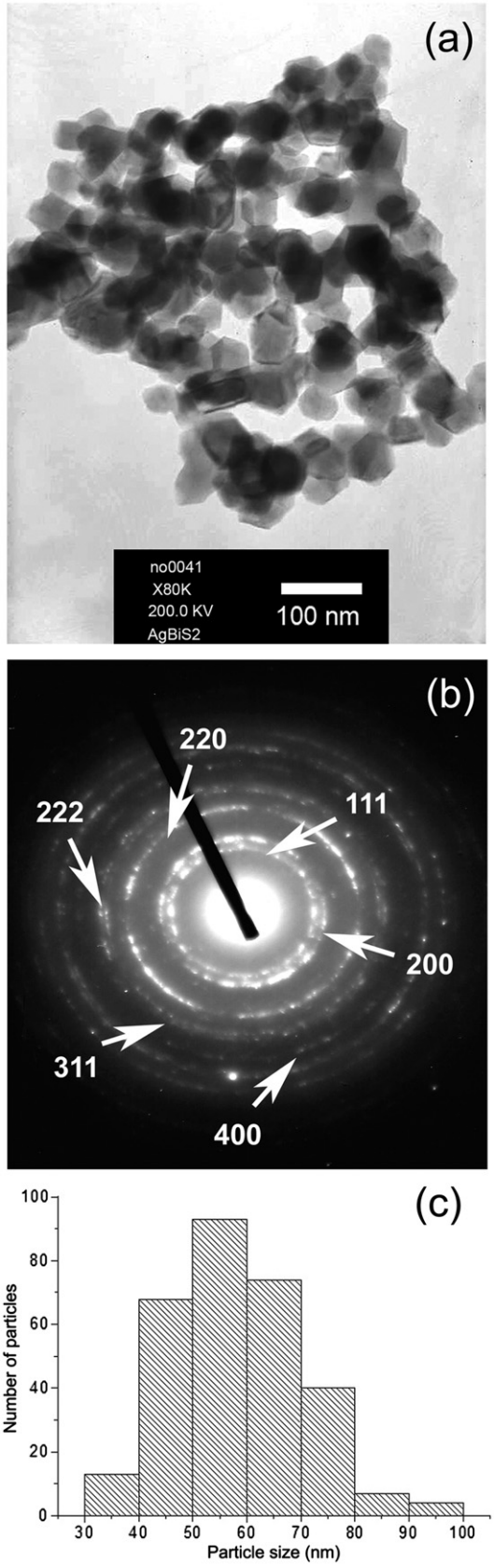

Fig. 3. (a) TEM image, (b) SAED pattern and (c) size distribution of $AgBiS_2$ nanoparticles synthesized by 100 W microwave refluxing method in EG for 60 min.

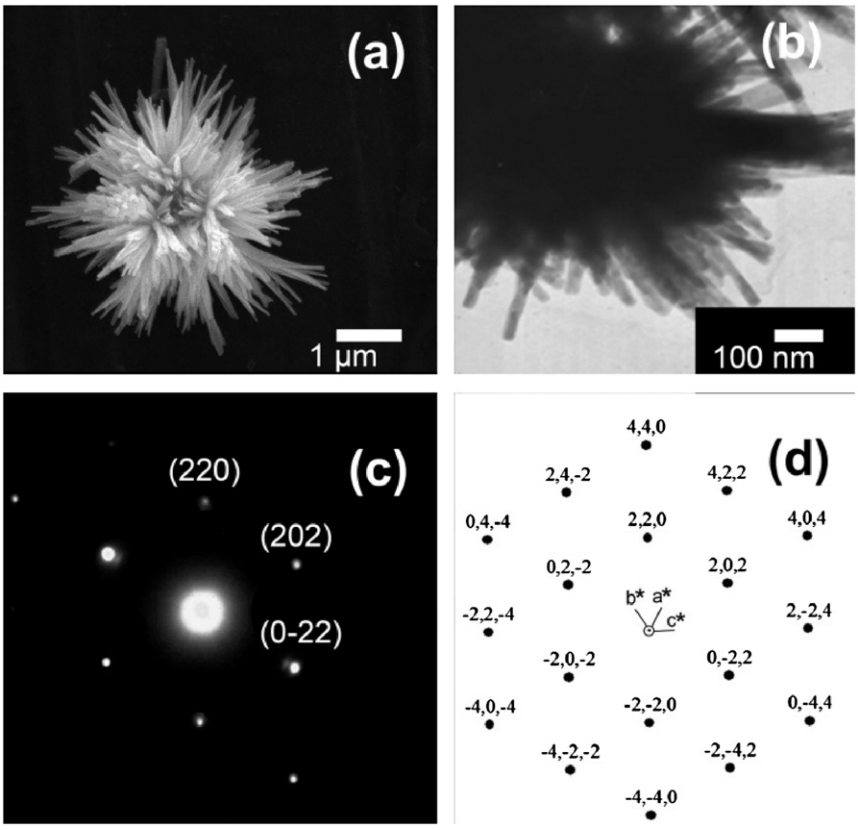

Fig. 4. (a, b) TEM images, (c) SAED pattern of a petal of $AgBiS_2$ flower synthesized by 800 W microwave refluxing method in EG for 60 min, and (d) its simulated pattern.

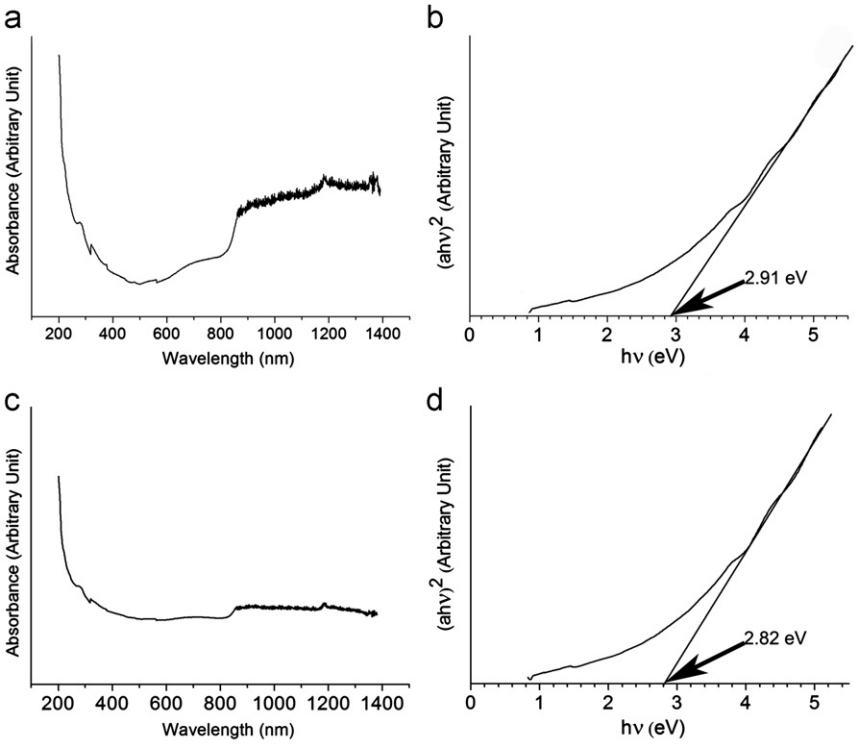

Fig. 5. UV–visible absorption and the $(\alpha h\nu)^2$ and $h\nu$ plots of $AgBiS_2$ (a, b) nanoparticles, and (c, d) flower-like clusters.

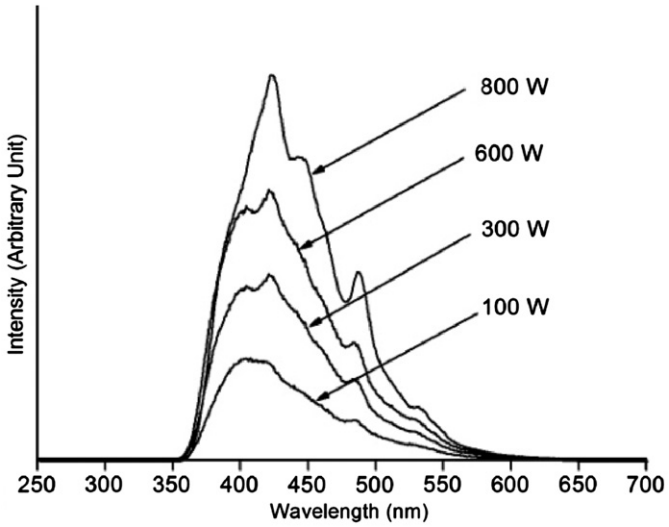

Fig. 6. PL emissions of $AgBiS_2$ synthesized by 100, 300, 600 and 800 W microwave refluxing in EG for 60 min.

reaction. Finally, $AgBiS_2$ nuclei were synthesized in EG by the microwave-assisted refluxing method.

$$Ag^+ + Bi^{3+} + TS \rightarrow Ag\text{–}Bi\text{–}TS \text{ complexes} \quad (1)$$

$$Ag\text{–}Bi\text{–}TS \text{ complexes} \rightarrow (AgBiS_2)_n \quad (2)$$

$$(AgBiS_2)_n \rightarrow n(AgBiS_2) \quad (3)$$

Alternately, Ag–TS and Bi–TS complexes could form and were decomposed to synthesize $AgBiS_2$ nuclei.

$$Ag^+ + TS \rightarrow Ag\text{–}TS \text{ complexes} \quad (4)$$

$$Bi^{3+} + TS \rightarrow Bi\text{–}TS \text{ complexes} \quad (5)$$

$$Ag\text{–}TS \text{ complexes} + Bi\text{–}TS \text{ complexes} \rightarrow n(AgBiS_2) \quad (6)$$

Due to the 100 W microwave refluxing, $AgBiS_2$ nanoparticles were synthesized by the orientation growth process. At higher refluxing power, the atoms were vibrated violently by a very strong force. Thus the nanoparticles gradually transformed into flower-like clusters at 800 W. In this research, the microwave refluxing played a key role in the decomposition of the complexes, formation of $(AgBiS_2)_n$ nuclei (nucleation), and the oriented growth of $AgBiS_2$ crystals [1,2].

3.4. Absorption and emission

UV–visible absorption (Fig. 5) of the as-synthesized nanoparticles and flower-like clusters indicated an exponential decreasing of optical absorption attenuated through the $AgBiS_2$ solids. Their allowed direct energy gaps were determined, by extrapolating linear portions of the curves to zero absorption, to be 2.91 eV for nanoparticles and 2.82 eV for flower-like clusters—in accordance with 2.88 eV of thin film reported by Ibrahim and Soliman [6].

PL emissions of different products (Fig. 6) were characterized using 300 nm excitation wavelength at room temperature. Their emission peaks were detected at the same wavelengths of 422.5 nm (2.93 eV) with two shoulders at 444.5 nm and 486.0 nm. The main emission peaks were specified as the recombination of electrons and holes in trapped surface states residing in the forbidden region [7,8]. But for the shoulders, they were caused by the shallow levels of donors and acceptors between the valence and conduction bands [9]. The present result corresponded to the 435 nm (2.85 eV) of $AgBiS_2$ nanostructured flowers and hexapod [10].

4. Conclusions

Pure cubic $AgBiS_2$ crystals the shape and size of nanoparticles and flower-like clusters were successfully synthesized by 100 W and 800 W microwave refluxing in ethylene glycol for 60 min. The phase was detected by XRD and SAED. SEM and TEM revealed the transformation of the as-synthesized nanoparticles at 100 W into flower-like clusters at 800 W. Their allowed direct energy gaps were determined to be 2.91 eV for nanoparticles and 2.82 eV for flower-like clusters, including their PL emission wavelengths were 422.5 nm.

Acknowledgments

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