

## Research Article

# Characterization of Cubic AgSbS<sub>2</sub> Nanostructured Flowers Synthesized by Microwave-Assisted Refluxing Method

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Cubic AgSbS<sub>2</sub> nanostructured flowers of nanorods were successfully synthesized by microwave-assisted refluxing of AgNO<sub>3</sub>, Sb(CH<sub>3</sub>COO)<sub>3</sub>, and L-cysteine (C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>S) dissolved in ethylene glycol at the pH of 4, characterized by X-ray diffraction (XRD) and electron microscopy (EM). The 1.89 eV direct energy gap was determined by UV-visible absorption, including two 688 and 857 nm emission wavelengths by photoluminescence (PL) spectroscopy. A possible formation mechanism of AgSbS<sub>2</sub> nanostructured flowers was also proposed according to the experimental results.

## 1. Introduction

Presently, silver antimony sulfide (AgSbS<sub>2</sub>) is a very attractive material, due to its promising candidate for a number of applications: active recording films, micromechanical and optical memories, electrical switching and transmission in midinfrared [1–4]. AgSbS<sub>2</sub> crystallizes as two main crystal systems: monoclinic and cubic [5].

Microwave-assisted refluxing is a distillation process of which the system is heated by a microwave radiation. It involves the condensation of vapors and the return of this condensate to its original. It has been developed and widely used in industrial and laboratory distillations [6]. This process is very fast, simple, effective, and environmentally friendly. It can solve the problems of temperature and concentration gradients and provides uniform growth media.

To the best of our knowledge, there are not many reports on the synthesis of AgSbS<sub>2</sub>: amorphous AgSbS<sub>2</sub> thin films by pulsed laser deposition [1], ternary AgSbS<sub>2</sub> thin films by direct fusion process [4], and Ag(As<sub>x</sub>Sb<sub>1-x</sub>)S<sub>2</sub> with  $x = 0-1$  by solid state heating process [7]. Our motivation is to synthesize cubic AgSbS<sub>2</sub> nanostructured flowers of nanorods

by microwave-assisted refluxing method. No one has ever succeeded in synthesizing them by a solution method.

## 2. Experimental Procedures

To synthesize AgSbS<sub>2</sub>, 1 mmol AgNO<sub>3</sub>, 1 mmol Sb(CH<sub>3</sub>COO)<sub>3</sub>, and 2 mmol L-cysteine (C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>S, LC) (1:1:2 molar ratio Ag:Sb:S) were dissolved in 50 mL ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, EG) and followed by pH adjusting to 0, 1, 2, 3, 4, 5, and 6 using HCl and NaOH. These solutions were processed by refluxing method irradiated with a 300 W microwave radiation for 10, 30, and 60 min. Finally, black precipitates were synthesized, separated by filtration, washed with deionized water and ethanol, and dried at 70°C for 12 h, for further characterization.

Crystalline phases of the as-synthesized nanostructured products were analyzed by an X-ray diffractometer (XRD, Philips X'Pert MPD) operating at 20 kV 15 mA and using Cu-K<sub>α</sub> line in  $2\theta = 10-80$  deg. An XRD pattern was also simulated in order to show the real existence of cubic AgSbS<sub>2</sub> phase in this research. The morphology investigation was carried out by a field emission scanning electron microscope

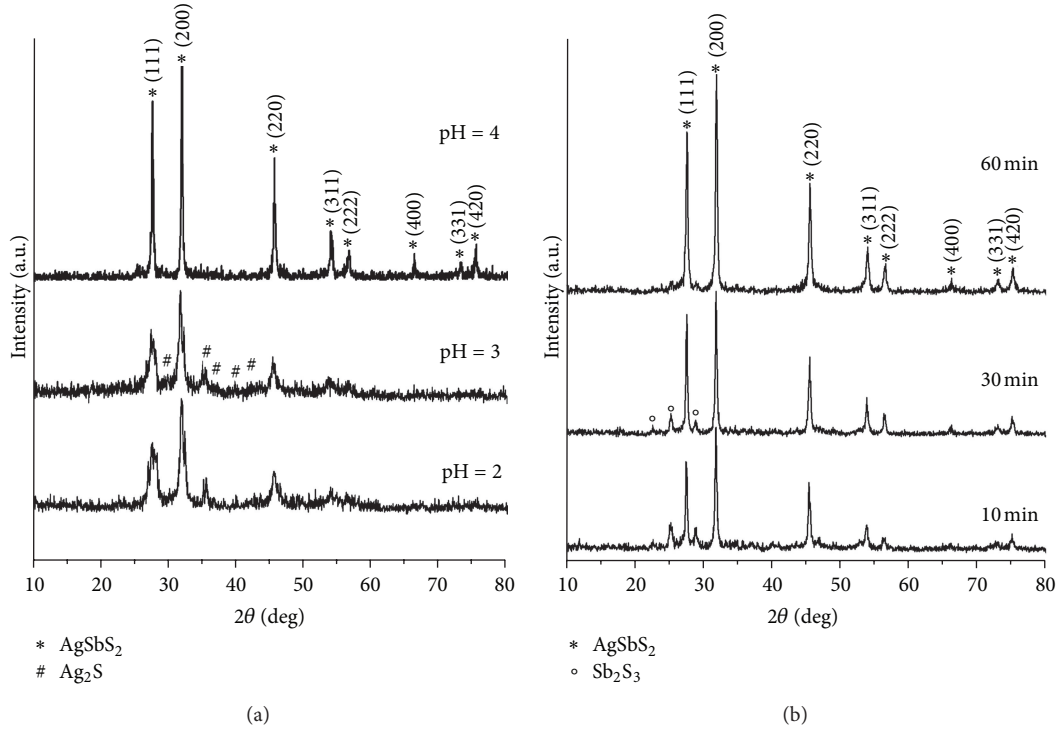


FIGURE 1: XRD patterns of cubic  $\text{AgSbS}_2$  synthesized in the solutions (a) with the pH 4, 3, and 2 for 60 min and (b) with the pH 4 for 60, 30, and 10 min.

(FE-SEM, JEOL JSM-6335F) operating at 35 kV and a transmission electron microscope (TEM, JEOL JEM-2010), high-resolution transmission electron microscope (HRTEM), and selected area electron diffractometer (SAED) operating at 200 kV. Their optical properties were studied by a UV-visible spectrometer (Lambda 25 PerkinElmer) using a UV lamp with the resolution of 1 nm and a fluorescence spectrophotometer (LS50B PerkinElmer) using 300 nm excitation wavelength at room temperature.

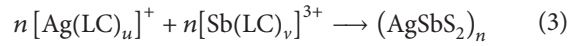
### 3. Results and Discussion

At the pH 6 and 5, different phases were detected in the products. Upon further decreasing in the pH to 4, cubic  $\text{AgSbS}_2$  (JCPDS number 17-0456) [5] was synthesized as the main product (Figure 1(a)). It was the only one cubic crystal system of the  $\text{AgSbS}_2$  phase [5] with no impurity detection. At the pH 3, 2, 1, and 0, the patterns were specified as cubic  $\text{AgSbS}_2$  mixed with  $\text{Ag}_2\text{S}$  (JCPDS number 09-0422) [5] impurities.

In the solution containing  $\text{Ag}^+$ ,  $\text{Sb}^{3+}$ , and L-cysteine ( $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ , LC) at the pH 6 and 5 (very close to the isoelectric point of LC), the solubility of LC was the lowest. The molecules often precipitated out of the solution [6] with the formation of different phases. At the pH 4, the  $\text{H}^+$  ions formed bonds with oxygen ions of carboxylate groups, leaving sulfur ions of L-cysteine (LC) to form complex ions with  $\text{Ag}^+$  and  $\text{Sb}^{3+}$  ions [8] at room temperature:



During microwave refluxing, these complex ions were decomposed with the formation of  $(\text{AgSbS}_2)_n$ :



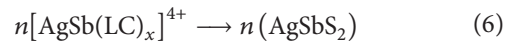
Due to their stabilities, the decomposition proceeded with rather slow rates. The concentration of  $(\text{AgSbS}_2)_n$  was lower than that synthesized by the direct ion-exchange reaction. Finally,  $\text{AgSbS}_2$  was synthesized [9, 10]:



Alternately,  $\text{Ag}^+$  and  $\text{Sb}^{3+}$  formed complex ions with LC at room temperature:



Then the complex ions were decomposed by microwave refluxing to synthesize  $\text{AgSbS}_2$ :



At the pH 3, 2, 1, and 0, additional impurities were synthesized. At high acidic solutions,  $\text{H}^+$  ions have much chance to form bonds with LC, leaving  $\text{Ag}^+$  as free ions. During refluxing,  $\text{S}^{2-}$  ions were released from the LC and further reacted with  $\text{Ag}^+$  ions to synthesize  $\text{Ag}_2\text{S}$  precipitates.

By reducing the refluxing time of the solution with the pH 4 from 60 min to 30 min and 10 min (Figure 1(b)),  $\text{Sb}_2\text{S}_3$  (JCPDS number 02-0374) [5] precipitates were also detected caused by incomplete reaction.

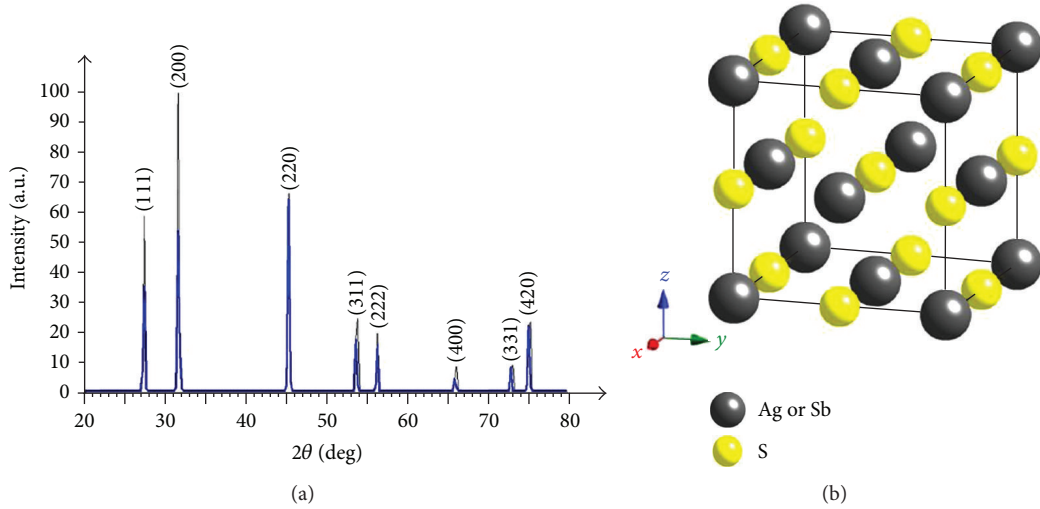


FIGURE 2: (a) XRD pattern and (b) unit cell of cubic  $\text{AgSbS}_2$  obtained by simulation.

TABLE 1: Intensities and  $2\theta$  Bragg's angles for different crystallographic planes of simulated, JCPDS database and experimental XRD peaks of cubic  $\text{AgSbS}_2$ .

Plane	Simulation		JCPDS number 17-0456 [5]		Experiment	
	$2\theta$ (deg)	Intensity (%)	$2\theta$ (deg)	Intensity (%)	$2\theta$ (deg)	Intensity (%)
(111)	27.3	59.0	27.3	65.0	27.4	82.2
(200)	31.6	100.0	31.6	100.0	31.7	100.0
(220)	45.3	66.6	45.4	40.0	45.4	56.2
(311)	53.7	25.3	53.8	20.0	53.7	22.6
(222)	56.3	21.3	56.3	16.0	56.4	13.7
(400)	66.1	9.1	66.1	8.0	66.2	12.3
(331)	72.9	8.7	72.9	6.0	72.9	8.2
(420)	75.1	23.5	75.1	8.0	75.1	16.4

In order to show the real existence of cubic  $\text{AgSbS}_2$  phase, its XRD pattern was simulated [11] and shown in Figure 2(a). The  $2\theta$  Bragg angles and peak intensities of the simulation, JCPDS database and experiment were summarized in Table 1. In this research, the experimental peaks were in good accordance with those of the simulation and the JCPDS database, including the intensities of the peaks that were controlled by different growth rates in different directions of unit cells. Simulated crystal structure [12] of  $\text{AgSbS}_2$  is also shown in Figure 2(b). Its unit cell was cubic structure with Ag or Sb coordinates at  $(0, 0, 0)$  and S at  $(1/2, 1/2, 1/2)$ , and vice versa. For each of  $\text{AgSbS}_2$  unit cell, Ag or Sb atoms are located at each of the corners and the centers of all the cube faces, including S atoms located in between them. Ag and Sb atoms have the same probability to reside in any of the crystal lattice, and they both have the same occupancy as S atoms in the unit cell.

SEM and TEM images (Figures 3 and 4(a)) show nanostructured  $\text{AgSbS}_2$  synthesized in the solutions with different pH values. At the pH 0, the product was composed of a number of nanoparticles oriented in different directions. Upon increasing of the pH from 0 to different values, they gradually transformed into different morphologies: clusters of nanoparticles (pH 1), mixed nanoparticles and incomplete

nanostructured flowers (pH 2), incomplete nanostructured flowers (pH 3), nanostructured flowers of nanorods grown out of cores (pH 4), and facet irregular microparticles with different orientations (pH 6). These products have different morphologies, controlled by the nucleation and growth processes. At the pH 4 and 60 min, nanorods of flower-like clusters were characterized by HRTEM (Figures 4(b) and 4(c)). The nanorods appeared as rough surfaces with the detection of the (111) and (200) crystallographic planes at an angle of 54.7 degree, specified as single crystal.

To synthesize nanostructured flowers,  $\text{AgSbS}_2$  molecules nucleated, followed by clustering of nuclei to form  $\text{AgSbS}_2$  cores. A number of nanorods grew out of these cores to form  $\text{AgSbS}_2$  flower-like clusters of nanorods (Figure 5). Due to the microwave-assisted refluxing process, the flower-like clusters were synthesized by the orientation growth, promoted by microwave refluxing. The atoms had more chance to arrange themselves in crystal lattice to form nanocrystalline flowers of nanorods. For the present research, microwave refluxing played a key role in the growth of flower-like crystals: decomposition of the complex ions, formation of  $(\text{AgSbS}_2)_n$  nuclei, and orientation growth of  $\text{AgSbS}_2$  crystals in the shape of flower-like clusters [9, 10].

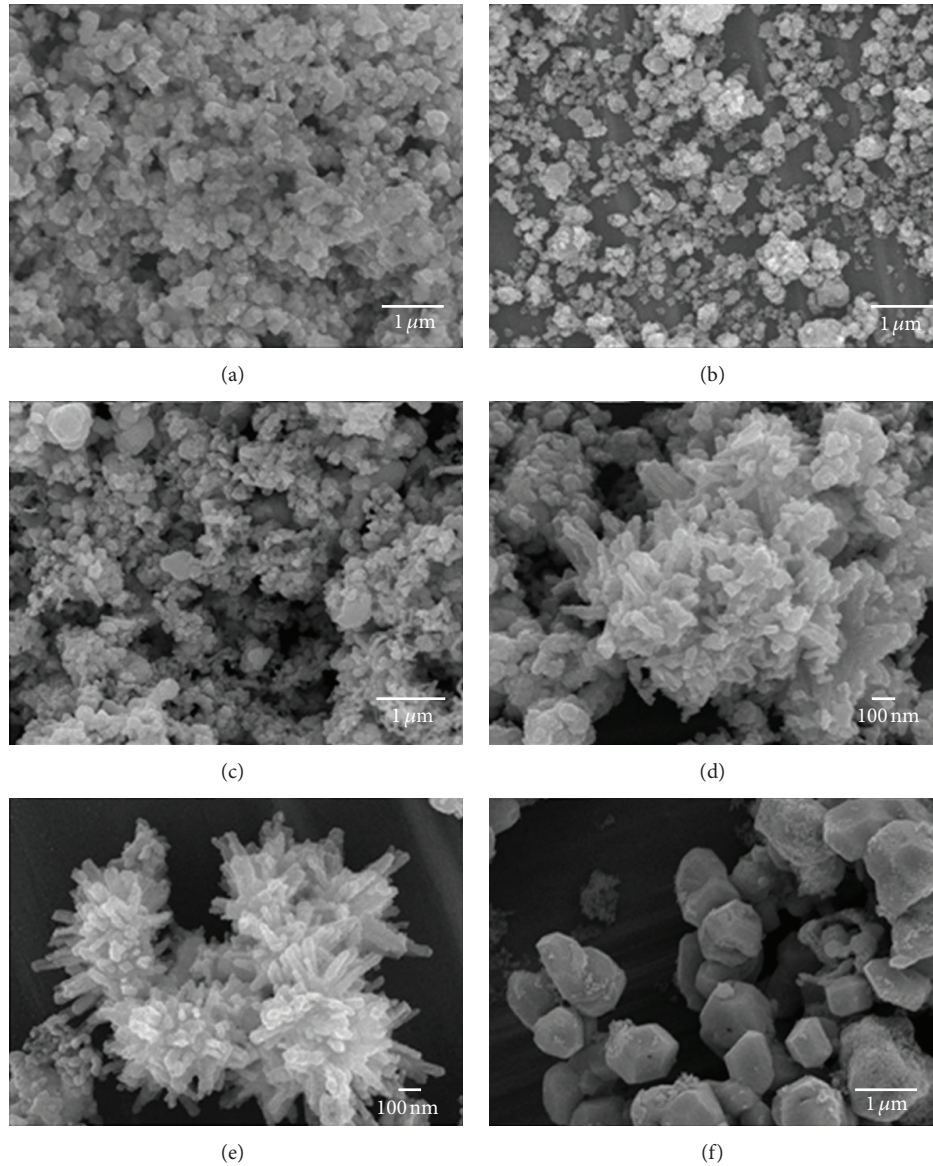


FIGURE 3: SEM images of the products synthesized in the solutions with the pH of ((a)–(f)) 0, 1, 2, 3, 4, and 6 for 60 min, respectively.

The SAED pattern (Figure 4(d)) appears as systematic spots corresponding to the (200), (202), and (002) crystallographic planes of a single crystalline nanorod of cubic  $\text{AgSbS}_2$  (JCPDS number 17-0456) [5], with the [0–10] as zone axis. A simulated electron diffraction pattern (Figure 4(e)) [13] was in accordance with that obtained by the experiment, indicating that the interpreted pattern could exist in reality.

Figure 6(a) shows the photonic absorbance attenuating through  $\text{AgSbS}_2$  nanostructured flowers of nanorods. It should be noted that the absorption was controlled by two photon energy ( $h\nu$ ) ranges, the high and low energies. When photon energy is greater than the energy band gap ( $E_g$ ), the absorption is linearly increased with the increase in the photon energy. The steep inclination of the linear portion of the curve was caused by the UV absorption for charged transition from the topmost occupied state of valence band

to the bottommost unoccupied state of the conduction band. For the photon energy with less than  $E_g$ , the absorption curve was different from linearity, caused by the UV absorption for charged transition relating to defects. By extrapolating the linear portion curve of the  $(\alpha h\nu)^2$  versus  $h\nu$  plot to zero absorption ( $\alpha = 0$ ), the direct energy gap ( $E_g$ ) was determined to be 1.89 eV, very close to the 1.77–2 eV energy gap of  $\text{AgSbS}_2$  thin films reported by Ibrahim [4].

Photoluminescence (PL) of  $\text{AgSbS}_2$  nanostructured flowers (Figure 6(b)) was excited by 300 nm wavelength at room temperature. The emission was detected at 688 nm (1.8 eV) as main peak, including the minor peak at 857 nm, very close to the optical transmission of  $\text{AgSbS}_2$  thin films for optical recording media reported by Wagner et al. [1]. The main emission peak was specified as the recombination of electrons and holes in trapped surface states residing in the forbidden

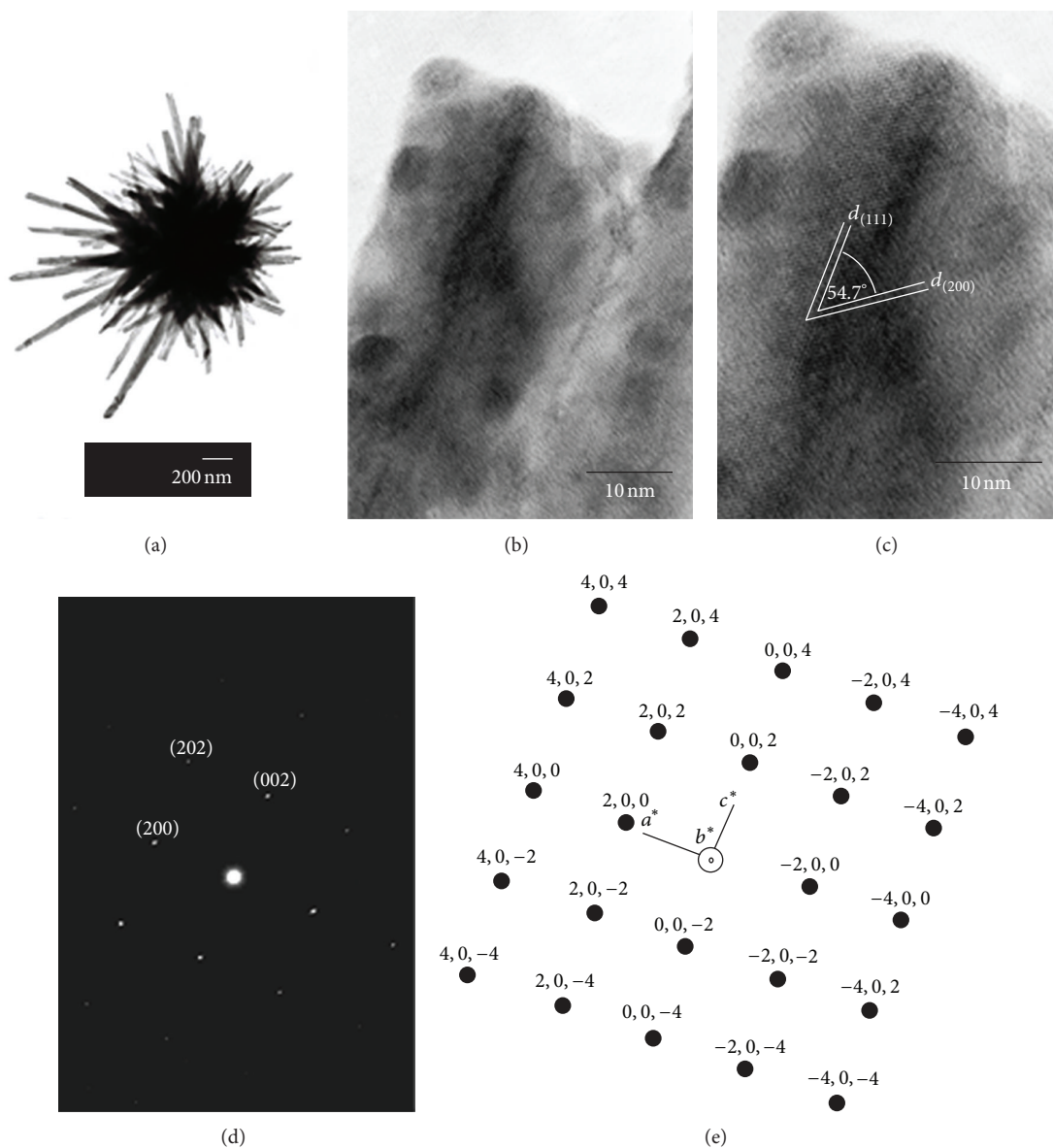


FIGURE 4: (a) TEM image, ((b), (c)) HRTEM images, and (d) SAED pattern of AgSbS<sub>2</sub> nanostructured flowers and (e) the simulated pattern of (d).

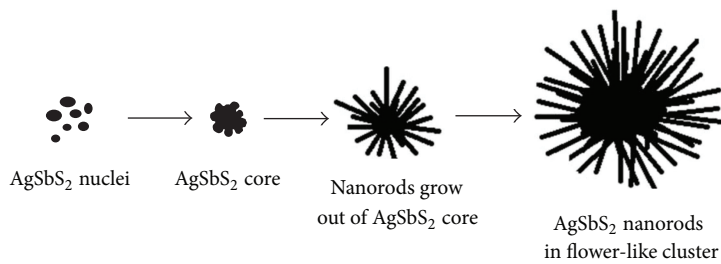


FIGURE 5: Schematic diagram for the formation of AgSbS<sub>2</sub> flower-like clusters of nanorods.

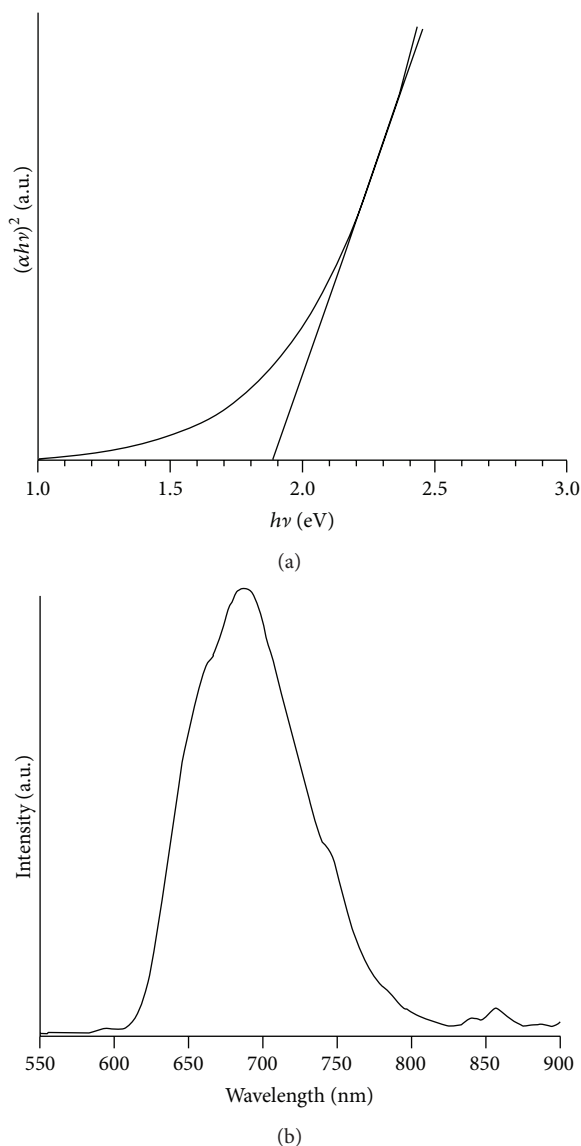


FIGURE 6: (a) The  $(\alpha h\nu)^2$  and  $h\nu$  plot and (b) photoluminescence of  $\text{AgSbS}_2$  flower-like clusters of nanorods.

region [1], but for the shoulders, they were caused by the shallow levels of donors and acceptors between the valence and conduction bands [14]. Furthermore, PL emissions could be controlled by different morphologies of the products, including crystalline degree, temperature, different types and concentrations of defects, different shapes and sizes of the products, and excitation wavelengths.

#### 4. Conclusions

$\text{AgSbS}_2$  nanostructured flowers were successfully synthesized by microwave-assisted refluxing of  $\text{AgNO}_3$ ,  $\text{Sb}(\text{CH}_3\text{COO})_3$ , and L-cysteine dissolved in ethylene glycol at the pH 4 for 60 min, according to the formation mechanism proposed in this report. Their direct energy gap was determined to be

1.89 eV, and their main and minor photoluminescence peaks were 688 and 857 nm, respectively.

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