CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 Chemical reagents and equipments

2.1.1 Chemical reagents

1) Copper chloride, CuCl, M.W. = 98.89 g/mol, 96.0 %, BDH
2) Copper acetate, $Cu(CH_3COO)_2$, M.W. = 181.63 g/mol, Carlo Erba
3) Bismuth(III)chloride, $BiCl_3$, M.W. = 315.34 g/mol, 98.0 %, Sigma-Aldrich
4) Antimony(III)chloride, $SbCl_3$, M.W. = 228.11, 99.0%, Fluka
5) Iron(II)chloride, $FeCl_2.4H_2O$, M.W. = 198.83, 99.0%, EMSURE
6) Iron(III)chloride, $FeCl_3.6H_2O$, M.W. = 270.30, 100.89%, Fisher Chemical
7) L-cysteine, $C_3H_7NO_2S$, M.W. = 121.16 g/mol, 99.0 %, MERCK
8) Thiourea, CH_4N_2S, M.W. = 76.12 g/mol, Sigma-Aldrich
9) Ethyleneglycol, CH_2OHCH_2OH, F.W. = 62.070 g/mol, 99.5%, Carlo Erba

2.1.2 Equipments

1) Analytical balance, model AB204-S, METTLER TOLEDO
2) Microwave oven, Electrolux model EMM2005
3) Hotplate & magnetic stirrer, model 502P-2, PMC Industries, Inc., San Diego, America
4) Oven, modelUE-400, Memmert, Germany

2.2 Experiments

2.2.1 Cyclic microwave-assisted synthesis of Cu_3BiS_3 dendrites using L-cysteine as a sulfur source and complexing agent

Firstly, the optimal condition for Cu_3BiS_3 preparation was investigated in order to obtain the single phase of the product. All the chemical reagents used are analytical pure grade. The Cu_3BiS_3 products with the yield of above 75% were prepared as the following describing. The synthesis was performed via a biomolecule and cyclic microwave radiation-assisted synthesis, in which 0.003 mol CuCl and 0.001 mol $BiCl_3$ were dispersed in 30 ml Ethylene glycol (EG) to form a solution, respectively. Then 0.003 mol of $C_3H_7NO_2S$ (L-cysteine) was added into the solution with 30 minute constant and vigorous stirring. After that, samples of the solution were irradiated using 300, 450, 600 and 700 W of microwave power, irradiated for 40 cycles (turning on for 30 second with every 30 second intervals). Finally, black precipitates were synthesized, separated by filtration, washed with de-ionized water and absolute ethanol, and dried at 70 °C for 24 hours. All of products were then characterized to determine their phases, morphologies and photoemission properties by XRD analysis, SEM, TEM, HREM, SAED and PL spectroscopy, respectively.

Table 2.1 Various reaction conditions for cyclic microwave radiation synthesis of Cu_3BiS_3

Condition	Radiation cycles	Microwave power (W)
CBIS1	40	300
CBIS2	40	450
CBIS3	40	600
CBIS4	40	700

2.2.2 Characterization of Cu_3SbS_4 microflowers produced by a cyclic microwave radiation

By separate dissolving of CuCl and $SbCl_3$ in ethylene glycol, and followed by NH_2CSNH_2 (thiourea, TU) adding, these solutions were thoroughly mixed to form 40 and 60 ml mixtures. In this research, a 300 W cyclic microwave radiation (40 second on for every 40 second interval) proceeded for 40, 30, 20, 10, and 2 cycles, and different molar ratios of Cu:Sb:S were varied. Finally, the precipitates were washed with absolute ethanol, and dried at 70 °C for 24 hours for further analyses. The phase purity of products was examined by XRD, SAED and Raman technique. The morphology of the as-synthesized sample was characterized by SEM, TEM technique. The EDX analysis showed the chemical composition of the products. UV-VIS-NIR spectroscopy was used for a study of optical properties in samples.

Table 2.2 Various reaction conditions for cyclic microwave radiation synthesis of Cu_3SbS_4

Condition	Cu:Sb:S mole ratio (mmol)	Solvent (ml)
CSbS1	3:1:4	40
CSbS2	3:1:5	40
CSbS3	3:1:6	40
CSbS4	3:2:4	40
CSbS5	3:3:4	40
CSbS6	3:3:4	60
CSbS7	2:2:4	40
CSbS8	1:1:4	40

2.2.3 Cyclic microwave-assisted synthesis of $CuFeS_2$ nanoparticles using biomolecules as sources of sulfur and complexing agent

All chemical reagent are analytical grade and used as received without further purification. Nanocrystalline $CuFeS_2$ were synthesized through a cyclic microwave radiation in which 1 mmol $Cu(CH_3COO)_2$ (or CuCl or $Cu(NO_3)_2.5H_2O$), 3 mmol $FeCl_3.6H_2O$ (or $FeCl_2.4H_2O$) and 2 mmol $C_3H_7NO_2S$ (L-cysteine) were mixed into 40

ml of ethylene glycol solvent. Samples of the solution were irradiated using 300 W of cyclic microwave radiation proceeded for 40 cycles (40 second on for every 40 second interval) and allowed to cool to room temperature. The brownish black precipitates were separated by filtration and washed with de-ionized water and absolute ethanol, and dried at 70^{o}C for 24 hour. Further characterizations were applied to these product including XRD, SEM, TEM, SAED, XPS analysis.

Table 2.3 Various reaction conditions for cyclic microwave radiation synthesis of $CuFeS_2$

Samples	**Cu-source**	**Fe-source**
CN	$Cu(NO_3)_2.5H_2O$	$FeCl_3.6H_2O$
CC	CuCl	$FeCl_3.6H_2O$
CA-1	$Cu(CH_3COO)_2$	$FeCl_3.6H_2O$
CA-2	$Cu(CH_3COO)_2$	$FeCl_2.4H_2O$

2.3 Characterization

2.3.1 X-Ray diffraction (XRD)

The crystallinity and phase purity of the products were analyzed using X-ray diffractometry (XRD) technique using Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV 35 mA, at a scanning rate of 0.02^{o}/s in the 2θ range of 20^{o} – 80^{o}. The identifications of products were analyzed by Philips X'Pert Highscore Computer Software (Search-Match Program) on the database of JCPDS software.

Figure 2.1 X-ray diffractometer

Sample preparation

The as-synthesized power was grinded in mortar agate and then packed in glass sample holder.

2.3.2 Field-emission scanning electron microscopy (FE-SEM)

The morphologies of the products were determined by a Field-emission scanning electron microscope (FE-SEM) on a JEOL instrument (JSM-6335F) at an accelerating voltage of 15 kV.

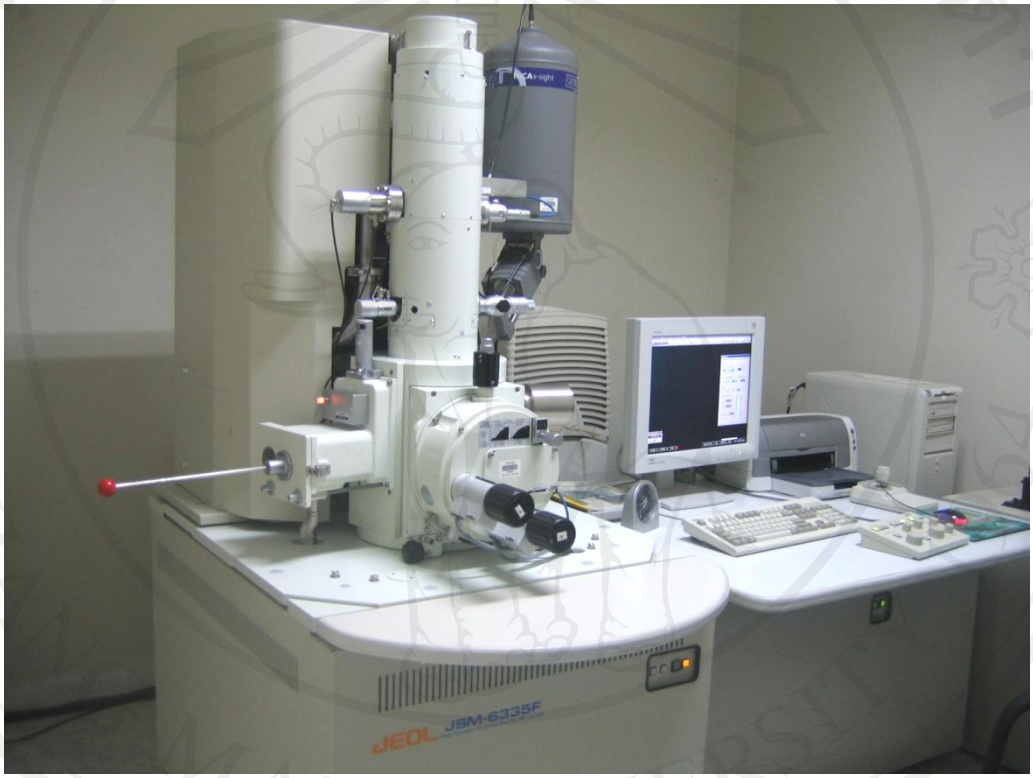

Figure 2.2 Scanning electron microscope

Sample preparation

A small amount of sample powder was dispersed in absolute ethanol using an ultrasonic bath. Afterwards, the dispersed sample was dropped on conductive copper tape which attached to the SEM sample's stub. The stub was then coated with gold particle by plasma sputtering under argon atmosphere, in order to increase sample's conductivity.

2.3.3 Transmission electron microscopy (TEM)

The structure and morphologies data of samples were also obtained from transmission electron microscopy (TEM) technique accompany with high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) analysis. The TEM, HRTEM and SAED images were recorded on a JEOL (JEM-2010) transmission electron microscope operate at an acceleration voltage of 200 kV.

Figure 2.3 Transmission electron microscope

Sample preparation

The preparing method of sample for TEM analysis was dispersing small amount of as-prepared powder in absolute ethanol, then, drop this solution on a copper grid coated with holey carbon film and leave the ethanol to slowly evaporate at room temperature.

2.3.4 Raman spectroscopy

Vibration modes of the crystalline products synthesized under the different conditions were studied using a Raman spectrometer operated at 50 mW Ar laser with $\lambda = 514.5$ nm.

Figure 2.4 Raman spectrometer

Sample preparation

Appropriate amount of the sample powders was pressed on glass slide and the slide attached with samples was further analyzed using a Raman spectrometer

2.3.5 Luminescence spectroscopy

The luminescence emission spectra of the samples were investigated using Perkin Elmer Luminescence spectrometer LS50B at room temperature. Photoluminescence (PL) spectrometer was operated using a corresponding excitation wavelength with scanning mode of emission spectrum operation.

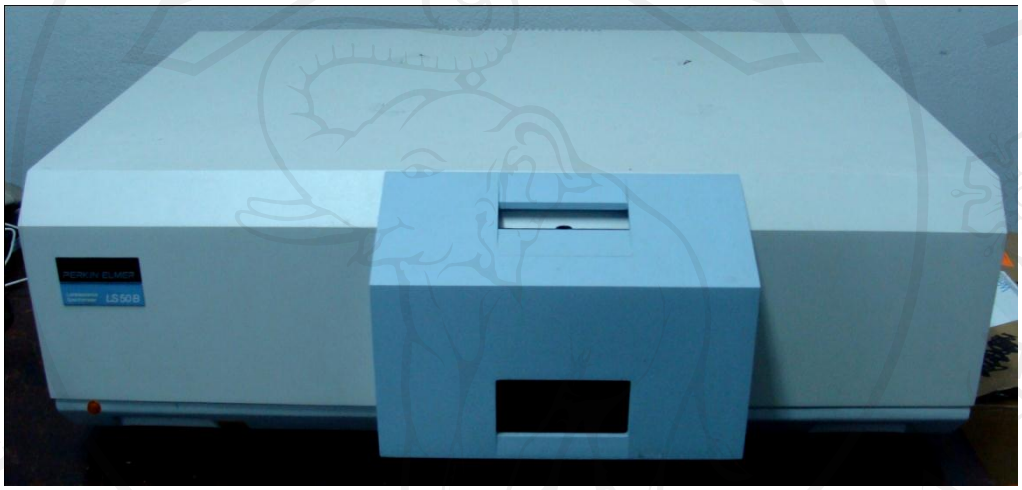

Figure 2.5 Luminescence spectrometer

Sample preparation

The appropriate amount of sample powders was dispersed in absolute ethanol using ultrasonic bath. This solution was transferred into quartz cuvette. The solid samples were also directly analyzed by using a solid holder instead of the quartz cuvette.

2.3.6 UV-Vis-NIR spectroscopy

To investigate optical properties of the product, the UV-Vis-NIR spectrum were measured by UV-Vis-NIR spectrophotometer (Perkin Elmer, Lampda 19) at room temperature by scanning mode of Perkin's software.

Figure 2.6 UV-Vis-NIR spectrophotometer

Sample preparation

The appropriate amount of sample powders was dispersed in absolute ethanol using ultrasonic bath. Then, solution was transferred into quartz cuvette. The absorption edge of the products was measured in the wavelength region from near-infrared to UV.

2.3.7 X-ray photoelectron spectroscopy

The XPS spectrum of sample was investigated by X-ray photoelectron spectrometer (XPS; AXIS ULTRADLD, Kratos analytical, Manchester UK.) The base pressure in the XPS analysis chamber was about $5x10^{-9}$ torr. The samples were excited with X-ray hybrid mode 700x300 μm spot area with a monochromatic Al Kα 1,2 radiation at 1.4 keV. X-ray anode was run at 15kV 10mA 150W. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45^{o} with respect to the normal to the sample surface.

Figure 2.7 X-ray photoelectron spectrometer

Sample preparation

The appropriate amount of sample powders was packed in the mold and compressed to be a circular disk by a manual hydraulic press machine. A circular disk sample was put on the carbon tape before loading into the X-ray photoelectron spectrometer.