CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 Chemical reagents

1. Cadmium acetate, $Cd(CH_3COO)_2.2H_2O$, Sigma-Aldrich, USA
2. Sulfur powder, S (powder), Sigma-Aldrich, USA
3. Bismuth oxide, Bi_2O_3, 99.5%, Riedel-de Haen, Germany
4. Thiocarbohydrazide, CH_6N_4S, Acros, USA
5. Copper (II) chloride, $CuCl_2.2H_2O$, M&B, USA
6. Ammonium sulfide, $(NH_4)_2S$, Sigma-Aldrich, USA
7. Hydroxyethyl cellulose, HEC, Fluka, Switzerland
8. Polyethylene glycol, PEG (MW = 6000, 8000, 10000, 20000), Fluka, Switzerland
9. Polyvinyl alcohol, PVA, (MW = 125000), Ajax, Australia
10. Polyvinyl pyrrolidone, PVP, (MW = 30000), Acros, USA
11. Ethylenediamine, $C_2N_2H_8$, Panreac, Spain
12. Absolute ethanol, C_2H_5OH, Merck, Germany
13. Ethanol 95%, C_2H_5OH, Merck, Germany
14. Hydrochloric acid, HCl, BDH, USA
15. Deionized water
16. Formic acid, HCOOH, 98%, BDH, USA
17. Zinc powder, Zn, RdH, USA
18. Iodine electrolyte, I^-/I^-_3, SOLAR TECH, Thailand

19. Eosin Y $C_{20}H_8Br_4O_5$, Sigma-Aldrich, USA
20. Titanium dioxide pates, TiO_2 pates, SOLAR TECH, Thailand
21. Chloroplatinic acid, $H_2C_{16}Pt$, SOLAR TECH, Thailand

2.2 Apparatus and instruments

1. Hotplate & magnetic stirrer (502P-2), PMC Industries, Inc., San Diego, U.S.A.
2. Analytical balance (Bb-210S), Sartorius AG. Goettingen, Germany
3. Homemade stainless steel autoclaves
4. Oven (UE-400), Memmert, Germany
5. X-ray Diffractometer (D-500), Siements, Germany
6. Raman Spectrometer (T64000), Horiba Jobin Yvon, France
7. Scanning Electron Microscope (JEM-6335), JEOL, Japan
8. Transmission Electron Microscope (JEM-2010), JEOL, Japan
9. Photoluminescence spectrophotometer, LS50B, Perkin Elmer, UK
10. UV-NIR spectrophotometer (Lambda 19), Perkin Elmer, UK

2.3 Experiments

2.3.1 Cadmium sulfide (CdS) [115]

Some hydroxy ethylcellulose (HEC) was dissolved into $Cd(CH_3COOH)_2$ aqueous solution (5 mmol $Cd(CH_3COOH)_2$ $2.5H_2O$ and 50 ml distilled water).The solution was stirred and dehydrated at 80 ^oC in order to achieve good dispersion of Cd^{2+}- HEC matrix and get polymer gel. The gel and 5 mmol sulfur powder was put into a home-made teflon liner autoclave which was filled with 60 ml ethylenediamine. The synthesis temperature varied from 100 to 200 ^oC and holding periods ranged from

24 to 72 hours. The obtained precipitates were filled and washed with distilled water and 95% ethanol several times to remove impurities and then the products were dried at 70 °C for 24 h. The obtained products were collected to future characterization. Table 2.1 and Figure 2.1 show the different reaction conditions and the flow chart for preparation CdS nanostructures.

Table 2.1 Reaction conditions for the preparation the CdS powders

Precursors	**Reaction temparatures(°C)**	**Reaction times (h)**
$Cd(Ac)_2$ + 0.25 g HEC	100	24
$Cd(Ac)_2$ + 0.25 g HEC	120	24
$Cd(Ac)_2$ + 0.25 g HEC	140	24
$Cd(Ac)_2$ + 0.25 g HEC	160	24
$Cd(Ac)_2$ + 0.25 g HEC	180	24
$Cd(Ac)_2$ + 0.25 g HEC	200	24
$Cd(Ac)_2$ + 0.25 g HEC	200	48
$Cd(Ac)_2$ + 0.00 g HEC	200	72
$Cd(Ac)_2$ + 0.25 g HEC	200	72
$Cd(Ac)_2$ + 0.50 g HEC	200	72
$Cd(Ac)_2$ + 0.75 g HEC	200	72
$Cd(Ac)_2$ + 0.10 g HEC	200	72

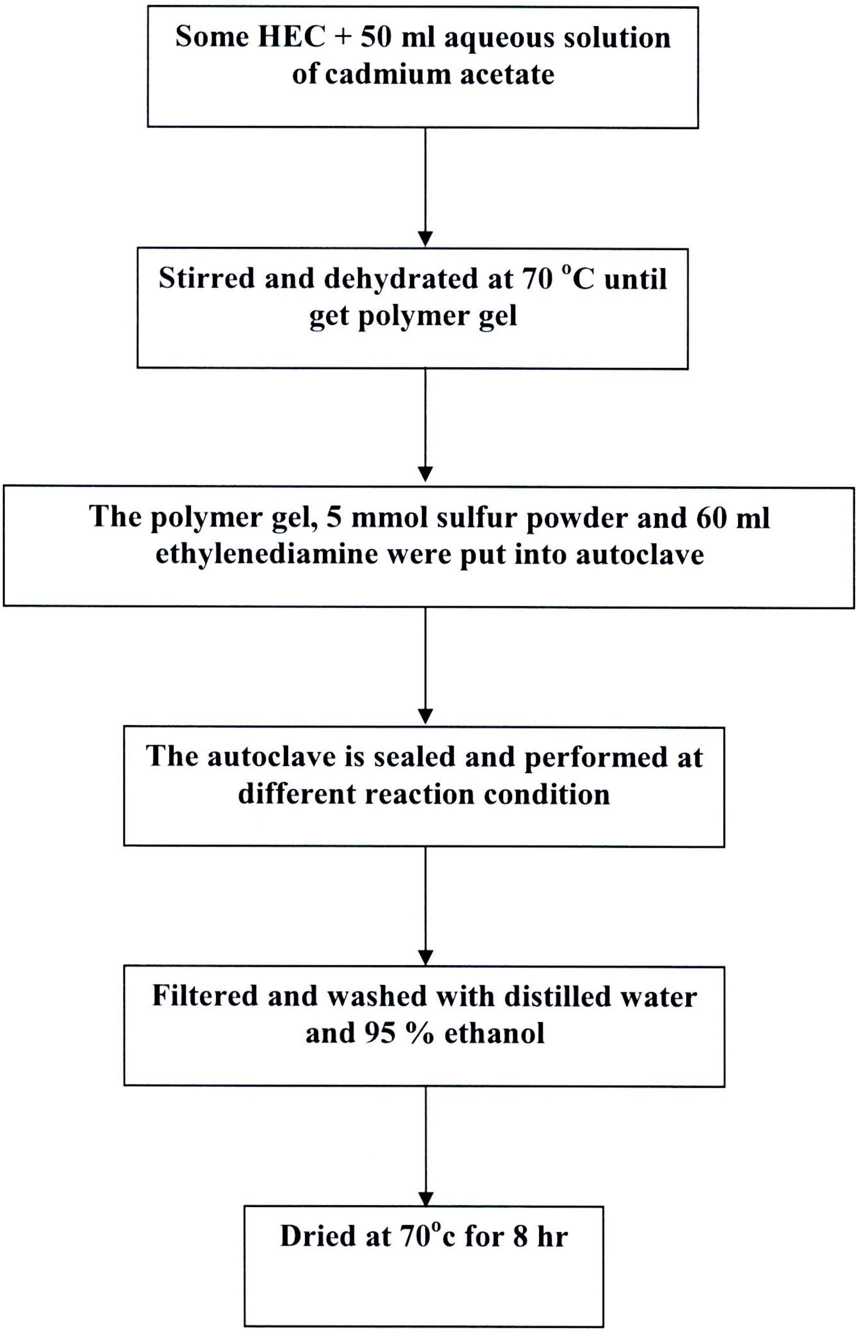

Figure 2.1 Schematic diagrams for the preparation of CdS by solvothermal method

2.3.2 Bismuth sulfide (Bi_2S_3) [123]

To produce nanostructured Bi_2S_3, 0.005 mol Bi_2O_3 and 0.010 mol thiocarbohydrazide (CH_6N_4S) were mixed in 20 ml H_2O containing 1 ml 37 % HCl. Subsequently, 1 g each of 125,000 MW PVA, 20,000 MW PEG and 30,000 MW PVP was also added to the solutions, which were stirred for 0.5 h in order to mix them thoroughly. At this stage, the solutions became yellow tea in color. They were further processed in home-made stainless autoclaves at 100 and 200 °C for 2 and 20 h. Finally, black precipitates were produced, separated by filtration, washed with de-ionized water and absolute ethanol, and dried at 80 °C for 24 h. The products were then characterized to determine their phase, morphologies, and vibration and emission properties. Table 2.2 and Figure 2.2 show the different reaction conditions and the flow chart for preparation Bi_2S_3 nanostructures, respectively.

Table 2.2 Reaction conditions for the preparation the Bi_2S_3 powders

Conditions	**Bi source**	**S source**	**polymers**	**Temp. + Time**
1	Bi_2O_3	CH_6N_4S	-	100 °C 2 h
2	Bi_2O_3	CH_6N_4S	-	120 °C 2 h
3	Bi_2O_3	CH_6N_4S	-	140 °C 2 h
4	Bi_2O_3	CH_6N_4S	-	180 °C 2 h
5	Bi_2O_3	CH_6N_4S	-	200 °C 2 h
6	Bi_2O_3	CH_6N_4S	-	200 °C 5 h
7	Bi_2O_3	CH_6N_4S	-	200 °C 10 h
8	Bi_2O_3	CH_6N_4S	-	200 °C 15 h
9	Bi_2O_3	CH_6N_4S	-	200 °C 20 h
10	Bi_2O_3	CH_6N_4S	PEG	200 °C 20 h
11	Bi_2O_3	CH_6N_4S	PVP	200 °C 20 h
12	Bi_2O_3	CH_6N_4S	PVA	200 °C 20 h
13				

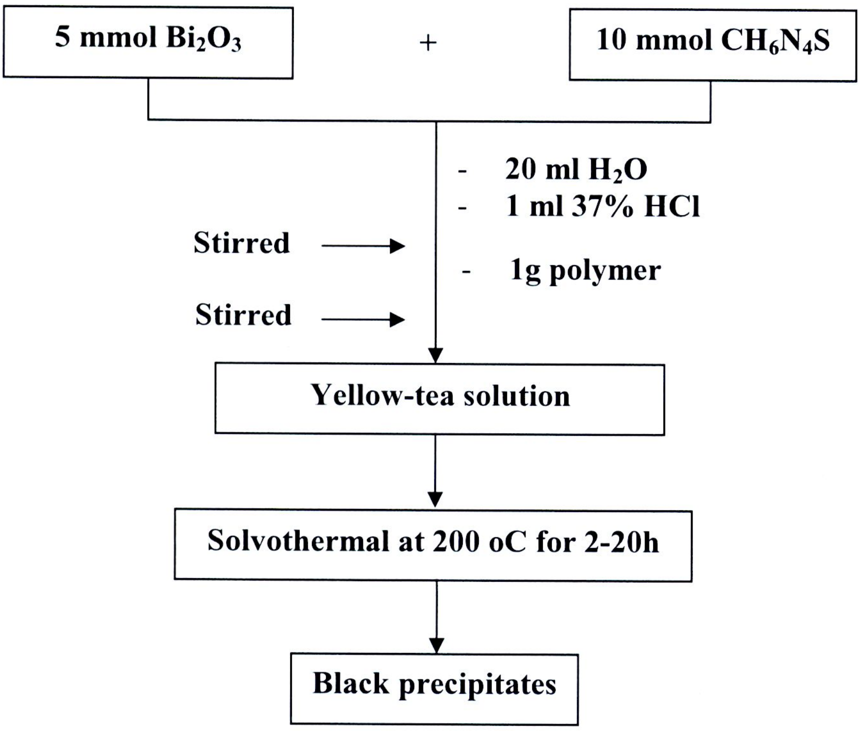

Figure 2.2 Schematic diagrams for the preparation of Bi_2S_3 by solvothermal method

2.3.3 Copper sulfide (CuS) [131,134]

The procedure was to dissolve 0.005 mol $CuCl_2.2H_2O$ and PEG with different amount and MWs in mixed solvents containing 9:1 volume ratio of C_2H_5OH:H_2O and 1.5 ml HCOOH (a pH stabilizer) each. The solutions (green) were continuous stirred, and each 0.005 mol $(NH_4)_2S$ was added. Solvothermal reactions proceeded at 200 °C for 1-5 h. Finally, black precipitates were separated by filtration, washed with distilled water and 95% ethanol, dried at 70 °C for 24 h, and intensively characterized. Table 2.3 and Figure 2.3 show the different reaction conditions and the flow chart for preparation CuS nanostructures, respectively.

Table 2.3 Reaction conditions for the preparation the CuS powders

No	Formic acid (ml)	Temp. and Time	Polymers
1	0.0	200 °C, 5 h	5 g, PEG 6000
2	1.5	200 °C, 5 h	5 g, PEG 6000
3	3.0	200 °C, 5 h	5 g, PEG 6000
4	5.0	200 °C, 5 h	5 g, PEG 6000
5	1.5	200 °C, 3 h	5 g, PEG 6000
6	1.5	200 °C, 1 h	5 g, PEG 6000
7	1.5	200 °C, 5 h	1 g, PEG 6000
8	1.5	200 °C, 5 h	10 g, PEG 6000
9	1.5	200 °C, 5 h	5 g, PEG 8000
10	1.5	200 °C, 5 h	5 g, PEG 10000
11	1.5	200 °C, 5 h	5 g, PEG 12000
12	1.5	200 °C, 5 h	5 g, PEG 20000

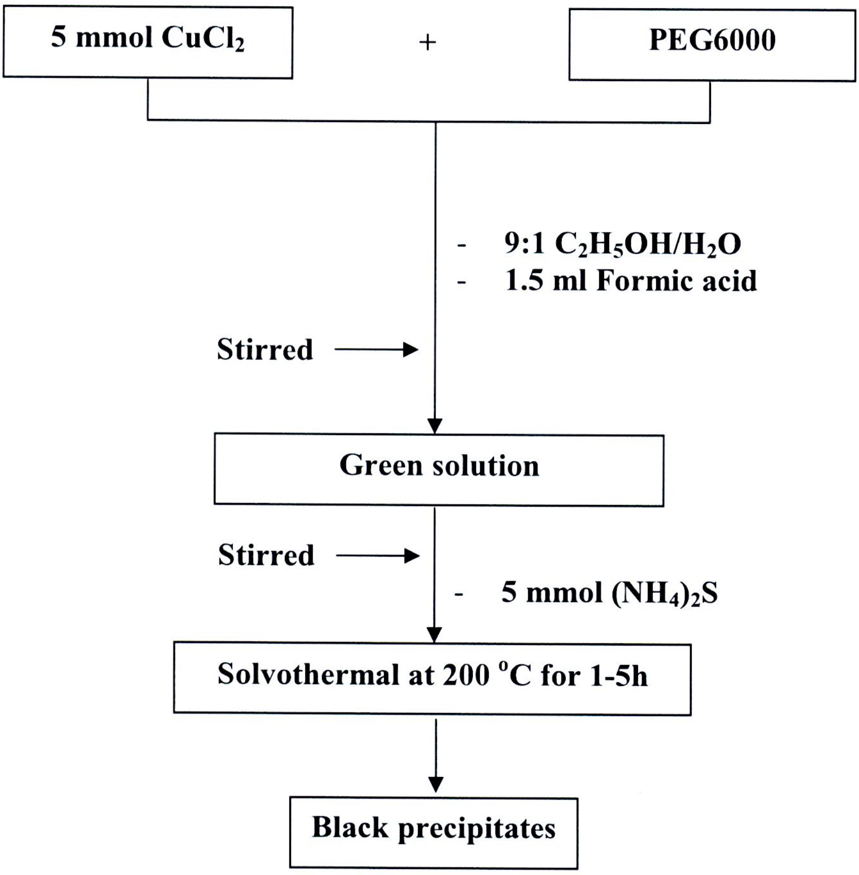

Figure 2.3 Schematic diagrams for the preparation of CuS by solvothermal method

2.4 Characterizations

2.4.1 X-ray diffraction (XRD)

Phase purity and crystallinity of the products were characterized by X-ray diffractometer.

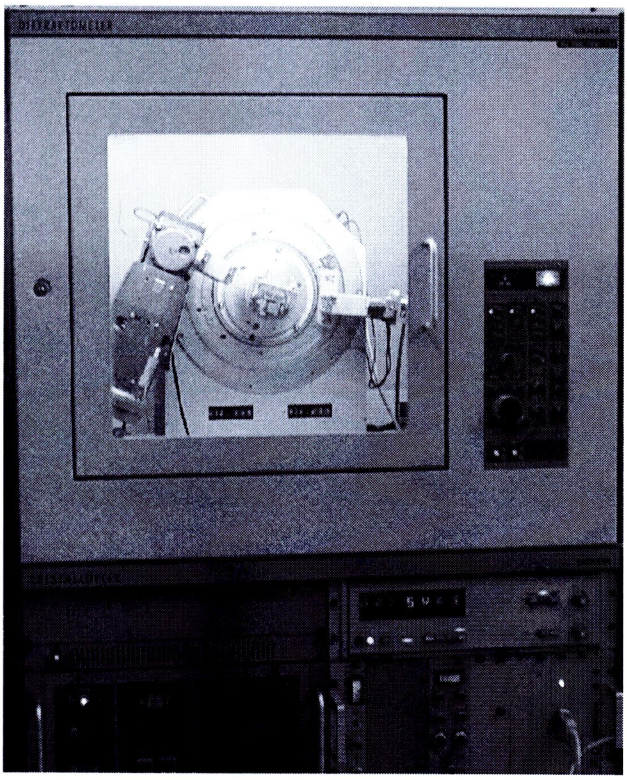

Figure 2.4 X-ray diffractometer

Sample preparation

The sample powders were finely grinded and then put on in sample holder. Crystallographic and phase analysis were performed on an X-ray diffractometer operating at a scanning rate of 0.04 $^{\circ}$ S^{-1} with Cu Kα radiation (λ = 1.54178 Å). Identification of crystalline structure was carried out by comparison of the experimental patterns with JCPDS standards.

2.4.2 Raman Spectroscopy

Vibration modes of the crystalline products synthesized under the different conditions were studied using a Raman spectrometer.

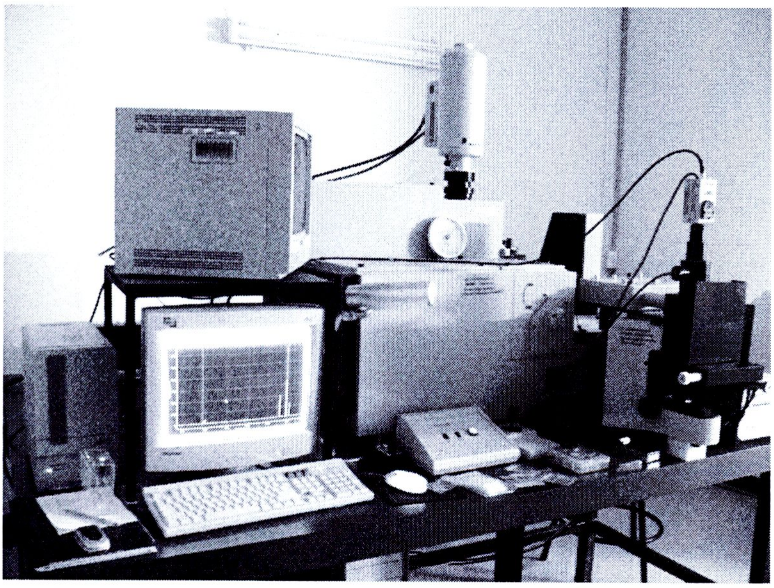

Figure 2.5 Raman spectrometer

Sample preparation

Appropriate amount of the sample powders was pressed on glass slide and ,then, the slide attached with samples was further analyzed using a Raman spectrometer operated at 50 mW Ar laser with λ = 514.5 nm

2.4.3 Scanning Electron Microscopy (SEM)

The surface morphologies of the products were investigated by using scanning electron microscope.

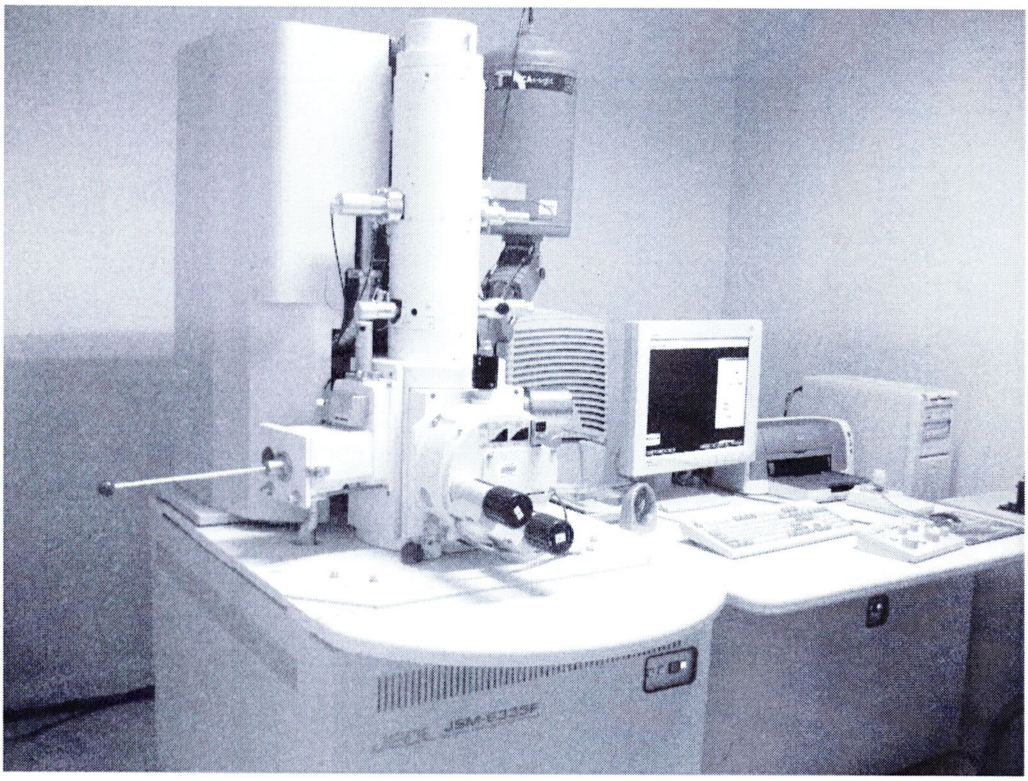

Figure 2.6 Scanning electron microscope

Sample preparation

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

2.4.4 Transmission Electron Microscopy (TEM)

The morphologies and electron diffraction of the samples were studied by using transmission electron microscope. The preferential growth direction was also studied by HR-TEM technique.

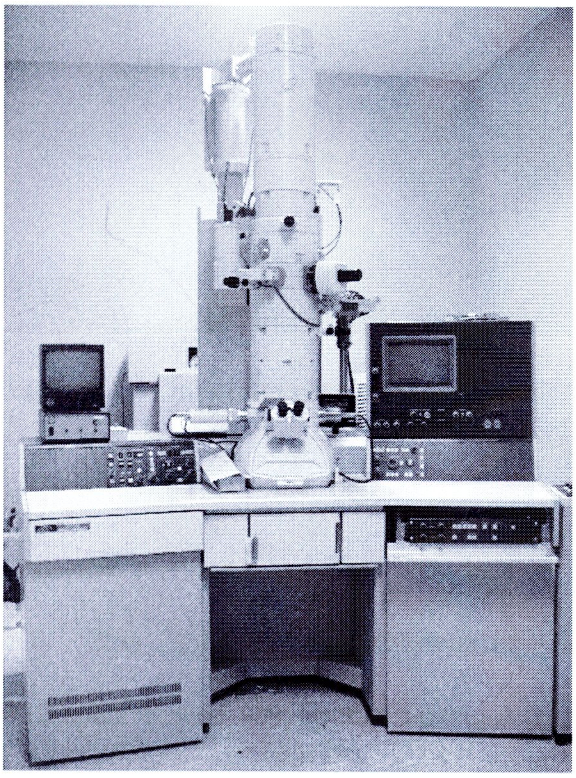

Figure 2.7 Transmission electron microscope

Sample preparation

Appropriate amount of the sample powders was dispersed in absolute ethanol using an ultrasonic bath. The samples were then dropped on thin amorphous carbon films supported by copper grid for further analysis.

2.4.5 Photoluminescence spectroscopy

Optical property of the products were analyzed by Perkin Elmer Luminescence spectrometer LS50B at room temperature

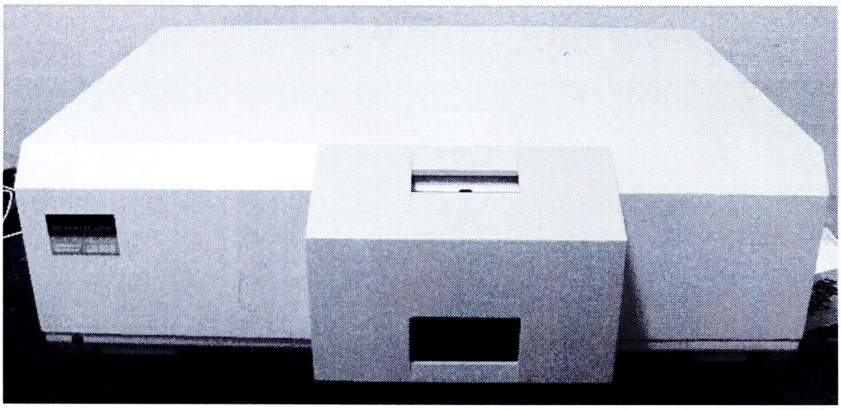

Figure 2.8 Photoluminescence spectrometer

Sample preparation

The appropriate amount of sample powders was dispersed in absolute ethanol using ultrasonic bath. This solution was transferred into quartz cuvette. Photoluminescence (PL) spectrometer was operated using a corresponding excitation wavelength. The solid samples were also directly analyzed by using a solid holder instead of the quartz cuvette.

2.4.6 UV-NIR Spectroscopy

Absorption edge or band gap energy of the solid samples was investigated using UV-NIR spectrophotometer.

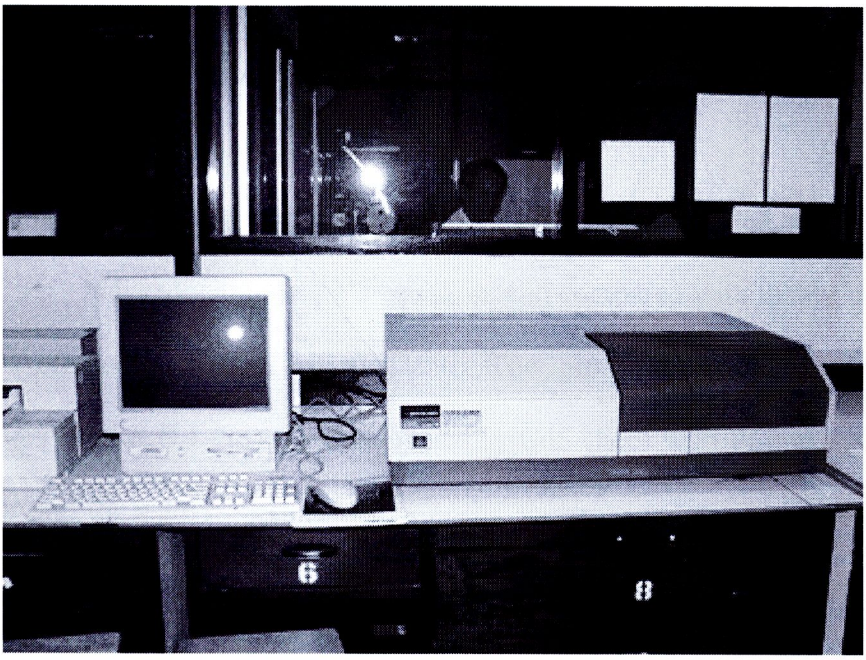

Figure 2.9 UV-NIR spectrophotometer

Sample preparation

The appropriate amount of sample powders was dispersed in absolute ethanol using ultrasonic bath. The solution was transferred into quartz cuvette. The absorption edge of the products was measured in the wavelength region of 200 – 1500 nm.