CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Chemical reagents, equipments and instruments

3.1.1 Chemical reagents

1) Strontium acetate , $Sr(C_2H_3O_2)_2$, MW= 205.71 , ALDRICH, Germany
2) Ammonium metatungstate hydrate, $H_{26}N_6O_4OW_{12} \cdot xH_2O$, MW= 2956.30 , Fluka
3) Polyvinyl alcohol , $(C_2H_4O)_x$, MW= 125,000 and 72,000 , ALDRICH, Germany
4) Magnesium acetate tetrahydrate $((CH_3COO)_2Mg \cdot 4H_2O)$= , 214.40 Fisher Scientific, India
5) Ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, MW= 1,235.86, Sigma-Aldrich, Singapore
6) Strontium nitrate, $Sr(NO_3)_2$, MW= 211.63, Sigma-Aldrich, Singapore
7) Strontium chloride hexahydrate, $SrCl_2 \cdot 6H_2O$, MW= 266.62, Sigma-Aldrich, Singapore

3.1.2 Equipments and instruments

1) Hotplate & magnetic stirrer, model 502P-2, PMC Industries, Inc., San Diego, America
2) Analytical balance, model BP-210S, Sartorius AG. Goettingen, Germany

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3) Thermometer
4) Aluminum foil
5) TGA, Shimadzu TGA-50 analyzer, Japan
6) X- ray diffractometry (XRD, SIEMENS D500, Germany)
7) FTIR, Bruker Tensor 27, Germany
8) Raman spectroscopy, model T64000 JY, Horiba JobinYvon, France
9) Scanning Electron Microscope, and Energy Dispersive X-ray Spectroscopy, model JEM-6335, JEOL, Japan
10) Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy, model S2600H, Hitachi, Japan
11) Transmission Electron Microscope, model JEM-2010, JEOL, Japan
12) Raman spectroscopy, model T64000 JY, Horiba JobinYvon, France
13) Luminescence spectrometer, model LS50B,Perkin Elmer
14) UV-Vis-NIR Spectrophotometer, model Lambda 19, Perkin Elmer
15) Electrospinning equipment.
    - High voltage power supply, Model HD 100 series Hipot Tester, Hipotronics Industries (Volt 0-40 kV)
    - Various speed controller, Crotech multifunction generator Model 4905,

      Hipotronics Industries (Volt 0-15)
    - Syringe pump (Flow rate 0-160 micro liter)
    - Grounded Aluminium collector (30 x 30 cm)
16) Microwave-Hydrothermal equipment.
    - Microwave oven, Electrolux Model= EMS3027X

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- Manometer
- Glass Vessel

3.2. Synthesis methods

3.2.1 Synthesis of $SrWO_4$ using electrospinning method

In the present research, 0.0045 mol $Sr(CH_3COO)_2$, 4.5 mmol ($H_{26}N_6O_40W_{12}\cdot xH_2O$), and different contents of poly (vinyl alcohol) (PVA, 125,000 MW) were separately dissolved in 10 ml deionized water each, mixed, and vigorously stirred at 80 ^oC for 30 min . The mixtures were encoded as M1, M2, M3, and M4 for using 1.0, 1.1, 1.2, and 1.3 g PVA, respectively in Figure 3.1. The schematic setup of the electrospinning process we used in this study was shown in Figure 3.2. Each of mixture was electrospun by a horizontal syringe needle biased with +15 kV from a d.c. power supply, to synthesize $SrWO_4$-PVA spiders' webs on a grounded vertical flat aluminum foil. The $SrWO_4$-PVA spider's web synthesized from the M4 mixture was selected to be calcined in air at 300 ^oC, 400 ^oC, 500 ^oC, and 600 ^oC for 3 h, to synthesize $SrWO_4$ nanoparticles joined together as a spider's web.

These products were characterized using thermogravimetric analyzer (TGA, Shimadzu TGA-50 analyzer, Japan) using a heating rate of 5 ^oC/min; X-ray diffractometer (XRD, SIEMENS D500, Germany) operating at 20 kV, 15 mA, and using Cu-Ka line, in combination with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) [91]; scanning electron microscope (SEM, JEOL JSM-6335F, Japan) operating at 15 kV; transmission electron microscope (TEM, JEOL JEM-2010, Japan), high resolution transmission electron microscope (HRTEM) and selected area electron diffractometer (SAED) operating at 200 kV; Fourier

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transform infrared spectrometer (FTIR, Bruker Tensor 27, Germany) with KBr as a diluting agent and operated in the range of 4000–400 cm^{-1}; Raman spectrometer (T64000 HORIBA Jobin Yvon, U.S.A.) using a 50 mW and 514.5 nm wavelength Ar green laser; UV–vis spectrometer (Lambda 25 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 245 nm excitation wavelength at room temperature.

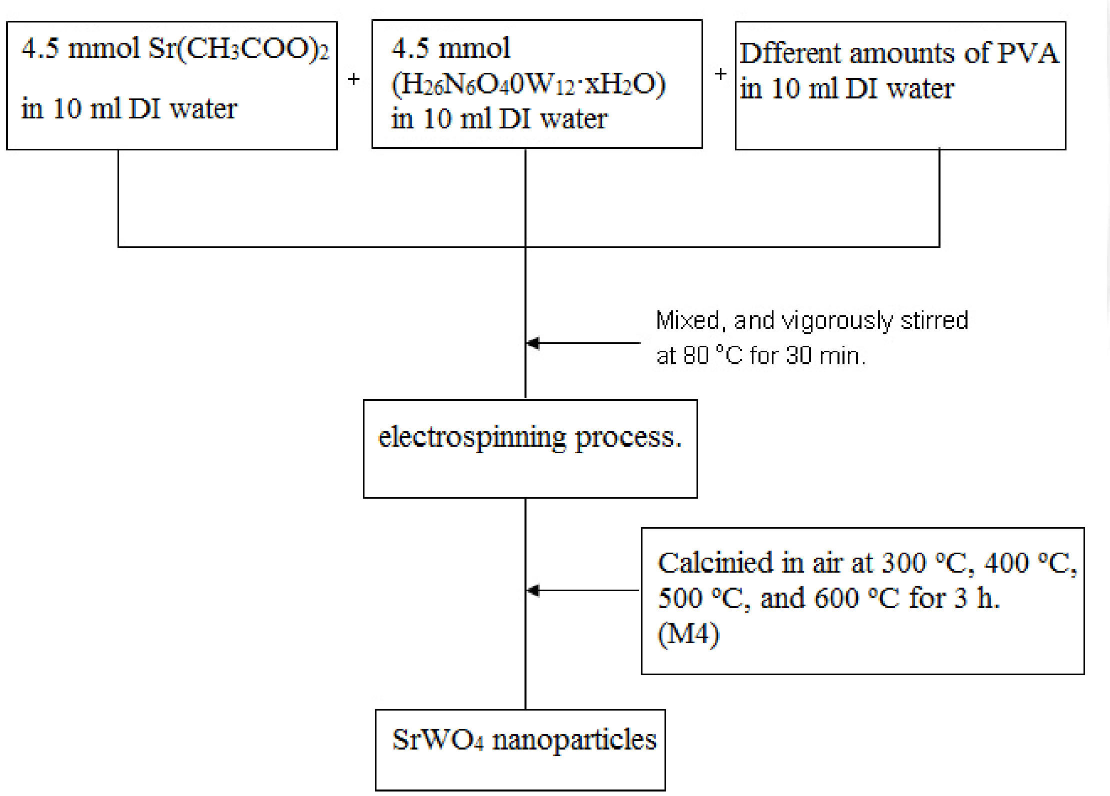

Figure 3.1 Schematic diagram used for preparation of $SrWO_4$.

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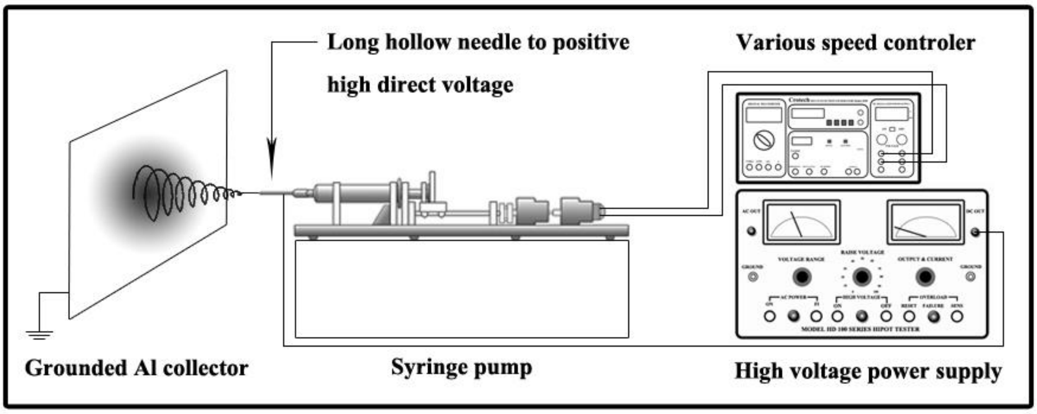

Figure 3.2 Schematic diagram of electrospinning equipment.

3.2.2 Synthesis of $MgWO_4$ using electrospinning

Different contents of magnesium acetate tetrahydrate ($(CH_3COO)_2Mg \cdot 4H_2O$), ammonium (meta) tungstate tetrahydrate ($(NH_4)_6W_7O_{24} \cdot 4H_2O$), and poly(vinyl alcohol) (PVA, 72,000 MW) were thoroughly mixed by dissolving in 30 ml deionized water each with 30 min stirring. The schematic setup of the electrospinning process we used in this study was shown in Figure 3.2. Each of these mixtures was electrospun through a horizontal plastic syringe, biased with a +15 kV direct voltage to form fibers on a ground flat aluminum foil placed 15 cm apart. The fibers were also calcined at 500, 600, and 700 ^{o}C for 3 h constant length of time, and left them cool down to room temperature. The products synthesized from different contents of the starting materials with and without subsequent calcination at high temperatures were summarized and encoded (Table 3.1).

These products were further characterized by X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV 15 mA, and using Cu-K line, in combination with the database of the Joint Committee on Powder Diffraction Standards (JCPDS)

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[92-93]; scanning electron microscope (SEM, JEOL JSM-6335F) operating at 15 kV; transmission electron microscope (TEM, JEOL JEM-2010), high resolution transmission electron microscope (HRTEM) and selected area electron diffractometer (SAED) operating at 200 kV, UV–visible spectrometer (Lambda 25 PerkinElmer) using a UV lamp with the resolution of 1 nm; and photoluminescence (PL) spectrometer (LS50B PerkinElmer) using a 290 nm excitation wavelength at room temperature.

Table 3.1 Product codes of the present research $MgWO_4$.

Product code	$(CH_3COO)2Mg\cdot 4H_2O$ (mmol)	$(NH_4)_6W_7O_{24}\cdot 4H_2O$ (mmol)	PVA (g)	temperature (^oC)/time (h)
MW1	1.5	1.5	0.9	None
MW2	1.5	1.5	1.1	None
MW3	1.5	1.5	1.3	None
MW3C1	1.5	1.5	1.3	500/3
MW4	3.0	3.0	1.3	None
MW4C1	3.0	3.0	1.3	500/3
MW5	4.5	4.5	1.3	None
MW5C1	4.5	4.5	1.3	500/3
MW5C2	4.5	4.5	1.3	600/3
MW5C3	4.5	4.5	1.3	700/3

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3.2.3 Synthesis of $MgMoO_4$ using electrospinning

$(CH_3COO)_2Mg{\cdot}4H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ each 4.5 mmol was dissolved in 30 ml deionized water, which was subsequently divided into three solutions with equal volume. Then 0.7, 1.0 and 1.3 g of PVA (125,000 MW) were added to form MM1, MM2, and MM3 mixtures. The schematic setup of the electrospinning process we used in this study was shown in Figure 3.2. Each was electrospun through a horizontal plastic syringe, biased with +15 kV direct voltage, to form a fibrous web on a ground flat aluminum foil, placed 15 cm apart. The webs produced from the MM3mixture were also calcined at 400, 500 and 600 ^{o}C, held at each of these temperatures for 3 h, and cooled down to room temperature and encoded (Table 3.2).

These products were characterized using thermogravimetric analyzer (TGA, Shimadzu TGA-50 analyzer, Japan) using a heating rate of 5 ^{o}C/min; X-ray diffractometer (XRD, SIEMENS D500, Germany) operating at 20 kV, 15 mA, and using Cu-Ka line, in combination with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) [94]; scanning electron microscope (SEM, JEOL JSM-6335F, Japan) operating at 15 kV; transmission electron microscope (TEM, JEOL JEM-2010, Japan), high resolution transmission electron microscope (HRTEM) and selected area electron diffractometer (SAED) operating at 200 kV; Fourier transform infrared spectrometer (FTIR, Bruker Tensor 27, Germany) with KBr as a diluting agent and operated in the range of 4000–400 cm^{-1}; Raman spectrometer (T64000 HORIBA Jobin Yvon, U.S.A.) using a 50 mW and 514.5 nm wavelength Ar green laser; UV–vis spectrometer (Lambda 25 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 245 nm excitation wavelength at room temperature.

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Table 3.2 Product codes of the present research $MgMoO_4$.

Product code	$(CH_3COO)2Mg\cdot 4H_2O$ (mmol)	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (mmol)	PVA (g)	temperature (^oC)/time(h)
MM1	4.5	4.5	0.7	None
MM2	4.5	4.5	1.0	None
MM3	4.5	4.5	1.3	None
MM3C1	4.5	4.5	1.3	400
MM3C2	4.5	4.5	1.3	500
MM3C3	4.5	4.5	1.3	600

3.2.4 Synthesis of $SrMoO_4$ using Microwave-Hydrothermal

To produce donut-like $SrMoO_4$, 5 mmol each of strontium salts [A = $Sr(NO_3)_2$, B = $Sr(CH_3CO_2)_2$ and C = $SrCl_2\cdot 6H_2O$] and 5 mmol ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] were separately dissolved in 25 ml distilled water to form strontium and molybdenum solutions, which were mixed, stirred for 10 min The schematic setup of the Microwave-Hydrothermal process we used in this study was shown in Figure 3.3. At room temperature and processed by a 270 W microwave-hydrothermal method for 5, 15, 30 and 90 min (encoded as 1, 2, 3 and 4 in sequence) to form precipitates. In this research, the products were encoded as MSA1, MSA2, MSA3, MSA4, MSB1, MSB2, MSB3, MSC1, MSC2 and MSC3. The MSA2 product implied that it was produced from $Sr(NO_3)_2$ + $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ for 15 min, the MSC3 product from $SrCl_2\cdot 6H_2O$ + $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ for 30 min, and similarly for other products. The details for the experiment show (Table 3.3).

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The products were characterized by an X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV and 15 mA to create Cu-Kα line for the analysis; a scanning electron microscope (SEM, JEOL JSM-6335F) operating at 15 kV; a transmission electron microscope (TEM, JEOL JEM-2010), high resolution transmission electron microscope (HRTEM) and selected area electron diffractometer (SAED) operating at 200 kV; a Raman spectrometer (HORIBA Jobin Yvon T64000) using a 50 mW and 514.5 nm wavelength Ar green laser; and a UV-visible spectrometer (PerkinElmer Lambda 25) using a UV lamp with the resolution of 1 nm.

Table 3.3 Product codes of the present research $SrMoO_4$.

Product code	$Sr(NO_3)_2$ (mmol)	$Sr(CH_3CO_2)_2$ (mmol)	$SrCl_2{\cdot}6H_2O$ (mmol)	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (mmol)	W/time (min)
MSA1	5.0	-	-	5.0	270/5
MSA2	5.0	-	-	5.0	270/15
MSA3	5.0	-	-	5.0	270/30
MSA4	5.0	-	-	5.0	270/90
MSB1	-	5.0	-	5.0	270/5
MSB2	-	5.0	-	5.0	270/15
MSB3	-	5.0	-	5.0	270/30
MSC1	-	-	5.0	5.0	270/5
MSC2	-	-	5.0	5.0	270/15
MSC3	-	-	5.0	5.0	270/30

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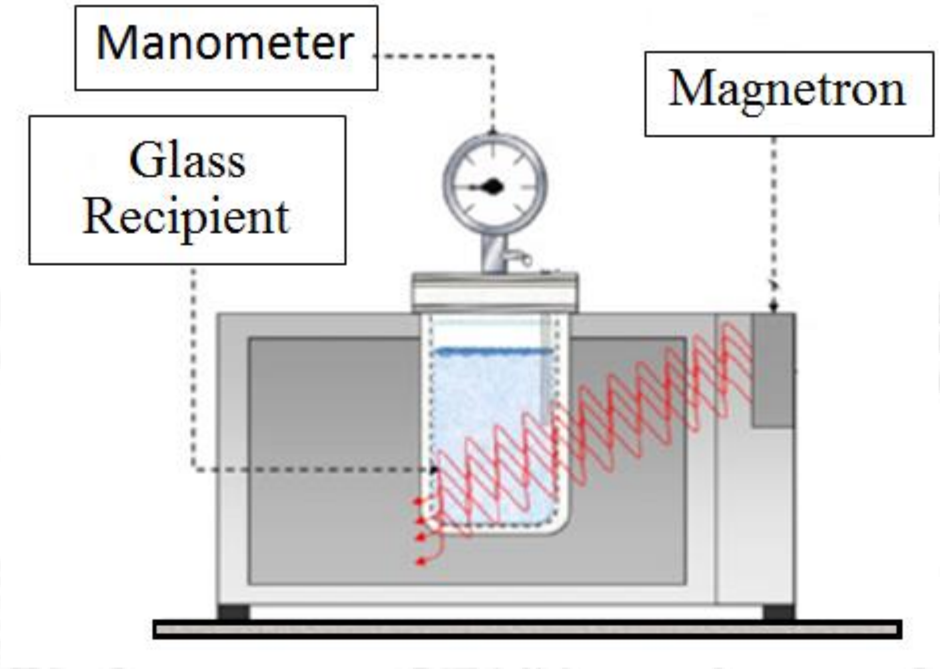

Figure 3.3 Schematic diagram of Microwave-Hydrothermal equipment.

3.3. Characterization

The thermal behavior of PVA and (SrWO$_4$–PVA, MgWO$_4$-PVA, MgMoO$_4$-PVA) electrospun fibers characterized using thermogravimetric analyzer (TGA, Shimadzu TGA-50 analyzer, Japan) using a heating rate of 5 ^{o}C/min.

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Figure 3.4 Thermogravimetric analyzer

The crystallinity and phase purity of the products were analyzed by using X-ray diffractometry (XRD, SIEMENS D500, Germany) with Cu Kα radiation (λ = 1.5418 Å) operating at 20 kV-15 mA, at a scanning rate of 5°/min in the 2θ range of 10°-90°. The identification samples were assisted by Philips X'Pert Highscore Computer Software (search-match program) on the database of JCPDS software.

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Figure 3.5 X-ray diffractometer

Fourier transform infrared spectrometer (FTIR, Bruker Tensor 27, Germany) with KBr pellet technique and operated in the range 400–4000 cm^{-1}. Raman spectrometer (T64000 HORIBA Jobin Yvon, U.S.A.) using a 50 mW and 514.5 nm wavelength Ar green laser

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Figure 3.6 Fourier transform infrared spectroscope

The Raman instrument provides a powerful tool for the definitive identification and characterisation of minerals and biomarkers. Raman spectroscopy is sensitive to the composition and structure of any mineral or organic compound. This capability provides direct information of potential organic compounds that can be related with present or past signatures of life on Mars as well as general mineralogical information for igneous, metamorphous, and sedimentary processes, especially water-related geo-processes. The T64000 Raman spectrometer triple monochromator with 30 mW and 632.8 (red) wavelength He-Ne laser by JobinYvon Horiba was used to investigate the pure phase of the samples as shown in Figure 3.8.

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Figure 3.7 Raman spectroscope

The morphology and particle sizes of as-obtained samples were determined by a Field emission-scanning electron microscope (SEM, JSM-6335F) operated at 15 kV accelerating voltage.

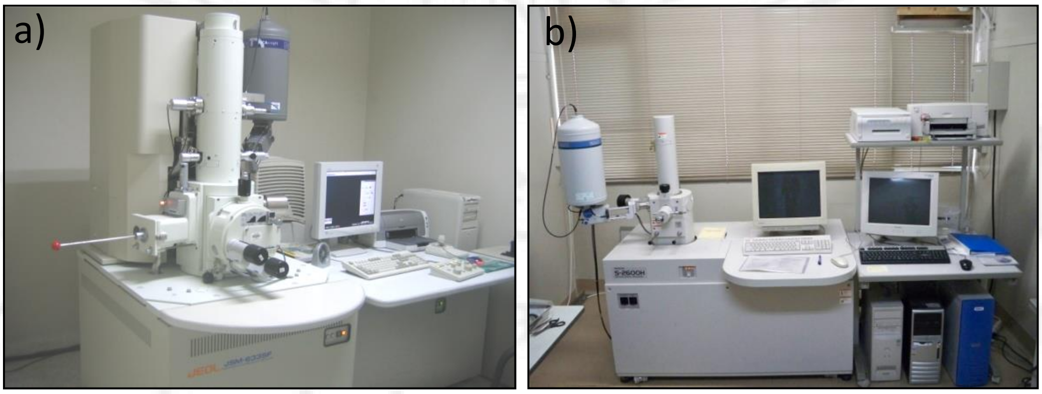

Figure 3.8 (a) Field emission-scanning electron microscope and (b) Scanning electron microscope.

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Transmission electron microscope (TEM, JEOL JEM-2010, Japan), high resolution transmission electron microscope (HRTEM) and selected area electron diffractometer (SAED) operating at 200 kV.The samples for TEM analysis were prepared by dispersing small amount of the powder in absolute ethanol and placing a drop of the solution onto a copper grid coated with holey carbon film and letting the ethanol evaporate slowly in air.

Figure 3.9 Transmission electron microscope

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The luminescence emission spectra of the samples were investigated using Perkin Elmer Luminescence Spectrometer LS50B (Figure 3.10) at room temperature.

Figure 3.10 Luminescence spectrometer

The transmission and absorption spectra of the samples were investigated using UV-Vis Spectrophotometer,model Lambda 19, Perkin Elmer (Figure 3.10) at room temperature.The optical property of the sample was studied using UV-Vis-NIR spectrophotometer with the aid of the following equations [95]:

$$(\alpha_{abs}h\nu) = A(h\nu - E_g)^n \qquad (3.1)$$

$$\alpha_{abs} = -(\log T)/t \qquad (3.2)$$

$$t = bC/d \qquad (3.3)$$

where α_{abs} is the total absorption coefficient, $h\nu$ is the photon energy, A is a constant, E_g is the indirect energy gap, $n = 1/2$ for the allowed direct transition, $n = 2$ for the allowed indirected transition, T is the transmittance of photon through the suspension in ethanol (concentration, $C = 0.001$ g/cm^3) containing in the cuvettes

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(spectroscopy cells) with the path length (*b*) of 10.00 mm, t is the effective thickness, and *d* is the density of sample. The curves of $(\alpha_{abs}\ h\nu)^2$vs$(h\nu)$ for direct allowed transition were plotted, and extrapolated to α_{abs} = 0.The absorption edge energies, corresponding to the energy gap of the samples.

Figure 3.11 UV-Vis Spectrophotometer.

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