CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Chemical reagents, equipments and instruments

3.1.1 Chemical reagents

1.) Copper powder, Cu, M.W. = 63.546 g/mol, purum, analytical grade, RdH

2.) Sulfur powder, S, M.W. = 32.066 g/mol, purum, analytical grade, M&B

3.) Zinc powder, Zn, M.W. = 65.39 g/mol, purum, analytical grade, RdH

4.) Antimony powder, Sb, M.W. = 121.76 g/mol, purum, analytical grade, M&B

5.) Aluminium powder, Al, M.W. = 26.98 g/mol, purum, analytical grade, M&B

6.) Argon gas, Ar, M.W. = 39.948 g/mol, >99.9%, TIG

7.) Poly(ethelene glycol), PEG, M.W ≈ 20,000 g/mol,analytical grade , Fluka

8.) Acetonitrile, CH_3CN, M.W. = 41.05 g/mol, 99.71%, Lab Scan

9.) Potassium iodide, KI, M.W. = 166.01 g/mol, purum, analytical grade, BDH

10.) Iodine, I_2, M.W. = 126.9 g/mol, purum, analytical grade, BDH

11.) Chloroplatinic acid, $H_2C_{l6}Pt$, M.W. = 409.8179 g/mol

12.) EosinY, $C_{20}H_8Br_4O_5$, M.W. = 647.92 g/mol, Sigma-Aldrich

13.) Copper sulfide powder, CuS, M.W. = 95.611 g/mol [11]

3.1.2 Equipments and instruments

1.) Vacuum Chamber
2.) Cooling system
3.) Microwave oven, Electrolux model 2820S
4.) Analytical balance, model BP-210S, Sartorius AG. Goettingen, Germany
5.) Diffusion pump: iLMVAC type DP 100/8 DM
6.) Rotary Vane pumps: EDWARDS, model RV12
7.) DC power supply: WELPRO , WELARC 200
8.) Active Invert Magnetron Gauge: BOC EDWARDS, AIM-X-NW25
9.) TIC Instrument Controller 3 head RS232/RS485
10.) Digital multimeter: FLUKE 8846A 6-1/2 digit precision multimeter
11.) Source measure units: KEITHLEY 236
12.) Gas flow meter: Cole Parmer scale 0-150

3.2 Synthesized methods

3.2.1 Synthesis of CuS via direct current heating

To produce CuS (hcp), 1:1 molar ratio of Cu:S (2 g dried powder each) was put in a bottle, mixed by rotation for 1 h at ambient temperature, loaded to fill a silica tube (11 mm I.D. × 10 mm long), and connected with two electrical stainless steel electrodes in a tightly closed chamber. Evacuation was done for removal of air to be 2×10^{-2} mbar absolute pressure, and argon was gradually fed into the chamber for replacement. Subsequently, argon in this chamber was evacuated to a constant absolute pressure of 2×10^{-4} mbar. To produce copper sulfide at the rapid rate, each solid mixture was heated by the direct flow of electricity (25 DC V and 20 A) through it for 1 s, 3 s and 5 s and left to cool down in the vacuum to room temperature (R_{temp}). A schematic diagram of the apparatus is shown in Figure 3.1 For the 1 s, 3 s, and 5 s heating samples. Finally, the products were intensively characterized to determine their phase, morphologies, vibrations and emissions.

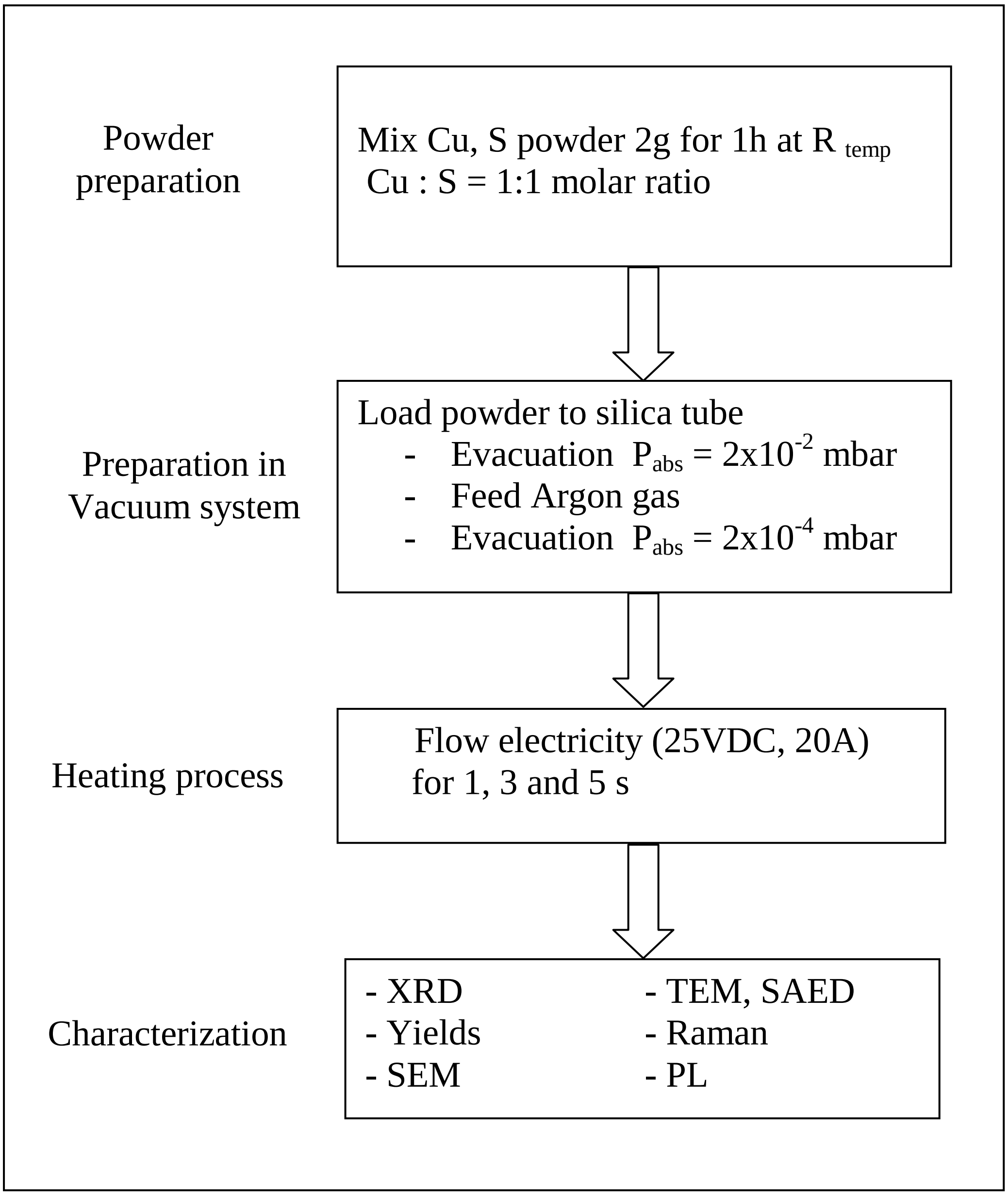

Figure 3.1 Schematic diagram used for preparation of CuS.

3.2.2 Synthesis of AlSb via direct current heating

To produce AlSb nanocrystals, 1:1 molar ratio of Al:Sb (total weight of 2 g dried powder) was put in a bottle, mixed by rotation for 1 h at room temperature. The analog gauge indicates force in one ton was used to press the powder for 1 min to form a short cylindrical rod, which was connected with two electrical stainless steel electrodes (Figure 3.3, 3.4) in a tightly closed chamber (Figure 3.5).

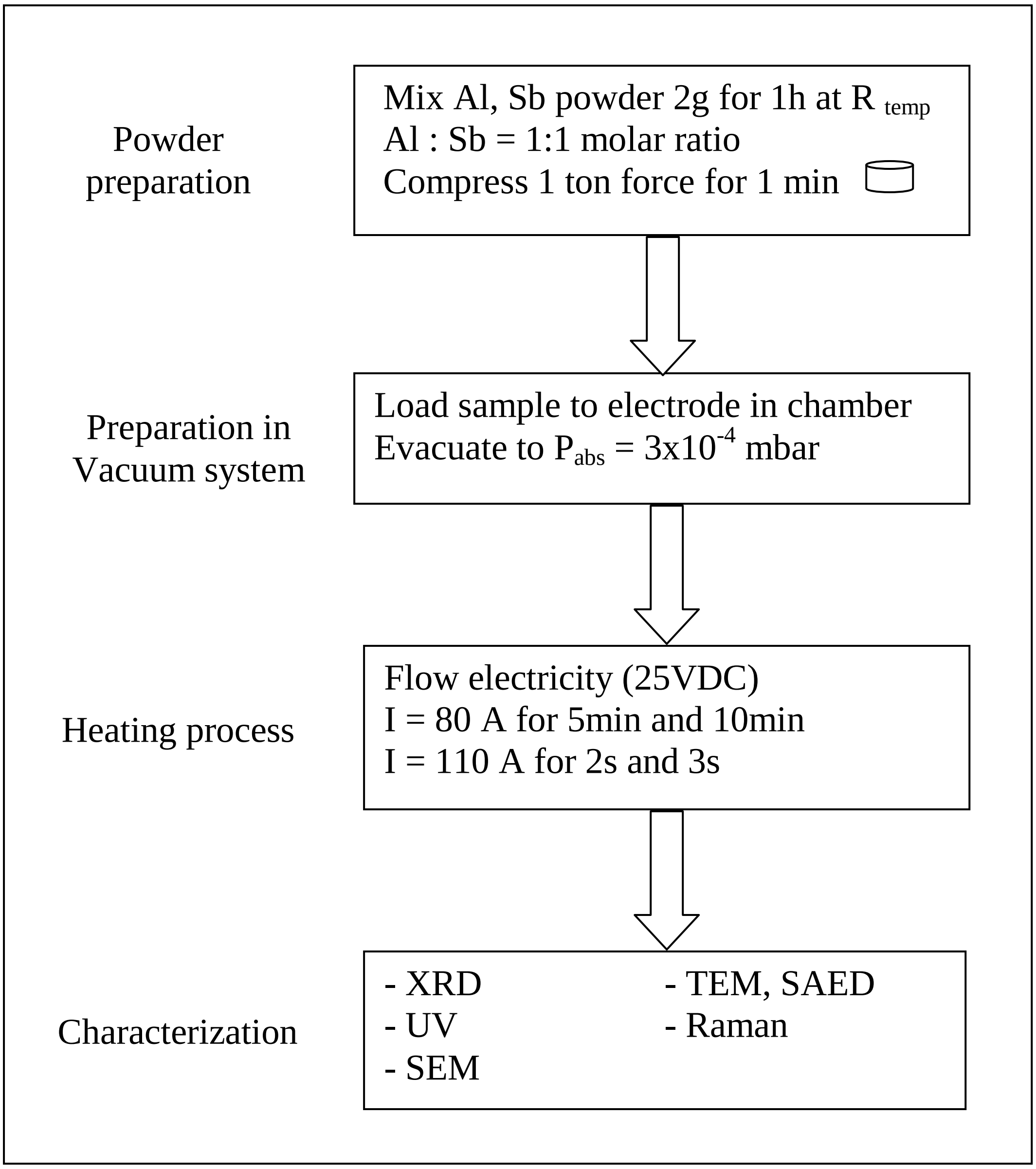

Figure 3.2 A schematic diagram of the apparatus.

Evacuation was done to achieve 3×10^{-4} mbar absolute pressure. Then each rod was heated by the direct flow of current using 25 DC V, under different conditions: A1 (80 A, 5 min), A2 (80 A, 10 min), A3 (110 A, 2 s) and A4 (110 A, 3 s), and left to cool down to room temperature. The phase, morphology, vibration modes, and optical property were further characterized.

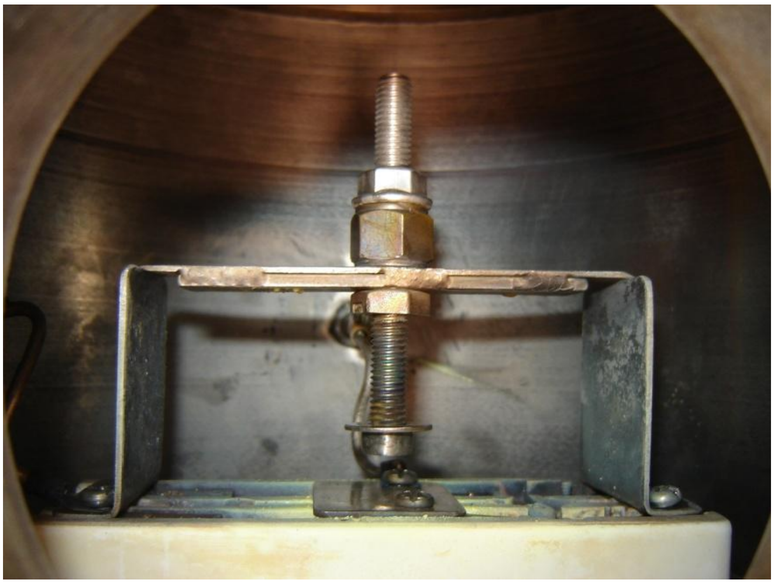

Figure 3.3 Photo of stainless steel electrodes.

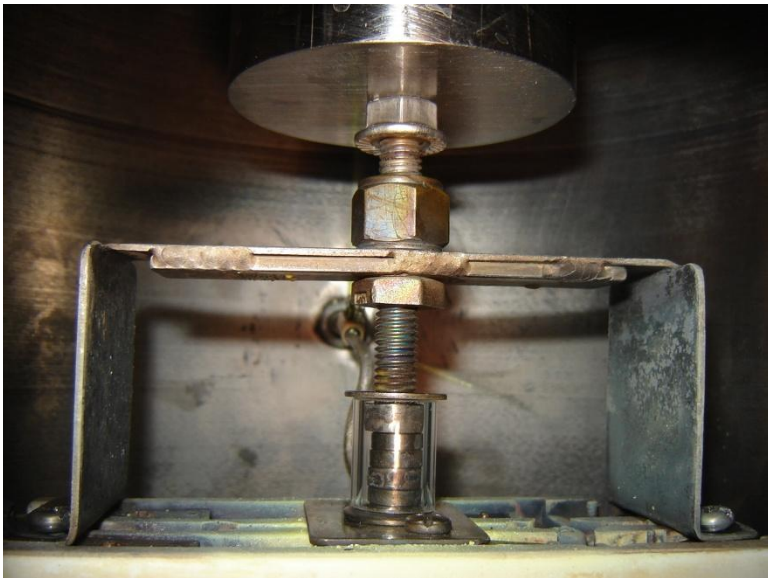

Figure 3.4 Photo of stainless steel electrodes contact with sample.

Figure 3.5 Vacuum and heating system image.

3.2.3 Preparation of quasi solid- state DSSCs

1.) Electrolyte preparation

The polymer electrolyte was prepared by adding 2.40 g of PEG (Mw ~20,000) to 30 ml of acetonitrile. 3.360 g of potassium iodide (KI) and 0.336 g of iodine were then added to the mixture under continuous stirring. Finally, copper sulfide nanoplate [11] was added. A total of four electrolyte solutions were made, with the CuS content varying from 0, 0.1, 0.3 and 0.5 wt.% of PEG electrolyte (Figure 3.6). The electrolytes were stirred continuously for 3h. All the electrolytes were stirred at room temperature to slow evaporate the solvent, up to the point that the final product had a gel-like character.

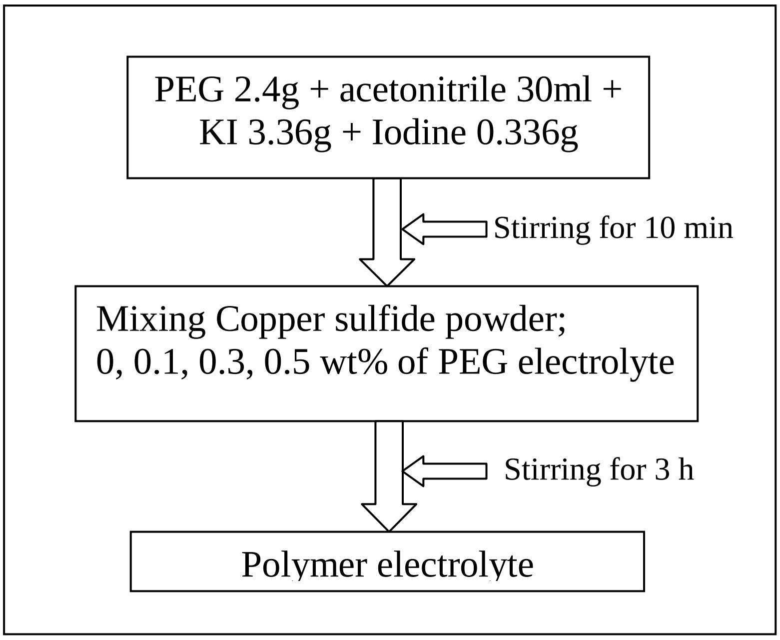

Figure 3.6 Preparation flow chart of electrolyte preparation.

2.) ZnO porous film synthesis and solar cell assembly

The fluorinated tin oxide glass (FTO) glass plate (1.5 cm x 2.5 cm , sheet resistance = 15-18 Ω/sq) was cleaned by acetone, dried by nitrogen blowing, and put in a quartz chamber containing 0.05 g Zn powder. Evacuation was done until the inside chamber was vacuum. The system was heated via microwave plasma for 5 min to produce porous Zn film on the FTO substrate, and followed by heating it in 21.2 mbar absolute air pressure for 3 min to produce porous ZnO film. To make the DSSCs the films were immersed in an ethanol solution contain 5 mM Eosin Y dye (2′,4′,5′,7′-tetrabromofluorescein), for 20 h at room temperature. Afterwards, the films were rinsed with ethanol and dried in air. Another FTO substrate was also coated with Pt on top. Then these two electrodes were composed to be a DSSC with different wt %

CuS-PEG electrolyte in between by the “Doctor Blade” technique, and sealed with silicone. The testing was done in a solar simulator (Xenon lamp) at AM 1.5 (100 mW/cm^2).

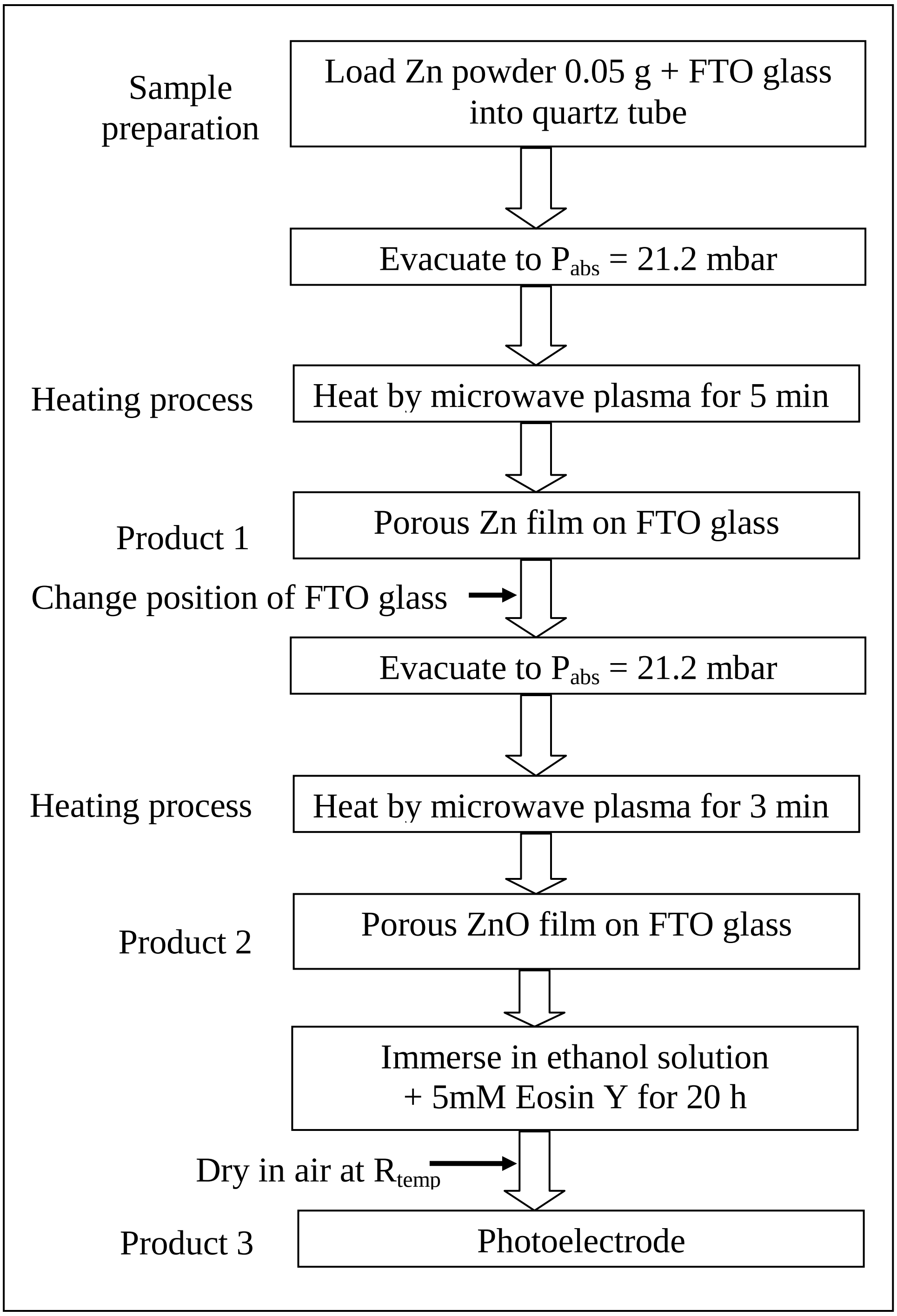

Figure 3.7 Preparation flow chart of ZnO photoelectrode.

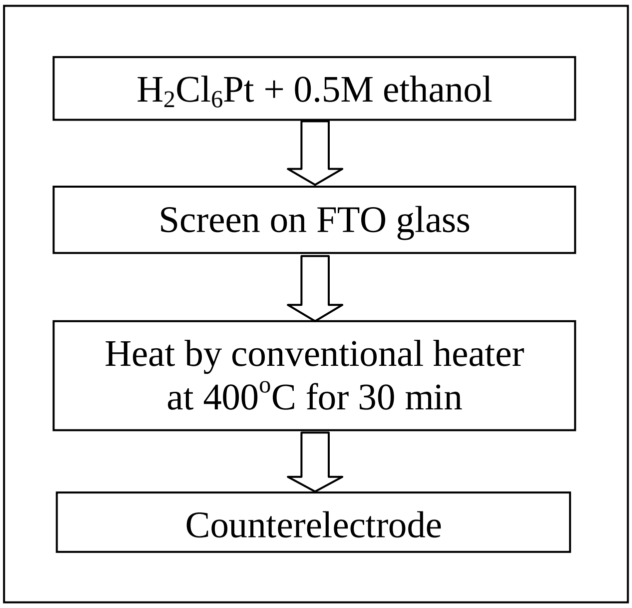

Figure 3.8 Preparation flow chart of Pt counterelectrode.

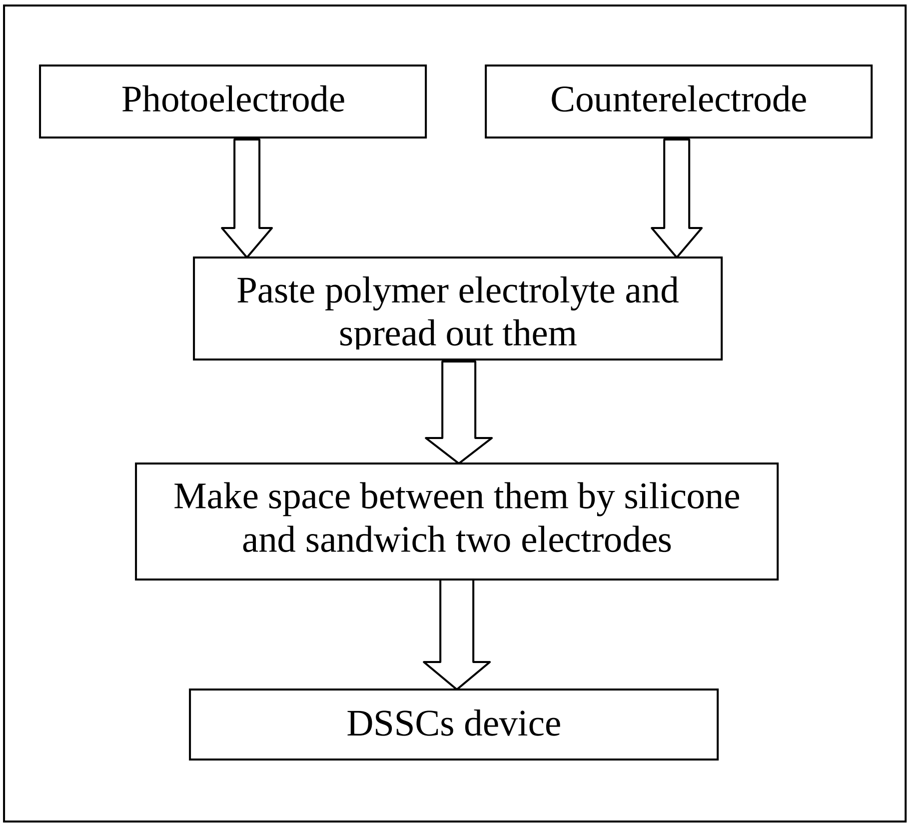

Figure 3.9 Preparation flow chart for fabrication of cell assembly.

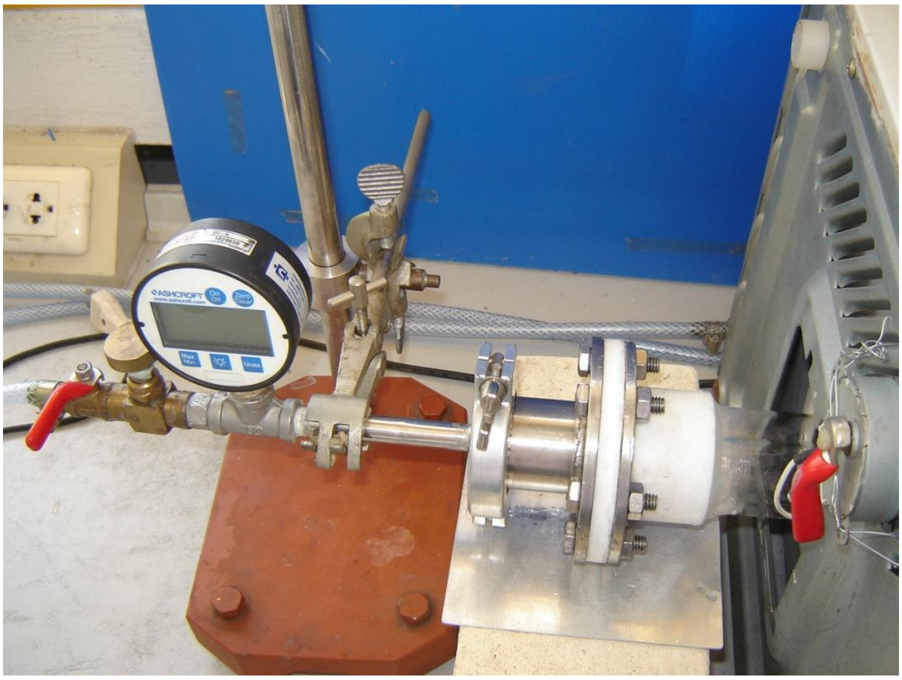

Figure 3.10 Pressure gauge of microwave plasma system.

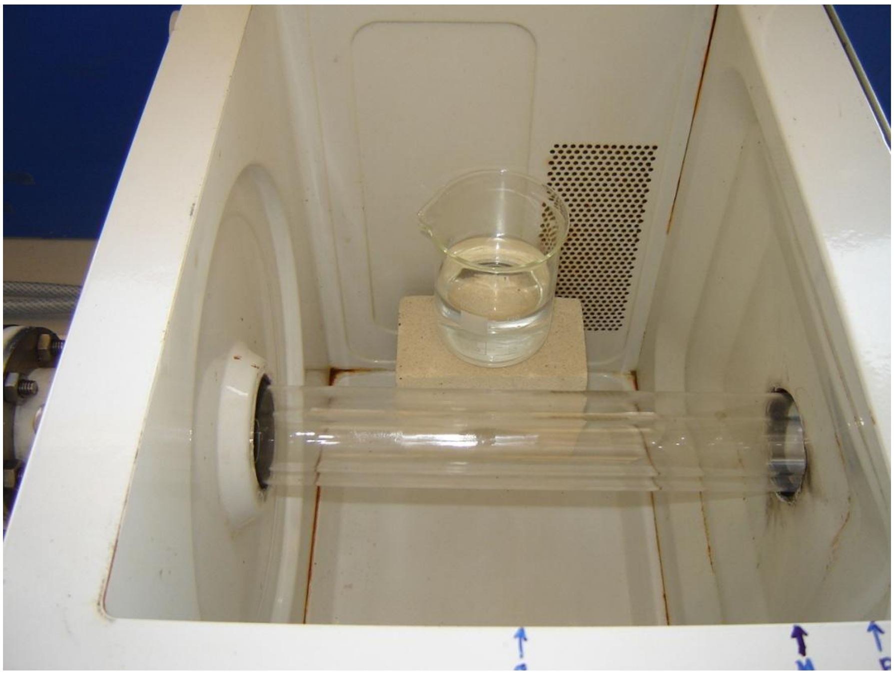

Figure 3.11 Position of quartz tube in the microwave oven.

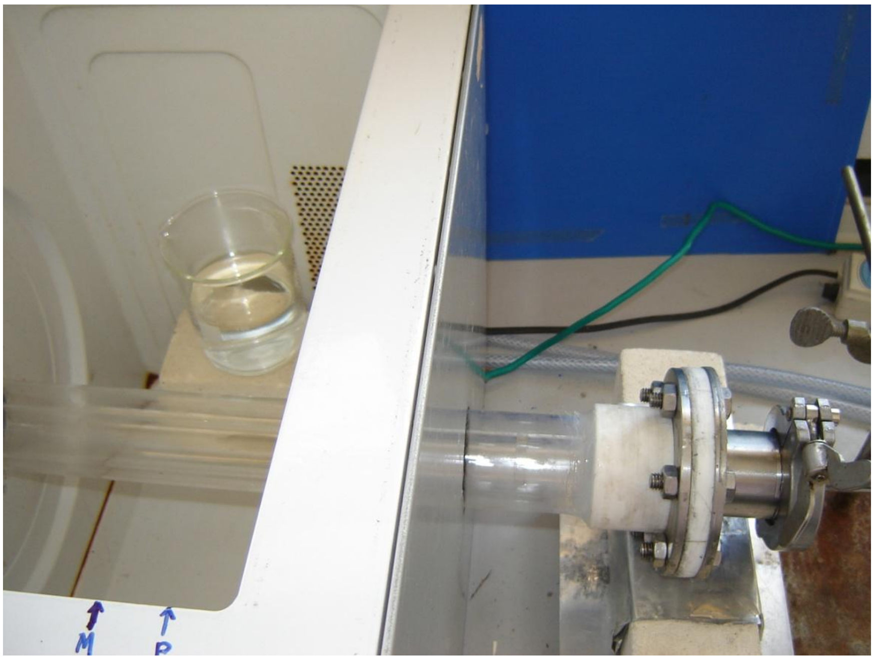

Figure 3.12 Junction of quartz tube and microwave oven.

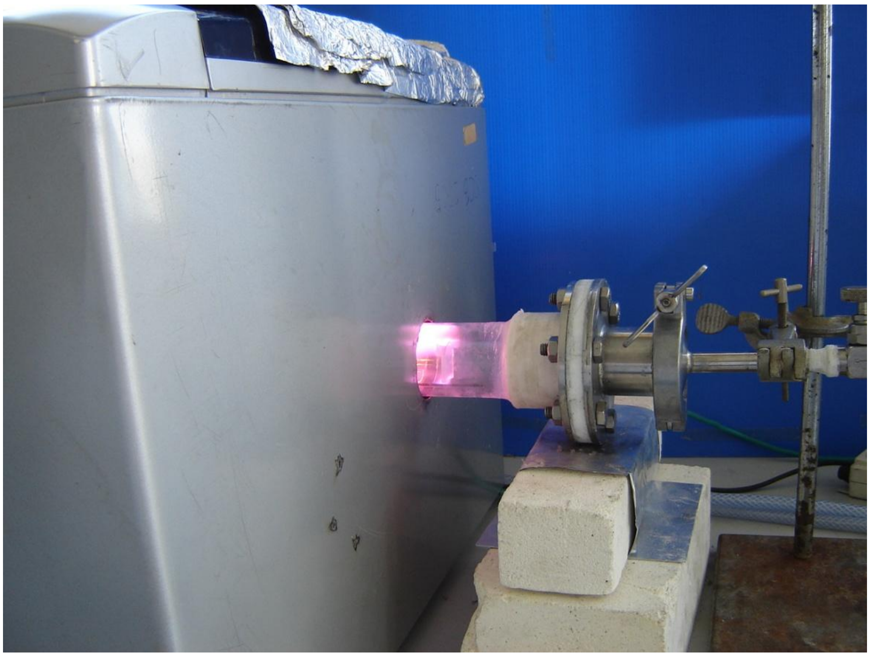

Figure 3.13 Microwave plasma as operated heating.

3.3 Characterization

3.3.1 X-ray diffraction (XRD)

The crystallinity and phase purity of the products were analyzed by using X-ray diffractometry (XRD) with Cu K_α radiation (λ = 1.5406 Å) operating at 20 kV, 15mA at a scanning rate of 0.04°/sec in the 2θ range of 10° - 120°(Figure 3.14). The identification of the products was assisted by Philips X'Pert Highscore Computer Software (search-match program) on the database of JCPDS software.

Figure 3.14 X-ray diffractometer.

3.3.2 Scanning electron microscope (SEM) and energy dispersive X-ray Spectroscopy

The morphology and particle sizes of as-obtained samples were determined by a Field emission-scanning electron microscope (FESEM, JSM-6335F) operated at 15 kV accelerating voltage. The chemical composition can be investigated by energy dispersive x-ray (EDX) analyzer equipped to SEM and controlled by Inca program used to determine the chemical composition.

Figure 3.15 Scanning electron microscope.

3.3.3 Transmission electron microscope (TEM)

The particle size and morphology was also observed by transmission electron microscope (TEM, JEOL JEM-2010) operating at 20 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 hole carbon film and letting the ethanol evaporate slowly in air.

Figure 3.16 Transmission electron microscope.

3.3.4 Raman spectrometer

HORIBA JOBIN YVON T64000 Raman spectrometer with 30 mW He-Ne laser with 632.8 nm (red) wavelength 50 mW and 514.5 nm (blue) wavelength Ar laser

Figure 3.17 Raman spectrometer.

3.3.5 Luminescence spectrometer

The luminescence emission spectra of the samples were investigated using Perkin Elmer Luminescence spectrometer LS50B at room temperature.

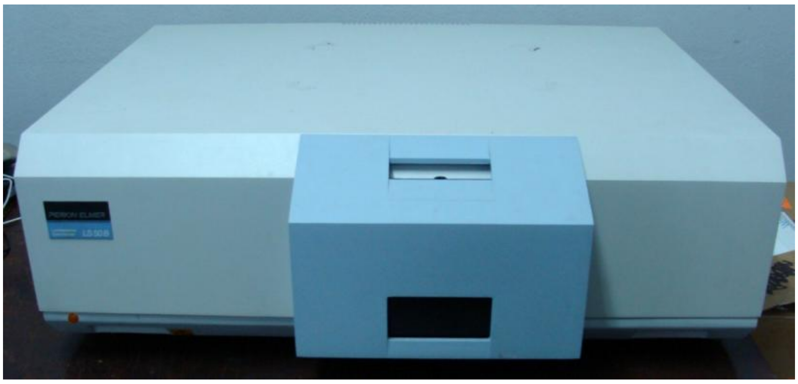

Figure 3.18 Luminescence spectrometer.

3.3.6 UV-Vis-NIR Spectrophotometer

The transmission and absorption spectra of the samples were investigated using UV-Vis-NIR Spectrophotometer, model Lambda 19, Perkin Elmer (Figure 3.19) at room temperature. The optical property of the sample was studied using UV-Vis-NIR spectrophotometer with the aid of the following equations [78, 79].

$$(\alpha h\nu) = B(h\nu - E_g)^n \tag{3.1}$$

$$\alpha = -(\log T)/t \tag{3.2}$$

$$t = bC/\rho \tag{3.3}$$

where α the total absorption coefficient, $h\nu$ the photon energy, B a constant, E_g the indirect energy gap; $n = 2$, for the allowed direct transition; $n = 1/2$, and for direct forbidden transition; $n = 3/2$, T the transmittance of photon through the suspension in ethanol (concentration, $C = 0.001$ g/cm^3) containing in the cuvettes (spectroscopy cells) with the path length ; b of 10 mm, t the effective thickness, and ρ the density of sample. The curves of $(\alpha h\nu)^2$ vs $(h\nu)$ for direct allowed transition were plotted, and extrapolated to $\alpha = 0$. The absorption edge energies, corresponding to the energy gap of the samples.

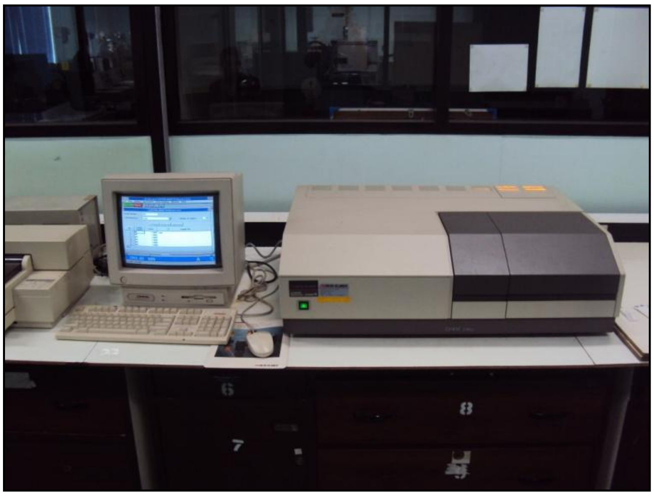

Figure 3.19 UV-Vis-NIR Spectrophotometer.