

## CHAPTER IV

### EXPERIMENTAL



This chapter discusses various material and method employed in this research. The experiments involved (i) preparation of  $\text{TiO}_2$  film and metal oxide dope  $\text{TiO}_2$  film, and measuring their characteristics. (ii) preparation of dye-sensitized solar cell components. (iii) assembled the DSSC by fit: the working electrode, the counter electrode and the electrolyte, and (iv) physical and electrochemical characterization.

#### 4.1 Preparation of $\text{TiO}_2$ film and metal oxide dope $\text{TiO}_2$ film

The preparation of the  $\text{TiO}_2$  film and metal oxide dope  $\text{TiO}_2$  film consisted of two steps: the preparation of  $\text{TiO}_2$  sol via sol gel method and the application of  $\text{TiO}_2$  sol onto electrode by ultrasonic spray coating.

##### 4.1.1 Preparation of $\text{TiO}_2$ sol

$\text{TiO}_2$  sol was prepared via a sol-gel method. A solution consisted of 14.44 ml of 70% nitric acid and 2000 ml of distilled water. Titanium (IV) isopropoxide in the amount of 166.80 ml was added slowly into the solution while being stirred continuously at room temperature. The mixture solution was stirred for 3-4 days until clean sol was obtained. Next, the clean sol underwent dialysis in a cellulose membrane. The distilled water used for dialysis was changed daily until a pH of 3.5 was obtained. And then,  $\text{TiO}_2$  sol was kept in a refrigerator until needed.

##### 4.1.2 Preparation of metal oxide dope $\text{TiO}_2$ sol

In this work, another oxide was added to  $\text{TiO}_2$  film. The metal oxide chosen for this study were  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , which were added to a  $\text{TiO}_2$  sol at concentrations of 0.25%, 1.0% and 2.0% (w/w).

#### 4.1.2.1 Preparation of $\text{Al}_2\text{O}_3/\text{TiO}_2$ sol

To prepare  $\text{Al}_2\text{O}_3$  sol, one mixed 2 g of aluminium iso-propoxide [AIP] in 44 ml of deionized water, which had been preheated to about  $90^\circ\text{C}$ . After the solution had been stirred thoroughly for one hour, 1.2 ml of 1 M HCl was added (the molar ratio of AIP : water : HCl is 1: 100: 0.05). Then the solution was stirred at  $90^\circ\text{C}$  for another hour. An almost transparent sol was.

To obtain 0.25%, 1.0% and 2.0% (w/w) of  $\text{Al}_2\text{O}_3/\text{TiO}_2$  mixture, one mixed 0.43 ml, 1.71 ml and 3.42 ml of  $\text{Al}_2\text{O}_3$  sol, respectively, with 80.44 ml, 79.84 ml and 79.03 ml of  $\text{TiO}_2$  sol, respectively. The solution was stirred until homogeneity was obtained. Then, the mixture solution underwent dialysis in a cellulose membrane until a pH of 3.5 was obtained.

#### 4.1.2.2 Preparation of $\text{MgO}/\text{TiO}_2$ sol

Preparation of  $\text{MgO}$  sol, this work mixed Magnesium nitrate hexahydrate  $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  and Oxalic acid  $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$  precursors in 1:1 molar ratio are first dissolved separately in ethanol and stirred to obtain two clear solutions.

To obtain 0.25%, 1.0% and 2.0% (w/w) of  $\text{MgO}/\text{TiO}_2$ , this work mixed 0.21 ml, 0.83 ml and 1.66 ml of magnesium sol with  $\text{TiO}_2$  sol with the volume of 80.44 ml, 79.84 ml and 79.03 ml respectively. The solution was stirred until homogeneity was obtained. Add then, the mixture solution underwent dialysis in a cellulose membrane until a pH 3.5 was obtained.

### 4.2 Preparation of dye-sensitized solar cell components and the fabrication procedure

The components of DSSC are mainly considered of transparent conducting glass, dye, electrolyte, counter electrode and anode electrode.

#### 4.2.1 Transparent conducting oxide glass

The conducting glass is transparent conducting oxide coated glass, which is the fluorine-doped tin oxide (FTO) coated on electrically conducting glass. The glass was purchased from Solaronix (Switzerland) under the commercial name TCO22-15. To identify the conducting side of fluorine doped tin oxide coated on glass, one used a multimeter to measure resistance. The conducting side would have a sheet resistance of ca. 15-20 ohm. The glass was cleaned with ethanol and dried with a hair-dryer.

#### 4.2.2 Dye sensitized

In this research, this work employed Cis-di(thiocyanate)bis(2,2'-bipyridine-4,4'-dicarboxylate)ruthenium (II) or N3 (R535) dye from Solaronix, which was widely used in dye-sensitized solar cell. To prepare the dye solution, 20 mg of N3 dye was dissolved in 100 ml of ethanol and the mixture was stirred until a homogeneous solution was obtained. The resulting product was a solution of 0.3 mM N3 dye in ethanol.

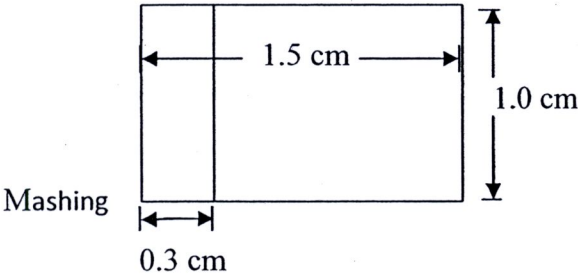
#### 4.2.3 Electrolyte

Electrolyte consisted of 0.5 M lithium iodine (LiI), 0.05 M iodide ( $I_2$ ), and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile, one mixed 2.00 g of LiI, 0.38 g of  $I_2$ , and 2.20 ml of TBP in 30 ml of acetonitrile. The solution was stirred until homogeneity was obtained.

#### 4.2.4 Counter electrode

The counter electrode for the DSSC was platinum coated on conducting glass. To prepare a platinum counter electrode by ion sputtering, one first cut a conducting glass to a rectangular piece that was  $1.0 \times 1.5 \text{ cm}^2$  in size. The glass was cleaned with ethanol and dried with a hair-dryer. Then, tape was placed on one side of the glass as seen in Figure 4.1. Wipe off any fingerprints using a tissue wet with ethanol. Then, platinum target was sputtering on the conducting glass using ion sputtering (JEOL



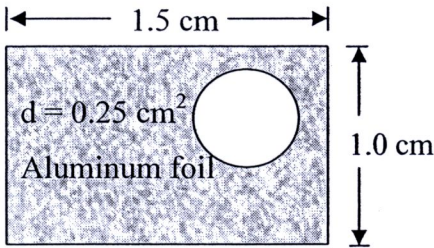


**Figure 4.1** The counter electrode before sputtering

JFC-1100E) at 10 mA of ion current for four minutes. After sputtering, masking tape was removed.

**4.2.5 Anode electrode**

Anode electrode consisted of  $\text{TiO}_2$  film or metal oxide dope  $\text{TiO}_2$  film on a conducting glass. To prepare the anode electrode, first we cut a conducting glass into a rectangular piece that was  $1.0 \times 1.5 \text{ cm}^2$ . The glass clean with ethanol and dry with a hair-dryer. Then the glass was masked with aluminum foil to a circle have radius 0.5 cm as seen in Figure 4.2. The cut out was located closer to one side of the foil than the other.



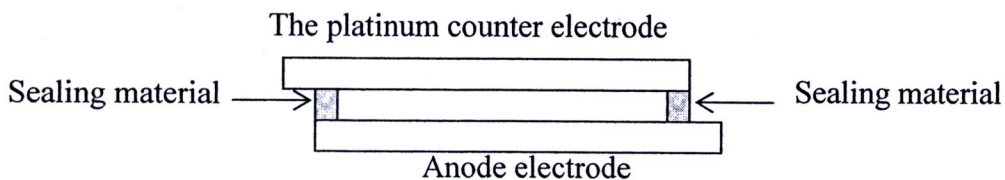
**Figure 4.2** The anode electrode before spray coating

After masking,  $\text{TiO}_2$  was coated on the conducting glass using ultrasonic spray coater. Stir well the  $\text{TiO}_2$  sol before use, not shake unless bubbles could be formed. The spraying liquid such as  $\text{TiO}_2$  sol was placed in a syringe pump, which fed the liquid at a rate 1 ml/min to an ultrasonic nozzle. The level speed of a moving stage was 4. The power of an ultrasonic nozzle, provided by a frequency generator until was 3.5 watts.

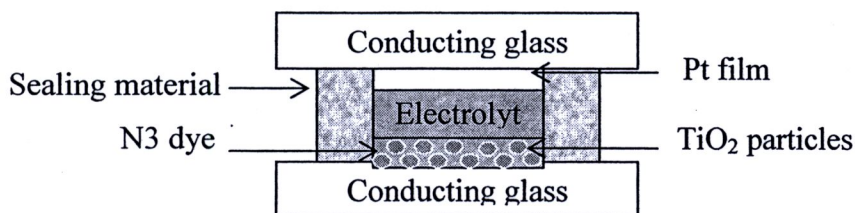
This study effect of modified  $\text{TiO}_2$  electrode then this work controlled the number of coats of  $\text{TiO}_2$  sol,  $\text{Al}_2\text{O}_3/\text{TiO}_2$  sol or  $\text{MgO}/\text{TiO}_2$  sol at 500 coats. After a few coats,  $\text{TiO}_2$  thin film was dried by a hair dryer. The thickness of film was measured using profilometer (Veeco Dektak 150). The anode electrode was sintered at  $400^\circ\text{C}$  for two hours. After anode electrodes was left to be cooled to  $30^\circ\text{C}$ . Before dye impregnation, we heat electrode on hotplate at  $70^\circ\text{C}$  for 10 minute, to avoid water absorption. Put slowly the anode electrode was immersed in a solution of 0.3 mM N3 dye for 12 hours in the dark. Then, the anode electrode rinsed with ethanol (The ethanol remove water from the porous  $\text{TiO}_2$ ) and dye with hair-dryer. Finally, the anode electrodes were assembled.

#### 4.3 Assembled and tested the DSSC

Assembly the two electrodes (counter and anode electrode), First this work cut two strips of a sealing material that were 0.15 cm wide and 1.2 cm long. The strips were inserted as spacer between the platinum counter electrode and anode electrode. The platinum counter electrode was placed on top of the anode electrode so that the conducting side of the counter electrode was on top of the  $\text{TiO}_2$  film. The cell was sealed by heating the sealing material with a hotplate at  $60^\circ\text{C}$  for 3 minute (see Figure 4.3)



**Figure 4.3** Cross-section of assembled dye solar cell showing sealing rim



**Figure 4.4** Fabrication of dye-sensitized solar cell assembly for testing

For electrolyte filling, in cell having a sealing rim with two small holes, the filling is done by putting a droplet onto only one hole, and let it soak up (see Figure 4.4), then clean carefully the area around the filling holes with acetone. The cell is ready for testing.

#### 4.4 Physical and electrochemical characterization

In this section discussed various techniques for physical and electrochemical properties of  $\text{TiO}_2$ , metal oxide dope  $\text{TiO}_2$  and dye sensitized, various characterization techniques were employed.

##### 4.4.1 X-ray diffractometry (XRD)

XRD was performed to determine crystal phase and crystallite size of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3/\text{TiO}_2$  and  $\text{MgO}/\text{TiO}_2$ . It was conducted using a SIEMENS D5000 X-ray diffractometer with  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.54439 \text{ \AA}$ ) with Ni filter. The spectra were scanned at a rate of  $0.04 \text{ min}^{-1}$  in the  $2\theta$  range of  $20-80^\circ$ .

##### 4.4.2 Nitrogen physisorption

To determine the specific surface area of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3/\text{TiO}_2$  and  $\text{MgO}/\text{TiO}_2$  were measured through nitrogen gas adsorption in a continuous flow method at liquid nitrogen temperature. A mixture of nitrogen and helium was employed as the carrier gas using Micromeritics ChemiSorb 2750 Pulse Chemisorption System instrument. The sample was thermally treated at  $200^\circ\text{C}$  for one hour before measurement.



#### 4.4.3 UV-Visible Absorption Spectroscopy (UV-Vis)

To determine the amount of dye adsorption was determined by a spectroscopic method by measuring the concentration of dye desorbed on the titania film into a mixed solution of 0.1M NaOH and ethanol (1:1 in volume fraction). The absorption spectra by UV-Vis Absorption Spectroscopy (Perkin Elmer Lambda 650,  $\lambda$  between 300-800 nm and step size 1 nm).

#### 4.4.4 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The amount of metal deposited on the surface of titanium dioxide ( $\text{TiO}_2$ ) was measured with an Optima 2100 DV spectrometer. The sample was solution, we dissolved 0.01 g of catalyst in 5 ml of 49% hydrofluoric acid (Merck) stirred until homogenous solution then the solution make to 100 ml with deionized water. The solution has concentration of 5 ppm ( $\text{mg}\cdot\text{l}^{-1}$ ) from the catalyst which was assumed to have metal content of 2.0 wt %.

#### 4.4.5 Zeta potential measurement

Zeta potential measurement were carried out on ZetaPlus (Malvern/Zetasizer), which uses the Doppler shift resulting from laser light scatter from the particles to obtain a mobility spectrum. A sample was suspended in deionized water and the pH of the suspension was adjusted using a 0.1M HCl and NaOH solution.

#### 4.4.6 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis of modified  $\text{TiO}_2$  was carried out in a Nicolet model 6700 of the IR spectrometer using the wavenumber ranging from 400-4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

#### 4.4.7 Current-Voltage Tester (I-V Tester)

The electrochemical properties of dye-sensitized solar cell were determined by I-V tester Current-Voltage measurements were performed using white light source under air mass (AM) 1.5G condition. To determine current density, open circuit voltage, cell resistance, and fill factor. This information was then converted to efficiency of the solar cell. An area of our solar cell was  $0.196 \text{ cm}^2$ . The equipment used was MV systems Inc., Xenon short ARC (Osram XBO 1000 W/HS).

The performance of each components is crucial and have been designated using the parameters: open-circuit voltage  $V_{oc}$ , fill factor FF and short circuit current density  $J_{sc}$  and expressed as efficiency ( $\eta$ ) using the equation:

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad (4.1)$$

and

$$FF = \frac{I_{max} V_{max}}{J_{sc} V_{oc}} \quad (4.2)$$

whereas ;  $V_{oc}$ , is the maximum voltage obtained at zero current

$J_{sc}$ , the shot circuit current is the maximum current obtained under less resistance (short circuit) condition

$P_{in}$  is the solar radiation intensity.

$I_{max}$  and  $V_{max}$  are the maximum current and maximum voltage, respectively