CHAPTER III
EXPERIMENTAL

3.1 Materials and Chemicals

1. Safflower, black rice and fresh noni leaves were purchased from a local market, Bfangkok, Thailand
2. Sappan wood were purchased from a traditional drug store in Singburi, Thailand
3. Fresh sunflower was purchased from Pak Khlong Market, Bangkok, Thailand
4. Commercial ZnO nanoparticles (ZoNoP®, 99.93% ZnO) was purchase from Nano Materials Technology Co., Ltd., in Thailand and used as received.
5. Thiophene monomer (≥ 99%) was purchased from Aldrich and used as received CAS No. 110-02-1
6. Acetylacetone (≥ 99.5%) was purchased from Fluka and used as received. CAS No. 123-54-6
7. Triton X-100 (laboratory grade) was purchased from Acros Organics and used as received. CAS No. 9002-93-1
8. Polyethylene glycol (PEG, MW 20,000) was purchased from Aldrich and used as received. CAS No. 25322-68-3
9. Lithium iodide beads (99%) was purchased from Aldrich and used as received. CAS No. 10377-51-2
10. Iodine was purchase from Suksapan panit, Thailand and used as received.
11. 4-tert-butyl pyridine (96%) was puschased from Aldrich. CAS No. 3978-81-2
12. Hydrogen Hexachloroplatinate (IV) Hydrate (~38% Pt basis) was purchased from Aldrich. CAS No. 26023-84-7

13. Lithium perchlorate (≥95.0%) was purchased from Sigma-Aldrich. CAS No. 7791-03-9
14. Absolute Ethanol (AR grade) was purchased from LAB-SCAN and used as received. CAS NO. 64-17-5
15. Acetonitrile (HPLC grade) was purchased from RCI Labsacn and used as received. CAS No. 75-05-8
16. Fluorine-doped SnO2 ({FTO) glass (sheet resistance of 8 Ω/cm^2) was purchased from Dyesol Company.

3.2 Instruments

1. Rotary Evaporator (Heidolph, WB2001)
2. Ultrasonic
3. Mechanical Stirrer (ALC, quiet-SL)
4. Potentiostat cyclic voltametry (PGSTAT101, Metrohm Netherlands)
5. X-ray Diffraction Microscope, XRD (Phillips, PW 1830/00)
6. Field Emission Scanning Electron Microscope, FE-SEM (HITACHI. S-4800)
7. Profilometer (Veeco Dektak 150)
8. UV-VIS spectrophotometer (SHIMADZU, UV-1800) for liquid sample
9. UV-VIS spectrophotometer (SHIMADZU, UV-2550) for solid sample
10. FTIR spectrometer (Thermo Nicolet, Nexus 670)
11. A digital Keithley 236 multimeter under an irradiation of white light from 1000 W/HS Xenon arc lamp

3.3 Experimental procedures

3.3.1 Preparation of natural dye sensitizers

Sappan wood, safflower, black rice, sunflower and noni leaves were cut into very small pieces and then extracted in water (sappan wood, safflower and black rice) or ethanol (sunflower and noni leaves) at room temperatue. Afterward, the solid residues were filtered out and the dye solutions were freeze-dried or evaporated. Finally, each extracted dye was dissolved in water (sappan wood, safflower and black rice) or ethanol (sunflower and noni leaves) to obtain concentration of 10 g/l before use.

3.3.2 Preparation of ZnO for doctor-blade methode

The pure ZnO paste was prepared by grinding 0.5 g of the commercial ZnO powder with 80 µl of acetylacetone, 40 µl of Triton X-100 and polyethylene glycol 0.25 g in 1.5 ml: 2 ml of water:ethanol before sonicated for 2 h.

3.3.3 Preparation of photoanode

3.3.3.1 Doctor-blade method

The prepared paste was spread on fluorine-doped SnO_2 (FTO) glasses with an area of 0.5 x 1.5 cm^2 by the doctor blading method and calcined at 500 °C for 1 h. to obtain the photoanode film. Then, the films were cooled to room temperature and drop 1 ml of natural dye solutions on the ZnO film at room temperature for 24 h. The excess dye molecules were washed out with water and ethanol. The ZnO photoanodes were keep in dry and dark container.

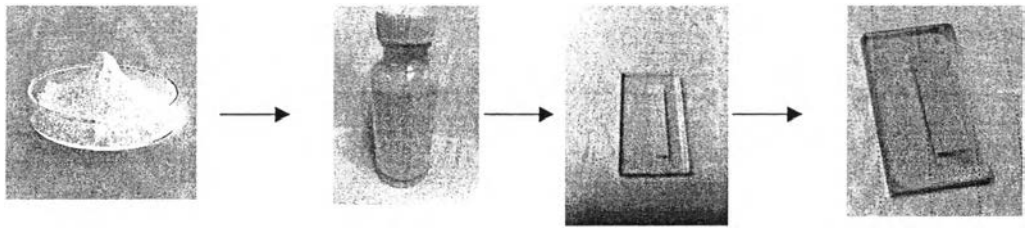

Figure 3.1 Preparation of ZnO photoanode (Doctor blade method).

3.3.3.2 Electrophoretic deposition (EPD)

A commercial nanocrystalline ZnO powder was dispersed well in ethanol (5 g/L) with 250 µl of acetylacetone and ultrasonicated for 2 h. After ultrasonication, the suspension was put in a container for electrophoresis. The electrophoretic cell contained two FTO glasses, one was used as the cathodic substrate and the second was used as anode. The distance between electrodes was 1 cm. The EPD was performed at a DC electric field. After EPD, the residual solvent on the as-deposited film was evaporated in air at ambient temperature and heated at 500 °C for 1 h in ambient conditions. The 1 ml of natural dye solution were dropped on the post heated electrodes in at room temperature and the excess dye molecules were washed out with water and ethanol and keep in dry and dark container.

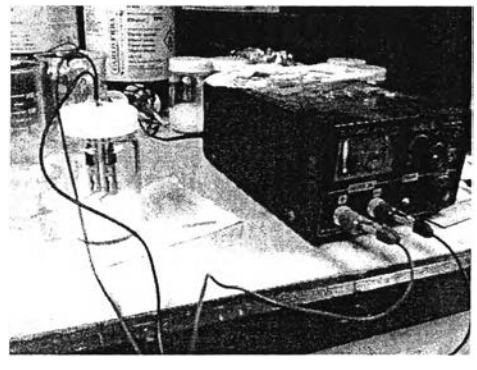

Figure 3.2 Preparation of ZnO photoanode (electrophoretic deposition).

3.3.3.3 Electropolymerization of thiophene

For the preparation of Polythiophene-ZnO electrode, the ZnO/FTO electrode as working electrode and Pt wire as counter electrode and Ag/Ag^{+} as reference were placed into thiophene (varied thiophene of 0.1 M, 0.2 M and 0.3M) and 0.2 M lithim perchlorate in acetonitrile. The thiophene was electropolymerized on the ZnO/FTO electrode under the potential of 3V with varied time of polymerization (1 min, 2 min and 5 min). Then, the polythiophene-ZnO coated the working electrode were

washed with acetonitrile to eliminate the un-reacted thiophene. The 1 ml of natural dye solution was dropped on the electrode at room temperature for 24 h.

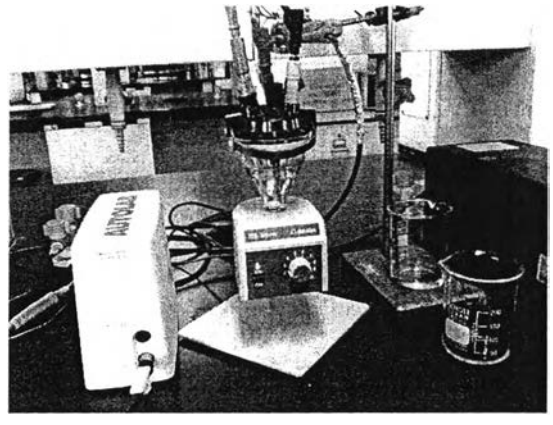

Figure 3.3 Electropolymerization of thiophene.

3.3.4 Cell assembly

To assemble the DSSC cells, the 127 μm-thick transparent parafilm® was used to make a narrow empty space inside the cell, by attaching around the four edges between the as-prepared semiconductor photoanode film and the Pt cathode film prepared from spreading 7 mM hexachloroplatinic acid in 2-propanol on FTO glasses by using doctor blade technique and calcining at 450 °C for 30 min. The electrolyte solution was composed of 0.025 M of iodine (I_2), 0.5 M of lithium iodide (LiI) and 0.2 M of *tert*-butyl pyridine that was dissolved in acetonitrile. Then, the electrolyte was injected to spread thoroughly in the as-prepared space between the two electrodes.

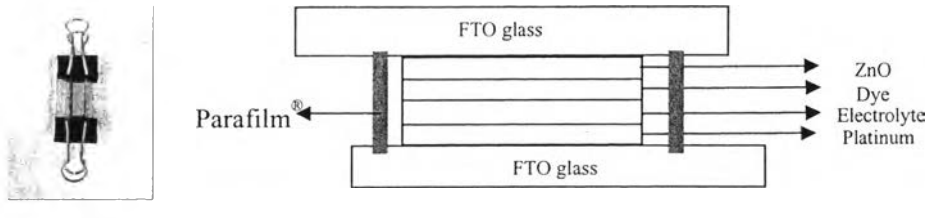

Figure 3.4 Cell assembly.

3.4 Characterizations

3.4.1 Physiochemical characterization

The crystal structure of the ZnO/FTO electrode (area 1cm x 1 cm) which was fabricated by doctor blading and electrophoretic deposition method were examined by X-ray diffractometer (XRD, Bruker AXS model Diffractrometer D8) with 2 theta (2θ) 20-60 degree.

The surface and cross-section morphologies of ZnO, ZnO/dye and ZnO/dye/polythiophene which were deposited on FTO glass were studied by field emission scanning electron microscope (FE-SEM, Hitachi S-4800) with 2k, 5k, 50k and 100k magnification.

The thicknesses of ZnO which were deposited on FTO glass were measured by using a profilometer (Veeco Dektak 150) with force 3 mg.

The optical absorption of extracted natural dyes (0.25 g/L) was measured by a UV-Visible spectrophotometer (Shimadzu Model UV-1800).

The optical absorption of ZnO and ZnO/dye (area 1.5cm x 2.5cm) which were deposited on FTO glass were measure by a UV-Visible spectrophotometer (UV-2550).

The FTIR spectra were recorded over a frequency range of 4000-400 cm^{-1} with 64 scan by using Nicolet Fourier transform infared spectrometer Nexus 670. The powdered samples were mixed with KBr and pressed in the form of pellets for analysis.

3.4.2 Photoelectrochemical measurement

The photovoltaic properties of the prepared DSSC, i.e. short circuit current (J_{sc}, mA/cm^2), open circuit voltage (V_{oc}, V), fill factor (FF) and efficiency (η, %) were determined from the I-V curve obtained by using a digital Keithley 236 multimeter under an irradiation of white light from 100 mW/cm^2 halogen-tungsten lamp. The active area of photoanode was 0.75 cm^2