CHAPTER III
EXPERIMENTAL

3.1 Materials and Chemicals

1. Red orchid was purchased from Pak-Khlong market, Bangkok, Thailand
2. Spirulina powder was purchased from Phu-Fah store, Jatujak market, Bangkok, Thailand
3. Indigo powder was purchased from Baan Tum-Tao, Sakonnakhon, Thailand.
4. Yellow cotton flower was collected from Nakhon Nayok, Thailand.
5. Commercial ZnO nanoparticles (ZoNoP®, 99.93% ZnO) was purchase from Nano Materials Technology Co., Ltd., in Thailand and used as received.
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. Acetonitrile (HPLC grade) was purchased from RCI Labsacn and used as received. CAS No. 75-05-8

15. Fluorine-doped SnO_2 ({FTO) glass (sheet resistance of 8 Ω/cm^2) was purchased from Dyesol Company.

3.2 Instruments

1. Ultrasonic
2. Mechanical Stirrer (ALC, quiet-SL)
3. X-ray Diffraction Microscope, XRD
4. Field Emission Scanning Electron Microscope, FE-SEM (JEOL, JSM-7001F)
5. UV-VIS spectrophotometer (SHIMADZU, UV-1800) for liquid sample
6. UV-VIS spectrophotometer (SHIMADZU, UV-2550) for solid sample
7. FTIR spectrometer (Thermo Nicolet, Nexus 670)
8. A digital Keithley 2400 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

Spirulina powder and indigo powder were used as received. Yellow cotton flower and red orchid were extracted using deionized water. Their solution was freeze and dried by freeze-drying process. Then solid sample were crushed and sieved before used. Finally, each dye powder was dissolved in water to obtain concentration of 10 g/l before used.

3.3.2 Preparation of ZnO for Doctor-blading Method

In order to prepare electrodes, the fluorine-doped SnO_2 (FTO) glass plates were washed with water and ethanol, respectively. The FTO-glass plates were fixed area by using transparent tape (size 1.0 cm x 1.0 cm). 1.0 g of ZnO nanoparticles was added into the 5.0 ml of PEG aqueous solution (0.1 g/ml) mixed with 0.1 ml of acetylacetone and 0.4 ml of triton X-100. The mixture was stirred for 1 day then it was extended onto the marked FTO-glass plates and calcined at 550 °C

for 1 h to obtain the photoanode film. Then 1 ml of natural dye solutions was dropped on the cooled ZnO film at room temperature for 24 h. The excess dye molecules were washed out with water.

3.3.3 Preparation of Pt Electrode

The Pt electrode was prepared by doctor blade method. The 7 mM of hexachloroplatinic acid in 2-propanol were dropped and spread on FTO-glass which was marked area by using transparent tape (size 0.5 cm x 1.5 cm). Finally, it was calcined at 450 °C for 30 min.

3.3.4 Fabrication of DSSC

In order to fabricate the DSSC, the 127 μm-thick transparent parafilm® was inserted between photoanode and cathode to prevent the short circuit current by attaching on four edges of photoanode film and the Pt electrode was covered on the top. The redox electrolyte solution contained with 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 in between two electrodes.

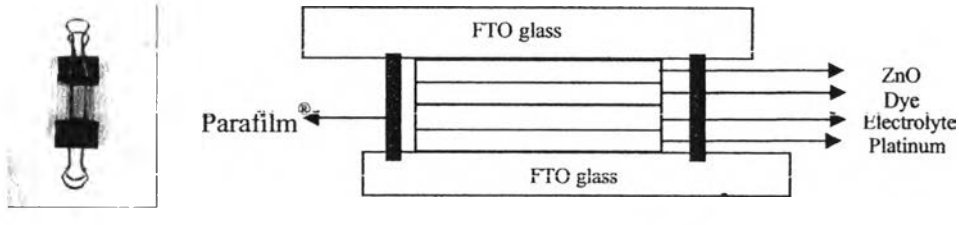

Figure 3.1 DSSC assembly.

3.3.5 Batch Adsorption Studies

For adsorption kinetics studies, dye solutions were prepared initial concentration at 100 mg/L with deionized water. 0.1 g of ZnO was used as absorbent. The concentrations of dye were monitored at different time intervals (from 60 to 600 min).

For adsorption isotherms, the different initial concentrations of dye in deionized water were prepared (10-1,000 mg/L). ZnO absorbent was immersed in

dye solution until equilibrium was reached. The concentrations of dye were determined at the maximum wavelength for each dye using UV-Visible spectrometer.

3.4 Characterizations

3.4.1 Physiochemical Characterization

The ZnO which was fabricated by doctor blading method and calcined at 550 °C was examined by X-ray diffractometer (XRD) with 2 theta (2θ) 20-70 degree.

The optical absorption, kinetics and isothermal adsorption studies of natural dyes in deionized water (2.5 g/L) were measured by a UV-Visible spectrophotometer (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 functional groups of each dye were determined by FTIR spectra which were recorded over a frequency range of 4000-400 cm^{-1} with 64 scan by using Nicolet Fourier transform infrared spectrometer Nexus 670. The powdered samples were mixed with KBr and pressed in the form of pellets for analysis.

The surface and cross-section morphologies of ZnO and ZnO/QDs which were deposited on FTO glass were studied by field emission scanning electron microscope (FE-SEM).

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 2400 multimeter under an irradiation of white light from 100 mW/cm^2 halogen-tungsten lamp. The active area of photoanode was 1.00 cm^2.