



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Dyes

Fresh red cabbage, dried rosella, and fresh blue pea were bought from fresh market. Ru(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)<sub>2</sub> (Z907) was kindly given from Laboratory for Photonics and Interfaces, EPFL. Methanol (analytical reagent grade) and absolute ethanol were purchased from RCI-Labscan Ltd.

#### 3.1.2 P25 TiO<sub>2</sub>/Bentonite Paste and Sol-Gel TiO<sub>2</sub>/Bentonite Paste

Commercial P25, titanium dioxide was from Degussa. Na-bentonite was kindly supplied from Thai Nippon Chemical Industry Co., Ltd. Acetylacetone and polyethylene glycol (PEG (MW. 10,000 and MW. 20,000)) were from Fluka. Cetyltrimethylammoniumbromide (CTAB) 99+%, acetylacetone 99.3% and triton® X-100 were from ACROS, and absolute ethanol was from RCI-Labscan Ltd. Diisopropoxytitanium bis(acetylacetonate) Ti(acac)<sub>2</sub>OiPr<sub>2</sub>, 75 wt.% was from Aldrich. Hydrochloric acid, 37% was from Carlo Erba. Nitric acid, 65% was from RCI-Labscan Ltd.

#### 3.1.3 Electrolyte

Potassium iodide and iodine was from Suksapan panish, Thailand. Lithium iodide beads, 99%, 4-tert-butylpyridine, 96%, 1-butyl-3-methylimidazolium iodide, 99%, 3-Methoxypropionitrile,  $\geq 98.0\%$  were from Aldrich. Acetonitrile HPLC was from Loba Chemie. Ethylene glycol, Pure P.A. was from Poch. Guanidine thiocyanate, 99% and valeronitrile, 98% were from ACROS. Z646, Z655, Z959, and sulfolane electrolyte were from Laboratory for Photonics and Interfaces, EPFL.

#### 3.1.4 Additive

4-(chloromethyl) benzoylchloride, 97% and 4-chloro-2,5 difluorobenzoic acid, 98% were from Aldrich.

#### 3.1.4 Counter Electrode and Conductive Glass

Chloroplatinic acid hydrate ~38% Pt-basis were from Sigma-Aldrich. Isopropanol was from RCI-Labscan Ltd.

#### 3.1.5 Polymethyl Acrylate

Methyl acrylate monomer,  $\geq 95\%$  was from Merck, and Potassium peroxodisulphate,  $\geq 98\%$  was from Fluka.

#### 3.1.6 Gelator

CTAB-modified Na-bentonite was from our lab (Muksing *et al.*, 2008, and Muksing, 2011), Laponite RD was from Rockwood Additives Ltd., and Purified Na-Bentonite was from our lab (3.22)

### 3.2 Experimental Procedures

#### 3.2.1 Preparation of Natural Dye Sensitizers

Fresh red cabbage, dried rosella, and fresh blue pea were cut into very small pieces and then extracted in a methanol/water mixed solvent at room temperature. Afterward, the solid residues were filtered out. Then, the dye solutions were concentrated by a rotary evaporator at 50°C and finally stored at 4°C before use.

#### 3.2.2 Na-Bentonite Purification

RO water with 30 times by weight was used to swell raw Na-bentonite under vigorous stirring for 12 h. The swollen Na-bentonite, which its main composition is shown in Table 3.1, was centrifuged at 10,000 rpm for 10 min. The supernatant containing highly dispersed swollen Na-bentonite was collected, dried,

and grinded in mortar. Its CEC is 67.5 meq/100g clay calculated from methylene blue testing (Chiappone *et al.*, 2004, Muksing, 2011).

### 3.2.3 Preparation of P25 TiO<sub>2</sub> and P25 TiO<sub>2</sub>/Bentonite Pastes

The pure TiO<sub>2</sub> paste was prepared by grinding 1 g of the commercial P25 TiO<sub>2</sub> powder with 0.1 ml of acetylacetone, 0.4 ml of Triton X-100, and polyethylene glycol in a mixture of water and ethanol before sonicated for 4 h. In the case of TiO<sub>2</sub>/clay paste, the TiO<sub>2</sub> powder was homogeneously mixed with the purified Na-bentonite with the Ti:Si molar ratios of 95:5 and 90:10, and also mixed with the Na-bentonite, initially modified by a method described in our previous work (Muksing *et al.*, 2008, and Muksing, 2011), with the Ti:Si molar ratios of 95:5, 90:10, and 85:15. Then the paste was prepared by the same method as the pure P25 TiO<sub>2</sub> paste.

### 3.3.4 Preparation of Sol-Gel TiO<sub>2</sub> and Sol-Gel TiO<sub>2</sub>/Bentonite

TiO<sub>2</sub> sol was prepared from diisopropoxytitanate bis(acetylacetonate) hydrolyzed with water at a molar ratio of 1:30 at 70°C until the solution became transparent. Then, polyethylene glycol was added into the sol. The purified Na-bentonite was swollen in RO water with 40 times by weight for 12 h before Na-exchanged with TiO<sub>2</sub> sol at 50°C for 6 h. The Ti:Si molar ratio of the purified Na-bentonite mixture was kept at 95:5, 90:10, and 80:20. Then, the gel was formed at 80°C.

### 3.2.5 Preparation of Photoanodes

The prepared paste or gel was spread on fluorine-doped SnO<sub>2</sub> (FTO) glasses (sheet resistance of 15 Ω/cm<sup>2</sup>) with an area of 0.5 × 2.0 cm<sup>2</sup> by the doctor blading method and calcined to obtain the photoanode film. All of the investigated electrodes are as follows:

- P25 TiO<sub>2</sub>/5 mol% Si CTAB-modified bentonite
- P25 TiO<sub>2</sub>/10 mol% Si CTAB-modified bentonite
- P25 TiO<sub>2</sub>/15 mol% Si CTAB-modified bentonite

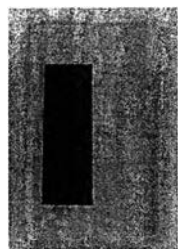
- P25 TiO<sub>2</sub>/5 mol% Si purified Na-bentonite
- P25 TiO<sub>2</sub>/10 mol% Si purified Na-bentonite
- Sol-gel TiO<sub>2</sub>/5 mol% Si purified Na-bentonite
- Sol-gel TiO<sub>2</sub>/10 mol% Si purified Na-bentonite

After calcination, the films were cooled to room temperature and then immersed into each of natural dye solutions for at least 20 h at room temperature, and the excess dye molecules were wash out with methanol. The films were dried in vacuum. Finally, the anode films (Figure 3.1) were obtained and kept in dark.

To investigate the effect of light scattering using UV-vis, TiO<sub>2</sub> films were calcined at 400°C for 10 min before overcoated with a light scattering layer, containing 5 or 10 mol% Si purified Na-bentonite.

**Table 3.1** Main compositions of bentonite

Compound	Content (wt.%)
SiO <sub>2</sub>	78.48
Al <sub>2</sub> O <sub>3</sub>	16.41
K <sub>2</sub> O	0.549
MgO	1.675
CaO	0.111
TiO <sub>2</sub>	0.307
MnO <sub>2</sub>	0.034
Fe <sub>2</sub> O <sub>3</sub>	2.403
ZnO	0.03



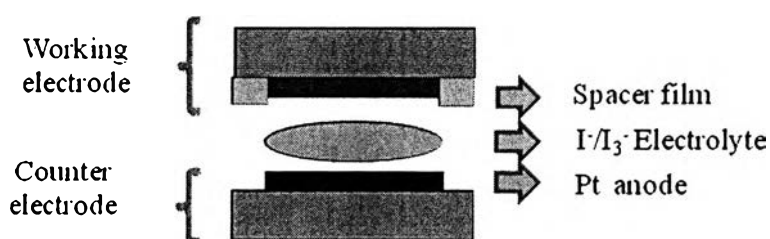
**Figure 3.1** The photoanode film.

### 3.2.6 Addition of Additive

To investigate the effect of adding 4-chloro-2,5-difluorobenzoic acid and 4-(chloromethyl)benzoyl chloride on the DSSC efficiency, the calcined P25 and P25/clay films were immersed into a 0.05 M methanol solution of these additives for 6 h at 60°C before immersed into the dye solution.

### 3.2.7 Cell Assembly

To assemble the DSSC cells (Figure 3.2), the 80  $\mu\text{m}$ -thick transparent sticker film 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 the spin-coating technique and calcining at 400°C for 15 min. The electrolyte was injected to spread thoroughly in the as-prepared space between the two electrodes.



**Figure 3.2** DSSC configuration.

### 3.3 Analytical Methods

The photoanodes were characterized using an X-ray diffractometer (XRD, Bruker Model-D8 Advance), a UV-visible spectrophotometer (UV-2550, Shimadzu), scanning electron microscopes (SEM and FE-SEM, JEOL JSM-6400 and Hitachi S4800, respectively) equipped by an energy dispersive X-ray analyzer (EDX), a Polarized optical microscope (POM, LEICA), and a BET surface area analyzer (Autosorb-1, Quantachrome). In addition, a step profile, Veeco Dektak 150 was used to measure film thickness.

The optical properties, rheological properties, and diffusion conductivity of gel electrolytes were investigated using a UV-vis spectrophotometer with integrating sphere, an Advanced Rheometric Expansion System (ARES) rheometer (Rheometrics Inc., Piscataway, NJ) with parallel-plate tool, and a potentiostat/galvanostat ( $\mu$ Autorlab type III/FRA 2).

The molecular weight of PMA was measured by using SHIMADZU GPC-RID10A with refractive index detector, and the morphologies of purified Na-bentonite aerogel/PMA composites were observed using FE-SEM (Hitachi S4800).

The photovoltaic properties of the prepared DSSCs, i.e. short circuit current ( $J_{sc}$ , mA/cm<sup>2</sup>), open circuit voltage ( $V_{oc}$ , V), fill factor (FF), and efficiency ( $\eta$ , %), were determined from the I–V curve obtained by using a digital Keithley 236 multimeter under an irradiation of white light from a 1000 W/HS Xenon arc lamp.