CHAPTER 7
SUMMARY AND OUTLOOK

This thesis reports on the fabrication of TiO$_2$-based and ZnO-based DSSCs which comprises of several steps: preparation of natural dye photosensitizer, synthesis and characterization of TiO$_2$ and ZnO nanoparticle, preparation of monolayer and bilayer TiO$_2$ or ZnO photoelectrode, preparation and performance measurement of DSSCs, and developing a novel approach to prepare ZnO photoelectrode by one-pot synthesis.

Selection of natural dye for DSSC sensitizer showed that anthocyanin dye, particularly cyanidin type, could generate better DSSC performance compared to DSSC sensitized with ternatin-anthocyanin dye and chlorophyll. The dye was extracted by using simple extraction method with ethanol and distilled water as the solvent. Carbonyl and hydroxyl groups in shorter chemical structure of cyanidin-antchoyanin dye (Figure 4.2b) are easy to bond with TiO$_2$ surface and generate higher efficiency by fast electron transport. The DSSC with cyanidin-anthocynain dye from mangosteen pericarp extract could generate conversion efficiency of 0.30% and high fill factor of 91.1% better than other employing ternatin-anthocyanin dye, i.e. Clitoria ternatea extract, that generates efficiency of 0.123% and fill factor of 77.3% (Table 4.1). The low conversion efficiency of DSSCs is ascribed to the weak stability of the dyes.

Synthesis and characterization of TiO$_2$ nanoparticles were conducted by using co-precipitation method. The synthesis involved TiCl$_3$ as starting chemicals. TGA curve of TiO$_2$ precipitate showed that the crystallization temperature of anatase TiO$_2$ was approximately at 375°C – 400°C. Widen peak of XRD pattern of synthesized TiO$_2$ (Figure 4.7) indicated the nanosize particle obtained. However, lower intensity of XRD peak implied to lower crystallinity of TiO$_2$ compared to commercial Degussa P25 and PA Merck (Figure 4.8). Raman spectra of TiO$_2$ nanoparticles indicated that energy level of anatase TiO$_2$ was higher than the rutile TiO$_2$ (Figure 4.10 & 4.11). BET test showed that high surface area of 113.03,
86.71, and 93.94 m²/g was obtained for anatase 1 (A₁, ± 67.11 nm), anatase 2 (A₂, ± 50.34 nm) and rutile (R, ± 80.88 nm). The BJH calculation presented the presence of mesopores and sub-micropores for the TiO₂ nanoparticles in the range of 3.04 – 3.745 nm. According to the low crystallinity, a study of retention time effect to the higher crystallinity of anatase TiO₂ without reducing the purity of the crystal phase is recommended.

Study of monolayer and bilayer TiO₂-based DSSCs were presented in Section 5.1. The dye sensitizers used are N719 dye and anthocyanin dye from mangosteen pericarp. DSSCs photoelectrode were monolayer (A₁, A₂, R) and bilayer (A₁A₂, A₁R and A₂R) TiO₂ which were coated to FTO glass using doctor blade technique with total active area of 0.25 cm². The photoelectrode were sensitized with N719 dye and anthocyanin dye for 5.5 hours and 12 hours, respectively. DSSCs were assembled using redox electrolyte I⁻I₃⁻ and Pt-catalyst counter electrode in sandwich structure.

Conversion efficiencies of 0.461% and 0.224% were achieved for DSSC using bilayer A₁A₂ and A₂R, respectively. Both efficiencies were much higher compared to that of monolayer anatase and rutile TiO₂ structure whose efficiencies in the range of 0.0189% to 0.0366% (Table 5.1). Similar result was obtained for DSSCs sensitized with N719 dye. Best performance of N719 dyed DSSC with conversion efficiency of 0.45% was generated by bilayer A₁A₂. However, bilayer A₂R was only able to produce conversion efficiency of 0.42%. The addition of rutile in bilayer structures could reduce the fill factor and open-circuit photovoltage of DSSCs. Among the fabricated DSSCs, all of bilayer DSSCs resulted higher peak of IPCE spectra in the wavelength range of visible light compared to monolayer DSSCs (Figure 5.3). These results reflected that the bilayer photoelectrode could enhance the light harvesting efficiency, i.e. extended optical path length, leading to higher conversion efficiency.

Fabrication of monolayer and bilayer ZnO-based DSSC were shown in Section 5.2. The monodisperse ZnO aggregates with average size of 423 nm exhibited high conversion efficiency of 0.421% and 0.568% for monolayer DSSC and bilayer DSSCs combined with smaller ZnO aggregates, respectively. High
photocurrent was obtained by enhancing IPCE spectra in visible light range (Figure 5.11). Overall, the monolayer and bilayer effect to the performance enhancement of DSSC was similar to the result of TiO$_2$-based DSSC. In accordance of conversion efficiency optimization, the effect of polydispersity to light harvesting efficiency is highly recommended for further study. In addition, sensitizing time of ZnO aggregate with Ru-based dye are also needed to be controlled to avoid the dissolution of Zn surface and the formation of Zn$^{2+}$ with dye complexes that might block the electron transport from the dye to ZnO layer.

A novel approach for ZnO photoelectrode preparation was conducted by using one-pot synthesis, i.e. dip coating, and hydrothermal growth (Chapter 6). The ZnO particles were synthesized in the form of nano spherical particles (SPs) and nanorods by using Zinc Acetate (ZnAc) dehydrate as the precursor and polyol (diethylene glycol and ethylene glycol) as the solvent. ZnO layer containing nano SPs are obtained in polydisperse and monodisperse by using the same method introduced in the Section 3.4.2. All of fabricated DSSC were sensitized with N719 dye. The DSSC with monodisperse ZnO nano SPs layer could produce high conversion efficiency of 1.827% by enhancing the light harvesting in both UV and visible light spectra. The DSSCs with ZnO nanorods layer also enlarged the photocurrent action spectra in visible light range and perform high conversion efficiency of 1.1% in average (Table 6.2) compared to DSSC with polydisperse ZnO nano SPs. This new method has been being promising to be developed. Nevertheless, several variables should be further studied since the reaction is quite difficult to be controlled. In order to maintain the ZnO photoelectrode in good contact on FTO substrate, the supernatant washing procedure is better to be conducted in several steps including pre heat treatment, evaporating, ethanol washing, and annealing.

Anthocyanin dye has comparable performance to N719-dye. This is indicated by the result in Table 4.1. Bilayer A$_1$A$_2$ could generate conversion efficiency of 0.461% and 0.45% for cyanidin - anthocyanin dye and N719-dye, respectively. However, another anthocyanin still has low efficiency low concentration dye since it is merely used simple extraction method. Thus, advance extraction method is suggested to obtain high concentration dye, i.e. soxhlet
extraction. Mixed dye is also proposed to enhance performance of DSSCs for further study.

Between TiO-based and ZnO-based DSSCs sensitized with N719, ZnO-based DSSCs has slightly higher performance. The best studied ZnO-based DSSC could generate 0.568% conversion efficiency by bilayer SP3-SP2 (see Table 5.2). The best studied TiO$_2$-based DSSC could only produce 0.4501% conversion efficiency by bilayer A$_1$A$_2$. Based on the result summary, TiO$_2$ nanoparticles could generate high photovoltage of DSSC and ZnO nanoparticles could generate high photocurrent. Thus, combination of ZnO and TiO$_2$ is possible to be further studied to obtain better DSSC performance compared to the result from this study.