



CHAPTER IV
PREPARATION AND APPLICATION OF
TITANIUMDIOXIDE/MODIFIED NATURAL CLAY
SEMICONDUCTOR AS A POTENTIAL ELECTRODE FOR
NATURAL DYE-SENSITIZED SOLAR CELL

4.1 Abstract

The TiO_2 /modified natural bentonite clay semiconductor, as a potential electrode of dye-sensitized solar cell, having a Ti:Si molar ratio of 85:15 was, for the first time, compared with the pure TiO_2 (commercial P25) electrode in terms of solar cell efficiency and characteristics. 4-chloro-2,5-difluorobenzoic acid and 4-(chloromethyl)benzoyl chloride were added to the electrodes to increase light harvesting ability of natural dyes extracted from red cabbage, rosella, and blue pea. The results showed that the TiO_2 /clay semiconductor provided a higher surface area but a slightly lower efficiency than the pure TiO_2 . The best natural sensitizer was found to be the dye extracted from red cabbage. Besides, the 4-(chloromethyl)benzoyl chloride provided a higher short circuit current for the TiO_2 /clay semiconductor.

Keywords: Modified natural bentonite clay; TiO_2 ; Dye-sensitized solar cell; Natural dye; Additive material

4.2 Introduction

Dye-sensitized solar cell (DSSC), a device converting light energy to electrical energy by imitating photosynthesis of plants [1], was firstly developed by Grätzel's group [2-4] and has widely known as a low-cost and easy-assembly solar cell, in which both synthetic and natural dyes can be used as a sensitizer. Electrical energy is generated when the cell is exposed to sunlight. Electrons in dye molecules

are excited and then injected to the conduction band of a wide-band gap n-type semiconductor (TiO_2 , ZnO_2 , etc.), on which the dye molecules adsorb. These electrons migrate through the host semiconductor particles until they reach the collector; also, the holes simultaneously generated are reduced by a redox electrolyte or hole carrier at the back electrode (Pt, graphite, etc.). Because of low material cost, simple preparation, and lack of heavy metals, natural dyes are more favorable to be applied in such device [5-8]. Thus, in this present work, three natural dye sensitizers extracted from red cabbage [8,9], rosella [10], and blue pea [10] were selected for use since they are indigenous in Thailand.

Recently, SiO_2 and Al_2O_3 have been applied as an energy barrier for suppression of charge recombination due to their insulation properties [11,12], which decrease the interaction between the photo-excited electrons in the semiconductor electrode and the electrolyte ions [13]. Moreover, synthetic nanoclay [14] was used to solidify a liquid electrolyte and induce a light scattering, which helps increasing the overall light absorption, especially in the red region [14-18]; however, the application of natural clay for the DSSCs has been scarcely reported. In the present work, natural Na-bentonite clay, which is abundantly available, was also applied for the DSSCs with the selected natural dyes. The Na-bentonite is an aluminosilicate mainly composed of montmorillonite with Na^+ as a dominant cation. Its particle size is less than 2 μm and its gap between two stacking platelet can significantly expand when being wet due to the fact that it can absorb water several times of its dry mass [19]. Montmorillonite is a member of the smectite family with 2 tetrahedral sheets sandwiching a central octahedral sheet in one platelet. There is a negative charge on the face of the clay platelet caused by structural substitutions or vacancies in the octahedral and/or tetrahedral layers [19]. For example, Mg^{2+} or other divalent cations may substitute Al^{3+} in the octahedral layer, or Al^{3+} or Fe^{3+} may replace Si^{4+} in the tetrahedral layer. Some cations, e.g. Na^+ and Ca^{2+} , are attracted to the spaces between the platelets due to the negative charge on the faces of the platelets and can be exchanged readily via a washing-modification technique. Chemically, it is identified as hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ [19]. Therefore, it is also believed to

function as energy barrier and the light scattering site in the DSSCs, owing to its inherent insulation property by aluminosilicate structure and its large platelet size, respectively.

Therefore, in this work, TiO₂/modified natural clay electrode having a Ti:Si molar ratio of 85:15 (modified bentonite clay content of ~20 wt.%) sensitized with the above mentioned natural dyes was, for the first time, compared with the commercial P25 TiO₂ electrode in terms of solar cell efficiency and semiconductor characteristics to verify the potential application of the natural clay for the DSSCs. Furthermore, to increase light harvesting ability of the studied natural dyes, some additives, i.e. 4-chloro-2,5-difluorobenzoic acid [20] and 4-(chloromethyl)benzoyl chloride, were also added to the electrodes in order to improve the interaction between the natural dyes and the electrode surface.

4.3 Experimental

4.3.1 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 (1:1 by volume) mixed solvent. 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.

4.3.2 Preparation of Photoanodes

The pure TiO₂ paste was prepared by mixing 1 g of the commercial P25 TiO₂ powder (Degussa) with 0.1 ml of acetylacetone, 0.4 ml of Triton X-100, and 0.2 g of polyethylene glycol (MW of 10,000) in 5 ml of a mixture of water and ethanol. In the case of TiO₂/clay paste, the Na-bentonite clay was initially modified by a method described in our previous work to have the main compositions of 78.5 wt.% SiO₂, 16.4 wt.% Al₂O₃, 2.4 wt.% Fe₂O₃, and 1.7 wt.% MgO [21], and the modified bentonite clay was then homogeneously mixed with the TiO₂ powder. The paste having a Ti:Si molar ratio of 85:15 (modified bentonite clay content of ~20 wt.%) was prepared by the same method as the pure TiO₂ paste. Afterwards, the paste

was spread on fluorine-doped SnO₂ (FTO) glasses (sheet resistance of 15 Ω/cm²) by the doctor blading method and calcined at 500°C for 2 h to obtain the photoanode film. Then, the calcined films were immersed into each of natural dye solutions.

To investigate the effect of adding 4-chloro-2,5-difluorobenzoic acid and 4-(chloromethyl)benzoyl chloride on the DSSCs efficiency, the calcined pure TiO₂ and TiO₂/clay films were immersed into a 0.5 M methanol solution of these additives for 6 h at 60°C before immersed into the dye solution.

4.3.3 Cell Assembly

To assemble the DSSCs, a 80 μm-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 7 mM hexachloroplatinic acid in 2-propanol by using a spin-coating technique. The electrolyte consisting of 0.5 M KI and 0.05 M I₂ in ethylene glycol [10] was dropped and spread thoroughly in the as-prepared space between the two electrodes.

4.3.4 Characterization and Measurement

The photoanodes were characterized by using an X-ray diffractometer (XRD, Bruker Model-D8 Advance), a UV-visible spectrophotometer (UV-2550, Shimadzu), a scanning electron microscope equipped by an energy dispersive X-ray analyzer (SEM-EDX, JEOL, JSM-6400), and a BET surface area analyzer (Autosorb-1, Quantachrome). The photovoltaic properties of the prepared DSSCs, i.e. short circuit current (J_{sc} , mA/cm²), open circuit voltage (V_{oc} , mV), 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 a 1000 W/HS Xenon arc lamp with a 100 mW/cm² light intensity, where the fill factor and efficiency were calculated based on the following equations:

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (4.1)$$

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (4.2)$$

where J_{max} is maximum power point current (mA/cm²), V_{max} is maximum power point voltage (V), and P_{in} is power of incident light (mW/cm²).

4.4 Results and Discussion

4.4.1 Photovoltaic Properties of DSSCs Sensitized with Different Natural Dyes

From the UV-visible analysis (Fig. 4.1), it was found that only the spectra of red cabbage and rosella dyes adsorbed on the photoanodes exhibited a red shift in both UV and visible regions, as compared to those in the corresponding dye solutions. This implies that these types of dye molecules were strongly bound to the oxide surface [7,8,10]. However, the spectrum of blue pea dye adsorbed on the photoanodes (Fig.4.1c) showed only red shift in UV region with much less absorbance in visible region, as also observed by Wongcharee *et al.* [10]. The results of the DSSCs shown in Table 4.1 reveal that from the overall consideration of the photovoltaic properties of both the pure TiO₂ and TiO₂/clay electrodes, the red cabbage dye provided the highest efficiency due to its high short circuit current and open circuit voltage. Meanwhile, the blue pea dye provided the highest fill factor but the lowest short circuit current since its absorption spectrum in range of 500-700 nm on both the TiO₂/clay and pure TiO₂ electrodes was not clearly observed (Fig. 4.1c). Therefore, among the three investigated natural dyes, the red cabbage dye is the most suitable to be applied for the DSSCs.

4.4.2 Characteristics and Photovoltaic Properties of Different Photoanodes

The XRD patterns of the pure TiO₂ and TiO₂/clay electrodes (Fig. 4.2) mainly show the mixed anatase and rutile phases, which are characteristic of the commercial P25 TiO₂. The presence of bentonite phase can be observed in the XRD pattern of the TiO₂/clay electrode (Fig 4.2a). Moreover, the SEM micrograph (top-viewed) and the corresponding EDX Si mapping of the TiO₂/clay electrode (Fig. 4.3a and b) show a uniform distribution of clay over the entire electrode in the form of Si, which is the main composition of the investigated clay. The high-resolution cross-sectional SEM micrograph (Fig. 4.3c) also shows a good dispersion of clay layers between the aggregated TiO₂ nanoparticles along the depth of the electrode. This implies that homogeneous mixing of the TiO₂ and clay can be easily achieved via the simple method used in this work.

Even though the specific surface area of the TiO₂/clay was found to be 61.8 m²/g, which is higher than that of the pure TiO₂ (50.8 m²/g) due to the effect of clay platelets on the sintering inhibition of TiO₂ particles, the efficiency of the TiO₂/clay electrodes were found to be somewhat lower compared to the TiO₂ electrodes (Table 4.1), but still acceptably high, typically regarding the use of natural dyes (not heavy metal-containing synthetic dyes) in the DSSCs. This reveals that the insulation property of the clay used in the TiO₂/clay electrode with the Ti:Si molar ratio of 85:15 played an important role on the DSSCs efficiency. However, a lower band gap energy after adding the clay in the TiO₂/clay electrode (i.e. 3.23 eV of pure TiO₂ and 3.00 eV of TiO₂/clay) might lead to a lower open circuit voltage of the TiO₂/clay electrode [13]. Although the effect of clay on lowering short circuit current seems to be obvious, the clay effect as an energy barrier to prevent the photoinduced charge recombination was not quite evident since the clay insulating phenomenon could be significant due to its well distribution (Fig. 4.3). In addition, the doctor blading method, which is commonly used to prepare the semiconductor electrode film for the DSSCs, only provided a moderate contact between the TiO₂/SiO₂ materials and the conducting FTO glass [13]. Hence, other methods that allow a better contact between the TiO₂/clay mixture and the FTO glass, such as spin-coating

and electrodepositing, are of great interest for our future work to prepare the TiO₂/clay film on the conducting glass.

4.4.3 Photovoltaic Properties of DSSC with Additives

To investigate the effect of additives, the red cabbage dye was selected as a sensitizer for the TiO₂/clay electrode due to its superior performance for the DSSCs, as above mentioned. When comparing with the case without additives, the UV-visible spectra of the dye adsorbed on the photoanodes with these additives shifted to the blue region (blue shift) by about 10 nm. These imply that these additives interacted with the red cabbage dye molecules. The comparative DSSCs results (Table 4.2) indicate that for the TiO₂/clay electrode, the benzoyl chloride aided to increase the short circuit current, with decreases in the open circuit voltage and fill factor; whereas, the benzoic acid aided to increase the open circuit voltage, with a decrease in the short circuit current.

Kang et al. [22] proposed that the influence of additives on the open circuit voltage and short circuit current was due to an alteration of the flat band potential of the TiO₂ electrode. The adsorption of additives with high donor groups on the TiO₂ surface may raise the flat band potential of the TiO₂ electrode [23]. In the present work, the benzoic acid adsorbed on the TiO₂ surface possessed a donor group (a negatively-charged carboxyl group when dissociated), thus resulting in an observed higher open circuit voltage (Table 4.2). On the other hand, the adsorption of positively-charged species onto the TiO₂ surface may lead to the potential drop in the Helmholtz layer, which depends on the types of adsorbed species. This potential drop normally increases with decreasing radius of positively-charged species and causes a positive shift in the conduction band level of the TiO₂ [24]. The adsorption of the benzoyl chloride (with a positively-charged carbonyl group when dissociated) in this present work depressed the open circuit voltage, but caused an increase in the short circuit current (Table 4.2) possibly due to its electron-withdrawing property. However, since the overall DSSCs efficiency was not significantly changed, the additive that could provide a higher short circuit current (benzoyl chloride) is

preferentially required, being more advantageous for a real application with an external load due to a higher electron flow.

In summary, although the TiO₂/clay electrode with the Ti:Si molar ratio of 85:15 (clay content of ~20 wt.%) showed a lower DSSC efficiency than the pure TiO₂ electrode, the possibility to replace a part of TiO₂ by the abundantly available and cost-effective natural clay may be proposed, thus greatly reducing the cost of TiO₂ used. Moreover, a suitable additive, which aided to increase the short circuit current, was identified. The ways to improve the DSSCs efficiency of the TiO₂/clay electrode need to be examined in the future studies by optimizing Ti:Si molar ratio and adjusting preparation method of the electrode semiconductor.

4.5 Conclusions

In this work, the TiO₂/modified bentonite clay electrode having the Ti:Si molar ratio of 85:15 was, for the first time, used as a potential electrode of the DSSCs. The red cabbage dye was found to be the best sensitizer for the DSSCs fabricated with TiO₂/clay electrode. Although the TiO₂/clay electrode provided a lower DSSC efficiency than the pure TiO₂ electrode, there is still the possibility to replace a part of TiO₂ by the naturally low-cost clay. Moreover, 4-(chloromethyl)benzoyl chloride aided to increase the short circuit current of the DSSCs fabricated with the TiO₂/clay electrode.

4.6 Acknowledgments

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4.7 References

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Table 4.1 Effect of natural dye sensitizers on photovoltaic properties of DSSCs fabricated with different photoanodes

Photoanode	Type of dyes	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	η (%)
100% TiO ₂	Red cabbage	0.35	540	0.65	0.13
	Rosella	0.29	420	0.61	0.07
	Blue pea	0.27	490	0.76	0.10
TiO ₂ /clay	Red cabbage	0.19	510	0.60	0.05
	Rosella	0.16	450	0.64	0.05
	Blue pea	0.14	460	0.69	0.04

Table 4.2 Effect of additives on photovoltaic properties of DSSCs fabricated with TiO₂/clay electrode and sensitized with red cabbage dye

Photoanode	Type of additives	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	η (%)
TiO ₂ /clay	None	0.19	510	0.60	0.05
	Benzoic acid	0.16	550	0.60	0.05
	Benzoyl chloride	0.21	470	0.52	0.05

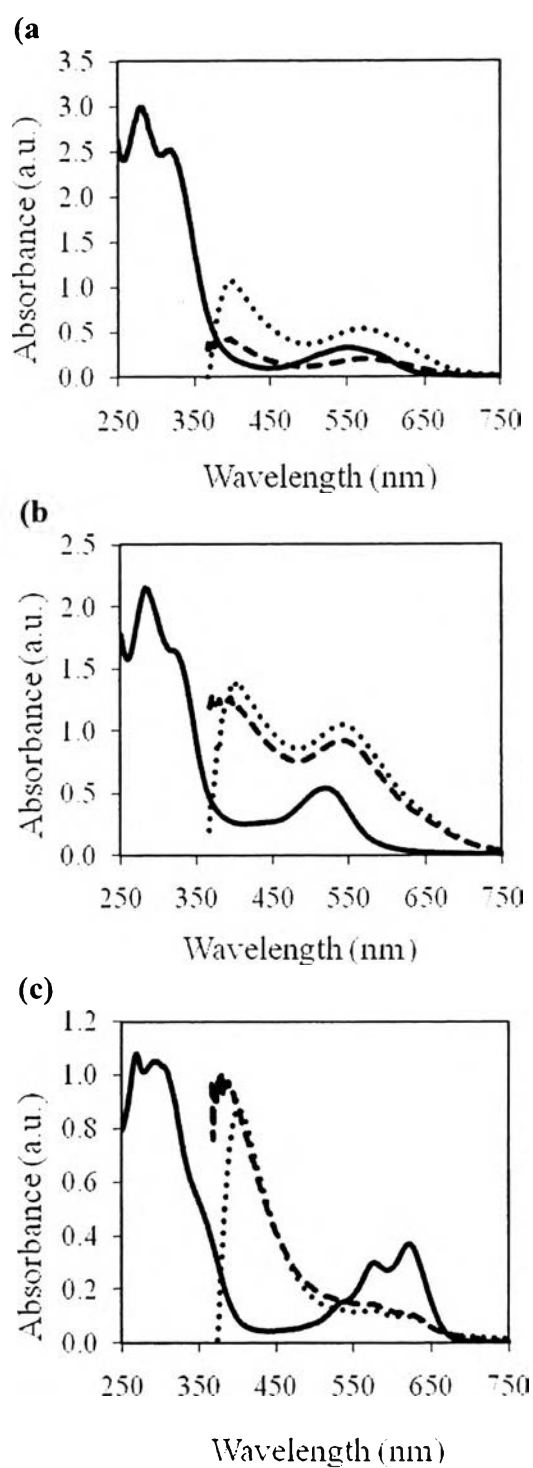


Figure 4.1 UV-visible absorption spectra of (a) red cabbage, (b) rosella, and (c) blue pea: (---) adsorbed on TiO_2/clay electrode, (.....) adsorbed on pure TiO_2 electrode, and (—) in as-prepared solution.

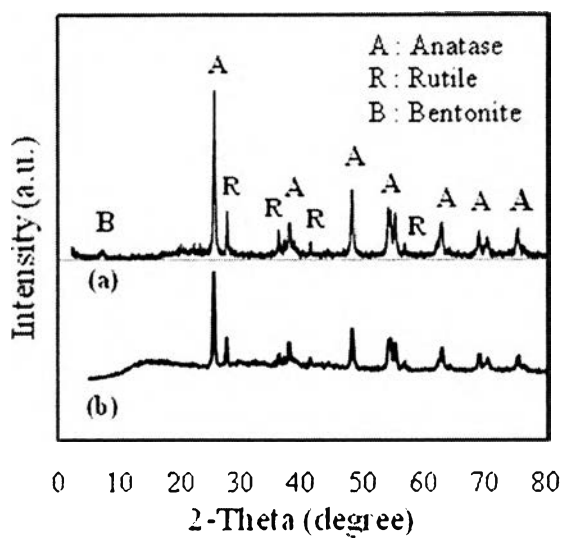


Figure 4.2 XRD patterns of (a) TiO₂/modified natural clay and (b) pure TiO₂ electrodes.

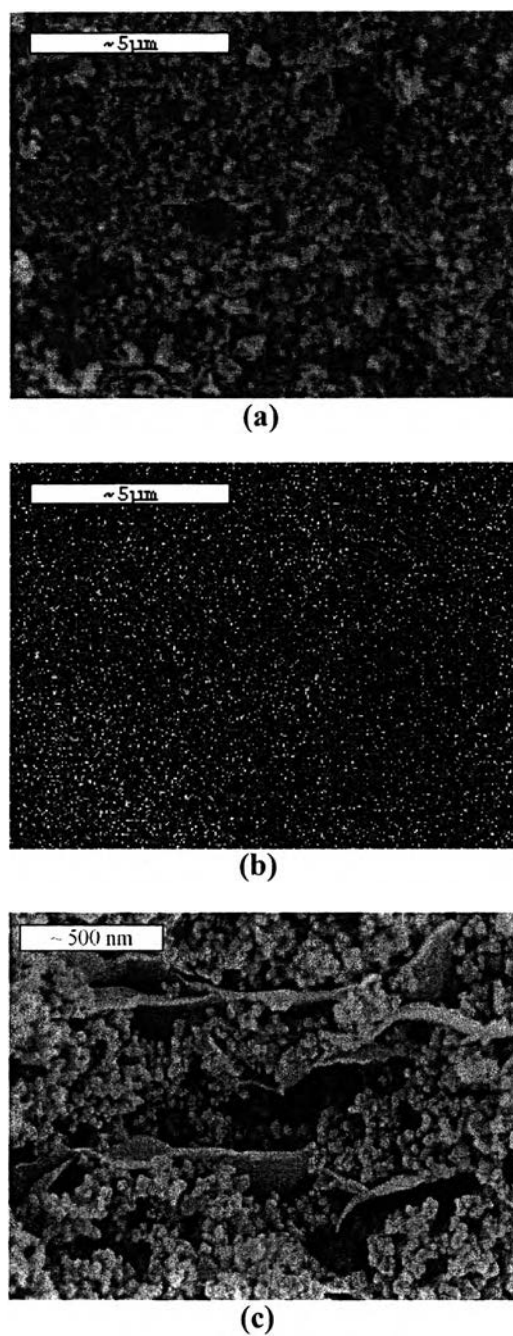


Figure 4.3 Top-viewed SEM micrograph (a), corresponding EDX Si mapping (b), and high-resolution cross-sectional SEM micrograph (c) of TiO₂/modified natural clay electrode.