CHAPTER IV
POTENTIAL OF ZnO-DYE SENSITIZED SOLAR CELL WITH VARIOUS NATURAL DYES

4.1 Abstract

This work aims to study the effect of natural dyes pigment on the efficiency of DSSC. Each of natural dyes pigment absorbed visible light in different wavelength region. Therefore, the natural dyes extracted from sappan wood, safflower, black rice, sunflower and noni leaves show different colors; red, yellow, purple, yellow and green. ZnO was used as a semiconductor and fabricated ZnO photoanode by the doctor blade method. It was observed that the noni leaves-ZnO DSSC exhibited the highest efficiency of 6.9 m% with the ZnO film thickness of 6 micrometers. The noni leaves dye which absorbed both visible and near infrared wavelength region enhanced the efficiency of DSSC. In addition, the various thicknesses of ZnO films (from 4 to 12 micrometers) were investigated. It was observed that the efficiency of noni leaves-ZnO DSSC increased with respect to the thickness of ZnO films. The performances of DSSC revealed the efficiencies in the range of 4.6 m% to 21.8 m%. This is due to the increment of ZnO nanoparticles and consequently the augmentation of dye loading.

4.2 Introduction

Dye sensitized solar cell (DSSC) is an attractive photovoltaic device due to low cost and relatively simple fabrication process. The semiconductors are one of components that used in DSSC photoanode. ZnO is one of the semiconductors and it is an attractive material in solar energy conversion due to its stability against photocorrosion and photochemical properties similar to TiO_2, having a band gap similar to TiO_2 at 3.2 eV and having higher electron mobility 115- 155 $cm^2/V\,s^2$ than that of TiO_2 (Chou *et. al.*, 2007). In addition, the dye or the sensitizer is an essential component of DSSC that is used to enlarge the spectral absorbance. The sensitizers can be divided into two kinds, synthetic dyes and natural dyes. The synthetic dyes as ruthenium polypyridyl complexes are mostly used, and the result was obtained with the maximum conversion efficiency of 11% (Gratzel, 2005). However, the cost of synthetic dyes and environment effect are concerned, natural dyes have been applied to DSSC. The natural dyes that found in plant, fruits and other natural products show various colors and contain several pigments that can be easily extracted and then employed in DSSC. Chang and co-workers prepared TiO_2 DSSC by using pomegranate leaf and mulberry fruits as dye-sensitizers and the conversion efficiency of fabricated DSSC were 0.597% and 0.548%, respectively (Chang et al., 2010). Wongcharee and co-workers have fabricated solar cells using natural dyes extracted from rosella, blue pea and a mixture of the extracts and has reported the efficiency of 0.37%, 0.05% and 0.15%, respectively (Wongcharee *et al.*, 2007). Recently, Thambidurai and co-workers reported the fabrication of dye sensitized ZnO nanorod based solar cells from natural dyes extracted from Ixora coccinea, Mulberry and Beetroot, and the solar cell efficiency is found to be 0.33%, 0.41% and 0.28%, respectively (Thambidurai et al., 2011). In 2012, Murugiah prepared ZnO based DSSC by using dragon fruit extracted dye and reported the efficiency of 25% under the natural sunlight (Murugiah et al., 2012).

In this work, the natural dyes that exacted from sappan wood, safflower, black rice, sunflower and noni leaves were investigated as the sensitizers in the DSSC. ZnO photoanode was prepared by doctor blade method and characterized the efficiency of DSSC with various natural dyes. Furthermore, the effect of thickness (4 to 12 micrometers) on the efficiency of natural dye-sensitized solar cell was studied.

4.3 Experimental

4.3.1 Materials

Safflower, black rice and noni leaves were purchased from Sam-Yan market, Bangkok, Thailand. Sappan wood was purchased from a traditional drug store in Singburi, Thailand. Sunflower was purchased from Pak Khlong Market, Bangkok, Thailand. Commercial ZnO nanoparticles (ZoNoP®, 99.93% ZnO) was purchase from Nano Materials Technology Co., Ltd., in Thailand. Acetylacetone ($\geq$ 99.5%) was purchased from Fluka. Triton X-100 (laboratory grade) was purchased from Acros Organics. Polyethylene glycol (PEG, MW 20,000), Lithium iodide beads (99%), 4-tert-butyl pyridine (96%) and hydrogen hexachloroplatinate (IV) hydrate (~38% Pt basis) were purchased from Aldrich. Iodine was purchase from Suksapan panit, Thailand. Fluorine-doped SnO_2 (FTO) glass (sheet resistance of 8 Ω/cm^2) was purchased from Dyesol Company.

4.3.2 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.

4.3.3 Preparation of ZnO for doctor-blade method

The 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. 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.

4.3.4 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.

4.3.5 Characterizations

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) 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) 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 (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 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 digital Keithley 236 multimeter under an irradiation of white light from 100 mW/cm^2 halogen-tungsten lamp.

4.4 Results and discussion

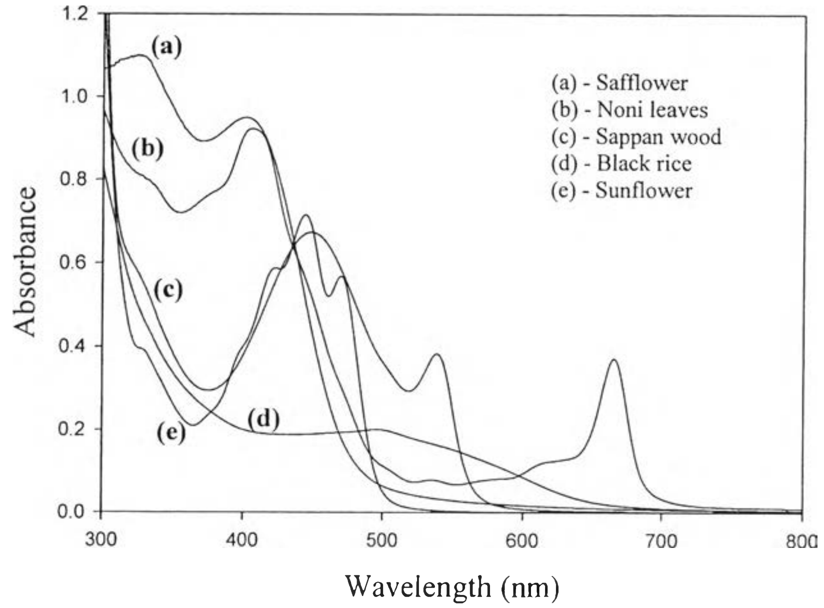

Figure 4.1 UV-Visible spectra absorbance of natural dyes: safflower (a), noni leaves (b), sappan wood (c), black rice (d), and sunflower (e).

Figure 4.1 shows the UV-Visible spectra of natural dyes. As shown in figure 4.1, the yellow pigments of safflower dye are carthamidin and carthamin, show the maximum absorption wavelength at 401 nm (Machewad *et al.,* 2012). The green pigments of noni leaves are chlorophyll, show the absorption wavelength at 406 and 665 nm (Amao *et al.*, 2004). The orange pigments of sappan wood dye which are the combination of yellow and red pigments are brazilin. They show the two maximum absorption wavelengths at 448 and 539 nm (Lee *et al.,* 2008). The purple pigments of black rice dye are anthocyanin, show the absorption wavelength at 495 nm (Hou *et al.,* 2013). The yellow pigments of sunflower dye are lutein, which are considered as the carotenoid family, show the absorption wavelength at 444/469 nm (Kumar et al., 2010). Their absorption is attributed to different chemical component of natural dyes.

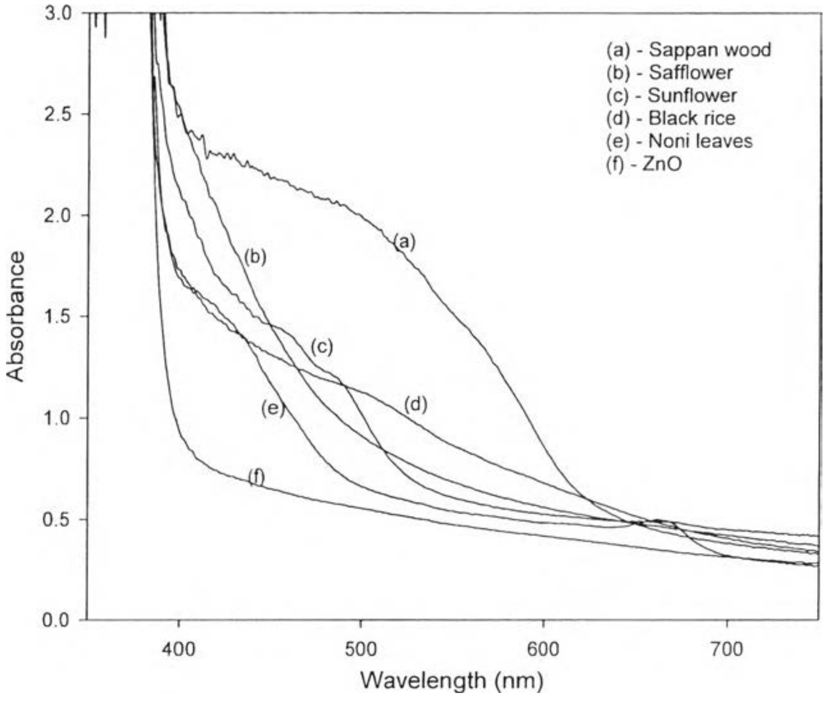

Figure 4.2 UV-Visible spectra of natural dyes absorbed on ZnO prepared by doctor blade method.

Figure 4.2 and table 4.1 show the UV-Visible spectra and the data acquired from the natural dyes absorbed on ZnO film with the ZnO film thickness of 4 micrometers (1 time of coating). The ZnO film only absorbed UV wavelength region. The natural dyes absorbed on ZnO films induced the absorption spectra in visible region. Sappan wood absorbed on ZnO shows strong absorption in wide range about 400-650 nm, while the safflower shows the absorption in the range of 400-450 nm. The noni leaves dye absorbed on ZnO film shows two maximum absorption bands around 414 and 670 nm. The ZnO film with the black rice dye and sunflower dye show weak absorption at 550 nm and 450-500 nm, respectively. The red shift of absorption spectra was observed due to the probability of the dye molecules interact with ZnO. (Calogero *et al.,* 2009) The hydroxyl groups in dye molecule interact with ZnO which oxygen atom in hydroxyl bounds with Zn atom (Matsumura et al., 1980 and Jin et al., 2013).

Table 4.1 Maximum absorption wavelength of natural dyes solution and natural dyes absorbed on ZnO

Natural dyes	Natural dyes solution	Natural dyes absorbed on ZnO
	λ (nm)	λ (nm)
Sappan wood	448 / 539	400-650
Safflower	401	400-450
Black rice	495	550
Noni leaves	406 / 665	414 / 670
Sunflower	444 / 469	450-500

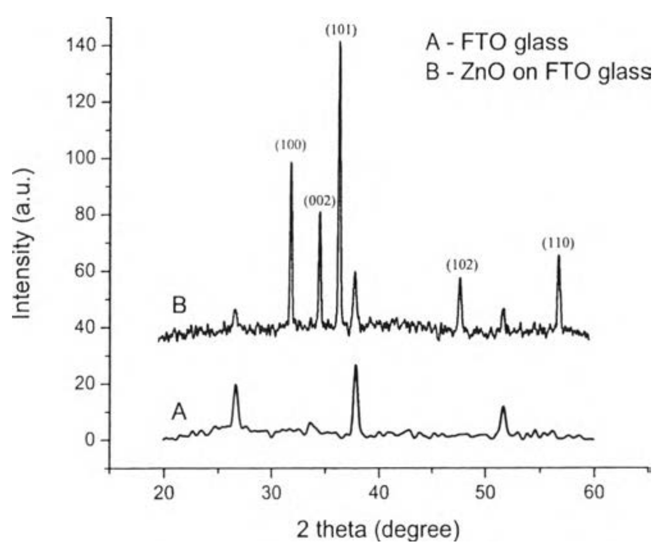

Figure 4.3 XRD pattern of ZnO film fabricated by doctor blade method.

Figure 4.3 shows the XRD pattern of ZnO on FTO glass fabricated by doctor blade method. The XRD pattern corresponds to the hexagonal ZnO structure (wurzite) (JCPDS database card No. 36-1451) with the diffraction peaks of (100), (002), (101), (102) and (110) crystal plane. The diffraction peaks at scattering angle 26.61, 37.85 and

51.62 degree correspond to FTO (fluorine doped tin oxide) glass (JCPDS database card No. 46-1088). (Liao *et al.*, 2005)

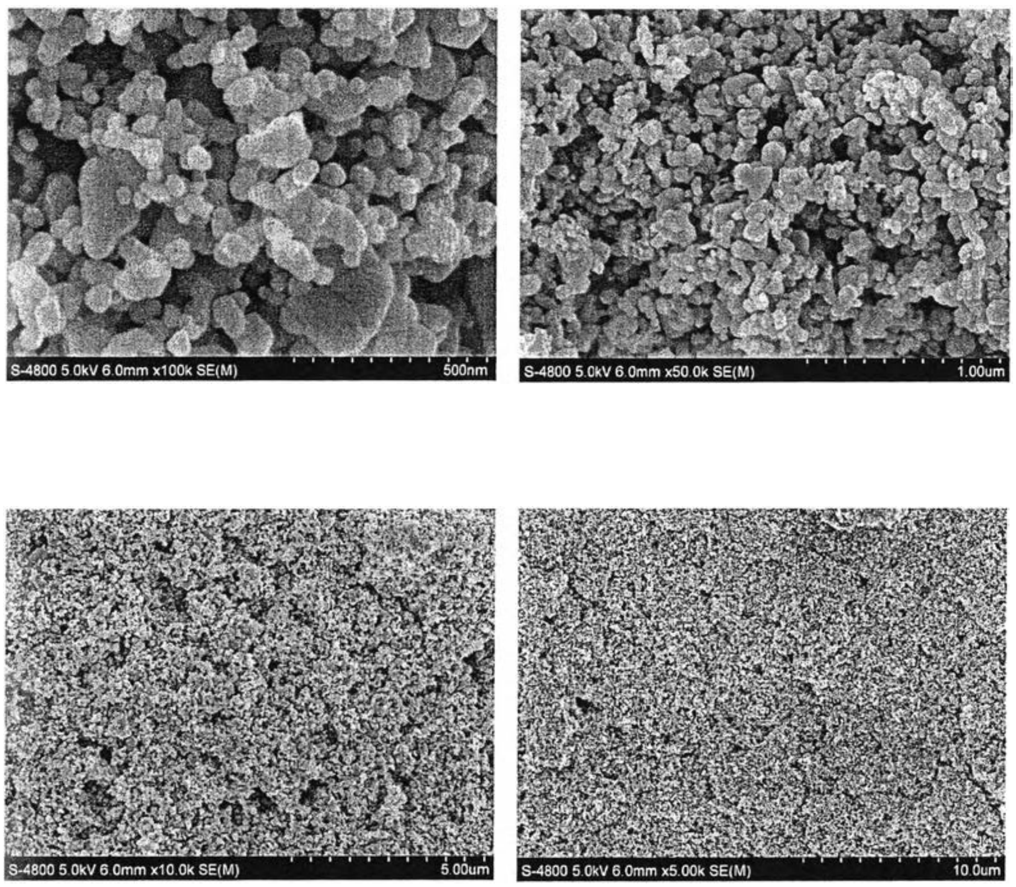

Figure 4.4 Top view FE-SEM images of ZnO film with different magnifications.

Figure 4.4 show the top view FE-SEM images of ZnO coated on FTO glass prepared by doctor blade method. The images reveal the particle sizes of ZnO about 50-200 nm and show porous structure of ZnO film due to the evaporation of organic solvent, organic additive (acetyl acetone), binder (polyethylene glycol, PEG) and surfactant (Triton X-100). The acetylacetone was added into the ZnO paste for prevent the coagulation and improve the porosity of ZnO films. The polyethylene glycol acts as the binder to decrease voids and prevent the cracking in ZnO electrode that influenced the efficiency of DSSC. (Saito *et al.*, 2009) The surfactant was added into the ZnO paste to reduce surface tension and enable even spreading on FTO glass. (Giannouli *et al.*, 2012)

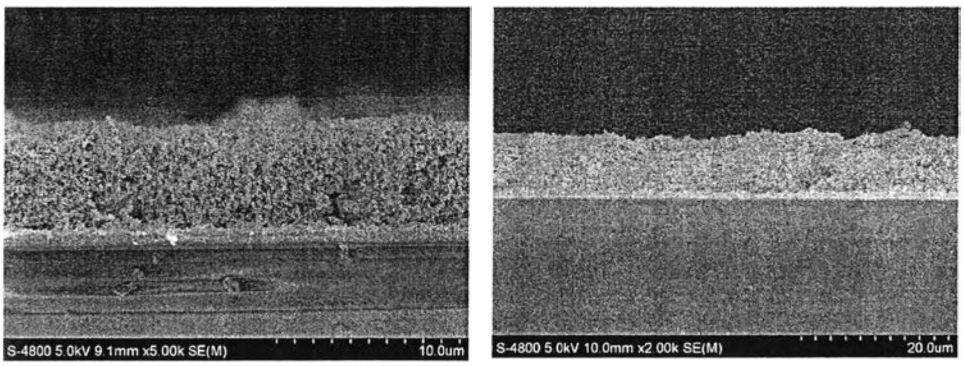

Figure 4.5 Side view FE-SEM images of ZnO film with different magnifaication.

Figure 4.5 show the cross-section of FE-SEM images of ZnO film. The thickness of film is about 6 nm with 2 times of blade-coated ZnO.

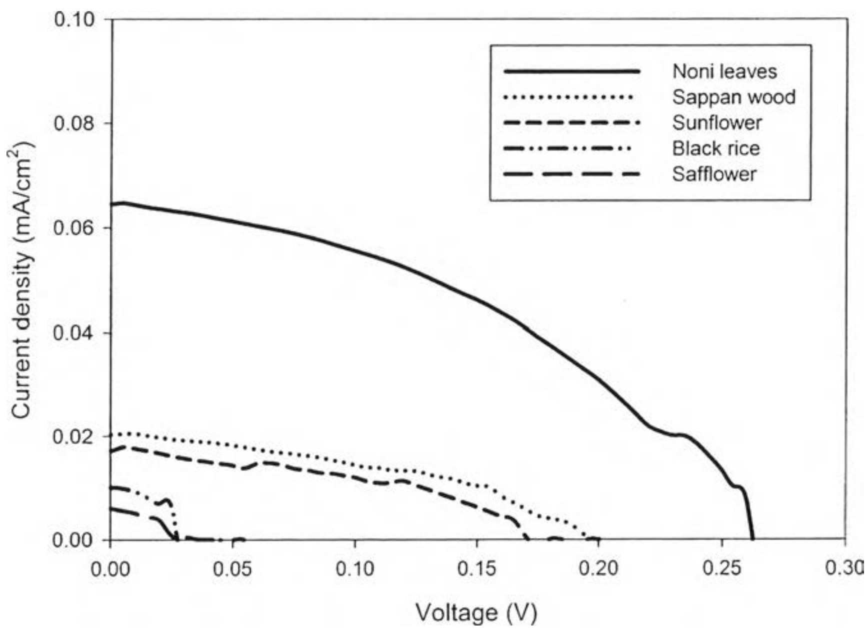

Figure 4.6 The J-V characteristics of DSSC with natural dyes.

Table 4.2 The efficiencies of DSSC with natural dyes (the thickness of ZnO film is about 6 μm)

Natural dyes	**J_{sc} (mA/cm^2)**	**V_{oc} (V)**	**ff**	**η (%)**
Sappan wood	0.020296	0.2	0.407	0.001654
Black rice	0.010129	0.027	0.551	0.0001507
Safflower	0.006105	0.045	0.267	0.0000734
Sunflower	0.017201	0.17	0.465	0.001359
Noni leaves	0.064540	0.275	0.393	0.006978

Figure 4.6 shows J-V characteristic of DSSC that sensitized with natural dyes. Table 4.2 shows the data acquired from measuring the photoelectric conversion efficiency of DSSC. The highest efficiency of DSSC prepared by chlorophyll dye from noni leaves extraction is 0.00697% with short-circuit current (J_{sc}) of 0.06454 mA/cm^2, open circuit voltage (V_{oc}) of 0.275 and fill factor of 0.393. The minimize efficiency of DSSC prepared from safflower extraction is 0.0000734 %. The safflower DSSC showed the lowest efficiency due to the only UV wavelength absorption and the high energy need for exciting the electron of safflower dye. The DSSC prepared from noni leaves extraction shows the highest efficiency because the noni leaves dye absorbed both visible and near-infrared wavelength region which needed the less of energy to excite electron. Hence, the electron in the excited state of noni leaves dye increased as a result of the increment of J_{sc} value. Although the sappan wood absorbed on ZnO film showed the highest absorbance, the efficiency of DSSC is 0.001654%. One possible reason that the sappan wood-ZnO DSSC exhibited the low efficiency was the excited state level of sappan wood overlaped the conduction band of ZnO and resulted in the electron mobility problem and the low J_{sc}. (Go´mez-Ortı´z *et al.*, 2010) The high efficiency of DSSC depends on the absorption of dye that has good absorption in visible region. In addition, the dye sensitizer which has the absorption spectrum near infrared wavelength region improves the efficiency of DSSC. (Nwanya *et al.*, 2011)

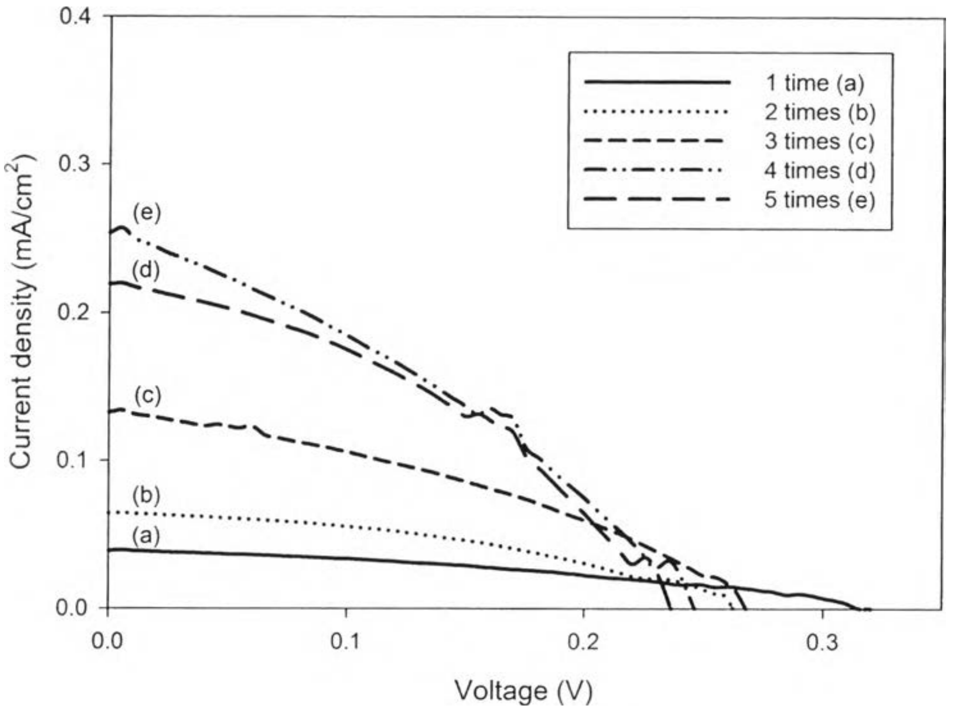

Figure 4.7 The J-V characteristics of DSSC using noni leaves as sensitizer with different number of coating.

Table 4.3 The efficiencies of DSSC with different number of coating

Number of coating	Thickness (μm)	Jsc (mA/cm^2)	Voc (V)	ff	η (%)
1	4.2	0.038907	0.32	0.371	0.0046218
2	6.3	0.06454	0.265	0.393	0.0069781
3	8.2	0.132680	0.27	0.364	0.0130438
4	10.7	0.253867	0.245	0.337	0.0218048
5	12.7	0.021949	0.24	0.379	0.0204062

Figure 4.7 and table 4.3 show the data of noni leaves dye DSSC with different number of coating ZnO. The short circuit current increases with increasing the thickness of ZnO films. This is because an increase in the ZnO film thickness increases the dye absorption area. The Jsc value decreases when the number of coating was 5 times, in which the ZnO film started to crack. In turn, the open-circuit voltage decreases with increasing the thickness of ZnO films. This phenomenon is due to the additional charge recombination, recapture of electrons by the oxidized form (I_3^-) of redox couple in electrolyte and oxidized sensitized occur more easily before reaching the FTO glass, resulting in the decrease efficiency of DSSC. (Yin *et al.*, 2010 and Saito *et al.*, 2009)

4.5 Conclusions

In summary, the natural dyes pigments had influenced to the efficiency of ZnO DSSC. The ZnO layer was fabricated by doctor blade method. The noni leaves-ZnO DSSC revealed the highest conversion efficiency of 6.4 m% with the ZnO layer thickness of 6 micrometers because the noni leaves dye absorbed both visible and near-infrared wavelength region that the excited energy need is not high resulted in the J_{sc} and efficiency enhancement. Furthermore, an increase in the efficiency of noni leaves-ZnO based DSSC was related to the thickness of ZnO films. The higher thickness resulted in an increase in the short-curcuit current (J_{sc}) due to higher dye absorption. The open-curcuit voltage (V_{oc}) decreased, as the ZnO film thickness increased because of the additional charge recombination.

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