CHAPTER VI

FABRICATION OF THE HYBRID POLYTHIOPHENE-ZnO DYE SENSITIZED SOLAR CELL WITH NONI LEAVES AS THE SENSITIZER

6.1 Abstract

In this work, the effect of a polythiophene layer on ZnO dye-sensitized solar cell was investigated. The polythiophene layer was polymerized on ZnO film by electropolymerization with varied concentration of thiophene monomer (0.1M, 0.2M and 0.3M) and electropolymerization time (1 min, 2min and 5 min). ZnO films were prepared by doctor blade and electrophoretic deposition method. The optimum condition for polymerized thiophene was 0.1M thiophene under a constant applied potential of 3 volt (versus Ag/Ag^+) and polymerization time of 1 min. The hybrid polythiophene-ZnO DSSC exhibited the conversion efficiency of 5.8 m% for doctor blade method and 4.8 m% for electrophoretic deposition method. These results indicated that the dark current reduced and consequently improved the conversion efficiency of DSSC in the presence of the polythiophene layer.

6.2 Introduction

The reason that DSSCs exhibit the low efficiency is due to the electron recombination reaction. This reaction involved two processes: the photoinduced electrons recombined with the oxidized sensitizer and/or with I_3^- in the electrolyte. The dark current usually represented the recombination between the electrons in the conduction band and the I_3^-. The dark current phenomenon affects the low conversion efficiency of DSSC. Since the I_3^- could penetrate into the porous semiconductor electrode, the electrons in the conduction band of the semiconductor could reduce the I_3^- to $3I^-$, which generates the dark currents (Lee *et al.*, 2009).

Photoinduced electrons have to travel the several different layers inside the cell to give the photocurrent; these layers trap the photoinduced electrons and delay the transportation of these electrons into the electrode side. This phenomenon enhances the unwanted charge carrier recombination (Lim et al., 2012). For this reason, it has been attempted to form interfacial layers by coating the thin energy barriers reducing recombination reaction. Lee and co-worker observed that the efficiency of DSSC with polythiophene layer increased from 4.60% to 6.01%, compared to one without polythiophene. These results indicated that the polythiophene as energy barrier formed between electrolyte and $N_3/TiO_2/FTO$, which reduced the recombination reaction (Lee *et al.,* 2009). Recently, Lim and co-workers fabricated dye-sensitized TiO_2 solar cell with a thin film of iodine doped polythiophene. It found that the polythiophene layer helped to suppress the recombination and enhance the power conversion efficiency by the factor of 27.52%, leading to the final efficiency of 6.44% (Lim et al., 2012). In addition, Hao and co-workers reported that the DSSC was based on nanostructured ZnO/Ru(II)/polypyrrole electrode as photoanode. The conversion efficiency of 1.3% was obtained. (Hao *et al.,* 2000)

In this work, polythiophene (PTh) is used as a conductive polymer. It is intensively studied due to their easy synthesis, high conductivity, photochemically and thermally stable under photoirradiation. Whiffen et al. (1979) proposed a two-step mechanism for the polymerization of thiophene monomer. Polymerization starts with the formation of a cation radical that is formed by a loss of an electron from the monomer. Thiophene radical can give either a substitution or combination reaction. The oxidation of thiophene is irreversible and the cation radical can be formed in the first step. Thiophene is extremely reactive. Polythiophene can be synthesized either electrochemically (Sari *et al.,* 2003) or chemically (Zhu *et al.,* 2008) by using simple oxidation. Electrochemical polymerization can be carried out by using a suitable power supply (potentiogalvanostat). Generally, potentiosatatic conditions are recommended to obtain thin films, while galvanostatic conditions are recommended to obtain thick films. The electrochemical technique is attractive because of both the simplicity and the advantage of obtaining a conductive polymer being simultaneously doped (Kumar *et al.*, 1998).

ZnO layer increases the electrode resistivity during electropolymerization of thiophene (Valaski *et al,* 2010). Hence, its thickness should be thin for less resistivity. In this study, the optimum condition for polymerized thiophene was 4 micrometers of ZnO layer for doctor blade method and set at 15V 5 min for EPD of ZnO because its thickness is thinner and less resistivity than other conditions. Moreover, the natural dye from noni leaves was used as the sensitizer. For doctor blade method, polythiophene was synthesized with varied electropolymerization time and concentration of monomer. The condition of polythiophene synthesis that obtains the highest conversion efficiency of the hybrid DSSC was applied to DSSC by EPD method. The efficiency of DSSC that prepared by EPD method was investigated in the presence of polythiophene, as compared with the conventional DSSC (without polythiophene).

6.3 Experimental

6.3.1 Materials

Fresh noni leaves were purchased from Sam-Yan market, Bangkok, Thailand. Commercial ZnO nanoparticles (ZoNoP®, 99.93% ZnO) was purchase from Nano Materials Technology Co., Ltd., in Thailand. Acetylacetone (≥ 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%), hydrogen hexachloroplatinate (IV) hydrate (~38% Pt basis) and Thiophene monomer (≥ 99%) 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. Lithium perchlorate (≥95.0%) was purchased from Sigma-Aldrich.

6.3.2 Preparation of ZnO by doctor-blade methode

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 keep in dry and dark container.

6.3.3 Preparation of ZnO by Electrophoretic deposition (EPD)

A commercial nanocrystalline ZnO powder was dispersed well in ethanol (5 g/L) with 250 μl of acetylacetone and ultrasonicated for 2 h. After ultrasonication, the suspension was put in a container for electrophoresis. The electrophoretic cell contained two FTO glasses and the distance between electrodes was 1 cm. The EPD was performed at a DC electric field. After EPD, the residual solvent on the as-deposited film was evaporated in air at ambient temperature and calcined at 500 °C for 1 h in ambient conditions. Then, the films were cooled to room temperature and keep in dry and dark container.

6.3.4 Electropolymerization of thiophene

For the preparation of polythiophene-sensitized ZnO nanoparticles electrode, electrochemical experiments were carried out with potentiostat (PGSTAT101, Metrohm Netherlands). A three-electrode system was used. The as-prepared ZnO/FTO electrode as working electrode and Pt wire as counter electrode and Ag/Ag^+ as reference were placed into 0.2 M lithim perchlorate with varied concentration of thiophene (0.1 M, 0.2M and 0.3M) in acetonitrile. The thiophene was electropolymerized on the ZnO/FTO electrode under the potential of 3V with different time (1 min, 2 min and 5 min). Then, the polythiophene-ZnO coated the working electrode were washed with acetonitrile to eliminate the un-reacted thiophene. The 1 ml of noni leaves dye solution was dropped on the post heated electrodes at room temperature and the excess dye molecules were washed out with ethanol and keep in dry and dark container.

6.3.5 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.

6.3.6 Characterizations

The FTIR spectra were recorded over a frequency range of 4000-500 cm^{-1} with 64 scans by using Nicolet Fourier transform infared spectrometer Nexus 670. The powdered samples were mixed with KBr and pressed in the form of pellets for analysis.

The optical transmittance of ZnO and hybrid ZnO-polythiophene films which were deposited on FTO glass were measure by a UV-Visible spectrophotometer (UV-2550).

The surface and cross-section morphologies of ZnO, ZnO/dye and ZnO/polythiophene which were deposited on FTO glass were studied by field emission scanning electron microscope (FE-SEM) with 10k, 20k and 30k magnification.

The photovoltaic properties of the prepared DSSC (The ZnO photoanode active area was 0.75 cm^2), 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.

6.4 Results and discussion

6.4.1 Polythiophene

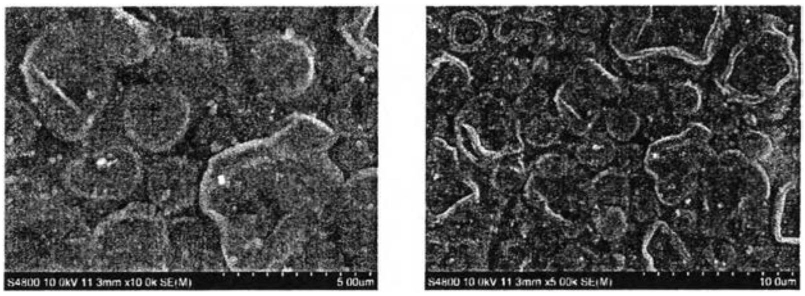

Figure 6.1 FE-SEM images of polythiophene under the constant applied potential of 3V and electropolymerization time of 10 min.

According to FE-SEM images, the morphology of polythiophene which is coated on the conductive glass shows cauliflower-like appearance (Uzun et al., 2010).

6.4.2 Doctor blade method

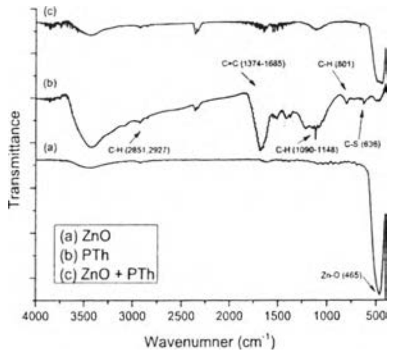

Figure 6.2 FTIR spectra of ZnO (a), polythiophene (b) and ZnO + polythiophene (c).

FTIR spectra of ZnO, polythiophene (0.1M thiophene, 0.2M $LiClO_4$, 1 min) are given in figure 6.2(a) and 6.2(b), respectively. As shown in figure 6.2(a), the absorption band observed at 465 cm^{-1} is attributed to the ZnO stretching vibrations (Saito *et al.*, 2009). In figure 6.2(b), the spectrum showed the C-H stretching vibration band at 2851, 2927 cm^{-1}; C=C stretching band at 1347-1685 cm^{-1}; C–H in-plane bending band at 1090– 1148 cm^{-1}; C–H out of plane bending band at 801 cm^{-1} and C–S bending band 636 cm^{-1} (Sari *et al.*, 2003). FTIR spectrum of ZnO-polythiophene is given in Figure 6.2(c). There are characteristic bands of ZnO and polythiophene in this spectrum. Due to the less amount of polythiophene in the hybrid material, the spectrum bands are not marked.

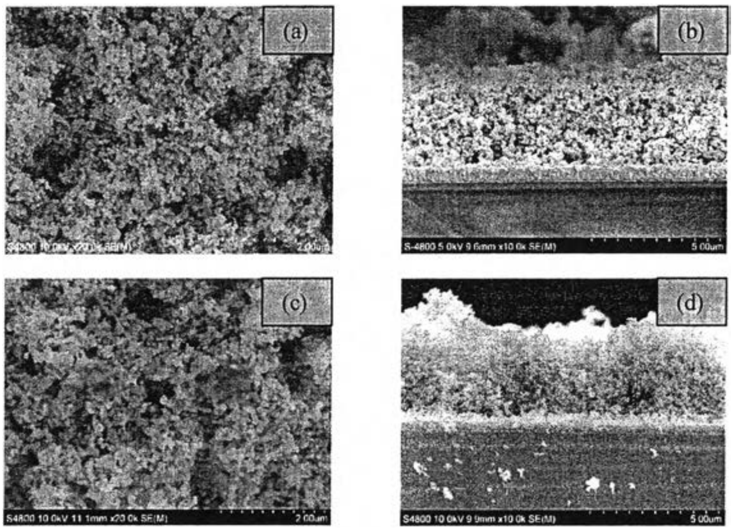

Figure 6.3 FE-SEM images of ZnO (a), (b) and ZnO + polythiophene (c), (d).

Figure 6.3(a) and (b) show the morphology of ZnO which is coted on the conductive glass and figure 6.3 (c) and (d) show the morphology of polythiophene-ZnO. The polythiophene was synthesized by electrochemical on the conductive glass surface. Because the thiophene is oxidized to radical cations at anode surface, then the couplings of its radicals proceed until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface (Figa et al., 2008). As shown in figure 6.3(c), polythiophene both coated on ZnO nanoparticles and precipitate on conductive glass. It found that around 0.28% of sulfur atoms were dispersed on ZnO film (from EDX information).

6.4.2.1 Electropolymerization time

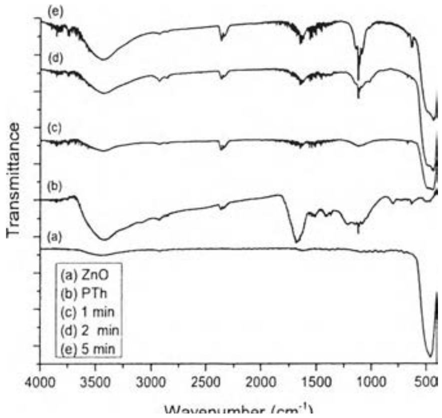

Figure 6.4 FTIR spectra of ZnO+polythiophene with varied electropolymerization time; 1 min (c), 2 min (d) and 5 min (e) in comparison to ZnO (a) and polythiophene (b).

From FT-IR spectra, the electropolymerization time increased with the increasing of polythiophene layer on ZnO films. It is notice that the spectra of polythiophene were obvious with the increment of polymerization time, as shown in figure 6.4(c), 6.4(d) and 6.4(e). For figure 6.4(a) and 6.4(b) have already been explained in figure 6.2

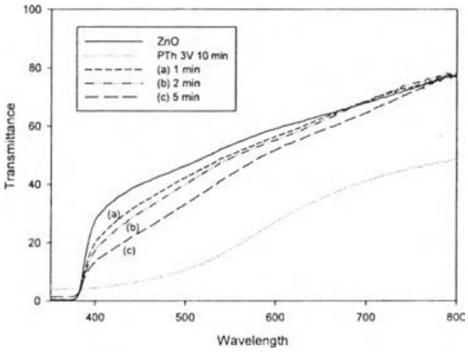

Figure 6.5 UV-Vis transmittance of ZnO, Polythiophene and various polymerization times of hybrid ZnO-Polythiophene films.

The transmittance of photoanode is one factor that affects the conversion efficiency of DSSC (Oftadeh *et al.*, 2012). Figure 6.5 shows the variation of UV-Vis transmittance of ZnO, polythiophene (0.1M Thiophene, 3V, 10 min) and various electropolymerization times of hybrid ZnO-polythiophene films with the wavelength of incident radiation in the range of 350 to 800 nm. It is observed that the increased electropolymerization time of thiophene layer resulted in the decrease in the transmittance of ZnO films. Thick polythiophene layer reduced the visible light transmittance of ZnO/FTO electrode and consequently, decreased the efficiency of DSSC (Ding *et al.*, 2013).

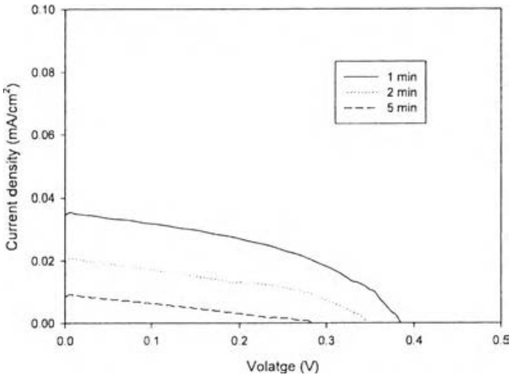

Figure 6.6 J-V characteristic of polythiophene-ZnO DSSC with varied polymerization time; 0.1M thiophene and 0.2M $LiClO_4$

Table 6.1 The efficiencies of polythiophene-ZnO DSSC with varied polymerization time

Time	J_{sc} (mA/cm^2)	V_{oc} (V)	Ff	η (%)
1 min	0.03473	0.39	0.44	0.0058671
2 min	0.01980	0.36	0.41	0.0028953
5 min	0.00858	0.30	0.29	0.0007401

Table 6.1 shows the performances of DSSC with the various electropolymerization times. The DSSC with the polythiophene (1 min) shows the conversion efficiency of 5.87m% with short-circuit current (J_{sc}) = 0.0347 mA/cm^2, open-circuit voltage (V_{oc}) = 0.385 V and fill factor (ff) = 0.44. On the other hand, the efficiency of polythiophene-ZnO DSSC with electropolymerization time of 2 min and 5 min significantly decreased to 2.89m% and 0.74m%, respectively. The increment of V_{oc} value is caused by the polythiophene layer acts as a charge energy barrier for dark current suppression. However, the thickness of the polythiophene film should not be too thick which diminished the J_{sc} and fill factor. Consequently, the solar cell efficiencies were decreased because of the increase in internal resistance of the system (Lee et al., 2009) and the decrease in visible light transmittance of the electrode with the

introduction of polythiophene-ZnO photoanode (Kim et al., 2009). In addition, the problem about the contact between ZnO film and the conductive glass also affects the efficiencies of the polythiophene-DSSC because the electrochemical process initiates polymerization at the conductive glass surface when the polymerization is performed on the electrode covered with the ZnO film (Lim et al., 2012).

6.4.2.2 Concentration of thiophene

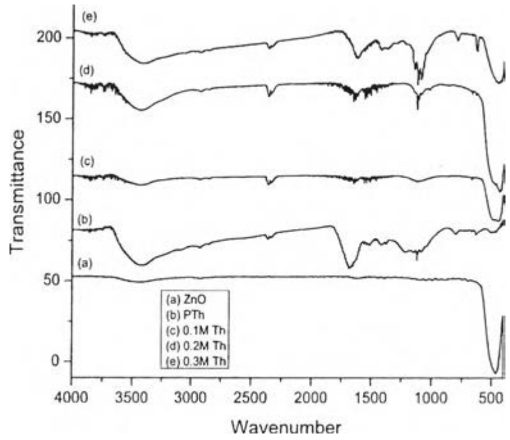

Figure 6.7 FTIR spectra of ZnO+polythiophene with varied concentration of thiophene; 0.1M (c), 0.2M (d) and 0.3M (e) in comparison to ZnO (a) and polythiophene (b).

From FT-IR spectra, the concentration of electropolymerization increased with increasing polythiophene layer on ZnO films. It is notice that the spectra of polythiophene were obvious with the increment of concentration, as shown in figure 6.7(c), 6.7(d) and 6.7(e). For figure 6.7(a) and 6.7(b) have been already explained in figure 6.2

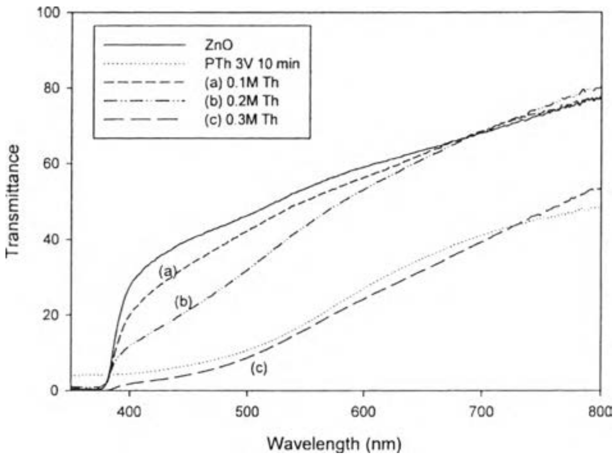

Figure 6.8 UV-Vis transmittance of ZnO, Polythiophene and various concentration of thiophene in hybrid ZnO-Polythiophene films.

The transmittance of photoanode is one parameter that influenced on the conversion efficiency of DSSC (Oftadeh et al., 2010). Figure 6.8 shows the variation of UV-Vis transmittance of ZnO, polythiophene (0.1M Thiophene, 3V, 10 min) and various concentration of thiophene in hybrid ZnO-polythiophene films with the wavelength of incident radiation in the range of 350 to 800 nm. It is observed that the increased concentration of thiophene resulted in the decrease in the transmittance of ZnO films. The 0.1M and 0.2M of thiophene showed the slight decrease in the transmittance of hybrid films but 0.3M of thiophene showed the significant decrease in the transmittance of hybrid film in comparison to the ZnO film. Thick polythiophene layer reduced the visible light transmittance of ZnO/FTO electrode and, consequently, decreased the efficiency of DSSC (Ding *et al.*, 2013).

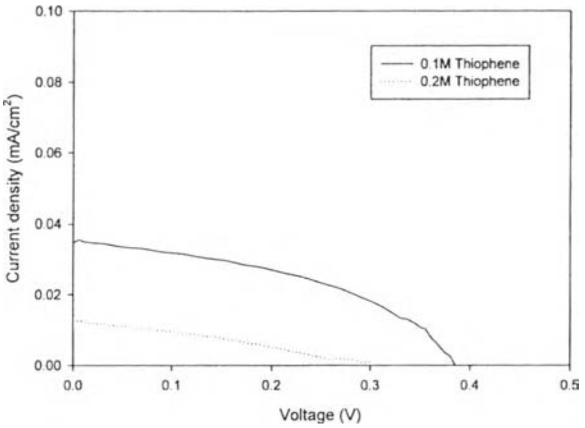

Figure 6.9 J-V characteristic of polythiophene-ZnO DSSC with varied concentration of thiophene.

Table 6.2 The efficiencies of polythiophene-ZnO DSSC with varied concentration of thiophene

Concentration of thiophene	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)
0.1M	0.03473	0.385	0.439	0.0058671
0.2M	0.01203	0.315	0.307	0.0011638
0.3M	-	-	-	N/A

The performances of DSSC with the various concentration of thiophene monomer were shown in figure 6.9 and Table 6.2. The DSSC with 0.1M of thiophene shows the conversion efficiency of 5.87m% with short-circuit current (J_{sc}) = 0.0347 mA/cm$_2$, open-circuit voltage (V_{oc}) = 0.385 V and fill factor (ff) = 0.44. Meanwhile, the efficiency of DSSC with 0.2M thiophene decreased to 1.16m% with short-circuit current (J_{sc}) = 0.01203 mA/cm$_2$, open-circuit voltage (V_{oc}) = 0.315 V and fill factor (ff) = 0.307. The decrease in the efficiency was observed and this may be due to the decrease in visible light transmittance of the photoelectrode with the presence of polythiophene layer. However, the transmittance was high enough to measure the efficiency of DSSC. On the other hand, the DSSC with 0.3M thiophene cannot measure the efficiency because the thicker polythiophene layer increased the internal resistance of the DSSC (Lee et al., 2009) and the visible light transmittance of film decreased (Kim et al., 2009). The resistance of DSSC influenced on the J_{sc} and fill factor, and resulted in the low efficienciey of DSSC when the concentration of thiophene increased although the thiophene layer reduced the dark current reaction. In addition, the less J_{sc} value attributed to the filling of electrolyte into the porous of ZnO was limited by the thicker polythiophene layer (Ding et al., 2010).

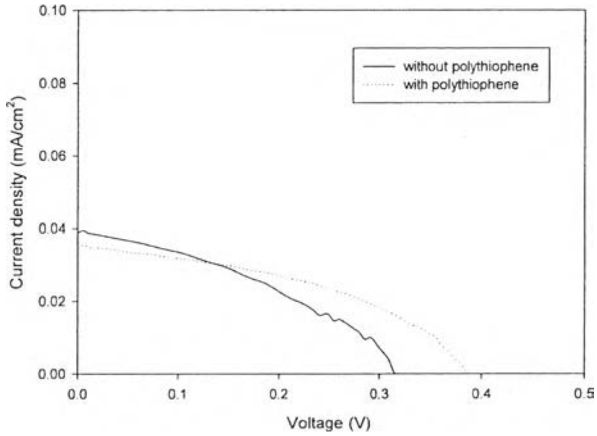

Figure 6.10 J-V characteristic of polythiophene-ZnO DSSC with and without polythiophene.

Table 6.3 The efficiencies of DSSC of ZnO with and without polythiophene

Material	**J_{sc} (mA/cm^2)**	**V_{oc} (V)**	**ff**	**η (%)**
ZnO with polythiophene	0.03473	0.385	0.439	0.0058671
ZnO without polythiophene	0.03891	0.320	0.371	0.0046217

Figure 6.10 and table 6.3 shows the performances of DSSC with and without polythiophene layer which polythiophene was polymerized under the 0.1M of thiophene

0.2M $LiClO_4$ in acetonitrile at apllied voltage of 3V for 1 min. It is important to notice that the DSSC with the polythiophene layer shows the conversion efficiency of 5.87m% with open-circuit voltage (V_{oc}) = 0.385 V and short-circuit current (J_{sc}) = 0.0347 mA/cm^2. On the other hand, the DSSC without polythiophene layer exhibited the efficiency of 4.62 m% with V_{oc} of 0.32V and short-circuit current (J_{sc}) = 0.0389 mA/cm^2. The presence of the polythiophene layer on DSSC improved the V_{oc} but diminished the J_{sc}. The V_{oc} value increased in the presence of polythiophene protecting layer indicating the reduction of recombination reaction. (Lee et al., 2009) The polythiophene layers function as the charge energy barrier which shielded the electrons in conduction band of ZnO recombine with the tri-iodide in electrolyte. On the contrary, the J_{sc} value decreased in the presence of polythiophene layer due to the internal resistance of DSSC and the limited of filling electrolyte into the porous ZnO (Lee et al., 2009 and Ding et al., 2010).

6.4.3 Electrophoretic deposition method

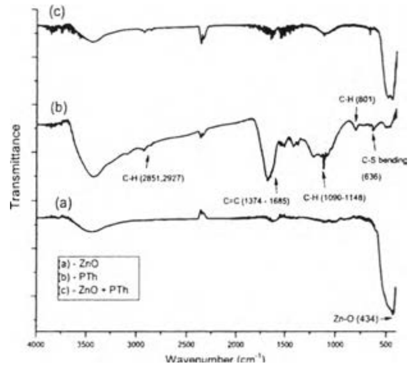

Figure 6.11 FTIR spectra of ZnO (a), polythiophene (b) and ZnO-polythiophene (c).

As shown in figure 6.11(a), the absorption band observed at 434 cm^{-1} is attributed to the ZnO stretching vibrations (Saito *et al.*, 2009). In figure 6.11(b), the spectrum showed the C-H stretching vibration band at 2851, 2927 cm^{-1}; C=C stretching band at 1347-1685 cm^{-1}; C–H in-plane bending band at 1090– 1148 cm^{-1}; C–H out of plane bending band at 801 cm^{-1} and C–S bending band 636 cm^{-1} (Sari *et al.*, 2003). FTIR spectrum of ZnO-polythiophene is given in figure 6.11(c); there are both characteristic bands of ZnO and polythiophene appearing in this spectrum. However, the bands are not distinct because of the less amount of polythiophene in the hybrid material.

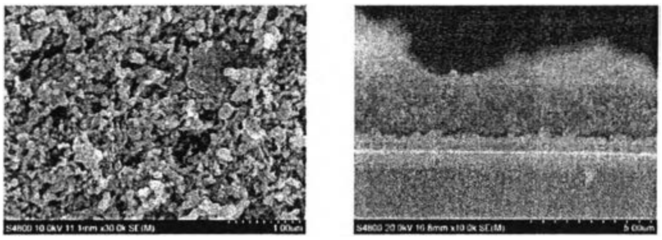

Figure 6.12 FE-SEM images of polythiophene - ZnO film.

The polythiophene was synthesized on the conductive glass surface by the electrochemical process. The thiophene is oxidized to radical cations at anode surface, and then the couplings of its radicals proceed until the oligomer becoming insoluble in the electrolytic medium and precipitates onto the electrode surface (Figa et al., 2008). As shown in figure 6.8, polythiophene was coated on ZnO particles and found that around 0.29% of sulfur atoms were dispersed on ZnO film (from EDX information).

Figure 6.13 J-V characteristic of DSSC with (dashed line) and without (solid line) polythiophene.

Table 6.4 The efficiencies of DSSC of ZnO with and without polythiophene

Material	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)
ZnO without polythiophene	0.03273	0.34	0.33	0.003704
ZnO with polythiophene	0.02816	0.39	0.44	0.004882

Figure 6.13 and table 6.4 show the performances of DSSC with and without polythiophene layer which polythiophene was polymerized under the 0.1M of thiophene 0.2M $LiClO_4$ in acetonitrile at apllied voltage of 3V for 1 min. It was found that the DSSC with the polythiophene layer showed the conversion efficiency of 4.8 m% with short-circuit current (J_{sc}) 0.0282 mA/cm^2 and open-circuit voltage (V_{oc}) 0.39 V. On the other hand, the DSSC without polythiophene layer exhibited the efficiency of 3.7 m% with J_{sc} of 0.0327 mA/cm^2 and V_{oc} of 0.34 V. The presence of the polythiophene layer on DSSC improved the open-circuit voltage (V_{oc}). The dark currents were reduced in the presence of polythiophene layer indicating the reduction of recombination reaction (Lee et al., 2009).

6.5 Conclusion

In conclusion, the polythiophene layer on ZnO dye-sensitized solar cell was prepared by electropolymerization method with varied concentration of thiophene and electropolymerization time. The efficiency of hybid polythiophene-ZnO DSSC which ZnO layer was fabricated by doctor blade and electrophoretic deposition method were investigated. Their conversion efficiencies improved from 4.6 m% to 5.8 m% and from 3.7m% to 4.8m%, respectively. Furthermore, the V_{oc} value increased in the presence of the polythiophene layer. This phenomenon is attributed to the polythiophene layer acts as the charge energy barrier which suppressed the dark current reaction. However, the J_{sc} value decreased because of the thicker polythiophene layer and then the increment of resistance of the DSSC and the decrease in the visible light transmittance. Therefore, the polythiophene layer has influenced on the efficiency of DSSC. The thickness of polythiophene layer should not too thick in order to enhance the efficiency of DSSC.

6.6 Acknowledgements

This work was financially supported by the government budget. Authors would like to thank Department of Physics and Department of Chemistry, Faculty of Science, Chulalongkorn University for I-V measurement and potentiostats for electrochemistry, respectively. The author gratefully thanks Polymer Processing and Polymer Nanomaterials Research Unit, The Petroleum and Petrochemical College, Chulalongkorn University for the chemical and equipment laboratory support.

6.7 References

Ding, I.K., Kyriazi, J.M., Cevey, N.L., Chittibabu, K.G., Zakeeruddin, S.M., Grätzel, M., and McGehee, M.D. (2010) Deposition of hole-transport materials in solid-state dye-sensitized solar cells by doctor-blading. Organic Electronics, 11, 1217–1222.

Ding, J.N., Li, Y., Hu, H.W., Bai, L., Zhang, S., and Yuan, N.Y. (2013) The influence of anatase-rutile mixed phase and ZnO blocking layer on dye sensitized solar cells based on TiO_2nanofiber photoanodes. Nanoscale Research Letters, 8, 1-9.

Figa, V., Luc, J., Baitoul, M., and Sahraoui, B. (2008) NLO properties of polythiophenes galvanostatically electrodeposited on ITO glasses. Journal of optoelectronics and advanced materials, 10 (8), 2123-2128.

Han, Y.Z., Yang, M.Z., Li, W.H., Qiao, X.B., Zhang, L., and Cai, S.M. (2000) A photoelectrochemical solar cell base on ZnO/dye/polypyrrole film electrode as photoanode. Solar Energ Materials & Solar Cells, 60, 349-359.

Hasiah, S., Ibrahim, K., Senin, H.B., and Halim, K.B.K. (2008) Electrical Conductivity of Chlorophyll with Polythiophene Thin Film on Indium Tin Oxide as *P-N* Heterojunction Solar Cell. Journal of Physical Science, 19(2), 77–92.

Kim, S.R., Parvez, M.K., and Chhowalla, M. (2009) UV-reduction of graphene oxide and its application as an interfacial layer to reduce the back-transport reactions in dye sensitized solar cells. Chemical Physics Letters, 483, 124–127.

Kumar, D., and Sharma, R.C. (1998) Advance in conductive polymers. European Polymer Journal, 34(8), 1053-1060.

Lee, W.J., Roh, S.J., Hyung, K.H., Park, J.Y., Lee, S.H., and Han, S.H. (2009) Photoelectrochemically polymerized polythiophene layers on ruthenium photosensitizers in dye-sensitized solar cells and their beneficial effects. Solar energy, 83, 690-695.

Lim, I., Yoon, S.J., Lee, W.J., Nah, Y.C., Shrestha, N.K., Ahn, H.K., and Han, S.H. (2012) Interfacially Treated Dye-Sensitized Solar Cell with in Situ Photopolymerized Iodine Doped Polythiophene. ACS Applied Materials & Interfaces, 4, 838–841.

Oftadeh, M., Aghtar, A., Esfahani, M.N., Salavati, M.N., and Mir, N. (2012) Fabrication of highly efficient dye-sensitized solar cell and CO2 reduction photocatalyst using TiO2 nanoparticles prepare by spin coating-assisted sol–gel method. Journal of the Iranian Chemical Society, 9(2), 143-149.

Sari, B., Talu, M., Yildirim, F., and Kurs, E.B. (2003) Synthesis and characterization of polyurethane/polythiophene conducting copolymer by electrochemical method. Applied Surface Science, 205, 27–38.

Saito, M., and Fujihara, H. (2009) Fabrication and photovoltaic properties of dye-sensitized ZnO thick films by a facile doctor-blade printing method using nanocrystalline pastes. Journal of the Ceramic Society of Japan, 117(7), 823-827.

Uzun, O., Basman, N., Alkan, C., Kolemen, U., and Yılmaz, F., (2010) Depth sensing indentation analysis of electrochemically synthesized polythiophene. Materials Chemistry and Physics, 124, 196–202.

Valaski, R., Yamamoto, N.A.D., Canestraro, C.D., Micaroni, L., Mello, R.M.Q., Quirino, W.G., Legani, C., Achete, C.A., Roman, L.S., and Cremona, M. (2010) Polythiophene thin films electrochemically deposited on sol–gel based TiO2 for photovoltaic applications. Thin Solid Films, 519, 1511–1515.