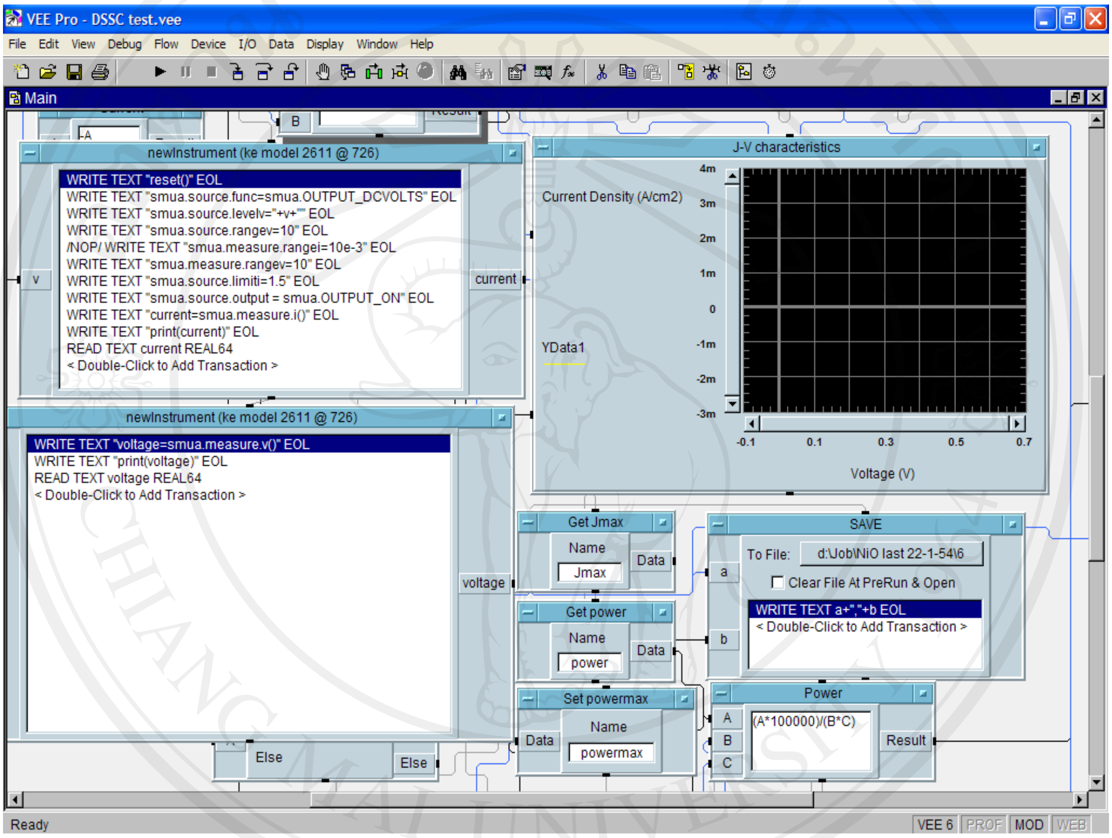
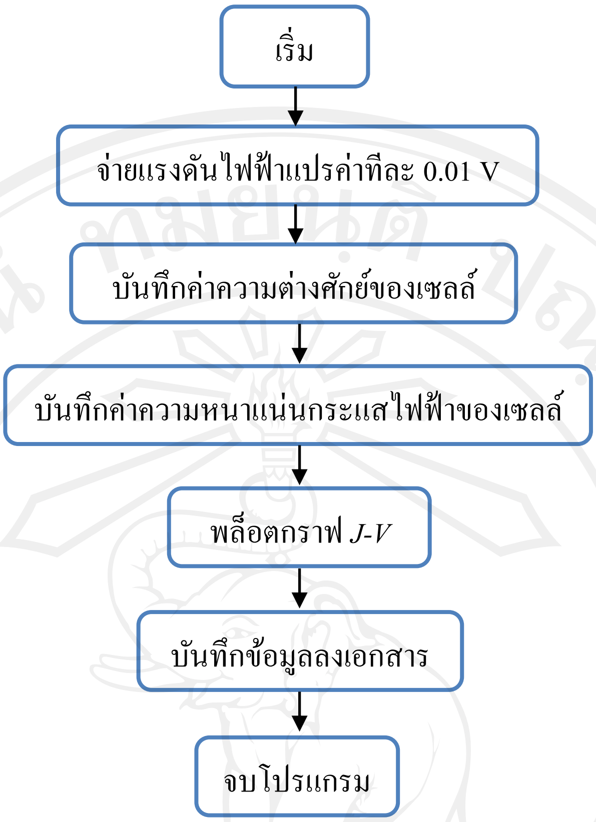
ภาคผนวก ก

โปรแกรมคอมพิวเตอร์ VEE Pro 6.0 ที่ใช้สำหรับวัดประสิทธิภาพการเปลี่ยนพลังงานแสงเป็นพลังงานไฟฟ้าของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง

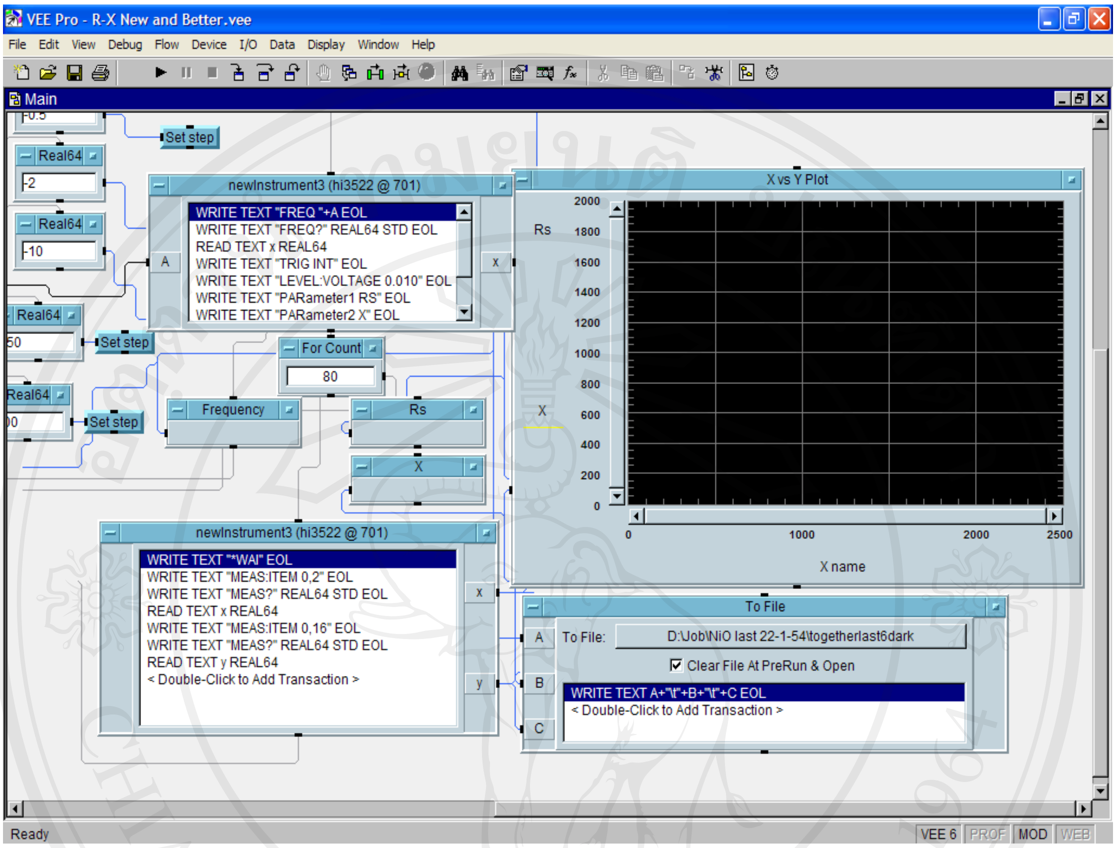


รูปที่ ก1 แสดงลักษณะของโปรแกรม VEE Pro 6.0 ที่ใช้สำหรับการวัดประสิทธิภาพ

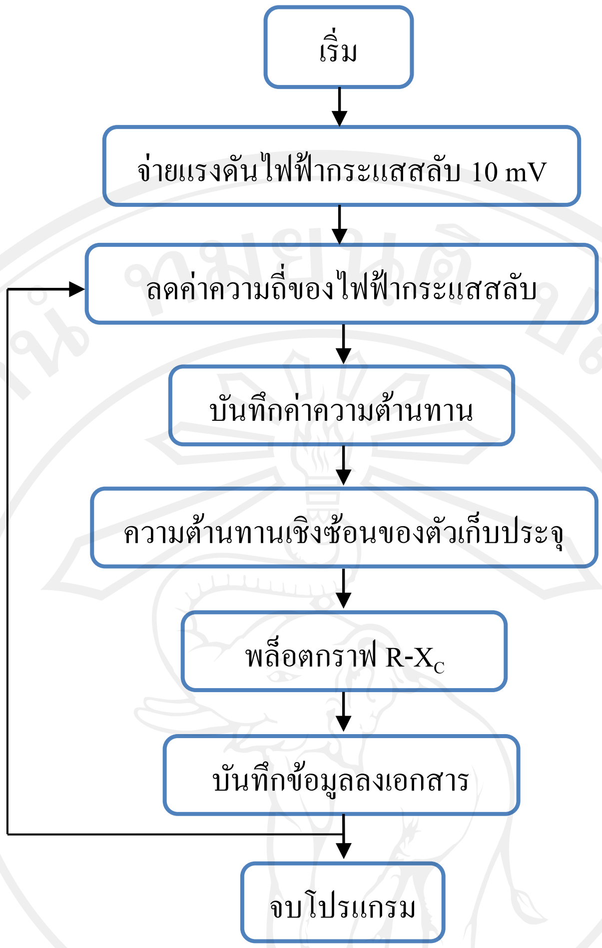


รูปที่ ก2 แสดงแผนผังการทำงานของโปรแกรม VEE Pro 6.0 ที่ใช้วัดประสิทธิภาพ

โปรแกรมคอมพิวเตอร์ VEE Pro 6.0 ที่ใช้สำหรับวัดอิมพิแดนซ์ทางเคมีไฟฟ้าสเปกโทรสโคปีของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง



รูปที่ ก3 แสดงลักษณะของโปรแกรม VEE Pro 6.0 ที่ใช้สำหรับการวัดอิมพิแดนซ์ทางไฟฟ้าเคมี



รูปที่ ก4 แสดงแผนผังการทำงานของโปรแกรม VEE Pro 6.0 ที่ใช้วัดอิมพิแดนซ์ทางไฟฟ้าเคมี

ภาคผนวก ข

ผลงานทางวิชาการ

1) นำเสนอผลงานแบบบรรยาย (Oral) ในงานประชุมวิชาการระดับประเทศ "SIAM PHYSICS CONGRESS 2011" จัดโดย สมาคมฟิสิกส์ไทย ร่วมกับมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี ระหว่างวันที่ 23-26 มีนาคม 2554 ณ โรงแรมแอมบลาสเดอร์ซิตี้ จอมเทียน พัทยา ชลบุรี โดยมีรายละเอียดดังนี้

THAI JOURNAL OF PHYSICS, SERIES 7, pp. 48-51 (2011)

EFFICIENCY ENHANCEMENT IN DYE-SENSITIZED SOLAR CELLS BY USING MIXTURE OF ZnO NANOPARTICLE AND ZnO POWDER

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In this work, the photoelectrochemical characteristics of ZnO dye-sensitized solar cells (ZnO-DSSCs) with the mixing of ZnO nanoparticle and ZnO powder were investigated. The structure of DSSCs was composed of ZnO layer (ZnO nanoparticle and ZnO powder) as a semiconductor, Eosin Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt/FTO as a counter-electrode. The photo-electrode was fabricated by screening mixed ZnO onto fluorine-doped tin oxide glass (FTO glass). The thickness of ZnO film was controlled by varying layer number of adhesive tape (1–4 layers). The ratios of mixed ZnO between ZnO nanoparticle and ZnO powder were 1:3, 1:1, and 3:2 by weight. The ZnO layers were characterized by FE-SEM and Raman spectroscopy. The photoelectrochemical characteristics of ZnO DSSCs were measured under stimulated sunlight AM 1.5 from a solar simulator with the radiant power of 100 mW/cm^2. It was found that all ratios of mixture ZnO film with 3 layers of adhesive tape exhibited higher photoconversion efficiency (1.07%) than those of only ZnO nanoparticle or ZnO powder. Thus, mixing ZnO nanoparticle and powder can be used for enhancement of efficiency in ZnO DSSCs.

Keywords: Dye-sensitized solar cells; Photoconversion efficiency; ZnO nanoparticle

INTRODUCTION

The dye-sensitized solar cells (DSSCs) are one of the promising organic solar cells. They have been widely investigated due to their low fabrication cost, environmental friendly (non-toxic gases) easy to produce and relatively high power conversion efficiency. Recently, Michael Grätzel has used nanocrystalline TiO_2 with *cis*-$Ru(SCN)_2L_2$ dye sensitizer as a photo-electrode. It exhibits high power conversion efficiency over 11% [1]

ZnO is a promising metal oxide semiconductor that can be used as an alternative photo-electrode in DSSCs. It has a wide band gap, electron affinity and electron injection efficiency similar to those of TiO_2 [2, 6]. Several works have been reported on DSSCs based on ZnO with Eosin Y dye sensitizer as a photo-electrode and the highest power conversion efficiency is 2.4% [3]. However the efficiencies of DSSCs based on ZnO are still lower than that of TiO_2.

One of the techniques that use to enhance the efficiency of ZnO DSSC is by increasing the dye adsorption surface area of the film photo-electrode on conducting glass. It is expected that the larger of the surface area by using nanostructure the higher the efficiency. Several methods have been applied to improve the power conversion efficiencies of DSSCs [2-7]. For example, Kakiuchi et al. improved dye-loading in ZnO photoelectrode by the formation of mesoporous microstructure and obtained power conversion efficiency as high as 4.1% [4]. Junting Xi et al. have used TiO_2 aggregates/nanocrystallites mixed photoelectrodes for a high power conversion efficiency of 7.59% [5]. In this work, we have investigated the effect of ZnO NP, ZnO powder and ZnO NP/powder mixtures on the photoelectrochemical properties of DSSCs.

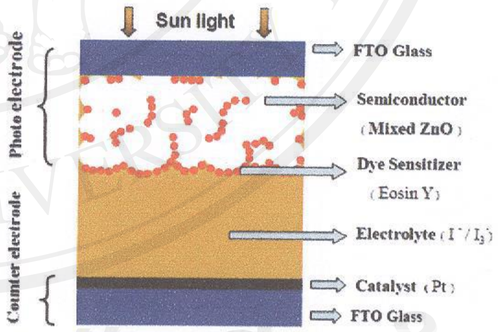

FIGURE 1. Schematic diagram of DSSC structures with mixture of ZnO nanoparticle and ZnO powder photo-electrode.

EXPERIMENT

The ZnO DSSC structures used in this experiment were shown as schematic diagram in Fig.1. The photo-electrodes were based on ZnO nanoparticle (NP), ZnO powder, and mixture of ZnO NP and powder (NP/powder). First, paste of ZnO NP and powder were prepared by mixing ZnO NP (purity of 99.5+%,

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ZoNoP) or powder (purity of 99.9%, Sigma Aldrich) with polyethylene glycol (PEG 20000, Sigma Aldrich) in distilled water and stirring for 30 min. For the ZnO mixture paste (ZnO NP/powder paste), it was prepared as the same condition as ZnO powder paste with ratios between ZnO NP and powder of 1:3, 1:1, and 3:2 by weight.

Next, the photo-electrode was prepared by screen printing the ZnO paste on transparent conducting oxide glass (fluorine doped-tin oxide: FTO, sheet resistance of 8 Ω/sheet) with an active area of 0.5x2 cm^2. The thickness of ZnO film was controlled by varying number layers of adhesive tape (1–4 layers). The FTO glasses coated with ZnO film were sintered at 400°C for 1 h under normal atmosphere.

Then, the photo-electrodes were soaked in Eosin-Y organic dye solution with a concentration of 0.6 mM (0.04 g of Eosin Y, $C_{20}H_6Br_4Na_2O_5$, in ethanol 100 cm^3) for 2 h. The dye-loaded ZnO photo-electrodes and the Pt counter-electrode (0.5 mM Hydrogen hexachloroplatinate (IV) Hydrate, $Cl_6H_2Pt.aq$, in acetone solution) were assembled into a sealed device using a hot-melted double layer parafilm (50 μm thick/sheet). The redox electrolyte (0.3 M LiI + 0.03 M I_2 in polyethylene carbonate) was introduced into the inter-space between the photo-electrode and the counter-electrode through two predrilled holes on the side of the device.

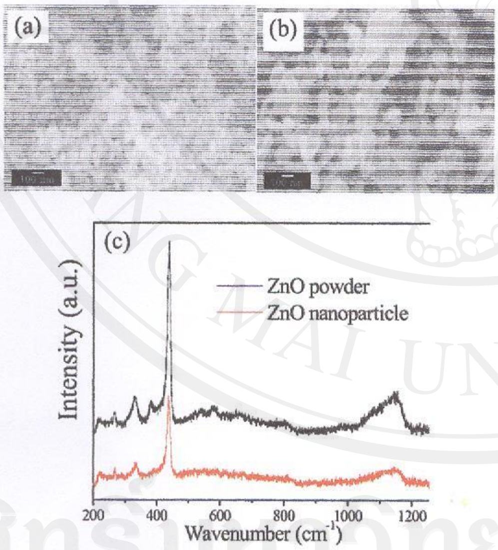

FIGURE 2. FE-SEM image of (a) ZnO NP, (b) ZnO powder, and (c) Raman spectra of ZnO NP and ZnO powder.

The photoelectrochemical characteristics of ZnO DSSCs were measured under illumination of simulated sunlight came from a solar simulator with the radiant power of 100 mW/cm^2 (xenon lamp with AM-1.5 filter). The incident light intensity was calibrated with a standard Si solar cell. The photocurrent densities versus photovoltage (J-V) characteristics were measured with dc voltage and current source which were interfaced and controlled by a computer.

The fill factor (*FF*) and the power conversion efficiency (η) were calculated from *J-V* curves by the equations

$$FF = \frac{J_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}} \quad (1)$$

and

$$\eta = \frac{J_{sc} \cdot V_{oc}}{P_{in}} \cdot FF \quad (2)$$

Electrochemical impedance spectroscopy was performed by using a impedance analyzer (Hioki model 3522-50) with DSSC under sunlight condition in the frequency range of 10,000 Hz to 1 Hz. Z-view software with a equivalent circuit modeling was used to fit the data in order to obtain a charge transfer resistance of ZnO photo-electrodes.

In addition, morphology of ZnO NP and ZnO powder was characterized by field emission scanning electron microscope (FE-SEM). ZnO photoelectrodes were also characterized by Raman spectroscope (T6400, Ar-laser λ = 514.53 nm).

RESULTS AND DISCUSSIONS

Figure 2 (a) and (b) showed FE-SEM images of ZnO NP and ZnO powder. A particle-like structure was observed with particle size less than 50 and 300 nm for ZnO NP and powder, respectively. Figure 2 (c) showed Raman spectra of ZnO NP and ZnO powder. The peaks in spectra ZnO NP and ZnO powder was similar confirming ZnO phase.

Figure 3 (a), (b), and (c) showed FE-SEM images of ZnO NP/powder mixture with the ratio of 1:3, 1:1, and 3:2 by weight, respectively. Compared to that of ZnO powder, the particle size of NP/powder mixtures was smaller.

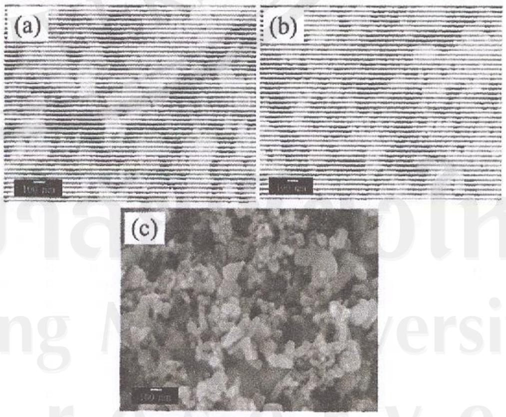

FIGURE 3. FE-SEM images of ZnO NP/powder mixture with the ratio of (a) 1:3, (b) 1:1, and (c) 3:2 by weight.

Figure 4 showed plot of efficiency of DSSCs based on ZnO NP/powder mixtures at various weight ratios as a function of number layers of adhesive tapes (film thickness). It was found that DSSCs based on pure ZnO NP (1:0 ratio) and pure ZnO powder (0:1 ratio) showed the optimum photoconversion efficiencies at 2 layers of adhesive tapes for 0.96% and 0.89%, respectively. However, DSSCs based on ZnO NP/powder mixtures with ratios of 1:3, 1:1, 3:2 showed the optimum photoconversion efficiencies at 3 layers of adhesive tapes for 1.06%, 1.07% and 1.07%, respectively. Thus, the condition of three layers of adhesive tapes was selected for further investigation.

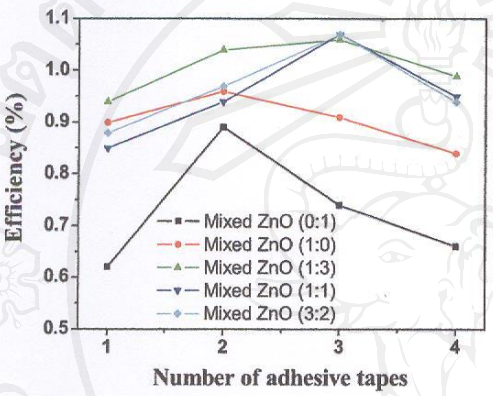

FIGURE 4. Plot of efficiency of DSSCs based on ZnO NP/powder mixtures at various weight ratios as a function of number layers of adhesive tapes of adhesive tapes.

Figure 5 shows *J-V* characteristics of DSSCs based on ZnO NP/powder at various weight ratios at 3 layers of adhesive tapes.

The photoelectrochemical parameters such as the short circuit density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (*FF*), the overall power conversion efficiency (η) which determined from the measured *J-V* curves, and their charge transfer resistance (R_{ct}) was summarized in Table 1. It can be seen that DSSC based on ZnO NP exhibited the highest current density (J_{sc} = 4.35 mA/cm^2) but DSSC based on ZnO powder exhibited the highest fill factor (*FF* = 0.57).

Surprisingly, J_{sc} and FF of DSSCs based on NP/powder mixtures exhibited the values in between those of ZnO NP and powder, respectively. Thus, the mixtures gave a combined effect from both ZnO NP and powder with the power conversion efficiency of about 1%.

In order to investigate the electron transport property in ZnO DSSCs, a electrochemical impedance spectroscopy (EIS) was performed. Figure 6 showed the EIS spectra of DSSCs based on ZnO NP/powder at various weight ratios under light condition. The EIS spectra were then fitted using Z-view software to obtain charge transfer resistance (R_{ct}) as listed in Table 1. It is found that ZnO DSSCs based on ZnO NP/powder mixtures exhibited the lowest resistance. This suggested that more efficient electron transfer at ZnO/dye/electrolyte interface was occurred in the case of NP/powder mixtures [8]. Therefore, using mixture of NP/powder is one of the techniques that can be applied for enhancement of power conversion efficiency in DSSCs.

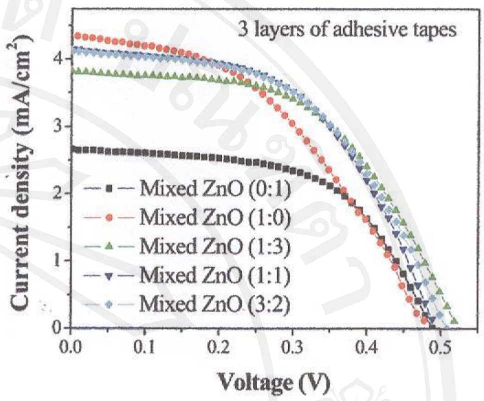

FIGURE 5. *J-V* characteristics of DSSCs based on ZnO NP/powder at various weight ratios at 3 layers of adhesive tapes.

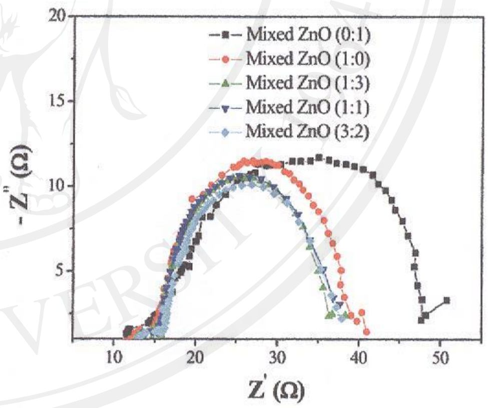

FIGURE 6. EIS spectra of DSSCs based on ZnO NP/powder at various weight ratios under light condition.

Table 1. Summary of the electrochemical parameters such as short current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (*FF*), the overall power conversion efficiency (η) which determined from the measured *J-V* curves, and their charge transfer resistance (R_{ct}).

DSSCs	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η(%)	R_{ct} (Ω/cm^2)
Mixed ZnO (0:1)	2.66	0.49	0.57	0.74	27.72
Mixed ZnO (1:0)	4.35	0.48	0.44	0.91	23.26
Mixed ZnO (1:3)	3.83	0.52	0.53	1.06	21.09
Mixed ZnO (1:1)	4.16	0.49	0.53	1.07	21.47
Mixed ZnO (3:2)	4.13	0.51	0.51	1.07	20.59

CONCLUSION

The photoelectrochemical characteristics of ZnO dye-sensitized solar cells (ZnO-DSSCs) with the mixing of ZnO NP and ZnO powder at mixture ratios of 0:1, 1:3, 1:1, 3:2, and 1:0 by weight were investigated. From photoconversion results, it was found that the mixtures gave a combined effect from both ZnO NP and powder with the power conversion efficiency of about 1%. Also, EIS results suggested that electron transfer at ZnO/dye/electrolyte interface was more efficient in the case of NP/powder mixtures. Therefore, using mixture of NP/powder is one of the techniques that can be applied for enhancement of power conversion efficiency in DSSCs.

ACKNOWLEDGMENTS

We are grateful to Commission of Higher Education (CHE). Apirak Apiwong-ngarm would like to acknowledge the Graduate School, Chiang Mai University for financial support.

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A-PO4-42

Efficiency Improvement of ZnO Dye-sensitized Solar Cells by Using Double-layer of ZnO nanoparticle/ZnO powder

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ABSTRACT

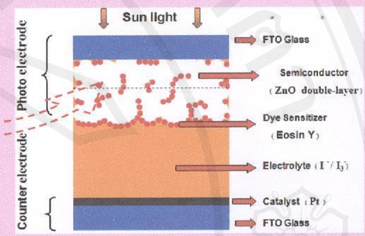
In this work, the photoelectrochemical characteristics of ZnO dye-sensitized solar cells (DSSCs) with double layer of ZnO nanoparticle/ZnO powder were investigated. The structure of DSSCs was ZnO nanoparticles/ZnO powder as a semiconductor, Eosin Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt/FTO as a counter-electrode. The photo-electrode was fabricated by screening ZnO nanoparticle as underlayer and ZnO powder as upper layer. The ZnO double-layers with thickness ratio of 1:1, 1:2, 1:3, 2:1, 2:2 and 3:1 were studied. The films were characterized by FE-SEM and Raman spectroscopy. The photoelectrochemical characteristics of ZnO DSSCs were measured under stimulated sunlight AM 1.5 from a solar simulator with the radiant power of 100 mW/cm². It was found that DSSCs with thickness ratio of 1:3 exhibited the highest photoconversion efficiency of 1.10%. The improvement of photoconversion efficiency with double layer can be explained in term of low transfer resistance.

Keywords : Dye-sensitized Solar Cells, Photoconversion Efficiency, ZnO nanoparticle

INTRODUCTION & EXPERIMENTAL

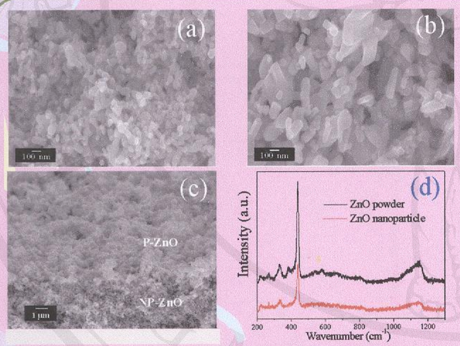
Objective: to improve the efficiency of DSSCs by using double-layer ZnO films

The ZnO double-layer with thickness ratio of 1:1, 1:2, 1:3, 2:1, 2:2 and 3:1

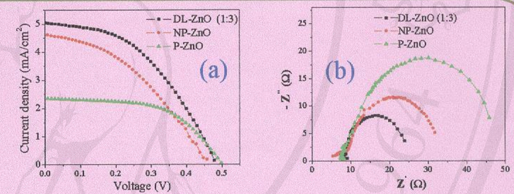


ZnO-DSSCs Structure

RESULTS & DISCUSSION



(a) and (b) showed FE-SEM images of NP-ZnO and P-ZnO , (c) Cross-sectional FE-SEM image of a double-layer film, and (d) Raman spectra of NP-ZnO and P-ZnO



(a) *J-V* characteristics of DSSCs, (b) EIS spectra of DSSCs

Summary of the electrochemical parameters such as short current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (*FF*), the overall power conversion efficiency (η) which determined from the measured *J-V* curves, and their charge transfer resistance (R_{ct}).

Ratios	Jsc (mA/cm²)	Voc (v)	FF	η(%)
1:1	4.01	0.43	0.47	0.81
1:2	4.53	0.43	0.49	0.96
1:3	5.05	0.48	0.45	1.10
2:1	3.97	0.48	0.45	0.85
2:2	3.23	0.45	0.42	0.61
3:1	3.48	0.48	0.45	0.75

Comparison of J_{sc} , V_{oc} , *FF*, and η for DL-ZnO films

Samples	Jsc (mA/cm²)	Voc (V)	FF	η (%)	Rct (Ω/cm²)
NP-ZnO	4.62	0.46	0.40	0.84	23.23
P-ZnO	2.35	0.50	0.56	0.66	36.98
DL-ZnO	5.05	0.48	0.45	1.1	16.44

CONCLUSIONS

- The double-layer film at thickness ratios of 1:3 enhanced the highest photoconversion efficiency of 1.10%.
- EIS data analysis proved that DL-ZnO film-based cell possessed the lowest charge transfer resistance.
- The double-layer film is one of the techniques that use to enhance the efficiency of ZnO DSSC is by increasing the dye adsorption surface area of the film photo-electrode on conducting glass.

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ประวัติผู้เขียน

ชื่อ - นามสกุล นาย อภิรัก อภิวงค์งาม

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ผลงานตีพิมพ์
A. Apiwong-ngarm, D. Wongratanaphaisan, A. Gardchareon and S. Choopun "Efficiency enhancement in dye-sensitized solar cells by using mixture of ZnO nanoparticle and ZnO powder," Thai Journal of Physics, Series 7, 2011, 48-51.

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