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Contributed Paper

Energy Conversion Efficiency Improvement of ZnO Dye-sensitized Solar Cells by Dye Re-adsorption and N-P Junction Technique

Surat Futemvong [a,b], Niyom Hongsith [b,d], Duangmanee Wongratanaphisan [b,c], Atcharawon Gardchareon [b,c] and Supab Choopun*[b,c]

[a] Department of Science, Muangpan Wittaya School, Lampang 52240, Thailand.
[b] ThEP center, CHE, Bangkok 10400, Thailand.
[c] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.
[d] School of Science, University of Phayao, Phayao 56000, Thailand.
*Author for correspondence; e-mail: supab99@gmail.com

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ABSTRACT

In this work, ZnO Dye-sensitized solar cells (DSSCs) with dye re-adsorption technique and NiO thin films coated as n-p junction were investigated. The general structures of ZnO DSSCs were FTO/ZnO as a photo-electrode, Eosin-Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt/FTO as a counter-electrode. For dye re-adsorption technique, ZnO photo-electrodes were soaked into Eosin-Y solutions as dye adsorption, then soaked into ethanol as dye desorption (3-step sequence). From the absorption spectra, the absorbance values depended on the dye re-adsorption steps suggesting the removal of the excess dye molecules during the process. For n-p junction, NiO thin films were coated on ZnO with 0.6 mg to form a barrier layer in photo-electrode called ZnO/NiO. The optimum conditions for the dye re-adsorption technique were selected with n-p junction DSSCs. The DSSCs were investigated by using J-V measurement and electrochemical impedance spectroscopy. It was found that ZnO and ZnO/NiO DSSCs with first dye re-adsorption exhibited the highest energy conversion efficiency of 0.99% and 1.10%, respectively. The improvement of energy conversion efficiency due to dye re-adsorption and n-p junction can be explained in terms of reduction of dye aggregation and decrease of charge recombination in photo-electrode.

Keywords: dye-sensitized solar cell, energy conversion efficiency, zinc oxide, nickel oxide, dye re-adsorption

1. INTRODUCTION

Dye-sensitized solar cell (DSSC) is a novel type of solar cell that discovered by Michael Grätzel in 1991 [1]. It has caught great attention due to low production cost, ease of fabrication, and environmental friendly (non-toxic gases). Since the work of Brian O'Regan and Michael Grätzel, DSSC with TiO_2 as semiconductors and ruthenium bipyridyl complexes [Ru(4,4/-dicarboxylic acid-2-2/-bipyridine)$_2$(NCS)$_2$] as a dye

sensitizer. The highest energy conversion efficiency obtained from TiO_2 DSSCs was 10.8% [1] and recently reported up to 11% [2]. Thus, TiO_2 has been a popular metal oxide in DSSCs.

ZnO is one of a promising metal oxide semiconductor which can be used as an alternative material in DSSCs due to its energy band gap, electron affinity and electron injection efficiency close to those of TiO_2 [3]. Recently, Woo-Jin Lee and coworkers [4] had studied ZnO as a semiconductor and Eosin-Y as a dye sensitizer in DSSCs. They obtained the highest energy conversion efficiency of 2.4%. However, DSSCs based on ZnO showed lower energy conversion efficiency than those of based on TiO_2 [5]. The important effects that attribute to reduce the efficiency are the dye aggregation [6] and the charge recombination at semiconductor/dye/electrolyte interface. Several methods have been applied to improve the energy conversion efficiency of ZnO DSSCs [7-11]. For example, dye desorption and re-adsorption post-treatments on electrodeposited ZnO/Eosin-Y hybrid thin films [9] have been used to improve the energy conversion efficiency from 0.8% to 2.3%. Moreover, the fabrication of n-p junction as a barrier layer for minimizing the charge recombination [7] has been also improved the energy conversion efficiency in ZnO DSSCs.

Nickel Oxide (NiO) is one of a p-type metal-oxide semiconductor with a wide band gap of ~4.0 eV [12, 13]. Thus, it can be used to form n-p junction in order to control charge recombination for improvement of photoconversion efficiency in ZnO DSSCs. Recently, p-NiO has been successfully used to form n-p junction with n-TiO_2 and obtained higher photoconversion efficiency from 3.21% to 4.16% [14].

In this work, the dye re-adsorption technique was applied to ZnO DSSCs in order to reduce the dye aggregation. Moreover, the n-p junction technique by using NiO thin films as a barrier layer at the photo-electrodes was used in order to reduce charge recombination. The both techniques were used as combining techniques for better efficiency improvement.

2. MATERIALS AND METHODS

First, ZnO paste was made by mixing ZnO powder (purity of 99.9%, Sigma Aldrich) and polyethyleneglycal (PEG 20000, Sigma Aldrich) in distilled water in a weight ratio of 5:1.2:12. Next, the photo-electrode was fabricated by screening ZnO paste on transparent conducting oxide glass (fluorine dope-tin oxide: FTO-8 Ω/sheet) with an active area of 0.5×2 cm^2. The FTO covered with ZnO was heated at 400°C for 1 h under normal atmosphere. To study the effects of dye re-adsorption on the energy conversion efficiency, the dye re-adsorption steps was performed. ZnO photo-electrodes were firstly soaked into Eosin-Y solutions as a dye adsorption for 1h (ZnO-Ad), then soaked into ethanol as the first dye desorption for 1h (ZnO-De(1), then soaked into Eosin-Y solutions as the first dye re-adsorption for 1h (ZnO-Re(1)), then soaked into ethanol as the second dye desorption for 1h (ZnO-De(2)), and finally soaked into Eosin-Y solutions as the second dye re-adsorption for 1h (ZnO-Re(2)). The optimal condition obtained from dye re-adsorption technique was selected for further study of n-p junction technique [8]. For n-p junction, the ZnO films on FTO were then coated with thin layer of NiO by thermal evaporation technique. NiO powder (Sigma Aldrich) of 0.6 mg was used as an evaporating material at base pressure of $\sim 5.0 \times 10^{-5}$ mbar. After evaporation, NiO films were heated at

400°C for 0.5 h (ZnO/NiO-Re(1)).

The counter-electrode was fabricated by screening the mixed solution of 20 mM hydrogen hexachloroplatinate (IV) hydrate (Cl_6H_2Pt) in acetone on FTO glass with an active area of 0.7 × 2 cm^2 and then heated at 400°C for 0.5 h.The photo-electrode and the counter-electrode were assembled using a hot-melted double layer parafilm (50 μm thick) to create the inter-spacing between two electrodes. The electrolyte (0.3 M LiI, 0.03 M I_2 in propylene carbonate) was introduced into the inter-spacing.

The desorbed dye solutions were characterized by using the UV-visible spectrophotometer (Varian Model Cary 50). The photocurrent density–photovoltage (*J-V*) characteristics were measured by source meter potentiostat (Keithley 2611) interfaced and controlled by pc computer under stimulated sunlight obtained from solar simulator with the radiant power of 100 mW/cm^2. The short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (*FF*) and energy conversion efficiency (η) were determined from the *J-V* curve. Electrochemical impedance spectroscopy (EIS) was performed by LCR tester (Hioki 3522-50) in the frequency range of 1 Hz - 10 kHz with the magnitude of the alternative signal of 10 mV. EIS spectra were recorded under forward bias (-0.4 V) in the light condition. The obtained EIS spectra were then fitted using Z-view software to obtain series resistance (R_S) and charge transfer resistance (R_{CT}) of ZnO DSSCs. Figure 3 showed the *J-V* characteristics of the ZnO and ZnO/NiO DSSCs with dye re-adsorption method.

3. RESULTS AND DISCUSSIONS

3.1 Optical Properties

Figure 1 (a) showed the absorption spectra of the first and the second desorbed dye solution from ZnO photo-electrode. The spectra were dominant at 527 nm corresponding to the absorption of Eosin-Y molecules. After the second desorption, this Eosin-Y peak decreased suggesting in removing excess Eosin-Y dye molecules on ZnO surface.

Figure 1 (b) showed the absorption spectra of dye coated ZnO films with different re-adsorption steps. The absorption of dye coated on ZnO photo-electrode was observed at two regions, at below 380 nm and between 400-600 nm corresponding to ZnO absorption and Eosin-Y absorption, respectively.

It was found that after desorption step, the absorbance value decreased indicating the removal of the excess dye molecules. Moreover, the first desorption showed the lowest adsorbed dye molecules on ZnO films. and the second re-adsorption showed the highest adsorbed dye molecules on ZnO films.

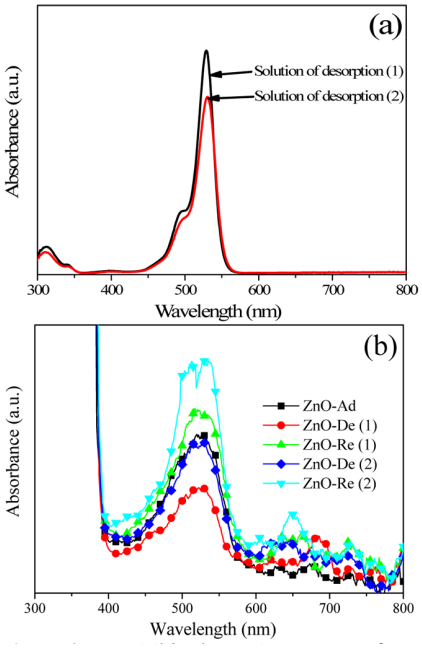

Figure 1. UV-visible absorption spectra of (a) desorbed dye solution and (b) the dye coated ZnO films with different re-adsorption steps.

3.2 Electrical Properties

The photoelectrochemical parameters such as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and energy conversion efficiency (η) were determined from J-V curve in Figure 2 and summarized as shown in Table 1. It can be seen that the reference cell of ZnO adsorption step exhibited the lowest photocurrent density of 3.36 mA/cm^2 resulting in the lowest energy conversion efficiency of 0.90%.

For the first dye desorption (1) step, the higher photocurrent density of 3.80 mA/cm^2 and energy conversion efficiency of 0.97% were observed and can be explained by a decrease of the excess dye molecules as confirmed by absorption spectra. For both first dye re-adsorption (1) and second dye desorption (2) steps, the highest energy conversion efficiency of 0.99% was observed. However, first dye re-adsorption (1) step exhibited higher photocurrent density (3.68 mA/cm^2) than second dye desorption (2) step (3.64 mA/cm^2) suggesting the optimum condition for adsorbed dye molecules on ZnO surface due to re-adsorption process. For the second dye re-adsorption (2) steps, the energy conversion efficiency (0.94%) became lower than the first dye re-adsorption (1) step. Even though the second dye re-adsorption (2) step exhibited the highest amount of dye adsorbed on ZnO surface as seen on adsorption spectra, the lower energy conversion efficiency was still observed. This was due to the dye aggregation on the ZnO surface and forming the insulating Zn^{2+}/dye complex layer when soaking at longer times [9]. This insulating layer blocks the injection of electrons from the dye molecule to the ZnO conduction band resulting in lower photocurrent density and energy conversion efficiency.

The results were in agreement with the previous work on the dye desorption and re-adsorption post-treatments on electrodeposited ZnO/Eosin-Y hybrid thin films [9]. They found that the more dye loading on ZnO were caused a dye aggregation and decrease of the photocurrent density from 5.9 mA/cm^2 to 0.33 mA/cm^2 resulting in lower the efficiency.

Thus, the optimum condition for dye re-adsorption technique is the first dye re-adsorption step and this condition was used for n-p junction technique. As expected, the DSSCs with combination effect of dye re-adsorption technique and n-p junction technique exhibited the highest energy conversion efficiency of 1.10% and highest photocurrent density of 3.90 mA/cm^2 as shown in Table 1. The results of efficiency improvement by ZnO/NiO junction were in agreement with our previous results [8] that improved the energy conversion efficiency from ZnO reference cell of 0.75% to ZnO/NiO junction cell of 1.00%.

Table1. Summary of photoelectrochemical parameters of ZnO and ZnO/NiO DSSCs.

Steps	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
ZnO-Ad	3.36	0.51	0.53	0.90
ZnO-De(1)	3.80	0.50	0.51	0.97
ZnO-Re(1)	3.68	0.50	0.54	0.99
ZnO De(2)	3.64	0.50	0.54	0.99
ZnO-Re(2)	3.60	0.49	0.54	0.94
ZnO/NiO-Re(1)	3.90	0.51	0.55	1.10

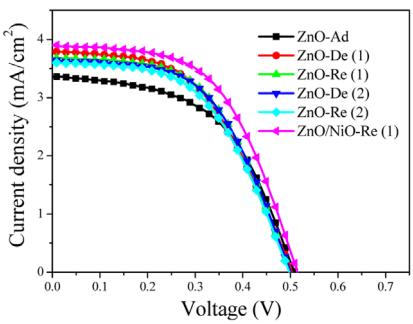

Figure 2. J-V characteristics of ZnO DSSCs with dye re-adsorption technique and n-p junction technique.

For investigation the electrical properties, electrochemical impedance spectroscopy (EIS) or the Nyquist plot was used to characterize the kinetics of electrochemical process such as electron transport, charge recombination and electron life time. Figure 3 (a) and (b) showed EIS spectra of ZnO and ZnO/NiO DSSCs with different re-adsorption steps and plot of series resistance (R_s) and charge transfer resistance (R_{CT}) as a function of re-adsorption steps, respectively. It can be seen that only one semicircle at the medium frequency was observed. A starting point of all semicircles at high frequency represented the series resistance, R_s, accounting for the transport resistance of FTO. It was found that R_S was about 15-20 W of each samples which indicating the sheet resistance of FTO glasses. Typically, the radius of these semicircles can be related to the charge transfer resistance, R_{CT}, across the photoelectrode-electrolyte layer. The larger the radius of the semicircle indicated the higher the charge transfer resistance.

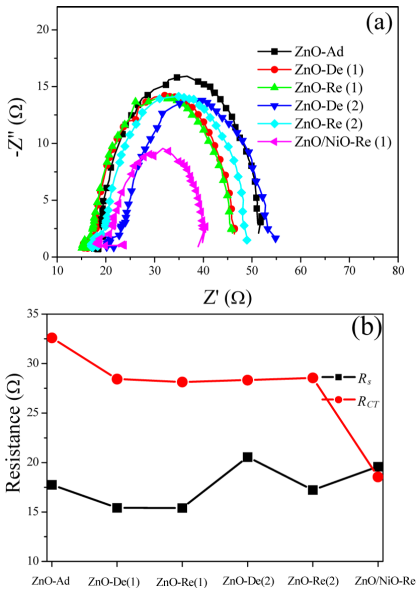

Figure 3. (a) EIS spectra of ZnO DSSCs with different re-adsorption steps and (b) plot of series resistance (R_s) and charge transfer resistance (R_{CT}) as a function of re-adsorption steps.

It can be seen that ZnO DSSCs with dye re-adsorption technique and n-p junction technique exhibited the lowest charge transfer resistance indicating the lowest charge recombination. Therefore, the improvement of energy conversion efficiency due to dye re-adsorption effect and n-p junction effect can be explained in terms of reduction of dye aggregation and decrease of charge recombination [10, 11] in photo-electrode.

4. CONCLUSION

The effects of dye re-adsorption technique and n-p junction technique on photoelectrochemical performance of ZnO dye-sensitized solar cell were investigated. From the absorption spectra, the absorbance values depended on the dye re-adsorption steps suggesting the removal of the excess dye molecules during the process. It was found that ZnO DSSCs with first dye re-adsorption step exhibited the highest energy conversion efficiency of 0.99%. This is due to the reduction of dye aggregation and optimal adsorbed dye onto ZnO surface. Moreover, it was found that ZnO/NiO DSSCs with first dye re-adsorption exhibited the highest energy conversion efficiency of 1.10%. This is due to the decrease of charge transfer resistance. Therefore, the improvement of energy conversion efficiency due to combination effect of dye re-adsorption effect and n-p junction effect can be explained in terms of reduction of dye aggregation and decrease of charge recombination in photo-electrode. Finally, these techniques of the efficiency improvement can be applied with other techniques such as antireflection coating in order to further improvement of DSSC efficiency.

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