Research Article

Surface Modification of Porous Photoelectrode Using Etching Process for Efficiency Enhancement of ZnO Dye-Sensitized Solar Cells

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Surface modification of porous ZnO photoelectrode using one- and two-step etching process is investigated for enhancing power conversion efficiency of ZnO dye-sensitized solar cells. ZnO films are modified by the diluted NH_4OH solutions for one-step etching process and used as photoelectrode of dye-sensitized solar cells. Rough porous films are observed after one-step etching process. The fabricated cells based on the optimized one-step etched films show a significant increase in short-circuit current density. The short-circuit current density is directly changed with amount of dye adsorption, which is related to specific surface area. The etched films exhibit higher specific surface area over two times than nonetched films. Thus, the large specific surface area is the key success for increasing amount of dye adsorption. Internal electrochemical property of fabricated cells is also improved, indicating that chemical surface of ZnO films is modified in the same time. The DSSCs fabricated on two-step etched films with NH_4OH and mixed acid $\text{HCl}:\text{HNO}_3$ show the maximum power conversion efficiency of 2.26%. Moreover, fill factor is also increased due to better redox process because of the formation of fine porous structure during the etching process. Therefore, these results implied that the roles of etching processes are improving specific surface area and fine porous formation which can provide better dye adsorption and redox process for dye-sensitized solar cell application.

1. Introduction

Dye-sensitized solar cell (DSSC) is one of the attractive solar cells over the past two decades due to various advantages such as relative high efficiency, easy and simple fabrication process on both rigid and flexible substrates, and nontoxicity, low cost, and environmental friendly raw materials [1, 2]. In addition, DSSCs can open huge opportunities for commercial large-scale production such as possibilities to design solar cell with shape flexibility, lightweight, color, and transparency products [3]. Typically, DSSC consists of photoelectrode (PE), counterelectrode (CE), and electrolyte (EL) [4, 5]. Each component of DSSC is intensively researched in order to enhance power conversion efficiency (PCE). Photoelectrode

is considered to be an effective component of DSSC in PCE enhancement due to a key role in controlling photoconversion process such as dye adsorption, light scattering, charge separation, and electron transportation [6–8]. To improve the photoconversion process, surface modification of photoelectrode has been successfully applied for PCE enhancement by using various techniques. The surface treatment of ZnO photoelectrode by controlling temperature has been studied [9] and it was found that PCE is higher at optimum temperature due to an increase of surface area for dye adsorption. The other technique is using double-layer structure films with different particle size to improve light scattering in the photoelectrode [7]. The larger particle size is coated on the smaller particle size to form a scattering layer

which plays an important role in increasing light scattering and decreasing electron scattering in the photoelectrode and at the same time resulting in higher PCE. Plasma etching is also an attractive technique for surface modification. The etching process creates porous structure via reactive ion etching (RIE). The pore size, shape, and distribution can be controlled by selecting appropriate reactive gases and flow rate [10]. However, plasma etching is an expensive technique due to vacuum system requirement. Wet chemical etching is an alternative technique which gains a lot of attention due to a low cost, simple, and short-time process. The chemical reaction in chemical etching can create crater-like morphology of oxide films which increases specific surface area and provides better dye adsorption [11]. Moreover, there are a large variety of chemical etchants that can be used in the etching process such as HCl, HF, HNO₃, KOH, NaOH, and NH₄Cl [11–14].

In this work, surface modification of porous ZnO photoelectrode using one- and two-step etching process is investigated for enhancing power conversion efficiency of ZnO dye-sensitized solar cells. Wet chemical etching process of diluted base (NH₄OH) solutions in distilled water is a promising simple process to improve specific surface area of ZnO photoelectrode, and mixed acid solution of HCl : HNO₃ in distilled water is used to form fine porous structure. Increment of dye adsorption is expected due to the increased specific surface area after the surface modification. The amount of dye adsorption is directly correlated to the amount of generated electrons which can be observed in terms of short-circuit current density (J_{sc}). Finally, power conversion efficiency of DSSC is expected to be enhanced by the optimized condition.

2. Experimental Details

2.1. Preparation of Photoelectrode. ZnO nanoparticle films were deposited onto fluorine-doped tin oxide (FTO) glass substrates by screen printing technique. Commercial FTO glass substrates were carefully cleaned with detergents, distilled water, acetone, and ethanol in an ultrasonic bath for 10 min each. They were then dried in air before depositing ZnO nanoparticle films. ZnO paste for screen printing was prepared by mixing ZnO nanoparticle in polyethylene glycol (PEG) solution. The PEG solution was prepared by dissolving 10% PEG by weight in distilled water, mixed by magnetic stirrer at room temperature. The ZnO paste was then screened onto FTO glass substrates and sintered at 400°C for 1 hr for calcinations and removal of any residual in the films.

2.2. Wet Chemical Etching Process of Photoelectrode. The calcined ZnO films were modified using a wet etching process. In the one-step etching process, a 5% concentration of NH₄OH in distilled water was used to etch the ZnO films at different etching times of 1, 2, and 3 min. Then, the films were immediately rinsed several times with flowing distilled water and dried in air using hot air blower. Finally, the films were annealed at 120°C for 30 min. In the two-step etching process, the one-step etched films were repeatedly etched by mixed acid solution of HCl : HNO₃ : distilled water in volume ratio of 3 : 7 : 44 for 10 s, rinsed, dried and annealed.

2.3. Fabrication of Dye-Sensitized Solar Cell. Dye molecules were loaded into the etched films using readsorption technique similar to that reported elsewhere [15]. The ZnO films, as photoelectrode, were immersed in dye solution at room temperature under dark condition for 1 hr for adsorption process. After the adsorption process, the photoelectrode was immersed in ethanol for 1 hr for deadsorption process. Finally, the photoelectrode was repeatedly immersed in dye solution with the same condition for readsorption process. After 1 hr, it was rinsed with ethanol for several seconds. Eosin-Y (EY) and N719 are used as dye sensitizers. The dye solution was prepared by dissolving 0.6 mM EY in absolute ethanol and stirring for 1 hr to form a homogenous solution and dissolving 0.6 mM N719 in acetone nitride/tert-butanol (1/1, v/v).

Pt counterelectrode was prepared by dropping a 20 μ L H₂PtCl₆ solution in acetone onto FTO glass substrates and sintered at 550°C for 1 hr. A DSSC was fabricated by sandwiching a loaded-dye photoelectrode, a Pt counterelectrode, a polymer film, and electrolyte. The electrolyte for EY was prepared by dissolving 0.2 M LiI and 0.02 M I₂ in propylene carbonate, and the electrolyte for N719 was prepared by dissolving 0.2 M LiI, 0.02 M I₂, and 0.2 M DMPII in acetone nitride.

2.4. Characterization. Morphology and cross section of ZnO films were observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) operating at a voltage of 15.0 kV. Specific surface area (SSA) was measured by the Brunauer-Emmett-Teller (BET, Quantachrome Autosorb 1 MP) method using N₂ gas. Dye adsorption was measured using UV-Vis-NIR spectroscopy (Varian Cary 50, wavelength range 190–1100 nm). Raman shifts were characterized by Raman spectroscopy (T64000 HORIBA Jobin-Yvon) using 50 mW and 514.5 nm wavelength Ar green laser. Photovoltaic characteristics were measured under standard simulated solar radiation of 100 mW/cm² (AM1.5). Electrochemical properties were characterized using electrochemical impedance spectroscopy (EIS) with frequency range of 10 kHz to 1 Hz and AC amplitude of 20 mV.

3. Results and Discussion

3.1. Morphological Characteristics of Etched ZnO Films. Surface morphology of one-step etched ZnO films was shown in Figure 1. The porous structures were observed from the top view FE-SEM images after etching process. The rough porous formation on the ZnO films was observed due to chemical reactions that can be represented by the following equations [16, 17]:

FIGURE 1: Morphology of ZnO films etched by NH_4OH solutions with various etching time; (a) 0 min, (b) 1 min, (c) 2 min, (d) 3 min, and (e) cross-sectional image.

Hydronium ion (H_3O^+) reacts on electron at oxygen site of ZnO. The OH^- will continuously react with Zn^{2+} at the surface to form $\text{Zn}(\text{OH})_2$ and remove ZnO particles from the surface. The reaction creates the pore position at the reaction site forming a rough porous structure. Since the base solutions have slow reaction, 1 min etching time is not enough to remove the dense particles as seen in Figure 1(b). On the other hand, 3 min etching time is too long and porous structure is destructed (Figure 1(d)). However, the etching time of 2 min showed optimum time with high-ordered porous films (Figure 1(c)).

The one-step etched ZnO films thickness was estimated from the cross-sectional FE-SEM image (Figure 1(e)) using

image-J software. The nonetched films showed the maximum thickness of $18.02 \pm 0.28 \mu\text{m}$. After surface modification for 1, 2, and 3 min, the thickness was decreased as 16.20 ± 0.31 , 14.01 ± 0.60 , and $13.79 \pm 0.44 \mu\text{m}$, respectively. The thickness is slightly decreased with increasing etching time due to ZnO removal during chemical process. The etching rate of ZnO films by diluted NH_4OH solution was estimated to be $1.49 \mu\text{m}/\text{min}$ by assuming the linear relation between thickness decreasing and etching time increasing.

3.2. The Brunauer-Emmett-Teller (BET) Analysis. The specific surface area of one-step etched films was measured using BET analysis to understand effects of specific surface area

FIGURE 2: Dye adsorption with various etching time of (a) EY sensitizer and (b) N719 sensitizer.

TABLE 1: Specific surface area and dye adsorption of etched ZnO films.

Etching time (min)	Specific surface area (m ² /g)	Dye adsorption (10 ⁻⁹ mol/cm ²)	
		EY	N719
0	2.52	9.33	43.67
1	5.71	9.65	44.85
2	5.30	11.04	53.03
3	4.29	10.19	43.10

on DSSC performance. The measured specific surface areas were listed in Table 1. It was found that the specific surface area of the etched films is rapidly increased over two times compared with the nonetched films. The specific surface area reached maximum value of 5.71 m²/g for 1 min etching time and slightly decreased for longer etching time. The result suggested that a simple modification of ZnO films can be effectively improved by wet chemical etching process.

3.3. Dye Adsorption Analysis. Dye concentration was investigated by extract the adsorbed dye molecules and measured absorbance spectra via UV-Vis-NIR spectroscopy as shown in Figure 2. The absorbance peaks showed the maximum value at 2 min etching time for both EY and N719. The amount of dye adsorption was evaluated by the Beer-Lambert law at the major peak wavelength as listed in Table 1:

$$A = c\varepsilon L, \quad (5)$$

where A is absorbance, c is dye concentration, ε is molar extinction coefficient ($\varepsilon = 89,560 \text{ M}^{-1} \text{ cm}^{-1}$ at wavelength of 532 nm for EY [18–20] and $\varepsilon = 14,100 \text{ M}^{-1} \text{ cm}^{-1}$ at wavelength of 515 nm for N719 [21, 22]), and L is length of dye solution (1 cm). It can be seen that dye adsorption is increased at

increasing etching time and optimized at the etching time of 2 min which corresponded to high-order porous film. Therefore, dye adsorption plays a key role in etching process of ZnO photoelectrode to enhance PCE of ZnO DSSC because change in light harvesting efficiency at a particular wavelength, $\phi_A(\lambda_{\text{ex}})$, is directly considered with amount of dye adsorption according to the relation [23]

$$\phi_A(\lambda_{\text{ex}}) = (1 - 10^{-A}), \quad (6)$$

where A is absorbance of dye adsorption at a particular wavelength. $\phi_A(\lambda_{\text{ex}})$ in etched films might be improved due to increased amount of dye adsorption which exhibited the most significant change for 2 min etching time.

3.4. Photovoltaic Characteristics. Current density-voltage (J - V) characteristics were measured under standard test condition (AM1.5) as shown in Figure 3. In addition, calculated photovoltaic parameters including short-current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) are summarized in Table 2. J_{sc} increased, reaching maximum values of 4.77 mA/cm² and 7.15 mA/cm² for EY and N719, respectively, at 2 min etching time whereas V_{oc} has small change. The result showed that PCE is improved with a direct correlation of J_{sc} where the films were etched by NH₄OH solutions for both EY and N719. J_{sc} is considered as a major factor for PCE enhancement which is related to the amount of dye adsorption as shown in Figure 4. It is clearly observed that J_{sc} increased with the increasing amount of dye adsorption. It was attributed that J_{sc} is governed by the amount of dye adsorption [24] which can be seen in terms of light harvesting efficiency, Φ_{LH} , according the relation [23]

$$J_{\text{sc}} \propto \Phi_{\text{LH}}\Phi_{\text{G}}\Phi_{\text{C}}, \quad (7)$$

FIGURE 3: Photovoltaic characteristics of ZnO DSSC fabricated on etched films with various etching time for (a) EY sensitizer and (b) N719 sensitizer.

FIGURE 4: Relation of J_{sc} and dye adsorption with various etching time for (a) EY sensitizer and (b) N719 sensitizer.

TABLE 2: Photovoltaic parameters and dye adsorption of ZnO DSSC fabricated on etched films.

Sensitizer	Etching time (min)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
EY	0	3.48 ± 0.08	0.45 ± 0.01	0.42 ± 0.01	0.67 ± 0.02
	1	4.22 ± 0.06	0.45 ± 0.01	0.37 ± 0.03	0.70 ± 0.05
	2	4.77 ± 0.47	0.44 ± 0.01	0.39 ± 0.04	0.80 ± 0.02
	3	4.35 ± 0.30	0.44 ± 0.01	0.35 ± 0.01	0.66 ± 0.05
N719	0	6.61 ± 0.26	0.57 ± 0.01	0.48 ± 0.02	1.80 ± 0.01
	1	6.87 ± 0.25	0.56 ± 0.01	0.47 ± 0.01	1.81 ± 0.01
	2	7.15 ± 0.32	0.57 ± 0.01	0.49 ± 0.02	2.00 ± 0.01
	3	6.96 ± 0.13	0.57 ± 0.01	0.47 ± 0.01	1.85 ± 0.08

where Φ_G is electron generation efficiency of dye molecule under excitation condition and Φ_C is charge collection efficiency of ZnO.

3.5. Electrochemical Impedance Spectroscopy (EIS) Analysis. Internal electrochemical reaction of electron in fabricated

DSSC was investigated by electrochemical impedance spectra measurement in the dark with forward bias voltage of -0.7 V for steady state as shown as Nyquist plot in Figure 5. The EIS parameters were fitted using Z-view software under equivalent circuits according to the inset of Figure 5(a) [6, 25]. Three main internal resistances of R_s , R_{ct1} , and R_{ct2}

FIGURE 5: Nyquist plots of ZnO DSSC fabricated on etched films with various etching time for (a) EY sensitizer and (b) N719 sensitizer.

FIGURE 6: Bode phase plots of ZnO DSSC fabricated on etched films with various etching time for (a) EY sensitizer and (b) N719 sensitizer.

correspond to series resistance and charge transfer resistance at electrolyte/Pt interfaces and at ZnO/dye/electrolyte interfaces, respectively [26]. Constant phase element (CPE) is used for smooth fitting. Electron lifetime (τ), which means duration of electron movement in conduction band of ZnO before recombination with oxidized dye or electrolyte [27], was calculated from the following equation [28]:

$$\tau = \frac{1}{2\pi f_{\text{peak}}}, \quad (8)$$

where f_{peak} is the frequency at the maximum peak from the Bode phase plots [28] as shown in Figure 6. The parameters were summarized in Table 3. All of the fabricated cells based on etched ZnO films exhibit larger $R_{\text{ct}2}$ compared with the

nonetched films. This result indicated lower recombination phenomenon at the ZnO/dye/electrolyte interfaces due to lower number of electrons (n) involved in the reaction at the interfaces according to the following equation [29]:

$$R_{\text{ct}} = \frac{RT}{nFJ_0}, \quad (9)$$

where R is the gas constant, T is the absolute temperature, F is Faraday's constant, and J_0 is exchange current density. The recombination is reduced resulting in reduction of J_0 and increase of J_{sc} .

Small change in R_s can be described by change in surface resistance of FTO due to chemical reaction during the etching process. $R_{\text{ct}1}$ changed due to counterelectrode

FIGURE 7: Morphology of two-step etched ZnO films (a) and comparative pore area distribution (b).

TABLE 3: Electrochemical impedance parameters of ZnO DSSC fabricated on etched films.

Sensitizer	Etching time (min)	R_s (Ω)	R_{ct1} (Ω)	R_{ct2} (Ω)	f_{peak} (Hz)	τ (ms)
EY	0	16.8	22.3	169.6	8	19.9
	1	18.1	21.8	178.7	10	15.9
	2	17.8	32.2	179.9	8	19.9
	3	18.3	20.1	185.9	10	15.9
N719	0	20.1	10.7	243.6	8	19.9
	1	21.7	7.3	267.5	10	15.9
	2	20.5	8.0	256.3	12	13.3
	3	21.2	9.5	287.7	12	13.3

surface. Calculated electron lifetime showed no trends. In addition, small change in electron life time indicated that duration of electron movement in conduction band of etched ZnO is not much changed while the R_{ct2} increased. The results suggest an improvement of electron transport in the fabricated cell. However, these internal phenomena do not significantly affect PCE when compared with the effects of dye adsorption.

3.6. Two-Step Etching Process Performance. The optimized one-step etched films with NH_4OH etching process for 2 min were repeatedly etched by mixed acid solution for short time of 10 s. It is well known that ZnO rapidly reacts with acid ions, and the small aggregate ZnO particles are removed to form a fine porous structure as shown in Figure 7(a). To evaluate porous structure in two-step etched film, one-step etched films, and nonetched films, image-J software is used for analyzing the pore area distribution from ordinary FE-SEM image. The FE-SEM image was converted as gray scale with 8 bits (image $\gg$ type $\gg$ 8 bits) and analyzed for pore area (image $\gg$ adjust $\gg$ threshold $\gg$ auto). All

samples exhibited similar trends for pore size distribution. The dominated pore size was observed in ranks of 0–40 nm^2 and the count frequency of small pore size exhibited higher number of pores (>3 times) than other ranks. Moreover, the two-step etched films exhibited the highest count frequency for the small pore size. This result can be described by the notion that large pore size might be etched during etching process. After the large pore size was etched, the small pore size was formed and relatively increased as seen in Figure 7(b). The increase of small pore size (0–40 nm^2) can ensure that fine porous structure (mesoporous structure) is formed for two-step etched films. The fine porous structure provides high specific surface area which was confirmed by the BET result. Moreover, the result agrees with the increase in number of small pore sizes. The specific surface area of two-step etched films exhibits a significant increment of value as 7.07 m^2/g compared with one-step etched films (5.30 m^2/g) and nonetched films (2.52 m^2/g).

In addition, the simulated 3D profiles as shown in Figure 8 exhibited that the one-step etched films become rough films because the peak and trough are very different in ranks. While the two-step etched films exhibited better smooth surface, it is confirmed that rough pores are modified, and fine pores are formed after the two-step etching process. Therefore, image-J analyzing technique which is a simple image processing technique can be used to preliminarily evaluate surface area. The Raman shift was shown in Figure 9; the intensity decreased after etching process due to thickness decrease. However, Raman shift was clearly not changed after the fine porous structure formation by chemical etching process. These results indicated that fine porous structure is formed by chemical corrosion and removed small aggregate particle from ZnO films without leaving any species such as O vacancies. Therefore, high specific surface area was improved due to fine porous structure formation, which was modified by two-step etching process.

FIGURE 8: Simulated 3D profile of (a) nonetched films, (b) one-step etched films, and (c) two-step etched films.

FIGURE 9: Raman shift of (a) nonetched films, (b) one-step etched films, and (c) two-step etched films.

Due to the fine porous structure formation, the PCE of DSSC fabricated on two-step etched films is enhanced as $2.26 \pm 0.01\%$ for N719 sensitizer, which is higher than both the one-step etched films and the nonetched films as shown in Figure 10. In addition, photovoltaic parameters including J_{sc} , V_{oc} , and FF are $7.49 \pm 0.05 \text{ mA/cm}^2$, $0.58 \pm 0.01 \text{ V}$, and 0.52 ± 0.01 , respectively. An improvement of FF indicated that fine porous structure offered better interfacial contact between ZnO/Dye/electrolyte providing better redox process in the DSSC. This result indicated that mixed acid solution can be used to modify ZnO films to improve FF and enhance PCE in

FIGURE 10: Comparative J - V characteristics of DSSC fabricated on nonetched, one-step, and two-step etched ZnO films.

DSSC. It can be seen that the enhanced cell in this work shows a quite low PCE compared with reports and commercial cells which are in wide ranges of 0.2–11.3% [30–32]. High PCE in several reports is maybe due to the use of a different semiconductor material such as TiO_2 with nanostructures such as nanorods, a complicating treatment in many parts of DSSCs, and production technology for device development. However, a simple method for photoelectrode modification

using etching process in this report is applied effectively and confirmed an ability to enhance cell performance.

4. Conclusions

Power conversion efficiency of ZnO dye-sensitized solar cell fabricated on modified photoelectrode is enhanced due to high specific surface area, which is supported by the fine porous structure. The optimized etched ZnO photoelectrode by the wet chemical etching process can also improve higher dye adsorption due to an increase in specific surface area. Increased amount of dye adsorption resulted in high short-circuit current density. Thus, high specific surface area is the major factor for increasing dye adsorption to enhance power conversion efficiency of DSSC. Moreover, the fabricated cell based on two-step etched films exhibits maximum power conversion efficiency and better fill factor due to the formation of fine porous structure. Therefore, these results implied that the roles of etching processes are improving specific surface area and fine porous formation which can provide better dye adsorption and redox process for DSSC application.

Additional Points

The paper highlights the following points. (i) Power conversion efficiency of ZnO dye-sensitized solar cell is enhanced by surface modification of porous photoelectrode. (ii) Porous ZnO films are successfully modified by etching process, providing increased dye adsorption and better redox process. (iii) Short-circuit current density is directly changed with the amount of dye adsorption, resulting in enhanced power conversion efficiency.

Competing Interests

The authors declare that they have no competing interests.

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