

Sulfuric acid treatment of ZnO photoelectrode for photovoltaic improvement in dye-sensitized solar cell

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Abstract. Chemical wet treatment of ZnO films using the diluted sulfuric acid for dye-sensitized solar cell application was performed. The ZnO films were prepared from commercial ZnO nanoparticles using screen printing method and annealed. The films were treated by dipping into diluted sulfuric acid for different treatment times. Morphology of the treated ZnO films shows the nanowire formation for long treatment time. The treated ZnO films were then used as photoelectrode of dye-sensitized solar cell. The power conversion efficiency is achieved to be maximal value for the dye-sensitized solar cell fabricated with the treated ZnO films. It reveals the higher than the dye-sensitized solar cell fabricated with the non-treated ZnO films. The enhancement is due to the increased open-circuit voltage, the increased fill factor, the increased shunt resistance, and the decreased charge transfer resistance. In addition, the effect of sulfuric acid treatment is found to improve the charge transfer behaviour due to the nanowire formation. Therefore, the sulfuric acid treatment of ZnO photoelectrode has potential to provide charge transfer rate for better dye-sensitized solar cell application.

1. Introduction

Surface treatment of photoelectrode is widely investigated for enhancing dye-sensitized solar cells (DSSCs) due to their advantages including simple process and effective method [1]. The surface treatment has ability to improve dye adsorption, light harvesting efficiency (LHE), electron transport efficiency, and electrochemical property [2,3]. Thus, the chemical wet treatment is considered as alternative method for DSSC application. There are different improved photovoltaic parameters after treatment with different chemicals. For example; the H_3BO_3 and $(\text{NH}_4)_2\text{TiF}_6$ treatment can reduce charge recombination and increase charge collection [4]. The effect finally led the enhanced power conversion efficiency (*PCE*) in DSSCs. The increased short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (*FF*) were demonstrated using KOH treatment [5]. The increase of dye adsorption was presented using NH_4OH and mixed acid $\text{HCl}:\text{HNO}_3$ [6]. The charge transfer improvement is one of the efficient improvements developed using porous photoelectrode because the porous structures are flexibility for full-filling electrolyte. The H_2SO_4 treatment of ZnO films demonstrated that it has possible for porous film formation due to the corrosion which might be possible for DSSC application [7]. In addition, the corrosion rate can be easily controlled using

various conditions such as concentration, temperature, or time. Therefore, H₂SO₄ treatment of ZnO films was carried out by varying treatment time for improving charge transfer behavior in DSSCs. The treated ZnO films were characterized and applied as photoelectrode of DSSCs.

2. Experimental

ZnO nanoparticles (NPs) were dissolved into 10 wt.% polyethylene glycol (PEG) solution (10 wt.% PEG in distilled water) and stirred for 1 h to obtain viscous ZnO precursor. The precursor was coated onto F:SnO₂ (FTO) substrate. The coated precursor was then annealed at 450 °C for 1 h to obtain ZnO films. For treatment process, 0.5 vol.% H₂SO₄ solution was dissolved into distilled water. The ZnO films were vertically dipped into the diluted H₂SO₄ solution for different treatment times of 0, 15, 30, 45, and 60 s. After the treatment, the ZnO films were rinsed with distilled water for several times, followed by heated at 100 °C for 30 min to obtain the treated ZnO films.

The treated ZnO films were used as photoelectrode by immersing into the dye solution in the dark for 1 h. After the immersion, the ZnO films were rinsed with ethanol for several times and stocked in the dark. The dye solution was prepared by dissolving 0.6 mM N719 dye into absolute ethanol. For counterelectrode preparation, 0.05 mM H₂PtCl₆ was dissolved into a mixture of acetone/propanol by volume (9/1). Pt solution of 20 μL was dropped onto FTO substrate and sintered at 550 °C for 1 h to obtain Pt counterelectrode. The photoelectrode and counterelectrode was sandwich-fabricated and sealed with polymer to obtain DSSC structure. After fabrication, the electrolyte of 0.2M LiI/0.02M I₂ in acetone nitride was injected between the cell gap for measurement.

For characterization, morphology of ZnO films was observed using scanning electron microscopy (SEM). Dye adsorption was measured using ultraviolet-visible (UV-Vis) spectroscopy. The dye molecules were extracted from ZnO films by immersing into 0.1 M NaOH solution. Photovoltaic characteristics of DSSCs were performed by measuring current density (*J*) and voltage (*V*) under simulated standard light intensity of 100 mW/cm². Internal electrochemical behavior was measured using electrochemical impedance spectroscopy (EIS).

3. Results and discussion

Figure 1 shows morphology of ZnO films treated with H₂SO₄ solution. All of the treated ZnO films exhibit quite smoother than the non-treated ZnO films. The result may be due to chemical reaction between ZnO and H₂SO₄ which can be assumed from the possible relations.

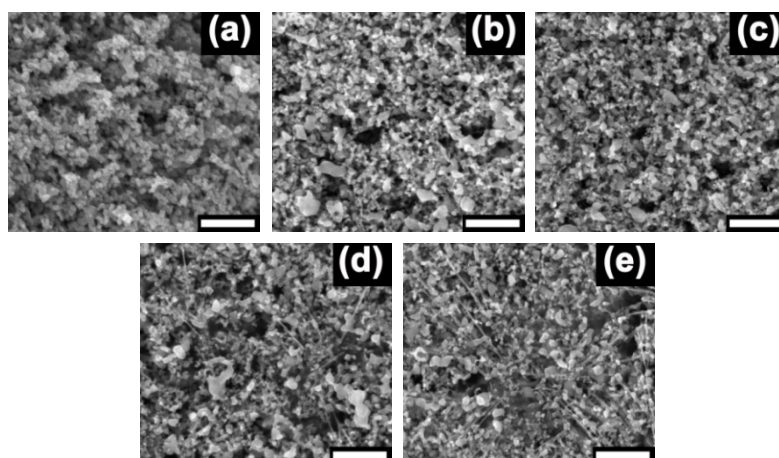
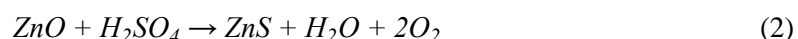
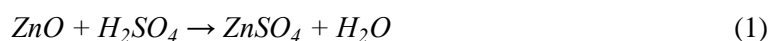


Figure 1. SEM images of (a) non-treated ZnO films, and the treated ZnO films for treatment time of (b) 15 s, (c) 30 s, (d) 45 s, and (e) 60 s, the scale bar is 1 μm.

The reaction may remove the aggregate ZnO particles from the surface and create smooth ZnO surface. Note that, the nanowires are found for the treatment time of 45s and 60s.

Figure 2 shows J - V curves of DSSC fabricated with different treatment time of ZnO films and the corresponding photovoltaic parameters are listed in table 1. The treated ZnO films for 15 s reveal the maximal PCE while the J_{sc} decrease. The decreased J_{sc} is due to the decreased dye adsorption as shown in figure 3(a). The result can be described that the ZnO films may be etched and removed during chemical reaction for longer treatment time. When ZnO films react with H_2SO_4 solution, the chemical reaction may transform ZnO to $ZnSO_4$ or ZnS due to chemical reaction [7]. The reaction occurs when the protons (H^+) react with O-site at the ZnO surface. The effect may decrease the surface area for the dye molecule adhesion [3]. For the longer reaction time of 60 s, numerous O-site of ZnO films may be reduced which result a very low efficient surface for dye molecule adhesion. However, the other parameters including V_{oc} and FF are increased in comparison to the non-treated film. The V_{oc} is generally determined by the different of energy level between the Fermi level of ZnO and the redox potential of electrolyte. The increased V_{oc} may be due to the electron concentration achievement of ZnO because the defect position of ZnO was treated by H_2SO_4 .

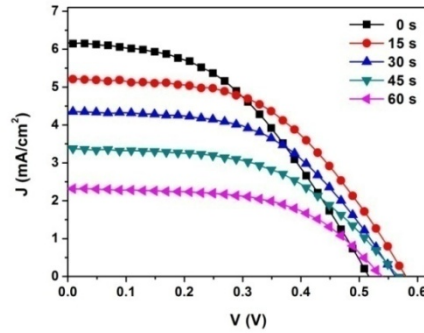


Figure 2. Current density versus voltage of DSSC fabricated with different treatment times of ZnO photoelectrodes.

Table 1. Photovoltaic parameters of DSSCs fabricated with treated ZnO photoelectrodes.

Treatment time (s)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_{sh} (Ω)	R_s (Ω)
0	6.17±0.12	0.52±0.02	0.45±0.02	1.43±0.08	739.70±36.21	40.44±0.08
15	5.20±0.13	0.58±0.01	0.51±0.01	1.53±0.02	1594.96±274.99	41.53±0.24
30	4.35±0.15	0.56±0.01	0.53±0.02	1.28±0.01	2756.22±495.46	44.08±0.11
45	3.39±0.13	0.56±0.01	0.52±0.01	1.00±0.01	1798.63±277.39	57.18±2.05
60	2.33±0.11	0.54±0.01	0.56±0.01	0.70±0.02	2315.32±280.76	62.03±4.02

The FF is assumed due to the improvement of internal resistance which will be further investigated. Thus, the PCE of DSSC fabricated with the treated ZnO films exhibits a quite enhancement because the achievement of V_{oc} and FF which is described from the relation.

$$PCE = \frac{J_{sc}V_{oc}FF}{P_{in}} \quad (3)$$

where P_{in} is incident sunlight power.

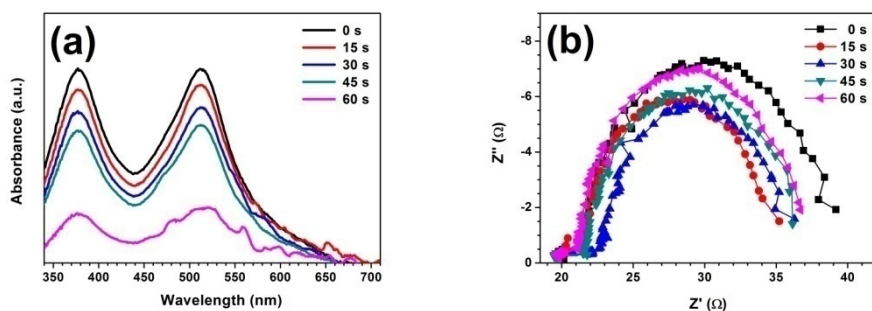


Figure 3. (a) Dye adsorption extracted from the treated ZnO films, and (b) EIS of DSSCs fabricated with the treated ZnO photoelectrodes.

To investigate internal resistance, shunt resistance (R_{sh}) and series resistance (R_s) are analyzed. Generally, high R_{sh} and low R_s are required for a good DSSC performance. From the photovoltaic results, The R_{sh} of DSSCs fabricated with the treated ZnO films show over double value compared with the non-treated films, while R_s shows small increased. This is believed a reasonable factor for the FF improvement. In addition, the EIS measurement in figure 3(b) confirmed that the charge transfer may be improved after the treatment according to the decreased diameter of the semi-circle curves. The 15 min treatment shows the smallest diameter of semi-circle curve indicating the low charge transfer resistance (R_{ct}) which may be due to nanowire structure of the treated ZnO films. The result can be interpreted that most of the injected electrons can transfer through ZnO to external load with better transferring rate.

4. Conclusion

Surface change of the treated ZnO films is observed compared with the non-treated ZnO films due to chemical reaction. The decrease of ZnO bulk is found after the treatment affecting the lower dye adsorption. The low dye adsorption causes the corresponding lower J_{sc} for the dye-sensitized solar cell application. However, the V_{oc} and FF are improved to achieve the PCE . The increased V_{oc} may be caused by electron concentration achievement and the increased FF is believed due to the improved internal resistances including the increased R_{sh} and the reduced R_{ct} . Therefore, chemical wet treatment of ZnO films using sulfuric acid demonstrates a potential chemical to enhance DSSC performance.

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