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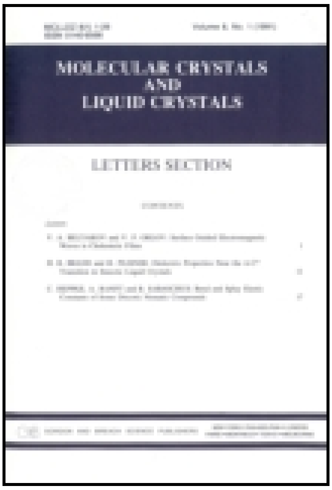

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Dye-Sensitized Solar Cells Composed of Well-Aligned ZnO Nanorod Array Grown with Chemical Bath Deposition Method as the Photo-Electrode

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Dye-Sensitized Solar Cells Composed of Well-Aligned ZnO Nanorod Array Grown with Chemical Bath Deposition Method as the Photo-Electrode

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Well-aligned ZnO nanorod arrays were prepared at different deposition times to determine the correlation between the length of the photoelectrodes and the photovoltaic performance in dye-sensitized solar cells. The length of the ZnO photoelectrode was controlled to 1.2, 2.7 and 4.0 μm by the deposition time. The DSSCs composed of the longer ZnO nanorods showed much better photovoltaic performance due to the enhanced amount of dyes adsorbed and electron injection, as determined by the intrinsic photon-to-current efficiency and electrochemical impedance spectroscopy. The photon-to-current efficiency of the DSSC containing ZnO photoelectrode was considered with the aspect of the length of ZnO nanorods.

Keywords ZnO nanorod array; two-step chemical deposition method; dye-sensitized solar cell; photovoltaic performance

1. Introduction

Nanostructured metal oxide materials are becoming an important research area with many potential applications [1]. For example, solar cells based on dye-sensitized metal oxides, such as TiO_2 and ZnO, are promising for highly efficient and low-cost solar energy conversion devices [2–5]. The structure of DSSCs is composed of a dye-adsorbed wide band gap semiconductor electrode, liquid type electrolyte containing the I^-/I_3^- redox couples, and a Pt-coated counter electrode [6–11]. The mechanism of DSSCs is based on the injection of

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electrons from photosensitizers (mainly Ru-complex, such as N3 and N719) to the conduction band of the electrode with an adsorbed photosensitizer. The oxidized photosensitizers were reduced by electron transfer from the electrolyte. Nanoparticle TiO_2 has been the most studied electrode material that can be sensitized with Ru-complex dyes, such as N719 or N3, giving a solar-to-electric–conversion efficiency of approximately 11%.

Although the highest overall conversion efficiency obtained from the sensitized ZnO electrodes has not reached that of sensitized TiO_2 electrodes, the use of ZnO as a photoelectrode in DSSCs has many advantages, such as high optical transmittance, wide range of configurations, direct band gap (3.3eV), no toxicity and a large exciton binding energy [12]. Furthermore, the electrode composed of ZnO nanorod has a much higher electron mobility than that of anatase TiO_2 nanoparicles [13]. Despite the many attempts to improve the photon-to-current efficiency of ZnO-DSSCs, such as vapor-phase transport, pulsed-laser deposition, chemical vapor deposition, and electro chemical deposition, the photovoltaic performance is much lower than that of TiO_2-DSSCs. The lower performance of ZnO is due mainly to chemical instability on the ZnO surface [14]. Many research groups reported that the photo current of ZnO-DSSCs decreased with increasing concentration of sensitizers on the ZnO surface because of the formation of agglomerates between the Ru-complex sensitizer and Zn^{2+} ions [13].

A previous study reported the photovoltaic performance of the ZnO electrode-DSSCs, in which the electrode showed relatively low performance due mainly to the chemical instability and short length of the ZnO nanorods ($<1\ \mu$m).

In this study, well-aligned ZnO nanorods longer than 4 μm were fabricated using the two-step chemical bath deposition (CBD) method. The uniformly-aligned ZnO nanorods arrays with different diameters and lengths were prepared to apply it as a photoelectrode in DSSCs. The photovoltaic performance of the DSSCs composed of a ZnO nanorod array was observed to confirm the grain length effect of the photoelectrode with the I-V curve and incident photon-to-current efficiency. Scanning electron microscopy and X-ray diffraction measurements were performed to observe the morphology of the ZnO array.

2. Experimental

2.1. Synthesis of ZnO Nanorods

ZnO nanorods were grown on fluorine-doped tin oxide (SnO_2:F, FTO) substrates as the working electrode. A solution of 0.01 M zinc acetate dehydrate ($Zn(CH_3COOH)_2 \cdot 2H_2O$) in acetone was prepared under vigorous stirring at 70 °C for 1 h. The resulting solution was transparent with a suspension of ZnO particles in solution. The solution was spin-coated onto the working electrode substrate in the first step at 500 rpm for 50 s and dried at room temperature for 1 h. The substrate was then annealed at 150°C for 4 h to remove the solvent and organic substances to prepare a film of crystal seeds. The deposited ZnO seed substrate was immersed several times into an aqueous solution of 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 25 mM hexamethylenetetramine ($(CH_2)_6N_4$) at 90°C for the hydrothermal reaction for 3 h(ZnO1), 7 h (ZnO2) and 12h(ZnO3). The grown ZnO nanorods were calcined at 450°C for 30 min. The size and morphology of the aligned ZnO nanorods were observed by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800). The crystallographic structure of the ZnO nanorods was analyzed by an X-ray diffraction (XRD, PANalytical MPD for thin films).

2.2. Fabrication of the DSSCs

DSSCs were prepared by immersing the ZnO chemical bath deposited films into a dye solution of 0.5 mM *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis tetrabutylammonium (N719, Solaronix) in ethanol for 2 h at room temperature. After washing with acetonitrile, the Pt- (Dyesol Co. Platinum Paste PT1) coated FTO substrates were used as the counter electrode. The substrates were then annealed at 450°C for 3 h in air. The Pt counter electrode was placed over the dye-adsorbed ZnO electrode, and the edges of the cell were sealed with a sealing sheet, 60 μm in thickness (Solaronix SX1170-60). The electrolyte, consisting of 0.5 mM LiI, 0.05 M I_2, and 0.2 mM *tert*-butyl pyridine in acetonitrile, was introduced to the cell through one of two small holes drilled into the counter electrode. The holes were then covered and sealed with a small square of sealing sheet. The active area of the dye-coated ZnO film was 0.240 cm^2.

2.3. Measurements of the Cell Performance

A monochromatic beam was generated using a 150 W Xenon lamp and the IPCE data was obtained under bias light. The I-V data was collected under the 1 sun condition (100 $mWcm^{-2}$, AM1.5), which was calibrated using a Si standard solar cell. The impedance spectra were examined at the open-circuit potential under the same illumination conditions used for the I-V measurements. The obtained data was fitted using Z-view software.

3. Results and Discussion

The morphology and grain size of the nanostructured photoelectrode is extremely important for improving the photovoltaic performance in DSSC [15]. In particular, the nanoparticles of the electrode cause problems, such as the possible recombination of electrons at the interface of particles. Therefore, the one-dimensional morphology, such as a nanorod array, would enhance the electron life time in DSSCs, as shown in Fig. 1. Thus, the ZnO nanorods can be a promising candidate for the photoelecrode material for the DSSC which is grown easily on fluorine-doped tin oxide substrates.

Well-aligned ZnO nanorod arrays were grown using a simple two-step process. In the first step, a ZnO seed layer was prepared on the working electrode substrate by spin-coating. The nanorods were grown in a zinc nitrate hexahydrate and hexamethylenetetramine solution at 90°C for different times, 3 h (ZnO1; 1.2 μm length), 7 h(ZnO2; 2.7 μm), 12 h (ZnO3; 4.0 μm), to obtain nanorods with different lengths. Fig. 2 shows SEM images of the pre-treated FTO surface and ZnO arrays at different growth times. The top surface of the nanorod had a hexagonal shape, and the mean diameter of the ZnO nanorods increased with increasing growth time, as shown in Fig. 2.

Figure 3 shows the XRD patterns of the ZnO nanorod arrays grown on the pre-treated FTO substrates. The typical sharp peaks of the ZnO nanorod were observed, which are in agreement with previous data [16]. Sharp peaks, particularly the (100), (002) and (101) peaks of the aligned ZnO nanorods, indicated good crystallite structures. The intensity of these peaks increased with increasing deposition time, which enhances the crystallinity and number of nanorods. The relative intensity ratio between the (002) and (101) XRD peaks is normally used to characterize the orientation of the ZnO nanorods. Figure 3 shows that the nanorods are oriented in the C-axis direction, which indicates that the ZnO nanorods tend to grow perpendicular to the FTO electrode surface. This is due mainly to the parallel direction of the planes of the ZnO seed particles spin-coated and treated thermally at 150°C on the FTO electrode. The morphology and direction of the photoelectrode are quite important

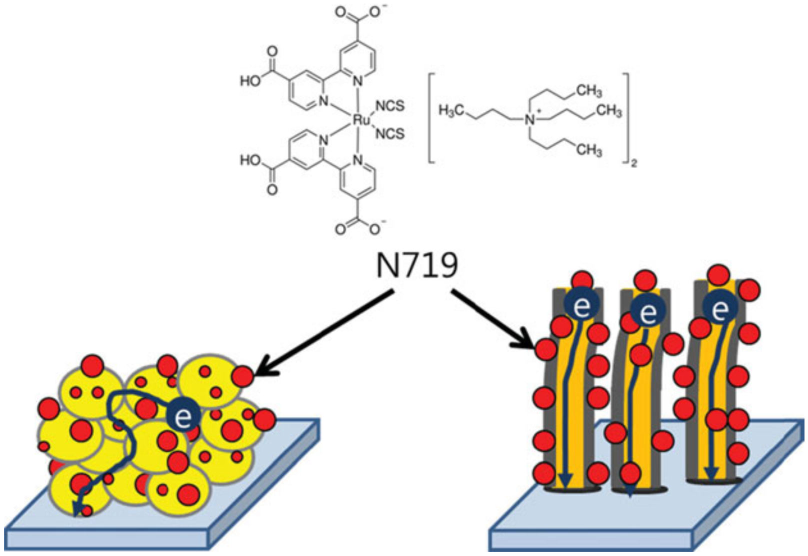

Figure 1. Chemical structure of photosensitizer used in this study and schematic diagram of the electron path taking place on different nanostructured electrodes of DSSCs composed of TiO_2 nanoparticles (left) and composed of ZnO nanorod array (right).

factors in DSSC due to the electron transfer pathway and the recombination rate from photoelectrode into the electrolyte.

We prepared DSSCs containing with different lengths of ZnO nanorod as the working electrode. Figure 4 and Table 1 shows the current density–voltage (I–V) curves and incident

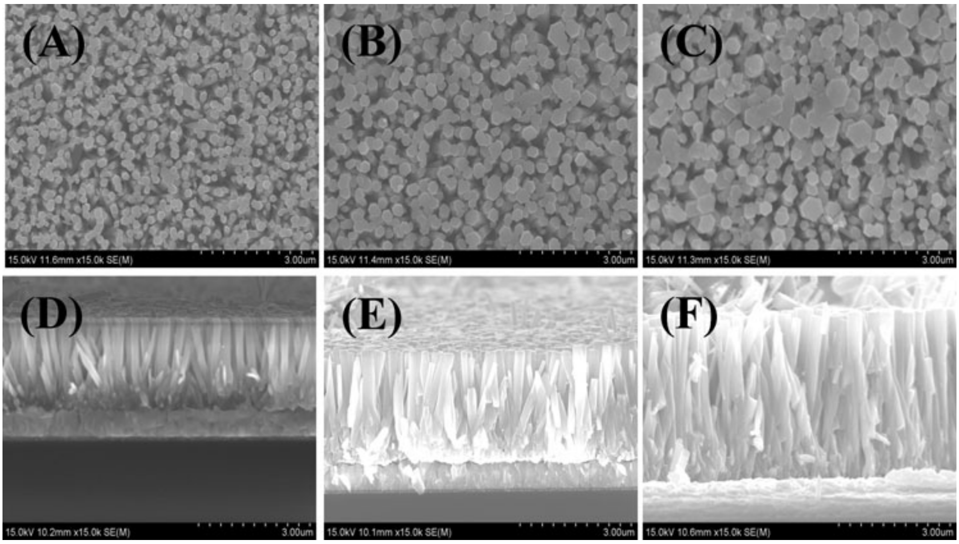

Figure 2. Scanning electron micrographs of the ZnO materials. (A) top view of the ZnO1. (B) top view of the ZnO2. (C) Top view of the ZnO3. (D) Cross sectional view of the ZnO1. (E) Cross sectional view of the ZnO2. (F) Cross sectional view of the ZnO3. (ZnO1 nanorod diameter: 200 nm, length: 1.2 μm, ZnO2 nanorod diameter: 300 nm, length: 2.7 μm and ZnO3 nanorod diameter: 500 nm, length: 4.0 μm).

Table 1. Photovoltaic performance and amounts of dye uptakes for the DSSCs composed of a ZnO electrode

Devices	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	Dye Uptake amounts[a] (mol/L)
ZnO1	0.61	0.63	0.38	0.15	1.12×10^{-6}
ZnO2	0.89	0.61	0.40	0.21	1.49×10^{-6}
ZnO3	1.37	0.58	0.39	0.31	1.52×10^{-6}

[a] The desorption was conducted with 0.1 M NaOH, 50% EtOH in Aq.solution.

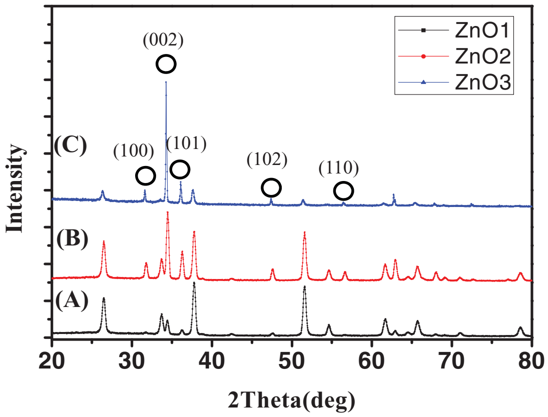

Figure 3. X-ray diffraction pattern of the ZnO of nanorods. (A) ZnO1, (B) ZnO2, (C) ZnO3.

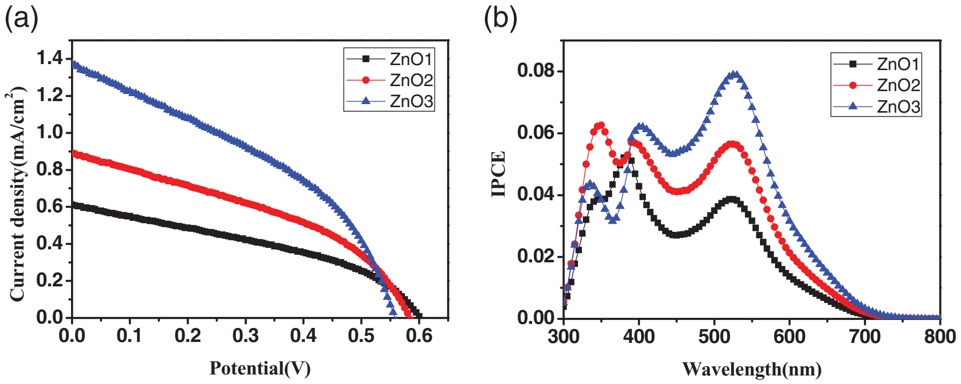

Figure 4. (A) I-V curves of DSSCs with ZnO1, ZnO2 and ZnO3 of DSSCs under illumination of simulated solar light (AM 1.5, 100 mW/cm^2). (B) IPCE spectra of the DSSCs.

Table 2. Impedance results of the DSSCs composed of a ZnO electrode

Devices	R_1 [a]/(Ω)	R_2 [b]/(Ω)	R_3 [c]/(Ω)
ZnO1	20.9	6.8	825.8
ZnO2	21.8	7.2	589.3
ZnO3	29.2	7.6	307.5

[a] R_1 is FTO interface resistance. [b] R_2 is due to the resistance at the interface between the counter electrode and the electrolyte. [c] R_3 is originated from the backward charge transfer from ZnO to the electrolyte and the electron conduction in ZnO nanorod array.

photon-to-current efficiencies (IPCE) of the DSSCs fabricated with the ZnO nanorod array grown for different deposition times. The cell composed of the ZnO nanorods showed relatively low J_{sc} values and cell efficiencies due to the chemical instability of the ZnO surface. On the other hand, the DSSCs containing the longer ZnO nanorods (ZnO3, 4.0 μm) showed better photovoltaic performance than that of the shorter nanorods (ZnO1, 1.2 and 2.7 μm). This was attributed to the enhanced amount of sensitizer adsorbed on the ZnO electrode surface. The amounts of the adsorbed dye on different length of ZnO electrode were also expressed in Table 1.

The IPCE of a solar cell is the product of the light harvesting efficiency for photons with a wavelength in λ; LHE(λ), the electron injection efficiency from the excited sensitizer to the conduction band of semiconductor oxide; η_{inj}, and the electron collection efficiency; η_{cc}, as shown in Equation (1)

$$\mathrm{IPCE}(\lambda) = \mathrm{LHE}(\lambda) \cdot \eta_{inj} \cdot \eta_{cc} \tag{1}$$

The LHE is determined from the amount of attached photosensitizer, light scattering, and concentration of redox species, η_{cc} is determined by the competition between recombination rate and charge transport, and η_{inj} is obtained from the driving forces related to the energy levels of TiO_2, dyes, and redox couple. Thus, the J_{sc} value of ZnO-DSSCs was increased as the length of ZnO nanorod increased.

Electrochemical impedance spectroscopy was also performed to clarify the charge transfer properties of the ZnO nanorod electrode. Figure 5 shows the AC impedance curve of the DSSCs fabricated with the ZnO nanorod electrode. The ohmic serial resistance, R_1 corresponds to the resistance between the electrolyte and FTO substrate. The R_2 and R_3 are the resistances retarding the charge transfer process occurring at the Pt electrode and the ZnO electrode, respectively. Thus, the R_3 value originates from the charge transfer process at the interfaces of the ZnO/dye/electrolyte. The ZnO nanorod electrode DSSCs had a lower R_3 value with an increased deposition time. The low surface resistance of the electrode suggests rapid electron transfer and a high surface resistance indicates slow electron transfer. Therefore, the low value of R_3 in the ZnO3 nanorod electrode DSSCs can be attributed to the larger amounts of sensitizers adsorbed on the photoelectrode than that of the ZnO1 electrode. The low value of R_3 in the DSSC indicates high electron transfer through the ZnO nanorod electrode, which enhances the electron injection from the exited sensitizers onto the ZnO resulting in enhanced J_{sc} values in the DSSCs.

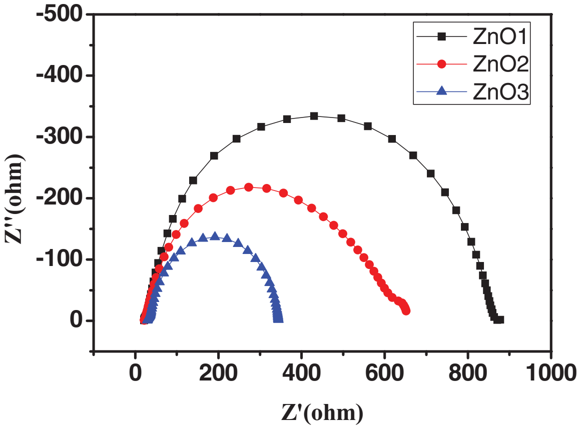

Figure 5. The impedance spectra of ZnO DSSCs under the forward bias applied condition in the dark.

4. Conclusions

Well-aligned ZnO nanorod arrays with different lengths (1.2 μm, 2.7 μm and 4.0 μm) were grown on FTO substrates using the two-step of chemical bath deposition process, respectively. The ZnO nanorods were grown on pre-treated substrates using the spin-coating technique. The DSSCs containing the ZnO nanorod photoelectrode showed relatively low photovoltaic performance due to the chemically unstable character of the ZnO surface. The longer ZnO nanorod electrode showed a better IPCE in the DSSCs due to the larger amount of photosensitizer on the electrode surface. The ZnO nanorod-DSSCs have promising potential to replace the TiO_2 electrode-based DSSCs due to their one-dimensional morphology and electron conductivity. Well-aligned ZnO nanorod arrays, 4.0 μm in length, were prepared to enhance the DSSC performance.

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