

Flexible dye-sensitized solar cells using ZnO coated TiO₂ nanoparticles

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Abstract

A photoelectrode using ZnO coated TiO₂ nanoparticles was prepared for use in flexible dye-sensitized solar cells. To provide an inherent energy barrier between the electrode and electrolyte interface, the surface of the TiO₂ nanoparticles was modified by thin ZnO layer. X-ray photoelectron spectroscopy and transmission electron microscopy image confirmed the formation of ZnO with a thickness of ca. ~0.5 nm, possible thickness for tunneling process in particle-to-particle transport of electrons, on the TiO₂ surface. The overall conversion efficiency was increased from 0.71 to 1.21% under a light intensity of 20 mW/cm² (0.2 sun) due to the reduced recombination of photoinjected electrons without any post-treatment.

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1. Introduction

The dye-sensitized solar cell (DSSC) is a type of photoelectrochemical solar cell composed of a dye-modified wide band semiconductor electrode, a counter electrode, and an electrolyte containing a redox couple (I⁻/I₃⁻). When a DSSC is illuminated by sunlight, the dye molecules adsorbed on the surface of the wide band semiconductor absorb light and become excited. The absorption of light by the dye molecules is followed by the injection of an electron from the excited state of the dye to the conduction band of the semiconductor and its subsequent transfer to the transparent oxide. Finally, the electron flows through the external circuit [1–4].

Due to its low fabrication cost, permanence, environmental compatibility, and simple fabrication process, interest in its application to low power devices such as small electronic devices and photoelectrochromic windows has grown considerably [5]. To make DSSC a commercially competitive technology, a new method that permits a film prepared on

flexible organic substrate is needed for purposes of flexibility, weight, and overall device thickness. Recently, some methods for preparing semiconductor films on a flexible substrate such as low-temperature annealing at the temperature of ~100 °C and a compressing method at the pressure of ~2000 kg/cm² s to achieve electrically connected TiO₂ network have been reported [5–8]. Expect on these methods, preparation of semiconductor film from the colloidal solution using doctor blade or screen printing followed by low-temperature annealing or compression, electrophoretically deposited nanoporous semiconductor film was introduced by Miyasaka et al. [9,10]. Miyasaka et al. reported improve performance of flexible DSSC using new post-treatment methods such as chemical vapor deposition (CVD) of TiO₂ followed by UV-illumination and local heating of nanoporous semiconductor film using microwave irradiation [9,10]. In addition, a study of the stability of flexible DSSC by electrochemical impedance spectroscopy has been reported [11,12].

In a DSSC, because the individual particle size is smaller than the Debye length of the material space charge region can not be formed. As a result, many studies to reduce the recombination at the interface were tried such as fabrication of bilayer electrode, preparation of composite semiconductor electrode, and passivation of semiconductor

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electrode using electropolymerization method and so on [13–19]. Specially Zaban et al. modified sintered TiO₂ coated film with Nb₂O₅ by dipping in niobium precursor solutions, followed by heat treatment at ~500 °C [19]. Due to the requirement of heat treatment at ~500 °C, it can not be applied to the fabrication of flexible DSSC. In addition, we reported on the modification of a sintered TiO₂ coated film with ZnO/Eosin Y layer by one-step electrochemical deposition method at room temperature [13]. This method is also very difficult to apply to flexible DSSC as the result of insufficient electrical connecting of TiO₂ network resulted from the absence of sintering process at ~450 °C. In this study, we applied ZnO coated TiO₂ nanoparticles to flexible DSSC as a photoelectrode to reduce recombination rate by providing energy barrier and efficient flexible DSSC was fabricated without any post-treatments such as low temperature annealing, static pressing, CVD, microwave irradiation and so on.

2. Experimental

2.1. Synthesis of ZnO coated TiO₂ powder

ZnCl₂ from the Aldrich Chemical Co. and TiO₂ powder (Degussa P25 powder) were used to modify the TiO₂ with a thin ZnO layer without any purification process. TiO₂ powder was first added to a 10 mM solution of ZnCl₂ in absolute ethanol and stirred for 2 min, followed by spraying this solution into liquid N₂. ZnO coated TiO₂ powder was obtained by freeze-drying of pre-frozen sample followed by sintering at 500 °C in air for 1 h. To minimize the difference in conditions between standard TiO₂ and ZnO coated TiO₂ powder, standard TiO₂ powder was added to absolute ethanol and followed by stirring, spraying, freeze-drying, and sintering under the same conditions.

2.2. Preparation of TiO₂ and ZnO coated TiO₂ electrodes

Viscous suspensions of TiO₂ and ZnO coated TiO₂ powder were prepared by adding the sintered powder to absolute ethanol without any organic surfactant and these suspensions were deposited on an ITO coated conducting plastic substrate (Toyobo Co. Ltd., 60 Ω/M) by doctor blade coating method with a glass rod and scotch tape as a frame and spacer. Here, absolute ethanol was used as the suspending agent due to its low surface tension, resulting in a deposition of smooth film [7]. In contrast to the conventional method of fabricating a TiO₂ film on a flexible substrate as a photoelectrode, the deposited film was not subjected to low temperature annealing or static pressing.

2.3. Cell fabrication

The two types of photoelectrodes prepared using TiO₂ and ZnO coated TiO₂ powder were immersed in an absolute ethanol solution of Ru 535 dye (Solaronix Co. Ltd.). Counter electrodes were prepared by the sputtering of Pt on the ITO coated conducting plastic substrate and the electrolyte was composed of 0.5 M LiI, 0.05 M I₂, and 0.5 M *tert*-butyl pyridine in methoxypropionitrile. Using these components, a sandwich type configuration was fabricated and this was employed to measure the performance of the cell. Here, the active area of the cells was adjusted to 0.5 cm².

2.4. Characterization of electrodes

X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM) images were used to study the formation of ZnO on TiO₂ surface. The surface morphology of the deposited film was observed from scanning electron microscopy (SEM) images.

2.5. Photovoltaic property measurement

Cell performance was measured using a 20 mW/cm² xenon light source and the white light was illuminated to the cells through an AM 1.5 filter. Photocurrent-voltage (I–V) measurements were performed using an Autolab PGSTAT30 Potentiostat/Galvanostat by Eco Chemie. Using same cells, photocurrent according to the incident light was measured by taking a wavelength in the ultraviolet and visible wavelength range using a monochromator (Dongwoo Optron Co. Ltd., Korea).

3. Results and discussion

Fig. 1 shows XPS spectra of films deposited from suspensions of TiO₂ and ZnO coated TiO₂ powder. In Fig. 1(a), the XPS peaks with binding energies of 458.1 and 529.4 eV correspond to Ti 2p_{3/2} and O 1s, respectively. For ZnO coated TiO₂ powder, an additional peak with a binding energy of 1021.5 eV corresponding to Zn 2p_{3/2} was present in Fig. 1(b). These XPS spectra serve as evidence for the formation of ZnO on the TiO₂ powder. Fig. 1(c) shows O 1s XPS spectra for the two types of deposited films. The peak position of the film prepared with ZnO coated TiO₂ nanoparticles was shifted to a high binding energy due to the O 1s band position at higher binding energy in ZnO compared with that in TiO₂. This also confirms the formation of a ZnO layer on TiO₂. In addition, the thickness of the ZnO layer on the TiO₂ was calculated to be ca. ~0.5 nm from the Zn/Ti ratio with the assumption of a uniform coating due to the specific adsorption of Zn²⁺ on TiO₂.

When Zn²⁺ is present in the aqueous solution with TiO₂ nanoparticles, the formation of a uniform ZnO layer due to

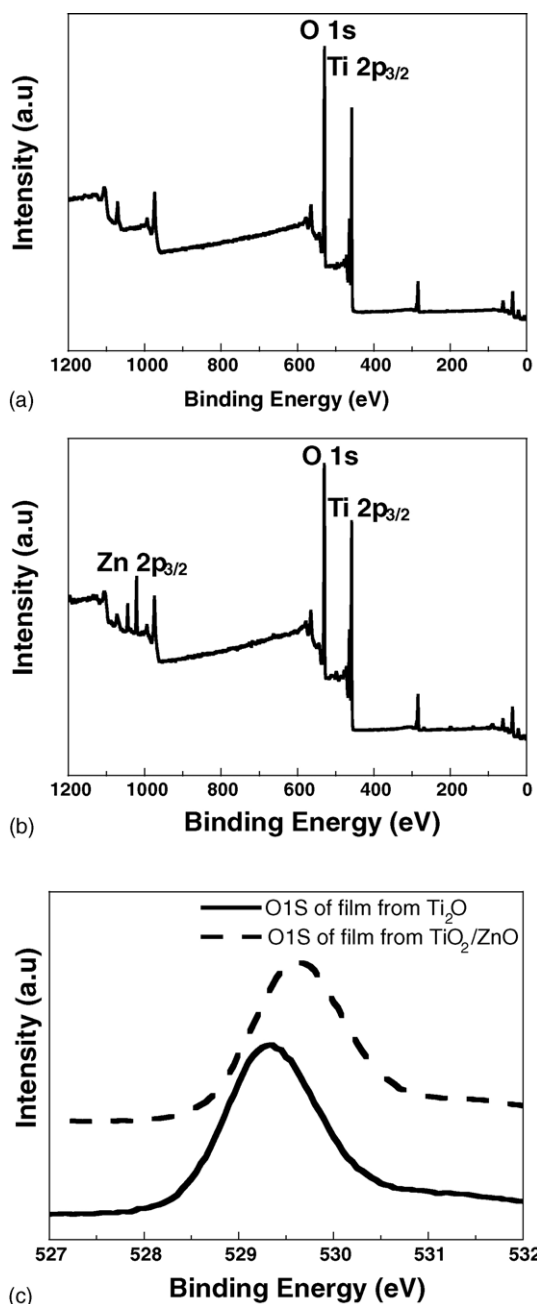


Fig. 1. X-ray photoelectron spectra of films deposited from suspensions of (a) TiO₂ and (b) ZnO coated TiO₂ powder. (c) O 1s X-ray photoelectron spectra of the two films.

the specific adsorption of Zn²⁺ on TiO₂ nanoparticles can be expected [14]. The formation of a uniform thin ZnO layer on the TiO₂ is confirmed by the TEM images shown in Fig. 2. Fig. 2(a) shows that the size of ZnO coated TiO₂ nanoparticles was similar with that of the bare TiO₂, having a value of ~20 nm and the size distribution was very narrow. From this fact and the HRTEM images (Fig. 2(b)) the formation of uniform thin ZnO layer on the surface of TiO₂ can be confirmed. In contrast to the smooth surface of the bare TiO₂ (Fig. 2(c)), the surface modified by a thin ZnO layer is shown

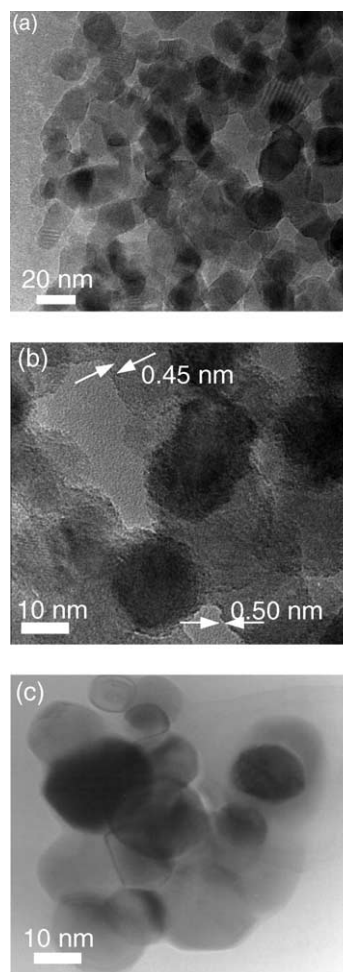


Fig. 2. (a) Transmission electron microscopy image of ZnO coated TiO₂ nanoparticles. (b) High resolution transmission electron microscopy image of ZnO coated TiO₂ nanoparticles. (c) High resolution transmission electron microscopy image of bare TiO₂ nanoparticles.

in Fig. 2(b). From the enlarged HRTEM image of Fig. 2(b) the thickness of the ZnO layer was evaluated to be ~0.45 to ~0.50 nm, which is in good agreement with the value obtained from the XPS measurement. Due to the very thin ZnO layer (~0.5 nm), possible thickness range in tunneling phenomenon, particle-to-particle transport of electrons necessary to efficient charge collection could occur smoothly. In the EDX spectrum, a small peak corresponding to Zn L was also observed around 1 keV (not shown here).

Fig. 3 shows SEM images of films deposited from the suspensions of TiO₂ and ZnO coated TiO₂ powder. Fig. 3(a) shows an electron micrograph demonstrating the formation of porous TiO₂ film, having high surface area. From Fig. 3(b), the deposited film from the suspensions of ZnO coated TiO₂ has also a moderate porosity and high surface area to which dye molecules could be adsorbed.

For comparison with a conventional photoelectrode composed of dye modified TiO₂, two types of flexible DSSC were fabricated and cell performance was compared. Fig. 4 shows the resulting photocurrent-voltage curves for the

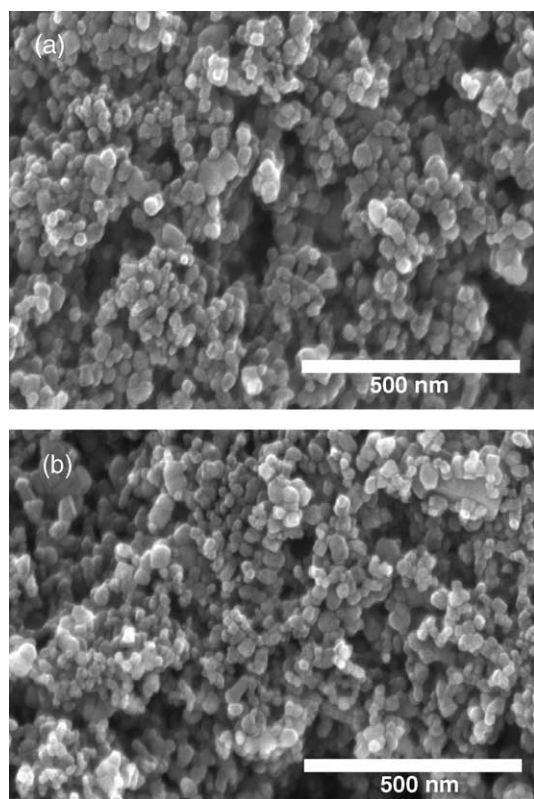


Fig. 3. Scanning electron microscopy images of films deposited from suspensions of (a) TiO_2 and (b) ZnO coated TiO_2 powder.

DSSCs fabricated using two types of photoelectrodes, dye modified films from the suspensions of TiO_2 and ZnO coated TiO_2 powder. By providing an inherent energy barrier that led to a decrease in recombination, the value of J_{SC} , V_{OC} , the fill factor, and overall conversion efficiency were increased from 0.35 to 0.49 mA/cm^2 , from -0.67 to -0.72 V, from 61.1 to 69.0%, and from 0.71 to 1.21%, respectively, without any heat treatment or static press processing. In addition, the amount of adsorbed dye on both electrodes was compared by the UV/vis absorption spectra measurements. Since the

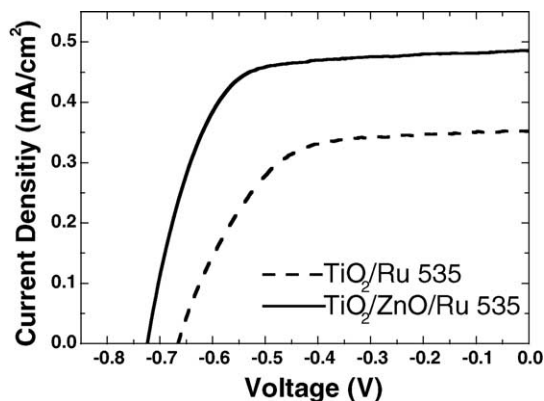


Fig. 4. I–V curves for flexible DSSCs fabricated using two types of photoelectrodes, dye modified films from the suspension of TiO_2 (dashed line) and ZnO coated TiO_2 powder (solid line).

amount of adsorbed dye was similar, the surface area can be assumed to be similar and the effect of the amount of dye on cell performance can be ignored. From these results the fabrication of more efficient flexible DSSC by applying ZnO coated TiO_2 nanoparticles to conventional fabrication method of flexible DSSC, low temperature annealing or static pressing to achieve the connection of TiO_2 nanoparticles, could be expected. Further studies applying some post-treatments, low temperature annealing, static pressing, CVD, and microwave irradiation, to nanoporous film of ZnO coated TiO_2 particles are currently underway.

The V_{OC} and J_{SC} represent the maximum photovoltage and photocurrent density obtainable from the cell, respectively, and the fill factor was calculated from these values and can be expressed by the following equation:

$$\text{FF} = \frac{J_{\text{m}} \times V_{\text{m}}}{J_{\text{SC}} \times V_{\text{OC}}} \quad (1)$$

In this equation ($J_{\text{m}} \times V_{\text{m}}$) is the maximum power density that can be obtained from the cell. When the fill factor value is close to one, it can be considered to be an efficient cell. To reduce the recombination, we provided an inherent energy barrier using ZnO, the conduction band edge of which was more negative than that of the TiO_2 . The possibility of the formation of an energy barrier by ZnO was ensured from the voltammograms of films prepared from suspensions of TiO_2 , ZnO, and ZnO coated TiO_2 powder (not shown here). The steady-state cathodic current was increased with the applied cathodic potential and the onset potential indicates the conduction band (CB) edge of the semiconductor. From a comparison of the onset potential of ZnO and TiO_2 , the formation of an energy barrier by the ZnO layer was confirmed.

Wavelength dependence of the Photocurrent density was measured using the same cells as were used in the I–V curve measurements. Here, the wavelength was controlled by a monochromator from 400 to 700 nm and electrochemical measurements were performed using a potentiostat. Under the controlled light illumination, the steady-state current density was measured by means of potentiostat and this value was shown in Fig. 5.

Fig. 5 shows photocurrent density for flexible DSSCs using a TiO_2/Ru 535 electrode (filled circles) and a $\text{TiO}_2/\text{ZnO}/\text{Ru}$ 535 electrode (opened circles) fabricated from suspensions of TiO_2 and ZnO coated TiO_2 powder, respectively. The photocurrent density was determined at the short-circuit state. In other words, 0 V was applied to the photoelectrode during the photocurrent density measurement process. The improved photocurrent density due to the reduced recombination rate was observed by using ZnO coated TiO_2 powder in the fabrication of the photoelectrode. When -0.5 V was applied to the photoelectrode instead of 0 V, the same tendency, an increased photocurrent compared with the flexible DSSC using TiO_2/Ru 535 electrode, was observed. From this result, increase of photocurrent density due to the existence of ZnO layer, improvement of incident photon-to-current conversion efficiency (IPCE) can be expected. IPCE was calculated us-

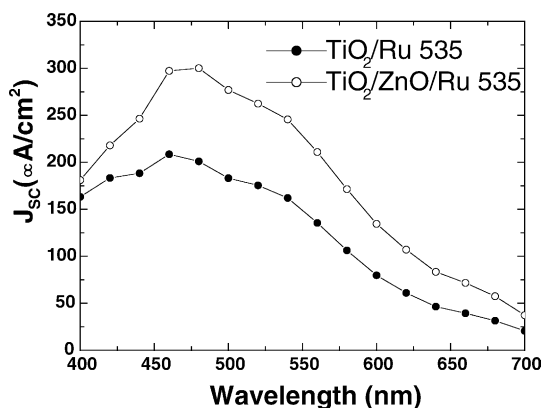


Fig. 5. Wavelength dependence of photocurrent density for conventional flexible DSSC (filled circles) and modified flexible DSSC (open circles) fabricated by TiO_2 and ZnO coated TiO_2 powder, respectively.

ing the following equation and the highest photoresponse was found to be around the λ_{max} of the Ru 535 dye in both flexible DSSCs (not shown here).

$$IPCE = \frac{1240 \times J_{ph}}{P \times \lambda} \quad (2)$$

where J_{ph} (in $\mu A/cm^2$) and P (in $\mu W/cm^2$) are the photocurrent density and the power density of the incident light, respectively, and λ (in nm) is the wavelength of the light.

4. Conclusions

In this study, for commercial competitiveness of a DSSC, a method for preparing a flexible dye-sensitized solar cell was examined. A new photoelectrode using ZnO coated TiO_2 nanoparticles was fabricated to provide an inherent energy barrier at the electrode/electrolyte interface leading to a reduced recombination of photoinduced electrons. XPS and EDX data confirmed the formation of ZnO, with a thickness of ca. ~ 0.5 nm on the TiO_2 surface. Cell performance was compared through I–V curve and wavelength dependent photocurrent measurements of the two types of DSSC. The value of J_{SC} , V_{OC} , fill factor, and overall conversion efficiency increased from 0.35 to 0.49 mA/cm^2 , from -0.67 to -0.72 V, from 61.1 to 69.0%, and from 0.71 to 1.21%, respectively without any post-treatments. The improvement

of cell performance by applying some post-treatments, low temperature annealing, static pressing, CVD, or microwave irradiation, to nanoporous film of ZnO coated TiO_2 particles can be expected.

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