Photovoltaic Properties of TiO_2 -ZnO Composite Electrodes for Dye-Sensitized Solar CellsJunichi HOJO¹, Hui TONG², Shunsuke SHINTANI², Miki INADA¹, Yumi TANAKA¹ and Naoya ENOMOTO¹¹Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan.²Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan.

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ABSTRACT

Photovoltaic properties of wet-type dye-sensitized solar cells were investigated with emphasis on the structures of two types of TiO_2 -ZnO composites as photoelectrodes. One was the mixed electrode of TiO_2 and ZnO powders. Another was the TiO_2 -coated ZnO nanorod array prepared by a sol-gel process. The composite films were loaded on a transparent electrode and calcined at 450–500 °C, on which dye molecules were adsorbed. The current-voltage characteristics were measured in iodide electrolyte solution under a simulated solar light. The mixed electrode exhibited a significant decrease in current density and photovoltaic efficiency compared to TiO_2 electrode. Although the photovoltaic efficiency of ZnO was lower than that of TiO_2 , TiO_2 coating of ZnO nanorod array improved the photovoltaic properties. The addition of triblockcopolymer as pore former in TiO_2 coating was effective to increase the photovoltaic efficiency. The control of the concentration of TiO_2 slurry was also important for homogeneous penetration into ZnO nanorod array.

KEY WORDS

dye-sensitized solar cell, titanium oxide, zinc oxide, composite, sol-gel

1 Introduction

Dye-sensitized solar cells have been receiving a lot of attention since the discovery by Gratzel et al.¹⁾ in 1991 because of the high photovoltaic efficiency and the low cost. The typical device is a wet-type solar cell. The photoelectrode is composed of oxide semiconductor (TiO_2) nanocrystalline porous film and adsorbed dye molecules, and operated in a redox electrolyte such as I^-/I_3^- couple. The photovoltaic efficiency was achieved over 10 % in full sunlight²⁾. During the operation of the solar cell, electrons are excited in dye molecules by light irradiation and injected into the conduction band of TiO_2 , whereas the oxidized dye molecules are regenerated by the redox system³⁾. In order to achieve high photovoltaic efficiency, the optimum structural design of the oxide film is important: (1) high electrical conduction for electron transfer, (2) large specific surface area to adsorb a large amount of dye molecules for light harvesting, (3) appropriate pore size to ensure the diffusion of dye molecules and redox electrolytes into the pores. The electron back transfer from oxide surface to electrolyte is a negative factor to decrease the photovoltaic efficiency³⁾. To restrict the electron back transfer, the whole oxide surface should be covered with dye molecules.

The use of ZnO nanorod array has been proposed because of the higher electron mobility of ZnO (200–300 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) than that of TiO_2 (0.1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)⁴⁾. The band gap (E_g) and conduction band energy (E_c) of ZnO and TiO_2 are close to each other: $E_g = 3.37\text{ eV}$ and $E_c = -4.3$ to -4.45 eV in ZnO; $E_g = 3.23\text{ eV}$ and $E_c = -4.4$ to -4.5 eV in anatase-type TiO_2 ^{3–5)}. Furthermore, TiO_2 coating of ZnO nanorod array was reported to suppress the electron back transfer from ZnO to electrolyte^{6,7)}. The ZnO/ TiO_2 core/shell nanorod-array structures have been fabricated by vapor phase deposition^{6–8)} or solution process⁹⁾. The thin film coating of TiO_2 on ZnO nanorod array increased the photovoltaic efficiency to about 2 %⁶⁾. However, the increase in surface area of electrode is desired to enhance the performance of the composite photoelectrode. Recently, the authors fabricated TiO_2 /ZnO nanorod array composite electrodes by sol-gel techniques to penetrate mesoporous TiO_2 into the space of ZnO nanorod array, and reported that the organic additives to TiO_2 slurry and the density of ZnO nanorod array are important for the penetration into ZnO nanorod array^{10,11)}.

In the present work, two types of TiO_2 /ZnO composite electrodes were investigated. One was the mixture of TiO_2 and ZnO powders to clarify the effect of TiO_2 and ZnO

combination on the photovoltaic property. Another was the TiO_2/ZnO nanorod array composite to discuss the appropriate structure of TiO_2 coating by sol-gel method.

2 Experimental procedures

2.1 Fabrication of TiO_2/ZnO powder composite

Commercial powders of TiO_2 (Nippon Aerosil Co., Ltd.) and ZnO (Wako Pure Chemical Ind., Ltd.) were used as starting materials. TiO_2 and ZnO slurries were separately prepared by a planetary ball milling with the following solvent: water, acetylacetone as dispersing agent, Triton X-100 as surfactant and polyethyleneglycol (PEG20000) as viscosity modifier. The slurries were mixed by ultrasonic agitation, and the composite films were loaded on an indium-tin oxide (ITO) glass substrate by a squeeze method, followed by calcination at 500°C for 2 h (film thickness: $3\text{--}6\mu\text{m}$).

2.2 Fabrication of TiO_2/ZnO nanorod array composite

2.2.1 Preparation of ZnO nanorod array

Zinc acetate (10 mM) and diethanolamine (10 mM) were dissolved in isopropanol, spread by spin coating on a fluorine-doped tin oxide (FTO) glass substrate, and heat-treated at 350 and 500°C to form ZnO seed layer. ZnO nanorods were grown on the seeded substrate in an aqueous solution of 25 mM zinc nitrate, 25 mM hexamethylenetetramine and 6 mM polyethyleneimine at 90°C ¹²⁾. After then, the substrate was calcined at 400°C for 0.5 h. To control the density of ZnO nanorod array, titanium isopropoxide (TIP) was added to the solution on seed preparation, in which co-deposited TiO_2 nanoparticles diluted ZnO seed layer and reduced the density of ZnO nanorod array.

2.2.2 Preparation of TiO_2/ZnO nanorod array composite

TiO_2 slurry was prepared essentially according to the reported sol-gel process by hydrolysis of titanium alkoxide¹³⁾. The process was modified by changing alkoxide and solvent, and using tetraethylammonium hydroxide (TEAOH) as peptizer, triblockcopolymer (P123) as pore former and PEG20000 as viscosity modifier. The mixture of 0.6–2 ml TIP and 1 ml isopropanol including P123 was added dropwise to 1 ml water at room temperature to prepare TiO_2 precipitate. TEAOH was added to the turbid solution, heated at 50°C to peptize the TiO_2 precipitate, and then PEG was added to the solution. ZnO nanorod array was coated with the TiO_2 slurry by dip coating. The composites were dried in vacuum and finally calcined at 450°C for 0.5 h.

2.3 Characterization and evaluation of solar cell properties

The morphologies of TiO_2 and ZnO powders and TiO_2 -coated ZnO nanorod array were observed by scanning

electron microscopy (SEM: Hitachi S-5200). The specific surface areas of TiO_2 and ZnO powders were determined from nitrogen adsorption isotherm (BET method: BELSORP-mini II, BEL Japan, Inc.). The crystalline phases were identified by X-ray diffraction (XRD: Shimadzu corp., XD-D1) with a thin-film attachment. The solar cell properties were measured as follows⁶⁾. Dye compound, cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis (tetrabutylammonium) (N719: Solaronix SA, Switzerland), was dissolved in a mixture of acetonitrile and tert-butyl alcohol (1 : 1 v/v) at the concentration of $3 \times 10^{-4}\text{M}$. Composite electrodes were immersed in the dye solution at room temperature to adsorb dye molecules. The dye-covered electrode and Pt-counter electrode were assembled in a sandwich-type cell. The electrolyte solution was composed of 0.1 M LiI, 0.05 M I_2 , 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in acetonitrile. Photocurrent density-voltage characteristics (J-V curves) were measured on an aperture area of 0.25cm^2 by using an automatic polarization system (Hokuto Denko Corp., HSV-110) and a solar simulator (Peccell Technologies, Inc., PEC-L01 with Xe lamp and AM1.5G filter, $100\text{mW}/\text{cm}^2$). The light intensity was calibrated with a standard silicon solar cell (Bunkoukeiki Co., Ltd., BS-520).

3 Results and discussion

3.1 Photovoltaic property of TiO_2/ZnO powder composites

Figure 1 shows the SEM images of commercial TiO_2 and ZnO powders. The commercial TiO_2 powder was very fine with a particle diameter of 21 nm and a specific surface area of $48\text{m}^2/\text{g}$. The crystalline phase was mainly anatase, including a small amount of rutile. The commercial ZnO powder consisted of large rod-like grains with a length of $0.15\text{--}0.80\mu\text{m}$ and a diameter of $0.12\text{--}0.45\mu\text{m}$ and had a small specific surface area of $4\text{m}^2/\text{g}$. The crystalline phase was wurtzite-type.

The J-V curves of TiO_2/ZnO mixed electrode under a simulated solar light are demonstrated in Fig. 2. Table 1 summarizes the short-circuit current density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (FF) and the photovoltaic conversion efficiency (η). The J_{sc} and η of TiO_2 electrode were not so high because the film thickness was small compared to an ordinary film thickness of about $10\mu\text{m}$ ¹⁾. The V_{oc} of TiO_2 electrode was located within the reported ones of $0.75\text{--}0.78\text{V}$ ¹⁴⁾. Compared to TiO_2 electrode, the J_{sc} and η of ZnO electrode were significantly low and the V_{oc} was also low. According to the mechanism of dye-sensitized solar cell³⁾, the low J_{sc} is attributed mainly to the

Fig. 1 SEM images of commercial powders: (a) ZnO and (b) TiO₂.

Fig. 2 J-V curves of TiO₂/ZnO mixed electrodes: (a) TiO₂; (b) TiO₂:ZnO=9:1 (mol ratio); (c) TiO₂:ZnO=7:3 (mol ratio) and (d) ZnO.

Table 1 Photovoltaic properties of TiO₂/ZnO mixed electrodes.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
TiO ₂	6.150	0.752	0.60	2.80
TiO ₂ :ZnO=9:1	0.505	0.797	0.70	0.30
TiO ₂ :ZnO=7:3	0.107	0.685	0.68	0.05
ZnO	0.780	0.698	0.65	0.40

decrease in the average specific surface area. However, the decrease of J_{sc} was so serious compared to the small amount of added ZnO. Therefore, the influence of electron back transfer on ZnO should be considered in the mixed electrode. However, the FF and V_{oc} were not small or the FF was rather high in the mixed electrode. The high electron conduction of ZnO seemed to bring the positive effect on the FF. Anyway, the dispersion of ZnO particles in TiO₂ film was not effective to enhance the photovoltaic properties of TiO₂ electrode.

3.2 Photovoltaic property of TiO₂-coated ZnO nanorod array composites

The process factors on the fabrication of TiO₂-coated ZnO nanorod array by sol-gel methods were investigated in the previous works^{10,11}. The photovoltaic property of ZnO nanorod array was improved by TiO₂ coating. However, TiO₂ agglomerates tended to segregate on the top of ZnO nanorod array, resulting in the decrease in photovoltaic efficiency. TEAOH was effective for the peptization of TiO₂ agglomerates to be penetrated into ZnO nanorod array. The concentration of TiO₂ slurry had to be controlled because the large agglomerates formed at the high concentration. The density of ZnO nanorod array also had to be controlled because TiO₂ slurry was difficult to penetrate into the dense ZnO nanorod array.

amount of dye molecules adsorbed on ZnO powder with a small specific surface area. The low V_{oc} is ascribed to the electric discharge inside cell by electron back transfer. The electron back transfer from electrode to electrolyte is more serious in ZnO than in TiO₂⁶. The low J_{sc} and V_{oc} lead to the decrease in η . However, the FF was higher in ZnO electrode than in TiO₂ electrode. The FF is a measure of decrease in photocurrent with increase in photovoltage, which is characterized by a shunt resistance (R_{sh}) and a series resistance (R_{se})³. The R_{sh} is determined from the slope of J-V curve near J_{sc} and the R_{se} from the slope of J-V curve near V_{oc} . They are related to electron back transfer and resistance of electric conduction path. If R_{sh} is infinite and R_{se} is zero, FF is ideally 1. High FF in ZnO electrode might be due to the high electron conduction.

Compared to TiO₂ and ZnO electrodes, the mixed electrodes exhibited the low J_{sc} and η . The decrease in J_{sc} by addition of ZnO to TiO₂ may be explained partly by the

TiO₂/ZnO nanorod array electrodes were fabricated on the basis of the optimized process, and the photovoltaic properties were investigated with emphasis on TiO₂ concentration and pore forming agent (P123). Figure 3 shows the SEM images of TiO₂-coated ZnO nanorod arrays. The length and diameter of ZnO nanorods were 3.0–4.5 μm and 0.10–0.35 μm , respectively. The concentration of TiO₂ slurry was controlled by TIP concentration. When the TiO₂ concentration was low, TiO₂ nanoparticles penetrated inside ZnO nanorod array. On the other hand, when the TiO₂ concentration was high, TiO₂ nanoparticles tended to cover the top of ZnO nanorod array. Figure 4 shows the XRD patterns of TiO₂-coated ZnO nanorod array. Amorphous TiO₂ deposits transformed to anatase phase after calcination. The crystalline phase of ZnO was wurtzite-type. The content of TiO₂ was smaller at the low TiO₂ concentration than at the high TiO₂ concentration in the slurry. The J–V curves of TiO₂/ZnO nanorod array electrodes are shown in Fig. 5. Table 2 summarizes the photovoltaic properties. The J_{sc} increased by addition of P123 at both low and high TiO₂ concentrations, leading to the increase in photovoltaic efficiency. This may be due to the pore forming effect by P123 to increase the surface area and the amount of adsorbed dye. However, the addition of a large amount of P123 suppressed the penetration of TiO₂ slurry, which may be due to the increase in slurry viscosity. When the TiO₂ concentration was high and P123 was added, the current density gradually decreased with an increase in voltage, meaning a small R_{sh}. Furthermore, the V_{oc} and FF were small. These results indicate that the electron back transfer was serious, which was caused by insufficient TiO₂ penetration and bare ZnO surface. On the other hand, the V_{oc} and FF were high at low TiO₂ concentration, resulting in the high photovoltaic efficiency

Fig. 3 SEM images of TiO₂-coated ZnO nanorod array: (a) 0.67 mol/l TIP and (b) 1.28 mol/l TIP. TEAOH/TiO₂ = 0.25 (mol ratio), 0.01 g/ml PEG.

Fig. 4 XRD patterns of TiO₂-coated ZnO nanorod array: (a) 0.67 mol/l TIP and (b) 1.28 mol/l TIP. TEAOH/TiO₂ = 0.25 (mol ratio), 0.01 g/ml PEG.

Fig. 5 J–V curves of TiO₂/ZnO nanorod array electrodes: (a1) 0.67 mol/l TIP, P123/TiO₂ = 0 (mol ratio); (a2) 0.67 mol/l TIP, P123/TiO₂ = 0.02 (mol ratio); (b1) 1.28 mol/l TIP, P123/TiO₂ = 0 (mol ratio) and (b2) 1.28 mol/l TIP, P123/TiO₂ = 0.005 (mol ratio). TEAOH/TiO₂ = 0.25 (mol ratio), 0.01 g/ml PEG.

Table 2 Photovoltaic properties of TiO₂/ZnO nanorod array electrodes.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
0.67 mol/l TIP, P123/TiO ₂ =0	0.622	0.646	0.62	0.25
0.67 mol/l TIP, P123/TiO ₂ =0.02	0.926	0.652	0.76	0.46
1.28 mol/l TIP, P123/TiO ₂ =0	0.581	0.669	0.60	0.23
1.28 mol/l TIP, P123/TiO ₂ =0.005	1.006	0.629	0.55	0.35

in the presence of P123. This is due to an effective TiO₂ covering of ZnO nanorod array. Compared to TiO₂/ZnO mixed electrodes, the TiO₂/ZnO nanorod array electrodes exhibited the high photovoltaic efficiency, suggesting the effect of one dimensional ZnO nanorod array on electron conduction. However, the V_{oc} was low, meaning that the covering of ZnO by TiO₂ was not complete.

4 Conclusions

The photovoltaic properties of TiO₂/ZnO mixed electrode and TiO₂/ZnO nanorod array electrode were compared to clarify the appropriate structure of the composite electrodes. The TiO₂/ZnO mixed electrode exhibited a significantly low photovoltaic efficiency compared to TiO₂ electrode. This seemed to be due to electron back transfer on ZnO from electrode to electrolyte. The photovoltaic property of ZnO nanorod array was improved by TiO₂ coating through sol-gel process. The low TiO₂ concentration for penetration into ZnO nanorod array and the addition of P123 as pore former were effective, but the photovoltaic efficiency was still low as 0.46%. The photovoltaic efficiency of about 2% has been achieved by vapor phase deposition of TiO₂ on ZnO nanorod array over 10 μm^2 . However, the homogeneous penetration of TiO₂ into long ZnO nanorod array is difficult by the sol-gel method. Rather, the full coverage of short ZnO nanorod array with mesoporous TiO₂ coating is important for decrease of electric conduction path and increase of specific surface area to adsorb more dye. The quantitative investigation will be continued on the structure of TiO₂/ZnO nanorod array composite and the specific surface area and pore size of TiO₂ coating.

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