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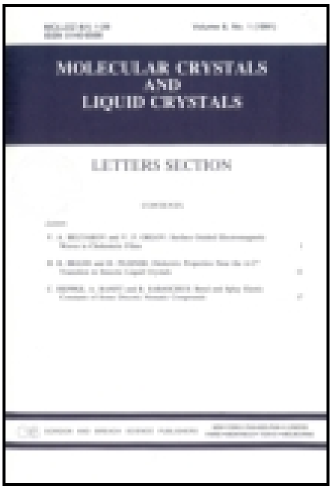

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Surface-Modified TiO_2 Photoelectrode for More Efficient Dye-Sensitized Solar Cells

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The time dependence in the surface treatment of TiO_2 photoelectrode on the photovoltaic properties of dye-sensitized solar cells (DSSCs) was studided. Nanoporous TiO_2 electrodes were modified with aqueous sodium sulfate (Na_2SO_4) solution (0.05 M) by a dip coating process at varied dipping time, and the resulting electrodes were applied to DSSCs. Fill factor values were significantly decreased with increasing dipping time, and short circuit current values were ranged from 18.11 to 21.53 mA/cm^2. However, there were no meaningful changes in open circuit voltage. The power conversion efficiency (PCE) of 6.59 $\sim$ 9.35% was obtained from the DSSCs with Na_2SO_4-modified TiO_2 photoelectrode. Even small differences in dipping time, PCEs were significantly changed.

Keywords Surface treatment; dye-sensitized solar cell; dip coating; sodium sulfate; power conversion efficiency

Introduction

Much attention has been paid to dye-sensitized solar cells (DSSCs) based on nanoporous TiO_2 photoelectrode, due to their low-cost production, non-vacuum processability, flexible devices, environment-friendly energy conversion system and fairly high performance [1–6]. A typical DSSC consists of nanostructured TiO_2 photoelectrodes covered with Ru dyes, a redox electrolyte solution of $I^-/I_3{}^-$ and a Pt counter electrode. Recently, DSSCs with a power conversion efficiency (PCE) of over 12% has been reported by A. Yella et al. [7]. They employed porphyrin dyes and cobalt (II/III)–based redox electrolyte instead of Ru dyes and iondine electrolyte, respectively. However, further improvements in the power conversion

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efficiency (PCE) are necessary to successfully commercialize DSSCs. In DSSCs, PCE is achieved by ultra-fast injection of an electron from a photo-excited dye into the conduction band of a semiconductor (TiO_2), subsequent completion of dye regeneration and hole transportation to the counter electrode. Thus, as a media of dye adsorption, electron transport, and electrolyte diffusion, the nanocrystalline TiO_2 photoelectrode plays a key role in the DSSCs [8]. The electrons injected into the TiO_2 layer are sometimes able to return to the sensitizer or the electrolyte due to an electron recombination phenomenon. This back electron transfer causes a reduction in conversion efficiency. Many researchers have investigated effects on the performance of DSSCs by modifications of TiO_2 surface using various metal oxides [9], organic co-adsorbates [10–12], and some insulating materials [13–15].

In a previous study [16], we could successfully introduce sodium sulfate (Na_2SO_4) on TiO_2 surfaces by a very simple dip coating process using aqueous solutions, and the resulting DSSCs with Na_2SO_4-treated TiO_2 layer showed an enhanced conversion efficiency due to an increase in open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}). In this study, we further examined our simple dip coating process at various dipping time to get higher conversion efficiency of DSSCs, and the time dependence of the surface treatment on the performance of the DSSCs was also investigated.

Experimental Details

Materials

Commercial fluorine-doped tin oxide (FTO, sheet resistance ~7 Ω/square) glass (TCO22-7), TiO_2 pastes for photoelectrode (Ti-nanoxide T/SP) and scattering layer (Ti-nanoxide R/SP), N719 dye (Ruthenizer 535-bisTBA) and iodide-based electrolyte (AN-50) were purchased from Solaronix. Sodium sulfate (SS, Na_2SO_4) was selected as the surface modifiers. Chloroplatinic acid ($H_2PtCl_6 \cdot 5.5H_2O$; Kojima Chemicals) as a Pt source were selected. All of the chemicals were used without any further purification.

Preparation of DSSCs

To prepare working electrodes, FTO glasses were cleaned in a detergent solution by sonication for 20 min, and thoroughly rinsed with deionized water and ethanol. After the treatment with UV-O_3 for 20 min, FTO glasses were immersed into a 40 mM $TiCl_4$ solution at 70 °C for 30 min. An active TiO_2 layer was formed on the FTO glass via a doctor-blade method followed by a calcination process at 500°C for 30 min in a furnace. Then, a scattering layer was additionally deposited, and then calcined. Finally, the TiO_2 films were treated with 40 mM $TiCl_4$ solution again, and annealed at 500°C for 30 min. Thus, TiO_2/FTO electrodes with 15-nm TiO_2 layers were prepared. The Na_2SO_4-modified TiO_2 electrode (SS-TiO_2) was fabricated by dipping the pristine TiO_2/FTO electrode into the aqueous Na_2SO_4 solution (0.05M) for $10 \sim 1200$ sec, followed by rinsing with deionized water and drying at 100°C for 30 min to give SS-TiO_2/FTO. To keep similar conditions between the standard and modified electrodes, the pristine TiO_2/FTO electrodes were also rinsed, and then dried at 100°C for 30 min. The pristine TiO_2/FTO and SS-TiO_2/FTO were separately immersed into a 0.5 mM of N719 dye solution for 24 h. To prepare the counter electrode, two holes were formed in the FTO glass by a drill, and cleaned using the method described above. A drop of 3 mM H_2PtCl_6 solution was placed on the rinsed FTO glass, and then it was calcined at 400°C for 30 min. Thermally treated counter electrodes were placed on

Table 1. Performance comparison of DSSCs employing SS-TiO_2/FTO as photoanodes

Applied electrodes		V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	η (%)
SS-TiO_2/FTO	SS(10)-TiO_2/FTO	0.64	19.77	69.60	8.81
	SS(30)-TiO_2/FTO	0.64	21.39	66.90	9.16
	SS(60)-TiO_2/FTO	0.65	21.53	66.81	9.35
	SS(300)-TiO_2/FTO	0.61	22.01	63.39	8.54
	SS(1200)-TiO_2/FTO	0.65	18.11	56.01	6.59

the dye-absorbed TiO_2/FTO and SS-TiO_2/FTO electrodes, and sealed with a 60 μm-thick sealing material (SX1170-60PF; Solaronix). The electrolyte was introduced into the cells through one of the two small holes drilled on the counter electrodes to give DSSCs with 25 mm^2 active area.

Measurements

Photocurrent-voltage measurements were performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system equipped with a 1 kW xenon arc lamp (Oriel). Light intensity was adjusted to 1 sun (100 mWcm^{-2}) with a Radiant Power Energy Meter (model 70260, Oriel).

Results and Discussion

TiO_2/FTO electrodes were soaked in SS (Na_2SO_4) solutions and the rinsed electrodes were dried at 100° to give the SS-TiO_2/FTO. The soaking time was adjusted because it determines the coating amount in the dip coating process. By varying the soaking time from 10 to 1200 sec, i.e., 10, 30, 60, 300 or 1200 sec, we prepared five different photoelectrodes such as SS(10, 30, 60, 300 or 1200)-TiO_2/FTO. The DSSCs with SS-TiO_2/FTO electrodes were fabricated, and their photovoltaic properties were characterized. The resulting photovoltaic properties of DSSCs are compared in Table 1 and the performance variations as a function of dipping time are presented in Figure 1.

As can be seen from Figure 1(a), open circuit voltage (V_{oc}) value was almost independent on the variation of dipping time. When considering that V_{oc} value is determined by the potential difference between Fremi level (E_F) of TiO_2 photoelectorde and the redox potential of the electrolyte, we can see that surface-treatment time does not affect the E_F of TiO_2. The short circuit voltage (J_{sc}) value was found to increase when the dipping time in the aqueous Na_2SO_4 solution was below 300 sec as shown in Fig. 1(b). However, a decrease in J_{sc} was observed in 1200 sec. Fill factor value was decreased with increasing the dipping time, ranging from 69.60 to 56.01%. In general, fill factor (*FF*) is influenced by internal resistance in cells. It seems that internal resistance to the electron transfer at the interface of the TiO_2/dye/electrolyte was increased by the surface modification [17]. Overall, the power conversion efficiency (PCE) of 6.59~9.35% was obtained from the DSSCs with Na_2SO_4-modified TiO_2 photoelectrode, indicating that, even small differences in dipping time, PCEs were significantly changed. The DSSC with the SS(60)-TiO_2/FTO exhibited the highest PCE of 9.35% with $J_{sc} = 21.53$ mA/cm^2, $V_{oc} = 0.65$ V, and $FF = 66.81\%$. Fig. 2 shows the current density (J) and voltage (V) curves of the DSSC with SS(60)-TiO_2/FTO. In previous work [16], the TiO_2 photoelectrtode was treated with aqueous Na_2SO_4 solution

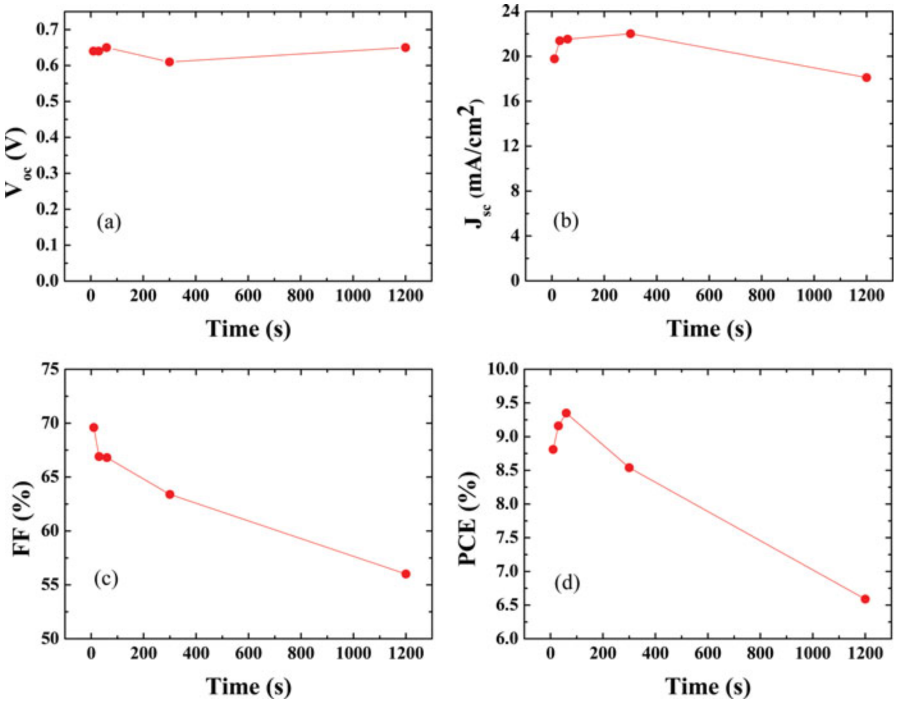

Figure 1. Performance variations with dipping time; (a) V_{oc}, (b) J_{sc}, (c) *FF* and (d) *PCE* of DSSCs characterized under AM 1.5 irradiation.

for 600 sec, and the PCE of the DSSC with such surface-modified TiO_2 layer [we here designate this photoelectrode as SS(600)-TiO_2/FTO] was compared with that of the reference device with pristine TiO_2/FTO, i.e., without any surface treatment. A 17.3% enhancement in PCE was achieved from the device with SS(60)-TiO_2/FTO in comparison with that

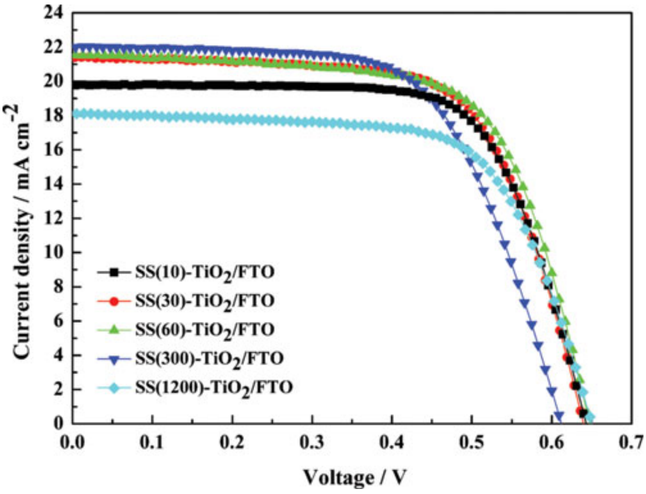

Figure 2. *J*-*V* characteristics of DSSCs with Na_2SO_4-modified TiO_2 electrodes.

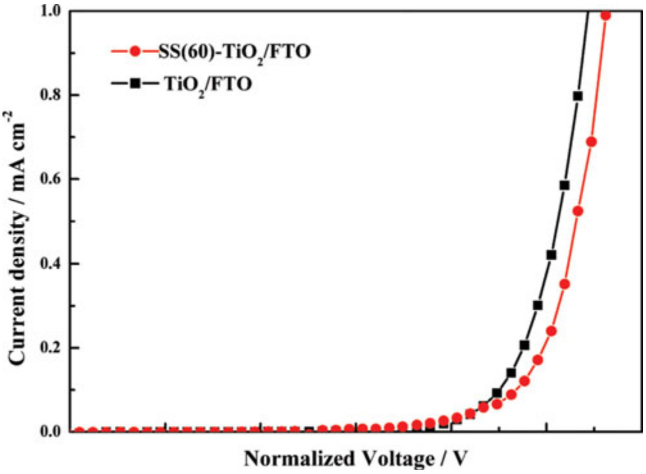

Figure 3. Dark currents with a normalized onset potential measured from the DSSCs with pristine- and SS(60)-TiO_2/FTO electrodes.

($\eta = 7.97\%$, $V_{oc} = 0.620$ V, $J_{sc} = 18.38$ mA/cm^2 and $FF = 69.97\%$) of the reference device. Except the device with SS(1200)-TiO_2/FTO, V_{oc}, J_{sc} and PCE were increased from those of the reference device. In addition, by optimization of surface treatment time, an additional improvement from 9.01% for the device with SS(600)-TiO_2/FTO to 9.35% for SS(60)-TiO_2/FTO was obtained.

It was revealed in our previous report [16] that the enhanced PCE was mainly due to a prolonged lifetime of electrons injected from the LUMO (lowest unoccupied molecular orbital) level of dye to the conduction band edge (CBE) of TiO_2 electrode. The presence of Na_2SO_4 on the TiO_2 electrode could play a role of energy barrier to charge recombination between TiO_2 and electrolyte. This decrement in recombination rate can increase electron collection efficiency, leading to an enhancement in J_{sc}. The rate of recombination between the photoinjected electrons (i.e. the electrons in the TiO_2) and ions in electrolyte can be inferred from the rate of increase in the dark current by the normalization of onset potential. As shown in Fig. 3, the normalized onset-voltage curves shows that the dark currents of DSSC with SS(60)-TiO_2/FTO was larger than those of the reference cell throughout the measured potential range. This means that the Na_2SO_4 treatment decreases the recombination rate of the photoinjected electrons.

The enhancement in V_{oc} of the DSSCs with SS(10, 30, 60, 300 and 1200)-TiO_2/FTO compared to the reference device could also be explained by the formation of an energy barrier on the TiO_2 surface. The modification of the TiO_2 surface can influence the V_{oc} value of DSSCs. Some semiconductors and insulators coated on the TiO_2 surface have been reported to form an energy barrier that allows the electron injection but hinders the recombination [18–21]. This barrier decreases the recombination rate for a given electron population. If the amount of electrons injected from the dyes is unchanged, then the electron concentration in the modified TiO_2 layer will be higher than that in the unmodified TiO_2 layer. A larger electron concentration in the TiO_2 layer can cause a more negative shift of the E_F [22, 23] and thus a larger V_{oc} as shown in Fig. 4. In our case, we believe that the sulfate (SO_4^{2-}) groups serve as an insulator, and form an energy barrier between the TiO_2 layer and the electrolytes. This energy barrier can induce a larger electron concentration

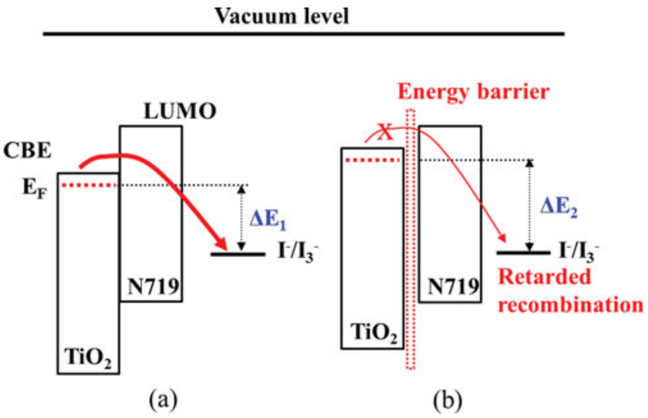

Figure 4. Schematic energy band diagram of (a) reference device and (b) DSSCs with SS-TiO_2/FTO showing the negative shift of Fremi level.

(or an increased electron lifetime) in the TiO_2 layer, leading to a more negative E_F. This resulted in the larger potential difference ($\Delta E_1 < \Delta E_2$, refer to Fig. 4) between E_F of TiO_2 and redox potential of electrolyte, Thus, V_{oc} can increase when SS-TiO_2/FTO was used as the photoelectrodes.

Conclusions

In summary, a dip coating process of modifying surfaces of a nanoporous TiO_2 was optimized to obtain higher performance of DSSCs. The TiO_2/FTO electrodes were immersed in aqueous Na_2SO_4 solution to give Na_2SO_4-modified TiO_2/FTO (SS-TiO_2/FTO). The dipping time was adjusted from 10 to 1200 sec, and such electrodes were used as the photoanodes of DSSCs. The device with the SS(60)-TiO_2/FTO, which is a 60-sec treated photoelectrode, exhibited the highest PCE of 9.35% with $J_{sc} = 21.53$ mA/cm^2, $V_{oc} = 0.65$ V, and $FF = 66.81\%$. Thus, by the optimization of surface treatment condition, a higher PCE was obtained, compared to our previous result.

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