



Enhanced power conversion efficiency of dye-sensitized solar cells with Li_2SiO_3 -modified photoelectrode



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ABSTRACT

The effects of lithium silicate (LS) as a surface modifier on the performance of dye-sensitized solar cells (DSSCs) were studied. LS-modified TiO_2 electrodes (LS- TiO_2 /FTO) prepared by a soaking process were applied to the photoelectrodes of DSSCs. The reference device without any modification showed performance of 0.68 V of open-circuit voltage (V_{oc}), 21.40 mA/cm^2 of short-circuit current (J_{sc}), and 63.21% of fill factor (FF), which led to a power conversion efficiency (PCE) of 9.20%, whereas for the device with the LS- TiO_2 /FTO electrode, the PCE was increased to 10.58% ($V_{oc} = 0.79$ V, $J_{sc} = 20.22$ mA/cm^2 , and $FF = 66.21\%$). By monitoring the changes in dark current–voltage characteristics, normalized IPCE spectra, and electrochemical impedance spectra, it was revealed that the LS modification induced the formation of a surface dipole on the TiO_2 photoelectrode, leading to the conduction band edge shift of TiO_2 toward a negative direction, and thus to an enhancement in V_{oc} and a decrease in J_{sc} .

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1 Introduction

Wide attention has been paid to dye-sensitized solar cells (DSSCs) due to their reasonable photovoltaic efficiency, low production cost, and brief fabrication process [1–3]. In addition, DSSCs are especially attractive for building integrated photovoltaics because the color of the device can be easily varied by choosing different dyes, and semi-transparent cells are regarded as excellent candidates for window-compatible photovoltaics [4,5]. Although an impressive power conversion efficiency (PCE) of 13% in DSSCs with porphyrin dye and the cobalt(II/III) redox shuttle has been reported by the Grätzel group [6], further improvements in PCE are necessary to successfully commercialize DSSCs.

In DSSCs, photoelectric conversion is achieved by ultra-fast injection of electrons from photoexcited dyes into the conduction band of TiO_2 (the photoelectrode), subsequent completion of dye regeneration, and hole transportation to the counter electrode. A mesoporous nanocrystalline structure, i.e., TiO_2 film, is essential in order to adsorb sufficient dye molecules for photoelectron generation and to favorably soak hole-carrying electrolytes into the photoelectrode, and it is also a good transporter of electrons injected from the photoexcited dyes to the TiO_2 conduction band.

Thus, high short-circuit current (J_{sc}) can be achieved from the TiO_2 cells. However, open-circuit voltage (V_{oc}) in DSSCs with a TiO_2 layer maintains low values. For example, the recombination between the photoinjected electrons and the oxidized dye or ions in the electrolyte may cause a reduction of approximately 300 mV of the V_{oc} from the theoretical value, leading to a rapid decrease in the conversion efficiency [7]. Interfacial modifications of the TiO_2 layer could improve the V_{oc} . By modification of the TiO_2 surface, the conduction band edges (CBEs) could shift to the negative direction, resulting in an increase in V_{oc} . For example, SrTiO_3 [8], ZnO [9], chenodeoxycholate [10], BaCO_3 [11], and MgO [12] were applied to modify TiO_2 electrodes, and the resulting DSSCs showed an enhancement in PCE, mainly due to an enhancement in V_{oc} . Meanwhile, surface modification of TiO_2 could lead to a reduction of interfacial charge recombination between the TiO_2 electrode and electrolytes by formation of an energy barrier on TiO_2 surfaces. For example, SrO [13], Al_2O_3 [14], Nb_2O_5 [15], BaCO_3 [16], CaCO_3 [17], ZnO nanorods [18], and graphite carbon nitride [19] were applied to modify TiO_2 electrodes, and the resulting DSSCs showed an enhancement in PCE attributed to an improved V_{oc} .

In this paper, we selected lithium silicate (LS, Li_2SiO_3) as a TiO_2 -surface modifier. The TiO_2 surfaces were directly treated with aqueous LS solution via a simple dipping process, and the resulting electrodes were applied to the photoelectrodes of DSSCs. We expected the LS to form a surface dipole or an energy barrier on TiO_2 surfaces, resulting in an improvement in the performance of

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the DSSCs. DSSCs with LS-modified photoelectrodes (LS-TiO₂/FTO) were fabricated, and the effects of the surface treatment on the photovoltaic performance of the cells were discussed.

2 Experimental

2.1. Materials

A commercial fluorine-doped tin oxide (FTO; sheet resistance $\sim 7 \Omega/\text{square}$) glass (TCO22-7), TiO₂ paste for the photoelectrode (Ti-nanoxide T/SP), N719 dye (Ruthenizer 535-bisTBA), and iodide-based electrolytes (AN-50) were purchased from Solaronix. The LS was purchased from Alfa Aesar. Chloroplatinic acid (H₂PtCl₆·5.5H₂O; Kojima Chemicals) was selected as the platinum (Pt) source. All of the chemicals were used without any further purification.

2.2. Preparation of DSSCs

To prepare the working electrodes, the FTO glasses were cleaned in a detergent solution with sonication for 20 min, then thoroughly rinsed with deionized (DI) water and ethanol. After treatment with a UV-O₃ for 20 min, the FTO glasses were immersed in a 40-mM TiCl₄ solution at 70 °C for 30 min, then washed with DI water and ethanol. An active TiO₂ layer was formed on the FTO glass via a doctor-blade method followed by a calcining process at 500 °C for 60 min. Next, a TiO₂ layer composed of ca. 400-nm particles was additionally deposited, then calcinated. Finally, the TiO₂ films were again treated with a 40-mM TiCl₄ solution and annealed at 500 °C for 60 min; thus, TiO₂/FTO electrodes with 12-nm TiO₂ layers were finally prepared. The electrodes were soaked in the aqueous solutions (5×10^{-4} M) of LS for 1–20 min to deposit LS onto the TiO₂ layers. Next, the resulting electrodes were rinsed with DI water and ethanol, then dried at 65 °C for 10 min to produce modified photoelectrodes [LS(1–20)-TiO₂/FTO]. The bare TiO₂/FTO and LS(1–20)-TiO₂/FTO photoelectrodes were separately immersed into 0.5 mM of N719 dye solution (acetonitrile/tert-butyl alcohol, $v/v = 1$) for 24 h. To prepare the counter electrode, two holes were formed in the FTO glass with a drill, then cleaned with the method described previously. A drop of 7-mM H₂PtCl₆/isopropanol solution was placed on the rinsed FTO glass, then calcined at 400 °C for 30 min. Thermally treated platinum counter electrodes were placed on the TiO₂/FTO electrodes, then 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 produce DSSCs with a 25-mm² active area.

2.3. Measurements

X-ray photoelectron spectroscopy (XPS) was performed using VG Multilab ESCA 2000 (ThermoVG scientific) with Mg K α radiation. The C 1s photoelectron peak (binding energy at 284.6 eV) was used as an energy reference. The amount of LS introduced onto the TiO₂ layer was measured using inductively coupled plasma mass spectrometry (ICP/MS, Elan 6100, PerkinElmer). Field emission scanning electron microscopy (FE-SEM) was used to study the morphology of the photoelectrodes. SEM measurements were performed on a Supra-55VP (Zeiss & Kleindiek). The UV-vis absorption spectra were obtained from a Jasco V-650 spectrophotometer. Electrochemical impedance spectroscopy (EIS) was performed using an electronic-chemical analyzer (Iviumstat Tec.). Photocurrent-voltage measurement was performed using a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with a 1-kW xenon arc lamp, Oriol). Light intensity was adjusted to 1 sun (100 mW cm⁻²) with a Radiant

Power Energy Meter (model 70260, Oriol). The incident photo-to-current conversion efficiency (IPCE) results were acquired from IPCE G1218a (PV Measurement). The active areas of the dye-adsorbed TiO₂ films were estimated using a digital microscope camera (Olympus SZ61) with image-analysis software.

3 Results and discussion

3.1. Modification of TiO₂ surface

We prepared four different electrodes by varying the soaking time from 1 to 20 min, i.e., LS(1, 5, 10, and 20)-TiO₂/FTO, where '(1)' means that the dipping time was 1 min. From the ICP measurements, the amount of Li deposited on the TiO₂ layer was determined to be 0.45, 0.56, 0.64, and 0.75% for the soaking times of 1, 5, 10, and 20 min, respectively. The amount of lithium was slightly increased with extending the soaking time. In order to further confirm the incorporation of LS on the TiO₂ surface, an XPS measurement was also conducted. Fig. 1(a) shows the XPS spectrum for whole survey scan measured from LS(5)-TiO₂/FTO photoelectrode. Peaks detected at 55.6 eV agreed with the binding energy of 1s in Li, indicating the existence of Li, as shown in Fig. 1(b). A peak at 102.1 eV attributed to the binding energy of 2p in Si was also displayed in Fig. 1(c), supporting the presence of Si on the surface of the photoelectrode.

In order to investigate the morphological changes by the Li₂SiO₃ modification, SEM images were obtained. However, a comparison of the images revealed no noticeable change in morphology as shown in Fig. 2. A similar result was reported by Lee et al. [20]. The morphology of TiO₂ films treated with an aqueous TiCl₄ solution (15–200 mM) was not changed. Wu et al. also reported that the TiO₂ nanoparticles, which were electrophoretically modified with TiCl₃ (250 mM), were similar to those in the bare photoelectrode [21]. It was because the concentration of the solution for the surface treatment was low. In this study, the Li₂SiO₃ solution with a very low concentration (0.5 mM) was used to modify the surface. Thus, we believe that the low concentration does not affect the surface morphology.

3.2. Photovoltaic performance of DSSCs with pristine and LS-modified TiO₂

The LS-modified photoelectrodes were applied in the fabrication of the DSSCs, and then their photovoltaic properties were characterized. The photovoltaic properties of the DSSCs as a function of surface-modification time are presented in Fig. 3. As can be seen from Fig. 3(a), the V_{oc} values were increased by the treatment of the TiO₂ surface with diluted LS solution. A V_{oc} enhancement of about 15.6% on average was achieved in all of the surface-treated devices, as compared to the reference cell with bare-TiO₂/FTO, i.e., without any treatment. However, the J_{sc} was observed to decrease with increasing the soaking time, as shown in Fig. 3(b). A slight increase (about 3.5% on average) in FF was observed in the devices with LS-TiO₂/FTO, compared to that of the control device. The overall efficiencies of DSSCs with LS-TiO₂/FTO were enhanced over that of the reference cell, because the improvement in V_{oc} overrode the reduction in J_{sc} . Thus, it is worth revealing how the incorporation of LS on photoelectrode surfaces improves the performance of DSSCs. Because the DSSCs with the LS(5)-TiO₂/FTO electrode, corresponding to a soaking time of 5 min, showed the best performance (10.58%) due to an increase in both V_{oc} and FF , we focused on this device to reveal the origin of the efficiency enhancement.

Fig. 4 shows the current density (J) and voltage (V) curves of DSSCs with LS(5)-TiO₂/FTO and bare TiO₂/FTO electrodes, and the device performance is compared in Table 1. The DSSCs with the

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