

Effect of increased surface area of stainless steel substrates on the efficiency of dye-sensitized solar cells

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In order to increase the electrical contact area between TiO₂ particles and stainless steel (StSt) substrates of the dye-sensitized solar cells (DSSCs), StSt foil was roughened electrochemically using sulfuric acid with some additives. Compared with the DSSC with nontreated StSt substrate, DSSC with this roughened StSt substrate showed a 33% increase in light-to-electricity conversion efficiency with negligible effect on open circuit voltage (V_{oc}) and fill factor. Electrochemical impedance spectroscopy clearly confirmed that the increased performance was due to a decreased electrical resistance at the TiO₂/StSt interface. © 2008 American Institute of Physics.

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Dye-sensitized solar cells (DSSCs) have attracted significant attention due to their superior light-to-electricity conversion efficiency (>11%), low cost, and eco-friendly properties.¹ During recent decades, efforts have been made to endow DSSCs with flexibility to extend their application. DSSCs with flexible substrates, which are generally fabricated using conductive-layer-coated plastic films,² can be produced in continuous roll-to-roll processes at a relatively low cost.³ However, conductive-layer-coated plastic films degrade at the TiO₂ sintering temperature of approximately 500 °C. In addition, sintering of TiO₂ particles below the plastic-degeneration temperature causes poor necking of TiO₂ particles.⁴ To fabricate a nanoporous TiO₂ electrode on a conductive-layer-coated plastic film, several low-temperature processes have been proposed, such as hydrothermal crystallization,⁵ electrophoretic deposition,⁶ and low-temperature sintering.⁷ However, these methods result in poor electrical contact between nanoporous particles and conductive substrates. Rather than conductive-layer-coated plastic films, Electronics and Telecommunications Research Institute (ETRI) have proposed metal substrates, in particular, stainless steel (StSt) substrate.⁸ Metal substrates are excellent alternatives to indium tin oxide coated plastic films because they do not require limitation of the sintering temperature.

In the present study, we report increased light-to-electricity conversion efficiency and decreased electrical resistance of DSSCs with the roughened StSt substrates. Figure 1 shows a schematic of dye-coated TiO₂ particles on the roughened StSt substrate. Roughening of the StSt foil (Good-Fellow, Fe/Cr18/Ni10) was electrochemically realized using sulfuric acid including hydrated sodium thiosulphate and propargyl alcohol.⁹ Anatase TiO₂ particles were synthesized using a sol-gel method¹⁰ and the diameter of the TiO₂ par-

ticles was adjusted to 20 nm. The synthesized TiO₂ particles were converted into a paste using an organic vehicle.¹¹ Photoelectrodes were fabricated on StSt substrates using the TiO₂ paste by the doctor blade method. Sintering of TiO₂ particles was performed at 550 °C for 30 min under an air atmosphere. Sintered TiO₂ films were coated with sensitizing dye by immersion in a solution of RuL₂(NCS)₂ (Solaronix) and ethanol overnight. The liquid electrolyte was composed of 0.70M 1-vinyl-3-methyl-imidazolium iodide, 0.10M LiI, 40 mM iodine, and 0.125M 4-tert-butylpyridine in 3-methoxypropionitrile. The prototype DSSCs were fabricated using fluorine-doped tin oxide (FTO) glass as the counterelectrode. The FTO glass was coated with the Pt catalyst using a drop of H₂PtCl₆ in ethanol, followed by heating at 400 °C for 30 min.¹² The photoelectrode and counterelectrode were sealed with a Surlyn layer (DuPont) under a pressure of 200 kPa/cm² at 100 °C.

The area of the active TiO₂ layer was approximately 0.20 cm², as measured using a video microscope system (SOMTECH). The cross-sectional microstructures of the interface between StSt and TiO₂ were analyzed using scanning transmission electron microscopy (STEM) (Hitachi, HD2300A). The actual surface areas of the nontreated and

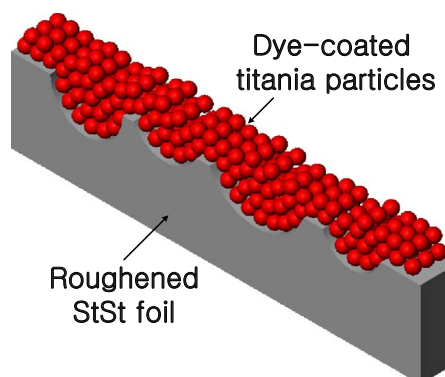


FIG. 1. (Color online) Schematic of dye-coated TiO₂ electrode using roughened StSt substrate.

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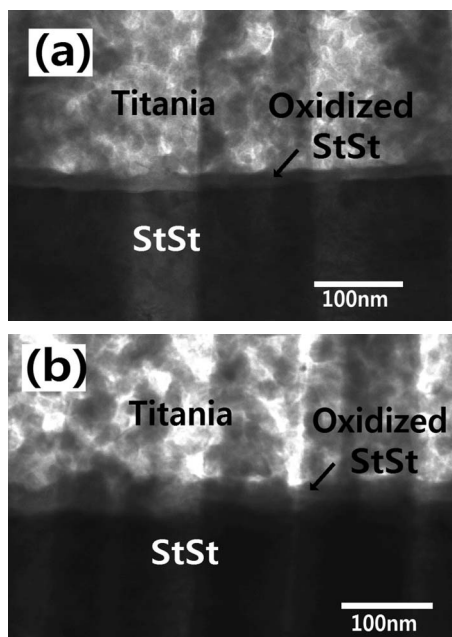


FIG. 2. Cross-sectional STEM images of StSt substrates (a) before and (b) after roughening in a sulfuric acid bath at 60 °C for 20 min.

roughened StSt substrates were identified with atomic force microscope (AFM) (Park Systems, XE-100) and image processing software (Image Metrology, SPIP™). J - V characteristics and electrochemical impedance spectra were measured using a Keithley 2400 source meter and an impedance analyzer (Solartron Analytical, 1255B) equipped with a potentiostat (Solartron Analytical, 1287), respectively. The electrochemical impedance spectra were measured over a frequency range of 10^{-1} – 10^6 Hz. A 1000 W xenon lamp (Oriol, 91193) served as the light source. The light intensity was adjusted with a reference Si cell (Fraunhofer Institute for Solar Energy System) to 1 sun light intensity of 100 mW/cm².

Sulfuric acid-based solutions are effective StSt pickling reagents.¹³ Additives, such as hydrated sodium thiosulfate and propargyl alcohol, endowed the StSt with pores and increased the surface area.⁹ Figure 2 shows cross-sectional STEM images of interface between StSt substrates and sintered TiO₂ particles. When the nontreated StSt was adopted as a substrate, the interface of the StSt and TiO₂ appeared flat as is shown in Fig. 2(a). However, when the roughened StSt was employed, some roughness was observed at this interface, which is shown in Fig. 2(b). To identify the actual surface area and to correlate the morphology to the photovoltaic performance, an AFM study on the StSt surfaces was also performed. Figure 3 shows the obtained AFM images. Compared with the projected area of 4.0 μm², the actual surface area of nontreated StSt substrate proved to be 4.063 μm²—a 1.6% increase. However, in the case of roughened StSt substrate, the actual surface area was measured to be 4.942 μm²—a 23.6% increase. In DSSCs with this rough-

TABLE I. Estimated resistance from electrochemical impedance spectra using an equivalent circuit model shown in Fig. 4(b).

Substrates	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)
DSSC with nontreated StSt substrate	7.5	17.1	18.7	31.0
DSSC with roughened StSt substrate	7.5	3.9	22.0	29.0

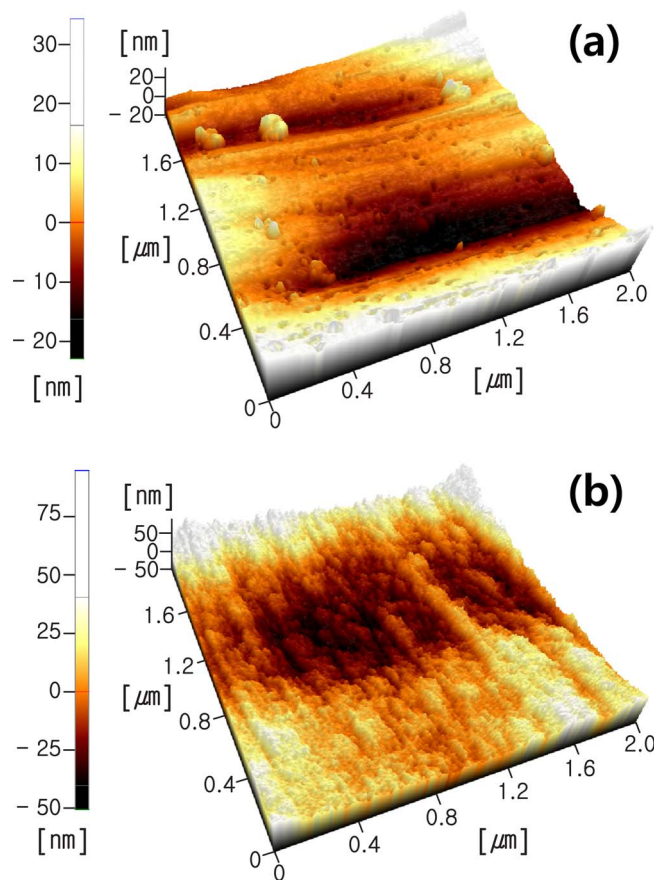


FIG. 3. (Color online) AFM images of StSt surface (a) before and (b) after roughening process.

ened substrate, the electrical contact area between StSt and TiO₂ particles was increased consequently.

Figure 4(a) shows the J - V characteristics of DSSCs with nontreated and roughened StSt substrates. The J_{sc} of the DSSC increased from 7.65 to 9.74 mA after roughening, which was a 27% increase. Light-to-electricity conversion efficiency also increased from 4.3% to 5.7%—a 33% increase. However, open circuit voltage (V_{oc}) and fill factor (FF) remained nearly constant. V_{oc} changed from 800 to 807 mV and FF varied from 70.3% to 72.4% after roughening. The increased surface area of StSt substrate enhanced J_{sc} and conversion efficiency with a negligible effect on V_{oc} and FF. To identify the cause of the increased J_{sc} and efficiency, electrochemical impedance spectra were also measured in the frequency range of 10^{-1} – 10^6 Hz. According to Hoshikawa *et al.*¹⁴ and Park *et al.*,¹⁵ typical electrochemical impedance spectra exhibit four semicircles in the Nyquist plot. Based on the model circuits for dye-sensitized solar cells, the semicircles are assigned as follows:

- (1) R_s : Ohmic resistance of the DSSC, especially the resistance of the base conductive layer.
- (2) Z_1 : impedance at the TiO₂/conductive layer interface.
- (3) Z_2 : impedance between TiO₂ particles plus the interface of the Pt /electrolyte solution.
- (4) Z_3 : impedance at the TiO₂/electrolyte solution and TiO₂/dye interface.
- (5) Z_4 : impedance due to diffusion of I^-/I_3^- redox electrolytes; negligible in this experiments due to very thin layer of electrolyte.

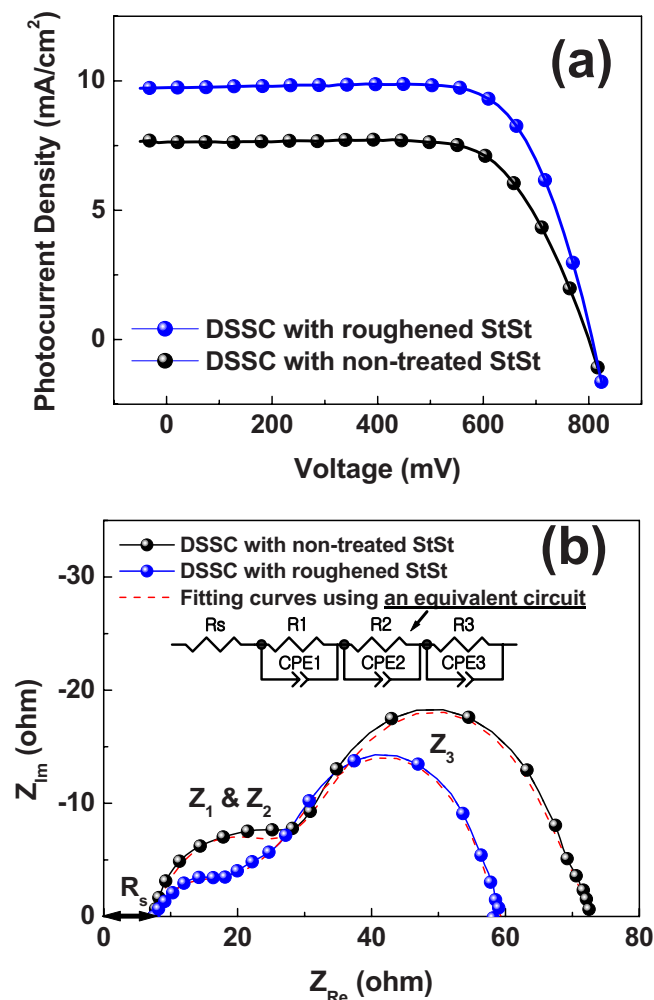


FIG. 4. (Color online) Under AM 1.5 irradiation (100 mW/cm²) with a xenon lamp. (a) J - V curves of DSSC with nontreated StSt substrates and roughened StSt substrates. (b) Electrochemical impedance spectra measured at the frequency range of 10^{-1} – 10^6 Hz and fitting curves using an equivalent circuit model including three CPEs.

Figure 4(b) and Table I show the electrochemical impedance spectra and estimated resistance of the DSSCs with nontreated and roughened StSt substrates. For the estimation of the resistance from electrochemical impedance spectra, the equivalent circuit model including three constant phase elements (CPEs) shown in inset of Fig. 4(b) was adopted. Even though there were small differences in R_2 and R_3 after roughening, R_1 was reduced from 17.1 to 3.9. The largely

reduced R_1 clearly comes from the reduced electrical resistance of the TiO₂/StSt interface because R_1 represents the electrical resistance at this interface. Considering the same electrical resistance between the TiO₂ particles and the interface with the Pt/electrolyte in DSSCs with both nontreated and roughened substrates, the small difference in R_2 after roughening is the expected result. The value of R_3 is closely related to the reverse electron transfer from TiO₂ to the electrolyte.¹⁴ In detail, as the number of electrons returning to the electrolyte increases, the arc of Z_3 increases. Therefore, the fact that R_3 remains unchanged after roughening clearly indicates that the increased electrical contact area does not cause an increase in the reverse electron transfer.

In conclusion, the solar cell performance of a StSt substrate DSSCs was significantly improved by this proposed method, which enhances electrical contact by roughening the substrates. The electrochemical impedance spectra measurements confirmed that both J_{sc} and efficiency were enhanced by a reduction in electrical resistance at the TiO₂/conductive layer interface.

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