Enhanced Photocurrent of Ru(II)-Dye Sensitized Solar Cells by Incorporation of Titanium Silicalite-2 in TiO_2 Film

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TiO_2 has been widely used as the photoanode material in a novel type solar cell for the last decade,[1] although several studies have explored other semiconducting metal oxides such as SnO_2,[2-3] ZnO,[4-7] Nb_2O_5,[8,9] CeO_2,[10] and $SrTiO_3$.[11] The novel solar cell is based on the sensitization of TiO_2 to visible and near infrared light by adsorbed dye molecules to the photoanode.

Efforts have been focused on improving the solar conversion efficiency of presently reported value of about 10%. The conversion efficiency decreases due to recombination losses of photoinjected electrons with oxidized dye molecules or redox couple at the surface of nanocrystalline TiO_2. Recent studies reveal that the addition of larger TiO_2 particles (up to 400 nm) to the nanocrystalline TiO_2 (15-20 nm diameter) colloidal solutions increases the scattering and the absorption in the red portion, which increases the photocurrent of the dye-sensitized solar cells.[12-15]

On the other hand, the photocatalytic activity toward the decomposition of phenol is improved with TiO_2-SiO_2 composite and titanium silicalite-2 (TS-2), a kind of zeolite, relative to TiO_2.[16-18] The enhancement is attributed to the presence of a Ti-O-Si phase at the TiO_2/SiO_2 interface, with the SiO_2 providing better adsorption sites in the vicinity of the TiO_2.

In the present study, we report the improvement of the photocurrent and conversion efficiency of dye-sensitized solar cells by homogeneously incorporating large TS-2 particles (~500 nm long) in the TiO_2 film electrodes without deteriorating the photocurrent stability.[19] TS-2 was prepared by a sol-gel method. The relations of TS-2 particles in the mixed film electrodes, morphology, and surface properties of the films to the photocurrent are discussed.

Experimental Section

TS-2 was crystallized by hydrolysis of tetraethylorthosilicate and tetrabutylorthotitanate, using tetrabutylammonium hydroxide as a template under static condition, followed by washing, drying and annealing at 500 °C for 5 h.[20] Anatase TiO_2 colloids were prepared from a sol-gel hydrolysis, autoclaving, and condensation of titanium isopropoxide in acetic acid solution as described elsewhere.[21]

TS-2 was added to the TiO_2 colloidal solution. To control the viscosity of the solution and prevent the cracking of the mixed oxide TiO_2/TS-2 thin film, 20 wt% polyethylene glycol (Fluka, MW 20,000) and 20 wt% polyethylene oxide (Aldrich, MW 100,000) with respect to the amount of TiO_2 present were added. The viscous solution was coated on SnO_2:F conducting glasses (Libbey-Owens-Ford Co., 8 ohm/sq 80% transmittance in the visible) by the simple doctor blade technique. The film was annealed at 500 °C for 30 min in air and its thickness was estimated to be about ~8 μm as measured by Tencor alpha-step profiler.

To sensitize the film, the TiO_2/TS-2 electrodes were immersed in ethanol containing 3×10^{-4} M Ru(II)L_2(NCS)$_2$: 2TBA (L = 2,2′-bipyridyl-4,4′-dicarboxylic acid, TBA = tetrabutylammonium, Solaronix, N719 dye) for 24 h at room temperature. Transparent Pt counter electrodes with small holes were prepared by spreading a drop of 5 mM hexachloroplatinic acid (Aldrich) in 2-propanol on a conducting glass, followed by heating at 450 °C for 30 min in air. The dye-coated TiO_2/TS-2 electrode and the Pt-coated conducting glass were sandwiched, using 30-μm thick Surlyn (Dupont 1702) under a pressure of 200 kPa/cm^2 and a temperature of about 100 °C. The redox electrolyte, consisted of 0.8 M 1,2-dimethyl-3-octyl-imidazolium iodide (homemade) and 40 mM iodine in 3-methoxypropionitrile (Aldrich), was introduced into the cell by capillary action. The active area of the cell was about ~0.25 cm^2.

A HP 8453A diode array spectrophotometer was used for measuring absorption spectra. X-ray diffraction (XRD) analysis was performed with Cu K_α (λ = 1.5406 Å) line using a Philips XPERT MPD. A Bomem, Hartman & Braun MB-series spectrometer utilizing KBr pellets was used to obtain FT-IR spectra. The surface morphology and thickness of the films were observed using a Hitachi S-4300 field emission scanning electron microscope (SEM).

Short-circuit photocurrent (J_{sc}) and open-circuit voltage (V_{oc}) were measured using a Keithley Model 2400 source measure unit. A 1000-W Xenon lamp (Oriel, 91193) served as the light source. The light was homogeneous up to 8×8 inch, and its intensity (or radiant power) was adjusted with a Si solar cell (Fraunhofer Institute for Solar Energy System; Mono-Si + KG filter; Certificate No. C-ISE269) for approximating AM-1.5 radiation.

Results and Discussion

TS-2 was characterized by XRD and IR. The XRD patterns confirmed the characteristic peaks of TS-2 at 2θ =

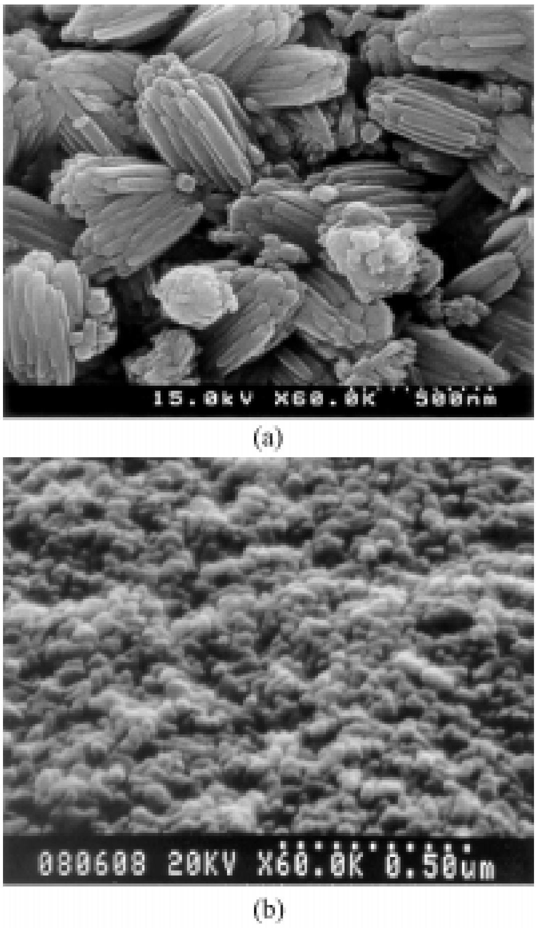

Figure 1. Plain-view SEM images of (a) TS-2 and (b) TiO_2 prepared by sol-gel methods.

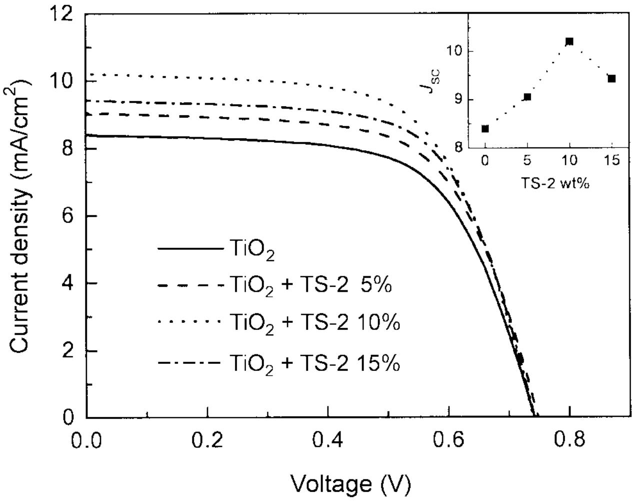

Figure 2. Dependence of *J-V* curves of dye-sensitized TiO_2/TS-2 solar cells on the wt% of TS-2.

Table 1. Dependence of the photovoltaic characteristics of the dye-sensitized solar cells on the wt% of TS-2 in the TiO_2/TS-2 film

Wt % TS-2	0	5	10	15
J_{sc} (mA/cm^2)	8.40	9.05	10.21	9.43
V_{oc} (V)	0.74	0.75	0.74	0.74
FF	0.64	0.64	0.64	0.66
Efficiency (%)	4.00	4.33	4.80	4.59

7.9, 8.8, 23.2, and 24.0 degrees. The IR spectrum of TS-2 presented a band peaking at 960 cm^{-1}. This band has been assigned to the stretching vibration of Si-O-Ti, suggesting that Ti atoms are effectively incorporated into the SiO_2 lattices.[22] A plane-view SEM image (Figure 1a) revealed that the average size of the cylindrical TS-2 clusters was 260 nm in diameter and 500 nm long, and the clusters were in the form of bundles consisting of large numbers of rods having an average dimension of 40 × 300 nm. We found that the Ru(II) dye molecules hardly adsorb to the TS-2 surface. This is presumably caused by the TS-2 surface being more hydrophobic than TiO_2, based on the observation that negligible absorption spectral change of the dye solution occurred in contact with TS-2 particles for 1 h. The TiO_2 particles prepared by the sol-gel method were confirmed to be anatase of about 20 nm in diameter on average by their XRD patterns and SEM images (Figure 1b).

Figure 2 shows the effect of the incorporation of TS-2 in the TiO_2 film on the *J-V* characteristics of dye-sensitized cells. In the presence of TS-2, J_{sc} increased regardless of the TS-2 wt%, with the V_{oc} being nearly a constant. The J_{sc} increased about 20% with incorporation of 10 wt% TS-2 in nanoparticle TiO_2. The results of the comparative study are quantitatively summarized in Table 1. Over the range of the TS-2 content, the V_{oc} and the fill factor (FF) remained nearly constant, and the overall conversion efficiency increased about 20% almost entirely due to an increase of J_{sc}.

An interesting observation is that the V_{oc} remained constant despite the increase in the J_{sc}. One explanation for the V_{oc} behavior may be related to the decreased density of surface states in the electrodes. The relatively larger TS-2 clusters effectively reduced the surface area of the TiO_2/TS-2 electrodes for dye adsorption, and consequently decreased the number of surface recombination centers, leading to an increase of V_{oc}.[23] On the other hand, a smaller dye adsorption implies that a smaller injection current from dye to the conduction band of the TiO_2/TS-2 electrodes. This leads to the V_{oc} decrease based on the relationship

$$n = n' \times \exp[qV_{oc}/kT],$$

where n and n' are the electron density in the conduction band under illumination and in the dark, respectively, assuming that the collection efficiency of the conduction band electrons remains the same. The combination of both the decreased density of surface states and the decreased adsorption of dye molecules apparently resulted in the invariance of the V_{oc}.

The J_{sc} increase regardless of wt% of TS-2 is most likely explained by the enhanced light scattering due to the larger TS-2 clusters in the TiO_2/TS-2 film electrode. Contrary to the V_{oc} behavior, the J_{sc} apparently showed a maximum at around 10 wt% TS-2. The increase in the photocurrent by the light scattering may be partially offset by the decreased

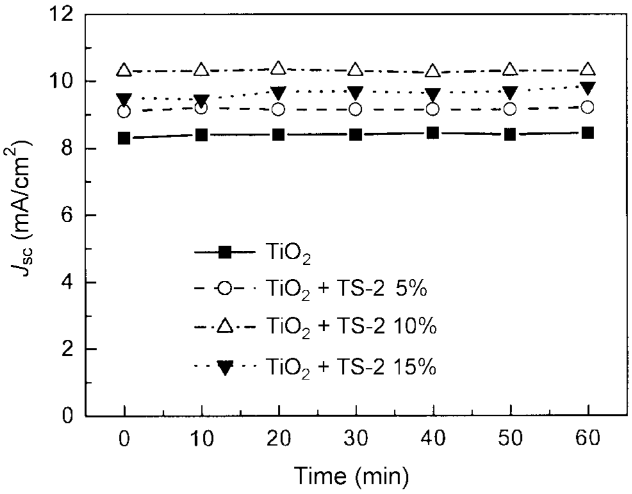

Figure 3. Comparison of time-dependent J_{sc} of dye-sensitized solar cells prepared with TiO_2 and TiO_2/TS-2 at several wt% of TS-2.

adsorption of dye molecules in the electrode surface. In addition, the incorporation of the TS-2 clusters reduced the connectivity between the contacting TiO_2 particles and/or the pathways of electrons to the tin oxide surface, compared with the electrode without TS-2.[24] As a result, the J_{sc} increase was further offset by the loss of inter-connectivity among the particles in the electrode film.

The stability of operation of sealed cells under prolonged light soaking was evaluated by measuring time-dependent current-voltage characteristics. The measurements showed that the *J-V* curves remained stable for 1 h with minimal fluctuation. To show the degree of stability, the time-dependent photocurrent is presented in Figure 3. Furthermore, almost identical *J-V* curves were obtained from the solar cells with TiO_2/TS-2 electrodes that had been left for 1 month in the laboratory, indicating that the solar cells should be suitable for long-term applications.

Further investigation of the effect of the variation of the particle size and cavity of TS-2 on the photocurrent-voltage enhancement appears worthwhile, since they are detrimental to the concentration of recombination centers and the extent of light scattering.

Conclusion

The effect of the incorporation of TS-2 into the TiO_2 film on photocurrent-voltage characteristics of dye-sensitized solar cells was investigated. We found that dye molecules hardly adsorbed to TS-2 prepared by a sol-gel method. J_{sc} of the dye-sensitized TiO_2/TS-2 solar cells were enhanced, whereas their V_{oc} remained the same. Analyses of SEM data indicated that the J_{sc} increase is explained predominantly by the enhanced light scattering by the larger TS-2 clusters. It is possible that the J_{sc} increase by the light scattering is partially offset by the reduced dye adsorption and loss of interconnectivity among particles in the electrode film. The offsetting effects of the reduced surface recombination sites and decreased number of injected electrons into the conduction band explains the V_{oc} invariance irrespective of wt% of TS-2.

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