Dependence of TiO$_2$ Film Thickness on Photocurrent-Voltage Characteristics of Dye-Sensitized Solar Cells

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To realize high energy conversion efficiency, mesoporous TiO$_2$ nanocrystalline electrodes of a large surface area have been investigated extensively as a key material for dye-sensitized solar cells (DSSC). One of the strategies to improve conversion efficiencies is to increase light harvesting efficiency by increasing the amount of dye in the electrodes using thick TiO$_2$ films. A thick nanocrystalline film may, however, increase charge recombination between injected electrons and electroactive agents arising from low drift mobility of electrons in the film ($10^{-4}-10^{-5}$cm/Vs), which limits the conversion efficiency. Furthermore, surface states increase with increasing film thickness, offsetting the injection efficiency achieved by the large surface area.

Though it would be interesting to evaluate the TiO$_2$ film thickness for optimum conversion efficiency, systematic studies on thickness dependence of photocurrent-voltage are limited. Hara et al. reported that short-circuit photocurrent density ($J_{sc}$) increased up to about 16 µm-thick film for a mercuochrome-sensitized TiO$_2$ solar cell due to an increased amount of dye, but corresponding energy conversion efficiencies ($\eta$) and fill factors (FF) were not examined. Park and coauthors correlated $J_{sc}$ increase of a dye, cis-dithiocyanate-$N,N'$-bis(4-carboxylate-4-tetramethylammoniumcarboxylate-2,2'-bipyridine)-Ru(II) (N719), sensitized rutile TiO$_2$ solar cell with two different film thickness, 6.6 and 11.5 µm. Recently, Yanagida and collaborators reported that light-to-electricity conversion efficiencies ($\eta$) decreased in films beyond about 12-µm thickness that were fabricated by repetitive coating followed by combustting at 500 ºC for 30 min, but thickness-dependent $J_{sc}$ and open-circuit voltage ($V_{oc}$) were not analyzed. The most commonly utilized TiO$_2$ thickness in the various studies has been around 11 µm, although it can be thicker than that because the diffusion length of injected electrons in DSSC is expected to be longer than 20 µm, according to a recent report.

In this paper, the effect of increasing thickness of nanocrystalline anatase TiO$_2$ film of DSSC on photocurrent-voltage ($J$-$V$) characteristics and incident-photon-to-current conversion efficiency (IPCE) was studied. The films ranging from 6 to 27 µm in thickness, were fabricated by repetitive coating with TiO$_2$ colloids made by a sol-gel hydrolysis and characterized by SEM and electrochemical impedance spectroscopy. Optimum conditions are reported regarding the film thickness.

Experimental Section

Fabrication of the cells and measurement of $J$-$V$ curves have been described in detail elsewhere. The TiO$_2$ film thickness increased by repeated coating and annealing. The films were immersed in 3 × 10$^{-4}$ M N719 dye (Solaronix) ethanol solution for 36 h. The redox electrolyte composed of 0.80 M 1,2-dimethyl-3-hexyl-imidazolium iodide (homemade) and 40 mM iodine in 3-methoxypropionitrile (Aldrich). $J$-$V$ curves were measured with a Keithley 2400 source meter. A 1000 W Xenon lamp (Oriel, 9113) was utilized at 100 mW/cm$^2$. IPCE was measured at the low chopping speed of 5 Hz using a system by PV Measurement, Inc., equipped with a halogen source and a broad band bias light for approximating one sun intensity. The IPCE system was calibrated using a silicon reference photodiode (GS87, PV Measurement, Inc.). The surface morphology and thickness of the films was obtained with a Philips XL30SFEG field emission SEM. Nyquist plots were recorded over a frequency range from 10$^{-2}$ to 10$^{4}$ Hz with an AC amplitude of 5 mV using an EG&G PARC M273A potentiostat with an M1025 frequency-response detector.

Results and Discussion

Figure 1 shows FE-SEM images of the top and cross-sectional views of a TiO$_2$ film on SnO$_2$: F prepared by three repetitive coatings. The film is about 22 µm thick and consists of TiO$_2$ particles of about 25 nm in diameter. No cracks on the surface and no gaps between the coatings are observed, indicating excellent inter-particle connectivity and inter-layer attachment. Four repetitive coatings can produce
a smooth film of 27 µm thickness without cracks and gaps. However, above 11 µm, it proved difficult to obtain crack-free thick films in a single coating. The dependence of $J-V$ curves of DSSC on the film thickness is shown in Figure 2a and their characteristics are plotted in Figures 2b and 2c. It is noted that $J_{sc}$ increases from 6.8 to 13.3 mA/cm$^2$, a 96% increase, with increasing film thickness from 6 to 22 µm. Over the same thickness range, $V_{oc}$ and FF decrease from 0.74 to 0.68 V and from 0.64 to 0.57, respectively. With films thicker than 22 µm, however, the $J_{sc}$ decreases by about 6% compared with the value at 22 µm, while the $V_{oc}$ and FF values are essentially saturated. As a result of these variations, the $\eta$ increases linearly from 3.2% to about 5.2%, a 62% increase, with a change from 6 to 15 µm, but the $\eta$ remained nearly the same above 15 µm. The variations of the $J_{sc}$ and $\eta$ are similar, indicating that the $\eta$ increase is largely due to the $J_{sc}$ increase.

The $J_{sc}$ enhancement is a result of unfailing improvement of IPCE as shown in Figure 3a. The maximum IPCE occurs at the absorption maximum of the dye,$^8$ 540 nm, with the highest IPCE being 0.74 for 22 µm. Analysis of the IPCE (Figure 3b) indicates that the relative enhancement at 640 nm with an increase in film thickness is larger than those at 410 and 540 nm. At 640 nm, where the dye absorbs weakly and thus depth of penetration of light in the film is large, the IPCE value increases linearly with film thickness at least up to 19 µm, implying uniform charge generation throughout the film.$^7$ At 540 nm, on the other hand, the IPCE values are saturated above 12 µm, indicating that the light absorption is not homogeneous due to the high molar absorption coefficient of the dye. At 410 nm, the values fluctuate, but essentially remains the same regardless of film thickness, since a change in thickness has no effect upon the photo process. The results suggest that a dye having larger absorption coefficients in the long wavelength region would be more beneficial in obtaining higher photocurrents for cells with thick films.

Undoubtedly, the $J_{sc}$ increase is predominantly related to the increase in injection current from excited dyes to the conduction band of TiO$_2$, arising from the increased surface area. The $J_{sc}$ increase can also be related to the $V_{oc}$ decrease observed in Figure 2. The $V_{oc}$ decrease implies that the conduction band edge of TiO$_2$ shifts positively, assuming that both the energy levels of the dye and the standard reduction potential of I$_3^-$/I$^-$ do not vary irrespective of film thickness. The positive shift with respect to dye energy levels narrows the energy difference between TiO$_2$ and dye and thus allows low lying excited states of the adsorbed dye to inject electrons, resulting in enhanced photocurrent.$^7$ For films thicker than 22 µm, however, the $J_{sc}$ shows a slight decrease. This implies that the $J_{sc}$ enhancement mentioned above is more than offset by the increased loss of the conduction band electrons in TiO$_2$ and/or SnO$_2$ through their back electron transfer to I$_3^-$ ions, I$_3^-$ + 2 e$^-$ = 3 I$^-$, the regeneration of oxidized dyes by the conduction band electrons being assumed negligible.$^9$

The $V_{oc}$ decrease in Figure 2 can be related to the enhancement of the above-mentioned back electron transfer.$^{10}$ Increasing the surface area of the electrode with increasing the film thickness mostly likely leads to an increase in the number of trapping surface states,$^{2,11}$ through which the back electron transfer would be facilitated, resulting in a lowering
of the $V_{oc}$. This result is consistent with the relationship that $V_{oc} = (kT/e)\ln(I_{inj}/R)$, where $I_{inj}$ is the charge flux from the sensitized injection and $R$ is the rate of the back electron transfer. Finally, the FF of the cells shows about 10% decline as the thickness increases from 6 to 22 µm (Figure 2c), which is attributable to the increase of resistance in the cell. Figure 4 compares Nyquist plots of the cells with film thickness. Each cell may be visualized as consisting of a multiplayer structure to which an RC circuit in series can be fitted. Analysis of the data by using ZView software reveals that the TiO$_2$ film resistance increases with increasing its thickness, with other resistances being essentially unaltered, providing supporting evidence for the FF decline.

**Conclusion**

The dependence of increasing thickness of nanocrystalline anatase TiO$_2$ film of DSSC on $J$-$V$ characteristics and IPCE was studied. The films were formed by repetitive coating of anatase TiO$_2$ colloid and characterized by FE-SEM and SEM. With increasing film thickness from 6 to 22 µm, the $J_{sc}$ increases by 96%, but $V_{oc}$ and FF decrease monotonically. The $\eta$ of the cell increases linearly with thickness increases up to 15 µm, due mainly to the surface area increase. The $V_{oc}$ decrease is related to the increase of back electron transfer between I$_3^-$ ions and conduction band electrons in the TiO$_2$ electrode. It is suggested that optimum $\eta$ can be attained with around 15 µm thickness for N719 dye.

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**References**


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**Figure 4.** Nyquist plots of DSSC against TiO$_2$ film thickness from 10 kHz to 10 mHz with an AC amplitude of 5.0 mV.