Effect of Cations on the Open-Circuit Photovoltage and the Charge-Injection Efficiency of Dye-Sensitized Nanocrystalline Rutile TiO₂ Films

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Dye-sensitized nanocrystalline rutile TiO₂ solar cells were prepared, and the influence of Li⁺ and 1,2-dimethyl-3-hexyl imidazolium ions in the electrolyte on the photovoltaic properties was compared. The electrolyte containing Li⁺ ions produced a lower open-circuit photovoltage than the electrolyte with 1,2-dimethyl-3-hexyl imidazolium ions, suggesting that the adsorption of Li⁺ ions to the rutile TiO₂ surface causes a shift in the band edges toward more positive potentials. At the same time, both the short-circuit photocurrent and the maximum value of the incident-photon-current conversion efficiency (IPCE) of the electrolyte containing Li⁺ ions were relatively higher. Data analysis suggests that presence of adsorbed Li⁺ ions improves via the phenomenon of band-edge movement the charge-injection efficiency by altering both the energy and number of excited state levels of the dye that participate in electron injection.

Introduction

A new type of solar cell technology has emerged in the past ten years.[1] It is based on the sensitization of nanocrystalline titanium oxide thin films, a material used as a pigment in house paints, to visible and near infrared light. Interest in dye-sensitized solar cells stems from their high solar conversion efficiency (> 10%) and potential low cost.

Figure 1 illustrates the basic underlying phenomenon that occurs in dye-sensitized solar cells.[2] When dye molecules (e.g., RuL₂(NCS)₂, where L is 2,2'-bipyridyl-4,4'-dicarboxylic acid) absorb visible photons, electrons in the t_{2g} orbital of Ru(II) are injected, *via* the π^* orbital of the carboxylated bipyridyl ligand, into the conduction band of *n*-type semi-conducting particles. The photoinjected electrons travel through the mesoporous network of the nanostructure and are collected at the transparent conducting layer, where they pass into the external circuit. The electrons re-enter the cell at the platinium counter electrode, where they reduce, in a net process, I_3^- to I^-. The I^- ions diffuse into the pores of the TiO₂ network and reduce the oxidized dye molecules back to their original state. Concomitantly, the I^- is oxidized to I_3^-, completing the redox cycle.

Selecting semiconducting oxide materials with the proper characteristics and developing the methodology for synthesizing the materials are of importance considerations in this emerging solar cell technology. Materials that have been studied for this purpose include TiO₂,[3] SnO₂,[4] ZnO,[5] and Nb₂O₅.[6] Of these, nanocrystalline anatase TiO₂ has been found to exhibit the most favorable photovoltaic properties. Until recently,[7] little attention has been paid to rutile TiO₂ despite the fact that it is thermodynamically the more stable form of TiO₂. The lack of interest in rutile TiO₂ probably arose from the expectation that solar cells based on it would have a lower photovoltage than that based on anatase TiO₂ because of the more positive conduction band potential of anatase as measured in the solid state. However, recently we showed[7] that the photovoltages of anatase and rutile TiO₂ based photochemical solar cells were essentially the same. This surprising discovery suggests that additional research on dye-sensitized rutile TiO₂ based solar cells is warranted.

In this paper, we report on the effect of cation species in the electrolyte on the photovoltaic properties of the dye-sensitized nanostructured rutile TiO₂ films.
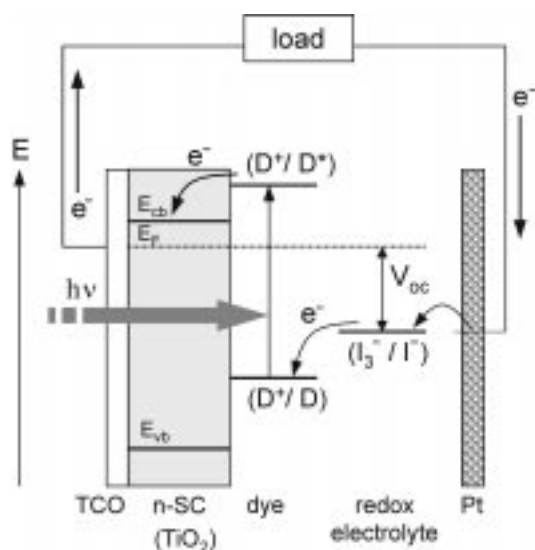

Figure 1. Schematic of the dye-sensitized nanocrystalline semiconductor solar cell showing the electron transfer processes that occur upon the absorption of light by the dye.

Experimental

Rutile TiO₂ particles formed from the hydrolysis of TiCl₄ were deposited on the surface of transparent SnO₂ conduct-

ing glass (Libbey-Owens-Ford Co., TEC-10 (10 ohm/sq), 75% transmittance in the visible) by two distinct methods and then heated in air for 1 h at 500 ℃. The first method[7a] involved the direct (*in situ*) deposit of rutile TiO_2 films onto the conducting glass. In the second method,[7b] the TiO_2 particles were prepared as a slurry and then deposited onto the glass substrate with a doctor blade. The slurry was prepared as follows[7b]: the TiO_2 particles were formed as a precipitate from the hydrolysis of $TiCl_4$ (Aldrich); $TiCl_4$ was added dropwise to chilled water (*ca.* 4 ℃) to produce a concentration of 2 M TiO_2. Subsequently, the solution was diluted to 0.5 M TiO_2 and set aside in a closed, air-filled vessel for 5 days. The liquid was then removed with a rotary evaporator. The resulting white precipitate was subjected to repeated purification by adding and removing water and then repeating the steps with methanol. The dried precipitate was collected and redispersed in distilled water to produce a solution containing 15 wt % TiO_2. With respect to the amount of TiO_2 present, 20 wt % poly ethylene glycol (Aldrich, average MW 2,000) and 15 wt % poly ethylene oxide (Polysciences, average MW 100,000) were added to the TiO_2 colloid solution, which was then stirred for 2 days with a magnetic stirring bar, to yield the slurry.

X-ray diffraction measurement was performed with Cu Kα radiation (λ = 1.5406 Å) using SCINTAG DMS-2000. Raman spectra were taken in the backscattering geometry using the 514.5 nm line of an Ar ion laser. The thickness of the transparent rutile films was measured with a Tencor Alpha-step profiler. The morphology of TiO_2 films was investigated by field emission scanning electron microscopy (SEM; JEOL Model 6320F).

For photosensitization studies, the TiO_2 electrodes were immersed in acetonitrile/*t*-butanol (50 : 50 v/v%) containing 3×10^{-4} M $Ru(LL')(NCS)_2$ (where L = 2,2-bypyridyl-4,4'-dicarboxylic acid, and L' = 2,2'-bipyridyl-4,4'-ditetrabutyl-ammoniumcarboxylate) for 24 h at room temperature. The dye-covered electrodes were then rinsed with the acetonitrile/*t*-butanol mixture and dried under a N_2 stream. Pt counter electrodes with a mirror finish were prepared by electron beam deposition of a 60-nm layer of Pt on top of a 40-nm layer of Ti on a glass plate. The Pt electrode was placed over the dye-coated TiO_2 electrode and the edges of the cell were sealed with 0.5-mm wide stripes of 25-μm thick Surlyn (Dupont, grade 1702). Sealing was accomplished by pressing the two electrodes together at a pressure of 900 psi and a temperature of about 120 ℃. The redox electrolyte was introduced into the cell through one of two small holes drilled in the counter electrode. Two different electrolytes were used in this experiment. One electrolyte consisted of 0.8 M 1,2-dimethyl-3-hexyl imidazolium iodide (C6DMI) and 40 mM I_2 in acetonitrile and the other contained 0.8 M LiI and 40 mM I_2 in acetonitrile. The holes were then covered and sealed with small squares of Surlyn 1702 and microscope objective glass. The resulting cell had an active area of about 0.3 cm^2.

Photocurrent–voltage *J–V* measurements were performed using a Keithley Model 236 source measure unit. A 1000-W

sulfur lamp (Fusion Lighting Inc.) served as a light source, and its light intensity (or radiant power) was adjusted with a Si solar cell equipped with KG-5 filter (Schott) for approximating AM-1.5 radiation. The light source for the incident photon-to-current conversion efficiency IPCE measurements was a 150-W Quartz halogen lamp equipped with a Photon Technology International Model 1492 monochromator. The intensity was measured with a UDT Instrument Model S370 optometer and a UDT Instrument Model 221 calibrated photodiode. Absorption and reflectance spectra were measured with an HP 8450A diode array spectrophotometer and a Cary 5E UV-Vis-NIR spectrophotometer, respectively.

Results and Discussion

Figure 2 shows the X-ray diffraction patterns and Raman spectra for annealed TiO_2 films that were deposited either directly or from a slurry onto the surface of the conducting glass (Experimental section). In both cases, the phase of the films was confirmed to be pure rutile TiO_2. SEM measurements (Figure 3(a)) indicate that the slurry-based TiO_2 film is made up of non-oriented, homogeneously distributed particles having a dimension of approximately 20×80 nm. In contrast, the SEM micrograph (Figure 3(b)) of the directly deposited TiO_2 film consists of cluster-like spherical bundles with an average dimension of about 500 nm. The individual needles appear to radiate out from the bundles.
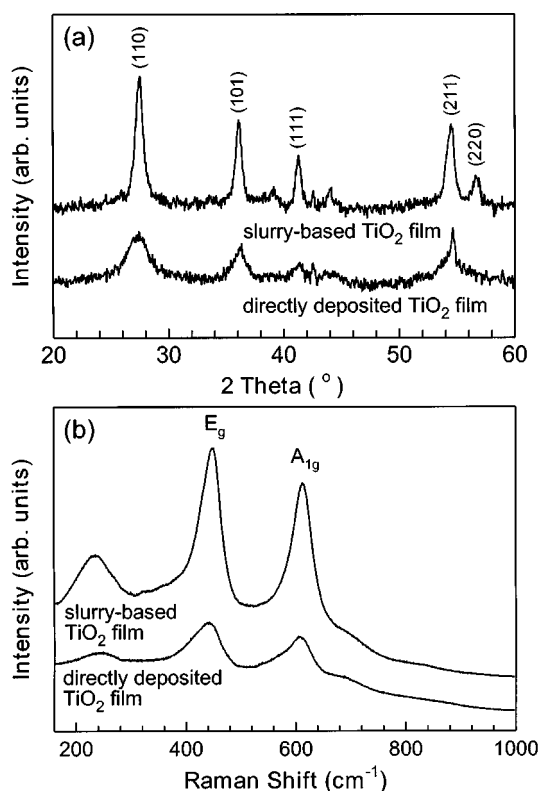

Figure 2. (a) X-ray diffraction (XRD) patterns and (b) Raman spectra of TiO_2 rutile films deposited directly and from a slurry onto the surface of conducting glass.
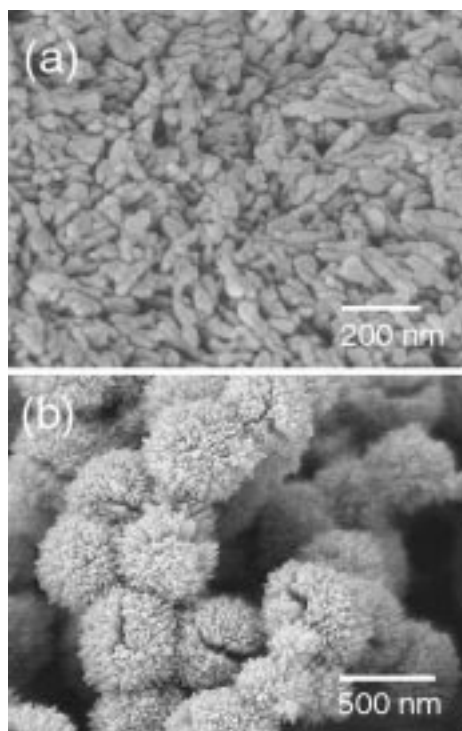
Figure 3. Scanning electron microscope micrographs of TiO₂ rutile films deposited onto the surface of conducting glass (a) from a slurry and (b) directly.
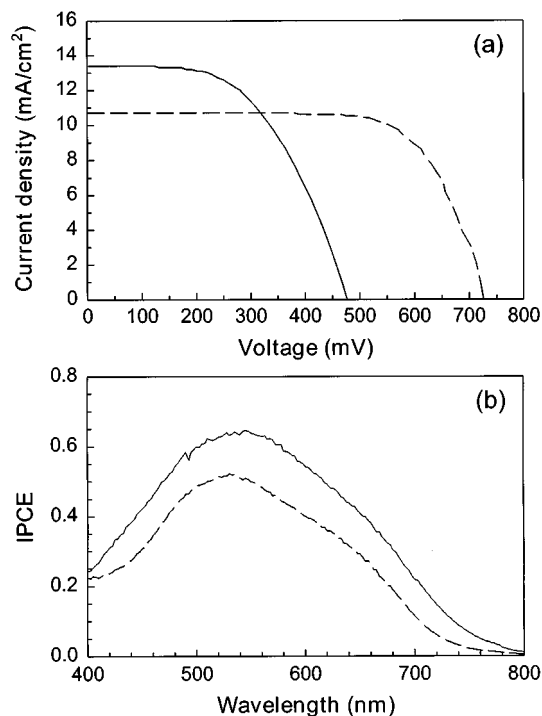

Figure 4. Effect of cation in the electrolyte on (a) the current-voltage characteristics and (b) short-circuit IPCE of dye-sensitized, slurry-based TiO₂ cells containing 0.8 M LiI and 40 mM I₂ (solid line) and 0.8 M 1,2-dimethyl-3-hexyl imidazolium iodide and I₂ (dashed line). The thickness of the rutile TiO₂ film was 11.5 μm, and the light intensity was about one sun.

Figure 4(a) compares the influence of the Li⁺ and the 1,2-dimethyl-3-hexyl imidazolium (C6DM⁺) ions in the electrolyte on the *J–V* characteristics of the dye-sensitized, slurry-based TiO₂ solar cell at 1 sun light intensity. The short-circuit photocurrent J_{sc} of the Li⁺ ions-containing electrolyte (13.4 mA/cm²) is about 25% higher than that observed for the C6DM⁺ electrolyte (10.7 mA/cm²). On the other hand, the open-circuit photovoltage V_{oc} of the Li⁺ electrolyte (470 mV) is 260 mV lower than that measured for the C6DM⁺ electrolyte (730 mV). A similar cation effect was observed in the case of dye-sensitized, directly-deposited rutile-based TiO₂ solar cells; the Li⁺ electrolyte produced a higher J_{sc} and a lower V_{oc} than the C6DM⁺ electrolyte. Consistent with the relative J_{sc} values, the maximum value of the incident monochromatic photon-to-current conversion efficiency (IPCE) of the Li⁺ containing electrolyte is approximately 25% higher than that of the electrolyte with C6DM⁺ (Figure 4(b)). Moreover, the maximum IPCE value of the cell with the Li⁺ ion based electrolyte (545 nm) is about 15-nm red-shifted with respect to that of the C6DM⁺ ion based electrolyte (530 nm).

The dependence of the photovoltage on the cation of the electrolyte suggests the possibility that the cation alters the energetics at the TiO₂/electrolyte interface. A similar effect has been observed for anatase TiO₂-based solar cells, where it was shown that small cations, such as Li⁺, produced a smaller photovoltage than larger cations, such as those of the alkali metal ions[8] or tetrabutylammonium ion.[9] In sufficient amount, cation adsorption can change the potential drop across the Helmholtz layer, causing the band edges to shift to

more positive potentials. Considering the small size of the Li⁺ ion compared with that of 1,2-dimethyl-3-hexyl imidazolium ion, it is reasonable to anticipate that the amount of Li⁺ ions adsorbed to the TiO₂ surface will exceed that of C6DM⁺ ions, producing a more significant shift of the band edges and, consequently, a more substantial drop of V_{oc}. In the case of anatase TiO₂, adsorption of Li⁺ ions is known to change the conduction-band edge position.[10]

Cation adsorption can also alter the photocurrent (Figure 4a) and the IPCE (Figure 4b) by affecting the light-harvesting efficiency or the electron-injection efficiency of the dye. In principle, electronic interactions between the cation and the dye can alter the light-harvesting efficiency of the dye. To explore this possibility, we compared the effect of the Li⁺ electrolyte and the C6DM⁺ electrolyte on the absorption spectrum of the adsorbed dye on TiO₂ particles suspended in an acetonitrile solution. The Li⁺ ions were found to cause less than a 2 nm red shift of the absorption maximum of the dye with respect to that observed for the C6DM⁺ electrolyte under otherwise identical condition. The relatively small spectral shift suggests that both Li⁺ and C6DM⁺ ions have essentially the same effect on the energy levels of the adsorbed dye. In turn, this implies that the difference in the IPCE response (Figure 4b) is not due to electronic interactions of the cation with the dye. These results suggest that cation adsorption to the TiO₂ surface affects the photocurrent (Figure 4a) and the IPCE (Figure 4b) by altering the electron-injection efficiency of the dye. The electron-injection

efficiency of the dye can be changed by band-edge movement with respect to energy level of the excited state of the dye from which the electron is injected. As discussed above in connection with V_{oc} (Figure 4a), one expects the adsorption of Li^+ ions to shift the conduction band edge of TiO_2 toward positive potentials by 260 mV with respect to the position of the conduction band edge in the presence of the $C6DM^+$ ions. Assuming that the energy level of the dye molecules either do not shift with the band edges or shift less than the 260 mV, one expects that increasing the difference in energy between the excited state of the dye and the conduction band edge position may affect the energy and number of excited state levels of the dye involved in electron injection. In particular, one can understand both the increase in the magnitude and the 15-nm red shift of the IPCE resulting from the presence of Li^+ ions (Figure 4b) in terms of the participation of low lying excited states of the adsorbed dye in the electron injection process. In other words, the positive shift of the conduction band edge of TiO_2 with respect to the excited state levels of the dye allows low lying excited states of the adsorbed dye to inject electrons into the conduction band of TiO_2 and therefore to contribute to the photocurrent and the IPCE.

Conclusions

The influence of Li^+ and 1,2-dimethyl-3-hexyl imidazolium ions in the electrolyte on the photovoltaic performance of dye-sensitized nanocrystalline rutile TiO_2 solar cells was investigated. The electrolyte containing Li^+ ions produced a lower open-circuit photovoltage and a higher short-circuit photocurrent than the electrolyte with 1,2-dimethyl-3-hexyl imidazolium ions. The adsorption of Li^+ ions to the nanocrystalline film is shown to have a significant effect on the band-edge position, which, in turn affects the photovoltage, photocurrent, and IPCE. The influence of cations on the photocurrent and the IPCE is attributed to the effect of band-edge movement on both the energy and number of excited state levels of the dye that participate in the electron-injection process. This study indicates that in the development of

high efficiency dye-sensitized solar cells, the nature of the cation must be a major consideration when optimizing the composition of the electrolyte.

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