Solid-state dye-sensitized solar cells of the type TiO$_2$/dye/CuSCN have been made with thin Al$_2$O$_3$ barriers between the TiO$_2$ and the dye. The Al$_2$O$_3$-treated cells show improved voltages and fill factors but lower short-circuit currents. Transient photovoltage and photocurrent measurements have been used to find the pseudo-first-order recombination rate constant ($k_{pfo}$) and capacitance as a function of potential. Results show that $k_{pfo}$ is dependent on $V_{oc}$ with the same form as in TiO$_2$/dye/electrolyte cells. The added Al$_2$O$_3$ layer acts as a "tunnel barrier", reducing the $k_{pfo}$ and thus increasing $V_{oc}$. The decrease in $k_{pfo}$ also results in an increased fill factor. Capacitance vs voltage plots show the same curvature ($\sim$150 mV/decade) as found in TiO$_2$/dye/electrolyte cells. The application of one Al$_2$O$_3$ layer does not cause a significant shift in the shape or position of the capacitance curve, indicating that changes in band offset play a lesser role in the observed $V_{oc}$ increase. Cells made with P25 TiO$_2$ have, on average, 2.5 times slower recombination rate constants (longer lifetimes) than those made with colloidal TiO$_2$. The cells with P25 also show 2.3 times higher trap density (DOS), which results in little change in the $V_{oc}$ between the two types of TiO$_2$. It is further noted that the recombination current in these cells cannot be calculated from the total charge times the first order rate constant.
applied to solid-state dye-sensitized cells using Cul as the hole conductor. In several publications, insulator-coated TiO\textsubscript{2} films have given an increase in efficiency relative to that of control cells. However, to the best of our knowledge, it has not yet been possible to surpass the best efficiencies reached by cells without insulator layers in either the electrolyte or solid-state case. It is clear that a more detailed understanding of the function of the coating is required to optimize performance.

There are three ways a surface coating can cause an increase in the $V_{oc}$ of a dye-sensitized cell. In case 1, the insulating nature of the coating material means that photoinjected electrons in the TiO\textsubscript{2} can only recombine with a positive charge in the electrolyte or hole conductor by tunneling through the insulator. This is the “tunnel barrier” effect. The barrier causes a decrease in the “per electron” recombination rate constant for a given electron population. If, at 1 sun illumination, the flux of injected electrons from the dye is unchanged, then the electron concentration at $V_{oc}$ will be higher for the cell with the coating. A larger electron concentration in the TiO\textsubscript{2} means a more negative Fermi level and thus a larger $V_{oc}$.

In case 2, the “surface dipole” effect, the surface coating changes the distribution of charge across the TiO\textsubscript{2}/hole conductor interface relative to the uncoated case. If the coating results in more negative charge closer to the TiO\textsubscript{2} surface, and more positive charge closer to the CuSCN, then the resulting electric field will increase the band offset between the two materials. This will not directly cause a decrease in the recombination rate constant at $V_{oc}$, so there will be no change in the concentration of electrons in the TiO\textsubscript{2} at $V_{oc}$. The increased band offset is the source of the increase in $V_{oc}$. In case 3, the coating removes, or moves out of the gap, a significant fraction of the surface states at potentials near $V_{oc}$, so that the total density of states at these potentials is reduced. This might directly reduce the recombination rate constant if recombination occurred through surface states. There are indications that recombination is not limited by surface-state density, but rather by transport; thus, we can expect no change in the recombination rate constant for this case as well.

To improve the understanding of how the mix of these three effects results in the observed increase in voltage and fill factor, we have fabricated more than 40 cells with varying TiO\textsubscript{2} sources and thicknesses and number of Al\textsubscript{2}O\textsubscript{3} layers. For 20 of these cells, we have used transient photovoltage measurements to determine the recombination rate constants as well as the density of states distribution (DOS). In this paper we present an initial analysis of these results.

**Methods**

Transparent conductive SnO\textsubscript{2} glass, “LOF Tec 8”, nominal resistance 8 $\Omega$\textpercm, was purchased from Pilkington. A thin solid film of TiO\textsubscript{2} (30–100 nm) was deposited on the SnO\textsubscript{2} by spray pyrolysis. Following this, 3–5 $\mu$m mesoporous layers of TiO\textsubscript{2} were deposited by one of two methods. For films of Degussa P25, we used an approach based on that of Lindström et al.\textsuperscript{17} further described in ref 26. For films of colloidal TiO\textsubscript{2}, colloidal anatase particles of mean diameter 30 nm were fabricated by hydrolysis of titanium isopropoxide (Aldrich) using a modification of standard recipes.\textsuperscript{2,38,39} In this case, the autoclaving temperature was 230 °C for 12 h. The particles were dried at 60 °C and resuspended in a mixture of 2-propanol and terpinol. The viscosity was modified by the addition of methylcellulose.

The films were doctor bladed onto the substrates with the spray pyrolysis underlayer. All TiO\textsubscript{2} layers were heated for 1 h at 450 °C in air. Thin Al\textsubscript{2}O\textsubscript{3} layers were deposited into the mesoporous TiO\textsubscript{2} films following ref 11. Briefly, a 0.15 M solution of aluminum tri-tert-butoxide (Aldrich) was made in dry 2-propanol. The solution was made in a glovebox, but all further steps were performed in air. Prior to immersion in the coating solution, the TiO\textsubscript{2} films were rinsed in distilled water and then dried at 60 °C for 30 min. After immersion, the solution plus films was placed in a closed vessel and held at 60 °C for 30 min. The coated TiO\textsubscript{2} films were removed from the coating solution and quickly and thoroughly rinsed in either water or 2-propanol. We found that, under some conditions, water rinse tends to leave traces of Al\textsubscript{2}O\textsubscript{3} on the outer surface of the TiO\textsubscript{2} film as well as on the exposed SnO\textsubscript{2} and the back of the glass support. The Al\textsubscript{2}O\textsubscript{3} coating solution was stored in closed vessels, and air exposure was minimized. We found that, in humid conditions, there is a reaction of air humidity with the coating solution, leading to thicker and inhomogeneous coatings that can block the pores in the TiO\textsubscript{2}.

After Al\textsubscript{2}O\textsubscript{3} coating, the films were heated again to 450 °C, allowed to cool to ~100 °C in air, and then placed in the ethanolic dye solution. The dye, RuL\textsubscript{2}(SCN)\textsubscript{2}, where C = 4,4’-dicarboxy-2,2’-bipyridine, known as “N3”, was purchased from Solaronix under the name Ruthenium 535. In this form, the dye is intended to have four protons as counterions. After dyeing overnight, the films were removed from the dye solution and then dried by pressing the TiO\textsubscript{2} side down on absorbent paper. Directly after drying, the samples were placed onto the 80 °C hotplate used for CuSCN deposition.

CuSCN was deposited from solution into the pores of the TiO\textsubscript{2} films with slight modifications of the previously described technique. Briefly, CuSCN (Aldrich) was dissolved to saturation (~2 g/L) in dipropylsulfide (Merck or ACROS). In most cases, the CuSCN solutions were doped with 1–10 mol % Cu(II)(SCN)\textsubscript{2} several days prior to use. Cu(II)(SCN)\textsubscript{2} was made by precipitation from water solution of LiSCN and CuClO\textsubscript{3} followed by filtration, water rinse, and drying in vacuum. Before deposition, the solutions were diluted 20% by additional dipropylsulfide. The doped and diluted solutions provided the highest and most reproducible efficiencies. The CuSCN solution was spread onto the TiO\textsubscript{2}/dye film at 80 °C in air by using a special apparatus. The resulting composite cells were treated under low vacuum (~5 × 10^{-2} millibar) for 2 h and then stored under nitrogen for several days before measurement. An improvement in performance was noted during storage in nitrogen, presumably because of the continued slow outgassing of the solvent from the CuSCN layer. Alternatively, after deposition, the cells were heated for an additional 10–15 min at 80 °C in air and then stored in flowing nitrogen at 60 °C for 1 h. This treatment also seemed to remove the last vestiges of solvent.

Electrical contact was made to the CuSCN using a cell holder that presses a one-cm\textsuperscript{2} pad of fine graphite powder (Aldrich) onto the surface. Evaporated gold contacts were found to give identical results. Potentials reported herein refer to the TiO\textsubscript{2} contact; thus, negative potentials indicate more electron-rich TiO\textsubscript{2}.

Photocurrent vs voltage measurements were made using illumination from a Steuernagel solar simulator that contains a metal–halogen arc lamp. Photocurrent and photovoltage transients were taken using a pump pulse generated by a ring of red LEDs controlled by a fast solid-state switch. Pulse times of 100 µs were used, with a rise and fall time of ≤2 µs. The pulse
was incident on the SnO$_2$ side of the cell. The pulse intensity was controlled to keep the $\Delta V$ due to the pulse below 10 mV. White bias light, incident on the SnO$_2$ side of the cell, was supplied by 10 W “Solarc” lamps (WelchAllyn) that are also of the metal–halogen type. The bias light was attenuated when needed by neutral-density filters. When the pulse intensity from the red diodes was insufficient to give voltage signals greater than 0.5 mV, a white flash lamp was used. The flash time was also 100 $\mu$s, with a fall half time of 20 $\mu$s. The time resolution of the potentiostat is 20 $\mu$s; thus, we could measure transient phenomena with time constants $\geq 40$ $\mu$s. It is important to note that both the Steuernagel and Solarc light sources contain a UV component similar to that found in sunlight. The TiO$_2$/N3/CuSCN cells usually show much better performance under such illumination than under incandescent (tungsten halogen) lamps lacking UV.$^{25}$

**Analysis**

It has been previously shown that the transient photovoltage measured at the external contacts is a good measure of the transient offset of the Fermi level in the TiO$_2$ phase of the i-het.$^{23}$ This is because the doped CuSCN used in these cells has an acceptor density at least 1000 times higher than the donor density in the TiO$_2$.$^{40}$ Thus, in the dark, the Fermi level in both materials will be equal to the work function of the CuSCN. Under bias and/or pulse illumination, the same number of electrons are added to the TiO$_2$ and holes to the CuSCN. In the CuSCN, the proportional change in the hole density will be small, and the Fermi level will move much less than that in the TiO$_2$. Thus, both the $V_{oc}$ generated by the bias light and the $\Delta V$ created by the pulse measure shifts of the Fermi level in the TiO$_2$.

In the photovoltage transients, the decays are very close to single exponential (see Figure 3). We have fit a single exponential to the decay and extracted the pseudo-first-order recombination rate constant ($k_{p\text{-reco}}$). We use “pseudo” here, as the rate constant is not independent of electron concentration. We have also used the transient voltage data to calculate the capacitance and density of trap states (DOS) at each $V_{oc}$. The capacitance of the TiO$_2$/CuSCN interface can be calculated as $C = \Delta Q/\Delta V$, where $\Delta V$ is the peak of the transient and $\Delta Q$ is the number of electrons injected by the pulse. We find $\Delta Q$ by integrating a photocurrent transient at $V = 0$, caused by an identical pulse. This will underestimate the actual injected charge by the fraction of electrons that are lost to recombination during transport. We estimate this error to be less than 30% in the worst cases. More importantly, the error will affect only the magnitude and not the shape of the calculated capacitance or DOS vs potential curves. (We note that this capacitance is a “chemical capacitance” i.e., it is controlled by the density of states at the Fermi level. This capacitance will thus have a dependence on the applied voltage not found in a classical capacitor of two metallic conductors separated by an insulator.)

As a check on this method of measuring the capacitance, we have compared the total charge ($Q_{tot}$) in the cell at $V_{oc}$ found by integrating the capacitance with that found by “charge extraction”. In this latter method, a 1 sun LED illumination of press$\underline{\text{t}}$s and sintered P25 particles. The effect of one Al$_2$O$_3$ layer was to increase the voltage from 550 to 690 mV, while the photocurrent decreased from 7.2 to 5.1 mA. The fill factor increased from 0.46 to 0.53, and the efficiency increased from 1.8 to 2.1%. The addition of a second Al$_2$O$_3$ layer caused a further increase in the voltage to 0.79 V; however, photocurrent decreased to 3.3 mA and the fill factor to 0.57, leading to an efficiency decrease to 1.5%. This set of IVs shows one of the largest effects of Al$_2$O$_3$ layers that we have measured. As will be seen below, the trend shown in Figure 1a is always reproduced, although the magnitudes of the effects vary substantially.

Figure 1b shows three 1 sun IVs for cells where the nanoporous TiO$_2$ layer consisted of $\sim$4 $\mu$m of pressed and sintered P25 particles. For this example, the effect of one Al$_2$O$_3$ layer is to increase the voltage from 0.61 to 0.67 V and to decrease the photocurrent from 5 to 4 mA/cm$^2$. The fill factor is increased from 0.45 to 0.56, and the efficiency increases from 1.4 to 1.5%. The addition of a second layer causes a further increase in the voltage to 0.71 V and an increase in the fill factor to 0.58; however, the decrease in the photocurrent to 3.4 mA results in a decrease in the efficiency to 1.4%.

We have found that the quantitative effect of the Al$_2$O$_3$ layer depends not only on the thickness of the layer but also on the type of TiO$_2$ used, the characteristics of the CuSCN solution, and other uncontrolled factors. Figure 2 shows a bar graph summary of the IV results of six separate comparisons of cells with varying Al$_2$O$_3$ layers. The bars give the average percent change in the IV characteristics for one and two Al$_2$O$_3$ layers relative to that for the cells without Al$_2$O$_3$. The error bars give the range of the percent change across the six comparisons. For example, the application of one Al$_2$O$_3$ layer caused an average increase in $V_{oc}$ of 17%, with a range from 8 to 28%. This was accompanied by an average decrease in photocurrent of 14%. Thus, on average, the photovoltage increase is nearly negated by the photocurrent decrease. The biggest change was in fill
factor, where the average increase for one Al₂O₃ layer was 27%. The average increase in efficiency for one Al₂O₃ layer was 25%. For cells with two Al₂O₃ layers, the percent changes in photocurrent, voltage, and fill factor were all slightly larger, but the mean increase in efficiency was no better than for one Al₂O₃ layer.

Several important correlations are not apparent from the presentation in Figure 2. In general, the fractional increase in efficiency given by an Al₂O₃ layer was smaller when the comparison cell without Al₂O₃ had higher-than-average efficiency. Thus, the effect of the Al₂O₃ layers is not completely additive with respect to other methods of improving cell efficiency. For this reason, our record cell efficiencies are 2.3% for cells with and without Al₂O₃ layers. More promisingly however, voltage increase and photocurrent decrease are not always linked. If the best measured voltage and FF increases that occurred without photocurrent loss could be added to the record cell without Al₂O₃, the efficiency should be around 3%.

Unsurprisingly, the largest increases in fill factor came in comparison to base cells with the lowest fill factors. More interestingly, the largest increase in fill factor was also correlated with the largest decrease in photocurrent. Because of this, the largest increase in fill factor does not translate into an equivalent increase in efficiency. The largest increase in fill factor came from the thickest films (5 μm P25), consistent with the hypothesis that the low initial fill factor comes from the poor competition between transport and recombination in these cells. It is not clear why these cells should also show the largest decrease in photocurrent, but it could be related to lower success in pore filling with CuSCN because of the slightly smaller pore necks after Al₂O₃ addition.

As mentioned in the Introduction, there are several mechanisms by which the Al₂O₃ layer can cause an increase in Voc. Photovoltage transients at Voc can help elucidate which of these mechanisms is dominant. Figure 3 shows representative photovoltage transients for cells with zero, one, and two Al₂O₃ layers. The transients were taken at Voc with 1 sun bias light. The signals have been normalized to the same height at time zero. The actual voltage peak of all transients was ~3 mV. The lines through the data are fits to a single-exponential decay. The fits are quite good, as expected for the very small voltage perturbations. For TiO₂/dye/CuSCN layers, the decay of the voltage signal has been shown to depend on the rate of electron–hole recombination across the TiO₂/CuSCN interface. 23 From the exponential fits, we extract a pseudo-first-order rate constant (kₚₒ) for the recombination reaction. The inverse of the rate constant is equivalent to the electron lifetime. From the data in Figure 3, the kₚₒ for the cell with no Al₂O₃ is 1.3 × 10⁻³/s (lifetime 75 μs). Application of one Al₂O₃ layer decreases kₚₒ to 5.5 × 10⁻³/s (lifetime 180 μs). The second Al₂O₃ layer causes
Figure 4. Pseudo-first-order recombination rate constant ($k_{pfo}$) vs $V_{oc}$ for TiO$_2$(Al$_2$O$_3$)/dye/CuSCN cells with zero, one, and two Al$_2$O$_3$ layers. $V_{oc}$ was varied by varying the bias light intensity. Flash intensities were varied to maintain a peak $\Delta V$ below 10 mV. (a) $k_{pfo}$ vs $V_{oc}$ for cells with colloidal TiO$_2$ layers. (b) $k_{pfo}$ vs $V_{oc}$ for cells with P25 TiO$_2$ layers. The lines plotted in the figure are guides to the eye with this slope.

Figure 5. Recombination rate constant, $k_{pfo}$, at $V_{oc}$ for TiO$_2$(Al$_2$O$_3$)/dye/CuSCN cells with either P25 or colloidal TiO$_2$ and zero, one, or two Al$_2$O$_3$ layers. Bias illumination was ~100 mW/cm$^2$.

Figure 4b displays similar data for a less extensive data set with P25 TiO$_2$ layers. Here again, the decrease in $k_{pfo}$ for one and two Al$_2$O$_3$ layers is obvious. The slope of the lines shown on this graph varies from 10% steeper than that shown by the colloidal TiO$_2$ cells, (for zero and one Al$_2$O$_3$ layer) to 13% flatter for two Al$_2$O$_3$ layers. Given these small deviations, it is reasonable to assume that the underlying recombination mechanism is the same for the two kinds of TiO$_2$.

Figure 5 shows the recombination rate constant $k_{pfo}$ at 1 sun $V_{oc}$ plotted vs the number of Al$_2$O$_3$ layers. Data are shown for 12 colloidal TiO$_2$ cells and 7 P25 cells. For the colloidal cells, the average recombination rate constant without Al$_2$O$_3$ is 1.1 $\times$ 10$^{4}$/sec, decreasing to 6.2 $\times$ 10$^{3}$/sec when one Al$_2$O$_3$ layer is present, and further to 2.3 $\times$ 10$^{3}$/sec with two Al$_2$O$_3$ layers. The decreasing $k_{pfo}$ at $V_{oc}$ is already strong evidence that the tunnel barrier effect is providing some of the increase in $V_{oc}$. If only surface-dipole or surface-state passivation were occurring, then $k_{pfo}$ at 1 sun $V_{oc}$ would be expected to remain unchanged or possibly increase. For the P25 cells, almost the same trend is seen, except that the average recombination rate constants are ~2.5 times slower than those for the colloidal TiO$_2$ cells.

The transient voltage data can also be used to calculate the capacitance and density of states (DOS) of the TiO$_2$ film at each $V_{oc}$. The capacitance is equal to the charge injected during the flash divided by the peak voltage of the transient. The capacitance can be converted directly to the density of trap states, taking into account the thickness and porosity of the TiO$_2$ films. Details are discussed in the Methods section. Figure 6a shows capacitance vs $V_{oc}$ curves for five TiO$_2$/dye/CuSCN cells with P25 or colloidal TiO$_2$ and various Al$_2$O$_3$ layers. The right axis in Figure 6a shows the corresponding DOS scale appropriate for the 3 $\mu$m colloidal TiO$_2$ films. (The axis cannot hold simultaneously for the P25 data because of the different layer thickness.) We have fit the capacitance/DOS data to a single exponential using eq 1.

$$C(V) = K + C_0 e^{-V/m_c}$$  \hspace{1cm} (1)

The value of $m_c$, the “characteristic energy”, describes the curvature of the DOS distribution. The DOS vs $V_{oc}$ curve is fit well by a single exponential, as has been found by other authors.42,47,49 For the colloidal TiO$_2$/dye/CuSCN cells, $m_c$ lies between 50 and 65 mV with uncertainties on the order of $\pm 15$ mV at the 95% confidence level. Using the same transient
At the same $V_{oc}$ in a “standard” electrolyte cell (containing imidazolium iodide, LiI, and tert-butylpyridine), we measured a DOS of $4 \times 10^{18}$, or 5.3 times higher than for the CuSCN cells. In Figure 6b, we have assumed that the surface dipole at the TiO$_2$/hole conductor) interface is identical in the two types of cells. This allowed us to set the difference between the TiO$_2$ Fermi levels at $V_{oc} = 600$ mV equal to the difference in work function of $\Gamma_f$/$\Gamma_{l^-}$ and CuSCN. The data support this assumption in the following way. The observed 5.3-fold increase in DOS for the electrolyte cell, in combination with a DOS distribution with $m_c = 65$ mV, implies that the TiO$_2$ Fermi level is 110 mV closer to the conduction band in the electrolyte cell than in the CuSCN cell. This is in fair agreement with the 150 mV smaller work function for $\Gamma_f$/$\Gamma_{l^-}$ relative to CuSCN.

In Figure 6a, it can be seen that there are shifts in the “onset potential” for the DOS distributions of the different cells. These shifts can be due to changes in the band offset between CuSCN and TiO$_2$. Alternately, the change in the DOS onset could be caused by chemical changes in the nature of the trap states caused by the application of the Al$_2$O$_3$ layer. It would seem likely that passivation of $>50\%$ of the surface states would result in some change in the shape of the DOS distribution. Therefore, the shape of the DOS curve ($m_c$) is only very slightly modified by the Al$_2$O$_3$ application, it seems that chemical changes are less likely than surface dipole changes. Overall, from the 14 colloidal TiO$_2$ cells measured, we find that the DOS onset varies up to 40 mV for supposedly identical cells.$^{31}$

The variation in “identical” cells makes it difficult to determine if the Al$_2$O$_3$ layer causes a shift in the DOS onset. The average shift for cells with one Al$_2$O$_3$ layer is $\sim 15$ mV and, thus, is buried beneath the intrinsic variation. Note that for the colloidal TiO$_2$ example shown in Figure 6a, the apparent shift in the capacitance onset for the one Al$_2$O$_3$ layer cell is $+30$ mV, where the same cell showed a shift in $V_{oc}$ of $-20$ mV. Thus, in this particular case, the shift in band offset worked against the voltage increase caused by the reduction in the recombination rate constant.

For the cells with two Al$_2$O$_3$ layers, the negative shift in the capacitance onset is at most 50 mV, also barely above the variation of identical cells. Comparing the onset shift of each cell with the increase in $V_{oc}$, we conclude that surface dipole effects from Al$_2$O$_3$ explain less than 50% of the observed increase in the $V_{oc}$. For the smaller P25 TiO$_2$ data set, the three P25 cells with Al$_2$O$_3$ showed a negative shift in the capacitance curve relative to the three cells without Al$_2$O$_3$. However, the size of the shift did not correlate with the increase in the $V_{oc}$. In sum, the presence of a clear change in $k_{reco}$ and an upper limit on the effects of band offset, shows that the tunnel barrier effect is the most significant contributor to the increase in $V_{oc}$.

We now consider the effect of the Al$_2$O$_3$ layers on the fill factor. We have recently presented a model that explains the low fill factors in TiO$_2$/dye/CuSCN cells based on the relationship of recombination rate and electron mobility in the TiO$_2$ as a function of the Fermi level.$^{23}$ We refer the reader to ref 23 for the details of the argument. The model predicts that a $V_{oc}$ increase caused by a decrease in the recombination rate constant should be accompanied by an increase in the fill factor, whereas increasing the band offset between TiO$_2$ and CuSCN will not increase the fill factor. The increases in fill factor seen in the data, along with the lack of obvious band edge shift, are consistent with this model. Going further, there is one matched pair of one Al$_2$O$_3$ layer cells with a 45 mV difference in the
position of the capacitance onset. Consistent with the model, the cell that showed a capacitance onset at the lower voltage, meaning the smallest contribution of band offset, showed a significantly higher fill factor, 56% compared to 47%. This one comparison is clearly not proof, but it does indicate the power of combined capacitance, recombination, and IV measurements to construct and test models of the cell’s operation.

We can use the recombination rate constant and capacitance data to examine the internal consistency of the conclusions reached in the previous paragraphs. We note that, at \( V_{oc} \), eq 2 relates the injection and recombination current to \( k_{pfo} \) and \( Q_{tot} \), where \( Q_{tot} \) is the number of electrons added to the TiO_2 film between \( V = 0 \) and \( V_{oc} \).

\[
J_{rec} = J_{inj} = \alpha Q_{tot} k_{pfo}
\]  

(2)

By definition, at \( V_{oc} \) the recombination current \( (J_{rec}) \) is equal to the injection current \( (J_{inj}) \). Under the assumption that all electrons are indistinguishable over the time scale of the recombination, \( \alpha \) is equal to one. This assumption is not always valid for dye-sensitized TiO_2 cells.\(^{52} \) The value of \( \alpha \) does not affect the following consistency check. We discuss the actual value of \( \alpha \) further below.

We make the assumption that the decrease in photocurrent for the one-layer Al_2O_3 cells (average \( \sim 20\% \)) results from decreased injection. From eq 2, we calculate the increase in the \( Q_{tot} \) implied by the change in \( J_{inj} \) and \( k_{pfo} \) between zero and one Al_2O_3 layer. The observed factor 2 decreases in \( k_{pfo} \) (Figure 5) gives an increase in \( Q_{tot} \) by a factor of 1.6. Following the capacitance vs voltage curve with \( m_e = 65 \) mV, a factor of 1.6 increase in \( Q_{oc} \) implies a 30 mV increase in \( V_{oc} \). This is most of the \( \sim 40 \) mV average shift seen in the samples used for transient studies.

This approach can also be used to rationalize why the lower recombination rate constants seen for the P25 films (Figure 5) did not result in a higher \( V_{oc} \). We measured three P25 cells with no Al_2O_3. These films showed \( \sim 3 \) times higher capacitance for a given voltage than the colloidal TiO_2 films. Because the P25 films are 33% thicker, the capacitance normalized to the same thickness will be 2.3 times higher. At a given \( V_{oc} \) the number of electrons (\( Q_{tot} \)) in the P25 film will be 2.3 times higher. From formula 2, we see that the 2.5-fold decrease in \( k_{pfo} \) will be canceled by the 2.3-fold increase in \( Q_{tot} \) so that the recombination current for a given \( V_{oc} \) hardly changes. For a given injection current, the \( V_{oc} \) for the P25 and colloidal films will be similar. More significantly this observation is consistent with the hypothesis that the recombination rate is limited by transport, which is in turn limited by trap density.\(^{34,35,53} \)

The fact that the second Al_2O_3 layer always causes a decrease in efficiency indicates that the present deposition technique gives layers that are too thick. This implies the need for a thinner layer at each deposition step, which might be accomplished by drying the TiO_2 at a higher temperature before immersion in the deposition solution. It has been hypothesized that the deposition of the Al_2O_3 layer depends on the water absorbed at the TiO_2 surface after the 60 °C drying.\(^{11} \) If so, this might explain some of the thickness variation, as the amount of adsorbed water may depend on the drying time and the ambient humidity. More careful drying of the TiO_2 will only work if water in the Al_2O_3 solution plays no role in the deposition, which is not yet known. Deposition of 1 nm of Al_2O_3 on 10 cm² of 3-μm thick colloidal TiO_2 requires only 0.7 mg of water. A typical cell holder will use at least 15 mL for the deposition. For the water on the TiO_2 to be limiting, 15 mL of solution should have less than 1 mg water, equivalent to \(< 0.005 \) wt %.

No source of 2-propanol is this dry, and in any case, a few minutes exposure to humid air could suffice to supply more than this amount of water. The preheating step mentioned in ref 11 may help reduce the water content of the deposition solution before insertion of the TiO_2 film. It is important to determine the role, if any, of air humidity on the deposition before further optimization can occur.

We now return to the fact that \( \alpha \) in eq 2 is significantly smaller than one for dye-sensitized TiO_2 cells. For example, for one cell without Al_2O_3, integrating the capacitance from \( V = 0 \) to \( V_{oc} \) gives 2 μC/cm² for \( Q_{tot} \) and the charge-extraction method gives a lower bound of 1.7 μC/cm². For this cell, the recombination rate constant at \( V_{oc} \) was 1.4 × 10⁷. Applying eq 2 with \( \alpha = 1 \) gives an estimated recombination current of 28 mA/cm², with a lower bound of 24 mA/cm² using the \( Q_{tot} \) from charge extraction. These estimates are clearly too large. For this cell, the 1 sun plateau photocurrent was 5.7 mA/cm². The injection current cannot have been higher than 7 mA/cm², given the dye used and the TiO_2 film thickness of \( \sim 2 \) μm. For another cell with two layers of Al_2O_3, the integrated capacitance gives \( Q_{tot} = 2.9 \) μC/cm², and the recombination rate constant is 1 × 10⁷. The estimated recombination current is thus 29 mA/cm², again clearly much too high for a 2-μm TiO_2 film. Although the value of \( Q_{tot} \) found by integrating the capacitance can have several sources of error, the value of \( Q_{tot} \) from charge extraction is a secure lower bound, thus an \( \alpha < 1 \) is required. In general, values of \( \alpha \) between 0.2 and 0.3 give recombination currents no higher than the maximum possible injection currents. We have also measured seven dye-sensitized electrolyte cells that also gave \( \alpha = 0.2–0.35 \).

A full discussion of \( \alpha \) is not within the scope of this paper. Values of \( \alpha < 1 \) might arise from transport-limited recombination and/or by trapping/detrapping times that are longer than the recombination time scale. An analogous discrepancy has been observed when comparing the measured \( Q_{tot} \) at short circuit and the \( Q_{tot} \) calculated from the short-circuit photocurrent and the photocurrent characteristic time.\(^{52} \)

Conclusions

From our analysis, the Al_2O_3 layer does produce the intended tunnel barrier effect. The similar trends of rate constant with \( V_{oc} \) indicate that the aluminum oxide does not cause a significant change in the recombination mechanism. The similar curvatures and positions of the DOS curves indicate there is little change in the band edge potential and the curvatures and positions are consistent with little change in the existence or occupation of surface states. It should be possible to construct Al_2O_3-coated cells that surpass the record efficiencies of uncoated cells. To achieve this, control of the coating thickness will need to be improved to avoid photocurrent losses from reduced injection and to avoid blocked pores. However, as the unexpected value of \( \alpha \) in eq 2 makes clear, it is important to achieve a better understanding of the mechanism of recombination. If there are indeed widely spaced recombination “hot spots”, then treatments aimed directly at these spots may be more rewarding than coating all of the particles with tunnel barriers.

References and Notes

Al2O3 Layers in TiO2/Dye/CuSCN Photovoltaic Cells


