Charge Recombination Kinetics in Dye-Sensitized Nanocrystalline Titanium Dioxide Films under Externally Applied Bias

Saif A. Haque, Yasuhiro Tachibana, David R. Klug, and James R. Durrant*

Centre for Photomolecular Sciences, Departments of Biochemistry and Chemistry, Imperial College, London SW7 2AY, U.K.

The kinetics of charge recombination were determined following low intensity optical excitation of Ru^{II}-$(2,2'$-bipyridyl-$4,4'$dicarboxylate$)_2(NCS)_2$ sensitized nanocrystalline TiO_2 films as a function of externally applied bias voltage V. These kinetics were found to be multiexponential. The median time ($t_{50\%}$) for charge recombination was found to depend strongly upon bias voltage, reducing from $t_{50\%} \sim 200$ ms for $V = 0$ V versus Ag/AgCl to < 30 ns for $V \leq -500$ mV. This reduction in $t_{50\%}$ was found to follow the equation $t_{50\%} \propto \exp(qV/1.7k_{B}T)$. These results are consistent with the charge recombination kinetics being strongly dependent upon the accumulation of electrons in intraband/conduction band states of the TiO_2 film. For biases $V \leq -400$ mV, the rate of charge recombination was found to exceed the rate of rereduction of the dye cation by an I^-/I_3- redox couple in solution.

Introduction

There is currently considerable interest in the interfacial charge-transfer kinetics of dye-sensitized nanocrystalline semiconductors, which is largely due to recent developments in nanocrystalline electrochemical photovoltaic devices.[1,2] The function of these devices is based upon electron injection from a photoexcited state of the dye into the conduction band of a wide band gap semiconductor (see Figure 1). The resulting dye cation is then rereduced by redox species in the electrolyte. To achieve a high photocurrent quantum yield, this rereduction must be much faster than the charge recombination reaction between the oxidized dye and injected electrons in the semiconductor. Transient spectroscopies have been widely employed to study the rates of electron injection and charge recombination for several different sensitizer dyes and semiconductor materials,[1,3,4] although a detailed understanding of the parameters controlling these interfacial electron-transfer kinetics remains to be established.

Photoelectrochemical solar cells currently under commercial development employ nanocrystalline titanium dioxide (TiO_2) films and the sensitizer dye $Ru^{II}(2,2'$-bipyridyl-$4,4'$dicarboxylate$)_2$-$(NCS)_2$ ($Ru(dcbpy)_2(NCS)_2$). We have recently shown that pulsed excitation of such films in the absence of a redox active electrolyte and applied bias results in electron injection with a time constant of $\leq 10^{-12}$ s.[5] Charge recombination between the dye cation and the injected electron (e^-_{sc}) in these films was found to be multiexponential over the microsecond−millisecond time scales.

Both the rates of electron injection and charge recombination are likely to be influenced by the application of a potential difference across the semiconductor/electrolyte interface, as illustrated in Figure 1. This dependence upon applied potential is particularly important for applications in photoelectrochemical solar cells, as electrical power is only generated from such devices under forward bias conditions (when the sensitized

electrode is at a negative potential relative to the electrolyte). Several studies have investigated the bias voltage dependence of the charge recombination kinetics of dye-sensitized nanocrystalline electrodes in the absence of a redox active electrolyte, but with widely differing conclusions. O'Regan et al.[6] reported that application of negative bias voltages to $Ru(dcbpy)_3$ sensitized TiO_2 films resulted in a 10^3 reduction in the time constant for charge recombination from ~ 1 ms to 1 μs. In contrast, Kamat et al.[7] reported microsecond charge recombination kinetics for $Ru(bpy)_2(dcbpy)^{2+}$ sensitized tin oxide films which were independent of bias voltage. Yan and Hupp[8] have studied the nanosecond charge recombination kinetics of TiO_2 films sensitized by hexaphosphonated $Ru(bpy)_3$ and reported a strong dependence upon applied potential, but only for potentials approaching (within 200 mV) the TiO_2 conduction band edge. It is unclear whether these differences result from differences in the sensitizer dye, or other details of the experimental procedures employed, as will be discussed in detail below.

Recent models[9,10] of photocurrent generation in $Ru(dcbpy)_2$-$(NCS)_2$ sensitized photoelectrochemical solar cells have assumed that, for all bias voltages, rereduction of the oxidized dye by semiconductor electrons is much slower than rereduction of the oxidized dye by the redox active electrolyte (reported as $\sim 10^8$ s^{-1} [11]). However, no data have previously been reported for the bias dependence of the charge recombination kinetics for this sensitizer dye. In this paper we extend our previous study[5] of such dye-sensitized films by considering the influence of externally applied bias upon the charge recombination kinetics in this system.

Materials and Methods

$Ru(dcbpy)_2(NCS)_2$ sensitized nanocrystalline TiO_2 films were prepared on fluorine-doped SnO_2 conducting glass supports (17 Ω). The film preparation method followed Nazeerudin et al.[11] (method A), resulting in a 10-μm thick film comprising 20-nm diameter anatase TiO_2 colloidal particles. Dye adsorption was achieved by immersion in 2×10^{-5} M ethanolic solutions

* Corresponding author: e-mail, j.durrant@ic.ac.uk, fax, 44 171 225 0960.
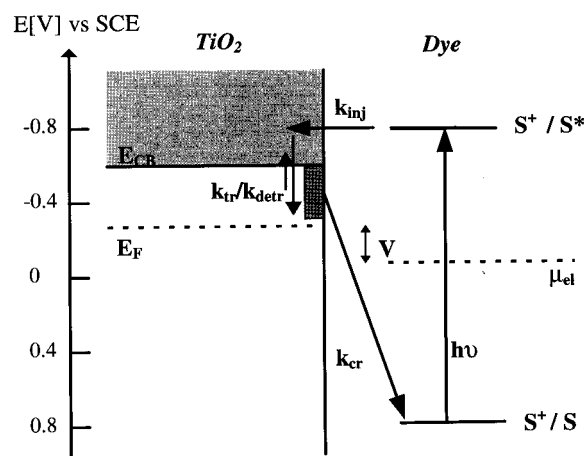
Figure 1. Schematic representation of the electron-transfer processes in a dye-sensitized TiO$_2$ film under applied bias in a three-electrode photoelectrochemical cell. The chemical potential of the electrolyte solution is held constant by an Ag/AgCl reference electrode. A potential difference *V* is applied between the reference electrode and the sensitized TiO$_2$ working electrode. Assuming no voltage drop at the conducting glass/TiO$_2$ interface, and a uniform potential throughout TiO$_2$ film (no band bending), the applied voltage modulates the Fermi level of the TiO$_2$. The application of a negative potential results in the accumlation of electrons in conduction and intraband states of the TiO$_2$. Intraband states include both surface and bulk defect states (see text for details). Optical excitation of the sensitizer dye initiates ultrafast electron injection (k_{inj}) into conduction band states of the TiO$_2$. The injected electron subsequently thermalizes with electrons accumulated in conduction band/intraband states of the TiO$_2$ (k_{tr}/k_{detr}). The oxidized dye cation is rereduced by back electron transfer from electrons accumulated or photoinjected in the TiO$_2$ conduction band/intraband states (k_{cr} − charge recombination). The principal purpose of this study is to determine the effect of electron accumulation induced by the applied bias upon charge recombination. In a functioning photoelectrochemical cell, rereduction of the dye cation by an I$^-$/I$_3^-$ redox couple in solution must be faster than this charge recombination pathway for the cell to achieve a high photocurrent quantum yield.

at room temperature for 8 h. This resulted in film optical densities of ∼0.5 at film absorption maximum at 538 nm, corresponding to dye coverages of approximately one-fifth of a monolayer. Films were stored in the dark under anhydrous conditions. All experiments were performed at room temperature.

Experiments without external bias were conducted as previously,[5] by covering the film with a 1:1 ethylene carbonate/propylene carbonate solution and glass cover slide. For experiments under external bias, the dye-sensitized semiconductor film formed the working electrode (∼2 cm^2 macroscopic surface area) in a three-electrode photoelectrochemical cell employing a platinum counter electrode and a Ag/AgCl reference electrode. Potential control was provided by a home-built potentiostat. The electrolyte solution was 0.1 M tetrabutylammonium trifluoromethanesulfonate (99% grade Aldrich) (TBAS) in ethanol; this solution was degassed with argon gas prior to and during all optical experiments.

Nanosecond−millisecond transient absorption spectroscopy was performed as previously [5] except that the excitation wavelength was 560 nm. Data were collected employing low-intensity excitation pulses (0.3 mJ/cm^2, repetition rate 2 Hz), resulting in excitation of approximately 3% of dye molecules per pulse, corresponding to approximately one injected electron per colloidal particle. Reduction in the excitation intensity by a factor of 3 resulted in no change in the kinetics of charge recombination, while increase of the excitation power above 0.6 mJ/cm^2 resulted in a significant increase in the rate of

the charge recombination (e.g., ∼10-fold increase in rate at 1 mJ/cm^2) [R.Willis, Y.T., D.R.K., and J.R.D., unpublished data]. Incidence on the sample of the probe and excitation light beams did not result in any change in the current drawn by the potentiostat due to the low light intensities used and the redox inactive electrolyte employed in electrochemical cell.

The effect of applied bias upon the transient data was fully reversible, with indistinguishable data at 0 mV bias being obtained at the beginning and end of data collection. Moreover, absorption spectra of the sensitized films were determined at the beginning and end of all data collection runs after rinsing the film in ethanol. Indistinguishable spectra were obtained before and after the transient experiments (absorption maximum at 538 ± 2 nm), indicating that both dye degradation and desorption were negligible.

Results

Figure 1 shows the decay of the transient absorption induced at 820 nm by pulsed excitation of a Ru(dcbpy)$_2$(NCS)$_2$ sensitized TiO$_2$ film in a three-electrode photoelectrochemical cell. The decay kinetics were determined as a function of the bias potential applied to the TiO$_2$ electrode (the potential of the electrolyte solution was held at a constant potential by the Ag/AgCl reference electrode). We have previously shown that the transient signal at 820 nm results primarily from an absorption band of the Ru(dcbpy)$_2$(NCS)$_2$ cation, although the induced absorption from electrons transiently injected into the TiO$_2$ may also contribute to the data.[5] As previously, we assign the decay of the induced absorption to charge recombination between the dye cation and electrons in the TiO$_2$. Indistinguishable decay kinetics were also observed at 540 nm, corresponding to bleaching of a MLCT ground-state absorption band of the sensitizer dye, consistent with this assignment. The dye excited state also gives rise to a relatively weak absorption increase at 820 nm; however, the lifetime of this state is ∼10−50 ns, and contributions to the data from this state can therefore be ruled out (except possibly for the data collected at biases ≤−400 mV). Moreover, redox reactions between the electrolyte solution (TBAS in ethanol) and the sensitized film can be ruled out, as similar data were collected both in the photoelectrochemical cell (prior to the application of an applied bias voltage) and for isolated films covered by propylene carbonate/ethylene carbonate without any added electrolyte, thus confirming that the TBAS/ethanol solution was redox inactive.

The charge recombination data shown in Figure 2 are plotted on a logarithmic time scale. They exhibit multiexponential kinetics which are strongly dependent on the applied potential. Data collected at a bias potential of 0 V show similar kinetics to those we have reported previously in the absence of applied bias. However, increasing the potential to −500 mV versus Ag/AgCl results in an approximately 10^4-fold increase in the median rate of charge recombination.

In photoelectrochemical solar cells, this charge recombination must compete with rereduction of the oxidized dye by a I$^-$/I$_3^-$ redox couple in solution. Figure 3 contrasts the nanosecond dye cation decay kinetics in the presence (A) and absence (B) of a 0.3 M I$^-$/I$_3^-$ couple. Data were collected with the sensitized film covered in a 1:1 ethylene carbonate/propylene carbonate solution as previously, in the absence of an applied bias voltage. In the absence of the iodide redox couple, only slight recovery of the dye cation signal is apparent on this nanosecond time
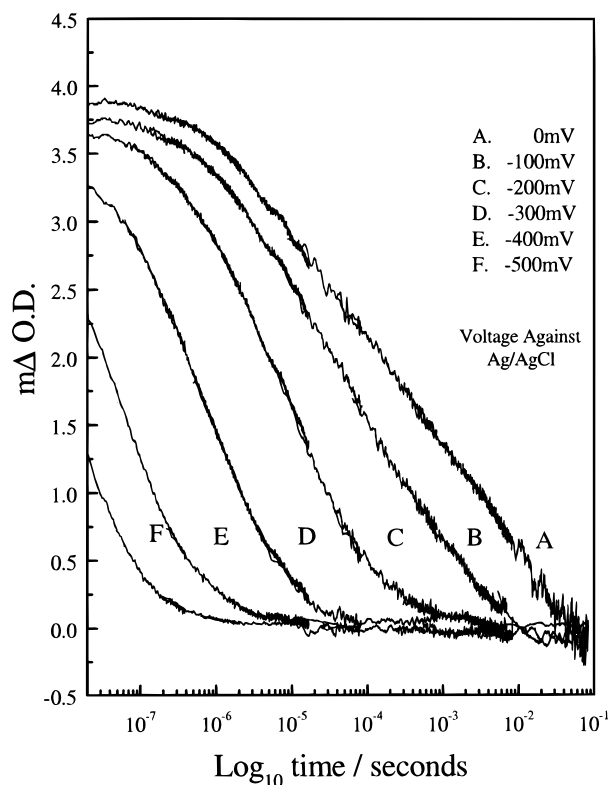
Figure 2. Transient absorption data following the decay of the cation state of Ru(dcbpy)$_2$(NCS)$_2$ adsorbed on a TiO$_2$ nanocrystalline electrode as a function of applied potential. Cation decay is attributed to charge recombination with electrons in trap/conduction band states of the TiO$_2$. Data were collected at a probe wavelength of 820 nm in a three electrode photoelectrochemical cell at room temperature, employing 560-nm excitation pulses. The electrolyte was maintained at a constant potential by an Ag/AgCl reference electrode (+40 mV versus SCE). Voltages are quoted versus the reference electrode.
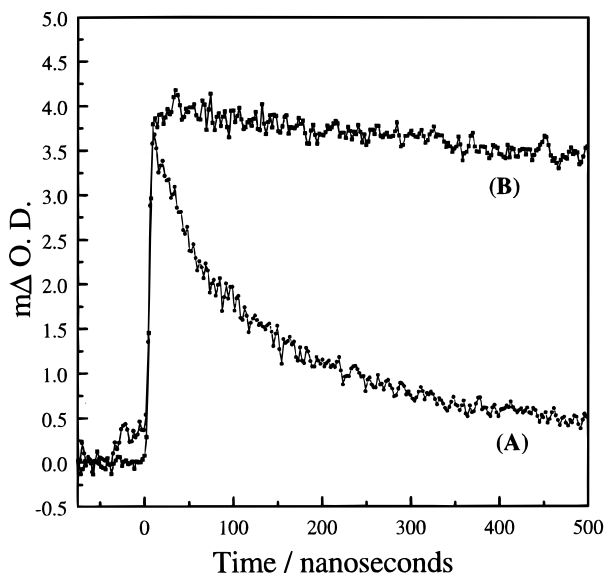

Figure 3. The nanosecond decay kinetics of the cation state of Ru-(dcbpy)$_2$(NCS)$_2$ adsorbed to a TiO$_2$ film in the presence (A) and absence (B) of 0.03 M I$_2$ and 0.3 M KI in propylene carbonate/ethylene carbonate. Data were collected without externally applied bias.

scale, consistent with our previous measurements. In the presence of the redox couple, a rapid decay of the cation signal is observed. A reasonable fit was obtained to a monoexponential decay, yielding an exponential time constant of 110 ns ($t_{1/2}$ ∼ 100 ns) for the rereduction of the dye cation by I$^-$.

Discussion

Electron Accumulation in Nanocrystalline TiO₂. Nanocrystalline TiO$_2$ is an n-type semiconductor, with a high density of intraband defect/surface states lying below the conduction band edge.[1,12] It has been suggested that trapping of conduction band electrons by these intraband states strongly influences the charge-transport properties of these films, with the electron dynamics being dominated by the kinetics of trapping/detrapping.[13] The application of an external potential to nanocrystalline TiO$_2$ films modulates the Fermi level of the TiO$_2$ electrode. Moreover, this external potential modulates the occupancy of both the trap states and the conduction band states according to Fermi−Dirac statistics. The accumulation of electrons within the conduction band/intraband states can be monitored as a function of applied potential by the onset of a broad absorption band with a maximum near 800 nm,[14] allowing determination of the flat band potential of the TiO$_2$ electrode, which corresponds approximately to the conduction band edge.[1] Following this procedure, we determined that, for the ethanol electrolyte employed in our studies, the conduction band edge of our dye-sensitized electrodes is at −0.65 ± 0.1 V versus Ag/AgCl.[15] It should be noted that a significant density of trap states is expected at potentials more positive than this. Previous spectroelectrochemical and voltammetry measurements have suggested a density of intraband surface states of (1−4) × 10^{17} m^{-2}, corresponding to 100−400 states per colloidal particle, attributed to coordinatively unsaturated Ti^{4+} centers.[12,14]

Bias Dependence of Charge Recombination. It is reasonable to suppose that, in the absence of a redox active electrolyte, the rate of rereduction of oxidized dye molecules will be strongly dependent upon the concentration of electrons [e$^-_{sc}$] accumulated by the applied potential within the TiO$_2$ conduction band and intraband states. Such a possibility has been addressed in several studies,[6,16] although to our knowledge not previously tested quantitatively for such nanocrystalline films. Following Fermi−Dirac statistics, for bias potentials below those of the conduction band/trap states we expect [e$^-_{sc}$] to follow the equation [e$^-_{sc}$] ∝ exp($-qV/k_BT$) assuming that the Fermi level within the TiO$_2$ electrode corresponds to that applied to the conducting glass back contact (see, however, ref 18).

The charge recombination data shown in Figure 2 clearly exhibit nonmonoexponential behavior. A detailed kinetic analysis is beyond the scope of this paper. To obtain a crude quantification of the rate of recombination, we determined the time taken for 50% of the initially formed dye cations to be rereduced ($t_{50\%}$) [17] (the experimentally observed median time). This crude estimate of the apparent rate of charge recombination is justified at least in part by the observation that the effect of bias voltage is primarily to induce a lateral shift of the transient data on the logarithmic time scale, without a large qualitative change in the form of the decay curve. Figure 4 shows a plot of ln ($t_{50\%}$) versus applied potential V, showing that ln ($t_{50\%}$) is linearly dependent upon V. We thus conclude that $t_{50\%}$ shows qualitatively the same dependence upon applied bias as [e$^-_{sc}$], consistent with the variation in recombination rate with bias potential being essentially dominated by the concentration of electrons accumulated in the TiO$_2$ film. This dependence upon [e$^-_{sc}$] suggests that under negative bias the charge recombination is primarily not geminate, but associated with electrons accumulated in the TiO$_2$ intraband states due to the applied potential.

From determination of the gradient of the linear fit shown in Figure 4, we find that $t_{50\%}$ ∝ exp($qV/n\ k_BT$), where $n = 1.7 ±$ 0.2. This deviates significantly from the "ideal" behavior,
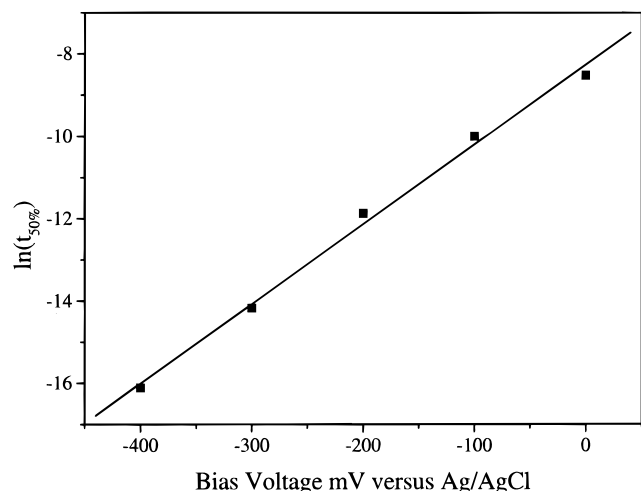
Figure 4. Plot of ln ($t_{50\%}$), where $t_{50\%}$[17] is determined from the data shown in Figure 2, versus applied potential to the dye-sensitized TiO$_2$ electrode.

corresponding to $n = 1$. There are several possible origins of this apparently nonideal behavior. These include the possibility that, due to limited conductivity of the TiO$_2$ film relative to that of the electrolyte, [e$^-_{sc}$] differs significantly between the front and back surfaces of the TiO$_2$ film,[18] and secondly the possible invalidity of our assumption that the Fermi level lies below the potential of the intraband states, both of which could result in the observed nonideal behavior. However, it is interesting to note that the current output of photoelectrochemical solar cells employing the same sensitizer dye has also been found to exhibit a similar dependences upon voltage ($n \sim 1.4-2$).[9,19,20] Both the current transport properties[13] and the charge recombination kinetics[5,6] have been suggested to be strongly influenced by trapping/detrapping from a distribution of trap sites, and it is therefore possible that the voltage dependencies of these two processes are also related, consistent with the results presented here.

The above analysis makes a number of crude approximations. It makes no distinction between charge recombination from conduction band and intraband states of the TiO$_2$, implying that the photoinjected electrons rapidly achieve thermal equilibrium between these states. This assumption is consistent with recent observations that trapping of directly excited conduction band electrons by intraband surfaces states occurs in 10^{-13} s in TiO$_2$ colloids.[21] It should be noted, moreover, that the potentials employed in this study are 150−650 mV below the conduction band edge of the TiO$_2$ electrode. The thermalized occupancy of conduction band states is therefore likely to be very low and the recombination kinetics primarily associated with recombination from intraband states of the TiO$_2$. Our analysis also neglects any shift in the quasi-Fermi level caused by injected electrons. This approximation can be crudely justified by the low density of injected electrons relative to the density of intraband states (approximately 1 and 100 per colloidal particle respectively [22]), although a more rigorous analysis taking consideration of the energy distribution of intraband states is clearly required.

Bias Dependence of Electron Injection. The amplitude of the initial absorption change shown in Figure 2 (20-ns time delay) is reduced as the applied negative bias is increased. Following the analysis given above, this can be readily attributed to an acceleration in the rate of charge recombination, resulting in an increasing proportion of charge recombination occurring in <20 ns. This reduction in amplitude could, however, also

be attributable, at least in part, to a reduction of the yield for electron injection at large negative biases. A strong bias dependence upon injection yield has previously been reported for similar experimental systems.[6,7] Further data with an improved time resolution are required to address this issue. However, it must be emphasized that, in the discussion above, the quantitative analysis given in Figure 4 for voltages between 0 and −400 mV is only marginally dependent upon any possible reduction in electron injection yield caused by the applied negative bias. For example, between 0 and −200 mV, $t_{50\%}$ changes by a factor of 20, while the initial amplitude, and therefore the injection yield, changes by <10%. Analysis of the recombination data assuming that all of the reduction in the initial amplitude was due to a reduction in the injection yield [17] resulted in a plot of ln ($t_{50\%}$) versus V indistinguishable within experimental error from that shown in Figure 4.

Comparison with Previous Studies. Previous studies of the charge recombination dynamics for dye-sensitized TiO$_2$ differ widely both in the typical time constants for charge recombination and their dependence upon applied bias voltage.[6−8,12,16,23,24] While a comprehensive review of these studies is beyond the scope of this paper, two points can be made which are of particular relevance. First, considerable care was taken for the results reported here to minimize the light incident upon the sample. Previous studies have generally used much higher light intentities, resulting in the possibility of nonlinear effects due to both the injection of several electrons into each colloidal particle, and the concomitant transient filling of intraband states causing a large laser-induced shift in the Fermi level.[22] Second, our data indicate the recombination kinetics are strongly dependent upon the concentration of electrons accumulated in the TiO$_2$ ([e$^-_{sc}$]), which is in turn dependent upon the difference between the applied potential and the potentials of the conduction band/intraband states. Fitzmaurice and co-workers have shown that the potential of the conduction band edge is strongly dependent upon the presence of small "potential determining" cations (H$^+$, Li$^+$) in the electrolyte solution,[14] while the density of intraband states is likely to depend upon the details of film preparation and subsequent surface treatment. Differences in recombination kinetics observed experimentally by different studies may, therefore, orginate either from differences in the preparation of the sensitized films and/or the concentration of potential determining ions in the electrolyte solution. In our current study we have addressed this issue, at least in part, by determining the conduction band edge of the TiO$_2$ spectroelectrochemically under experimental conditions identical with those used for our transient recombination data. However, as discussed above, we have not explicitly taken account of the density of intraband states in our analysis of the recombination kinetics; further studies in this area are clearly required.

Relevance to Photoelectrochemical Solar Cells. It is not possible to make a direct correlation between the results presented here and studies of the electrical performance of Ru-(dcbpy)$_2$(NCS)$_2$ sensitized TiO$_2$ photoelectrochemical solar cells, such as those reported recently.[9,10,20] First, the results reported here employ only an applied bias potential and minimal current flow, rather than a photovoltage and concomitant photocurrent generated by solar illumination. Second, as discussed above, the results presented here suggest the recombination kinetics may be very sensitive to the details of the electrode preparation and surface treatment. A detailed study of the correlation between charge recombination kinetics and electrical performance of identical samples is currently in progress.

Given the above caveat, it is still pertinent to note, at least for the experimental system under study here, that for bias

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voltages of ≤ -0.4 V, the kinetics of charge recombination between the oxidized dye and electrons within the TiO$_2$ are faster than rereduction of the oxidized dye by I$^-$ (compare Figure 2, traces E and F, with Figure 3, trace A). If these kinetics were indicative of those found in a photoelectrochemical cell, these would suggest that, for cell output voltages > 0.6 V,[25] direct recombination between the oxidized dye and electrons in the TiO$_2$ would result in a signficant loss of photocurrent. This contrasts with recent models of the electrical performance of photoelectrochemical solar cells, which have explicitly assumed this recombination pathway to be negligible and attributed the loss of current at high output voltages solely to recombination between I$_3^-$ ions and TiO$_2$ electrons.[9,10] Our results clearly call into question this assumption and emphasize the possibility that direct recombination between oxidized dyes and TiO$_2$ electrons may be a important process limiting the performance of photoelectrochemical cells.

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