

## Frequency-Resolved Optical Detection of Photoinjected Electrons in Dye-Sensitized Nanocrystalline Photovoltaic Cells

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Electron accumulation in illuminated dye-sensitized nanocrystalline TiO<sub>2</sub> photovoltaic cells has been detected by measuring the photoinduced change in transmission at 940 nm. The sensitivity of the transmission measurement was enhanced by using intensity-modulated visible light (514 nm) to excite the photosensitizer dye. The intensity modulation was superimposed on a larger dc illumination level in order to allow linearization of the intensity-modulated transmission, photovoltage, and photocurrent responses. The dye-sensitized photovoltaic cell was also characterized by measuring its frequency-dependent impedance under steady illumination. Comparison of the normalized modulated transmittance  $\Delta T/T$  at open circuit with the corresponding modulated photovoltage response was used to derive the optical absorption cross section of electrons in the cell ( $\sigma_n \approx 10^{-17} \text{ cm}^2$  at 940 nm). The net electron injection efficiency was found to be 1 at short circuit but only 0.3 at open circuit, indicating that under strong accumulation the reaction of electrons from the TiO<sub>2</sub> with the oxidized dye competes with dye regeneration by iodide ions.  $\Delta T/T$  was also measured under short-circuit conditions, and the results showed that the decrease in electron density is less than that predicted for the case of trap free electron transport. Complex plane plots of the frequency-dependent  $\Delta T/T$  response were found to be semicircular for both open-circuit and short-circuit conditions. The minima of the semicircles occurred at the same frequencies in the two cases, indicating that the majority of the detected electrons are trapped and that their concentration relaxes predominantly via back reaction with I<sub>3</sub><sup>−</sup>.

### Introduction

Nanocrystalline dye-sensitized solar cells with efficiencies in excess of 10% have been developed by Grätzel and co-workers.<sup>1–3</sup> The novel feature of the cells is the use of a ruthenium sensitizer dye adsorbed on a thin (10  $\mu\text{m}$ ) porous film of nanocrystalline TiO<sub>2</sub>. Light absorption by the dye results in rapid electron injection into the oxide,<sup>4</sup> and the dye is then regenerated from its oxidized state by electron transfer from iodide ions present in the electrolyte phase. Collection of the photoinjected electrons at the transparent back contact appears to occur by rather slow diffusion. Values of the electron diffusion coefficient derived from photocurrent transients<sup>5,6</sup> and from intensity-modulated photocurrent spectroscopy (IMPS)<sup>6,7</sup> are of the order of  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . This means that electrons photogenerated in the middle of a 10  $\mu\text{m}$  thick TiO<sub>2</sub> film require a transit time,  $\tau_d$ , of several milliseconds to diffuse to the back contact. It is a remarkable feature of optimized cells that the lifetime,  $\tau_n$ , for the back reaction of photoinjected electrons with I<sub>3</sub><sup>−</sup> is longer than the transit time  $\tau_d$ , so that the short-circuit collection efficiency for injected electrons can exceed 90%.

Under open-circuit conditions, photoinjected electrons are not extracted at the substrate contact and back-react instead with I<sub>3</sub><sup>−</sup> or with the oxidized state of the dye. Schlichthörl et al.<sup>8</sup> have shown that the electron lifetime under open-circuit conditions can be derived using intensity-modulated photovoltage spectroscopy (IMVS). These authors showed that  $\tau_n$  depends

on the concentration of I<sub>3</sub><sup>−</sup> in the electrolyte and on illumination intensity. For the cells used in our experiments,  $\tau_n$  at intensities of about 1 sun is of the order of 10 ms. It follows that substantial electron accumulation is expected to occur under illumination at open circuit. For typical solar illumination levels, the rate ( $G$ ) of photoinjection of electrons in a 10  $\mu\text{m}$  thick sensitized TiO<sub>2</sub> film is of the order of  $10^{20} \text{ cm}^{-3} \text{ s}^{-1}$ , so that steady-state electron densities of up to  $10^{18} \text{ cm}^{-3}$  are expected under open-circuit conditions. Under short-circuit conditions, by contrast, the steady-state electron density is expected to be lower because electrons are removed by diffusion to the back contact. The objective of the present work was to detect electron accumulation optically and to relate it to the dynamic photocurrent and photovoltage responses.

Accumulation of electrons in nanocrystalline TiO<sub>2</sub> electrodes has been studied in the absence of sensitizer dye by optical absorption spectroscopy.<sup>9,10</sup> In these studies, electron accumulation was brought about by controlling the potential of the electrode. The present work has established that the optical absorption due to electrons in the TiO<sub>2</sub> can also be followed in dye-sensitized cells by choosing a wavelength in the near-infrared that lies beyond the onset of absorption by the sensitizer dye and I<sub>3</sub><sup>−</sup>. Accumulation of photoinjected electrons in a dye-sensitized TiO<sub>2</sub> solar cell was effected using intensity-modulated visible excitation in the absorption band of the dye. The resulting modulation of the near-IR optical transmittance arising from perturbation of the electron density was measured as a function of modulation frequency under open-circuit and short-circuit conditions. The frequency-resolved modulated transmittance  $\Delta T/T$  was compared with the modulated photocurrent and

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photovoltage measured with the same illumination. Analysis of these responses confirmed that substantial electron accumulation occurs even under short-circuit conditions. The majority of electrons that are detected by modulated transmission appear to be located in traps.

### Theory

**Photomodulated Transmittance.** Expressions for the integrated modulated electron density have been derived (see Supporting Information). In the general case where electrons may be located either in the conduction band or in traps, the near-IR optical transmittance,  $T$ , associated with photogenerated electrons in a  $\text{TiO}_2$  film of thickness  $d$  is given by

$$T = \frac{I_t}{I_0} = \exp - \left( \int_0^d (\sigma_f(\lambda)n_f(x,t) + \sigma_t(\lambda)n_t(x,t))dx \right) \quad (1)$$

Here  $n_f(x,t)$  and  $n_t(x,t)$  are the position- and time-dependent densities of free and trapped electrons, respectively, and  $\sigma_f(\lambda)$  and  $\sigma_t(\lambda)$  are the corresponding optical absorption cross sections at the wavelength  $\lambda$ . The optical cross section for trapped electrons is associated with excitation to the conduction band. In these experiments, the energy of the near-IR source is 1.3 eV. It follows that electrons located in very deep traps ( $E_c - E_{\text{trap}} > 1.3$  eV) will not be detected.

If the electron concentrations are perturbed from their initial photostationary values by modulated illumination superimposed on a larger dc level, it can be shown that the ratio  $\Delta T/T$  is given by

$$\frac{\Delta T}{T} = - \int_0^d (\sigma_f(\lambda)\delta n_f(x) + \sigma_t(\lambda)\delta n_t(x))dx \quad (2)$$

where  $\delta n_f(x)$  and  $\delta n_t(x)$  are the photoinduced perturbations of the free and trapped electron densities, respectively, and  $\Delta T$  is the resulting change in transmittance. Analytical expressions for  $\delta n_f(x,t)$  and  $\delta n_t(x,t)$  are given in the Supporting Information. Here it suffices to note that  $\Delta T/T$  is a measure of the total (i.e., integrated) time-dependent area density of free and trapped electrons.

**Intensity Modulated Photovoltage Spectroscopy (IMVS).** Schlichthörl et al.<sup>8</sup> have discussed the relationship between the small amplitude-modulated photovoltage and the corresponding modulation of the number density of free and trapped electrons. Their treatment makes use of an empirical “conduction band capacitance” and a “surface state capacitance”. The physical origin of these terms is explored briefly in this section.

In the dark, the Fermi levels,  $E_F$ , in the  $\text{SnO}_2$ ,  $\text{TiO}_2$ , and electrolyte phases are all equal.  $n_0$ , the equilibrium density of electrons in the conduction band of the  $\text{TiO}_2$ , is given by

$$\frac{n_0}{N_c} = e^{\frac{-(E_c - E_F)}{kT}} \quad (3)$$

where  $N_c$  is the density of states in the conduction band and  $E_c$  is the conduction-band energy.

Under illumination, the total electron population,  $(n_0 + \Delta n)$  in the conduction band defines the electron quasi-Fermi level  $nE_F$

$$\frac{n_0 + \Delta n}{N_c} = e^{\frac{-(E_c - nE_F)}{kT}} \quad (4)$$

where  $\Delta n$  is the increase in electron concentration brought about by illumination.

The photovoltage is a measure of the change in the Fermi level in the  $\text{TiO}_2$ . The distance dependence of  $nE_F$  at open circuit is neglected for simplicity: this approximation is valid for open circuit conditions and  $\alpha d \approx 1$ . For short-circuit conditions,  $nE_F$  becomes distance-dependent since the excess electron concentration tends to zero at the substrate if electron collection is diffusion controlled. The open-circuit photovoltage is related to the change in the Fermi level by

$$qU_{\text{photo}} = nE_F - E_F \quad (5)$$

Equation 4 can therefore be rewritten in the form

$$\frac{n_0 + \Delta n}{N_c} = e^{\frac{-(E_c - E_F - qU_{\text{photo}})}{kT}} = e^{\left(\frac{E_c - E_F}{kT}\right)} e^{\frac{qU_{\text{photo}}}{kT}} \quad (6)$$

If a small periodic intensity modulation is superimposed on the background dc level, eq 6 becomes

$$\frac{n_0 + \Delta n + \delta n}{N_c} = e^{\left(\frac{E_c - E_F}{kT}\right)} e^{\left(\frac{qU_{\text{photo}}}{kT}\right)} e^{\left(\frac{q\delta U_{\text{photo}}}{kT}\right)} \quad (7)$$

where  $\delta n$  is the periodic component of the excess electron density and  $\delta U_{\text{photo}}$  is the periodic photovoltage. Linear expansion of the last term in eq 7 gives

$$\frac{\delta n}{N_c} = e^{\left(\frac{E_c - E_F}{kT}\right)} e^{\left(\frac{qU_{\text{photo}}}{kT}\right)} \frac{q\delta U_{\text{photo}}}{kT} \quad (8)$$

The modulation of the conduction-band electron density per unit area ( $\delta Q_{\text{cb}}$ ) in a film of thickness  $d$  is therefore given by

$$\delta Q_{\text{cb}} = qd\delta n = \frac{q^2 N_c d}{kT} e^{\left(\frac{E_F - E_c}{kT}\right)} e^{\left(\frac{qU_{\text{photo}}}{kT}\right)} \delta U_{\text{photo}} \quad (9)$$

The so-called conduction band capacitance introduced empirically by Schlichthörl et al.<sup>8</sup> to relate the modulated photovoltage to the modulated charge is identified as

$$C_{\text{cb}} = \frac{q^2 N_c d}{kT} e^{\left(\frac{E_c - E_F}{kT}\right)} e^{\left(\frac{qU_{\text{photo}}}{kT}\right)} \quad (10)$$

This allows one to write the relationship between the intensity-modulated photovoltage and the corresponding perturbation of the free electron charge in the simple form

$$\delta Q_{\text{cb}} = C_{\text{cb}} \delta U_{\text{photo}} \quad (11)$$

The preceding treatment gives no information about the trapped electrons. In the dark at equilibrium, the trapped electron density is given by

$$n_t^0 = \int_{E_v}^{E_c} N(E)f(E)dE \approx \int_{E_v}^{E_F} N(E)dE \quad (12)$$

Here  $N(E)$  is the density of states function for traps in the band gap and  $f(E)$  is the Fermi–Dirac function.

Under illumination, the trapped electron density is determined by the quasi Fermi level  $nE_F$  for electrons, and  $n_t$  under open-circuit conditions ( $nE_F$  independent of distance) is given to a good approximation by

$$n_t = \int_{N_v}^{nE_F} N(E)dE \quad (13)$$

It can be shown that the change in electron density  $\delta n_t$  arising from a small additional optical perturbation of the electron quasi

Fermi level is

$$\delta n_t = N(E_F) \delta E_F = N(E_F) q \delta U_{\text{photo}} \quad (14)$$

Here  $N(E_F)$  is the density of electron traps at the electron quasi Fermi level. The modulated trapped charge per unit area in a film of thickness  $d$  is

$$q d \delta n_t = q^2 N d (E_F) \delta U_{\text{photo}} \quad (15)$$

This allows one to define the “surface state” capacitance discussed by Schlichthörl et al.<sup>8</sup> as

$$C_t = q^2 N d (E_F) \quad (16)$$

It is worth noting that electrons need not be trapped at the surface for eq 16 to be valid, so that the term “trap capacitance” would be preferable.

It is now possible to relate the intensity-modulated photovoltage to the perturbation of the trapped charge density:

$$\delta Q_t = C_t \delta U_{\text{photo}} \quad (17)$$

It follows that the total photomodulated charge in the nanocrystalline electrode is given by

$$\delta Q_{\text{total}} = (C_{\text{cb}} + C_t) \delta U_{\text{photo}} = C_{\text{total}} \delta U_{\text{photo}} \quad (18)$$

where  $C_{\text{total}}$ , the total capacitance of the nanocrystalline electrode under illumination, is the sum of  $C_{\text{cb}}$  and  $C_t$ .

The limiting low-frequency value of the total modulated charge at open circuit can be related to the rate of electron injection and the pseudo-first-order lifetime,  $\tau_n$ , for the reaction of electrons with  $\text{I}_3^-$ . If all injected electrons are collected at short circuit, the injection rate is given by the short-circuit current density  $j_{\text{photo}}$  so that

$$\delta Q_{\text{total}} = \eta(U_{\text{photo}}) j_{\text{photo}} \tau_n \quad (19)$$

where  $\tau_n$  is the electron lifetime determined by back reaction with  $\text{I}_3^-$ . Here the term  $\eta(U_{\text{photo}})$  ( $\leq 1$ ) has been introduced to take into account the fact that electrons can be transferred not only to  $\text{I}_3^-$  but also to the oxidized state of the dye,  $\text{D}^+$ . The rate of this process depends on the electron concentration. Under short-circuit conditions, it can be neglected but is reported to occur on a nanosecond time scale under conditions of strong electron accumulation.<sup>11</sup> It is therefore possible that the net electron injection efficiency  $\eta(U_{\text{photo}})$  under open-circuit (zero net current) conditions is lower than unity. As shown in the Supporting Information, the value of  $\eta$  at open circuit is related to the rate constants for the two processes by

$$\eta = \left[ \frac{k_{\text{reg}} n}{k_{\text{back}} n + k_{\text{reg}} [I^-]} \right] \quad (20)$$

where  $k_{\text{reg}}$  and  $k_{\text{back}}$  are the second-order rate constants for the regeneration and back reactions, respectively.

Schlichthörl et al.<sup>8</sup> have used eq 19 to calculate the modulated charge and hence the photocapacitance of a dye-sensitized electrode. It is important to note here that their approach assumes that  $\eta(U_{\text{photo}}) = 1$ . In the present paper, we show that the measured photocapacitance is smaller than the value calculated assuming  $\eta(U_{\text{photo}}) = 1$ . In fact, under the illumination conditions used in the present experiments,  $\eta(U_{\text{photo}})$  was found to be 0.3, showing that the back reaction of electrons with  $\text{D}^+$  cannot be neglected at open circuit.

### Intensity-Modulated Photocurrent Spectroscopy (IMPS).

Analytical IMPS expressions for the case of diffusional electron transport and kinetically limited extraction have been derived previously.<sup>7</sup> It is important to note that the theoretical treatment is not limited to diffusion-controlled extraction; it includes the rate constant,  $k_{\text{ext}}$ , for electron transfer from the  $\text{TiO}_2$  to the  $\text{SnO}_2$  substrate as a variable, and solutions for the excess electron density profiles can therefore be obtained for the open-circuit case, when  $k_{\text{ext}}$  becomes zero (cf. Supporting Information). The treatment also includes consideration of the situation where electrons are trapped at a set of levels that are located at the same energy. In both cases, integration of the electron-density profiles for short-circuit and open-circuit conditions yields the total modulated charge densities as a function of modulation frequency. In the limit of homogeneous illumination at open circuit, the expressions for the free and trapped electron densities become identical to those derived by Schlichthörl et al.<sup>8</sup> The IMPS response appears in the lower quadrant (real positive, negative imaginary) of the complex plane as a result of the transit delay associated with the collection of electrons by diffusion. Values of the apparent diffusion coefficient are obtained by fitting the experimental IMPS plot to the expressions given in ref 7. A convenient order of magnitude estimate of the diffusion coefficient can be obtained by noting that the minimum in the IMPS response occurs at an angular frequency corresponding to the inverse of the mean transit time for electrons diffusing to the substrate.

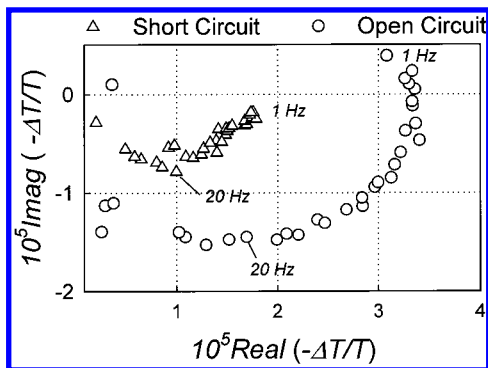
### Experimental Section

**Materials.** Dye-sensitized  $\text{TiO}_2$  cells were prepared following the methods described by Nazeeruddin et al.<sup>2</sup> The thickness of the  $\text{TiO}_2$  layer was limited to  $2.7 \mu\text{m}$  in order to permit reliable transmission measurements in the near-IR and to minimize unwanted effects of the RC time constant.<sup>7</sup> The electrolyte was composed of methyl-hexylimidazolium iodide (MHImI), iodine, *tert*-butylpyridine, and acetonitrile. MHImI was prepared according to the method given by Papageorgiou et al.<sup>12</sup> Iodine was purchased from Fluka and used without further purification. Acetonitrile and *tert*-butylpyridine were purchased from Fluka and distilled under nitrogen before use.

Nanoporous  $\text{TiO}_2$  layers were prepared from a colloidal  $\text{TiO}_2$  dispersion obtained by hydrolysis of titanium isopropoxide. The preparation method of O'Regan and Grätzel<sup>1</sup> was modified to yield only the anatase modification. The colloidal dispersions were dried and the powders ground with pine oil until a smooth dispersion was obtained, which was then screen printed on conducting glass plate glass (TEC 8, fluorine-doped  $\text{SnO}_2$  on 3 mm float glass purchased from Libby Owens Ford). The film was fired in air at  $450^\circ\text{C}$ . The  $\text{TiO}_2$  films were dipped in a  $3 \times 10^{-4} \text{ M}$  solution of the ruthenium dye *cis*-di(thiocyanato)-*N,N*-bis(2,2'-dicarboxylate)ruthenium(II) in ethanol for 2 h. A sandwich cell was prepared with a second transparent platinum-modified conductive glass plate, and both plates were glued together with a transparent poly(ethylene) (PE) hot melt. Electrolyte was introduced through holes drilled in the back electrode, and these were subsequently sealed with microscope cover plates and PE hot melt.

**Apparatus.** The cell was illuminated with the 514 nm line of an argon-ion laser. The intensity of the laser beam was modulated using an Isomet acousto-optic modulator driven by a Solartron 1250 frequency response analyzer in an arrangement that has been described elsewhere.<sup>13</sup> The maximum incident power was 14 mW, and the peak to peak modulation depth was 18%. The laser beam was expanded to illuminate an area of





**Figure 1.** Complex plane plots of the photomodulated transmittance ( $\Delta T/T$ ) response of the dye-sensitized cell showing the accumulation of electrons under conditions of optical injection. Excitation wavelength 514 nm. Detection wavelength 940 nm. See text for further details. (○) Open-circuit response. (●) Closed-circuit response. Note that the characteristic relaxation frequency,  $\omega_{\min}$ , is the same in both plots.

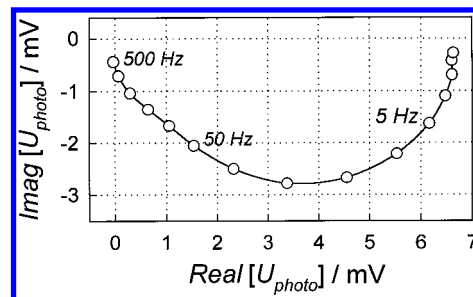
$0.8 \text{ cm}^2$ . The short-circuit current of the cell was measured and used to calculate the photocurrent conversion efficiency (defined as the ratio of electron flux to the incident photon flux, corrected for reflection). The conversion efficiency of 0.31 obtained in this way agreed closely with the value calculated from the measured absorbance of the cell at 514 nm by assuming that the quantum efficiency for electron injection ( $\eta(V=0)$ ) is unity, i.e., no back reaction of electrons with the oxidized dye occurs at short circuit. An identical value of 0.31 for the photocurrent conversion efficiency was calculated from the low-frequency intercept of the modulated photocurrent response.

For the short-circuit photocurrent and modulated transmittance measurements, the voltage of the cell was controlled by a potentiostat operating in two-electrode mode. The cell was illuminated from the substrate side, and the periodic components of the cell photocurrent or transmittance were measured by the frequency response analyzer. Photovoltage measurements were made by connecting the cell to the frequency response analyzer via a high-impedance low-noise preamplifier (Stanford model SR560). Open-circuit photomodulated transmittance measurements were performed with no external connections to the cell. The transmittance of the cell was measured at 940 nm using a Kodenshi GaAs (OPE5594) light-emitting diode (LED) source and Sharp silicon (PD481PI) diode detector with a built-in IR filter that eliminated stray light from the laser beam. The IR wavelength was chosen to lie beyond the absorption bands of the dye and of  $\text{I}_3^-$ . The source and detector were mounted slightly off axis relative to the laser beam, so that the transmittance was measured in the illuminated area. The measured photomodulated transmittance signal  $\Delta T$  was divided by the dc transmittance  $T$  to give the dimensionless complex quantity  $\Delta T/T$ , which was plotted in the complex plane.

Impedance measurements were made under white light illumination using a Solartron 1286 interface and a Solartron 250 frequency response analyzer. The illumination intensity was adjusted to give the same short-circuit dc photocurrent density as that measured in the photomodulated transmittance measurements, and the impedance was measured by perturbing the cell about its open-circuit voltage (typically  $V_{\text{oc}} = 0.65 \text{ V}$ ).

## Results and Discussion

**Calculation of the Optical Absorption Cross Section of Electrons.** Figure 1 shows the normalized photomodulated near-IR transmittance ( $\Delta T/T$ ) responses measured under open- and short-circuit conditions, respectively. The short-circuit dc photocurrent density was  $1.8 \text{ mA cm}^{-2}$ , and the low-frequency limit



**Figure 2.** Intensity-modulated photovoltage response of the dye-sensitized  $\text{TiO}_2$  cell under the same illumination conditions as those used in Figure 1. Note that the characteristic frequency  $\omega_{\min}$  is the same as that seen in the  $\Delta T/T$  responses.

of the ac photocurrent density was  $0.3 \text{ mA cm}^{-2}$ . The dc open-circuit voltage was 0.63 V, and the low-frequency limit of the modulated photovoltage was 6.6 mV (cf. Figure 2).

The  $\Delta T/T$  plots are semicircular as expected. They can be compared with the theoretical plots shown in the Supporting Information for the trap free case and for the case of a set of electron traps. The minima in both experimental plots occur close to 20 Hz. As expected, the low-frequency limit of  $\Delta T/T$  is smaller under short-circuit conditions because electrons are extracted at the substrate contact, whereas at open circuit they can relax only by back reaction with  $\text{I}_3^-$  or with  $\text{D}^+$ . It would have been interesting to obtain  $\Delta T/T$  plots for lower excitation densities, but this was not possible due to signal/noise limitations.

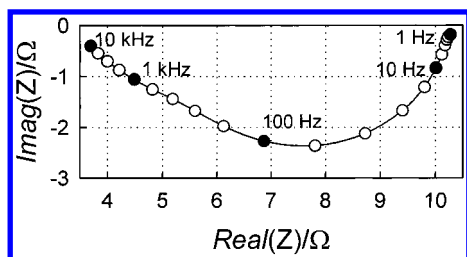
Figure 2 illustrates the intensity-modulated photovoltage response measured under the same illumination conditions as those used for the photomodulated transmittance. It can be seen that the minima in the photovoltage and open-circuit transmittance plots occur at the same frequency (20 Hz). The low-frequency intercept of the  $\Delta T/T$  plot on the real axis is related to the low-frequency limit of the total modulated charge by

$$-\frac{\Delta T}{T}|_{\omega \rightarrow 0} = \frac{\delta Q_{\text{tot}} \sigma(\lambda)}{q} = \frac{C_{\text{tot}} \sigma(\lambda) \delta U_{\text{photo}}}{q} \quad (21)$$

where  $\sigma(\lambda)$  is a weighted-average absorption cross section for free and trapped electrons,  $\delta Q_{\text{tot}}$  is the low-frequency limit of the total modulated charge per unit area,  $C_{\text{tot}}$  is the total capacitance ( $C_{\text{cb}} + C_{\text{t}}$ ), and  $\delta U_{\text{photo}}$  is the low-frequency limit of the modulated photovoltage.

The total capacitance derived from impedance measurements at open circuit at the same illumination level is  $1.12 \times 10^{-4} \text{ F cm}^{-2}$  (details of the impedance response of the dye-sensitized cell are given in the next section). The weighted-average optical absorption cross section  $\sigma(\lambda)$  can, therefore, be found from the data shown in Figures 1 and 2 using eq 21. The value of  $7.3 \times 10^{-18} \text{ cm}^2$  at 940 nm found in this way is in good agreement with the optical absorption cross sections calculated for electrons in  $\text{TiO}_2$  by Rothenberger et al.<sup>9</sup> ( $1.3 \times 10^{-17} \text{ cm}^2$  at 780 nm). Boschloo and Fitzmaurice<sup>10</sup> have measured the absorbance associated with potential-controlled electron accumulation in  $\text{TiO}_2$ . Their work has shown that for lithium electrolytes, the absorption cross section increases with the accumulated charge, providing evidence for the intercalation of lithium ions into  $\text{TiO}_2$ . The optical cross sections calculated from their data lie in the range from  $3 \times 10^{-18}$  to  $1.5 \times 10^{-17} \text{ cm}^2$  at 800 nm. The absorption cross section,  $\sigma_n$ , derived in the present work falls within this range.

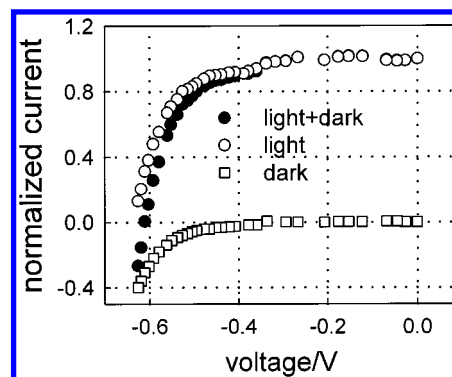
**Calculation of the Net Electron Injection Efficiency at Open Circuit.** To determine the net efficiency for electron



**Figure 3.** Impedance of the dye-sensitized cell under illumination (zero dc current). Electrode area  $3.5 \text{ cm}^2$ . Note that the (constant) illumination conditions were identical to the level used for the  $\Delta T/T$  and photovoltage measurements (Figures 1 and 2). The fitting parameters for the smaller semicircle (counter electrode impedance) are  $R = 1.7 \text{ } \Omega$  and  $C = 9.7 \times 10^{-5} \text{ F}$ . For the larger semicircle (dye-sensitized electrode impedance), the fit gives  $R = 4.8 \text{ } \Omega$  and  $C = 3.8 \times 10^{-4} \text{ F}$ .

injection at open circuit, it is necessary to make an independent measurement of the photocapacitance (cf. eqs 18 and 19). The results of a detailed impedance study will be reported elsewhere.<sup>14</sup> Figure 3 illustrates the impedance response of the cell measured under illumination. The illumination intensity was adjusted to give the same short-circuit dc photocurrent density ( $1.8 \text{ mA cm}^{-2}$ ) as that measured in the photomodulated transmittance and photovoltage measurements. The dc open-circuit voltage was measured as  $0.63 \text{ V}$ . The larger of the two semicircles can be attributed to the parallel combination of the recombination resistance with the photocapacitance  $C_{\text{total}}$ . The smaller semicircle arises from the Faradaic impedance of the  $\text{I}_3^-/\text{I}^-$  reaction at the transparent counter electrode in parallel with the counter electrode capacitance. Analysis of the impedance response gives  $C_{\text{tot}} = 1.12 \times 10^{-4} \text{ F cm}^{-2}$ . The low-frequency limit of the modulated charge can now be calculated by multiplying the measured value of  $C_{\text{total}}$  by the limiting low-frequency photovoltage shown in Figure 2. The value found in this way is  $7.3 \times 10^{-7} \text{ C cm}^{-2}$ . By contrast, the charge calculated from the product  $j_{\text{photo}}\tau_n$  is  $2.4 \times 10^{-6} \text{ C cm}^{-2}$ . The net injection efficiency  $\eta(U_{\text{photo}})$  given by the ratio of the measured modulated charge to the charge calculated from the  $j_{\text{photo}}\tau_n$  (c.f. eq 19) is therefore 0.3. This interesting result suggests that back reaction electrons with  $\text{D}^+$  can contribute significantly to the limitation of the open-circuit voltage in dye-sensitized cells. This conclusion is in agreement with the early work of O'Regan et al.<sup>15</sup> and the more recent work of Haque et al.<sup>11</sup> The latter authors have shown that the rate of decay of the  $\text{D}^+$  state following flash excitation is strongly potential dependent and occurs on a nanosecond time scale at potentials corresponding to  $V_{\text{oc}}$ .

The work of Haque et al.<sup>11</sup> shows that the reaction of electrons with  $\text{D}^+$  under accumulation conditions occurs on a nanosecond time scale. Their data indicate that the half-life for the reaction is reduced to  $100 \text{ ns}$  at a potential that corresponds to an open-circuit potential of  $600 \text{ mV}$ . Haque et al. also studied the rate of the  $\text{D}^+/\text{I}^-$  reaction and found a pseudo-first-order rate lifetime of  $100 \text{ ns}$  for  $0.3 \text{ mol dm}^{-3} \text{ KI}$  in propylene carbonate. It follows that the rates of reaction of  $\text{D}^+$  with electrons and with  $\text{I}^-$  are very similar at the open-circuit voltage, so that  $\eta(U_{\text{photo}})$  should be less than 1. A crude order of magnitude comparison of the rate reaction of electrons and of iodide ions with  $\text{D}^+$  can be made by considering the reactions to be quasi-homogeneous. The concentration of iodide in the cells used in the present study is  $0.5 \text{ mol dm}^{-3}$ . By contrast, the total open-circuit excess electron density estimated from the product  $j_{\text{photo}}(dc)\tau_n\eta(U_{\text{photo}})$  is  $2.7 \times 10^{13} \text{ cm}^{-2}$ , which corresponds to a volume density of electrons of  $1.7 \times 10^{-4} \text{ mol dm}^{-3}$ . Since the diffusion coefficients of electrons and  $\text{I}^-$  ions appear to be of the same



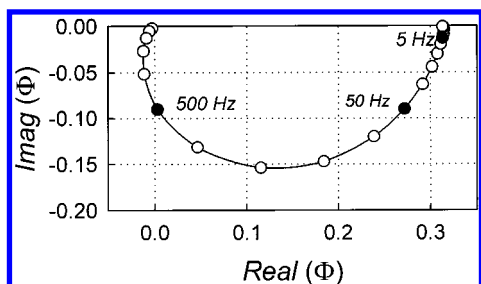
**Figure 4.** dc current-voltage characteristics of the dye-sensitized  $\text{TiO}_2$  cell in the dark and under illumination at the intensity level used for the measurements of  $\Delta T/T$ , IMVS, and IMPS. The photocurrent shown has been calculated from the difference between the current under illumination and in the dark. Note that  $V_{\text{oc}} = 0.61 \text{ V}$  and the net efficiency for electron injection,  $\eta(V_{\text{oc}})$ , = 0.3.

order of magnitude, the upper diffusion-limited second-order rate constants for the reaction of  $\text{D}^+$  with electrons and with iodide ions should be similar. Therefore, in order for electron capture by  $\text{D}^+$  to compete with the regeneration reaction, its rate constant must be  $10^3$  times higher than that of the  $\text{D}^+/\text{I}^-$  reaction. From the data of Haque et al., the second-order rate constant for the  $\text{D}^+/\text{I}^-$  reaction is  $3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The second-order rate constant for the reaction of electrons with  $\text{D}^+$  is, therefore, of the order of  $3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , suggesting that the process is diffusion controlled.

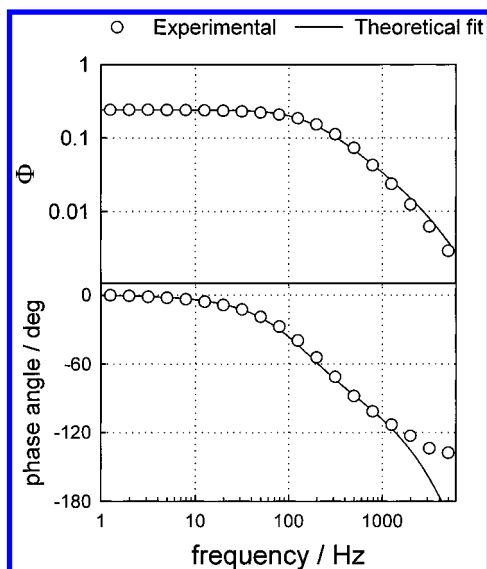
In principle,  $\eta(V)$  can also be obtained from the potential dependence of the photocurrent if it is assumed that the dark and photocurrents are additive. Figure 4 illustrates the potential dependence of the dc photocurrent measured under the same illumination conditions as those used for the modulated transmittance measurements. The net current ( $i_{\text{net}} = i_{\text{dark}} + i_{\text{photo}}$ ) is also shown. At open circuit  $i_{\text{net}} = 0$ , and the ratio of the photocurrents at open and short circuit ( $i_{\text{photo}}(\text{oc})/i_{\text{photo}}(\text{sc})$ ) is equal to  $\eta(V_{\text{oc}})$ . From the figure it can be seen that  $\eta(V_{\text{oc}}) \approx 0.3$ , which is in good agreement with the value calculated from the photovoltage and photocapacitance.

**Analysis of the Frequency Dependence of the Photomodulated Transmittance.** As shown in the Supporting Information, the short-circuit-modulated transmittance response for the trap free case is a semicircle with an  $\omega_{\text{min}}$  value identical to that measured by IMPS. In the short-circuit trap free case, the excess electron density relaxes primarily by transport to the substrate. By contrast, the open-circuit  $\Delta R/R$  response should give a semicircle with the same  $\omega_{\text{min}}$  as that measured by IMVS because the electron concentration can relax only by back reaction with  $\text{I}_3^-$ . Figure 5 illustrates the short-circuit IMPS response of the cell. The response appears in the fourth quadrant (positive real, negative imaginary) of the complex plane as the result of the time delay between the generation and collection of electrons. An order of magnitude estimate of the mean transit time for photogenerated electrons can be obtained from the frequency of the minimum in the complex plane plot:  $\tau_d \approx 1/\omega_{\text{min}} \approx 1 \text{ ms}$ . This approach is approximate of course; analytical treatment of the generation/collection problem allows the electron-diffusion coefficient to be determined by fitting the complete IMPS response.<sup>7</sup>

A surprising feature of the IMPS plot is that it crosses the imaginary axis. This is not expected for illumination from the substrate side.<sup>7</sup> Experiments with strongly absorbed UV illumination of dye-free nanocrystalline  $\text{TiO}_2$  from the substrate side also show this anomaly,<sup>18</sup> which may be associated with



**Figure 5.** Short-circuit IMPS response of the dye-sensitized cell under the same illumination conditions as those used for the  $\Delta T/T$  and IMVS measurements (Figures 1 and 2). The low-frequency intercept can be used to calculate the incident photon flux to electron flux conversion efficiency (in this case 0.31). Note that the characteristic relaxation frequency  $\omega_{\min}$  is much higher in the IMPS response than in the IMVS response because IMPS detects the transit of electrons to the substrate, whereas the other methods detect the (slower) relaxation of the electron density by reaction with  $I_3^-$ .



**Figure 6.** Bode plot of the IMPS response of the dye-sensitized  $TiO_2$  cell. The plot also shows the theoretical response calculated taking the nonhomogeneous dye distribution and the RC time constant of the cell into account. The electron diffusion coefficient obtained by fitting the IMPS response is  $2.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

trapping effects. In the present case, however, the illumination is much more uniform than in the case of the dye-free system, and a recent study of the IMPS response of sensitized  $TiO_2$  cells<sup>16</sup> has shown that the effect arises from nonhomogeneous dye distribution. If the dye does not penetrate uniformly through the film, the electron generation rate in the region close to the substrate may be much lower than in the bulk. This “dead layer” introduces a time delay in the collection of photoinjected electrons that is manifest in an excursion of the IMPS response into the third quadrant of the complex plane at high frequencies. In cells with uniform dye distribution, the IMPS response does not cross the imaginary axis. The effect of nonuniform dye distribution on the IMPS response has been modeled by solving the generation/collection problem for a series of lamina with dye concentrations varying from zero at the substrate to the bulk value at some distance from the surface.<sup>16</sup> Figure 6 compares the Bode plot of the measured IMPS response with a theoretical plot that takes in the reduction in dye loading near the substrate. The theoretical plot also takes into account the phase shift arising at high frequencies from the RC time constant of the cell.<sup>7</sup> It should be noted that the short-circuit IMPS response is insensitive to the electron lifetime since the collection efficiency

is close to unity, i.e.,  $\tau_d \ll \tau_n$ . The electron-diffusion coefficient calculated from the fitting of the IMPS response is  $2.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

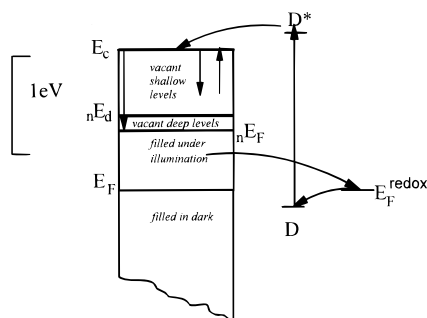
It is clear from the experimental complex plane plots of  $\Delta T/T$  measured at open and short circuit (Figure 1) that the  $\omega_{\min}$  values in the two cases are essentially identical to  $\omega_{\min}$  for the IMVS response. It follows that the short-circuit  $\Delta T/T$  response does not detect the relaxation of electrons by diffusion to the substrate. This must mean that most of the optically detected electrons are trapped at levels sufficiently deep that thermal release to the conduction band is slower than reaction with  $I_3^-$ . The surface area/volume ratio in nanocrystalline films is very high, and it therefore seems probable that energy levels at or near the surface of the  $TiO_2$  crystallites are responsible for trapping and back reaction of electrons. Electrons captured by these surface levels could be transferred subsequently to  $I_3^-$ , whereas electrons trapped in the bulk would have to be released first to the conduction band before they could recombine.

#### Trapping and Back Reaction in the Dye-Sensitized Cell.

The effect of electron trapping on the IMPS<sup>7</sup> and IMVS<sup>8</sup> response of dye-sensitized  $TiO_2$  solar cells has been treated in a first approximation using a single-level model, but a more realistic approach is to consider that traps are distributed in energy throughout the band gap. In the dark at open circuit, the Fermi level,  $E_F$  (and hence the trap occupancy), in the  $TiO_2$  particles is determined by electron exchange with the  $I_3^-/I_3^{2-}$  redox system. Under illumination, the trap occupancy is determined by the position of the quasi Fermi level for electrons  $nE_F$ , which is defined by eq 4. The competition between thermal release of electrons from traps and back reaction with  $I_3^-$  (effectively recombination) can be used to define an electron demarcation level  $nE_d$  that is analogous to the demarcation level for electron-hole recombination in semiconductors.<sup>17</sup> Electrons located in levels below  $nE_d$  will recombine with  $I_3^-$  before they can be released by thermal excitation. The converse is true for electrons in shallower levels: they will be released before they recombine with  $I_3^-$  and therefore contribute to the current under short-circuit conditions. The relaxation time for electrons above  $nE_d$  will be determined by trapping/detrapping and transport, and consequently, the collection process and hence the IMPS response can be described by an effective diffusion coefficient that determines  $\tau_d$ . The position of the demarcation level,  $nE_d$ , relative to the conduction band is defined by the equality

$$\frac{1}{\tau_t} = k_{\text{release}} = \nu e^{-\frac{(E_c - E_d)}{kT}} \quad (22)$$

where  $\tau_t$  is the recombination lifetime of the electron in the trap,  $k_{\text{release}}$  is the rate constant for thermal release from traps located at the demarcation level, and  $\nu$  is a preexponential factor, Figure 7. For example, for  $\tau_n = 10^{-2} \text{ s}$  and  $\nu = 10^{12} \text{ s}^{-1}$ , eq 22 shows that  $(E_c - nE_d) \approx 0.6 \text{ eV}$ . The fact that the steady-state collection efficiency for photoinjected electrons approaches 100% under short-circuit conditions places constraints on the rate at which electrons are trapped and recombine at deep levels. The integrated trapping rate ( $\text{s}^{-1}$ ) for these centers must be smaller than the inverse of the transit time for electrons generated furthest away from the collector electrode. An order of magnitude estimate of this transit time for a film of thickness  $d$  is given by  $d^2/D$ . For  $d = 2.7 \mu\text{m}$  and  $D_n = 2.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , the time required for an electron to reach the substrate from the other side of the film is 2.6 ms. The trapping lifetime must be at least 10 times longer than this, so that an upper limit to the trapping rate is  $10 \text{ s}^{-1}$ .



**Figure 7.** Energy-level diagram illustrating the equilibrium Fermi level ( $E_F$ ), the electron quasi Fermi level under illumination ( ${}_nE_F$ ), and the electron demarcation level ( ${}_nE_d$ ) defined by the competition between thermal release of electrons from traps and recombination with  $I_3^-$ . (a) Open-circuit conditions. (b) Short-circuit conditions.

## Conclusions

Measurement of the periodic component of the electron absorbance in dye-sensitized cells illuminated by an intensity-modulated laser has revealed that the majority of electrons are trapped at deep levels where they make no contribution to the measured photocurrent. Instead, they react slowly with  $I_3^-$ , so that their lifetime is a measure of the rate constant for the back reaction via surface states. At the intensities used in these experiments, the electron quasi-Fermi level over a major part of the film lies below the demarcation level that defines whether reaction with  $I_3^-$  or thermal release to the conduction band is the dominant relaxation process. The electrons collected under short-circuit conditions may be captured briefly by shallow traps and released again before reaction with  $I_3^-$  can occur. The electron transit time will be increased by the sequence of capture and release events, so that the effective diffusion coefficient will be considerably lower than the true diffusion coefficient for free electrons. The observed intensity dependence of  $D_n$  can be explained by the upward movement of the quasi-Fermi level through the distribution of shallow traps.

Efficient operation of the dye-sensitized cell places constraints on the maximum rate at which carriers are trapped by deep traps that act as recombination centers by localizing the electrons long enough to permit the back reaction with  $I_3^-$  to take place. The open-circuit voltage is limited partly by back reaction of electrons with the oxidized state of the dye. Under open-circuit

conditions, this reduces the net injection efficiency to around 30%.

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**Supporting Information Available:** Derivations of expressions for the light-modulated electron density, complex plane plots of the frequency dependence of the response for trapped and free electrons, and derivation of expression for the net electron injection efficiency (19 pages). Ordering information is given on any current masthead page.

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