

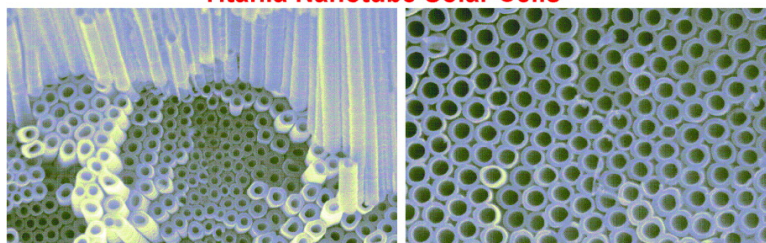
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Titania Nanotube Solar Cells



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Dye-Sensitized Solar Cells Based on Oriented TiO₂ Nanotube Arrays: Transport, Trapping, and Transfer of Electrons

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Abstract: Dye-sensitized solar cells fabricated using ordered arrays of titania nanotubes (tube lengths 5, 10, and 20 μm) grown on titanium have been characterized by a range of experimental methods. The collection efficiency for photoinjected electrons in the cells is close to 100% under short circuit conditions, even for a 20 μm thick nanotube array. Transport, trapping, and back transfer of electrons in the nanotube cells have been studied in detail by a range of complementary experimental techniques. Analysis of the experimental results has shown that the electron diffusion length (which depends on the diffusion coefficient and lifetime of the photoinjected electrons) is of the order of 100 μm in the titania nanotube cells. This is consistent with the observation that the collection efficiency for electrons is close to 100%, even for the thickest (20 μm) nanotube films used in the study. The study revealed a substantial discrepancy between the shapes of the electron trap distributions measured experimentally using charge extraction techniques and those inferred indirectly from transient current and voltage measurements. The discrepancy is resolved by introduction of a numerical factor to account for non-ideal thermodynamic behavior of free electrons in the nanostructured titania.

Introduction

Dye-sensitized solar cells (DSC)^{1,2} have continued to excite interest since the original work of O'Regan and Grätzel,³ and AM 1.5 solar conversion efficiencies of 11% have been reported for optimized devices.⁴ Normally, the light-harvesting component of the DSC is a ruthenium bipyridyl dye chemisorbed on the high internal surface area of a mesoporous film of nanocrystalline titanium dioxide. Photoexcitation of the dye leads to rapid electron injection into the TiO₂, and the dye is then regenerated from its oxidized form by electron transfer from iodide ions in the electrolyte that permeates the porous network of interconnected TiO₂ particles. The tri-iodide ions formed in the dye regeneration process diffuse through the liquid phase to the cathode, where they are reduced back to iodide ions to complete the cycle. When current is drawn from the cell, injected electrons move toward the anode contact either by hopping between sites (the hopping model) or by a random walk process in which the electrons spend some time immobilized in trap sites from which they are excited thermally back to the conduction band (the multiple trapping model). In either model, the electrons may be localized near the surface or in the bulk, and during their transit they may be lost by transfer across the

solid/liquid interface to I₃⁻ ions. The efficiency of collection of the photoinjected electrons, which is a critical factor in device performance, is determined by competition between electron transport to the anode and electron transfer to I₃⁻ ions in the electrolyte. A key parameter in this context is the electron diffusion length, $L_n = (D_0\tau_0)^{1/2}$, which is determined by the free electron diffusion coefficient D_0 and the free electron lifetime τ_0 . Efficient cells are characterized by L_n values that considerably exceed the TiO₂ film thickness.

The excellent light-harvesting efficiency achieved in the DSC using only a monolayer of adsorbed dye is due to the high surface area of the porous nanocrystalline TiO₂ layer, which is usually made by sintering a paste consisting of colloidal oxide particles with sizes in the 10–30 nm range. Oriented TiO₂ nanotube arrays prepared by anodization of titanium metal^{5–9} offer an attractive alternative to films fabricated by the sol–gel route because they combine high surface area with well-defined pore geometry.^{10–13} The vertical pore geometry of the nanotubes appears to be more suitable than the conventional random pore

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network for fabrication of solid-state cells utilizing polymeric sensitizer materials,¹⁴ and it has been reported that nanotube arrays give enhanced light scattering and improved collection efficiencies compared to conventional sol-gel-derived TiO₂ films of the same thickness.¹⁵ The objective of the present work was to achieve comprehensive characterization of DSC based on well-defined titania nanotube arrays using a range of techniques to probe injection efficiency, electron transport, trapping, and electron transfer to solution redox species.

A multiple trapping model has been used to explain why in dye-sensitized solar cells the electron diffusion coefficient D_n appears to increase strongly with light intensity, whereas the electron lifetime τ_n decreases in such a way that the product $D_n\tau_n$ remains almost constant over many orders of light intensity.^{16,17} However, in spite of the success of the multiple trapping model, the identity of the trapping states still remains obscure: possible origins include defect sites in the bulk or surface of the oxide nanoparticles as well as Coulombic interactions of electrons with ions in the electrolyte. The present study of nanotube dye-sensitized cells has revealed that the application of the multiple trapping model of electron transport in dye-sensitized cells leads to apparent inconsistencies that can be resolved by introduction of an empirical factor to account for non-ideal thermodynamic behavior of electrons in nanoscale systems consisting of interpenetrating solid-state and electrolyte phases. The results obtained in this study suggest that realistic microscopic modeling is required to achieve a better understanding of the interactions between electrons, ions, and solvent dipoles in these systems.

Experimental Section

Titania nanotube (TNT) samples were prepared by anodization of 2.5 × 1.5 cm × 125 μm pieces of titanium foil (99.6% purity, Advent) in a nonaqueous fluoride-containing electrolyte.¹⁸ The foil samples were sonicated successively in acetone and methanol and then rinsed with deionized water before drying in a nitrogen stream. The electrolyte, 0.2 M HF in ethylene glycol, was prepared from ethylene glycol containing less than 0.2 wt % H₂O (Sigma-Aldrich) and 48% HF (Merck). All anodizations were carried out at 25 °C using a two-electrode electrochemical cell with a platinum gauze counter electrode. The titanium foil samples were contacted with a copper back-plate and pressed against an O-ring in the cell wall, leaving 1 cm² exposed to the electrolyte. Anodization was performed using a high-voltage potentiostat (Jaisle IMP 88 PC) and a digital multimeter (Keithley 2000) interfaced to a computer. A voltage of 120 V was applied for 0.25, 0.5, 1, and 2 h to obtain 1, 5, 10, and 20 μm thick nanotube layers, respectively. The anodized samples were rinsed with deionized water and then dried in a nitrogen stream. A Hitachi FE-SEM S4800 field-emission scanning electron microscope was used for morphological charac-

terization of the samples. The nanotube length was obtained from SEM cross-sections after scratching through the nanotube layer with a sharp metallic tip. Details of XRD and XPS characterization are given in the Supporting Information.

The TNT samples were annealed in air at 450 °C for 30 min and then cooled to 80 °C before being immersed overnight in a 0.5 mM solution of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N719) in 1:1 acetonitrile/*tert*-butanol. The sensitized TNT layers were sandwiched together with transparent platinized counter electrodes fabricated from fluorine-doped tin oxide coated glass (TEC15, Hartford Glass). A hot melt polymer (Solaronix SX1170-25, 25 μm) was used as an adhesive spacer. The electrolyte, which contained 0.6 M butyl-methyl-imidazolium iodide, 0.03 M iodine, 0.5 M *tert*-butylpyridine, and 0.1 M guanidinium thiocyanate in acetonitrile/valeronitrile, 85:15 v/v, was introduced into the space between the electrodes through small holes drilled in the counter electrodes.

To establish the dye-loading of the sensitized TNT layers, samples sensitized with N719 were placed into a 10 mM solution of KOH (pH 13) to desorb the dye. The concentration of desorbed dye determined by UV-vis spectroscopy was used to calculate the amount of dye present in the sensitized TNT samples.

Incident photon-to-current conversion efficiency (IPCE) spectra of the cells were measured with a spectral resolution of 8 nm using monochromatic light provided by a xenon lamp and grating monochromator. The incident photon flux was measured with a calibrated silicon photodiode. The current-voltage characteristics of the cells were measured under simulated AM 1.5 illumination (100 mW cm⁻²) provided by a solar simulator (1 kW xenon with AM 1.5 filter, Müller) calibrated using a GaAs solar cell. Photovoltage decay measurements were carried out using a high-power green light-emitting diode (LED, λ = 530 nm) and an Autolab PGSTAT 12 potentiostat. The cell was illuminated under open-circuit conditions until a steady photovoltage was achieved. The LED was then switched off, and the photovoltage decay transient was recorded. Intensity-modulated photovoltage and photocurrent spectroscopy (IMVS and IMPS) measurements were carried out using modulated light (10% modulation depth) from a high-power green LED (λ = 530 nm). The modulation frequency was controlled by a Solartron 1260 frequency response analyzer (FRA), and the photocurrent or photovoltage of the cell was measured using a Solartron 1286 electrochemical interface and fed back into the FRA for analysis. The light-intensity incident on the cell was adjusted using neutral density filters (Schott NG) and measured using a calibrated silicon photodiode.

Three methodologies were employed for charge extraction experiments. The first method, which has been described elsewhere,^{19,20} involves determining the trapped electronic charge at a series of intervals along the open circuit photovoltage decay characteristic by short circuiting the cell and integrating the current. The second method, the dark charge extraction technique, involved applying a voltage across the cell in the dark using an Autolab PGSTAT12 equipped with an analogue integrator. Once a constant current was reached, the applied bias was switched to 0 V and the resultant current spike was integrated for 300 s to obtain the charge stored in the cell at a given bias voltage. The experiment was repeated for a range of voltages to obtain the trapped electronic charge as a function of the externally imposed bias voltage. The third method, which utilized a Solartron 1286 autoranging electrochemical interface and Corware software, involved illuminating the cell under short circuit conditions at different light intensities and integrating (300 s) the transient current that flowed after the illumination was switched off. When analyzing data obtained from

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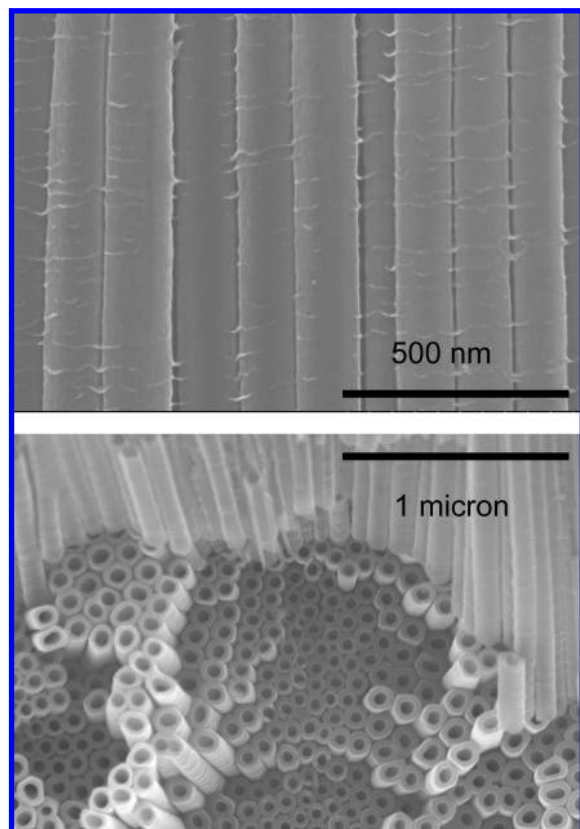


Figure 1. Cross-section and oblique SEM images of titanium nanotube (TNT) arrays used to fabricate dye-sensitized cells.

the dark charge extraction technique, a correction was made for the iR drop across the series resistance of the cell at high applied forward bias voltages that give rise to significant dark currents. The series resistance of the cell was obtained by impedance spectroscopy. For bias voltages below about 0.5 V the iR drop was <1 mV.

Results and Discussion

Structural Characterization and Dye Loading. Figure 1 shows representative cross-sectional and oblique view SEM images of titania nanotube arrays grown under conditions identical to those used to fabricate the solar cells used in this study. Detailed analysis of cross-sectional and face-on SEM micrographs revealed that the only geometric parameter that changes significantly from sample to sample is the tube length. Wall thickness, tube diameter, and tube packing are relatively constant across all samples. In agreement with Zhu et al.,¹⁵ it was observed that some bundling together of nanotubes occurs near the outer surface of the thicker samples.

The XRD patterns of as-prepared and annealed TNT samples (Supporting Information) show that as-grown nanotube arrays are almost entirely amorphous, whereas after annealing they consist of anatase. The average crystallite size was estimated by TEM to be 23 nm. XPS measurements showed that fluorine present in the as-grown films was removed during the annealing process (Supporting Information).

The total internal surface area of the inside and outside of the nanotubes, A_i , and the occupied volume, V , of the TNT layers were calculated using the expressions

$$A_i = \pi(D_i + D_o)lNA_p \quad (1)$$

$$V = \pi \left[\left(\frac{D_o}{2} \right)^2 - \left(\frac{D_i}{2} \right)^2 \right] lNA_p \quad (2)$$

Table 1. Dye Loading of TNT Layers of Varying Thickness

layer thickness (μm)	dye concentration (mM)	α (cm^{-1}) at 530 nm
1	87	2190
5	80	2010
10	79	1990
20	69	1740

where D_i is the inner diameter of the tubes, D_o is the outer diameter, l is the tube length, N is the number of tubes per unit projected area, and A_p is the projected area of the layer. D_i (90–120 nm), D_o (130–150 nm), and l and N were all obtained from evaluation of SEM micrographs. The specific surface area of the film is given by

$$A_s = \frac{A_i}{V\rho} \quad (3)$$

where ρ is the density of anatase. A specific surface area of $25 \pm 4 \text{ m}^2 \text{ g}^{-1}$ was obtained using average parameters representative of the TNT layers used in this study. A BET study on similar TNT layers by Grimes et al.⁹ gave a specific surface area of $38 \text{ m}^2 \text{ g}^{-1}$. Assuming the TNT layers were comparable with those used in the present work, the surface roughness of the tube walls can be estimated as the ratio of the BET specific surface area and the calculated specific surface area. This calculation yields a surface roughness factor of around 1.5.

The surface area available for dye adsorption was also investigated by measuring the loading of N719 by dye-desorption experiments. The concentrations of dye in the films and the corresponding absorption coefficients at 530 nm are shown in Table 1.

The dye concentration in the films expected for monolayer coverage of the inside and outside of the nanotubes (calculated from the mean nanotube dimensions assuming a dye molecule footprint of 136 \AA^2 and smooth tube walls) is 58 mM. If one assumes that the experimental dye loading values correspond to monolayer coverage, a surface roughness factor in the range 1.2–1.5 is obtained, which is consistent with the surface roughness factor from the calculation based on BET measurements.⁹

IPCE Spectra and Power Conversion Efficiencies. Figure 2 shows the IPCE spectra of devices fabricated using 1, 5, 10, and 20 μm thick TNT layers. A peak IPCE close to 90% was obtained for the device fabricated using a 20 μm thick TNT layer. To compare the measured IPCE spectra with values calculated from the dye loading of the TNT layers (cf. Table 1) and the wavelength dependent molar absorption coefficient of the dye in solution, the overall efficiency for injection and collection of electrons was taken to be unity. Light scattering by the TNT layers¹⁵ was not considered. Absorption losses due to the platinumized cathode (10%) and the tri-iodide electrolyte were quantified by separate transmittance measurements and incorporated into the calculation of the IPCE. It can be seen from Figure 2 that agreement between the calculated and measured IPCE spectra for the 5, 10, and 20 μm films is generally satisfactory, although the IPCE at longer wavelengths is somewhat lower than the predicted value, which may indicate a blue shift of the absorption spectrum of the adsorbed dye or lower injection efficiency. Figure 2 also includes the IPCE spectrum of the thickest TNT device calculated without correction for absorption losses due to the 20 μm thick layer of tri-iodide electrolyte. The calculation gives an indication of the substantial losses in the short wavelength region due to the electrolyte.

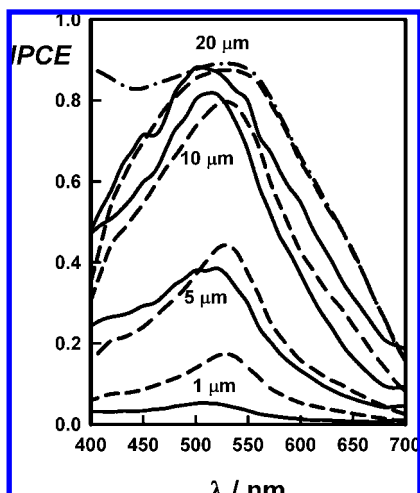


Figure 2. Comparison of measured IPCE spectra (continuous lines) with spectra predicted from the dye loading taking into account absorption losses due to the platinized cathode and the tri-iodide electrolyte (broken lines). The IPCE spectrum calculated for the 20 μm TNT layer cell from the dye coverage without including the absorption loss due to I_3^- is also shown (dot-dash line).

Table 2. Comparison of Measured Short Circuit Current Densities (AM 1.5, 1 sun) with Values Calculated from the IPCE Spectra

thickness (μm)	j_{sc} (mA cm^{-2})	
	predicted	measured
5	3.4	3.2
10	7.6	7.0
20	9.6	9.0

The good agreement between measured and calculated IPCE spectra in the case of the 20 μm film indicates that the collection of electrons is efficient, even when the penetration depth of the light is small relative to the film thickness. This means that the electron diffusion length must be significantly greater than the film thickness. By contrast, it has been reported that DSC fabricated using pressed nanocrystalline TiO₂ evidently have much lower electron diffusion lengths, leading to the loss of response in the blue part of the IPCE spectrum when the cells are illuminated from the electrolyte side.³¹

The current voltage characteristics of three cells were measured under simulated AM 1.5, 1 sun illumination (I_V characteristics are given in the Supporting Information). A power conversion efficiency of 2.61% was achieved for the 20 μm cell. The short-circuit currents of the devices can be predicted by convoluting the AM 1.5 irradiance spectrum and the IPCE spectra. In principle, the calculated and experimental results should agree provided that the current response is a linear function of light intensity (IPCE measurements are performed using much lower photon fluxes than those corresponding to 1 sun). Table 2 shows that the predicted and measured AM 1.5 short-circuit currents agree to better than 10% (the difference between predicted and measured currents is attributed to spectral mismatch³² in the simulated AM 1.5 spectrum).

Intensity Dependence of the Photovoltage. The open circuit photovoltage V_{oc} was measured as a function of the incident photon flux I_0 for all three nanotube cells (Supporting Information). In an ideal DSC, the free electron concentration n_c is determined by nondegenerate (Boltzmann) statistics and should vary as $\exp[V_{\text{oc}}/(k_B T)]$. Because the rates of electron injection and transfer to I_3^- must be equal at open circuit, and assuming

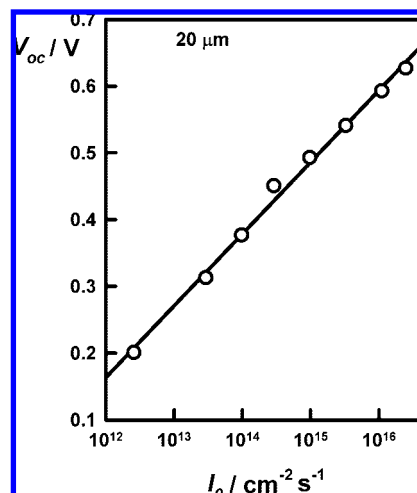


Figure 3. Intensity dependence of the photovoltage for 20 μm nanotube cell (illumination wavelength 530 nm) showing non-ideal diode behavior ($m = 1.9$). I_0 is the incident photon flux.

that the electron lifetime is independent of n_c , it follows that the slope of the V_{oc} versus $\log_{10}(I_0)$ plot is $k_B T/2.303q = 58$ mV/decade at 293 K. In non-ideal cells, the slope is $m k_B T/2.303q$, where m is a non-ideality factor. The slope of the semilogarithmic plot shown in Figure 3 for the 20 μm cell is close to 110 mV/decade, giving $m = 1.9$, which indicates that the nanotube cell is considerably less ideal than cells fabricated in our laboratory using commercial colloidal TiO₂ pastes (Solaronix and Dyesol), which typically give slopes between 70 and 85 mV/decade. Preliminary work has shown that the value of m for the nanotube cells depends on electrolyte composition, with significantly lower values ($m = 1.25$) being observed for ionic liquid electrolytes.²¹

A possible explanation of the non-ideal intensity dependence of the photovoltage is that it could be the consequence of electron transfer via surface states.²² However, as we show in this article, the intensity dependence of the quasi-Fermi level is also non-ideal under short circuit conditions, where electron transfer to I_3^- ions can be neglected. This non-ideality has important consequences for the analysis of electron transport in the nanotube cells.

IMPS and IMVS Measurements To Determine D_n and τ_n . Normally, the concepts of electron diffusion coefficient and electron lifetime are easily understood. However, in the case of the DSC, the time-dependent electron densities are affected by trapping and detrapping as well as by transport and electron transfer to redox species. As a consequence, measured apparent electron diffusion coefficients D_n and electron lifetimes τ_n differ substantially from the free electron values D_0 and τ_0 and are dependent on the (intensity dependent) trap occupation level.^{1,23} Under practical operating conditions, $D_n \ll D_0$ and $\tau_n \gg \tau_0$.

IMPS measurements were analyzed to obtain an effective diffusion coefficient D_n by fitting the frequency-dependent response using the analytical expression for the IMPS response given originally by Dloczik et al.²⁴ This expression does not take trapping/detrapping into account, and it is based on the assumption that the apparent electron diffusion coefficient D_n

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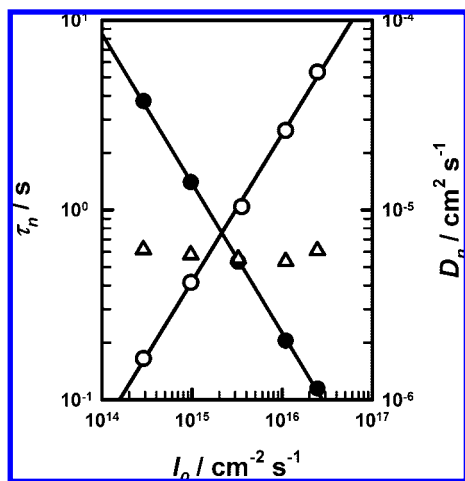


Figure 4. Intensity dependence of apparent electron diffusion coefficient (open circles) and electron lifetime (closed circles) for 20 μm nanotube cell. Note that the $D_n\tau_n$ product (triangles, right-hand y scale) is almost independent of illumination intensity.

is constant throughout the film. In fact, D_n varies with distance as a consequence of the fact that under short circuit conditions the free-electron density—and hence the electron QFL and the corresponding trap occupancy—vary with distance, falling steeply close to the anode. At first sight, this appears to present a problem for the interpretation of experimental IMPS data because the analytical solution is no longer valid (the breakdown of Fick's laws of diffusion under conditions where the diffusion coefficient varies with distance²⁵ is discussed in the Supporting Information). However, it can be assumed that the diffusion coefficient of *free* electrons is independent of position, so that the IMPS response with trapping/detrapping can be obtained numerically as described in the Supporting Information. The comparison of the IMPS responses calculated using the full numerical solution and the analytical (constant D_n) solution demonstrate that the analytical expression can be used to derive an effective D_n that is entirely adequate for estimation of the electron diffusion length, which was one of the objectives of the present work. The modeling also shows that the D_n values obtained using the simple analytical (constant D_n) solution are consistent with the value predicted using a mean QFL corresponding to averaging of the total electron density across the film.

The parameters used to fit the experimental IMPS response to the analytical expression were the absorption coefficient α (calculated from dye loading, Table 1) and the thickness of the TNT film. The effective electron lifetime, τ_n , was derived as a function of illumination intensity (and hence of the photovoltage) from the IMVS responses.

Figure 4 shows that the intensity dependences of D_n and τ_n balance in such a way that the product $D_n\tau_n$ is almost independent of intensity, as reported elsewhere.^{17,26} This behavior provides a strong indication that the rate of change of average free-electron density with illumination intensity is identical under open circuit and short conditions. Because the

solution of the continuity equation under short circuit conditions predicts that the local free-electron density should scale linearly with intensity (Supporting Information), we conclude from Figure 4 that the free-electron density at open circuit must also scale linearly with intensity. This effectively rules out electron transfer to I_3^- via surface states as an explanation of the non-ideal photovoltage behavior in Figure 3 because this is expected to lead to a nonlinear intensity dependence of the free electron concentration.

It would be tempting to conclude that the electron diffusion length can be obtained directly from Figure 4 using the relationship $L_n = (D_n\tau_n)^{1/2}$. This gives $L_n = 24 \mu\text{m}$, which is close to the film thickness. This value is not consistent with the high IPCE observed (generally one requires L_n to be 3 times the film thickness for 98% collection efficiency). However, as we have pointed out elsewhere, this approach is flawed since in order to calculate the correct value of L_n , it is necessary to take pairs of D_n and τ_n measured at the same value of the quasi-Fermi level.^{1,27} Because it is well established that the average quasi Fermi level in a DSC is considerably lower under short circuit conditions than under open circuit conditions,^{28,29} use of the $D_n\tau_n$ product in Figure 4 leads to substantial underestimation of L_n . This problem can be overcome if D_n and τ_n can be obtained as a function of the QFL rather than light intensity. The next section shows how this can be done.

Using the Trapped Electron Charge To Calculate the Relative QFL Positions at Open Circuit and Short Circuit. Boschloo et al.^{29,30} have determined the mean QFL under steady-state short circuit conditions by simultaneously switching off the illumination and open circuiting the cell. In these experiments, relaxation of the short circuit density profiles of free and trapped electrons at open circuit following interruption of the illumination leads to a uniform mean QFL that is around 200 meV lower than under open circuit conditions. This is similar to the difference observed in our laboratory using a titanium electrode evaporated onto the nanocrystalline layer.²⁸ Here, we note that this mean QFL should be almost the same as that obtained by averaging the short circuit electron density profiles across the film (see Supporting Information). In the present work, comparison of the trapped electronic charge under open circuit and short circuit conditions at the same illumination intensity provided a convenient measure of the relative mean positions of the QFL in the two limiting conditions. To relate the extracted electron charge measured in charge extraction experiments to the density of states function for trapping states, it is necessary for the electron diffusion length to exceed the film thickness so that all trapped electrons are collected. The results of the IPCE and dye-loading experiments provide strong evidence that the electron collection efficiency at short circuit is indeed close to unity.

When the cell is at open circuit under illumination, the QFL position $nE_F - E_{F,\text{redox}}$ is determined by the balance between electron injection by the photoexcited dye and electron transfer

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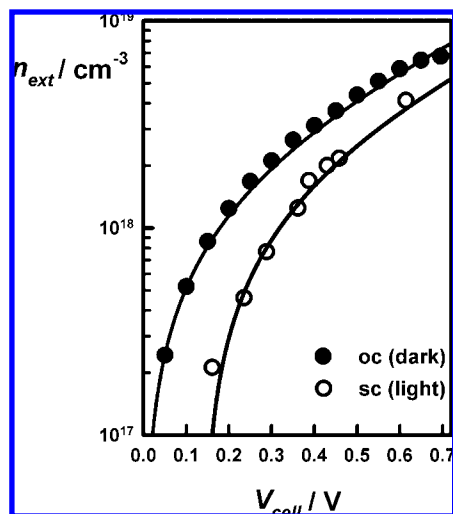


Figure 5. Extracted electron density vs cell voltage for a 20 μm nanotube cell obtained from voltage controlled measurements in the dark (filled symbols) and from integration of the short circuit photocurrent decay (open symbols). In the latter case the cell voltage is the open circuit photovoltage at the same light intensity as that used to measure the photocurrent transient. The lines are fits to eq 5 with $T_0 = 5500$ K, $N_{t,0} = 2 \times 10^{19}$ cm^{-3} , and $E_c - E_{F,\text{redox}} = 1.0$ eV.

to I_3^- , and it is almost constant throughout the film. Essentially identical conditions hold when the cell is under voltage control at a voltage equal to the photovoltage. However, when the cell is at short circuit and the electron diffusion length considerably exceeds the film thickness, the QFL position is determined by the balance between electron injection, and transport to the anode contact and electron transfer to I_3^- can usually be neglected. Calculations show that the QFL (which is considerably lower than at open circuit) is almost constant through the bulk of the film but decreases sharply near the anode (Supporting Information for calculated examples). The trapped electron density measured under these conditions corresponds to integration of the trap occupancy over the film thickness. For convenience, we can use the total trapped charge averaged over the film thickness to define the mean QFL under short circuit conditions. This value of QFL is expected to be almost identical to the one determined by Boschloo et al.^{29,30} by switching the cell to open circuit while simultaneously interrupting illumination.

The trapped electronic charge density in the TNT layers under open circuit (or potential-controlled) conditions was determined using charge extraction during open circuit photovoltage decay as well as by the charge extraction technique under voltage control in the dark. The data obtained by the two methods was nearly identical (Supporting Information), and therefore only the data obtained in the dark measurements is shown in the figure because they cover a wider voltage range. The electronic charge trapped under short circuit conditions was found by integration of a series of “off” photocurrent transients following illumination at short circuit at different light intensities. In the latter case, the open circuit voltage corresponding to each illumination intensity was also recorded.

Figure 5 compares the charges extracted from the 20 μm nanotube cell under controlled voltage and short circuit conditions. Both sets of data have been plotted against the cell voltage. In the case of the potential-controlled experiments, the cell voltage is equal to the difference between the quasi Fermi level nE_F and the redox Fermi level $E_{F,\text{redox}}$, provided that voltage losses at the cathode are negligible. In the case of short circuit

measurements at different illumination intensities, the cell voltage used in the plot is the corresponding open circuit photovoltage. The difference between the open circuit and short circuit mean QFL positions can be obtained as follows. For an exponential electron trap distribution $g_T(E_T)$ of the form^{19,20,26,31,32}

$$g_T(E_T) = \frac{N_{t,0}}{k_B T_0} \exp\left(-\frac{(E_C - E_T)}{k_B T_0}\right) \quad (4)$$

where $N_{t,0}$ is the total trap density, E_C is the conduction band energy, and T_0 is a characteristic temperature that describes the rate of change of trap density with trap energy, E_T .

The density of trapped electrons is given by

$$n_t \approx N_{t,0} \exp\left(-\frac{(E_C - E_{F,\text{redox}})}{k_B T_0}\right) \left[\exp\left(\frac{(nE_F - E_{F,\text{redox}})}{k_B T_0}\right) - 1 \right] \quad (5)$$

The experimental charge extraction data shown in Figure 5 were fitted to eq 5 with $T_0 = 5500$ K, $N_{t,0} = 2 \times 10^{19}$ cm^{-3} , and $E_C - E_{F,\text{redox}} = 1.0$ eV. Very similar values of T_0 and $N_{t,0}$ were obtained for the 5 and 10 μm cells. The high value of T_0 , which corresponds to a very flat distribution of trapping states, was obtained from charge-extraction measurements during photovoltage decay (Supporting Information) and confirmed (albeit over a smaller voltage range) by analysis of the voltage dependence of the chemical capacitance determined by impedance measurements.

Comparison of the charge extraction plots for dark (voltage controlled) and light (short circuit) charge extraction as a function of cell voltage show that they are separated by a constant 150 mV over a wide range. This means that the two curves can be superimposed if it is assumed that the mean QFL under short circuit conditions with illumination is 150 meV lower than at open circuit (or at the equivalent externally imposed voltage). In the case of a 5 μm thick conventional DSC illuminated from the substrate side, the difference has been found to be 0.25 eV using a titanium electrode evaporated onto the TiO₂ layer.²⁸

The constant separation between the two plots and hence between the open circuit and short circuit QFL values again indicates that the free-electron concentrations at short circuit and at open circuit have the same intensity dependence over the entire range, providing further evidence ruling out electron transfer via surface states as the source of non-ideality.

Estimation of the Electron Diffusion Length. The electron diffusion length of electrons in the nanotube DSC can now be estimated by taking into account the 150 meV difference between the mean QFL positions at short circuit and open circuit. Figure 6 illustrates the method. This approach gives an almost constant electron diffusion length of around 100 μm , which is considerably higher than the value of 24 μm obtained from the $D_n \tau_n$ product in Figure 4.

This estimation of the electron diffusion length is consistent with the observation that the IPCE of the 20 μm nanotube cell corresponds to complete collection of all photoinjected electrons, which requires that the diffusion length is considerably greater than the film thickness. The residual weak dependence of L_n on QFL (and hence light intensity) reflects the fact that the magnitudes of the best fit slopes of the D_n and τ_n plots are not exactly equal.

Fitting the IMPS and IMVS Data Using the Multiple Trapping Model with a Non-ideality Term. The presence of electron traps influences the relaxation times associated with

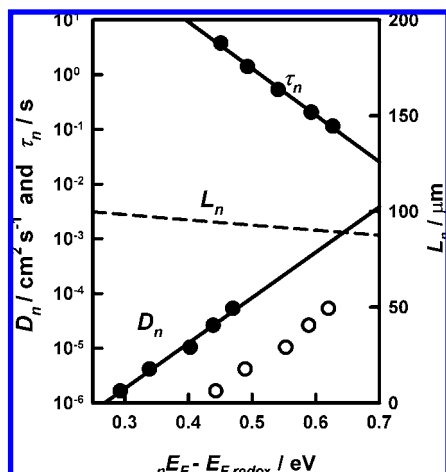


Figure 6. Estimation of the electron diffusion length for 20 μm nanotube cell based on experimental D_n and τ_n data. To account for the difference in QFL between open and short circuit, the D_n points (open circles) have been moved to the left by 0.15 eV (closed circles), which corresponds to the intensity independent difference between the open circuit and short circuit QFL estimated from the charge extraction experiment shown in Figure 5.

electron transport to the anode and also the relaxation of electron density in the conduction band associated with electron transfer to I_3^- . This problem has been analyzed by Bisquert and Vikhrenko²³ using the quasistatic approximation, which assumes that free and trapped electrons maintain a common equilibrium even when the system is displaced away from thermodynamic equilibrium. These authors showed that D_n , the apparent electron diffusion coefficient determined by transient or periodic perturbation, is related to D_0 , the diffusion coefficient of free electrons in the conduction band, by the expression

$$D_n = D_0 \left(\frac{\partial n_t}{\partial n_c} + 1 \right)^{-1} = D_0 \left(\frac{\partial n_t}{\partial n_c} \frac{\partial_n E_F}{\partial_n E_F} + 1 \right)^{-1} \quad (6)$$

An analogous treatment shows that τ_n , the apparent electron lifetime, is related to τ_0 , the conduction band electron lifetime, by

$$\tau_n = \tau_0 \left(\frac{\partial n_t}{\partial n_c} + 1 \right) = \tau_0 \left(\frac{\partial n_t}{\partial n_c} \frac{\partial_n E_F}{\partial_n E_F} + 1 \right) \quad (7)$$

For an exponential trap distribution (cf. eq 2), it can be shown that the slopes of the semilogarithmic plots of D_n and τ_n as a function of $nE_F - E_{F,\text{redox}}$ in Figure 6 should be given by

$$\frac{\partial \log_{10}(D_n/D_0)}{\partial_n E_F} = - \frac{\partial \log_{10}(\tau_n/\tau_0)}{\partial_n E_F} = \frac{1}{2.303k_B} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (8)$$

Surprisingly, the values of T_0 obtained from the plots in Figure 6 (570–580 K) are an order of magnitude lower than the T_0 value (5500 K) derived from the charge extraction plots in Figure 5.

The derivation of eq 8 assumes that the derivative $\partial n_c / \partial_n E_F$ is determined by the Boltzmann relationship

$$n_c = N_c \exp \left(- \frac{E_C - nE_F}{k_B T} \right) \quad (9)$$

where N_c is the effective density of conduction band states. Because the D_n and τ_n plots in Figure 6 both give very similar values of T_0 , we propose modification of the usual Boltzmann

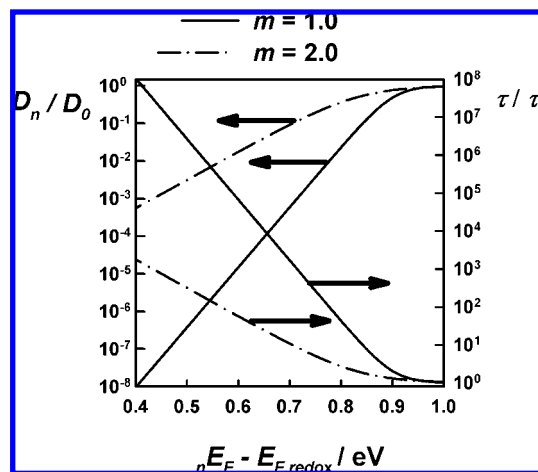


Figure 7. Plots showing how inclusion of a non-ideality factor m (cf. eq 11) affects the predicted dependence of the normalized apparent electron diffusion coefficient D_n/D_0 and electron lifetime τ_n/τ_0 on the position of the quasi-Fermi level $nE_F - E_{F,\text{redox}}$. $T = 295$ K, $T_0 = 5500$ K, $N_{t,0} = 5 \times 10^{19} \text{ cm}^{-3}$, $N_c = 10^{20} \text{ cm}^{-3}$, $E_C - E_{F,\text{redox}} = 1.0$ eV. m as shown.

expression by an empirical non-ideality factor m to account for the possibility of non-ideal thermodynamic behavior of conduction band electrons in the TiO_2 , so that eq 9 becomes

$$n_c = N_c \exp \left(- \frac{E_C - nE_F}{mk_B T} \right) \quad (10)$$

Equation 8 then becomes

$$\frac{\partial \log_{10}(D_n/D_0)}{\partial_n E_F} = - \frac{\partial \log_{10}(\tau_n/\tau_0)}{\partial_n E_F} = \frac{1}{2.303k_B} \left(\frac{1}{mT} - \frac{1}{T_0} \right) \quad (11)$$

The effect that introduction of m has on the plots of D_n and τ_n as a function of the QFL position is illustrated in Figure 7.

Using this approach, the experimental plots of D_n and τ_n for the 20 μm films can be fitted using $T_0 = 5500$ K and $m = 2.1$, which is similar to the non-ideality factor derived from the intensity dependence of the photovoltage ($m = 1.9$). At present, the origin of this non-ideality is unclear, but as shown in the Supporting Information, introduction of this empirical factor m is equivalent to assuming that the non-ideal thermodynamic behavior of electrons in the nanostructured two-phase system can be accounted for by an electron activity coefficient of the form

$$\gamma_n = 1 + an_c^{m-1} \quad (12)$$

where a is a constant and $an_c^{m-1} \gg 1$.

Determination of T_0 and τ_n from Open Circuit Voltage Decay: Further Evidence for Non-ideality. Open circuit photovoltage decay plots can be used to determine the characteristic temperature of the electron trap distribution and also the dependence of τ_n on photovoltage. At the same time, anomalies in the decay behavior can be used to identify shunting of the cell occurring by electron transfer to tri-iodide ions via the conducting substrate.^{33,34} In the case of the TNT cells, the photovoltage decay is remarkably slow, and the plot of U_{photo} versus $\log_{10} t$ shown in Figure 8 is linear at long times as expected for an exponential distribution of electron traps.³⁵ The fact that the plot remains linear up to 1000 s also shows that back reaction of electrons via the titanium substrate is negligible. This can be attributed to the existence of a barrier layer of TiO_2

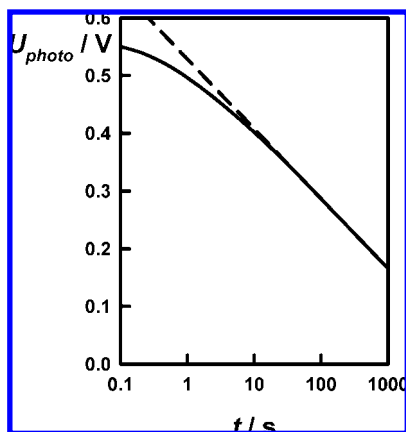


Figure 8. Semilogarithmic plot of the open circuit photovoltage decay for a TNT cell, showing the linear behavior characteristic of an exponential distribution of electron traps. The broken line corresponds to eq 15.

formed at the base of the nanotubes during anodization. Mor et al.¹¹ concluded from an analysis of the voltage decay of nanotube cells that the electron lifetime is higher in nanotube arrays than in conventional colloid films. However, the differences that they observed can be attributed primarily to back reaction via the substrate³⁴ in the case of the colloid-based films that had no blocking layer.

In the case where the electron trap distribution follows the exponential form of eq 4 and the transfer of electrons to redox species occurs only via the conduction band, the open circuit photovoltage decay is described by³⁵

$$U_{\text{photo}}(t) \approx -\frac{mk_{\text{B}}T}{q(1-mT/T_0)}(\ln|c_2| + \ln(t)) \quad (13)$$

where

$$c_1 = \exp\left[\frac{(mT/T_0 - 1)qU_{\text{photo}}(0)}{mk_{\text{B}}T}\right] \quad \text{and} \quad c_2 = k_{\text{cb}}\left[1 - \frac{mT}{T_0}\right]\frac{N_{\text{C}}T_0}{N_{\text{t},0}mT}\left(\frac{n_{\text{eq}}}{N_{\text{C}}}\right)^{(1-mT/T_0)} \quad (14)$$

Here, k_{cb} , the pseudo-first-order rate constant for electron transfer to I_3^- , is equal to the inverse of the free electron lifetime τ_0 . Note that the non-ideality factor m has been incorporated into eqs 13 and 14.

It follows that at long times a plot of $U_{\text{photo}}(t)$ vs $\ln(t)$ should have a slope given by

$$\frac{dU_{\text{photo}}(t)}{d \log_{10} t} = -\frac{2.303mk_{\text{B}}T}{q(1-mT/T_0)} \quad (15)$$

If m is taken as unity, the slope of the semilogarithmic plot in Figure 8 gives $T_0 = 600$ K, which is very similar to the values obtained from the IMPS and IMVS analysis. However, if non-ideality is taken into account and T_0 is taken as 5500 K, a value of $m = 1.8$ is obtained, in reasonable agreement with the value deduced from the analysis of the IMPS and IMVS data.

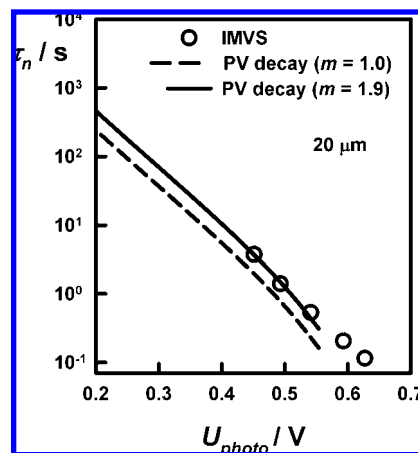


Figure 9. Dependence of apparent electron lifetime on photovoltage derived from the decay shown in Figure 8 using eq 16 with $m = 1$ and $m = 1.9$. The results are compared with the τ_n values measured by IMVS.

Values of τ_n can be derived from the intensity modulated photovoltage (IMVS) response^{36,37} or by analysis of the open circuit potential decay. Here, we modify the usual relationship^{38,39} to take account of non-ideality to obtain

$$\tau_n = -\frac{mk_{\text{B}}T}{q}\left(\frac{dU_{\text{photo}}(t)}{dt}\right)^{-1} \quad (16)$$

The analysis involved using a cubic fit of the decay in semilogarithmic form followed by numerical differentiation of the fitted U_{photo} versus t relationship. An example is shown in Figure 9 for the $20 \mu\text{m}$ cell. It can be seen that for $m = 1.0$, the analysis yields values of τ_n that are lower than those derived from IMVS. By contrast for $m = 1.9$, the lifetime plots for IMVS and photovoltage decay coincide, providing further support for the introduction of non-ideality factor into the analysis.

Conclusions

Dye-sensitized titania nanotube cells utilizing the iodide/triiodide redox couple exhibit high collection efficiencies for photoinjected electrons. The electron diffusion length has been estimated using a method that takes into account the fact that the occupancies of electron traps under open circuit and short circuit conditions are substantially different. The electron diffusion length estimated in this way is of the order of $100 \mu\text{m}$. This detailed study of transport, trapping, and transfer of electrons by experimental methods and numerical modeling has also revealed that the steady state and dynamic behavior of titania nanotube cells appear to be influenced by non-ideal electron statistics. This problem has been addressed empirically using a simple non-ideality factor. However, further work is clearly required to establish the origin of the observed non-ideal behavior.

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Supporting Information Available: XRD and XPS data, SEM of nanotube arrays, *IV* characteristics, photovoltage data, additional charge extraction data, discussion of inhomogeneous

diffusion, electron density profiles and mean QFLs, theoretical modeling of IMPS response, electron activity coefficient derivation, and complete ref. 4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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