

Mechanism of Molecular Control of Recombination Dynamics in Dye-Sensitized Nanocrystalline Semiconductor Films

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Recent experiments have shown that it is possible to switch between electron transport limited and interfacial electron transfer (IET) limited recombination dynamics of photoinjected electrons and the oxidized dye molecules anchored to the TiO₂ under the same spectroscopic conditions, by appropriate design of the dye. The kinetics not only is slower in the IET limited case but also single exponential, in contrast to the highly dispersive transport limited recombination kinetics. We suggest that exponential kinetics could be a result of the Coulomb trap effect. Once an electron reaches the cation, electrostatic interaction keeps it near the cation until recombination takes place. Otherwise, dispersive transport would not allow for the exponential kinetics to develop. An analytical expression for the cation survival probability is derived that shows very good agreement with available experimental data. Physically, the Coulomb trap effect is justifiable if the relative dielectric constant of the surrounding medium is low enough (less than 5).

1. Introduction

Recent extensive research has clarified significantly the mechanism of charge recombination in dye-sensitized nanocrystalline semiconductors (photoelectrochemical solar cells).^{1–9} This recombination takes place following the photoinduced electron injection from adsorbed dye molecules into the conduction band of the semiconductor. Recombination kinetics is typically highly dispersive with characteristic time scales spanning from picoseconds to milliseconds. The wide range of time scales is usually attributed to the trapping of electrons by localized states on the semiconductor surface. Recombination is controlled by electron transport between energetically distributed trap sites, which in turn is assumed to occur by full activation of electrons up to the conduction band. The dominant factor responsible for the observed dispersive recombination kinetics is redistribution of electrons among trap states with different energies rather than spatial diffusion. This concept is supported by experimental evidence of strong sensitivity of the recombination rate to the occupancy of the trap levels, which can be controlled by changing the intensity of the light source or the surrounding electrolyte composition or by applying the external bias.^{2,3}

A very nice experimental result has been reported recently by Clifford et al.¹⁰ They studied charge recombination between photoinjected electrons in nanocrystalline TiO₂ films and the anchored oxidized sensitizer dye. Two different dyes were employed, *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (dye **1**) and *meso*-5-(4-carboxyphenyl)-10,15,20-tris(4-diphenylaminophenyl)porphyrin (dye **2**). Dye **2** differs from dye **1** by the substitution of three carboxyphenyl peripheral groups with triphenylamine electron-donor groups. This modification of the dye structure led to a significant reduction in the observed recombination rate. What is most striking, however, the slow kinetics was monoexponential, allowing the authors to suggest that it was interfacial electron transfer that was the limiting step

of reaction rather than the usual electron transport. The slower recombination dynamics most probably derives from a larger physical separation of the dye cation state from the film surface (rather than differences in dye redox potential).¹⁰ This point is clear. However, the reason for monoexponentiality of the decay is far from being obvious.

Let us assume, in line with standard semiconductor theory, that recombination and trapping occur by the same mechanism (i.e., by activation to the conduction band) and differ only by the capture cross section. When the microscopic recombination rate k_r is slow, electrons can be assumed to be in thermal equilibrium (Fermi distribution) in the course of reaction. As the number of electrons decreases by recombination, the Fermi energy $\epsilon_F(t)$ decreases (its absolute value increases). Here and in what follows energy is in units of $k_B T$. Simple analysis shows⁹ that in this case the cation number density $n(t)$ satisfies the kinetic equation, $n^{-1}dn/dt \approx k_r \exp[-\epsilon_F(t)]$. Given the commonly assumed exponential trap energy distribution, $g(\epsilon) = \alpha \exp(-\alpha\epsilon)$, as would be expected for an Urbach tail at the conduction band edge,¹¹ there is a nonlinear relationship between $\epsilon_F(t)$ and $n(t)$, and therefore, although the decay is modulated by k_r , it is nothing like a single exponential. One can immediately object to these arguments and note that the recombination mechanism may be different. The recombination mechanism is most likely electron transfer between a localized trap state and a localized cation state, while the conduction band is not involved. As it will be shown below, this does not help, and the decay will still be nonexponential.

The decay would be monoexponential if recombination took place from a constant Fermi level. The concentration of photogenerated electrons in experiments of Clifford et al. was low, ~ 0.1 per nanoparticle. If the concentration of dark electrons was higher than that and k_r was slow enough to allow for complete intra- and interparticle equilibration of photogenerated electrons, one would observe an exponential decay determined by the dark Fermi level. However, the number density of dark electrons in TiO₂ is estimated to be just about 0.1 per nanoparticle.¹² Also, the time scale of the decay, when it

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becomes truly exponential, turns out to be too slow. In other words, one cannot fit the experimental decay curves of Clifford et al. for the two dyes simultaneously by changing only k_r .

This puzzle could be resolved, in our opinion, by taking Coulomb interaction between an electron and a cation into account. This interaction is certainly not long-ranged because of the screening effect of the surrounding electrolyte. However, it should be strong when the two charges are close. An electron trapped at one of the sites adjacent to the cation will have its activation energy increased by the Coulomb contribution. If we assume that the Coulomb energy is much larger than the usual trap energy, then an electron, once reaching a trap site adjacent to the cation, will no longer be detrapped. In this paper we provide a mathematical framework based on this physical idea. The new model, albeit simple, shows very good agreement with experiment. It is predicted that the initial decay is dispersive when k_r is large, but it becomes exponential when k_r is sufficiently small. The long-time behavior of the decay is predicted to be independent of k_r and determined by the trap energy distribution. That is, the decay curves for different k_r converge at long times.

2. Generic Random Flight Model

Pulsed excitation of the dye-sensitized TiO₂ leads to formation of a dye cation state that is then rereduced by charge recombination with a photogenerated electron. Experimentally one monitors the decay kinetics of the cation state, the cation survival probability $n(t)$. We assume that electrons are rapidly trapped and their concentration in the conduction band is negligible. The energy distribution of electron trap states $g(\epsilon)$ is taken to be exponential below the conduction band:

$$g(\epsilon) = \alpha \exp(-\alpha\epsilon) \quad (1)$$

Here the conduction band edge energy is set to zero. Exponential density of localized states is a standard assumption. Previous studies have demonstrated that it can fit experimental data both for transient photocurrent⁴ and charge recombination.^{4,5,9} The trap states are thought to arise from surface defects associated with oxygen vacancies and adsorbed species. α defines the depth of the distribution and is typically ~ 0.4 for TiO₂.⁴ One should note, however, that so far little evidence could be obtained either in spectroscopic studies^{13,14} or ab initio calculations¹⁵ that the energy distribution of surface states in TiO₂ is indeed exponential. As shown recently,¹⁶ the presence of a few deep traps could be totally responsible for the observed dispersive transport, and thus the assumption of the exponential density of localized states may not be required.

It is also assumed that electrons leave traps by thermal activation, with the corresponding detrapping rate constant given by

$$k_d(\epsilon) = \nu_0 \exp(-\epsilon), \quad (2)$$

where ν_0 is the attempt-to-escape frequency. According to the principle of detailed balance, ν_0 also defines the capture rate of a conduction band electron by a vacant trap. In what follows we set $\nu_0 = 1$, which is equivalent to measuring time in units of ν_0^{-1} . Hot photoexcited electrons most likely lose memory of their initial spatial position within the nanoparticle before they are trapped for the first time. Therefore, our time zero corresponds to a random distribution of electrons among traps, that is, according to $g(\epsilon)$. These are all standard assumptions.

In conventional semiconductor theory, there are two models of dispersive transport that implicitly include the distribution of localized states: the multiple trapping (MT) model^{17,18} and the continuous time random walk (CTRW) model.^{19,20} In the limit of low carrier density these two models give similar results,^{17,18} although they are not equivalent.²¹ The first application of the random walk simulation methodology to dye-sensitized TiO₂ films appears to be due to Nelson.⁴ Her approach is related to but not the same as the original CTRW model. She considered a nearest-neighbor random walk on a regular lattice of trap sites of different energy. Our model of electron transport is a modification of the MT model that we referred to as the random flight model.⁹ After an electron is thermally detrapped into the conduction band, it is assumed to have an equal chance to be captured by any of the vacant traps within the same nanoparticle. This mechanism implies that electron motion in the conduction band is rather fast (corroborated by a rather high value of $1.5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ quoted²² for the diffusion coefficient of the conduction band electrons in bulk TiO₂). Actually, the probability that an electron is captured by a certain trap will depend to some extent on the distance of that trap from the original trap from which the electron is detrapped. Comparison of different models with experiment^{4,5,9,23} and additional theoretical analysis⁹ show that spatial motion of the electron has only minor effect on the recombination kinetics and that the recombination kinetics is mainly governed by the energy redistribution of trapped electrons. So we choose the random flight model instead of the CTRW model. The random flight model can be solved analytically.

There is a fraction p of traps adjacent to the cation. Recombination is assumed to take place only from these adjacent traps by the electron-transfer mechanism with the rate constant $k_r(\epsilon)$. Since the dispersion of the trap energy levels is about $k_B T$ we may assume that $k_r(\epsilon)$ is independent of energy, $k_r(\epsilon) = k_r$. Finally, we assume that recombination is mainly an intra-particle event. This assumption appears to be justified experimentally: the decay kinetics become intensity (i.e., concentration)-independent as soon as the estimated average number of photoexcited cations per nanoparticle becomes less than one.³

Since the excitation efficiency in experiments of Clifford et al. is low, we can consider a single electron-cation pair. The most convenient analytical approach in this case is to employ the ensemble averaged waiting time distribution formalism.²⁴ We introduce the ensemble averaged waiting (detrapping) time distribution functions

$$\psi_d^0(t) = \int_0^\infty d\epsilon g(\epsilon) k_d(\epsilon) \exp[-k_d(\epsilon)t] \quad (3)$$

$$\psi_d(t) = \int_0^\infty d\epsilon g(\epsilon) k_d(\epsilon) \exp(-[k_d(\epsilon) + k_r(\epsilon)]t) \quad (4)$$

where subscript 0 refers to nonadjacent traps. The reaction time distribution function is given by

$$\psi_r(t) = \int_0^\infty d\epsilon g(\epsilon) k_r(\epsilon) \exp(-[k_d(\epsilon) + k_r(\epsilon)]t) \quad (5)$$

Functions $\psi_d^0(t)$ and $\psi_d(t) + \psi_r(t)$ are normalized so that their integrals over time equal unity. The Laplace transform of the cation survival probability,

$$\hat{n}(s) \equiv \int_0^\infty dt n(t) \exp(-st)$$

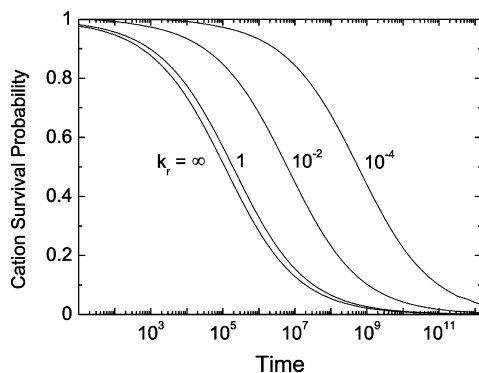


Figure 1. Cation survival probability $n(t)$ calculated by numerical Laplace inversion of eq 10 using the Crump algorithm for $\alpha = 0.4$, $p = 0.01$, and several values of k_r (numbers attached to curves). Time is in units of ν_0^{-1} . Lin/log plot.

is given by

$$\hat{n}(s) = \frac{1}{s} - \frac{p\hat{\psi}_r(s)}{s} \sum_{i=0}^{\infty} [(1-p)\hat{\psi}_d^0(s) + p\hat{\psi}_d(s)]^i$$

$$= \frac{1}{s} - \frac{1}{s} \frac{p\hat{\psi}_r(s)}{1 - (1-p)\hat{\psi}_d^0(s) - p\hat{\psi}_d(s)} \quad (6)$$

Equation 6 is easy to understand. Each surviving step of the electron (from the conduction band into the trap and back to the conduction band) is associated with the probability p to visit a trap adjacent to the cation and the associated probability $\hat{\psi}_d(t)$ to escape reaction and return to the conduction band. At the same time $(1-p)$ is the probability to choose a nonreactive trap and $\hat{\psi}_d^0(t)$ is the associated detrapping probability. Similarly, the product $p\hat{\psi}_r(t)$ determines the probability to react.

Given the trap energy distribution in eq 1, the detrapping rate constant in eq 2, and the recombination rate constant k_r , we obtain

$$\hat{\psi}_d^0(s) = 1 - {}_2F_1(1, \alpha, 1 + \alpha, -1/s) \equiv 1 - h(s) \quad (7)$$

$$\hat{\psi}_d(s) = 1 - h(s + k_r) \quad (8)$$

$$\hat{\psi}_r(s) = \frac{k_r}{s + k_r} h(s + k_r) \quad (9)$$

Here ${}_2F_1$ denotes the Gauss hypergeometric function. The final solution for the survival probability can be rewritten as follows:

$$\hat{n}(s) = \frac{1}{s} - \frac{k_r}{s(s + k_r)} \left[1 + \left(\frac{1}{p} - 1 \right) \frac{h(s)}{h(s + k_r)} \right]^{-1} \quad (10)$$

Because $h(s) \sim s^\alpha$ in the limit of $s \rightarrow 0$,²⁵ one can expect the power-law feature to persist in the decay kinetics at long times. Figure 1 shows that this is indeed the case. The decay curves actually look very similar at all times for different values of k_r . Although the decay is modulated by k_r , it never behaves as a single exponential. Here $\alpha = 0.4$ was chosen as in previous studies. Our choice of $p = 0.01$ is based on the quoted number of several hundred traps per nanoparticle¹² and a reasonable assumption that only a few of them are adjacent to the cation. Variation of these parameters does not change the general conclusion: this model does not explain experimental data for small k_r .

3. Coulomb Trap

There is electrostatic interaction between an electron and a cation. It is most likely short-ranged because of the screening

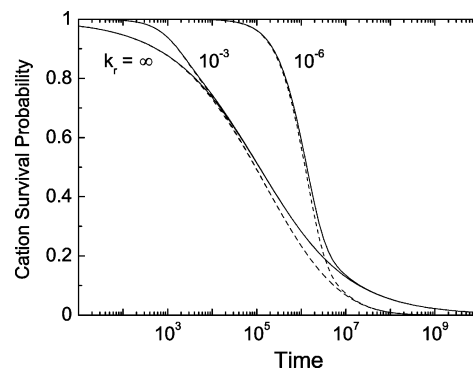


Figure 2. Same as Figure 1, illustrating eq 11 (solid lines) and eq 15 (dashed) with $\epsilon_F = 18k_B T$.

effect of the surrounding electrolyte solution. Instead of going into detail of electron motion in the complex electrostatic field we simply assume that the electron feels the Coulomb interaction only when it is trapped near the cation. Effectively, this corresponds to lowering the energy of all adjacent traps. In addition to the usual thermal activation, an electron in an adjacent trap has to overcome the Coulomb interaction with the cation in order to escape into the conduction band.

The idea of a Coulomb trap can be readily incorporated into the generic random flight model. We have only to assume that the adjacent trap energy distribution is shifted down by ϵ_c , the Coulomb energy. Analysis shows that the model is not sensitive to the value of ϵ_c when it is sufficiently large ($\epsilon_c \geq 12k_B T$), and so we assume further that adjacent electrons are never detrapped. In other words, $k_d(\epsilon) = 0$ for adjacent traps. Now $\hat{\psi}_r(s) = k_r/(s + k_r)$ and the solution for the survival probability reads

$$\hat{n}(s) = \frac{1}{s} - \frac{k_r}{s(s + k_r)} \left[1 + \left(\frac{1}{p} - 1 \right) h(s) \right]^{-1} \quad (11)$$

The difference between eqs 10 and 11 may not look significant, but it is. Absence of $h(s + k_r)$ in the denominator in eq 11 allows for an intermediate stage to develop where $(1/p - 1)h(s) \ll s/k_r$. This stage is exponential. Figure 2 shows transition from dispersive kinetics at high values of k_r to exponential kinetics at low values of k_r . The decay curves converge at long times. The long-time behavior is dispersive and independent of k_r .

Although it is already clear that the model is capable of explaining the experimental results of Clifford et al., detailed comparison indicates that the predicted long-time decay is somewhat too slow. This effect is familiar and is related to the chosen functional form of the trap energy distribution, $g(\epsilon)$. Equation 1 allows traps of infinite depth to exist, albeit with vanishingly small probability. This is definitely not realistic.¹³⁻¹⁵ A way around it is to introduce a certain cutoff energy. A more physical approach is to simply take dark electrons into consideration. As can be estimated from the natural doping density of TiO_2 ,¹² the average number of electrons per 10 nm radius semiconductor particle in the dark is only ~ 0.1 . The contribution of dark electrons to direct reduction of the dye cation may be negligible, but they fill deep traps and thus effectively increase the mobility of photogenerated electrons. We incorporate the effect of dark electrons by modifying the trap energy distribution as follows:

$$g_d(\epsilon) = \frac{g(\epsilon) - g_F(\epsilon)}{1 - n_d} = \frac{\alpha \exp(-\alpha\epsilon)}{(1 - n_d)[1 + \exp(\epsilon - \epsilon_F)]} \quad (12)$$

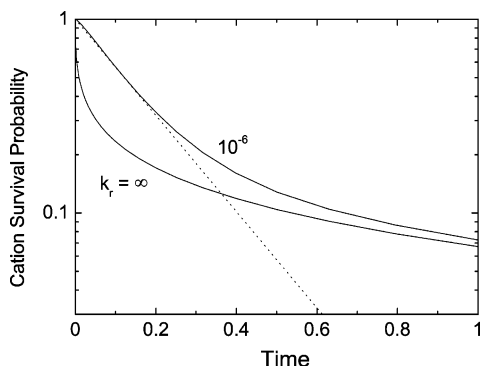


Figure 3. Same as Figure 1, illustrating eq 15 with $\epsilon_F = 18k_B T$. Log/lin plot. Dotted line is a single exponential, a guide to the eye.

where ϵ_F is the dark Fermi energy, $g_F(\epsilon)$ is the Fermi distribution

$$g_F(\epsilon) = \frac{g(\epsilon)}{1 + \exp(\epsilon_F - \epsilon)} \quad (13)$$

and n_d is the number density of dark electrons

$$n_d = \int_0^\infty d\epsilon g_F(\epsilon) \quad (14)$$

This soft cutoff is an approximation but not an unreasonable one. Equation 11 for the cation survival probability modifies into

$$\hat{n}(s) = \frac{1}{s} - \frac{k_r}{s(s + k_r)} \left[1 + \left(\frac{1}{p} - 1 \right) h_d(s) \right]^{-1} \quad (15)$$

where

$$h_d(s) = \frac{h(s) - n_d}{1 - n_d} \frac{s}{s - \exp(-\epsilon_F)} \quad (16)$$

Figures 2 and 3 confirm that the effect of dark electrons is to increase the decay rate at long times.

4. Comparison with Experiment and Discussion

We begin comparison of our model with experiment by fitting the dispersive decay curve, where the microscopic recombination rate is supposed to be high. In this case, eq 15 simplifies into

$$\hat{n}_0(s) = \frac{1}{s} \left[1 + \frac{p}{(1-p)h_d(s)} \right]^{-1} \quad (17)$$

This is very similar to the solution derived earlier from the master equation for the distribution function of trapped electrons.⁹ The difference is that previously we worked in the thermodynamic limit and now we consider a geminate electron-cation pair, which is more appropriate for low-intensity experiments. We fix $\epsilon_F = 18k_B T$ and $p = 0.01$ and vary α and ν_0 . The Laplace transform was inverted numerically using the Crump algorithm. Since our theoretical solution is given in dimensionless time units, we divide time by ν_0 after Laplace inversion. Reasonable agreement with experiment is achieved for $0.4 \leq \alpha \leq 0.5$, which is in accord with previous studies.^{4,5,9} After the dispersive kinetics for the first dye is fit, we adjust k_r to fit the kinetics for the second dye. Figure 4 shows the results for $\alpha = 0.5$, $\nu_0 = 3.2 \times 10^6 \text{ s}^{-1}$, and $k_r/\nu_0 = 3.5 \times 10^{-6}$. It appears that our qualitative model captures the physics of the phenomenon quite well. The value of ν_0 is somewhat smaller

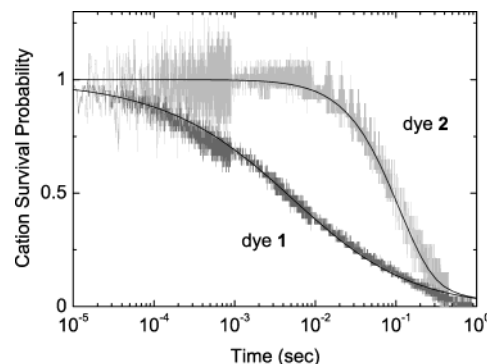


Figure 4. Normalized transient cation absorption data of Clifford et al. (grey lines) for TiO_2 films sensitized with *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (dye 1) and *meso*-5-(4-carboxyphenyl)-10,15,20-tris(4-diphenylaminophenyl)porphyrin (dye 2). Solid lines correspond to Laplace-inverted eq 15 (dye 2) and eq 17 (dye 1) with the following parameters: $\alpha = 0.5$, $p = 0.01$, $\epsilon_F = 18k_B T$, $\nu_0 = 3.2 \times 10^6 \text{ s}^{-1}$, and $k_r/\nu_0 = 3.5 \times 10^{-6}$ (dye 2). For dye 1, k_r is assumed to be very high.

than previously reported. This is due to a different choice of p . In our previous study, only one trap per cation was assumed to be reactive, which corresponds to $p \approx 0.002$.

The model currently assumes random electron retrapping within a nanoparticle. A more realistic model of retrapping biased for closer traps could be considered. However, as we have already mentioned, we do not expect any significant difference in model predictions, although mathematical transparency of the solution would certainly be sacrificed. Another direction in which our model can be extended is, of course, to include interparticle mobility of electrons. It will affect recombination kinetics at longer times but, most likely, will not change our main conclusion concerning the origin of the exponential stage. We would like to comment here in this respect that so far there is no consensus in the literature regarding the number of traps per nanoparticle. For example, by comparing their transient photocurrent measurements with random walk simulations Van de Lagemaat and Frank²⁶ have concluded that only one trap per nanoparticle is required to achieve consistency. This looks like a contradiction to our and others' assumption^{4,5,9,12} that this number is about several hundred. However, there is no contradiction in our opinion. Results of Van de Lagemaat and Frank only confirm that the conduction band in nanocrystalline TiO_2 films is not continuous through the sample but rather discontinuous at particle boundaries. Macroscopic electron transport is controlled by hopping through these boundaries. A nanoparticle itself acts as a trap. Consideration of the recombination kinetics, on the other hand, requires details of the intraparticle electron motion (energy redistribution) to be taken into account, where many trap states are involved.

One should not conceal a certain deficiency of the Coulomb trap idea. The Coulomb energy could be estimated in a usual way as follows: $\epsilon_c = e^2/(\epsilon r)$, where e is the electron charge, ϵ is the dielectric permittivity, and r is the distance between the trapped electron and the cation. Since a typical radius of a TiO_2 nanoparticle is $R = 7 \text{ nm}$,²⁷ our assumed fraction of adjacent surface traps $p = 0.01$ corresponds to $r \leq 2R\sqrt{p} = 1.4 \text{ nm}$. Therefore, to have $\epsilon_c \gtrsim 12k_B T$, the dielectric permittivity should be less than 5. The quoted values of ϵ for anatase range from 25 to 48,²⁸ while for propylene carbonate (the solvent used in experiments of Clifford et al.¹⁰) $\epsilon \approx 64.9$ and can be decreased by added salt (LiClO_4 in ref 10) only slightly.²⁹ However, in our model traps are assumed to be on the surface and hence it

is unlikely that the bulk dielectric constant of TiO_2 is a relevant quantity to be used in the estimation of the Coulomb energy. Concerning the effect of the solvent one can argue that adsorbed dye molecules reduce ϵ at the interface and that it is the local dielectric permittivity that matters at such short separations, i.e., there may be no intervening solvent molecules between the trapped electron and the center of charge density for the oxidized dye, only the atoms of the dye molecule itself. All these arguments weighed, the Coulomb trap model can be neither fully justified nor fully rejected. It remains our assumption that is supported by a good fit to experimental data.

We cannot completely deny the possibility that there are dye-specific traps on the surface of TiO_2 , namely, the possibility that adsorbed dye molecules modify the trap energy distribution. If these dye-induced traps were sufficiently deep, it might be possible to derive exponential stage in recombination kinetics. However, if this perturbation of the trap energy distribution did exist, it would have been observable spectroscopically, and so far there is no indication of that in the literature.

In conclusion, we suggest that the exponential stage of recombination kinetics in dye-sensitized nanocrystalline TiO_2 can be observed because of the Coulomb trap effect. That is, once an electron reaches the cation, electrostatic interaction keeps it near the cation until interfacial back electron transfer takes place. Otherwise, dispersive transport would not allow for the exponential kinetics to develop. Our model predicts that at long times the slow exponential decay curve for the dye **2** should become dispersive and converge with the decay curve for the dye **1**. On the other hand, the experimental decay curves appear to cross at long times. However, it must be stressed that the magnitude of these transient optical signals at long times is strongly dependent upon the accuracy of the background absorbance level and is not known more accurately than the noise level, which for these data appears to be at least 5% of the signal. Considering the experimental error we cannot say that the experimental results are inconsistent with our prediction. More detailed and elaborate experiments are needed to test it.

Acknowledgment. We would like to thank Prof. J. R. Durrant for providing us with experimental data.

Note Added in Proof. Very recently (*J. Am. Chem. Soc.* **2004**, *126*, 5225), Clifford et al. have confirmed that slower recombination results from a larger physical separation of the

dye cation HOMO orbital rather than from the change in the dye oxidation potential.

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