Dynamics of Semiconductor-to-Dye Electron Transfer for Anthracene Dyes Bound to Different Sized TiO₂ Particles

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The photosensitization of different sized TiO₂ nanoparticles by anthracenecarboxylic acid dye molecules has been studied using transient absorption spectroscopy. These experiments primarily yield information about the semiconductor-to-dye electron transfer reaction. Our measurements show that for TiO₂ particles in the 4 to 40 nm size range, the rate of this reaction does not depend on the particles' size. The results were analyzed using a model where the electrons are assumed to be evenly distributed over the surface of the particle. To reproduce our experimental results with this analysis, the scaling parameter that describes the distance dependence of the semiconductor-to-dye electron transfer reaction must be > 180 nm. We do not consider this to be physically reasonable. An alternative explanation is that the injected electrons are in localized trap sites that are spatially close to the dye radical cation, i.e., they are not randomly distributed over the particle surface. The observation of single exponential decays in the transient absorption data implies that these trap sites have a narrow energy distribution.

1. Introduction

Dye sensitization of wide band gap semiconductor electrodes has gained significant attention in recent years, largely because of the demonstration of dye-sensitized solar energy cells with conversion efficiencies as high as 10%.^{1,2} An important factor in the development of these solar cells was the introduction of nanoporous electrodes made from semiconductor particles, which greatly increased the density of bound dye molecules per unit area of electrode. In addition to the large surface-tovolume ratio, semiconductor nanoparticles may present quantum confinement effects, i.e., have electronic and optical properties that strongly depend on the particle size.^{3,4} The efficiency of dye-sensitized solar cells depends critically on the rates of the forward (dye-to-semiconductor) and back (semiconductor-todye) electron transfer reactions, thus, it is significant to ask how the rates of these reactions depend on the size of the nanoparticles. In this paper we are primarily concerned with the back electron transfer reaction in the sensitization process. This reaction has been extensively studied for TiO₂ particles, and it's rate varies from ca. 10 ps to μ s depending on the specific dye/semiconductor system.⁵⁻¹⁷ In many cases the dynamics show complex multiexponential decays, which could be the result of either a spatial or an energetic distribution of the trapped electrons in the semiconductor particles.

To the best of our knowledge no definitive study on the size dependence of dye sensitization has been published, however, some related work on the charge recombination after optical excitation in small semiconductor nanoclusters has been performed. For example, Serpone and co-workers studied the relaxation dynamics of TiO_2 in aqueous solution for three different nanoparticle sizes and demonstrated that the smaller the particle, the greater the fraction of electron/hole pairs that have recombined by the first 20 ps after band gap excitation.¹⁸

Kelley and co-workers examined MoS₂ nanoparticles of 3.0 and 4.5 nm diameter and found that the electron-hole recombination dynamics are slower for the larger particles.¹⁹ These workers also presented a kinetic model that successfully explained their results. In this model, the electrons and holes are assumed to be randomly distributed around the edge of the disklike nanoclusters (MoS2 is a two-dimensional layered semiconductor) and diffusion between trap sites is assumed to be slow compared to electron-hole recombination. This gives a distribution of reaction distances between the electron and the hole and, therefore, multiexponential decays.19 Recently, Kelly and co-workers have used this model to analyze the dynamics of semiconductor-todye electron transfer for a cyanine dye bound to MoS₂ and WS₂ nanoclusters.²⁰ The distance scaling parameters obtained for both the interfacial electron transfer reaction and the electron-hole recombination process were found to be equal to the radius of the bulk excitation in MoS₂/WS₂.^{19,20}

In this paper we present a study of the electron transfer dynamics for the 1-, 2-, and 9-isomers of anthracenecarboxylic acid bound to two different sized anatase TiO₂ particles. We have found that there is no size dependence for the rate of the back electron transfer reaction for particles in the 4 to 40 nm diameter size range. Moreover, all of the experimental data can be fit to single exponential decays, indicating that the back reaction takes place from trap sites with a narrow distribution of energies.¹⁶ An extension of Kelley's model to three-dimensional, spherical particles is applied to our results. It is important to note that the time scales for back electron transfer in the anthracenecarboxylic acid/TiO₂ systems (ca. 20–30 ps) are much faster than the average back electron transfer time for systems that show distributed kinetics.^{5–9,15,17}

2. Experimental Section

The experimental apparatus used in these studies has been described in detail elsewhere.¹¹ It consists of a regeneratively amplified mode-locked Ti-sapphire laser system (Clark-MXR

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CPA-1000; 100-120 fs fwhm sech² deconvolution; 0.6 mJ/ pulse; $\lambda = 780$ nm) pumped by a CW argon ion laser (Coherent I-90/6). The output of the regenerative amplifier is split by a 70/30 beam splitter (CVI). The 70% portion is doubled in a 1 mm type-I BBO crystal to supply the pump laser pulses (390 nm). The 30% portion is used as the probe beam, after being strongly filtered by neutral density filters. The cross-correlation between the 390 nm pump and the 780 nm probe pulses was measured by sum frequency generation in a 0.3 mm KDP crystal, producing a typical fwhm of 150-200 fs (sech² deconvolution). The polarization of the laser pulses was controlled by passing the pump and probe beams through $\lambda/2$ achromatic waveplates (Special Optics) and Glan-Laser calcite polarizers (Karl-Lambrecht). The probe beam was split into signal and reference beams which were detected by matched photodiodes (Thorlabs) for shot-to-shot normalization. The normalization, and data collection and analysis routines have been described elsewhere.¹¹ Numerical solutions to the equations presented in section 4 were obtained using Mathematica (ver. 2.2.2; Wolfram Research).

The TiO₂ nanoparticles were prepared by controlled hydrolysis in acidified water of a 20 mL solution of 1 mL titanium(IV) isopropoxide (ACROS, 98%) dissolved in 2-propanol.^{18,21-23} The hydrolysis was carried out under N2 at different temperatures. For the smaller particles, lower temperatures were required and the hydrolysis was performed at $1 \circ C.^{18,21-23}$ For the larger particles, the water was kept at room temperature (20 ± 1 °C) during the addition of the titanium(IV) isopropoxide solution (\sim 10 to 15 min). Ten minutes after the end of the addition the temperature was lowered to less than 5 °C to avoid precipitation of the TiO₂ particles.²¹ Note that the titanium(IV) isopropoxide/ 2-propanol solution was always at room temperature. After the reaction mixture was stirred for 3 h, the water was removed by rotatory evaporation yielding a white powder that was dried overnight and redissolved in absolute ethanol. Both preparations yielded TiO₂ particles with an anatase crystal structure, as judged from X-ray powder diffraction measurements and the absorption onset in the UV/vis spectra. ZrO2 nanoparticles were prepared in a similar way using zirconium(IV) isopropoxide (Aldrich, 99.9%).¹⁶ Dynamic light scattering measurements performed on both a Protein Solutions DynaPro-MSDC spectrometer and a Coulter N4 plus spectrometer showed that the smaller particles have a hydrodynamic radius of ca. 1.4 to 2 nm and the larger particles have a hydrodynamic radius of 20 to 30 nm. The larger TiO₂ particles were also examined by transmission electron microscopy (TEM, 100,000× magnification). To help locate the TiO₂ particles on the TEM grid, a small amount of a Au colloid solution was added to the TiO₂ particle solution before deposition. The Au particles (ca. 15 nm diameter) have a strong contrast and can be clearly seen by TEM. These measurements show that the larger TiO₂ particles are cylindrical, with an average short axis length of 20 nm, an average long axis length of 40 nm, and a fair amount of polydispersity. These particle sizes are consistent with the sizes reported in the literature for the above recipe.^{18,23}

1AC and 2AC were purchased from TCI (Tokyo-Kasei) and 9AC was purchased from Aldrich. All three isomers were used without further purification. Steady-state absorption spectra were recorded with a Perkin-Elmer Lambda 6 UV/vis spectrophotometer, and fluorescence emission and excitation spectra were obtained with a SLM Instruments MC-320 spectrometer.

3. Results

The absorption spectrum of the dye molecules bound to the small (ca. 4 nm diameter) TiO_2 nanoparticles is identical to the



Figure 1. (a) Absorption spectra of 1AC in ethanol (–) and 1AC bound to small (•••) and large (- -) TiO₂ nanoparticles. (b) Absorption spectra of 1AC in ethanol (–) and 1AC bound to ZrO_2 nanoparticles (-•-•). Excitation spectra of 1AC bound to TiO₂ nanoparticles (•••) and to ZrO_2 nanoparticles (-•-•).

absorption spectrum for the molecules bound to the larger (ca. 40 nm diameter) TiO₂ particles. Both spectra are red shifted with respect to the free dye in solution, as shown in Figure 1 (a) for 1AC.¹⁶ The TiO₂ absorption at $\lambda < 350$ nm shows a redder onset for the big particles; this is not due to the particle size but to the fact that a larger concentration of TiO₂ was used for the solutions of the larger particles. This was done to ensure that the majority of dye molecules are bound in both solutions (the larger particles have less surface sites per unit volume of semiconductor and, therefore, a higher concentration is needed to bind a given amount of dye). Freshly prepared dye/TiO₂ solutions show a significant quenching of their fluorescence emission compared to the free dye in solution, and to the dye molecules bound to ZrO₂.¹⁶

Although the fluorescence quenching is considerable (> 90%), it is not complete. To determine whether the remaining fluorescence is due to free molecules in solution or to bound molecules, we recorded excitation spectra of 1AC bound to the three different kinds of semiconductors (small and large TiO₂ particles and ZrO₂ particles). The results of these measurements, shown in Figure 1(b), suggest that for the two TiO_2 solutions there is only one fluorescing species – the free dye molecules. This assignment is indicated by the perfect overlap of the rising portion of the fluorescence excitation spectra of the 1AC-TiO₂ solutions with the absorption spectrum of the free dye in solution. On the other hand, for the ZrO₂ solution there is a substantial red-shift in the excitation spectrum that perfectly matches the red-shift of the absorption spectrum of the bound dye molecules, indicating that in this case the fluorescence emission has an important contribution from the bound mol-



Figure 2. Solid line: transient absorption data for 1AC (top) and 2AC (bottom) bound to small and large TiO_2 nanoparticles. Dashed line: fits to the data using a single-exponential decay plus an offset, see text for details.

ecules, see Figure 1(b). We have previously shown that the absorption spectra of the dye molecules bound to anatase TiO_2 particles are identical to the spectra obtained when the molecules are attached to the ZrO_2 particles, see ref 16. Thus, these results show that when the dye molecules are bound to TiO_2 they do not fluoresce. Similar results were obtained for the other two anthracenecarboxylic acid isomers.

Transient absorption measurements for all three anthracenecarboxylic acid isomers show that there is no difference in the dynamics for *freshly* prepared samples of the different sized nanoparticles. Figure 2 shows the magic angle transient absorption experiments for 1AC and 2AC performed with 390 nm pump and 780 nm probe pulses. This probe wavelength monitors the electronically excited dye molecules, the dye radical cation, and the trapped conduction band electrons.¹¹⁻¹³ By using a combination of transient absorption, time-resolved anisotropy and bleach recovery measurements we have determined that the decay in the transient absorption signal is due to the back electron transfer reaction which destroys the radical cation and the trapped electrons.^{11,13,16} Figure 2 shows that the data for the large and small particles almost perfectly overlap for 1AC and 2AC; similar results were obtained for 9AC. Thus, the time scale for the back electron transfer reaction is the same for the 4 and 40 nm particles.

Also shown in Figure 2 are the best fits to the experimental data obtained from the convolution of a sum of exponentials with a Gaussian instrumental response function. For the freshly prepared large particle samples, as well as for the small TiO₂ particle samples, the data recorded over a 100 ps delay range fits well to a single-exponential decay plus an offset. The time constants obtained for the small (4 nm) particles are 19 ± 1 ps for 1AC, 14 ± 1 ps for 2AC, and 33 ± 2 ps for 9AC. For the large (40 nm) particles the time constants are 19 ± 1 ps, 15 ± 1 ps and 36 ± 4 ps for 1AC, 2AC, and 9AC, respectively. The



Figure 3. Transient absorption data for 1AC (top) and 2AC (bottom) bound to freshly prepared large TiO_2 nanoparticles (—) and large TiO_2 nanoparticles that had been aged for ca. 1 week (•••).

offset, which accounts for $13 \pm 3\%$ of the signal for 1AC and $5 \pm 3\%$ for 2AC, is assigned to the free dye in solution, as shown by the excitation spectra. Experimental conditions were such that > 90% of the dye molecules are bound.

After aging the samples for periods of time ranging from a couple of days to a couple of weeks, the transient absorption results for the dye molecules bound to the *large* TiO_2 particles present a considerable increase in the background signal. This is shown in Figure 3 for 1AC and 2AC. These changes are accompanied by an increase in the fluorescence quantum yield of the dye-semiconductor solution. There is a 1:1 correspondence between the increase in the fluorescence and the increase in the background transient absorption signal. In addition, there is no change in the excitation spectra of the samples, i.e., the fluorescence from the dye-TiO₂ samples is still due to free dye molecules in solution. These results indicate that the increase in the offset is due to an increase in the concentration of free dye. This aging effect is not observed for the smaller TiO_2 particles.

We have previously shown that water molecules effectively compete with the anthracenecarboxylic acid dye molecules for adsorption sites at the surface of the semiconductor nanoparticles.¹³ For example, adding $\geq 0.1\%$ H₂O by volume to an ethanolic solution of small TiO₂ particles with adsorbed 9AC results in a noticeable increase in the background transient absorption signal. The large TiO₂ particles have approximately 10 times less surface area than the 4 nm diameter particles for a given TiO₂ concentration, hence, they are more susceptible to contamination by water. Thus, we propose that the increase in the background signal shown in Figure 3 is due to adsorption of water from the atmosphere onto the nanoparticle surface. This process depends on how tightly the samples are sealed, how they are stored, the relative humidity in the laboratory, etc., which also explains why different samples take different periods of time to develop the larger background.



Figure 4. Transient absorption data for 2AC bound to large (ca. 40 nm) TiO₂ nanoparticles (solid line) recorded over a 0-200 ps time range. Fits to the data using a single-exponential decay plus an offset are also presented (dashed line), as well as the difference between the fit and the experimental data (residuals).

To fit the data for the aged, large particle samples, a function that contains two exponential decays plus an offset must be used. This is necessary because of the greater amount of free dye present in these samples. The transient absorption signal from the free dye molecules shows a growth that distorts the decay due to the back electron transfer reaction for the bound dye molecules. Because of this complication, only the results from the freshly prepared solutions will be analyzed in the following discussion, as these results are more reliable (and meaningful) than the results from the aged samples.

Transient absorption data for 2AC bound to the large TiO₂ particles collected over a 200 ps time delay range is presented in Figure 4. In this experiment the data can be satisfactorily fitted using a single-exponential decay of 15 ± 1 ps plus an offset. In several other scans recorded over this longer delay range, multiexponential decay functions gave slightly better fits to the data compared to single exponential decays. However, the deviations from a single exponential were always small, and the weighted average of the time constants from the multiexponential fits always gave a decay time that was only 10% to 15% longer than that obtained from the single-exponential fits. Thus, we believe that a single-exponential decay function is sufficient to account for our experimental data in the 0-100 ps time range, which accounts for > 90% of the back electron transfer reaction, i.e., more complex multiexponential or stretched exponential fitting functions are not justified.

4. Discussion

The photoexcited dye molecules rapidly transfer an electron to the TiO₂ nanoparticles. The electrons are subsequently trapped into sites at the surface of the particle that can have a distribution of energies as well as a distribution of distances from the dye radical cation. The initial trapping process is believed to be very fast (ca. 100 fs),^{15,17,22} and we note here that very little information is available about the character of the trap sites. Our transient absorption experiments monitor the reaction between the trapped electrons and the dye radical cation. The results from these measurements show that the majority of the back electron transfer occurs with a single-exponential decay, and that there is *no difference* in the dynamics for the large and small TiO₂ particles in the 0–200 ps time range. The latter observation is the most important point for this paper. In general, we expect larger distances (on average) between the dye radical cation and the trapped electrons for the larger TiO₂ particles and, therefore, longer back electron transfer times.^{19,20} Thus, the observation that the transient absorption decays are identical for the small and large TiO₂ particles is somewhat surprising.

Before analyzing the experimental results, it is important to address the issue of quantum-size effects in TiO₂ particles. There is some controversy about whether TiO₂ shows size quantization at the typical sizes used in solar cells (2-50 nm diameter). Predictions of the threshold of quantum size effects depend critically on m_e , the effective mass of the electron.³ Early studies reported m_e values for TiO₂ ranging from 0.01 to 30 m_0 , where m_0 is the electron rest mass.^{24–26} Thus, estimates of the region where quantum size effects are expected for TiO₂ vary from 0.6 to 2000 nm. More recent studies suggest that TiO_2 nanoparticles do not present quantum size effects for particles as small as 2 nm diameter.²⁷ In addition, recent electrical resistivity measurements of anatase TiO₂ films indicate that the effective mass of the electrons is approximately $1 m_0$, which implies a Bohr radius for the exciton of ca. 1.6 nm for the conduction band electrons.²⁸ Thus, we do not believe that quantum size effects are important for TiO₂ particles in the 4 nm to 40 nm size range. For TiO₂, the surface charge density and, therefore, the conduction band energy also depend on the pH of the solution.²⁹⁻³² In our experiments, the small and large particles were synthesized under identical pH conditions so that the surface charge density should be the same for the two samples. Thus, in the following analysis we will assume that the conduction band energy and, therefore, the energetics for the back electron transfer reaction are the same for the different sized TiO₂ particles.

In the following discussion we will assume that the larger particles are spherical with a mean diameter of 40 nm, even though the TEM results show that they have an aspect ratio of \sim 2. This approximation is not expected to change the conclusions of this paper. The starting point in our analysis is to extend the model of Kelly et al.^{19,20} to spherical particles. This model describes radiative recombination between photoexcited electrons and holes in MoS₂ nanoclusters; however, it can be easily refined to account for the reaction between trapped electrons and an adsorbed dye molecule.²⁰ In this model the electrons are assumed to be randomly distributed over the surface of the particle. The distribution is described by the function $\tilde{g}(x,t)$, where *x* is the distance between the trapped electron and the radical cation. The back electron transfer reaction occurs with a distance dependent rate constant given by

$$k(x) = k_0 \exp[-2x/a] \tag{1}$$

where k_0 gives the magnitude of the back electron transfer rate constant, and *a* is a distance scaling factor. For the MoS₂ particles examined in ref 19, the value of *a* was found to be similar to the Bohr radius of the bulk exciton in MoS₂. Assuming that there is no diffusion between trap sites on the time scale of the back electron transfer reaction, the distribution function simply decays in time as

$$\frac{d\tilde{g}(x,t)}{dt} = -k(x)\tilde{g}(x,t) \tag{2}$$

In this model the close electrons (small values of x, large values of k(x)) react first and the far away electrons react at latter times, i.e., the distribution function changes its shape during the course

of the reaction, which causes multiexponential decay kinetics. The probability of finding an electron in the particle at time t is given by²⁰

$$N(t) = \int_0^{2R} \tilde{g}(x,t) \, dx \tag{3a}$$

$$= \int_0^{2R} \tilde{g}_0(x) \,\mathrm{e}^{-k(x)t} \,dx \tag{3b}$$

where $\tilde{g}_0(x) \equiv \tilde{g}(x, t = 0)$, and the distribution function is normalized so that $\int_0^{2R} \tilde{g}_0(x) dx = 1$. In these equations *R* is the radius of the particles, so that the maximum distance between the trapped electrons and the dye radical cation is 2*R*. The total number of the trapped electrons is equal to the number of dye radical cations, thus, N(t) is proportional to the absorbance of the sample, which is the observable in our experiments (disregarding the contribution from the free dye molecules in solution, which produce an offset in the transient absorption data).

To solve eq 3, an expression is needed for the distribution function $\tilde{g}_0(x)$. To derive this function we assume that the dye radical cation is at a fixed point on the surface of a sphere and the trapped electrons are randomly distributed over this surface. In this case it can be shown that $\tilde{g}_0(x)$ is given by

$$\tilde{g}_0(x) = x/2R^2 \tag{4}$$

where $0 \le x \le 2R$ (the derivation of this function is given in Appendix A). Substitution of eq 4 into eq 3b yields

$$N(t) = \frac{1}{2R^2} \int_0^{2R} x e^{-k(x)t} dx$$
 (5)

which can be easily integrated using Mathematica (for example). Equation 5 contains two adjustable parameters: k_0 and a. In MoS₂ the value of a was found to be the same as the Bohr radius of the bulk exciton, i.e., $a = \epsilon a_0/(m_e/m_0)$ where ϵ is the static dielectric constant of the semiconductor and $a_0 = 0.053$ nm. Reasonable values of ϵ and m_e/m_0 for anatase TiO₂ are $\epsilon = 31$ and $m_e/m_0 = 1$,²⁸ which yields a = 1.6 nm. Note that this value of the distance scaling parameter is strictly appropriate for an electron in the conduction band of TiO₂.

Calculated decays for the small and large TiO₂ particles using this value of a are shown in Figure 5 (a). In this calculation, k_0 was adjusted to give a decay that is consistent with a 19 ps back electron transfer time for the small particles (this value is appropriate for 1AC). Equation 5 clearly predicts very different dynamics for the 4 and 40 nm diameter particles. In addition, the calculated decay for the 4 nm particles is clearly multiexponential, which is not observed in our experiments. Increasing the value of *a* reduces the difference in the decay times for the large and small particles. For values of $a \ge 180$ nm the decay constants for the different sized particles are essentially equal. For example, using a = 200 nm and $k_0 = 0.06$ ps⁻¹ gives a decay time of ca. 19 ps for both the 4 and 40 nm particles. (Larger values of a and correspondingly smaller values of k_0 can give the same decay time.) Note that when $a \gg 2R$ the calculated decays are essentially single exponential.

The large value of *a* obtained from the above analysis is unphysical: if the Bohr radius of an electron in TiO_2 was \geq 180 nm, then TiO_2 should show enormous quantum size effects. This result means that the assumptions used to derive eq 5 must be incorrect. An alternative approach to this problem is to assume that diffusion between trap sites is much faster than the back electron transfer reaction (this is the opposite limit to



Figure 5. (a) Time-dependent populations for small (4 nm) and large (40 nm) particles calculated using eq 5 with a = 1.6 nm and $k_0 = 2.5$ ps⁻¹. (b) Ratio of rate constants for the large and small particles calculated using eq 7 versus *a*, the distance scaling parameter. See text for details.

that used to derive eq 5). In this case it can be shown that the probability of finding a trapped electron in the particle at a time t is given by the relatively simple expression

$$N(t) = N_0 \mathrm{e}^{-k(R)t} \tag{6}$$

where the particle size dependent rate constant k(R) is given by

$$k(R) = \int_0^{2R} \tilde{g}_0(x)k(x)dx \tag{7}$$

In this equation $\tilde{g}_0(x)$ is given by eq 4, i.e., the electrons are still assumed to be randomly distributed over the surface of the particle. Equations 6 and 7 are derived in Appendix B. In this model we would always expect to see single exponential decays (which is essentially what is observed experimentally), but the rate constant should be different for different sized particles. For example, choosing a = 1.6 nm and $k_0 = 0.69$ ps⁻¹ gives a back electron transfer time of 19 ps for the 4 nm particles and 1800 ps for the 40 nm particles. As was found for eq 5, using larger values of a reduces the difference in the electron transfer times. A plot of the ratio of the rate constants calculated using eq 7 for the small and large particles k(4 nm)/k(40 nm) is shown in Figure 5(b) as a function of the distance scaling parameter a. Note that this ratio is independent of the value of k_0 . This plot shows that the rate constants are essentially equivalent for values of $a \ge 200$ nm. However, once again such a large value for the distance scaling parameter for an electron in TiO₂ is unrealistic. Thus, allowing for fast diffusion between trap sites does not lead to a physically reasonable model. The two cases considered (no diffusion between trap sites and diffusion much

faster than back electron transfer) represent two opposite limits for the mobility of the trapped electrons. Thus, we conclude that all models where the electrons are assumed to be initially evenly distributed over the surface of the particle cannot explain our experimental results with physically realistic parameters.

An alternative approach is to assume that the electrons are randomly distributed within the volume of the particle rather than distributed over the particle surface (i.e., the electrons are in the conduction band and not surface trap sites). This situation is more difficult to quantitatively analyze. However, we would still expect to see a difference in the back electron transfer times for the different sized particles for this model. We note that the average time for a species that is randomly distributed inside a sphere to diffuse to the surface of the sphere is $\tau = R^2/\pi^2 D$, where D is the diffusion constant.³³ This equation describes the time scale for a reaction between a species inside a sphere and a second species that is located at the surface, assuming that the reaction occurs as soon as the diffusing species reaches the surface.^{33,34} In our experiments the electrons must diffuse to the dye radical cation, which is fixed at a specific position at the surface of the nanoparticle, i.e., the reaction does not occur as soon as the electron reaches the surface. Therefore, the reaction time will be longer than predicted by the above equation. We expect that the time scale for the reaction should increase by a factor that is related to the total surface area of the particle divided by the area of an adsorbed dye molecule. This factor is proportional to R^2 , which means that the difference in reaction times for different sized particles should scale as R^4 . (Note that this treatment neglects Coulombic interactions between the electron and the dye.) Thus, we expect a 10^4 difference in the time scales for diffusion of the electron to the dye radical cation for the two particles, if the electrons are randomly distributed inside the particles. This estimate of the difference in reaction times is not consistent with our experimental data.

The final possibility considered is that the electrons injected into the semiconductor particles are localized into sites that are spatially close to the dye radical cation. Furthermore, the back electron transfer reaction occurs before the electrons can escape from these sites. In this case the size of the particles would not be expected to have an effect on the rate of the semiconductorto-dye electron transfer reaction. The dye molecules used in this study attach to the TiO₂ particles through the carboxylate group, which binds to titanium atoms at the surface of the particles.² The surface electron trap sites are also located on the titanium atoms, and typical Ti-Ti distances in TiO₂ are ca. 3 Å.³⁵ Thus, if the electrons are localized on nearest neighbor, or next nearest neighbor Ti's, the back electron transfer reaction would be expected to be rapid and independent of the size of the particles. Of the three models considered for the electron sites, random distribution over the surface or within the volume of the semiconductor, or trapping into localized sites adjacent to the dye radical cation, the last is the only one that is consistent with our experimental data.

An interesting consequence of this conclusion is that if the dye molecules only interact with localized sites at the semiconductor surface, and not the delocalized conduction band levels, then the density of accepting states for electron transfer should be small. The ultrafast time scales for forward (dye-tosemiconductor) electron transfer observed in these systems are usually attributed to the high density of states in the conduction band of the semiconductor.³⁶ The anthracenecarboxylic acid dye molecules that were examined in this paper show forward electron transfer times that are < 200 fs.¹⁶ Thus, the exact role



Figure 6. Comparison of experimental transient absorption data for a $9AC-TiO_2$ solution (—) and the signal calculated using eqs 8-10 (···). The $9AC-TiO_2$ sample was in ethanol with ca. 1% added water. The water produces nonsingle exponential decay kinetics for these samples, see text for details and ref (13).

of the conduction band levels in electron transfer for the anthracenecarboxylic acid—anatase TiO_2 systems is unclear at the present time.

It should be noted that, in general, a distribution of energies is expected for the electron trap sites,² which should also lead to nonsingle exponential decay kinetics. The effect of a distribution of trap site energies can be modeled by writing the transient absorption signal as^{37}

$$S(t) = \int_{-\infty}^{\infty} P(E) e^{-k(E)t} dE$$
(8)

where

$$k(E) = k_0 e^{-(E-\lambda)^2/4\lambda kT}$$
(9)

In these equations P(E) is the energy distribution function for the sites, λ is the reorganization energy, E is the energy difference between the trap site and the redox potential of the dye, and we have assumed that the classical Marcus theory for electron transfer is sufficient.^{36–40} To simulate the experiments P(E) is assumed to be given by a Gaussian distribution function:

$$P(E) = e^{-(E - \Delta E)^2/\sigma^2}$$
(10)

where ΔE is the average energy difference between the trap sites and the redox potential of the dye,² and σ gives the width of the energy distribution. The choice of a Gaussian function is somewhat arbitrary; however, the exact function used in the present analysis is not expected to change the conclusions given below. Equation 8 is simply a sum of exponential decays for the different trap sites that is correctly weighted for the trap site energies. Note, we have assumed that the coupling element for electron transfer is identical for the different trap sites.

Equations 8–10 have been used previously to simulate transient absorption data for 9AC–anatase TiO₂ in ethanolic solutions with small (<2 vol %) amounts of added water.³⁷ Adding water to the ethanol/TiO₂ solutions changes the energy of the electron trap sites at the surface of the particles and produces nonexponential decays.¹³ For example, Figure 6 shows data collected for 9AC in a TiO₂/ethanol solution with 1% added water. Also shown is a fit to the data using eqs 8–10 and the following parameters: $\Delta E = 1.6 \text{ eV}$, $\lambda = 0.7 \text{ eV}$, and $\sigma = 0.043 \text{ eV}$ (the value of ΔE corresponds to the difference in energy between the flatband potential of the semiconductor and the redox potential of the dye). An offset has also been added

to account for the free dye molecules in solution. The calculated and experimental transient absorption signals are clearly in excellent agreement. A multiexponential fit to the experimental data shown in Figure 6 yielded time constants of 33 ps (35%), 8.7 ps (39%), and an offset (26%). These results are presented here to demonstrate that eqs 8-10 provide a good description of the multiexponential decays that can be observed in semiconductor-to-molecule electron transfer reactions. Note that for a given ΔE the deviation of the calculated decay from a single exponential increases as σ increases. For the experimental data shown in Figures 2 and 4, the values of σ used in eqn 10 must be less than 0.02 eV to obtain a reasonable fit to the data. This means that the fwhm of the trap site energy distribution must be less than 0.03 eV, which is on the order of kT. Thus, the back electron transfer reaction occurs from a fairly narrow energy distribution of trap sites for the anthracenecarboxylic acid-anatase TiO₂ systems.

5. Summary and Conclusions

The electron transfer dynamics for the 1-, 2-, and 9-isomers of anthracenecarboxylic acid bound to different sized anatase TiO₂ particles has been examined by ultrafast transient absorption experiments. The results from these measurements show that (i) greater than 90% of the back (semiconductor-to-dye) electron transfer reaction is complete within 100 ps, and that in this time range the observed decays in the transient absorption data can be fitted using a single exponential decay plus an offset. (The offset accounts for the unbound dye molecules.) (ii) The size of the TiO₂ particles does not affect the electron transfer dynamics for particles in the 4 to 40 nm size region. These experimental results can only be explained by assuming that the electrons are trapped in localized states that are adjacent to the binding site for the dye radical cation, i.e., their spatial distribution is not random. The trapped electrons undergo back electron transfer before they can diffuse away from the dye radical cation. These results also show that the shape of the nanoparticles should have very little effect on the semiconductorto-dye electron transfer times for this system. The observation of essentially single-exponential decays for the back electron transfer reaction in our data also implies that the trap sites for the electrons at the surface of the particle have a fairly narrow distribution in energy.

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Appendix A: Derivation of Equation 4

The distribution function for the distance between a species fixed at a point on the surface of a sphere and a second species randomly distributed over the surface can be derived as follows. The fixed species is considered to be located at the point **P** in Scheme 1. The second species (the trapped electron in our case) is located at a random position **A**, at the surface of the sphere of radius *R*. The angle θ goes from $-\pi/2$ to $\pi/2$ and is defined as the polar angle, and φ is the azimuth angle which goes from 0 to 2π .⁴¹ The probability of finding the species A at a distance between *x* and *x* + *dx* from the point **P**, g(x)dx, is

SCHEME 1



proportional to the area of the ring around the sphere defined by x and x + dx.

The area of this ring can be calculated by considering the area element in spherical coordinates, $dA = R^2 \cos\theta \ d\theta \ d\varphi$, and then integrating over the azimuth angle φ , to give

$$g(x)dx \propto 2\pi R^2 \cos\theta \ d\theta \tag{A1}$$

where *x* is the distance between **P** and **A**. From simple geometry and it can be shown that $x = R[2(1 - \sin\theta)]^{1/2}$. Equation (A1) can be rearranged to give

$$g(x) \propto \frac{2\pi R^2 \cos\theta}{|dx/d\theta|}$$
 (A2)

Performing the differentiation $dx/d\theta$ yields $g(x) \propto 2\pi x$, which in turn gives the normalized distribution function

$$\tilde{g}(x) = x/2R^2 \tag{A3}$$

where the normalization condition is $\int_{0}^{2R} \tilde{g}(x) dx = 1$.

Appendix B: Derivation of Equations 6 and 7

To derive the rate law for the case where diffusion between trap sites is much faster than the back electron transfer time, consider the distribution at time $t_1 = t_0 + \Delta t$. From the rate law $d\tilde{g}(x, t)/dt = -k(x)\tilde{g}(x, t)$ we have

$$\tilde{g}(x, t_1) = \tilde{g}(x, t_0) - k(x)\tilde{g}(x, t_0)\Delta t$$
(B1)

Integration of $\tilde{g}(x, t_1)$ over x gives $N(t_1)$, the probability of finding an electron on the particle at time t_1

$$N(t_1) = \int_0^{2R} \tilde{g}(x, t_1) \, dx = N(t_0) - \Delta t \int_0^{2R} k(x) \, \tilde{g}(x, t_0) \, dx$$
(B2)

and by comparison at time $t_2 = t_1 + \Delta t$

$$N(t_2) = N(t_1) - \Delta t \int_0^{2R} k(x) \,\tilde{g}(x, t_1) \, dx \tag{B3}$$

If we assume that $\tilde{g}(x, t_1) = N(t_1) \times \tilde{g}(x, t_0)$, i.e., the distribution at time t_1 has the same form as that at t_0 but is weighted by the population $N(t_1)$, then we can write

$$N(t_2) = N(t_1)[1 - \Delta t \int_0^{2R} k(x) \,\tilde{g}(x, t_0) \, dx]$$
(B4)

and in general

$$N(t_n) = N(t_{n-1})[1 - \Delta t \int_0^{2R} k(x) \,\tilde{g}(x, t_0) \, dx]$$
(B5)

The condition used to derive eqs B4 and B5 is equivalent to assuming that the electrons rapidly diffuse between trap sites, so that they are always randomly distributed over the surface of the particle. Equation B5 can be rewritten as

$$\frac{\Delta N(t)}{N(t)} = \left[-\int_0^{2R} k(x) \,\tilde{g}(x, t_0) \,dx\right] \Delta t \tag{B6}$$

which for small Δt can be trivially integrated to give

$$N(t) = N(t_0) e^{-k(R)t}$$
(B7)

where $k(R) = \int_0^{2R} k(x)\tilde{g}(x, t_0) dx$.

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