Effect of Structure on Electron Transfer Reactions between Anthracene Dyes and TiO₂ Nanoparticles

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Photoinduced electron transfer to TiO_2 nanoparticles has been examined for the 1-, 2-, and 9-isomers of anthracenecarboxylic acid. TiO_2 samples with either anatase or amorphous crystal structures were used for these experiments. The results from time-resolved transient absorption measurements show that the rates of the forward (dve-to-semiconductor) and reverse (semiconductor-to-dye) electron transfer reactions depend on the chemical structure of the dye and the method used to synthesize the particles. These effects arise from differences in both the energetics and the coupling elements for the reactions. Specifically, the reverse electron transfer reactions for the 1- and 2-isomers are significantly faster than that for the 9-isomer due to differences in the oxidation potentials of the dye molecules. In addition, both the forward and reverse electrontransfer times are faster for the anatase TiO_2 particles compared to the amorphous particles. For example, the forward electron transfer time for the anatase particles is ≤ 200 fs, whereas it is ca. 1.5 ps for the amorphous particles. This is due to a difference in the coupling elements for the forward electron transfer reaction. Finally, all the anthracenecarboxylate dyes examined show red shifts in their UV-vis absorption spectra when they are attached to the semiconductor particles. Experiments with ZrO2 show that these shifts are not due to a charge-transfer band. The spectra are more strongly perturbed when the dye molecules are attached to the anatase particles, which shows that for this series of compounds there is a correlation between the spectral shifts and the time scale for electron transfer.

Introduction

The demonstration of efficient solar-energy conversion using dye-sensitized semiconductor electrodes has generated considerable interest in the electron transfer dynamics of molecules bound to metal-oxide surfaces.^{1,2} In general, ultrafast laser studies show that the forward (dye-to-semiconductor) electron transfer reaction is extremely fast, usually less than 200 fs.^{3–15} On the other hand, the back reaction occurs on a range of time scales—varying from ~10 ps to microseconds—and often displays complex, multiexponential decays.^{5,6,9–19} Both the forward and reverse electron-transfer reactions are crucial to the solar-energy conversion process, therefore, it is important to understand how the rates of these reactions depend on the chemical properties of the dye and the semiconductor.

In a recent series of papers, we have examined the electron transfer dynamics of 9-anthracenecarboxylic acid (9AC) bound to TiO₂ particles.^{9,12} The TiO₂ particles in these studies were prepared by different techniques, and the time constants measured for the back electron transfer reaction were found to be different for the two types of particles.^{9,12} The back electron transfer rate was also found to depend on how the semiconductor particles were treated after they had been prepared. For example, adding small amounts of water to the ethanolic dye-TiO₂ solutions produces a red shift in the TiO₂ absorption spectrum and a decrease in the back electron transfer time.¹² The red shift implies a lower conduction band energy and, therefore, a smaller driving force for back electron transfer. These results are consistent with Marcus-inverted behavior for the back electron transfer reaction.¹² Analysis of the data using the weak coupling limit expression for electron transfer gave a reorganization energy of $0.75 \pm 0.05 \text{ eV}.^{12}$

In this paper, we report results for a series of carboxy– anthracene dyes: 9AC, 1-anthracenecarboxylic acid (1AC), 2-anthracenecarboxylic acid (2AC), and 9-anthraceneacetic acid (9AA). Time-resolved experiments were carried out for these species bound to the two types of TiO₂ particles used in our previous paper (which have anatase or amorphous crystal structures), as well as particles of ZrO₂. The conduction band of ZrO₂ is 1.2 eV higher in energy than that for TiO₂,²⁰ which means that photoinduced electron transfer does not occur to ZrO₂ for these systems.

The aim of these experiments is to gain a "chemical" understanding of the important factors in the dye-sensitization process. As will be shown below, both the oxidation potential of the dye and the crystal structure of the semiconductor play crucial roles in the electron transfer reactions. The experimental results also show that both the forward and reverse electron transfer rates are correlated to the shift in the UV–vis absorption spectra of the dye molecules that occurs when they bind to the semiconductor particles. However, these spectral changes are not due to the formation of a charge-transfer band. Analysis of the rate constants for back electron transfer shows that these reactions are in the intermediate coupling region (i.e., coupling elements of $50-200 \text{ cm}^{-1}$). Thus, calculations based on the simple nonadiabatic theory for electron transfer are not adequate for these systems.^{21–23}

Experimental Section

The transient absorption apparatus has been described in detail elsewhere.⁹ Briefly, the output of a regeneratively amplified Ti–Sapphire laser system (Clark-MXR CPA-1000; 100–120

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fs fwhm; 0.6 mJ/pulse; $\lambda = 780$ nm) was split by a 70/30 beam splitter (CVI). The 70% portion was doubled in a 1 mm type-I BBO crystal to supply the pump pulses (390 nm), and the 30% portion was used as the probe beam, after attenuation by neutral density filters. White light probe pulses were generated by focusing into a 6 mm BK-7 window; different wavelengths were selected by 10 nm band-pass interference filters (Oriel). Crosscorrelations between the pump and probe pulses were measured by sum frequency generation or parametric amplification in a 1 mm type-I BBO crystal. The fwhm of the cross-correlation trace was 150-200 fs (sech² deconvolution). The polarizations of the laser pulses were controlled by passing the 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. Steadystate absorption spectra were recorded with a Perkin-Elmer Lambda 6 UV-vis spectrophotometer, and fluorescence spectra were obtained with a SLM Instruments MC-320 spectrometer.

The anatase TiO₂ nanoparticles were prepared by controlled hydrolysis in water of titanium(IV) isopropoxide (ACROS, 98%) dissolved in 2-propanol.^{12,24-26} The hydrolysis was carried out under deareated conditions at 1 °C. ZrO2 nanoparticles were prepared in a similar way using zirconium(IV) isopropoxide (Aldrich, 99.9%).²⁶ The water was removed by rotatory evaporation, yielding a white powder that was dried overnight and redissolved in absolute ethanol. X-ray powder diffraction and UV-vis absorption spectra confirmed the anatase crystalline structure. TiO₂ nanoparticles were also synthesized by rapid hydrolysis of titanium(IV) isopropoxide in absolute ethanol.9,27 In this case, the X-ray powder diffraction patterns failed to show any peaks, indicating that the particles have an amorphous crystal structure. The absorption onset for the particles is similar to that of rutile TiO₂ (the amorphous particles have a red-shifted absorption spectrum compared to the anatase particles).²⁶ Dynamic light scattering measurements (DynaPro-MSDC, Protein Solutions) show that the anatase particles have an average hydrodynamic radius between 1.5 and 2.0 nm for samples prepared on different days. The amorphous particles only weakly scatter light, which means it was not possible to accurately record their size via light scattering.

9AC was purchased from Aldrich and was used without further purification. 1AC and 2AC were purchased from TCI (Tokyo-Kasei) and were also used without further purification. 9AA was synthesized by treating 9-(chloromethyl)anthracene (Aldrich, 98%) with magnesium turnings (1 equiv) in dry THF under reflux overnight. The resulting Grignard reagent was reacted with dry ice to produce 9AA. The product was recrystallized from toluene/ethanol and identified by IR, NMR, and mass spectroscopy. Cyclic voltammetry was performed for all three anthracenecarboxylic acid isomers in acetonitrile (Fisher) using ferrocene as the internal reference. The results from the cyclic voltammetry experiments show that the oxidation potentials of 1AC and 2AC are 0.1 eV more negative than the 9AC oxidation potential. From ref 28, $E(9AC/9AC^{\bullet+}) = 1.3$ eV versus NHE, therefore, $E(1AC/1AC^{\bullet+}) = E(2AC/2AC^{\bullet+}) = 1.2$ eV versus NHE.

Results

9-Anthraceneacetic Acid. Both the absorption spectrum and the transient absorption dynamics of the 9AA-TiO₂ solutions failed to show any differences from the free dye in solution. Also, no fluorescence quenching was observed for 9AA when TiO₂ was added to the solution. To test whether 9AA binds to the particles, the stability against flocculation of a solution of amorphous TiO2 with 9AA and a solution with a greater amount of 9-methylanthracene (9MA, which is not expected to adsorb onto TiO₂) were compared to as-prepared particles. Both the 9MA-TiO₂ and the straight TiO₂ solutions showed significant turbidity after several hours at room temperature. In contrast, the solution with 9AA remained clear, indicating that the 9AA molecules attach to the particles and protect them against precipitation. The observation of no fluorescence quenching or change in the transient absorption dynamics implies that the forward electron transfer time is longer than 10 ns for 9AA (i.e., longer than the estimated lifetime of the excited electronic state of the dye). This implies that the electronic coupling element for electron transfer from 9AA to TiO₂ (either the anatase or the amorphous forms) is at least 2 orders of magnitude smaller than the coupling elements for the other dye molecules in this study (vide infra).

Note that the sedimentation experiments do not definitively prove that 9AA adsorbs onto the TiO_2 particles, i.e., the observation of reduced electron-transfer efficiency may simply mean that the dye molecules are not attached to the particles. A possible reason why this may occur for 9AA is that adsorption requires deprotonation of the carboxylate group,^{11,29} which is unfavorable for 9AA because the negative charge on the deprotonated carboxylate cannot be stabilized by resonance with the anthracene ring.³⁰

Steady-State Spectra. When 9AC binds to the surface of either crystalline form of TiO₂, the absorption spectrum of the dye shifts to the red.^{9,12} Figure 1 shows the absorption spectra of 1AC and 2AC in solution and bound to the anatase and amorphous TiO₂ nanoparticles. There is a pronounced red shift in the spectra for both isomers, indicating a strong interaction with the particles. The stoichiometry of this reaction was studied by recording difference absorption spectra, shown in Figure 2 for 2AC. In these experiments, the absorption of the dye–TiO₂ system was measured against the same concentration of dye as a reference. A linear relation of the difference absorption with the dye concentration (insert of Figure 2) shows that the dye molecules do not form dimers at the surface of the TiO₂ particles.³¹ Similar results were obtained for 1AC.

The association constant K_a between the dye molecules and the semiconductor nanoparticles was calculated using the Langmuir adsorption isotherm³²

$$K_{\rm a} = \frac{\Theta}{\left[\mathrm{D}\right]_{\rm f} \left(1 - \Theta\right)} \tag{1}$$

where $[D]_{\rm f}$ is the concentration of free dye and Θ is the fraction of occupied sites at the particle surface. The fraction of occupied sites is given by $\Theta = [D]_{\rm b}/[S]_0$, where $[D]_{\rm b}$ is the



Figure 1. Top: Absorption spectra for 1AC in ethanol (···) and bound to anatase (–) and amorphous (- - -) TiO_2 . Bottom: Absorption spectra for 2AC in ethanol (···) and bound to anatase (–) and amorphous (- - -) TiO_2 .



Figure 2. Absorption spectra of 2AC bound to anatase $-\text{TiO}_2$ minus the absorbance of an equimolar solution of free 2AC. The concentration of 2AC increases from bottom-to-top at 410 nm. The inset shows the linear dependence of the absorbance difference at 410 nm on the concentration of 2AC.

concentration of bound dye and $[S]_0$ is the total concentration of sites. The total concentration of dye is $D_0 = [D]_f + [D]_b$ and $[S]_0 = \gamma$ [TiO₂], where γ is a proportionality constant that is related to the average number of binding sites per particle. Using the last two relationships in eq 1 yields

$$K_{\rm a}\gamma \frac{[{\rm TiO}_2]}{A/\epsilon l} - K_{\rm a} = \frac{1}{(D_0 - A/\epsilon l)}$$
(2)

where $A = \epsilon l[D]_b$ is the absorbance of the bound dye molecules. The effective association constant $K_a\gamma$ was calculated using data from a range of wavelengths. In these calculations the values of the ϵl were initially estimated from a solution with a high concentration of TiO₂. $K_a\gamma$ was then obtained from the slope of a plot of $1/(D_0 - A/\epsilon l)$ versus $[TiO_2]/(A/\epsilon l)$. The percentage of bound dye was then calculated, and the values of ϵl were reevaluated. This series of calculations was performed iteratively until the answers were self-consistent. For anatase TiO₂



Figure 3. Absorption spectra for 2AC bound to anatase TiO₂ (––), amorphous TiO₂ (•••), ZrO₂ (- –), 2AC in ethanol (-••–), and 2AC in an acidic ethanolic solution with an excess of Al^{3+} (-•–).

the following effective association constants were obtained for 1AC, 2AC, and 9AC, respectively, $K_a\gamma = 6000 \pm 1000$, 4300 \pm 800, and 1400 \pm 200. These results show that 1AC and 2AC have a significantly stronger chemical interaction with the semiconductor particles than 9AC.

For the amorphous TiO₂ particles, the smaller perturbation of the absorption spectra does not allow for an accurate determination of $K_{a\gamma}$ by this method. Thus, the association constants for the different dye molecules bound to the amorphous TiO₂ particles were determined using the fluorescence quenching method described in ref 9. The effective association constants were found to be within experimental error of the values obtained for the anatase TiO₂ particles. For ZrO₂, the effective association constants are approximately one-half of those for anatase TiO₂.

In Figure 3, absorption spectra are presented for 2AC in ethanol, bound to anatase TiO₂, amorphous TiO₂ and ZrO₂ particles, and in an acidified ethanol solution with excess Al³⁺. This figure shows that 2AC interacts with ZrO₂ and anatase TiO₂ in a similar way, but the perturbation of the spectrum for the amorphous TiO₂ particles is much weaker. This can be clearly seen in the $\lambda > 400$ nm spectral region. Also note that the red shift in the absorption spectrum of the dye induced by complexation with Al³⁺ is nearly identical to the shift induced by the amorphous particles. A red shift due to the formation of a dye—metal ion complex has been previously observed for a variety of dye molecules, see for example ref 10. It is important to note that the spectral shifts for the anatase TiO₂ and ZrO₂ particles are larger than that caused by complexation with Al³⁺. 1AC and 9AC show qualitatively similar results.

Fluorescence quenching measurements show that the fluorescence quantum yield for 1AC and 2AC bound to ZrO2 is ca. 90% of that for the free dye molecules in solution. For 9AC-ZrO₂, the relative fluorescence quantum yield is ca. 70%. This shows that photoinduced electron transfer to ZrO₂ is not significant for the anthracenecarboxylate dye molecules. These results are in agreements with recent fluorescence measurements performed by Levinger and co-workers for coumarin 343 bound to ZrO₂.³³ For the dye molecules bound to TiO₂, the fluorescence quantum yields are ca. 5% of those for the free dye in solution. Fluorescence excitation spectra show that the emission from the dye $-TiO_2$ solutions is due to free dye in solution. In contrast, for the dye-ZrO₂ solutions, the fluorescence excitation spectra show that the majority of the fluorescence (>90%) arises from bound dye molecules. These results are consistent with fast photoinduced electron transfer to TiO₂ but not to ZrO₂.

Transient Absorption and Time-Resolved Anisotropy Measurements. In our previous studies, we compared the



Figure 4. Magic-angle transient absorption data for 9AC bound to anatase TiO_2 , amorphous TiO_2 , and ZrO_2 . The dashed lines are the fits to the experimental data, the results of which are summarized in Table 1. The experiments were performed with 390 nm pump and 780 nm probe pulses. The experiments for amorphous TiO_2 were performed over a 200 ps total delay time.

transient absorption dynamics and time-resolved anisotropy of $9AC-TiO_2$ to the free dye in solution.^{9,12} In this paper, we introduce the results for 9AC bound to ZrO₂ nanoparticles. Figure 4 compares the dynamics of 9AC bound to the anatase and amorphous TiO₂ particles and the ZrO₂ nanoparticles. The best fits to the data using a sum of exponentials convoluted with a Gaussian instrument response function are also shown. All the scans presented in Figure 4 were measured at the magic angle (54.7°) to eliminate effects due to rotation.³⁴ In the ZrO_2 experiments, the 780 nm probe pulse interrogates the electronically excited dye molecules that are bound to the surface of the semiconductor particles (particle concentrations used are such that over 95% of the molecules are bound). The 9AC-ZrO₂ signal has a biexponential decay with time constants of 44 ps (28%) and 7 ps (22%) with a 50% offset. For the TiO₂ particles, the fluorescence quenching studies show that most of the excited 9AC molecules undergo electron transfer, creating trapped electrons in the TiO₂ particles and the 9AC⁺⁺ radical cation that strongly absorb the 780 nm probe light.^{9,10,12,35} The decay in the signal for 9AC-TiO₂ is assigned to the back electron transfer reaction.^{9,12} This reaction destroys both the electrons localized in the TiO₂ particles and the dye radical cation. The data in Figure 4 for the TiO₂ particles can be fitted using a singleexponential decay plus an offset. For anatase TiO₂ the decay time is 33ps (87% of the decay), and for amorphous TiO_2 the decay time is 54 ps (72% of the decay). The constant background that remains after the 9AC⁺⁺ signal has decayed is due either to bound 9AC molecules that do not transfer an electron⁹ or (more likely) to free dye molecules in solution. It is important to note that the back electron transfer time is faster for anatase TiO₂ compared to the amorphous particles.

Figure 5a shows time-resolved anisotropy measurements for 9AC bound to anatase TiO_2 and ZrO_2 . The positive anisotropy shown by the 9AC– ZrO_2 system is a signature of the excited electronic state of the neutral dye—the anisotropy indicates the presence of the radical cation in the 9AC– TiO_2 system. The difference in the sign of the anisotropy arises because the radical cation and the dye have different electronic structures. This causes the transition dipole moment for absorption at 780 nm to have a different alignment with respect to the molecular axis for the radical cation compared to the electronically excited dye molecules.¹² The decay in the negative anisotropy signal occurs because two different anisotropy signals (electronically excited dye molecules and the dye radical cation). Specifically,



Figure 5. (a) Time-resolved anisotropy data for 9AC-anatase TiO_2 and 9AC-ZrO₂. The dashed line for 9AC-anatase TiO_2 is a calculation of the time-dependent anisotropy using a 33 ps back-electron-transfer time. The dashed line for 9AC-ZrO₂ is a fit to the data using a sum of exponentials. See text for details. (b) Time-resolved anisotropy data for 1AC-anatase TiO₂ and 1AC-ZrO₂.

the time-resolved anisotropy in our experiments is given by $r(t) = n_{\rm D}(t)r_{\rm D}(t) + n_{\rm RC}(t)r_{\rm RC}(t)$,³⁶ where $n_{\rm D}(t)$ and $n_{\rm RC}(t)$ are the relative populations of the electronically excited dye and the radical cation, respectively, and $r_{\rm D}(t)$ and $r_{\rm RC}(t)$ are the corresponding anisotropies (which are time dependent due to rotation).

A simulation based on the above equation for r(t) assuming that the offset in the transient absorption signal (13% of the signal) is only due to free dye is included in Figure 5. In this calculation, the time-dependent anisotropy of the free dye $r_{\rm D}(t)$ was taken from ref 12 and that for the radical cation $r_{RC}(t)$ was assumed to have the same form as the anisotropy for ZrO₂ but with a different sign. (The anisotropy for 9AC-ZrO₂ decays with time constants of 40 (63%) and 10 ps (23%), with a 14% offset.) These calculations show that the decay in the anisotropy arises from a combination of rotation, and the decrease in the population of the radical cation compared to free dye due to the back electron transfer reaction. The agreement between the calculations and the experimental results supports the assignment of the 33 ps decay time to back electron transfer. Figure 5b shows time-resolved anisotropy data for 1AC bound to anatase TiO_2 and ZrO_2 . The anisotropy signals for $1AC-TiO_2$ and 1AC-ZrO₂ are significantly different, indicating that electron transfer occurs for 1AC-TiO2. However, in this case, the anisotropy is negative for both the radical cation and the electronically excited dye molecules. This makes it difficult to quantitatively analyze the results for 1AC. 2AC shows a similar behavior to 1AC.

Magic-angle transient absorption data for 1AC bound to ZrO_2 and TiO_2 are presented in Figure 6a, and data for 2AC are shown in Figure 6b. These species have very similar dynamics, i.e., there is almost no decay in the signal for ZrO_2 , and the decay for anatase TiO_2 is faster than that for amorphous TiO_2 . These results are similar to what was observed for 9AC, except that the 9AC- ZrO_2 data showed a significant decay on a 100 ps



Figure 6. Magic-angle transient absorption data for (a) 1AC and (b) 2AC bound to anatase TiO_2 , amorphous TiO_2 , and ZrO_2 . The dashed lines are the best fits to the experimental data; the results from these fits are summarized in Table 1.

time scale. The results from fitting the data to the convolution of the function $S(t) = A_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$ with a Gaussian instrument response function are summarized in Table 1 for all the samples. It is important to note that the back electron transfer time (τ_1) for the anatase TiO₂ particles is much faster for 1AC and 2AC than for 9AC. However, for amorphous TiO₂, 9AC presents the faster decay. Experiments performed with degenerate 390 nm pump/probe pulses are presented in Figure 7 for 1AC anatase-TiO₂. This signal has two components: a transient bleach that is maximized for parallel pump and probe polarizations and a transient absorption signal that is maximized for perpendicular polarizations. Experiments with ZrO₂ show that the transient absorption signal has an anisotropy of $r(0) = -0.18 \pm 0.01$ (which is close to the minimum allowed value). The transient absorption contribution in Figure 7 is due to free dye molecules in solution. The time scale for the bleach recovery is 23 ± 2 ps, which is consistent with the decay time in the 390 nm pump/780 nm probe experiments. Note that the bleach recovery can be seen in both the parallel and perpendicular polarization experiments. The combination of the bleach recovery and time-resolved anisotropy experiments confirm that the decays in Figures 4 and 6 for the TiO₂ particles are due to the back electron transfer reaction.

Finally, as shown in Table 1, 1AC and 2AC have a fast decay component (τ_2) whereas 9AC only shows a single-exponential decay when bound to TiO₂. To assign the process that gives rise to the faster decay, experiments were performed at different probe wavelengths. Figure 8 shows the short time dynamics for 1AC-TiO₂ recorded with 780 and 600 nm probe pulses. The instrument response function is also presented. The fast 850 fs decay at 780 nm (28%) shows up in the 600 nm scan as a fast 900 fs rise (15%). As discussed below, the forward electron transfer time for anatase TiO₂ is ca. 200 fs (i.e., within the instrument response time). Thus, the ~900 fs process is due to a blue shift or a decrease in the width of the absorption spectrum of the radical cation. For 2AC, the corresponding relaxation time is 650 ± 100 fs. These spectral changes are

consistent with either transfer of population from high to low vibrational levels (vibrational relaxation),³⁷ stabilization of the ground state of the radical cation via solvation,³⁸ or a blue shift in the absorption spectrum of the electrons in the TiO₂ particles.³⁹ At present we cannot determine which of these possibilities is primarily responsible for the short time dynamics in Figure 8. For 1AC and 2AC bound to amorphous TiO₂, the time scales for the spectral shifts for the radical cation are 2.3 \pm 0.3 and 2.2 \pm 0.5 ps, respectively.

Short time scans for 1AC and 2AC adsorbed at the surface of the amorphous TiO₂ particles are presented in Figure 9. The rise in this signal is much slower than that for anatase TiO₂ (see Figure 8 and Table 1: τ_3). As discussed in the next section, this slow rise is tentatively assigned to the forward electron transfer process. The short time anisotropy for 9AC bound to amorphous TiO₂ is shown in Figure 10, along with the corresponding anisotropy for anatase TiO₂. For the 9AC– amorphous TiO₂ system, the anisotropy becomes negative at ca. 1.5 ps, whereas for anatase TiO₂ the anisotropy is negative within the laser pulse. These results also suggest that the forward electron transfer reaction is slower for amorphous TiO₂ compared to anatase TiO₂.

Discussion

An energy-level diagram for the forward electron transfer process, based on the Gerischer model for electron transfer at semiconductor surfaces,^{40,41} is shown in Figure 11. In this model, the distribution of energies for the ground-state oxidation of the dye is represented by a Gaussian function that is separated from the standard redox potential by the reorganization energy (Λ). The curve shown in Figure 11 was calculated using a redox potential of 1.3 eV versus NHE (appropriate for 9AC) and a reorganization energy of 0.7 eV (vide infra). Note that the relative energy levels are not significantly different for 1AC and 2AC. The distribution of energies for the excited-state reaction was obtained by simply adding the $S_1 \leftarrow S_0$ frequency to the ground-state distribution. Figure 11 shows that the excited state of the dye is significantly above the conduction-band minimum (CBM) of TiO₂ but below the CBM of ZrO₂. The conduction band minima for anatase TiO₂ and ZrO₂ were taken from ref 20 and corrected for the pH of the solution.³² Thus, electron transfer into the conduction band is energetically possible for TiO_2 but not for ZrO_2 . This energy-level picture agrees with the fluorescence quenching results for the different dye molecules.

Steady-State Spectra. Figure 3 shows that there is a considerable shift in the absorption spectrum of the dye molecules upon binding to the nanoparticles that is not simply due to metal-ion complexation.¹⁰ There are several possible mechanisms for producing this shift. One possibility is a chargetransfer band. Coupling between the wave functions of the excited electronic state of the dye $\Psi(D^*)$ and the chargeseparated state $\Psi(D^{+\bullet} + e^{-})$ can give mixed states with energies $E_{\pm} \approx E_{\rm m} \pm \sqrt{\Delta + |V|^2}$, where $E_{\rm m} = \frac{1}{2}(E_1 + E_2)$, $\Delta = \frac{1}{2}(E_1 - E_2)$ E_2), V is the coupling constant for interaction between the states, and E_1 and E_2 are the energies of the unperturbed levels.^{42,43} Optical transitions to E_{-} give a red-shifted absorption spectrum. For TiO₂, the energy of the charge-separated state $E(D^{+\bullet} + e^{-})$ is less than the energy of the excited electronic state of the dye $E(D^*)$. Thus, the lower energy state for TiO₂ would be assigned to a charge-transfer state (the wave function for the lower energy mixed state is predominantly made up of the lower energy zeroorder state). In contrast, for $ZrO_2 E(D^*) \le E(D^{+\bullet} + e^{-})$, which means that the lower state for ZrO_2 would be mostly $\Psi(D^*)$.

TABLE 1: Best-Fit Values for the Transient Absorption Data Presented in Figures 4, 6, 8, and 9^a

compound ^b	A_0	A_1	τ_1 (ps)	A_2	$ au_2$ (ps)	A_3	$ au_3$ (ps)
1-Anthracenecarboxylic Acid							
TiO ₂ (a) (780 nm)	0.14 ± 0.02	0.58 ± 0.04	18 ± 1	0.28 ± 0.05	0.85 ± 0.2		
TiO ₂ (a) (600 nm)	0.3 ± 0.1	0.55 ± 0.1	19 ± 1			-0.15 ± 0.1	0.9 ± 0.2
TiO_2 (b)	0.07 ± 0.03	0.3 ± 0.1	73 ± 5	0.15 ± 0.1	2.3 ± 0.3	-0.5	1.6 ± 0.2
ZrO_2	0.7 ± 0.1					-0.3 ± 0.1	0.35 ± 0.1
2-Anthracenecarboxylic Acid							
$TiO_2(a)$	0.02 ± 0.02	0.11 ± 0.03	14 ± 1	0.37 ± 0.03	0.65 ± 0.2	-0.5	0.45 ± 0.2
TiO_2 (b)	0.08 ± 0.06	0.25 ± 0.1	55 ± 5	0.15 ± 0.1	2.2 ± 0.5	-0.5	1.7 ± 0.3
ZrO ₂	0.5					-0.5	0.35 ± 0.1
9-Anthracenecarboxylic Acid							
$TiO_2(a)$	0.11 ± 0.02	0.72 ± 0.02	33 ± 2			-0.17	2.3 ± 0.3
$TiO_2(b)$	0.14 ± 0.03	0.36 ± 0.03	54 ± 2			-0.5	0.3 ± 0.1
ZrO_2	0.25 ± 0.1	0.14 ± 0.11	44 ± 4	0.11 ± 0.1	7 ± 1	-0.5	0.3 ± 0.1

^{*a*} The fitting function used was $S(t) = A_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$. The negative A_3 coefficients indicate that this component corresponds to a rise in the transient absorption signal. The short and long time components were determined from separate experiments. ^{*b*} TiO₂ (a) = anatase crystal structure; TiO₂ (b) = amorphous crystal structure.



Figure 7. Degenerate 390 nm pump/probe experiments for 1ACanatase TiO₂ performed with parallel and perpendicular pump and probe laser polarizations. The transient absorption signal that dominates the perpendicular polarization experiments is due to free dye molecules in solution.



Figure 8. Short-time transient absorption data for 1AC-anatase TiO_2 measured at two different probe wavelengths. The solid lines are the experimental data, the dashed lines are the best fits to the experimental results, and the dotted line is the cross-correlation between the 390 nm pump and the 600 nm probe pulses.

Assuming that the coupling elements for TiO_2 and ZrO_2 are similar, the red shift should be larger for TiO_2 than for ZrO_2 because the conduction band of TiO_2 is lower in energy. Thus, the fact that the spectra are nearly identical for anatase TiO_2 and ZrO_2 implies that the spectral red shift for these particles is not due to a charge-transfer band.

At present, the exact mechanism for the larger red shift observed upon binding to the anatase TiO_2 and ZrO_2 particles



Figure 9. Short-time transient absorption data for 1AC-amorphous TiO_2 and 2AC-amorphous TiO_2 . The dashed lines are fits to the experimental data.



Figure 10. Short-time time-resolved anisotropy data for 9AC bound to anatase and amorphous TiO_2 . The dashed lines are exponential decays that estimate the experimental decays.

is unclear. One possible explanation for this effect is that electronic excitation of the dye molecules produces a change in their dipole moment, which creates an image dipole in the semiconductor.⁴⁴ The image dipole lowers the energy of the excited state, producing a red shift in the absorption spectrum compared to the free dye in solution. This effect should be essentially instantaneous. With this interpretation we would expect that all molecules that have a substantial change in dipole moment upon electronic excitation should have red-shifted absorption spectra. A second possibility is that the large charge density at the surface of the anatase TiO₂ and ZrO₂ particles creates a strong electric field which causes a Stark shift in the spectra of the bound dye molecules.⁴⁵ This effect would not occur for the amorphous particles because they have a signifi-



Figure 11. Energy-level diagram for photoinduced electron transfer for 9AC bound to anatase TiO₂ and ZrO₂ particles. The lower Gaussian represents the distribution function for the ground-state reaction of the dye, and the upper Gaussian represents that for the electronically excited dye molecules. $E_c(\text{TiO}_2)$ and $E_c(\text{ZrO}_2)$ are the conduction band minima for the two nanoparticles (assuming a sample pH of 3), E° (D/D⁺) is the redox potential for 9AC (1.3 eV), and Λ is the total reorganization energy (assumed to be 0.7 eV).

cantly lower surface charge density. The pH of the amorphous TiO₂ solutions is pH \approx 6, which is very close to the point of zero charge (pH \approx 5.0) for TiO₂.²⁶

Reorientation at the ZrO₂ Surface. Figures 4–6 show that the different dye molecules have different dynamics at the surface of ZrO₂. The transient absorption signal for 9AC decays with double-exponential kinetics (44 and 7 ps representing 28% and 22% of the decay, respectively), while the signals for 1AC and 2AC remain constant over the time scale of our experiments. The decay for 9AC–ZrO₂ also shows up in the time-resolved anisotropy data. We discard vibrational relaxation as the reason for the 9AC dynamics because the pump laser excites molecules very close to the origin of the absorption band. Experiments performed at different concentrations of 9AC give essentially equivalent results, which shows that resonant energy transfer between adsorbed dye molecules is not important in this system.⁴⁶

We believe that the decay for 9AC-ZrO₂ is due to reorientation of the bound dye molecules after electronic excitation. This motion must change both the orientation of the transition dipole moment with respect to the polarization of the pump laser (to give a decay in the anisotropy signal) as well as the energy of the first excited electronic state relative to the higher electronic states (to give a decay in the transient absorption signal). For free 9AC, the time-resolved anisotropy has a biexponential decay with time constants of 1 and 10 ps. In our previous paper, the 1 ps process was assigned to vibrational energy exchange between levels with different vibronic symmetry and the 10 ps process was assigned to overall rotation.9 The fact that the 1 ps component does not appear for 9AC-ZrO₂ is surprising and indicates that our original assignment is not correct. An improved assignment is that the 1 ps anisotropy decay for the free dye is due to internal rotation of the carboxylate group. This motion would be severely hindered when the dye molecules are bound to the metal oxide surface. The fact that the decay in the anisotropy is much slower for 9AC bound to ZrO₂ compared to free 9AC could be due to the following effects: (i) the environment at the surface of the particles is restricted compared to bulk solution and/or (ii) the internal rotation involves movement of the bulky anthracene ring when the carboxylate group is bound to the surface of the particle. The anisotropy does not decay to zero for the dye molecules bound to ZrO_2 on the time scale of our experiments. This is expected since the molecules are not free to rotate about all 3 axes when

they are attached to the ZrO_2 surface.³³ Note that for free 9AC, the anisotropy is essentially zero after \sim 30 ps, see Figure 9 of ref 9.

Electron Transfer Dynamics. A. Forward Electron **Transfer.** We previously reported that the negative anisotropy for 9AC is a signature of the radical cation.^{9,12} This assignment was based on a comparison of the anisotropies of the free dye and the dye bound to amorphous TiO₂. The results presented in Figure 5a for 9AC-ZrO₂ show that this assignment is correct-the negative anisotropy signal is not a consequence of the interaction of the excited dye molecules with the surface. Furthermore, as shown in Figure 5b, the different isomers of anthracenecarboxylic acid show a change in anisotropy when the radical cation is formed. Thus, polarized light experiments appear to be a general way of probing the forward electron transfer reaction in these systems. In contrast, the magic angle transient absorption experiments are more difficult to interpret for two reasons. (i) D^* and $D^{+\bullet}$ absorb in the same spectral region (a pathological problem in these experiments). Thus, the increase in the signal due to formation of $D^{+\bullet}$ is masked by the decay due to destruction of D^* . (ii) Vibrational relaxation, solvation dynamics, and intramolecular vibrational energy redistribution (IVR) also contribute to the short-time transient absorption signal.

Figure 10 shows that the negative anisotropy signal appears instantaneously when the dye molecules are bound to the anatase TiO₂ particles, suggesting that the forward electron-transfer process occurs within the time response of our laser system ($\tau_f \leq 200$ fs). However, for amorphous TiO₂, the dynamics are quite different: in this case, the negative anisotropy signal appears in ca. 1.5 ps. Figure 9 shows that the transient absorption signals for 1AC and 2AC bound to amorphous TiO₂ also have slow rise components of 1.6 ± 0.2 and 1.7 ± 0.2 ps, respectively, that are not observed when the dye molecules are bound to the anatase particles. These results indicate that the forward electron transfer process is much faster for the anatase particles (≤ 200 fs) compared to the amorphous particles (ca. 1.5 ps).

The current understanding of the forward electron transfer process is that the rate is proportional to the square of the electronic coupling element times the density of states in the conduction band of the semiconductor.41,47 Specifically, a Fermi's Golden Rule treatment yields $k_f = 2\pi/\hbar |V|^2 \rho(E)$ where $\rho(E)$ is the density of states.⁴⁸ Thus, differences in $k_{\rm f}$ could be due to differences in V or $\rho(E)$. In our experiments, the conduction-band minimum is approximately the same for the anatase and rutile particles (see eq 4 below). Thus, their density of states should be similar, which means that differences in $k_{\rm f}$ must be due to the coupling element. For bulk rutile TiO₂, $\rho(E) = 2 \text{ eV}^{-1} \text{ atom}^{-1}$.⁴⁹ Using this value for $\rho(E)$ yields $V \ge 1$ 130 cm⁻¹ for anatase-TiO₂ and $V \approx 50$ cm⁻¹ for the amorphous-TiO₂ particles. Note that in this calculation we have assumed that each dye molecule primarily interacts with one Ti atom and that quantum size effects (which drastically affect $\rho(E)$) are unimportant for TiO₂.²⁴

The conclusion that the coupling element for the forward electron transfer reaction is larger for the anatase particles compared to the amorphous particles is the major result of this section. The coupling element is related to the degree of wave function overlap between the excited electronic state of the dye and the delocalized conduction-band levels of the semiconductor. This quantity is strongly distance dependent.⁵⁰ The larger coupling element for anatase TiO₂ compared to amorphous TiO₂ implies that the chromophore is closer to the surface for the

anatase particles. The dye molecules used in this study bind through interaction between the carboxylate group and surface Ti atoms. For the amorphous TiO_2 particles, the geometry around the surface Ti atoms must force the dye molecules to be further away from the surface than for the anatase particles. This picture is consistent with the larger perturbation of the UV-vis absorption spectra when the dye molecules are bound to the anatase particles compared to the amorphous particles.

B. Back Electron Transfer. The transient absorption measurements show that the time constants for back electron transfer for the anatase and amorphous TiO_2 particles, respectively, are 18 and 73 ps for 1AC, 14 and 55 ps for 2AC, and 33 and 54 ps for 9AC. Thus, the general trend is that the back electron-transfer times are much faster for anatase TiO_2 than for amorphous TiO_2 . In terms of Marcus theory, this could be due to changes in the driving force, the reorganization energy, or the coupling element. The aim of this section is to determine whether we can separate these different contributions to the experimental data.

A classical formulation for the back electron transfer rate constant $k_{\rm b}$ is⁵⁰

$$k_{\rm b} = \left(\frac{2\pi}{\hbar}\right) \left|V\right|^2 \frac{1}{\sqrt{4\pi\Lambda kT}} \exp\left\{-\frac{\left(\Delta G^\circ + \Lambda\right)^2}{4\Lambda kT}\right\}$$
(3)

where Λ is the total reorganization energy, V is the coupling element, and ΔG° is the overall free energy of reaction. The existence of electron-trap sites at the surface of the semiconductor particles makes it difficult to determine accurate values for ΔG° . Recent spectroelectrochemistry measurements by Grätzel and co-workers show that the majority of trap sites for ca. 15 nm diameter anatase-TiO₂ particles cast in a film are within 0.3 eV of the conduction-band minimum.⁵¹ In addition, the observation of single exponential decays in our experiments for the back electron transfer reaction implies a narrow energy distribution of sites for the trapped electrons. Specifically, a wide distribution of trap sites should produce distributed kinetics and complex, multiexponential decays.^{12,15–19,52,53} This is not observed in the 100-200 ps time scale of our experiments when absolute ethanol is used as the solvent.^{12,52} Note that on longer time scales the back reaction may become nonsingle exponential. However, the majority of the back electron transfer process (>75%) occurs within 100 ps for the anatase TiO₂ particles and within 200 ps for the amorphous particles. These observations imply that in our experiments the energy levels for back electron transfer are narrowly distributed within 0.3 eV of the conduction-band minimum. Because we do not know the exact energy of the trap sites, we will assume that ΔG° is given by the difference between the conduction-band minimum and the redox potential of the ground state of the dye. This assumption means that the coupling elements derived in the following analysis are upper limits.

In our systems we expect that Λ should be the same for the different particles, as Λ is determined by the internal modes of the dye and the reorganization of the solvent.^{22,50} On the other hand, both V and ΔG° could be different for the anatase and amorphous TiO₂ particles. For semiconductor nanoparticles, band bending effects are negligible, so that the energy of the conduction band can be equated to the flatband potential of the semiconductor.² For TiO₂, the flatband potential depends on the pH and the crystal structure of the sample. For anatase TiO₂, the flatband potential is well-known.^{20,53,54} No measurements are available for the amorphous particles. However, because the band gap of these particles is similar to rutile TiO₂, it is

reasonable to use the flatband potential of rutile TiO_2 to calculate the conduction-band energy of the amorphous particles. Thus, the pH dependence of the conduction bands of the two types of particles are taken as^{20,53,54}

$$E_{\rm cb}({\rm anatase}) = -0.12 - 0.059 {\rm pH}$$

 $E_{\rm cb}({\rm amorphous}) = 0.06 - 0.059 {\rm pH}$ (4)

We have previously used eq 3 to show that the back electron transfer reaction for 9AC bound to anatase TiO₂ lies in the Marcus-inverted region with a reorganization energy of $\Lambda =$ 0.75 ± 0.05 eV.¹² For this calculation, we used a value of ΔG° = -1.8 eV for the driving force. This value does not properly include the effect of pH on the flatband potential. If we take into account that the anatase synthesis yields water solutions at pH 3 and assume the same proton activity for the ethanolic solutions, then the total reorganization energy is 0.7 ± 0.1 eV. Thus, correction for the proton activity of the solution does not have a large effect on the value of Λ derived in our previous paper.¹² In these calculations, only ratios of rate constants were calculated, i.e., we did not directly determine the coupling element. Attempts to use eq 3 to calculate a coupling element yield unrealistically large values of V, implying that the weak coupling limit used to derive eq 3 is not valid for these systems.

Equation 3 is a classical derivation for the electron transfer rate constant. It underestimates the rate for reactions that have a large ΔG° because it does not account for tunneling through the barrier.^{21–23,50} Therefore, direct calculations of the coupling element using eq 3 result in an overestimate of V. A more suitable expression for the rate of electron transfer in the inverted region is^{22,50}

$$k_{\rm b} = \left(\frac{2\pi}{\hbar}\right) |V|^2 \frac{1}{\sqrt{4\pi\lambda_{\rm s}kT}} \sum_{\nu'} \exp(-S) \frac{S^{\nu'}}{\nu'!} \times \exp\left\{\frac{-(\lambda_{\rm s} + \nu'\hbar\omega + \Delta G^{\circ})^2}{4\lambda_{\rm s}kT}\right\} (5)$$

where $S = \lambda_i / \hbar \omega$, λ_i is the reorganization energy of the single high-frequency mode of the dye, ω is the frequency of this mode, λ_s is the reorganization energy of the solvent, and v' are all the possible final vibrational states. Complications in the calculation of V from eq 5 arise from the uncertainty in the values of ΔG° , λ_{i} , λ_{s} , and ω . However, the ratio V_{anat}/V_{amorph} is relatively invariant to the above-mentioned variables. Our calculations show that the ratio of the electronic coupling elements for the two different crystalline structures of TiO2 are $V_{\text{anat}}/V_{\text{amorph}} = 2 \pm 0.5$ for 1AC and 2AC and $V_{\text{anat}}/V_{\text{amorph}} =$ 1.3 \pm 0.2 for 9AC for $\Lambda = \lambda_i + \lambda_s = 0.7$ eV. For all three isomers the square of $V_{\text{anat}}/V_{\text{amorph}}$ is very close to the ratio of the back electron-transfer rate constants, i.e., for a specific dye the difference in the back electron transfer times for the anatase and amorphous TiO₂ particles is due to the coupling elements. Furthermore, the different values of Vanat/Vamorph for 1AC/2AC compared to 9AC explain why the back electron transfer times for 1AC and 2AC are faster than that for 9AC for anatase-TiO₂ and slower for amorphous-TiO2. These calculations were performed using the same values of λ_i , λ_s , and ω for the two semiconductor samples and calculating ΔG° from eq 4 and the redox potential of the dye molecules. Note that the calculated ratios of the coupling elements are relatively insensitive to changes in ΔG° of $\leq 0.2 \text{ eV}$.

Equation 5 provides more realistic values for the coupling element than eq 3, however, the problem is severely underdetermined. For example, if we choose $\omega = 1500 \text{ cm}^{-1}$ and $\lambda_i =$ $\lambda_s = 0.35$ eV, then the rate constants for 1AC, 2AC, and 9AC bound to anatase TiO_2 can be reproduced with a value of V =60 cm⁻¹. On the other hand, using $\lambda_s = 0.6$ eV and $\lambda_i = 0.1$ eV requires V = 100-200 cm⁻¹. Although at present it is impossible to quantitatively determine all the parameters in eq 5, we can conclude that reasonable values of λ_i and λ_s (i.e., λ_i , $\lambda_{\rm s} = 0.2 - 0.6 \, {\rm eV}$) require coupling elements in the 50-200 cm⁻¹ range for the anatase TiO₂ particles and correspondingly smaller values for the amorphous particles. These values are on the verge of the strong coupling limit for electron transfer. Note that if the back electron transfer reaction occurs from trap sites below the conduction band, the driving force for the reaction would be smaller than that calculated by eq 4. In this case, the values of V needed to reproduce the rate constants would be smaller than those reported above.

The above analysis shows how the back electron transfer reaction for a specific dye molecule depends on the identity of the semiconductor. Equation 5 can also be used to investigate how the back electron transfer time for a specific semiconductor particle depends on the chemical structure of the dye. For anatase TiO₂, the differences in the rate constants observed for 1AC, 2AC, and 9AC are due to differences in the redox potentials of the dye molecules. Specifically, the calculated coupling elements for the three dye molecules vary by only $\sim 10\%$. This means that the factor of 2 difference in the time scales for back electron transfer is due to differences in ΔG° : 1AC and 2AC have smaller ΔG° values than 9AC and, therefore, faster back electron transfer times because of Marcusinverted behavior. This conclusion is unaffected by the presence of surface states that change ΔG° . (In these calculations we have assumed that λ_i , λ_s , and ω are the same for the three dye molecules.) For the amorphous TiO₂ particles, the different rate constants for the three dye molecules arise from differences in both the coupling elements and the redox potential.

Summary and Conclusions

The main conclusion from this work is that the time constants for electron transfer for dye molecules bound to semiconductor particles depend on the way the particles are prepared. Specifically, TiO2 (a common semiconductor for dye-sensitized solarenergy cells and photocatalysis) was synthesized with either anatase or amorphous crystal structures. We have shown that the rate of electron transfer is consistently and significantly faster for the anatase form of TiO₂-for both the dye-to-semiconductor and the semiconductor-to-dye reactions. For the forward electron transfer reaction, the differences are due to changes in the coupling between the adsorbed dye molecules and the semiconductor surface. Analysis of the forward electron transfer reaction using Fermi's Golden Rule gave coupling elements of \geq 130 cm⁻¹ for anatase TiO₂ and \sim 50 cm⁻¹ for the amorphous TiO₂ particles. The back reaction was analyzed using the quantum mechanical expression for electron transfer (eq 5). For all three isomers, the different rates for anatase TiO₂ compared to amorphous TiO₂ are primarily due to differences in the coupling elements. For example, for 1AC and 2AC, the coupling elements for the anatase TiO₂ particles are approximately a factor of 2 larger than those for the amorphous particles, yielding a factor of 4 difference in the back electron transfer times.

The experimental data can also be analyzed to compare the different isomers of anthracenecarboxylic acid bound to the same semiconductor. In this case, differences were principally observed in the back (semiconductor-to-dye) electron transfer reaction. For anatase TiO₂, the data can be satisfactorily explained by the different redox potentials for the three anthracenecarboxylic acid isomers. Specifically, 1AC and 2AC have smaller (less positive) oxidation potentials compared to 9AC and, therefore, smaller driving forces for the back electron transfer reaction. This produces faster back electron transfer times for 1AC and 2AC compared to 9AC because the back reaction is in the Marcus-inverted region. For the amorphous TiO₂ samples, the differences in the back electron transfer times for the three dye molecules arise from differences in both the driving force and the coupling elements.

Finally, all the dye molecules examined show a red shift in their steady-state absorption spectrum when they are attached to the particles. The perturbations of the absorption spectra of the bound dye molecules are larger for the anatase TiO_2 particles compared to the amorphous TiO_2 particles. Comparison of the spectra of dye molecules bound to TiO_2 and ZrO_2 show that the spectral shifts are not due to the formation of a charge-transfer band, i.e., the steady-state spectra do not provide direct information about the forward (dye-to-semiconductor) electron transfer process. However, our experimental results suggest that for anthracene dyes attached to TiO_2 , stronger perturbations in the absorption spectra are correlated to faster electron transfer times—for both the forward and reverse reaction.

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