

Photoinduced Charge Separation across Colloidal TiO₂ and Fluorescein Derivatives[†]

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The photoinduced interaction of the dyad of fluorescein's anthraquinone methyl ester (FL-AQ) and its model compound of fluorescein's butyl ester (FL4) with colloidal TiO₂ was examined by absorption, fluorescence spectroscopy, fluorescence lifetime, photoinduced ESR, and transient laser flash photolysis. The dyad and the model compound are adsorbed on colloidal TiO₂ through their phenolic groups. Their apparent association constants with colloidal TiO₂ (K_{app}) obtained from absorption spectra are 3060 and 3590 M⁻¹, and the degrees of association (α) are 0.84 and 0.86, respectively. In the photoinduced ESR study, the cation radical of fluorescein (FL^{•+}) was always observed for the FL4/TiO₂ colloid system no matter if fluorescein was excited at 532 nm or TiO₂ excited at 355 nm, while, for the FL-AQ/TiO₂ colloidal system, the cation radical of fluorescein was detected only when TiO₂ was excited at 355 nm. The charge-separated state of the FL-AQ/TiO₂ colloidal system formed by photoinduced intramolecular electron transfer was detected by nanosecond transient absorption spectroscopy immediately. The lifetimes of FL^{•+} at 480 nm and AQ^{•-} at 560 nm in the FL-AQ/TiO₂ colloidal system are 11.1 and 8.93 μ s, respectively. The related phenomena are discussed in this paper.

1. Introduction

Photosensitization of a stable large band-gap semiconductor is an interesting and useful phenomenon. Numerous studies in this area have been carried out in heterogeneous media.¹ Dyes with high extinction coefficients in the visible regions are often employed in the modification of semiconductor electrodes and particles.^{2–5} As in natural photosynthesis, these materials convert light into useful energy by efficiently separating charge: the electronically excited sensitizer injects an electron into the solid to form a charge-separated pair with the hole localized on the sensitizer. The research that explored the performance of the dyad of a sensitizer–donor has been reported.⁶ However, little research has been carried out on dyads such as a photosensitizer–acceptor in this area.

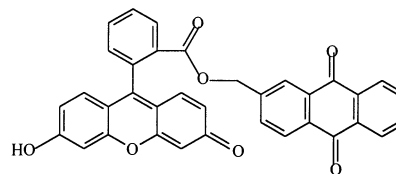
Fluorescein (FL) is a kind of xanthene dye. It contains two active groups that can link donors or acceptors to form dyads and even triads. It possesses a very high fluorescence quantum yield. Hence, it is often used as a singlet sensitizer for photoinduced electron transfer and energy transfer.⁷

When FL is excited by visible light, its photoinduced electron can be transferred to an organic acceptor, such as anthraquinone (AQ). It can also be injected into inorganic semiconductors, for instance, colloidal TiO₂. This paper compares the rate and efficiency between these two processes. For this purpose, the dyad of FL's anthraquinone methyl ester (FL-AQ, Chart 1) and its model compound of the butyl ester (FL4) were synthesized. And the effects of transferring the FL's photoinduced electron to AQ and of injecting it into colloidal TiO₂ were also studied.

2. Experimental Section

2.1. Syntheses. FL4 was synthesized from fluorescein (Sigma Chemical Co.) and 1-bromobutane (Beijing Chemical Co.). FL-

CHART 1: Structure of FL-AQ



AQ was synthesized from fluorescein (Sigma Chemical Co.) and 2-(bromomethyl)anthraquinone according to the procedure described in the literature.⁸ The compound 2-(bromomethyl)anthraquinone was synthesized from 2-methylantraquinone (Sigma Chemical Co.) and *N*-bromosuccinimide (Sigma Chemical Co.) according to a previous report.⁹ After separation and purification, the structures of these compounds were characterized by the UV–vis, IR, 300 M ¹H NMR, and MS spectra. The reagents used in this experiment were all of analytical grade.

2.2. Preparation of Colloidal TiO₂. The colloidal TiO₂ was prepared by hydrolysis of titanium(IV) 2-propoxide (Aldrich Chemical Co., 6.67 mL) in 100 mL of ethanol (containing about 2% water) with vigorous stirring. The concentration of TiO₂ colloid was ca. 0.22 mol·L⁻¹. The onset of the absorption of TiO₂ colloid in ethanol was at approximately 385 nm. No protective agent was added as the colloids were stabilized for a few months at 5 °C. Scanning transmission electron microscopy yielded a size range of 40–70 Å for the particles. The average diameter is 60 Å, and the average surface area of every particle is 1.13 × 10⁴ Å².

2.3. Photophysical Measurements. UV–vis absorption spectra were measured with a Hitachi U-2001 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence lifetimes were determined using a Horiba Naes-1100 single-photon counting apparatus. The lifetimes were calculated from the decay curves by using the reiterative least-squares method. Electron spin resonance (ESR) spectra were recorded at room temperature

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SCHEME 1: Possible Existing Forms of Fluorescein Esters

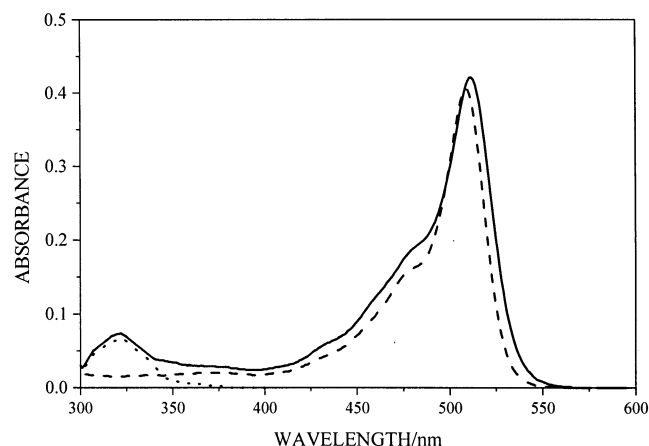
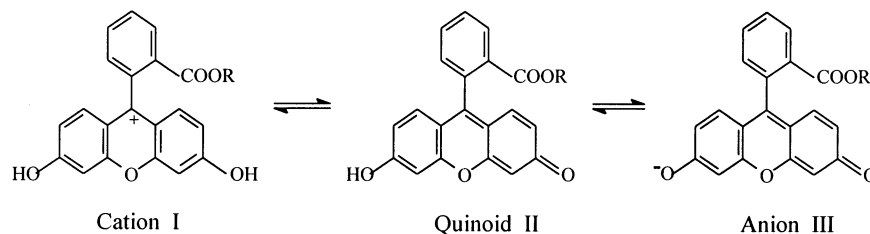


Figure 1. Absorption spectra of FL-AQ and its model in ethanol: (—) FL-AQ; (---) FL4; (···) MAQ.

(20–25 °C) using a Bruker ESR-300E spectrometer linked to a computer for data acquisition and instrument control. Samples were introduced into the specially made quartz cup and illuminated directly inside the microwave cavity. All samples were purged with argon for 30 min before measurements and irradiated directly in the cavity of the ESR spectrometer with a Quanta-Ray Nd:YAG laser. The transient absorption spectra and its kinetics were measured with a Quanta-Ray Nd:YAG nanosecond flash photolysis that employed 532 nm laser with a pulse width ca. 10 ns (10 mJ/pulse). For the data acquisition an EG&G OMAIII apparatus was used. All experiments were performed using a recycling sample cell with 5 mm path length and purged with argon through measurements. The anhydrous ethanol used in photophysical measurements was redistilled before use.

3. Results and Discussion

3.1. Absorption Characteristics. Absorption spectra of the dyad FL-AQ in ethanol (Figure 1) show two basic features from 300 to 350 nm that are those of the anthraquinone component, whereas the features between 400 and 550 nm correspond to absorption of fluorescein. This spectrum is nearly identical to the sum of the spectra of model compounds FL4 and 2-methyl-anthraquinone (MAQ), indicating that there is no ground-state interaction between the xanthene ring and anthraquinone. In addition, it is well-known that the fluorescein ester can exist in three states,¹⁰ i.e., the cation (I), the neutral quinoid (II), and the anion (III) state (Scheme 1). The maximum absorption wavelength of the cation state is ca. 438 nm. Those of the neutral quinoid state and the anion state are ca. 450 and 500 nm, respectively. So one can see that in ethanol for FL-AQ there exists an equilibrium between the neutral quinoid (II) state and the anion (III) state, mainly shifted toward the III state.

By observing the changes in the shape or position of the absorption band on addition of colloidal TiO₂, one can determine whether the adsorption has occurred. Figure 2 shows the

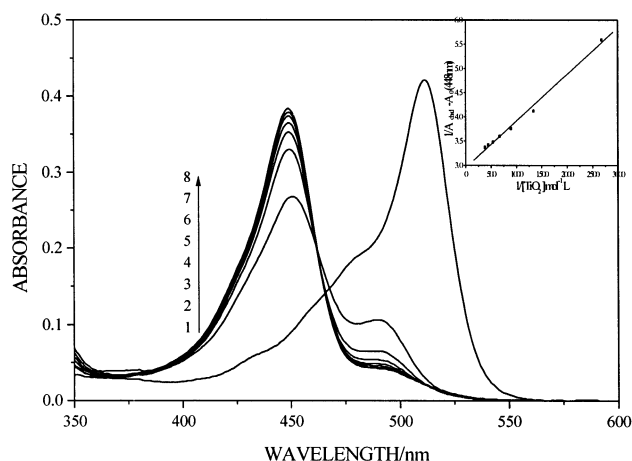


Figure 2. Absorption spectra of FL-AQ in ethanol (1.0×10^{-5} M) at various concentrations of TiO₂: (1) 0 M; (2) 3.7×10^{-4} M; (3) 7.5×10^{-4} M; (4) 1.1×10^{-3} M; (5) 1.5×10^{-3} M; (6) 1.9×10^{-3} M; (7) 2.2×10^{-3} M; (8) 2.6×10^{-3} M. The insert shows the dependence of $1/(A_{\text{obsd}} - A_0)$ on the reciprocal concentration of TiO₂.

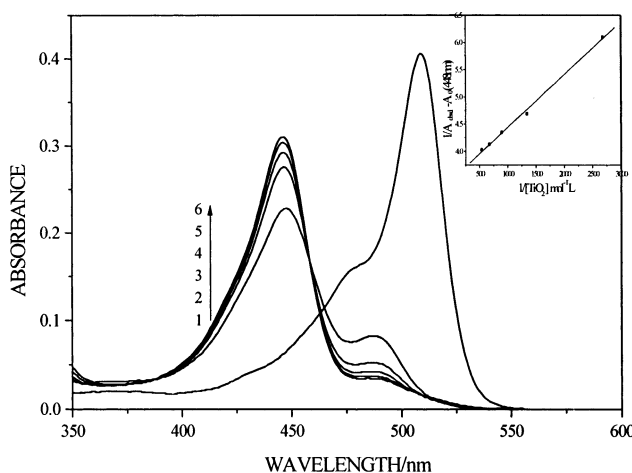


Figure 3. Absorption spectra of FL4 in ethanol (5.0×10^{-6} M) at various concentrations of TiO₂: (1) 0 M; (2) 3.7×10^{-4} M; (3) 7.5×10^{-4} M; (4) 1.1×10^{-3} M; (5) 1.5×10^{-3} M; (6) 1.9×10^{-3} M. The insert shows the dependence of $1/(A_{\text{obsd}} - A_0)$ on the reciprocal concentration of TiO₂.

absorption spectra of FL-AQ in neat ethanol and in ethanol containing colloidal TiO₂ at different concentrations. With increasing concentrations of colloidal TiO₂, the absorption band with maximum around 511 nm decreases, accompanied by an increase in the new absorption band appearing with maximum around 449 nm. (The absorption spectra of 2-methylanthraquinone are overlaid by the absorption of colloidal TiO₂.) Such an extensive change in the absorption spectra indicates a strong interaction between the dye and colloidal TiO₂. The absorption of FL4 exhibits the same effect as FL-AQ when colloidal TiO₂ is added in different concentrations (Figure 3). Because FL4 adsorbs on colloidal TiO₂ through the phenol

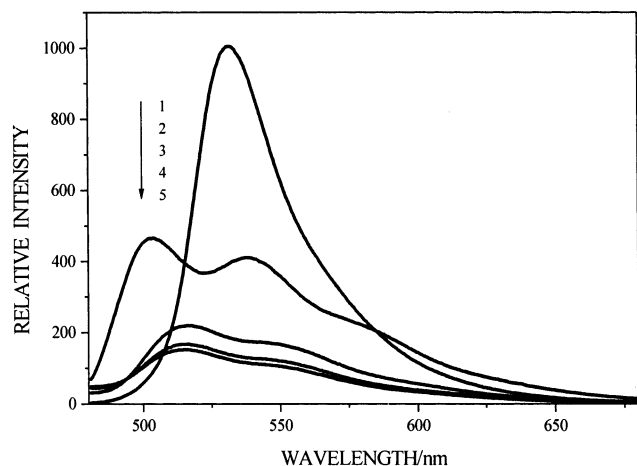
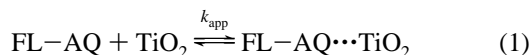


Figure 4. Fluorescence spectra of FL4 in ethanol (1.0×10^{-5} M) at various concentrations of TiO_2 : (1) 0 M; (2) 3.7×10^{-4} M; (3) 7.5×10^{-4} M; (4) 1.1×10^{-3} M; (5) 1.9×10^{-3} M. The excitation wavelength is 470 nm.

group,¹¹ we deduce that FL-AQ also adsorbs on colloidal TiO_2 through the phenol group to form a surface complex ($\text{TiO}_2 \cdots \text{FL-AQ}$) (eq 1).

This leads to extensive changes in the absorption spectra of FL-AQ (Figure 2), and the new absorbance feature at the shorter wavelength is due to the absorption of the complex. From the absorption spectra we infer that fluorescein in this surface complex exists mainly in the neutral quinoid (II) state (Scheme 1).



The apparent association constant in the formation of this surface complex, K_{app} , can be estimated from the changes of absorbance intensity of the new band at 449 nm from a Benesi-Hildebrand-type plot:¹²

$$A_{\text{obs}} = (1 - \alpha)A_0 + \alpha A_c \quad (2)$$

Here A_{obs} is the absorbance of the dye solution containing different concentrations of colloidal TiO_2 at 449 nm, α represents the degree of association between FL-AQ and TiO_2 , and A_0 and A_c are the absorbance of FL-AQ and of the complex ($\text{TiO}_2 \cdots \text{FL-AQ}$) at 449 nm, respectively. At relatively high TiO_2 concentrations, α can be equated to $\{K_{\text{app}}[\text{TiO}_2]/(1 + K_{\text{app}}[\text{TiO}_2])\}$. In this case, eq 2 becomes

$$\frac{1}{A_{\text{obsd}} - A_0} = \frac{1}{A_c - A_0} + \frac{1}{K_{\text{app}}(A_c - A_0)[\text{TiO}_2]} \quad (3)$$

Therefore, if the enhancement of absorbance at 449 nm is due to the absorption of the surface complex, a plot of $1/(A_{\text{obs}} - A_0)$ versus $1/[\text{TiO}_2]$ should yield a linear relationship with a slope equal to $1/(K_{\text{app}}(A_c - A_0))$ and an intercept equal to $1/(A_c - A_0)$. Indeed the linearity of the double reciprocal plot shown in the insert of Figure 2 confirms this behavior. The values of K_{app} and α of $\text{TiO}_2 \cdots \text{FL-AQ}$ as determined from this plot were 3060 M^{-1} and 0.84, respectively. A similar plot is obtained for FL4 (shown the insert of Figure 3), from which we estimated K_{app} and α of $\text{TiO}_2 \cdots \text{FL4}$ to be 3590 M^{-1} and 0.86, respectively.

3.2. Fluorescence Characteristics and Fluorescence Lifetimes. The fluorescence spectra of FL4 in neat ethanol and in ethanol containing colloidal TiO_2 in various concentrations are illustrated in Figure 4. With increasing concentration of colloidal

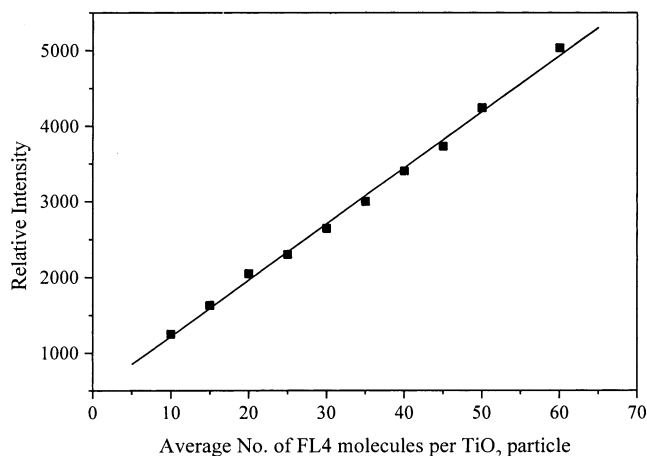


Figure 5. Plot of the relative fluorescence intensity versus the average numbers of FL4 molecules/ TiO_2 particle. The concentration of TiO_2 is 1.9×10^{-3} M.

TiO_2 , the fluorescence intensity decreases, and nearly 29% of the emission of 5.0×10^{-6} M FL4 can be quenched by 1.9×10^{-3} M colloidal TiO_2 . The decrease in fluorescence emission may be attributed to the interfacial electron transfer, the concentration quenching among the adsorbed dye molecules,¹³ or energy transfer between the dye and the colloidal TiO_2 .

The band-gap energy of TiO_2 semiconductor ($\Delta E = 3.2 \text{ eV}$)¹ is greater than the singlet excited-state energy of FL4 ($\Delta E = 2.42 \text{ eV}$),¹⁴ and no fluorescence emission of the dye can be absorbed by the colloidal TiO_2 . Thus, energy transfer from the singlet excited state of FL4 to colloidal TiO_2 is impossible. It can therefore be concluded that the fluorescence quenching shown in Figure 4 should not be caused by energy transfer.

At relatively higher TiO_2 concentrations, the fluorescence emission decreases continuously with increasing concentration of colloidal TiO_2 , indicating a negligible contribution from concentration quenching to the observed fluorescence quenching of FL4 shown in Figure 4. In addition, we can calculate² that the average number of FL4 molecules that adsorbed on each TiO_2 particle is 46. This means the occupied area for each FL4 molecule (A/M) on colloidal TiO_2 particle is 246 \AA^2 . According to the PC model of molecular mechanics, for the stable conformations of FL and FL4, the width of the chromophore, the height including the substituted phenyl, and the thickness are all about 10 \AA . When adsorbed on the surface of colloidal TiO_2 , every molecule should merely occupy about an area of 100 \AA^2 . Compared with the A/M above, FL4 on the TiO_2 surface should suppose to be quite commodious. Furthermore, we measured the fluorescence spectra of different concentrations of FL4 in ethanol containing 1.9×10^{-3} M colloidal TiO_2 . With increasing concentration of FL4, the fluorescence intensity increases. A plot of the relative fluorescence intensity versus the average numbers of FL4 molecules (less than 60 molecules) per TiO_2 particle shown in Figure 5 yields a good linear relationship. This confirms that the fluorescence quenching shown in Figure 4 (the average number of FL4 molecules that adsorbed on each TiO_2 particle is 46) was not caused by concentration quenching.

We measured the fluorescence lifetimes of FL4 in neat ethanol and in colloidal TiO_2 ethanol solution. The experimentally observed fluorescence lifetime of FL4 in neat ethanol is 4.66 ns, while in colloidal TiO_2 ethanol solution it is 3.57 ns. The fluorescence lifetime of FL4 in colloidal TiO_2 ethanol solution is also shortened. The dynamic quenching efficiency (Φ_{ET}) is about 23%, which can be calculated from the equation¹⁵

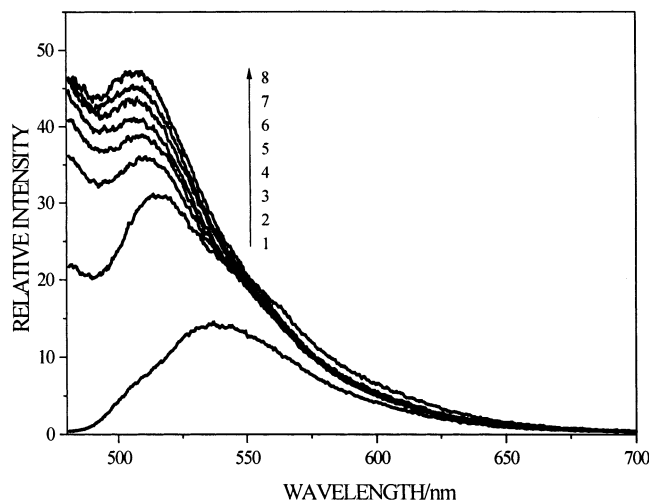
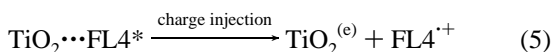
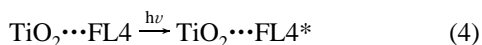


Figure 6. Fluorescence spectra of FL-AQ in ethanol (1.0×10^{-5} M) at various concentrations of TiO_2 : (1) 0 M; (2) 3.7×10^{-4} M; (3) 7.5×10^{-4} M; (4) 1.1×10^{-3} M; (5) 1.5×10^{-3} M; (6) 1.9×10^{-3} M; (7) 2.2×10^{-3} M; (8) 2.6×10^{-3} M. The excitation wavelength is 470 nm.

$\Phi_{\text{ET}} = 1 - \tau/\tau_0$ (τ_0 represents fluorescence lifetime of FL4 in ethanol; τ is the fluorescence lifetime of FL4 in colloidal TiO_2 ethanol solution). In other words, the quenching of the fluorescence quantum yield is mostly a dynamic one. The oxidation potential of the singlet excited state of FL4 is about -1.33 eV vs NHE¹⁴ (obtained from the oxidation potential of FL4 and its singlet state energy), and the energy level of the conduction band of colloidal TiO_2 lies around -0.5 eV.¹⁶ This makes possible the occurrence of the interfacial electron transfer. The quenching behavior which is similar to that of previously reported dyes^{2,17,18} is attributed to the electron injection from the singlet excited state of FL4 to the conduction band of colloidal TiO_2 (reactions 4 and 5).

According to the equation¹⁵ $k_{\text{ET}} = 1/\tau - 1/\tau_0$ (k_{ET} is the rate constant of electron injection process; τ_0 and τ represent the fluorescence lifetime of FL4 in ethanol and adsorbed onto the TiO_2 surface, respectively), we can calculate that k_{ET} of FL4 is $6.55 \times 10^7 \text{ s}^{-1}$.



For the dyad FL-AQ in neat ethanol (Figure 6, curve 1), the excitation wavelength is 470 nm at which only the fluorescein moiety is excited. Comparison the fluorescence spectra of FL-AQ with FL4 shows its fluorescence quenching is quite heavy. The fluorescence quantum yield decreases 98% (in comparison with the relative fluorescence quantum yield of 5.0×10^{-6} M FL4 in ethanol solution being 1.00). We measured the fluorescence lifetimes of FL-AQ in ethanol solution. The experimentally observed fluorescence lifetime of FL-AQ is 0.24 ns. The fluorescence lifetime of FL-AQ is also shortened significantly.

Because the singlet state energy of fluorescein ($\Delta E = 2.42$ eV) is less than that of 2-methylanthraquinone ($\Delta E = 2.88$ eV),¹⁹ when fluorescein is excited, there will be no energy transfer in FL-AQ. The free energy change of the electron-transfer reaction (ΔG_f) can be obtained with the Rehm–Weller equation:²⁰

$$\Delta G_f = E_0(\text{D}) - E_R(\text{A}) - E_D^* - C \quad (6)$$

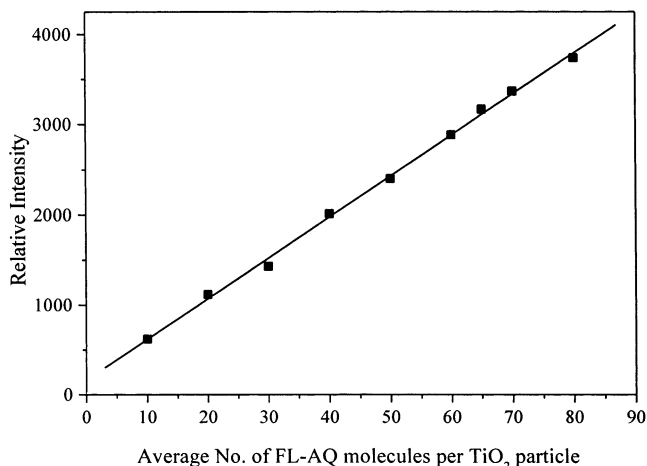


Figure 7. Plot of the relative fluorescence intensity versus the average numbers of FL-AQ molecules/ TiO_2 particle. The concentration of TiO_2 is 2.6×10^{-3} M.

$E_0(\text{D})$ represents the oxidation potential of the donor, $E_R(\text{A})$ is the reduction potential of the acceptor, E_D^* is the excited-state energy of the donor, and C is the stabilizing energy of D^{+}A^{-} , which usually can be regarded as 0.06 eV in polar solvent.²¹ The excited-state energy of fluorescein is 2.42 eV, the oxidation potential is 0.91 eV (vs Ag/AgCl, saturated KCl), and the reduction potential of 2-methylanthraquinone is -0.96 eV (vs Ag/AgCl, saturated KCl); thus, ΔG_f is -0.61 eV. This indicates that electron transfer from the singlet excited state of fluorescein to the ground state of 2-methylanthraquinone is feasible. It is thus reasonable to assume that the fluorescence quantum yield of FL-AQ decrease is due to photoinduced electron transfer between fluorescein and anthraquinone ($\text{FL-AQ} \rightarrow \text{FL}^{+} - \text{AQ}^{-}$). According to the equations¹⁵ $k_{\text{ET}} = 1/\tau - 1/\tau_0$ and $\Phi_{\text{ET}} = 1 - \tau/\tau_0$ (k_{ET} represents rate constant of electron transfer; τ_0 is the fluorescence lifetime of the model compound (FL4) in ethanol; τ is the fluorescence lifetime of the dyad (FL-AQ) in ethanol; Φ_{ET} is the efficiency of dynamic electron transfer), we can calculate that k_{ET} and Φ_{ET} of FL-AQ are $3.95 \times 10^9 \text{ s}^{-1}$ and 95%, respectively.

With the addition of nanometer colloidal TiO_2 to FL-AQ ethanol solution, the maximum fluorescence emission wavelength of FL-AQ is blue-shifted and the fluorescence intensity increases a little (curves 2–8, Figure 6). However, the fluorescence quantum yield decreases 88% in comparison with the relative fluorescence quantum yield of 5.0×10^{-6} M FL4 in ethanol solution being 1.00. This indicates that the interaction between FL-AQ and colloidal TiO_2 hinders just a little the electron transfer from FL to AQ. This point can be confirmed by the change of fluorescence lifetime. The fluorescence lifetime of FL-AQ in colloidal TiO_2 is 1.59 ns. The rate constant of electron transfer is $4.14 \times 10^8 \text{ s}^{-1}$, which lower than that of FL-AQ in ethanol solution without colloidal TiO_2 by about 10 times.

In the same way,² we can calculate that the average number of FL-AQ molecules that adsorbed on each TiO_2 particle is 65. This means the occupied area for each FL-AQ molecule (A/M) on colloidal TiO_2 particle is 174 \AA^2 . According to the PC model of molecular mechanics, for the stable conformation of FL-AQ (where FL and AQ are face-to-face),¹⁴ the width of the chromophore, the height including the substituted phenyl, and the thickness are all about 10 \AA . When adsorbed on the surface of colloidal TiO_2 , every molecule should merely occupy about an area of 100 \AA^2 . Compared with the A/M above, FL-AQ on the TiO_2 surface should suppose to be quite commodious.

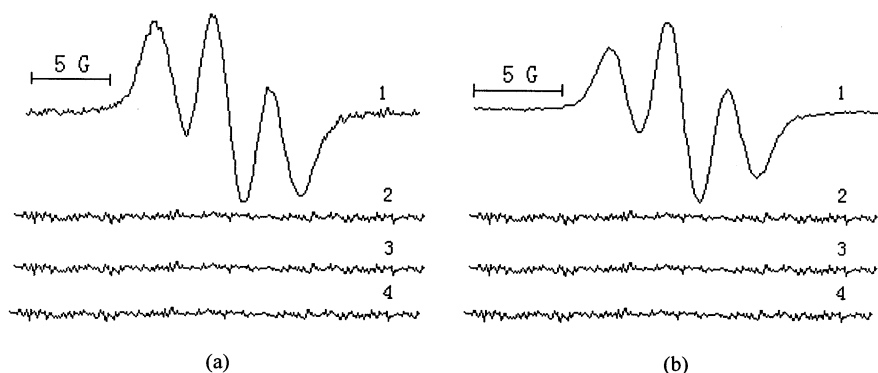


Figure 8. ESR spectra for samples of (1) 2.5×10^{-4} M FL4 in 2.5×10^{-2} M colloidal TiO_2 /ethanol solution under steady-state laser irradiation, (2) 2.5×10^{-4} M FL4 in 2.5×10^{-2} M colloidal TiO_2 /ethanol solution without irradiation, (3) 2.5×10^{-4} M FL4, and (4) 2.5×10^{-2} M colloidal TiO_2 in ethanol under steady-state laser irradiation: (a) 532 nm steady-state laser irradiation; (b) 355 nm steady-state laser irradiation.

Similarly, we measured the fluorescence spectra of different concentrations FL-AQ in ethanol containing 2.6×10^{-3} M colloidal TiO_2 . With increasing concentration of FL-AQ, the fluorescence intensity increases. A plot of the relative fluorescence intensity versus the average numbers of FL-AQ molecules (less than 80 molecules) per TiO_2 particle shown in Figure 7 yields a good linear relationship. It can therefore be concluded that the fluorescence quenching shown in Figure 6 (the average number of FL-AQ molecules that adsorbed on each TiO_2 particle is 65) was not caused by concentration quenching.

3.3. ESR Measurements under Steady-State Laser Irradiation. Interfacial electron injection between FL4 and the semiconductor colloid particles and electron transfer between FL and AQ were further elucidated by electron spin resonance spectroscopy under steady-state laser irradiation, a technique that has proven useful to examine photoinduced electron transfer²² and the reaction mechanism.²³

Figure 8a illustrates that the ESR spectra recorded under 532 nm laser irradiation lead to excitation of FL4; the relevant concentrations were 2.5×10^{-4} M FL4 and 2.5×10^{-2} M colloidal TiO_2 in ethanol (curve 1). In the absence of laser irradiation, no ESR signal was observed (curve 2). Also, no signal was detected when irradiated ethanolic solution contained either FL4 (2.5×10^{-4} M, curve 3) or colloidal TiO_2 (2.5×10^{-2} M, curve 4). The ESR signal of curve 1 is ascribed to the cation radical of fluorescein ($\text{FL}^{\cdot+}$).²⁴ This confirms that reaction 5 occurred.

A similar sequence of ESR spectra was obtained for the FL4/ TiO_2 system by exciting colloidal TiO_2 at 355 nm (Figure 8b, curve 1). No ESR signal was detected for the FL4/ TiO_2 system in the absence of irradiation (curve 2). The 355 nm steady-state laser irradiation of the ethanolic solution containing only FL4 or colloidal TiO_2 also gave no signal (Figure 8b, curves 3 and 4). The ESR signal of curve 1 is assigned to $\text{FL}^{\cdot+}$, which formed by the hole of the semiconductor TiO_2 obtaining an electron from the ground state of FL4.

However, no ESR signal was detected for the FL-AQ/ TiO_2 system under 532 nm steady-state laser irradiation and in the absence of this laser irradiation. This indicated no electron injection into colloidal TiO_2 under 532 nm steady-state laser irradiation of TiO_2 ••FL-AQ. Also, no signal was detected when irradiated ethanolic solution contained either FL-AQ (2.5×10^{-4} M) or colloidal TiO_2 (2.5×10^{-2} M). The FL's photoinduced behavior in TiO_2 ••FL-AQ is much like in FL-AQ; i.e., the FL's photoinduced electron transfer to AQ is a much faster process.

Under 355 nm steady-state laser irradiation of colloidal TiO_2 in the FL-AQ/ TiO_2 system, one can obtain the similar sequence of ESR spectra (Figure 9, curve 1). No ESR signal was detected

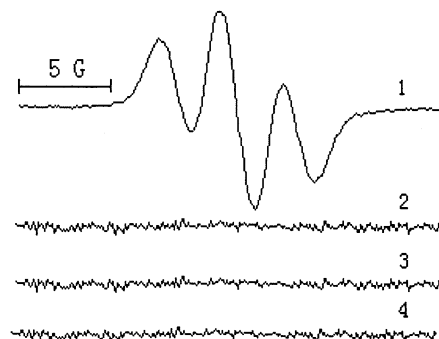


Figure 9. ESR spectra for samples of (1) 2.5×10^{-4} M FL-AQ in 2.5×10^{-2} M colloidal TiO_2 /ethanol solution under 355 nm steady-state laser irradiation, (2) 2.5×10^{-4} M FL-AQ in 2.5×10^{-2} M colloidal TiO_2 /ethanol solution without irradiation, (3) 2.5×10^{-4} M FL-AQ, and (4) 2.5×10^{-2} M colloidal TiO_2 in ethanol under 355 nm steady-state laser irradiation.

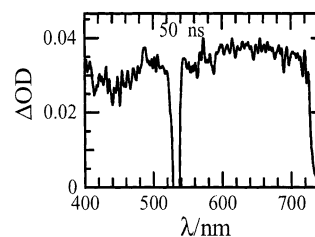


Figure 10. Absorption difference spectra of 1.0×10^{-5} M FL-AQ in argon-purged ethanol obtained 50 ns after pulse 532 nm light excitation (10 mJ/pulse, 10 ns fwhm).

for the FL-AQ/ TiO_2 system in the absence of irradiation (curve 2). The 355 nm steady-state laser irradiation of the ethanolic solution containing only FL-AQ or colloidal TiO_2 also gave no signal (Figure 9, curves 3 and 4). This is for the same reason as for the FL4/ TiO_2 system showed above.

3.4. Transient Difference Absorption Spectra. Time-resolved laser flash photolysis is very useful in the investigation of the interfacial charge-transfer processes in colloidal semiconductor systems.^{13,18,25} The dynamics of the photoinduced charge separation process of the FL-AQ/ TiO_2 colloid system was scrutinized by recording transient absorption at different time intervals.

Figure 10 shows the transient difference absorption spectrum of deaerated FL-AQ ethanol solution after the laser pulse ($\lambda_{\text{ex}} = 532$ nm). The signal is weak. According to the thermodynamic equation²⁶ $\Delta G_r = E_R(\text{D}) - E_O(\text{A})$ (ΔG_r represents the free energy change of electron recombination reaction; $E_R(\text{D})$ is the reduction potential of donor ($\text{AQ}^{\cdot-}$); $E_O(\text{A})$ is the oxidation potential of acceptor ($\text{FL}^{\cdot+}$)), we find that ΔG_r is also negative.

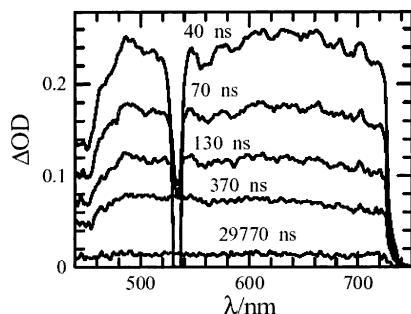


Figure 11. Absorption difference spectra of 1.0×10^{-5} M FL-AQ with 2.6×10^{-3} M TiO_2 colloids in argon-purged ethanol obtained after pulse 532 nm light excitation (10 mJ/pulse, 10 ns fwhm). The spectra were recorded 40, 70, 130, 370, and 29 770 ns from top to bottom after pulse excitation.

This shows that both electron transfer and electron recombination reactions can occur. This is presented in the following equation:



The reason for the weak signal in the transient difference absorption spectrum may be that rates of electron transfer and electron recombination both are too fast to form a long-lived photoinduced charge-separated state.

Figure 11 presents the transient difference absorption spectra of FL-AQ in colloidal TiO_2 measured at different times after 532 nm laser excitation. The shape of these spectra is similar to that of Figure 10, but the intensity increases obviously. According to the Corey–Pauling–Kuntz molecular model, the carboxyl phenyl is almost perpendicular to the chromophore. AQ is positioned face-to-face with the chromophore of FL in the FL-AQ solution.¹⁴ This favors increasing the rate and efficiency of electron transfer. But the rate of electron recombination is also enhanced. When FL-AQ is adsorbed on the colloidal TiO_2 surface with the free $-\text{OH}$ group, the polar bond of $\text{H}(\delta^+) \text{---} \text{O}(\delta^-)$ changes into an ionic bond of $\text{Ti}(+) \text{---} \text{O}(-)$. Correspondingly, the electronic densities and their contribution should be changed. This stabilizes the neutral quinoid (II) state of fluorescein ester and hampers the face-to-face configuration of FL-AQ. The change of configuration also hinders the electron-transfer process. This point can be confirmed by the change of fluorescence lifetime of FL-AQ with and without colloidal TiO_2 . In the same way, the change of configuration

also hinders the electron recombination process. Thus the charge-separated state is stabilized.

The signal at ca. 480 nm (Figure 11) can be ascribed to the absorption of the cation radical of fluorescein ($\text{FL}^{\cdot+}$).²⁷ The kinetics of the recombination, shown in Figure 12, was modeled as a biexponential decay, which yields lifetimes of $\tau_1 = 68$ ns (1.2%) and $\tau_2 = 11.1 \mu\text{s}$ (98.8%), respectively. In Figure 11 also appears a strong signal at ca. 560 nm that is assigned to the absorption of the anion radical of anthraquinone ($\text{AQ}^{\cdot-}$).²⁸ The absorption spectra of $\text{FL}^{\cdot+}$ and $\text{AQ}^{\cdot-}$ overlapped each other and so form a wide absorption signal. The kinetics of the recombination at 560 nm was also modeled as a biexponential decay, which yields lifetimes of $\tau_1 = 68.5$ ns (2.5%) and $\tau_2 = 8.93 \mu\text{s}$ (97.5%), respectively. The biexponential decay means that only about 2% of the radical anion (cation) recombines within 68 ns and 98% of the radical lives as long as about 10 μs . The solvation action and the change of FL-AQ's configuration induced by addition of colloidal TiO_2 slow the rate of the electron recombination and prolong the lifetimes of the radical to about 10 μs . According to the equation¹⁶ $k_R = 1/\tau$ (k_R represents the rate constant of electron recombination; τ is the lifetime of the radical), we can calculate that the rate constant of electron recombination of the radical is about 10^5 s^{-1} , which is lower than that of electron transfer from FL to AQ by about 10^3 times. Thus, we can detect the charge-separated state of FL-AQ.

These results further support the photoinduced intramolecular electron-transfer process taking place between FL^* and AQ in the FL-AQ/ TiO_2 colloid system. Therefore, exciting the fluorescein moiety in $\text{TiO}_2 \cdots \text{FL-AQ}$ with visible light results in a different direction of electron transfer as compared to exciting the TiO_2 component using ultraviolet light.

4. Conclusions

The dyad of FL-AQ adsorbs to the surface of colloidal TiO_2 particles through the phenolic group of the fluorescein moiety as well as FL4. But the way of photoinduced electron transfer in the FL-AQ/ TiO_2 and FL4/ TiO_2 colloid systems is different. The electron transfers from FL4 to colloidal TiO_2 in the FL4/ TiO_2 colloid system despite exciting fluorescein at 532 nm or TiO_2 at 355 nm. For the FL-AQ/ TiO_2 colloid system, exciting fluorescein at 532 nm results in electron transfer from FL to AQ, while exciting TiO_2 at 355 nm results in electron transfer from FL to colloidal TiO_2 . This result maybe useful in the study of the fabrication of a type of 3 response materials.

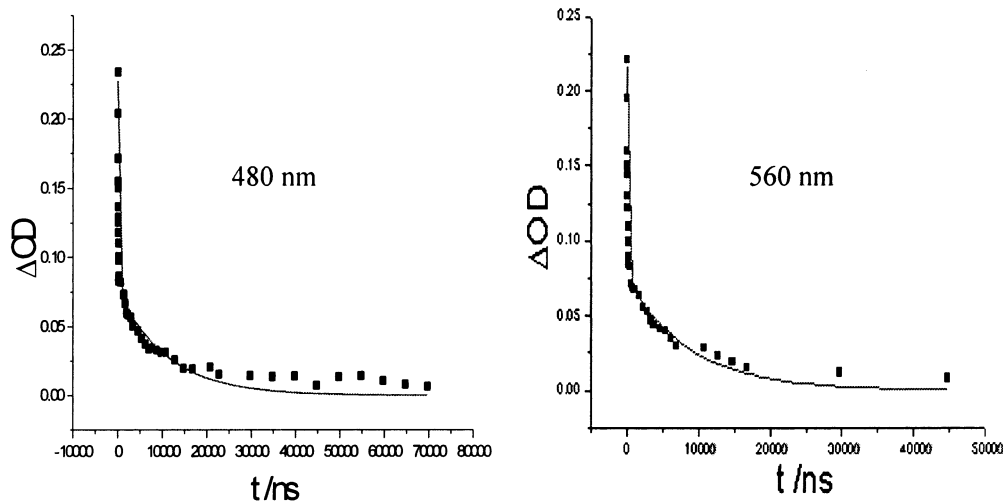


Figure 12. Transient absorption kinetics decay measured at 480 and 560 nm, respectively.

Current efforts are carefully adjusting the energy relationships among semiconductor (Sc), photosensitizer (Ps), and acceptor (Ac) to make a type of 3 response materials. In the system of Sc–Ps–Ac, there is no light and no signal (status 0). When Sc is excited by UV, the electron of the Ps will always inject into Sc (status +1). When Ps is excited by visible light, the Ps can donate an electron to the Ac first (forming $\text{Ps}^{*+}-\text{Ac}^{*-}$) and then Ps^{*+} obtains the electron from Sc (status –1).

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