Photochemical events during the photosensitization of colloidal TiO$_2$ particles by a squaraine dye

Chuan-yi Wang, Chun-yan Liu *, Wei-qin Wang, Tao Shen

Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, People's Republic of China

Abstract

The photochemical behaviour of a squaraine dye (2[4-ethylamino-2-hydroxyphenyl]-4[4-ethylaminophenyl]squaraine (SQ)) in a TiO$_2$ system was probed by UV–visible spectroscopy, fluorescence quenching measurements, single-photon counting and nanosecond time-resolved laser flash photolysis. A strong interaction was observed between SQ and the TiO$_2$ colloidal particles, with an apparent association constant of 2.275×10^3 M^{-1}. The fluorescence emission of the SQ dye was quenched by the TiO$_2$ colloid with an efficiency of 97%, resulting from electron transfer from the singlet excited state of the SQ dye to the conduction band of the semiconductor. The rate constant for the electron injection process was 1.97×10^8 s^{-1}, determined from the fluorescence lifetimes. Analysis of the transient absorption spectra confirmed the electron injection process from SQ to the TiO$_2$ particles. © 1997 Elsevier Science S.A.

Keywords: Adsorption; Colloidal TiO$_2$ particles; Fluorescence lifetimes; Fluorescence quenching; Photoinduced electron transfer; Squaraine dye

1. Introduction

Bulk semiconductor materials have been widely used as photocatalysts for solar energy conversion [1,2] and chemical transformation [3] and for the photodegradation of organic pollutants [4]. An important defect of metal oxide semiconductors is that their photoactivity is limited to the UV region. Therefore the photosensitization of stable, large-bandgap semiconductors by visible light using dyes is a long-term goal [5,6].

During the past decade, considerable interest has been shown in nanometre-sized semiconductor particles [1,7–10]. Such ultrasmall particles possess a unique catalytic behaviour and show size quantization effects, non-linear optical properties and unusual luminescence [11–15]. Unlike bulk materials, ultrasmall (colloidal) semiconductor particles are amenable to fast kinetic studies because of their transparent properties in solution. Therefore, with the availability of colloidal particles, the mechanism of dye sensitization can be probed easily using certain techniques.

Organic dyes, e.g. oxazines [16], erythrosin B [17], eosin [17], chlorophyllin [7], phthalocyanines [18] and Ru(bpy)$_3^{2-}$ and derivatives [19,20], have been extensively used in the sensitization of large-bandgap semiconductors, such as TiO$_2$, ZnO and SnO$_2$. Certain squaraine dyes (SQs)

are semiconducting and photoconducting. They have been applied in electrophotography, organic photovoltaic cells and, more recently, in optical storage systems [21]. However, less is known about the application of SQs in photosensitization. In this work, special attention was paid to the variation in the fluorescence lifetime of an SQ in a TiO$_2$ system in order to obtain a more detailed understanding of the photosensitization process. Furthermore, the surface-trapped electrons from the excited singlet state of SQ were observed by flash photolysis experiments.

2. Experimental section

2.1. Materials

The SQ dye was obtained from the Japanese Research Institute for Photosensitizing Dyes Co. Ltd., and used without further purification. The structure of the SQ dye is shown below:
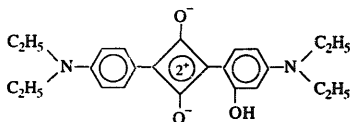
* Corresponding author.

Colloidal TiO_2 particles were prepared as follows:

1. 2 ml of 0.2 mol l^{-1} HCl was added to 86 ml ethanol and 2 ml of 2.5 wt.% polyvinylpyrrolidone (PVP-10; average molecular weight, 10 000; Sigma), which acted as a stabilizing agent for the colloidal TiO_2 particles, was dissolved in this solution;
2. 0.5 ml of titanium tetraisopropoxide (Aldrich) was dissolved in 9.5 ml of ethanol;
3. the titanium tetraisopropoxide–ethanol solution was slowly added dropwise to the solution in (1) at 0 °C with vigorous stirring
4. the resulting solution was peptized by further stirring for 3–5 h to give a transparent TiO_2 sol which contained 1.8×10^{-2} mol l^{-1} TiO_2.

The average diameter of the prepared TiO_2 particles was 2–3 nm determined by transmission electron microscopy.

All the other chemicals used in the experiments were analytical grade reagents, and doubly distilled deionized water was employed.

2.2. Apparatus and measurements

Absorption spectra were recorded on a Hewlett-Packard 8451A diode array UV–visible spectrophotometer.

Emission spectra were measured using a Perkin–Elmer Ls-05 fluorescence spectrophotometer, with a computer for data collection and reduction. The quantum yield of fluorescence of SQ was measured by the relative method using optically dilute solutions [3,22]. The fluorescence lifetime measurements were carried out on a multiplexed, time-correlated, single-photon counting spectrofluorometer (HORIBA, model NAES-1100), excited using the pulsed light of a hydrogen lamp (stable pulse halfwidth of less than 2 ns in the 200–700 nm range). Fluorescence lifetimes from 200 ps to several hundred microseconds can be accurately recorded with this spectrofluorometer. The steady state phosphorescence of the dye at 77 K was studied using a Hitachi MPF-4 fluorescence spectrophotometer equipped with a rotating can phosphoroscope.

Nanosecond laser flash photolysis experiments were performed with a 532 nm laser pulse (100 mJ; pulse width, 6 ns) from a Quanta Ray Nd:YAG laser system. A 300 W xenon lamp was used as the monitoring source. The transmitted monitoring light from the sample was collected and focused onto a monochromator, which was fitted to a photomultiplier tube, and the photomultiplier output was input to a TS-8123 Storagescope digitizer. Time zero in these experiments corresponds to the time at the end of the excitation pulse. The experiments were performed in a rectangular quartz cell with a path length of 5 mm along the monitoring light path. The signals were processed with a computer system. The samples were thoroughly deaerated by bubbling with N_2 for at least 30 min before the experiments.

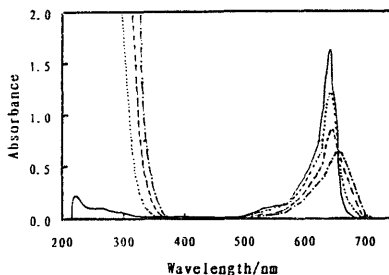All measurements were performed at room temperature unless specified otherwise.

Fig. 1. Absorption spectra of 5×10^{-6} mol l^{-1} SQ in ethanol solution containing TiO_2 colloid: ———, 0 mol l^{-1}; ···, 8×10^{-5} mol l^{-1}; – – –, 3.2×10^{-4} mol l^{-1}; – · –, 1.6×10^{-3} mol l^{-1}.

3. Results and discussion

3.1. Absorption spectra

SQ dyes exhibit strong optical absorption in the visible region, making them good candidates as sensitizers of semiconductor materials. As shown in Fig. 1, the SQ dye exhibits a maximum absorption peak at 641 nm. With the addition of TiO_2 colloid, however, the optical density (OD) of SQ decreases. The spectral absorption is broadened and the maximum is red shifted by about 15 nm. These changes in absorption indicate that an interaction occurs between SQ and the TiO_2 particles, changing the electronic state of SQ.

The surface of TiO_2 is polarized as a result of the protonation equilibria [23]

$$TiOH_2^+ = TiOH + H^+ \quad pK_a = 4.95 \quad (1)$$

$$TiOH = TiO^- + H^+ \quad pK_a = 7.8 \quad (2)$$
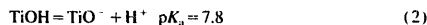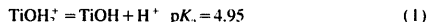
and the point of zero charge $pH_{pzc} = 1/2(4.95 + 7.8) = 6.4$. The pH value of the solution in the experiment is around pH 3.5 and thus lower than pH_{pzc}. Therefore the surface of the TiO_2 particles is positively charged, and the SQ dye, with high polarity, is easily adsorbed onto the surface of the colloidal TiO_2 particles due to an electrostatic interaction.

3.2. Fluorescence quenching

The addition of a TiO_2 colloid to a solution of SQ results in the quenching of the fluorescence emission of SQ. Fig. 2 shows the effect of increasing concentration of TiO_2 colloid on the fluorescence emission spectrum of SQ. More than 90% of the emission of SQ (1×10^{-5} mol l^{-1}) is quenched by TiO_2 (1.6×10^{-3} mol l^{-1}). This type of quenching behaviour is similar to that of other organic dyes used for the sensitization of large-bandgap semiconductor particles [17–20].

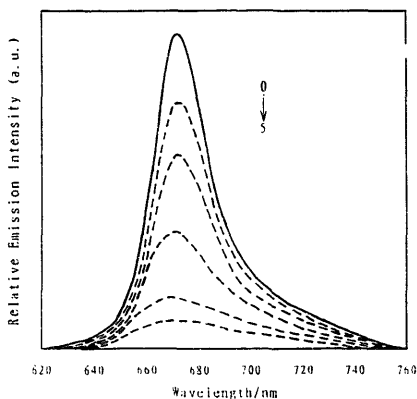The fluorescence emission quenching can be attributed to energy transfer or electron transfer from the excited singlet

Fig. 2. Emission spectra of 5×10^{-6} mol l^{-1} SQ in ethanol solution at various concentrations of colloidal TiO$_2$: 0, 0 mol l^{-1}; 1, 8×10^{-5} mol l^{-1}; 2, 1.6×10^{-4} mol l^{-1}; 3, 3.2×10^{-4} mol l^{-1}; 4, 6.4×10^{-4} mol l^{-1}; 5, 9.6×10^{-4} mol l^{-1}; $\lambda_{em} = 670$ nm; $\lambda_{ex} = 600$ nm.

state of SQ to the colloidal TiO$_2$ particles. From the spectral absorption of the TiO$_2$ colloid (strong absorption in the UV region in Fig. 1) and the emission spectrum of SQ (Fig. 2), there is no spectral overlap between them. Therefore the mechanism of energy transfer cannot be responsible for the fluorescence quenching of SQ by colloidal TiO$_2$ particles. The fluorescence quenching is caused by electron transfer, as interpreted from the potential of the excited singlet state of SQ (SQ$^*_{(S1)}$) and the conduction band of TiO$_2$. The oxidation potential of SQ$^*_{(S1)}$ is around -1.6 V (vs. normal hydrogen electrode (NHE)), determined from cyclic voltammetry and the excitation energy, whereas the energy level of the conduction band of TiO$_2$ is around -0.5 V (vs. NHE) [9]. Naturally, this provides a favourable driving force for the electron injection process (Fig. 3).

Kamat et al. [8,9] have proposed a fluorescence quenching model for a dye–TiO$_2$ system. According to their viewpoint, the fluorescence quenching is due to the strong adsorption of the dye on the colloidal TiO$_2$ particles. If this is also true of the SQ–TiO$_2$ system, an equilibrium will exist between the adsorbed and non-adsorbed molecules of the sensitizer, with an apparent association constant K_a (Eq. (3))

$$SQ + TiO_2 = [SQ \cdots TiO_2] \qquad (3)$$

The observed quantum yield (Φ_f) of the sensitizer in a colloidal TiO$_2$ solution is related to the fluorescence quantum yields of the non-adsorbed (Φ_f^0) and adsorbed (Φ'_f) molecules of the sensitizer, which can be expressed by the following relation [8,9]

$$\frac{1}{\Phi_f^0 - \Phi_f} \equiv \frac{1}{\Phi_f^0 - \Phi'_f} + \frac{1}{K_a(\Phi_f^0 - \Phi'_f)[TiO_2]} \qquad (4)$$
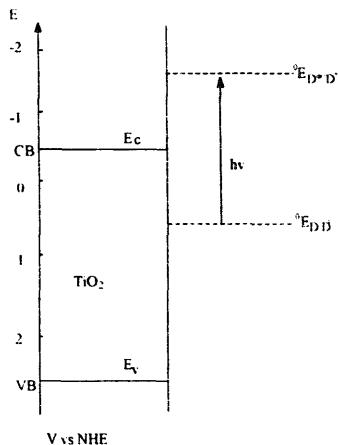

Fig. 3. Schematic diagram describing the conduction and valence band energy levels for TiO$_2$ and the electron-donating energy level for SQ. E_C and E_V are the energy levels of the conduction and valence bands respectively for TiO$_2$.
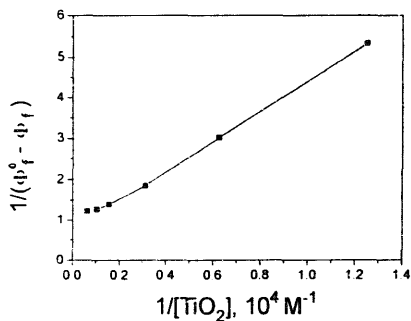

Fig. 4. Dependence of $1/(\Phi_f^0 - \Phi_f)$ on the reciprocal concentration of TiO$_2$.

This equation suggests that there is a linear dependence of $1/(\Phi_f^0 - \Phi_f)$ on the reciprocal concentration of the TiO$_2$ colloid. The experimental results follow this relationship (Fig. 4). Φ_f^0 was determined to be 0.85 using the relative method and optically dilute solutions. From the slope and intercept of the line in Fig. 4, K_a and Φ'_f can be determined: 2.275×10^3 M^{-1} and 0.025 respectively. The fluorescence quenching efficiency is $\eta = (\Phi_f^0 - \Phi'_f)/\Phi_f^0 = 97\%$. The value of K_a indicates that there is indeed a strong interaction between SQ and TiO$_2$. This agrees with the results observed by UV–visible spectroscopy (Fig. 1). In order to analyse the fluorescence quenching process further, fluorescence lifetime measurements were performed.

Table 1
Pre-exponential factor (A), fluorescence lifetime (τ (ns)) and reduced χ^2 for the luminescence decay of SQ at various concentrations of TiO_2 colloid ($\lambda_{em} = 670$ nm; $\lambda_{ex} = 600$ nm; $[SQ] = 5 \times 10^{-6}$ mol l^{-1})

$[TiO_2]$ (mol l^{-1})	A	τ (ns)	χ^2
0	0.124	4.78	1.15
1.6×10^{-4}	$A_1 = 0.0692$, $A_2 = 0.0538$	$\tau_1 = 5.42$, $\tau_2 = 2.62$	1.19
4.0×10^{-3}	0.12	2.41	1.18

3.3. Fluorescence lifetime measurements

Many workers have measured the fluorescence lifetimes of dye sensitizers in semiconductor systems. However, most report the results of the adsorption of the dyes on the semiconductors, and overlook the detailed variation of the lifetimes of the dye during sensitization. This is important for a more detailed understanding of the photosensitization process. The results of the fluorescence lifetime measurements for SQ are given in Table 1.

The fluorescence quenching process can be divided into three types, i.e. static, dynamic and combined static and dynamic, which can be determined from the fluorescence lifetimes [22]. As shown in Table 1, the fluorescence of the SQ dye in ethanol, in the absence of TiO_2, exhibits a single-exponential decay ($F(t) = A \exp(-t/\tau)$) with a lifetime of 4.8 ns. In the presence of TiO_2 colloid, however, it deviates from a single-exponential decay. At lower concentrations of TiO_2 colloid, the fluorescence exhibits a two-exponential decay ($F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$). There is an obvious component with a much shorter lifetime. A component with a lifetime similar to that of SQ alone in ethanol is also observed. Computer analysis of the decay gives a lifetime of 2.62 ns for the shorter lived component, which is assumed to be due to the adsorbed dye. The lifetime of the longer lived component is 5.42 ns, which is close to the lifetime of SQ in TiO_2-free solution (4.8 ns). This indicates that the fluorescence quenching process of SQ by the TiO_2 colloid is static due to the adsorption of SQ on the colloidal TiO_2 particles, in agreement with the quenching model proposed by Kamat et al. [8,9]. In the presence of higher concentrations of TiO_2 colloid, the fluorescence of SQ again shows a single-exponential decay, but with a lifetime of 2.41 ns. This lifetime of 2.41 ns is close to that of the shorter lived component ($\tau_2 = 2.62$ ns) of SQ in the presence of the lower concentration of TiO_2 (1.6×10^{-4} mol l^{-1}). In the presence of higher concentrations of TiO_2 colloid, nearly all SQ molecules are adsorbed, and the fluorescence exhibits a single-exponential decay of adsorbed SQ; therefore the lifetime of 2.41 ns can be attributed to the fluorescence emission decay of adsorbed SQ. The above analysis confirms that an interface complex is formed due to the adsorption of the SQ molecules on the TiO_2 particles.
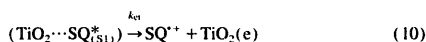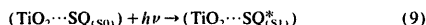
The deactivation of the excited singlet state generally includes radiative decay (k_f), internal conversion (k_{ic}) and intersystem crossing (k_{isc}) processes which are expressed by

$$SQ^*_{(S1)} \xrightarrow{k_f} SQ_{(S0)} + h\nu' \tag{5}$$

$$SQ^*_{(S1)} \xrightarrow{k_{ic}} SQ_{(S0)} \tag{6}$$

$$SQ^*_{(S1)} \xrightarrow{k_{isc}} SQ^*_{(T1)} \tag{7}$$

Therefore the observed fluorescence lifetime of SQ in TiO_2-free solution can be given as follows

$$\tau = 1/(k_f + k_{ic} + k_{isc}) \tag{8}$$

For SQ in the presence of TiO_2 colloid, in addition to the above deactivation pathways, there is another important process, i.e. electron injection from $SQ^*_{(S1)}$ to the conduction band of TiO_2, which can be described as follows

$$(TiO_2 \cdots SQ_{(S0)}) + h\nu \rightarrow (TiO_2 \cdots SQ^*_{(S1)}) \tag{9}$$

$$(TiO_2 \cdots SQ^*_{(S1)}) \xrightarrow{k_{et}} SQ^{\cdot+} + TiO_2(e) \tag{10}$$

where k_{et} is the specific rate of the charge injection process. The observed fluorescence lifetime of SQ associated with TiO_2 (τ') can be expressed by

$$\tau' = 1/(k'_f + k'_{ic} + k'_{isc} + k_{et}) \tag{11}$$

As shown in Eq. (11), the fluorescence lifetime (τ) for adsorbed SQ is determined by k'_f, k'_{ic}, k'_{isc} and k_{et}. Before we attribute the decrease in lifetime to electron injection from $SQ^*_{(S1)}$ to the conduction band of TiO_2, other possible causes must be considered. The phosphorescence of SQ with or without TiO_2 was too weak to be measured at 77 K. Consequently, the intersystem crossing process plays a negligible role in the observed decrease in the fluorescence lifetime. Another possibility is that the adsorption of SQ onto the surface of TiO_2 may change the rate of internal conversion from the excited singlet state to the ground state. Since the adsorbed SQ on the surface of TiO_2 is more rigid than that in the TiO_2-free system, dye adsorption will result in a decrease in internal conversion, leading to a longer fluorescence lifetime. The final possibility is that dye adsorption on the surface of TiO_2 may change the natural radiative rate constant k_f. Drexhage [24] has calculated such an effect for a dye adsorbed on the surface of silver halide. His results indicated that k_f should increase by a factor of 1.26 for an adsorbed dye relative to that of a non-adsorbed dye. Such a change in k_f should lead to a decrease in the fluorescence lifetime, but the decrease is quite small compared with the observed fluorescence lifetime decrease. Both silver halide and TiO_2 are semiconductors and, to a large extent, a dye on TiO_2 is similar to that on silver halide. Therefore the change in k_f in this case will only yield a small decrease in the fluorescence lifetime of SQ adsorbed on the surface of TiO_2.

As stated above, the estimated changes in k'_f, k'_{isc} and k'_{ic} for the adsorbed dye can account for, at best, minor differ-

ences in the fluorescence lifetime; therefore it is reasonable to attribute the major part of the observed lifetime decrease to electron injection from $SQ^*_{(S1)}$ to the conduction band of TiO_2. Therefore the following relation between τ and τ' can be obtained

$$1/\tau' = 1/\tau + k_{et} \qquad (12)$$

Substituting the lifetimes of 5.42 ns (τ) and 2.62 ns (τ') into Eq. (12), the electron transfer rate constant (k_{et}) can be obtained: 1.97×10^8 s^{-1}. This value of k_{et} is close to that of the anthracene-9-carboxylic acid–TiO_2 colloid system observed by Kamat [8]. The rate of the electron injection process is affected by the solvent environment and the energetics of the excited sensitizer.

3.4. Laser flash photolysis studies of the charge injection process

Time-resolved laser flash photolysis has been demonstrated to be very useful in the investigation of interfacial charge transfer processes in colloidal semiconductor systems [7–9,17,25]. The role of SQ^* in sensitizing TiO_2 colloids can be further elucidated by recording the transient absorption at different time intervals. Fig. 5 shows the transient absorption spectra obtained on 532 nm laser pulse excitation of the SQ dye (1×10^{-5} mol l^{-1}) in the presence of 8×10^{-4} mol l^{-1} TiO_2 colloid. The transient absorption spectrum recorded immediately after laser pulse excitation exhibits maxima at 625, 660 and 685 nm, and shows a single-exponential decay with a lifetime of approximately 2.2 µs (Fig. 6). Because of the interference from excitation pulse scatter, the absorption around 532 nm is masked in the experiments. No transient absorption of pure SQ in ethanol was measured under the same experimental conditions. This indicates that the transient absorption results from the interaction between SQ and TiO_2. The problem is how to identify the observed transient species. The observed transient signal may originate either from SQ^{*+} or from the surface-trapped electrons of the colloidal TiO_2 particles (Eq. (10)). The transient absorption of a similar squaraine dye radical cation at around 580 nm with a lifetime of 270 ps has been identified by Kamat et al. [26]. Due to the limitation of the experimental instrument, a signal at 580 nm could not be observed in our experiment. Therefore
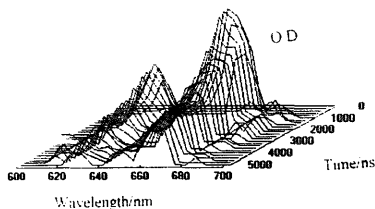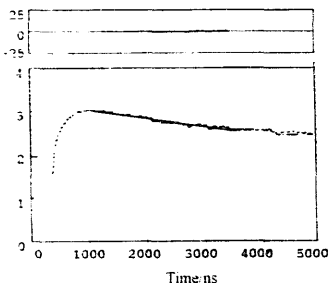

Fig. 6. Decay of the transient absorption at 660 nm. Full line is the calculated decay curve fitted to a single-exponential decay law with the following parameters: $A = 1.05 \times 10^3$; $\tau = 2.2$ µs; reduced $\chi^2 = 1.4$.

the observed absorption above 600 nm is not due to SQ^{*+}, but to the surface-trapped electrons of colloidal TiO_2 particles. A similar absorption at long wavelength for trapped electrons with a lifetime of 13 µs in a TiO_2 system has been observed by Kamat et al. [27]. It should be noted that, in the present experiment, the trapped electrons have a shorter lifetime (2.2 µs). We assume that this is caused by the back-reaction of the trapped electrons with SQ^{*+}. Moreover, the back-reaction proceeds with a first-order law and the rate constant derived from the lifetime is about 10^5 s^{-1}.

4. Conclusions

The fluorescence emission of the dye SQ can be efficiently quenched by TiO_2 colloids owing to charge injection from the excited singlet state of SQ to the conduction band of the colloidal TiO_2 particles (confirmed by time-resolved laser photolysis experiments). The adsorption quenching mode is supported by measurements of the fluorescence lifetime, and the apparent adsorption constant K_a was calculated. The fluorescence quenching efficiency of SQ by TiO_2 colloid is about 97%.

Acknowledgements

Fig. 5. Time-resolved transient absorption spectra of SQ (5×10^{-6} mol l^{-1}) in ethanol with colloidal TiO_2. $\lambda_{ex} = 532$ nm.

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