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Photosensitization of colloidal TiO_2 with a cyanine dye

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Abstract

Fluorescence quenching studies have been carried out to elucidate the processes of electron injection from the excited anhydro-1,1′-diethyl-3,3′-disulfobutyl-5,5′-dicyanimidazolo carbocyanine hydroxide (dye) into the conduction band of TiO_2 semiconductor colloid. The dye adsorbed strongly on colloidal TiO_2 with an apparent association constant of 3478 M^{-1}, and its fluorescence emission was quenched by TiO_2 colloid with an efficiency of 92%. Fluorescence lifetime measurements gave the rate constant for the electron injection process from the excited singlet state of the dye into the conduction band of the semiconductor as 4×10^9 s^{-1}. © 1997 Elsevier Science S.A.

Keywords: Cyanine dye; Titanium dioxide colloid; Photosensitization

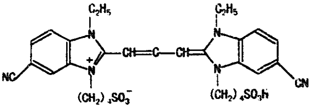
1. Introduction

The photosensitization of electron transfer across the semiconductor solution interface plays a vital role in silver halide photography [1–3] and electrophotography [4,5]. Recently, it has also gained interest with regards to light energy conversion in photoelectrochemical cells [6–8]. Effort in this area has concentrated on improving the visible light response of wide-band semiconductors, such as ZnO and TiO_2. Sensitization is achieved by adsorption of dye molecules at the semiconductor surface which, upon excitation, inject an electron into its conduction band.

Semiconductor particles of colloidal dimensions are sufficiently small to yield transparent solutions, allowing direct analysis of interfacial charge-transfer by a fluorescence quenching technique. Recently the erythrosin B sensitization of colloidal TiO_2 in acetonitrile has been studied by Kamat and Fox [9] the eosin sensitization of aqueous colloidal TiO_2 has been reported by Moser and Grätzel [10].

On the other hand, although cyanine dyes are widely used to spectrally sensitize photographic emulsions [2,3] and studies on photoinduced electron transfer of cyanine dyes on the surface of semiconductor powder such as ZnO, TiO_2, AgCl have been reported [11,12], cyanine dyes on the surface of semiconductor colloid have scarcely been studied in the past.

The present study employs cyanine dye as the sensitizer,



since its association with TiO_2 colloids extended the absorption into the visible wavelength (450–540 nm). We have investigated the process of charge injection from the excited cyanine dye adsorbed strongly on the colloidal TiO_2 into the conduction band of TiO_2 semiconductor colloid by absorption spectra and fluorescence spectra.

2. Experimental details

2.1. Materials

Colloidal suspensions of TiO_2 were prepared by slowly adding 1.5 ml of $TiCl_4$ to 100 ml of vigorously stirred water at 0 °C. The resulting sol was dialysed until the pH reached ca.6. Polyvinyl alcohol (2%) was added to stabilize the colloidal particles when $pH > 3$. The averge particle diameter, as measured from transmission electron microscopy was 100 Å. Anhydro-1,1′-diethyl-3,3′-disulfobutyl-5,5′-dicyanimidazolo carbocyanine hydroxide was purchased from No. 1 Film Factory of the Ministry of Chemical Industry, China.

2.2. Apparatus

Absorption spectra were recorded with a Shimadzu 160 spectrophotometer, and emission spectra were recorded with

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a Hitachi MPF-4 fluorescence spectrometer. The excitation wavelength was at 490 nm. Fluorescence lifetime measurements were performed by the time-correlated single-photon counting technique using a Horiba NAES-1100 single-photon counting fluorescence spectrometer.

3. Results and discussion

3.1. *The absorption characteristics of the dye*

The absorption spectra of the dye in aqueous solution, recorded in the presence and in the absence of colloidal TiO_2 are shown in Fig. 1. The percentage absorptance of the dye is characterized by the intense band located at 514 nm assigned to the molecular band. In the presence of colloidal TiO_2 this peak decreased markedly, but the location of the peak did not change. It is due to adsorption partly on the surface of TiO_2 colloid.

3.2. *Fluorescence quenching by colloidal TiO_2*

Addition of TiO_2 colloids to a solution of the dye resulted in the quenching of its fluorescence emission. Fig. 2 shows the effect of increasing the concentration of TiO_2 colloids on the fluorescence emission spectrum of the dye. More than 90% of the emission of 10 μM dye can be quenched with 2 mM TiO_2. This quenching behavior is similar to the previously reported fluorescence quenching of dyes such as erythrosin B [9], eosin [10] and chlorophyllin [13] and is attributed to the electron injection from the excited singlet of the dye to the conduction band of TiO_2 (reaction 1).

$$\mathrm{Dye^*(S_1) + TiO_2 \rightarrow Dye^{+\cdot} + TiO_2(e)} \qquad (1)$$

In order to verify this assumption, it is necessary to assess the relative energy levels of the excited singlet state of the dye molecules to the conduction band of TiO_2. The highest occupied level of the dye, E_{HO} and the lowest vacant level of the dye, E_{LV} can be calculated from the oxidation potential of the dye, E_{OX} and the energy E_{max} (eV), which is responsive to the wavelength of the maximum absorption of the dye according to following equation [14]:

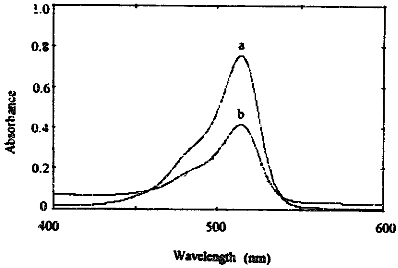

Fig. 1. Absorption spectra of 20 μM dye in water (a) without TiO_2 (b) with TiO_2, $[TiO_2]$ = 1 mM.

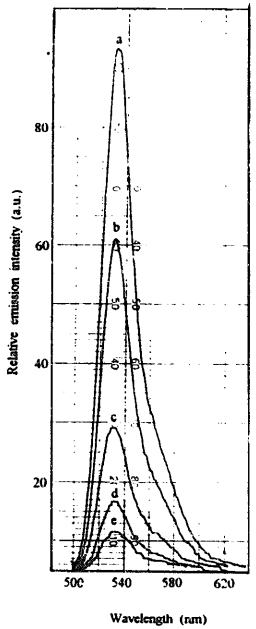

Fig. 2. Fluorescence emission spectra of 10 μm dye in water at various concentration of TiO_2 (a) 0 M, (b) 0.2 mM, (c) 0.5 mM, (d) 1 mM, (e) 2 mM.

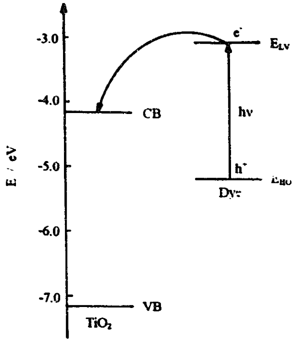

Fig. 3. Scheme of correlation between energy levels of dye and those of the conduction and valence bands of TiO_2.

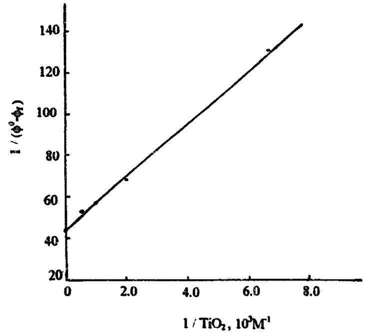

Fig. 4. The dependence of $1/(\phi_f^0-\phi_f)$ on the reciprocal concentration of TiO_2.

$$E_{HO} = -E_{OX}(\text{V vs. Ag/AgCl}) - 4.72 \quad (2)$$

$$E_{LV} = E_{HO} + E_{max}(\text{eV}) \quad (3)$$

Fig. 3 shows the energy levels of the dye relative to those of TiO_2. It would be thermodynamically allowed for the electron injection from the excited singlet of the dye to the conduction band of TiO_2.

The participation of TiO_2 in the quenching process was further analyzed by considering the equilibrium between adsorbed and unadsorbed molecules of sensitizer with an apparent association constant of K_{app} (reaction 4) [15].

$$\text{Dye} + TiO_2 \overset{K}{\rightleftarrows} [\text{Dye}\ldots TiO_2] \quad (4)$$

the observed quantum yield, $\phi_f(\text{obsd})$, of the dye in a colloidal TiO_2 suspension can be related to the fluorescence yields of unadsorbed (ϕ_f^0) and adsorbed (ϕ_f') molecules of the sensitizer by the equation

$$\phi_f(\text{obsd}) = (1-\alpha)\phi_f^0 + \alpha\phi_f' \quad (5)$$

where α is the degree of association between TiO_2 and the dye. At relatively high TiO_2 concentrations α can be equated to $(K_{app}[TiO_2]/(1+K_{app}[TiO_2]))$. Eq. (4) could then be simplified to

$$1/(\phi_f^0-\phi_f(\text{obsd})) \\ = 1/(\phi_f^0-\phi_f') + 1/K_{app}(\phi_f^0-\phi_f')[TiO_2] \quad (6)$$

If the observed quenching is due to the association of the dye with TiO_2 colloid, one would expect a linear dependence of $1/(\phi^0-\phi_f(\text{obsd}))$ on the reciprocal concentration of TiO_2 colloid with an intercept equal to $1/(\phi_f^0-\phi_f')$ and a slope equal to $1/(\phi_f^0-\phi_f')K_{app}$. Indeed the linearity of the double reciprocal plot shown in Fig. 4. confirms this behavior. The value of K_{app} as determined from this plot was 3478 M^{-1}. The large value of K_{app} indicates a strong interaction between the sensitizer and the semiconductor colloid, which is necessary for observing efficient electron injection.

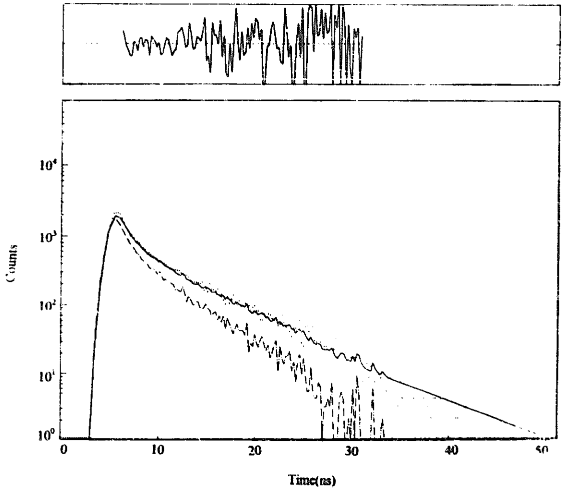

Fig. 5. Fluorescence decay and normalized instrument response curves for a sample of 50 μm dye in 1 mM TiO_2/H_2O suspension. Excitation was at 490 nm, and the emission was recorded at 530 nm. Solid line is a calculated decay curve dervived from nonlinear least-squares fit to a two-exponential decay law with the following parameters: $a_1=0.655$, $\tau_1=0.24$ ns, $a_2=0.0064$, $\tau_2=7.88$ ns, and reduced $\chi^2=1.38$.

3.3. Fluorescence lifetime measurements

It has been shown [15] that the sensitizer molecules adsorbed on the TiO_2 surface had a significantly shorter excited lifetime than in homogeneous solution and this decrease in lifetime could be correlated with the charge injection process. In neat aqueous solution, the fluorescence of the dye had a decay with a lifetime of 8.08 ns. However, in a TiO_2 suspension, the fluorescence emission of the dye followed a two-exponential decay. The fluorescence decay for the dye in 1 mM TiO_2 suspension and the calculated decay curve are shown in Fig. 5. The fluorescence lifetimes of the two components attributed to the dye adsorbed on TiO_2 colloid and unadsorbed the dye present in aqueous solution were 0.24 ns and 7.88 ns, respectively.

If we suppose the observed decrease in fluorescence lifetime is entirely due to the electron injection process (reaction 1) and the other radiation and nonradiation decay processes of the dye associated with TiO_2 colloid occur at the same rate as in neat solvent, we can correlate the observed lifetimes by the following expression [15].

$$1/\tau_{ads} = 1/\tau + K_{et} \qquad (7)$$

where τ and τ_{ads} are the lifetimes of the sensitizer in aqueous solution and adsorbed on to the TiO_2 surface and K_{et} is the specific rate of the charge injection process. The value of K_{et} obtained upon substitution of the values of τ (7.88 ns) and τ_{abs} (0.24 ns) in Eq. (7) was $4 \times 10^9\ s^{-1}$.

Acknowledgements

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