

Photochemistry of semiconductor particles

5. Location of dyes in reverse micelles containing TiO₂ nanoparticles and effects on photoinduced interfacial electron transfer

Ling Zang, Chun-Yan Liu, Xin-Min Ren

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

Received 23 November 1994; accepted 13 December 1994

Abstract

TiO₂ nanoparticles have been prepared in AOT–isooctane (AOT ≡ bis(2-ethylhexyl)sulphosuccinate sodium salt) reverse micelles. Three dyes, eosin (EO), methyl thionine (MT) and rhodamine B (RB), with different net charges were chosen as probes solubilized in the water phase to investigate the interaction with TiO₂ particles and AOT micelles. It was found from the spectral characteristics of the dyes that the three dye molecules were located at different places in the reverse micelles. EO was adsorbed on to the TiO₂ particles, whereas MT was transferred into the micelle phase. This was attributed to the different charges of the dyes, which determine their interaction with the micelle surface. The different locations of the dyes resulted in different efficiencies of photoinduced interfacial electron transfer from the dyes to the TiO₂ particles. This can be explained in relation to the contact of the dyes with the TiO₂ surface.

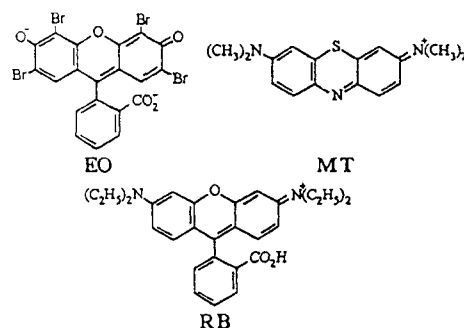
Keywords: Semiconductor particles; Dyes; Reverse micelles; Photoinduced interfacial electron transfer

1. Introduction

Colloidal semiconductor particles have been proved to be effective photocatalysts for the conversion and storage of light energy [e.g. 1]. Upon band gap excitation, semiconductor particles function as pools of photo-generated electrons and holes and initiate interfacial redox reactions. Alternatively, the adsorbed molecule can inject charge from its excited state into the semiconductor particle. This process is commonly referred to as photosensitization and plays a vital role in silver halide photography [2]. Recently it has also gained interest with regard to improving the visible light response of large band gap semiconductors such as TiO₂ and ZnO by adsorbing dyes on to the surface [3]. Many spectroscopic techniques have been employed to investigate the mechanism of such dye sensitization processes [4–7].

However, almost all the research on dye sensitization to date has been done in homogeneous media, mostly aqueous solution, and little has been done in micellar solution to our knowledge. Micellar solution, particularly reverse micelles (or microemulsion), can offer a unique

microenvironment for facilitating the charge separation between water and organic phase and hence increasing the quantum efficiency of conversion of the light energy [8,9]. In this regard it is indispensable to study the photosensitization of the large band gap semiconductor particles formed in reverse micelles and used as photocatalysts. In the present study we prepared TiO₂ nanoparticles in AOT–isooctane (AOT ≡ bis(2-ethylhexyl)sulphosuccinate sodium salt) reverse micelles. Three dyes, eosin (EO), methyl thionine (MT) and rhodamin B (RB), were chosen as probes solubilized in the water phase to investigate their interaction with TiO₂ particles and AOT micelles:



It will be of interest to see that the charge of the dye molecule plays a critical role in the adsorption on the TiO₂ surface, which in turn determines the charge transfer from the dye to the TiO₂ particle.

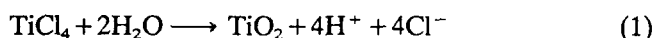
2. Experimental details

2.1. Materials

All the chemicals were of the purest quality commercially available and were used as received. TiCl₄, methyl thionine, rhodamine B and isooctane were purchased from Beijing Chemical Company. Eosin and AOT were obtained from BDH and Sigma respectively. Doubly distilled water was used throughout the experiments.

2.2. Preparation of TiO₂ nanoparticles

The preparation was carried out by a simple injection technique: 22 μl of TiCl₄ cooled to 0 °C was rapidly added under vigorous stirring to 100 ml of a 0.02 M AOT–isooctane micellar solution (0 °C) with a water-to-surfactant ratio ($w = [\text{water}]/[\text{surfactant}]$) of 5. This was then kept at 0 °C for 2 h. The colloidal TiO₂ (2×10^{-3} M) thus prepared was aged in a refrigerator at about 10 °C and used as a stock solution, which was stable for days at this temperature. The local concentration of H⁺ ions in the water pool of the reverse micelles can be estimated to be 5 M from the hydrolysis reaction of TiCl₄:



Since eosin is insoluble in acidic water, neutralization with a base was needed for the TiO₂ stock sol prior to its use in subsequent experiments. This was carried out by mixing 10 ml of the above stock solution with another 10 ml of micellar solution with the same content of water in which 5 M NaOH was solubilized. Vigorous stirring was again employed during the process. Owing to the stabilization effect of the reverse micelles, the neutral TiO₂ sol (10^{-3} M) thus obtained was quite stable. No flocculation was found within the time of the experiments. The absorption spectrum of the TiO₂ sol was very similar to that reported in Ref. [10], where the TiO₂ nanoparticles were prepared in aqueous solution. From the absorption onset the particle size of the TiO₂ colloids prepared in the present study can be estimated, based on the quantum size effect [11], to be 2–2.4 nm. This is in agreement with the results obtained by transmission electron microscopy (TEM).

2.3. Apparatus

Absorption spectra were measured with a Hewlett–Packard 8451A diode array spectrophotometer. Fluorescence spectra were recorded on a Perkin–Elmer LS-05 fluorimeter equipped with a computer for data acquisition, storage and manipulation. A Philips transmission electron microscope (EM-400) was used to determine the particle size of the TiO₂ colloids.

3. Results

3.1. Spectral characteristics

Fluorescence spectra of the three dyes were measured in various environments as shown in Fig. 1. Different shifts of the fluorescence maximum (λ_{max}) were found for these dyes. The emission spectrum of EO was red shifted by 10.5 nm in the reverse micelle relative to its aqueous solution. With the addition of 10^{-4} M TiO₂ colloids the spectrum was further shifted to the red by 2 nm. In contrast, for MT and RB, blue shifts of λ_{max} were observed under the same conditions. Compared with those of EO and MT, the λ_{max} shift of RB is much less, as indicated in Fig. 1c.

Fig. 2 shows the absorption spectra of EO in AOT–isooctane reverse micelles with the addition of TiO₂ colloids in various concentrations. When the concentration of TiO₂ was increased, the absorbance decreased markedly, accompanied by a steady red shift of the absorption maximum. Similar results were reported by previous authors using xanthene dyes, eosin [4] and erythrosin B [12] as the photosensitizer for TiO₂ colloids in aqueous solution. In contrast, little decrease in absorbance was found for MT and RB under the same conditions as for EO.

3.2. Fluorescence quenching

Addition of TiO₂ colloids to the reverse micelles resulted in not only the red shift of the emission spectrum of EO but also an effective fluorescence quenching. Fig. 3 shows the effect of increasing the concentration of TiO₂ colloids on the fluorescence spectrum of EO. Nearly 75% of the emission of 10^{-5} M EO was quenched with 10^{-4} M TiO₂. This quenching behaviour is similar to the previously reported fluorescence quenching of anthracene-9-carboxylic acid by TiO₂ colloids in aqueous solution [13]. A similar fluorescence quenching was also observed for RB, but the quenching efficiency was much lower than that of EO, as shown in Fig. 4, in which the relative fluorescence intensities (I/I_0) of EO and RB are plotted as a function of the concentration of TiO₂ added. An approximate linear relationship between I/I_0 and $[\text{TiO}_2]$ was obtained. Unlike those of

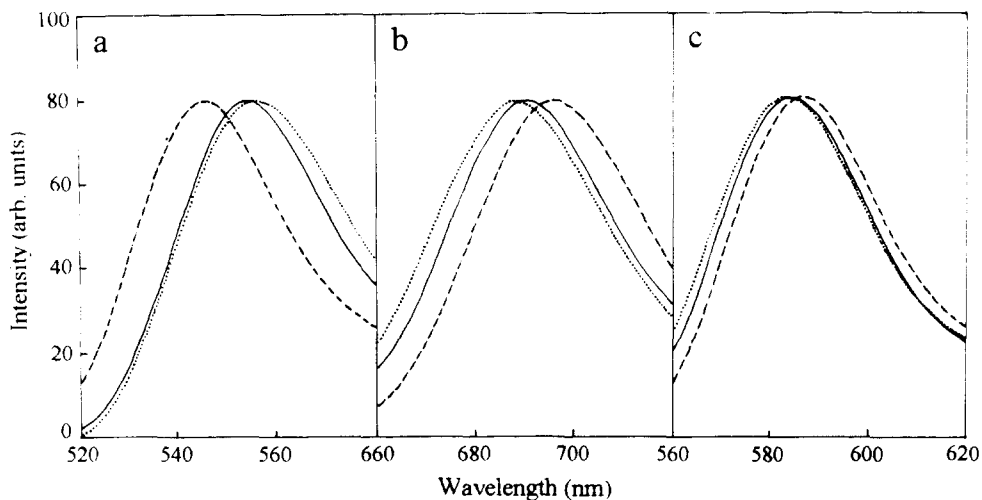


Fig. 1. Fluorescence spectra of dyes (10^{-5} M) in (---) water at pH 7, (—) AOT-isooctane reverse micelles (2×10^{-2} M) without TiO_2 colloids and (· · · · ·) reverse micelles with 10^{-4} M TiO_2 colloids. The local pH of the water pool of reverse micelles was kept at about 7 and the water-to-surfactant ratios (w) were maintained at 5.5–6. These two conditions were used throughout the experiments. Dyes: a, EO; b, MT; c, RB.

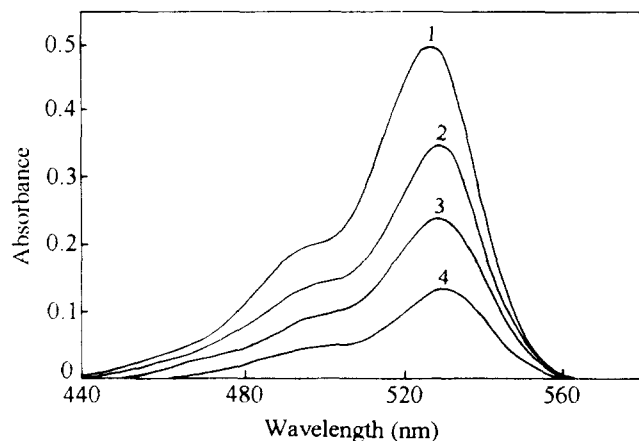


Fig. 2. Absorbance spectra of 10^{-5} M EO in AOT-isooctane reverse micelles at TiO_2 concentrations of (1) 0, (2) 10^{-5} , (3) 2×10^{-5} and (4) 5×10^{-5} M.

EO and RB, the emission of MT can hardly be quenched by TiO_2 colloids. The fluorescence spectrum of MT remained unchanged upon addition of TiO_2 colloids to the reverse micelles, even at quite high concentration (1.5×10^{-4} M).

4. Discussion

4.1. Location of dyes in reverse micelles

It has been widely recognized that the emission characteristics of many fluorophores are very sensitive to the solvent polarity [14]. For example, the fluorescence maximum shifts to longer wavelength with increasing solvent polarity. This is due to the solute-solvent, dipole-dipole reorientation of the polar

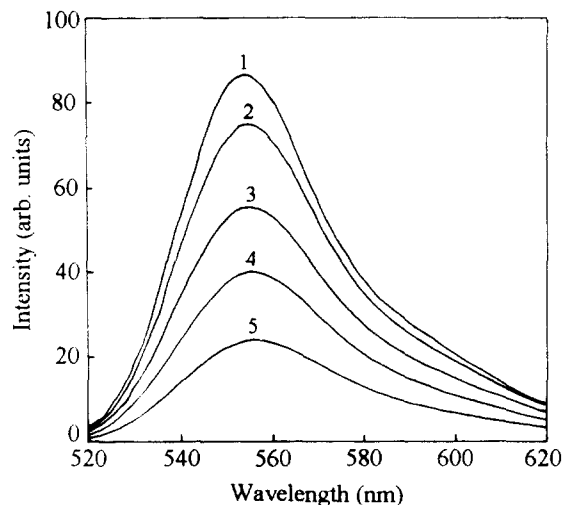


Fig. 3. Fluorescence spectra of 10^{-5} M EO in AOT-isooctane reverse micelles at TiO_2 concentrations of (1) 0, (2) 2×10^{-5} , (3) 4×10^{-5} , (4) 6.5×10^{-5} and (5) 10^{-4} M.

solvent molecules about the increased (relative to the ground state) dipole moment of the excited state. The negative charge of AOT molecules forms a spherical electrostatic field around the water pool, which causes an increase in polarity of the microenvironment. For the fluorophores solubilized in the water pool a red shift of the emission spectrum would be expected. The different observations in Fig. 1 for the three dyes can be attributed to their different locations in the reverse micelles. For EO, which possesses two negative charges at pH 7, most of the molecules are present in the central part of the water pool owing to the electrostatic repulsion of the micelles. Therefore the increase in polarity of the water pool results in a red shift of the emission spectrum (Fig. 1a). With the addition of TiO_2

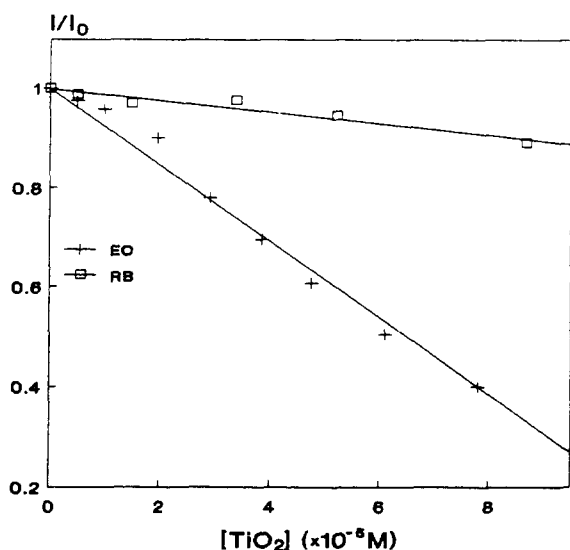


Fig. 4. Influence of TiO₂ concentration on relative fluorescence intensity (I/I_0) of EO and RB in AOT-isooctane reverse micelles. I is the observed fluorescence intensity and I_0 is that in the absence of TiO₂.

colloids the EO molecules are forced to adsorb on the TiO₂ surface by the electrostatic repulsion. As a result of this, the emission spectrum is further red shifted. This is due to the interaction of the EO molecules with the TiO₂ surface, which is believed to be of high polarity [4]. In addition to the effects on the emission characteristics, such an interaction can also cause some effects on the absorption characteristics, such as the decrease in absorbance and the red shift of the absorption maximum [4] (Fig. 2).

The positively charged MT molecule, however, was transferred by the electrostatic attraction from the highly polar phase of water to a less polar site in the micellar phase. As a consequence, the fluorescence maximum was blue shifted. This is in agreement with the results obtained by Sarpal and Dogra [15]. They investigated the spectral characteristics of aromatic amines in CTAB micelles and also found a blue shift in the fluorescence spectra relative to those of their aqueous solution. The further blue shift of the fluorescence maximum of MT upon addition of TiO₂ colloids indicated that the MT molecules were pushed into the deeper sites in the micellar phase by the TiO₂ particles. No MT molecules were adsorbed on the TiO₂ particles¹, however, otherwise a red shift in the fluorescence spectra would occur as in the case of EO.

The most interesting case is that of RB, which has a carboxyl group, -COOH. Owing to the electron-withdrawing effect of the substituted xanthenyl group (with a positive charge) at the ortho position, the acidic

dissociation constant of RB increases abruptly and is believed to be much larger than that of benzoic acid, 6.3×10^{-5} [17]. At the concentration of 10^{-5} M most of the RB molecules are in the deprotonated form which possesses a positive and a negative charge. The RB molecule is thus of apparent neutrality. It can neither be repulsed to the central part of the water pool nor be attracted into the micellar phase by the negative electrostatic field. From the small blue shift of the emission spectrum of RB (Fig. 1c) it can be concluded that most of the molecules in the reverse micelles are located in the region near the micelle surface, where the polarity is believed to be lower than that of water [15]. Addition of TiO₂ colloids facilitated the locating due to the space effects as discussed above for MT and thus caused a further blue shift of the fluorescence maximum.

4.2. Effects of location of dyes on interfacial charge injection

Two conditions are required for efficient interfacial charge injection from the sensitizer to the semiconductor particle. One is a sufficiently large energy difference between the excited state of the sensitizer and the conduction band of the semiconductor, since the difference acts as the driving force for charge injection. The other condition is that the sensitizer should be strongly bound to the semiconductor surface. For the three dyes used in this study the excited singlets lie at more negative positions with respect to the conduction band of TiO₂ and are therefore sufficiently energetic to inject electrons into the TiO₂ particles [4,18,19]. The sole factor controlling the interfacial charge transfer is the adsorption of the dyes on the TiO₂ colloids.

Owing to the effects of the electrostatic field formed by the negative charge of AOT, the dyes in the reverse micelles were located in different regions as described above. Upon addition of TiO₂ colloids the EO molecules were forced to bind strongly with the particle surface, whereas there was no direct interaction between the MT molecule and the TiO₂ colloid. One can then expect efficient electron transfer from the excited singlet of EO to the conduction band of TiO₂. This was confirmed by the observation presented in Fig. 3, where the emission of EO was effectively quenched by the addition of TiO₂ colloids. For MT, however, no fluorescence quenching was observed in accordance with the fact that the MT molecule does not adsorb on to the TiO₂ surface. Since the RB molecules were not located right in the micellar phase but in the region near the micelle surface, it was possible for some RB molecules to adsorb on the TiO₂ surface. This can be seen from the weak fluorescence quenching of RB by the addition of TiO₂ colloids (Fig. 4). The much lower quenching

¹ The point of zero charge (PZC) for TiO₂ is around pH 6 [16]. At pH 7 the TiO₂ surface is slightly negatively charged. No direct electrostatic interaction between MT and TiO₂ particles is expected to occur.

efficiency compared with EO was attributed to the small number of RB molecules binding with the TiO₂ surface.

4.3. Analysis of fluorescence-quenching data

In a previous work carried out in aqueous solution by Kamat [13], the participation of TiO₂ in the quenching process was analysed by considering the equilibrium between adsorbed and unadsorbed molecules of the sensitizer. An equation was derived to fit the experimental data. In the present study, however, this equation cannot be used to elucidate the quenching behaviour of the dyes by TiO₂ colloids. This is due to the unique microenvironment in the reverse micelle, which is quite different from the aqueous solution.

Owing to the slightly negatively charged surface of the TiO₂ particle at pH 7, it is almost impossible for EO or RB to adsorb spontaneously on the particle surface [4]. The adsorption of these two dyes on TiO₂ colloid in the AOT–isooctane reverse micelle is mainly caused by the electrostatic repulsion of the negative micelle surface. In such a case the adsorbance (C_a) of the dye at a given concentration (C_0) is proportional to the surface area of TiO₂ colloids, which in turn is proportional to the TiO₂ concentration ($[TiO_2]$):

$$C_a = K[TiO_2] \quad (2)$$

where K is the apparent adsorption constant of the dye. The observed fluorescence intensity of the dye (I) is determined by the concentration of free dye in the water pool:

$$I = k(C_0 - K[TiO_2]) \quad (3)$$

Thus the relative fluorescence intensity (I/I_0) can be written as

$$\frac{I}{I_0} = 1 - \frac{K}{kC_0} [TiO_2] \quad (4)$$

where I_0 is the fluorescence intensity in the absence of TiO₂. One can expect a linear dependence of I/I_0 on the concentration of TiO₂ colloids with a slope equal to $-K/kC_0$. This is indeed confirmed by the linearity of the plots for EO and RB shown in Fig. 4. The value of the slope can be used to evaluate the quenching efficiency of the TiO₂ colloids: the lower the slope, the higher is the quenching efficiency.

It is noteworthy that the quenching efficiency of TiO₂ colloids in reverse micelles was much higher than that in aqueous solution. For EO it was about 75 times higher than that reported in Ref. [4], where the work was carried out in aqueous TiO₂ solution. In addition to the electrostatic effect, such a marked increase in quenching efficiency was also due to the cage effect of the micelle, which concentrated the EO molecules at the TiO₂ interface. A similar cage effect was observed

in the case of the fluorescence quenching of CdS and ZnS nanoparticles by Ag⁺ ions in AOT–isooctane reverse micelles [20].

5. General conclusions

Owing to cage and electrostatic effects, reverse micelles offer a unique microenvironment for controlling the adsorption of additives with various charges on the semiconductor particles in the micelles. This is helpful for studying the dependence of the interfacial electron transfer on the interaction between the photosensitizer and the semiconductor surface. Three dyes were chosen in this study as probes to investigate the interaction with TiO₂ particles and the photoinduced interfacial electron transfer in AOT–isooctane reverse micelles. The results provide convincing proof for the argument that adsorption is a crucial condition for charge injection from the excited singlet of the photosensitizer into the semiconductor particle.

Acknowledgments

The support of this research by the National Natural Science Foundation of China and Eastman Kodak Company is gratefully acknowledged.

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