Coadsorption of Cationic Dyes with Surfactants on Colloidal TiO_2 Particles to Achieve Photosensitization in Highly Acidic Media

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Absorption and emission characteristics of rhodamine B (RB) were investigated in aqueous solutions of sodium dodecylbenzenesulfonate (DBS) at pH 0.9 in the absence and presence of colloidal TiO_2. From the spectral changes one can obtain detailed information about the interaction between RB, DBS and TiO_2. No adsorption of RB onto the surface of TiO_2 occurred at the quite low pH due to the strong electrostatic repulsion between RB molecules and the positively charged TiO_2 particles. Addition of DBS was found to be capable of improving the coadsorption of RB onto the surface of TiO_2 particles, and thus realizing and efficient charge injection from the excited state of RB into the conduction band of TiO_2.

Due to the high catalytic activity and photostability with respect to anodic dissolution, colloidal TiO_2 has been widely used as effective photocatalysts for light energy conversion and chemical transformation.[1,2] One severe disadvantage of this semiconductor material is the large band-gap, 3.2 eV for bulk TiO_2, which limits the photosensitivity to the ultra-violet region. To improve the visible light response, various dyes have been employed as photosensitizers to modify TiO_2 particles.[3,4] In a non-aqueous solution (e.g. acetonitrile), owing to the good stability of TiO_2 colloids, an effective photosensitization is readily achieved using anionic dyes, such as eosin and rose bengal.[4] However, in the aqueous solution, colloidal TiO_2 is only stable in highly acidic or highly basic media.[5] In such a case, it is impossible to attain a photosensitization using any cationic dye in highly acidic media, since the TiO_2 surface is positively charged. Even for the anionic dyes, the photosensitization is also quite difficult due to their weak solubility at low pH. In the present paper, we report on the preparation of a quite stable TiO_2 sol in aqueous solution at low pH, and on the ability of an anionic surfactant (sodium dodecylbenzenesulfonate, DBS) to modify the particle surface of colloidal TiO_2 in highly acidic solution (pH 0.9) to improve the adsorption of the cationic sensitizer, for which we choose rhodamine B (RB) as a suitable candidate. As one of the most readily available and useful laser dyes, RB is quite stable upon visible irradiation. Although the photochemical processes of adsorbed RB on solid TiO_2 surface have been investigated in recent years,[6] very few studies have been done in aqueous colloidal solutions.

All the chemicals were of the purest quality commercially available and were used as received. Deionized and doubly distilled water was used throughout the experiments. The preparation of colloidal TiO_2 was carried out by a simple injection technique: 110 µL (1 mmol) of $TiCl_4$ was rapidly added under vigorous stirring to 200 mL of a highly acidic solution, which was previously adjusted at pH 1.0 by adding HCl. Moderate stirring was then maintained for 2h. No stabilizing agents were used. The TiO_2 sol ($5x10^{-3}$ M, pH 0.9) thus prepared was quite stable even when kept at room temperature. No flocculation was detected over at least several months. From the absorption onset, the particle size of the TiO_2 colloids prepared in this study can be estimated, based on the quantum size effect,[5] to be ca. 2.5 nm. This is in agreement with the results obtained by transmission electron microscopy (TEM).

Absorption spectra were measured with a Shimadzu 1600A 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 TiO_2 colloids.

Figure 1 shows the effect of addition of TiO_2 colloids on the absorption characteristic of RB in the highly acidic aqueous solution. In the absence of DBS, no difference in the absorption spectra was observed between the TiO_2-free and TiO_2-containing solutions of RB. This is reasonable because in the acidic media, RB and the surface of TiO_2 are both positively charged.

One of the important criteria for and efficient photosensitization is to adsorb the dye molecule onto TiO_2 surface, thus making the charge injection attainable within the excited state lifetime of the dye. To improve the adsorption of RB on colloidal TiO_2, we tried to use DBS to modify the positively charged surface of TiO_2, since DBS was found to be able to strongly adsorb on TiO_2 particles.[7-9] A conceptual representation of coadsorption of RB with DBS onto the TiO_2 surface is proposed as shown in Scheme 1, in which several DBS molecules seize a RB molecule by electrostatic attraction to nestle closely to the particle surface of TiO_2. It is obvious that one prerequisite for achieving such a coadsorption is strong binding of RB with DBS. The absorption spectra of RB in the absence and presence of DBS provide direct evidence for the ground state association (Figure 1).

In the acidic water (pH 0.9), the visible spectrum exhibited a band maximum at 560 nm with a shoulder at 522 nm. The spectral structure is the same as that obtained in neutral aqueous solution. The 560 nm band is assigned to the RB monomer and the 522 nm band to the dimer.[10] When DBS was added at a concentration of $1.2x10^{-4}$ M, the absorbency at the maximum decreased markedly accompanied by an increase in absorption at the longer wavelength. This was attributed to the strong electrostatic interaction between RB and DBS, since these two molecules are opposite charged. The electrostatic association between these two molecules can also be seen from the changes in the fluorescence spectra of RB, in which the emission band shifted noticeably to the red with addition of DBS at the same concentration of $1.2x10^{-4}$ M.

It is expected that the positive charge on the TiO_2 surface counteracts in some degree the electrostatic interaction between RB and the head group ($-SO^{3-}$) of DBS (Scheme 1).

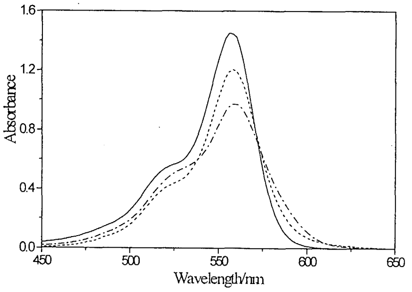


Figure 1. Absorption spectra of 1.7×10^{-5} M RB in various aqueous solutions at pH 0.9: (—) neat water with or without addition of 5.0×10^{-3} M TiO_2 colloids; (–·–) 1.2×10^{-4} M DBS; (----)1.2×10^{-4} M DBS and 5.0×10^{-3} M TiO_2. The pH of all the solutions was adjusted with HCl.

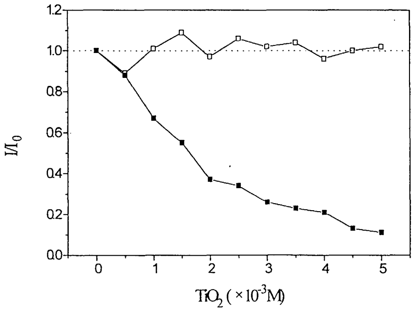
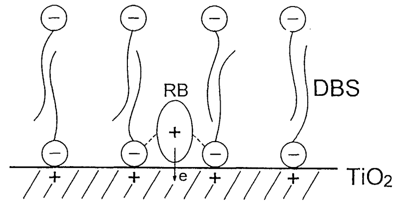


Figure 2. Influence of TiO_2 concentration on relative fluorescence intensity (I/I_0) of RB (5.0×10^{-7} M) in a neat water (□) and a 1.0×10^{-4}M DBS solution (■). I is the observed fluorescence intensity and I_0 is that in the absence of TiO_2. Both the solutions were adjusted at pH 0.9 with HCl (The excitation wavelength is 525nm, monitor wavelength is 540~700nm).



Scheme 1. Schematic diagram illustrating coadsorption of RB with DBS on the positively charged surface of TiO_2 colloids.

consequently, the absorption band of RB shifted to the blue and became narrower in comparison with that in the TiO_2-free DBS solution (Figure 1). Another parallel consequence was the observed blue shift of the fluorescence band of RB in the presence of TiO_2 colloids (about 2 nm).

As shown in Figure 1, addition of colloidal TiO_2 indeed leads to a notable increase in the quantity of RB monomer (main band) accompanied by a decrease in the number of the dimer (shoulder). It is commonly recognized that the RB monomer is fluorescent and dimer is nonfluorescent. However, the increase in the monomer component of RB did not result in any enhancement in the fluorescence intensity. On the contrary, (as shown in Figure 2), the fluorescence yield of RB deceased continuously with increasing the concentration of TiO_2 colloids, indicating an occurrence of the interfacial electron injection.

It has been shown earlier in the field of electrochemical catalysis that the surfactant films adsorbed on the electrode can effectively incorporate and protect the reaction mediators at the electrode surface, and at the same time, preconcentrate the substrates.[11] Especially for the nonpolar organic compounds (e.g. aryl or alkyl halides), which are insoluable in water and quite difficult to be adsorbed on the charged surface of the electrode, the reaction rate of the nonpolar substrate could be greatly enhanced by addition of aninic surfactants. We feel that the principles used to modify and control surface properties of electrodes in surfactant media could be harnessed for improving the photosensitization (charge injection) of the positively charged TiO_2 colloids by RB.

Figure 2 shows the effect of DBS on the fluorescence quenching of RB by TiO_2 colloids. In the absence of DBS, the relative fluorescence intensity (I/I_0) of RB remained almost constant with increasing the concentration of TiO_2, while in the presence of 10^{-4} M DBS, an increase in the concentration of colloidal TiO_2 brought about a steady decrease in the fluorescence intensity of RB. This obviously indicates that DBS molecules facilitate the coadsorption of RB molecules onto the surface of TiO_2 colloids, therefore making it possible for a photoinduced electron transfer from the excited state of RB to the conduction band of TiO_2. The microenvironment depicted in Scheme 1 seems suitable for dissociating the RB aggregate which readily forms in the DBS solutions.

Some further study on the influence of DBS concentration on fluorescence intensity of RB ($5.0\text{x}10^{-7}$ M) and 2-naphthalene sulfonic acid (NSA, $1.0\text{x}10^{-5}$ M) in aqueous solution of colloidal TiO_2 ($5\text{x}10^{-3}$ M) at pH 0.9 was also done. Increasing the amount of DBS was always conductive to enhancing the fluorescence quenching by TiO_2 colloids, since more and more RB molecules would be coadsorbed on the TiO_2 particle by the electrostatic interaction with DBS molecules. In contrast, DBS caused only a slight effect on the fluorescence quenching of NSA. With an increase in the concentration of DBS, the quenching efficiency of NSA by TiO_2 lessened to a small extent. Owing to the higher polarity of NSA compared with that of DBS, NSA adsorbed onto TiO_2 surface more strongly than DBS, i.e. a DBS molecule did not compete effectively with a NSA molecule for the same adsorption site ($\equiv$Ti-OH_2).[7,12,13] Control spectral measurements supported this assumption. Both absorption and emission bands of NSA shifted to the red in the presence of TiO_2 colloids, whereas further addition of DBS made little effect on the spectral characteristic. Nevertheless, the electrostatic repulsion between NSA and DBS would cause a negative effect on the adsorption of NSA, and consequently a slight decrease in the efficiency of fluorescence quenching.

In summary, the present study shows the ability of an anionic surfactant (DBS) to modify the positively charged surface of colloidal TiO_2 to improve a photoinduced charge transfer from rhodamine B to the TiO_2 particles. This provides a promising way for achieving an efficient photosensitization of colloidal TiO_2 by a cationic dye in highly acidic solutions.

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