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The effect of the potential of colloid titanium dioxide on fluorescence quenching

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Abstract

The dependences of the fluorescence quantum yields of pyrene-1,3,6-trisulfonate and pyrene-3,5,8,10-tetrasulfonate adsorbed onto TiO_2 colloid on the solution composition were investigated. The increases in pH and chloride concentration cause a decrease in the rate constants of fluorescence quenching. The results are discussed in terms of the potential of the surface of the colloid particles.

Keywords: Colloid titanium dioxide; Fluorescence quenching; Fluorescence quantum yields

1. Introduction

Many studies during the last few years have dealt with colloidal TiO_2, owing to its extreme photocatalytic activity and stability to photocorrosion [1–3]. There are only a few investigations of the fluorescence of photoexcited labels on the surface of TiO_2. Chandrasekaran and Thomas [4] studied the emission of optically excited pyrene, bromopyrene, pyrene aldehyde, anthracene, methylanthracene, naphthalene and perylene over the surface of suspended TiO_2 and found changes in the emission spectra and fluorescence kinetics compared with the homogeneous methanolic solution. Graetzel and coworkers [5,6] studied the fluorescence of Eosine Y and of [tetrakis(4-carboxyphenyl)porphyrinato]zinc(II) in colloidal solutions of TiO_2 and found that the fluorescence quenching of the label by the semiconductor surface is drastically decreased as pH of the solution is increased from 4 to 9, which was attributed to desorption of the label from the surface; however, it was also supposed that at high pH values the reaction of the electron transferring from the excited species to the conductance band has not enough driving force. Kamat and Fox [7] and later Kamat et al. [8] observed the emission of erithrosin in acetonitrile and of chlorophyllin in aqueous solutions bound to TiO_2 surface. A very detailed study of the electron transfer from anthracene-9-carboxylic acid to suspended TiO_2 was made by Kamat [9], including the measurement of the rate constant of the reaction. However, only the studies in [5,6] revealed directly the dependence of the quenching rate constant of the fluorescence of completely bound labels upon the composition of the aqueous solution and, as far as we were able to find, the only value taken into account was the pH. In the present work we studied the influence of the pH and pCl of the solution on the quenching of the fluorescence of completely adsorbed pyrene-1,3,6-trisulfonate (PTS) and pyrene-3,5,8,10-tetrasulfonate (PTTS). The results were discussed in terms of the change in the surface potential of the semiconductor particles due to the change of the pH and pCl of the solution.

2. Experimental details

Titanium dioxide colloid was prepared from titanium tetrachloride by hydrolysis in water according to the procedure in [10]. The size of the prepared particle was determined with an OPTON 10CR transmission electron microscopy (TEM) system. PTS and PTTS were purified by recrystallization from methyl alcohol. The purity was monitored by nuclear magnetic resonance (NMR). Because of the instability of dye molecules adsorbed onto titanium dioxide particles under UV irradiation, the dye was added to the colloid solution just before the measurement and the adsorption spectra measurements were made from 350 nm. However, the change in the scan rate produced no detectable effect upon the measured fluorescence intensity; so the influence of the photolysis of the label during one scan upon the results of the

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measurement was considered to be negligible. Light absorbance spectra were measured on a Specord-M40, the fluorescence on a Shimadzu RF5000, and the nanosecond fluorescence decay kinetics on a single-photon counting system with a flash lifetime shorter than 2 ns. The pH and pCl were measured with Econix (Russia) electrodes using an Ecotest-110 ionometer.

3. Results

The absorbance and fluorescence spectra of PTS in the presence and in the absence of titanium dioxide have already been described elsewhere [11]. When titanium dioxide is added, the absorbance is a little decreased without considerable changes in the shape of the spectrum. The fluorescence of both PTS and PTTS is decreased with increasing TiO_2 concentration to some limit and then remains constant, as was observed for other dyes in [4–7] (Fig. 1). The shape of the fluorescence spectra is unaffected by the addition of TiO_2. To know quantitatively which part of the label is bound to the surface and which remains in the bulk solution, we processed the dependence of the fluorescence quantum yield upon the concentration of colloidal TiO_2, using the following model. The total quantum yield ϕ of the fluorescence can be expressed as follows:

$$\phi = \alpha\phi_b + (1-\alpha)\phi_{aq} \qquad (1)$$

Here α and $1-\alpha$ are the part of the label bound to the surface of the colloid, and the part of the label in the bulk solution, ϕ_b and ϕ_{aq} are the quantum yields of the fluorescence of the label completely bound to the colloid microphase and in the bulk aqueous solution respectively. We can express α as usually for micelles [12]:

$$\alpha = \frac{K[TiO_2]}{1+K[TiO_2]} \qquad (2)$$

where K is the binding equilibrium constant. The substitution of Eq. (2) into Eq. (1) gives after simple transformations [12]

$$\phi = \phi_b + \frac{\phi_{aq}-\phi}{K[TiO_2]} \qquad (3)$$

Eq. (3) provides a possibility to build a linear anamorphose of the dependence, shown in Fig. 1 to extrapolate the fluorescence quantum yield to the 'infinite' concentration of TiO_2 and to estimate which part of the label is bound to the surface of colloid particles. The plot of ϕ vs. $(\phi_{aq}-\phi)/[TiO_2]$ is shown in Fig. 2. One can see that this anamorphose is almost linear, which makes it possible to obtain the values of ϕ_b. The small deviation from the linearity at low concentration of titania could be caused by the interaction of the label molecules with one another, when present simultaneously at the surface of the same colloid particle. One should mention that the change in the concentration of titanium dioxide colloid changes the pH and pCl of the solution simultaneously, which should be therefore carefully adjusted by the addition of perchloric acid or sodium chloride to obtain the above dependences. It is evident that the quantum yield of the fluorescence of the label on the surface is considerably smaller than in the bulk solution. One can consider this as a quenching of the fluorescence by the surface of the semiconductor. The surface of the solid phase is widely known to be non-uniform.

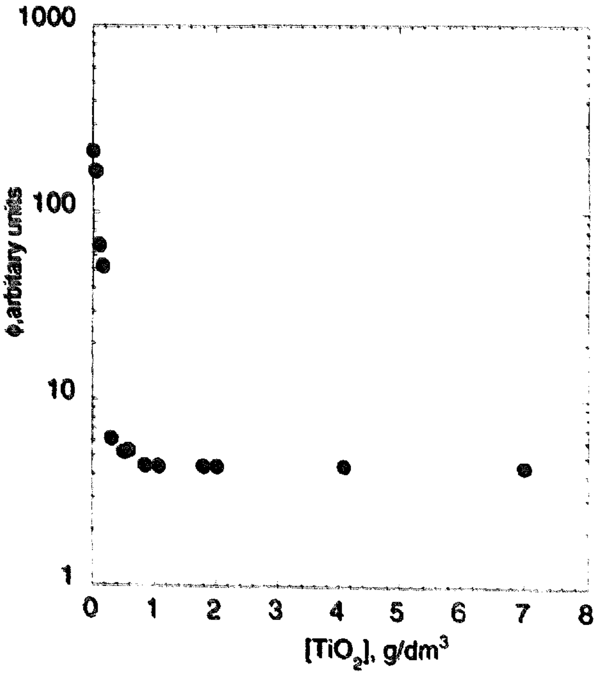

Fig. 1. The plot of the quantum yield of PTTS vs. the concentration of TiO_2 with pH 2.8 and pCl 2.7.

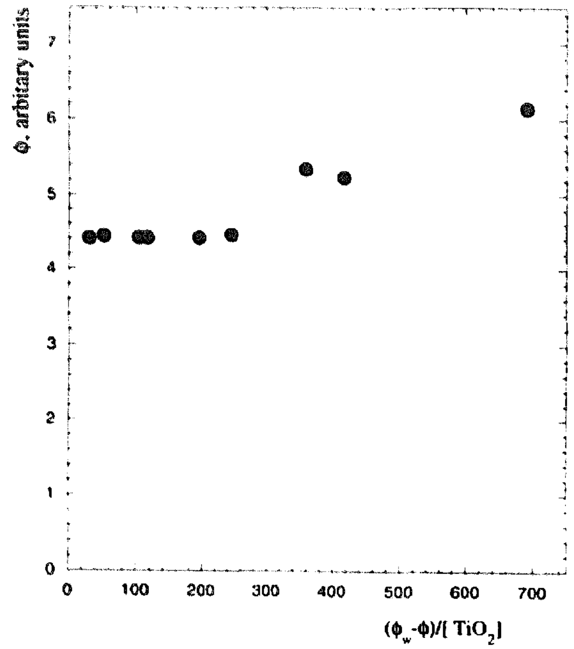

Fig. 2. The plot of the quantum yield of PTTS fluorescence in the presence of TiO_2 vs. $(\phi_w-\phi)/[TiO_2]$ at pH 2.8 and pCl 2.7.

So the equation occurs whether such a quenching can be characterized with a single quenching rate constant. For example, Chandrasekaran and Thomas [4] have found that the fluorescence decay of the pyrene label on TiO_2 is described by two exponential components. In this case, one cannot evidently use a single rate constant. However, the labels used by Chandrasekaran and Thomas were hydrophobic and placed directly on the surface of the semiconductor. We have used hydrophilic labels which are likely to be localized in the outer part of the electric double layer with other counterions and so one could expect more uniform reactivity than in the case described by Chandrasekaran and Thomas. So we tried to check the possibility of use of a single rate constant by comparing the ratios of the fluorescence decay times and the fluorescence quantum yields.

The fluorescence decay at high concentration of colloid particles as revealed by single-photon counting is single exponential with a lifetime much shorter than that in homogeneous aqueous solution. This also gives evidence that almost all dye molecules bound to the surface in the ground electronic state reach approximately equal states when photoexcited.

The fluorescence decay time for PTTS with pCl 1.6 and pH 2.7 in the presence of 0.5 g dm^{-3} of transparent TiO_2 colloid was 1.6 ns, while in the homogeneous aqueous solution its decay time was 10.8 ns. The first-order quenching rate constant k_1 can be calculated according to the following equation:

$$k_1 = \frac{1}{\tau} - \frac{1}{\tau_{aq}} \qquad (4)$$

where τ_{aq} and τ are the decay times of fluorescence in the absence and in the presence respectively of the quencher. For the above case, Eq. (1) gives $k_1 = 0.63 \times 10^9$ s^{-1}. The ratio of the fluorescence quantum yields is equal to the ratio of the fluorescence decay times within 3%. So the quenching process can be considered as monomolecular and purely dynamic. However in the general case the fluorescence decay times for both PTS and PTTS are too short for our equipment because some light scattering is present and, to measure the rate constants of the quenching, we have used the following expression, which could be obtained by the substitution of the approximation $\phi_{aq}/\phi_b = \tau_{aq}/\tau$ into Eq. (4).

$$k_1 = \frac{\phi_{aq}/\phi_b - 1}{\tau_{aq}} \qquad (5)$$

The rate constants thus determined with different pCl and pH values for both PTS and PTTS are given in Table 1. One can see that the rate constants are considerably dependent on both pH and pCl.

4. Discussion

Earlier we have shown [11], using the quenching of PTS bound to TiO_2 by iodide ions, that the potential dependence of TiO_2 surface on the concentration of protons and chloride ions in the pCl range from 1.0 to 4.0 and the pH range from 1.0 to 4.0 is as follows:

Table 1
The dependence of the rate constants of the fluorescence quenching for PTS and PTTS by the surface of colloid TiO_2

$\log[k_1\ (s^{-1})]$	pH	pCl	Label
9.84	2.7	3.36	PTS
9.676	2.7	2.16	PTS
9.584	2.7	2.06	PTS
9.342	2.7	1.8	PTS
8.84	2.7	1.6	PTS
9.706	2.9	2.62	PTTS
9.667	2.9	2.42	PTTS
9.618	2.9	2.13	PTTS
9.386	2.9	1.84	PTTS
8.532	2.9	1.50	PTTS
9.764	2.74	2.7	PTTS
9.841	2.5	2.7	PTTS
9.944	2.2	2.7	PTTS
9.973	1.9	2.7	PTTS
9.6	2.8	2.7	PTS
9.681	2.5	2.7	PTS
9.945	2.0	2.7	PTS

$$E = E^0 - \frac{RT}{F}\ln\left(\frac{[H^+]}{[Cl^-]}\right) \qquad (6)$$

Duonghong et al. [13] established the position of the zero-charge E_{fb} potential of the colloid TiO_2 to be −0.14 V vs. a normal hydrogen electrode (NHE) at pH 0. However, we cannot use this datum to obtain the fixed scale of E_{fb} for our particles, because the value of pCl in [13] is unknown. For our particles we can only introduce the scale of the potential ψ_l of the surface which characterize the behaviour of the label in the outer part of the double layer. To establish the zero of ψ_l we used turbodimetric titration [8]. With pCl 2.8, ψ_l was found to be zero at pH 5.9; so

$$\psi_l = 0.18 - 0.059(\mathrm{pH} - \mathrm{pCl})\ \mathrm{V\ vs.\ NHE} \qquad (7)$$

However, there are not sufficient data to establish the value of the overpotential for electron transfer from photoexcited labels to the conductance band during our measurements. First of all, the positioning of the Fermi level or of the flatband potential for such small particles, meets some difficulties and we are not able to use the values obtained in [1], because the chloride concentration was not quantitatively monitored in the work described in [1]. It was shown earlier [13] that the change in pH by one unit leads to a change in E_{fb} by some 59 mV. The only assumption that one can make is that ψ_l reflects the charging of the particle as a whole and the whole system of electronic terms within the particle is displaced as well. In spite of the fact that the dependence of the value of E_{fb} upon chloride concentration was not studied so far, the fact that the same is correct also for ψ_l leads to the conclusion that ψ_l equals F_{fb} within some constant:

$$E_{fb} = E_{fb}{}^0 - 0.059(\mathrm{pH} - \mathrm{pCl})\ \mathrm{V\ vs.\ NHE} \qquad (8)$$

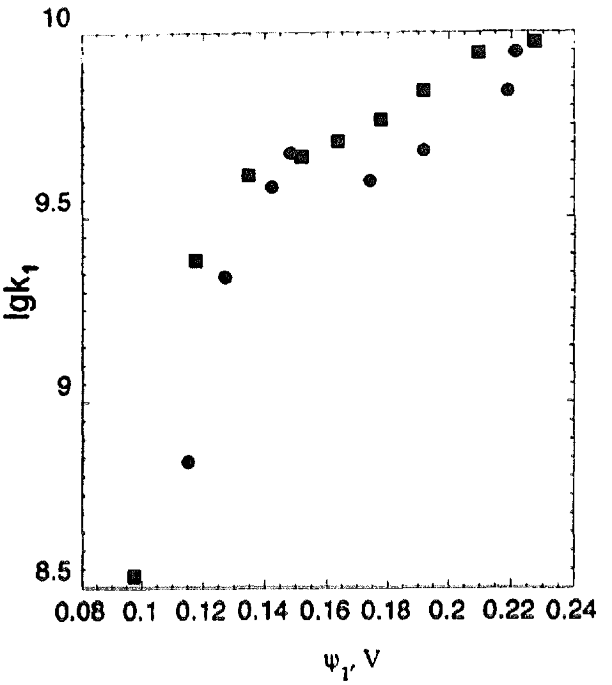

Fig. 3. The logarithm of the quenching rate constant k_1 vs. the surface potential ψ_1 of TiO_2 for PTS (●) and for PTTS (■).

We were not able to measure the reversible standard oxidation potentials for PTS and PTTS in water on both gold and platinum rotating electrodes, and these salts are almost insoluble in acetonitrile.

However, the rate constant of the quenching of the fluorescence of PTS and PTTS by the semiconductor surface, calculated as described above, is pH and pCl dependent. Fig. 3 shows the plot of the logarithm of the quenching rate constant k_1 vs. ψ_1, for both PTS and PTTS which proves to be non-linear and common for both labels.

5. Conclusions

One can see from Table 1 that the increase in the chloride concentration causes a decrease in the rate constant of quenching. We consider the electron transfer to be the only possible mechanism of quenching of the fluorescence of PTS and PTTS by TiO_2 due to the potential dependence of the rate constant. So the increase in chloride concentration results in decrease in the oxidative power of TiO_2. This enables us to understand the inhibiting power of hydrochloric acid on the photo-oxidation of organics in the presence of TiO_2 [14,15]. So far the dependence of E_{fb} on the concentration of chloride and other ions has not been described in the literature. Meanwhile, very often chloride is present in systems containing titanium dioxide owing to synthesis from $TiCl_4$, use of hydrochloric acid or photolysis of chlororganics. Also the work with titanium dioxide where there is no proper control of the chloride concentration should be considered as only semiquantitative. The coincidence of the plots for k_1 vs. ψ_1 for substances with different chemical natures shows that the processes in the double layer are responsible for the observed dependence. However, the occasional coincidence of the oxidation potentials of PTS and PTTS is also possible, as we could not measure these potentials. Anyway, shifts in the E_{fb} due to the change in the total potential of the particle affects the shape of the potential barrier for electron transfer, which evidently is the reason for the observed potential dependence of fluorescence quenching.

Acknowledgments

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