Research Article

Studies on the Photoinduced Interaction between Zn(II) Porphyrin and Colloidal TiO$_2$

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The interaction of Zn(II) porphyrin (ZnPP) with colloidal TiO$_2$ was studied by absorption and fluorescence spectroscopy. The fluorescence emission of ZnPP was quenched by colloidal TiO$_2$ upon excitation of its absorption band. The quenching rate constant (kq) is 1.24×10^{11} M^{-1} s^{-1}. These data indicate that there is an interaction between ZnPP and colloidal TiO$_2$ nanoparticle surface. The quenching mechanism is discussed on the basis of the quenching rate constant as well as the reduction potential of the colloidal TiO$_2$. And the mechanism of electron transfer has been confirmed by the calculation of free energy change (ΔG_{et}) by applying Rehm-Weller equation as well as energy level diagram.

1. Introduction

Wide-band gap semiconductor particles such as TiO$_2$ have been widely used for different applications in photocatalysis and the environment [1, 2]. Over the past decades, considerable interest has been shown in the modification of TiO$_2$ semiconductors by organic dyes to extend the photoresponse to visible light owing to their potential application in solar energy conversion [3–5]. Dye sensitization is considered to be an efficient method to modify the photo response properties of TiO$_2$ particles. The dyes used are erythrosine B [6], rose Bengal [7], metal porphyrin [8–10], and so forth.

Porphyrins, (including metal-free porphyrins, metalloporphyrins and supramolecular porphyrins) [11] are recognized to be the most promising sensitizers [12]. The chemistry of porphyrin derivatives has played an important role especially during the past decade in particular branches of new materials science, and many researchers have undertaken projects on the synthesis of variously substituted compounds to obtain new functional materials [13–15]. Metalloporphyrin may be an appropriate candidate because of its high absorption coefficient within the solar spectrum and its good chemical stability in comparison to that of other dyes. They are highly effective photocatalysts due to their very strong absorption in the 400 nm–450 nm region (Soret band) and in the 500 nm–700 nm region (Q-bands) and, in fact, the presence of p-electrons affords the condition for electron transfer during the photoreaction.

In the present work we have investigated the electron transfer from excited ZnPP (see Scheme 1) to the conduction band of TiO$_2$ colloid by using absorption and fluorescence spectroscopy.

2. Materials and Methods

2.1. Materials. Zn(II) porphyrin and tetrabutyl titanate were purchased from Aldrich. The doubly distilled water was used for preparing the solutions. All measurements were performed at room temperature (28°C).

2.2. Preparation of Colloidal TiO$_2$. The colloidal TiO$_2$ suspension was prepared by the hydrolysis of tetrabutyl titanate ($C_{16}H_{36}O_4Ti$). Typically, tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) in 2-propanol was injected by using syringe into water with constant stirring under nitrogen atmosphere (8 h) it giving
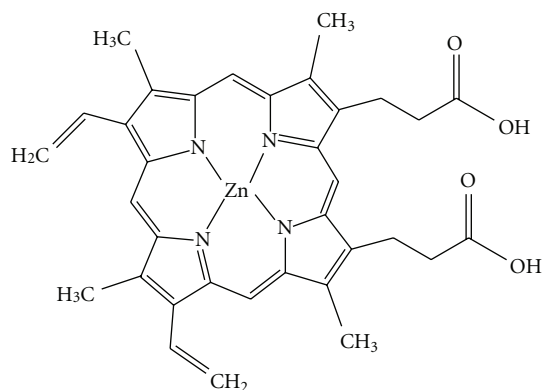
Scheme 1: Structure of ZnPP.

1×10^{-2} M titania stock solution. No stabilizing agents were used during the hydrolysis process. The colloidal suspensions of TiO_2 prepared by this method were stable for 3–5 days. Fresh colloidal TiO_2 dispersed in water was prepared before each set of experiments. No attempts were made to exclude the traces of 2-propanol present in the colloidal TiO_2 suspension and it was confirmed separately that the presence of 2-propanol did not affect the photochemical measurements as earlier reported [16].

2.3. Instrumentation. The steady-state fluorescence quenching measurements were carried out with Perkin Element LS-50B spectrofluorimeter. The excitation wavelength of ZnPP was 420 nm and the emission was at 589 nm. The excitation and emission slit widths (each 5 nm) and scan rate (600 nm/min) were maintained constant for all the experiments. The samples were carefully degassed using pure nitrogen gas for 15 min. Quartz cells (4 cm × 1 cm × 1 cm) with high vacuum Teflon stopcocks were used for degassing. Absorption spectral measurements were recorded using Varian Cary 5000 NIR-UV-Vis spectrophotometer.

3. Results and Discussion

3.1. UV-Vis and Fluorescence Spectra Studies. The absorption and emission spectra of ZnPP (Figure 1) were recorded in the absence and in presence of colloidal TiO_2 (Figures 2 and 3). From Figure 2 we can see in the region of 300 nm–500 nm, ZnPP has one characteristic absorption band with absorption maxima at 420 nm. After addition of different concentration of TiO_2 to ZnPP solution, the shape and band maxima of absorption spectra of ZnPP remain unchanged, but the intensities decreased greatly. The fluorescence spectra of ZnPP with varying concentrations of TiO_2 are shown in Figure 3; it is clear that the fluorescence spectra of ZnPP remain unchanged, and no other new emission band of the ZnPP is noticed. However, TiO_2 can quench the fluorescence of ZnPP effectively.

The above observations suggest that the ZnPP–TiO_2 interaction does not change the absorption and fluorescence spectral properties and the formation of any emissive exciplex may be ruled out.
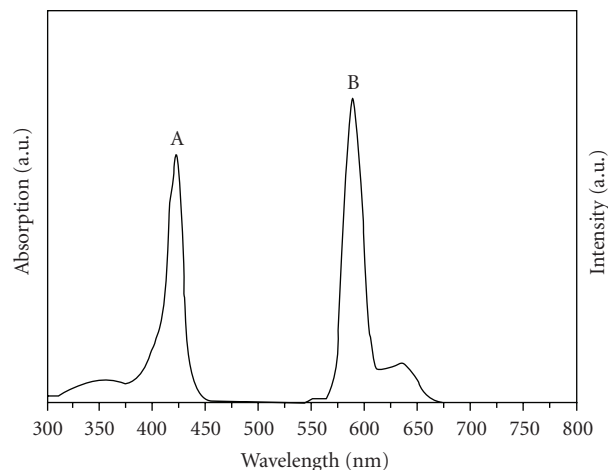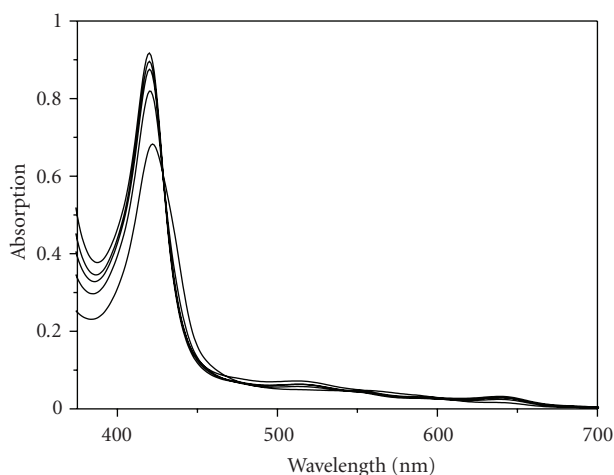

Figure 1: Absorption (A) and emission (B) spectrum of ZnPP.

Figure 2: Absorption spectrum of ZnPP in the presence of colloidal TiO_2 in the concentration range of $(0–5) \times 10^{-4}$ M in water.

The Stern-Volmer constant (K_{sv}) and the quenching rate constant (k_q) for the fluorescence quenching of ZnPP were determined from Stern-Volmer plots using emission intensity data

$$\frac{I_0}{I} = 1 + K_{sv}[Q], \tag{1}$$

where

$$K_{sv} = k_q \tau, \tag{2}$$

where I_0 and I correspond to the intensities of the sensitizer in the absence and presence of the quencher, respectively, $[Q]$ the concentration of the quencher and τ_0 the emission lifetime of sensitizer. The Stern-Volmer plot in the quenching of ZnPP is linear with a correlation coefficient (R^2) of greater than 0.9966 indicating the dynamic nature of quenching process and absence of static quenching (Figure 4). From the slope of the above plot, the K_{sv} values obtained are 4.48×10^4 M^{-1}, and using (2), namely, $K_{sv} = k_q \tau$, the k_q value calculated is found to be 1.24×10^{11} $M^{-1}s^{-1}$.
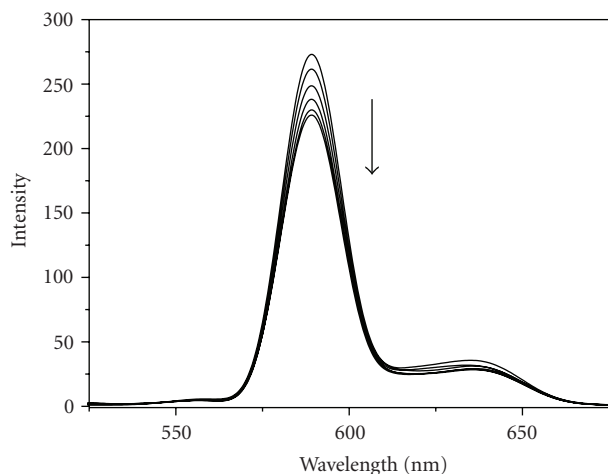
FIGURE 3: Steady state fluorescence quenching of ZnPP (2×10^{-6} M) with colloidal TiO$_2$ in the concentration range of $(0–5) \times 10^{-4}$ M in water.
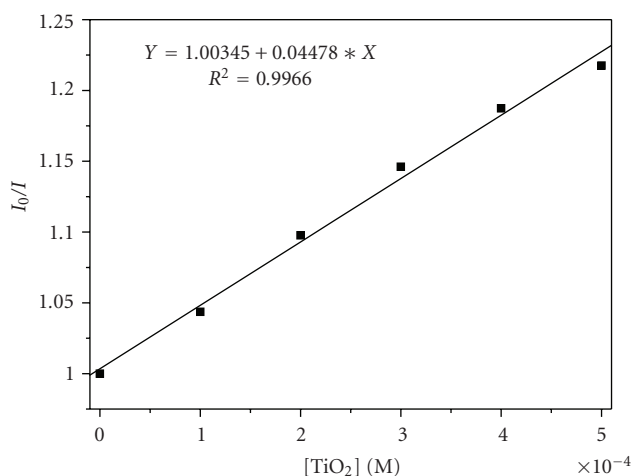

FIGURE 4: Stern-Volmer plot for the fluorescence quenching of ZnPP with various concentrations of TiO$_2$ $(0–5) \times 10^{-4}$ M in water.

FIGURE 5: Absorption spectrum of TiO$_2$ (A) and emission spectrum of ZnPP (B).

SCHEME 2: Energy level diagram for ZnPP and TiO$_2$.

The decrease in fluorescence emission may be attributed to the various possibilities such as energy transfer, electron transfer, or ground state complex formation between the ZnPP and colloidal TiO$_2$.

As shown in Scheme 2, the band gap energy of TiO$_2$ (3.2 eV) is greater than the excited state energy (2.11 eV) of ZnPP and there is no overlap between the fluorescence emission spectrum of ZnPP with the absorption spectrum of colloidal TiO$_2$ (Figure 5), so the above two inferences excluded the possibility of energy transfer from ZnPP to colloidal TiO$_2$. From the above discussion, we confirmed that the fluorescence quenching shown in Figure 3 should not be caused by energy transfer.

The possibility of surface complex formation between ZnPP and colloidal TiO$_2$ is the reason for quenching of ZnPP by colloidal TiO$_2$. While increasing the concentration of colloidal TiO$_2$, some of the ZnPP molecules were adsorbed on the surface of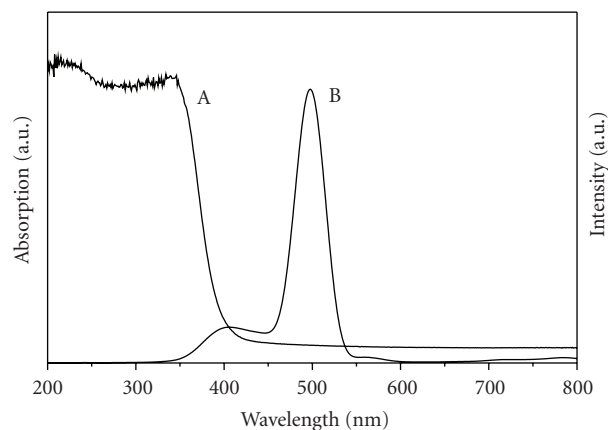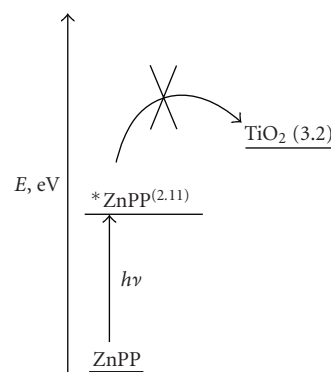 TiO$_2$, so the number of molecules available for the fluorescence is reduced, which is the reason for decrease in fluorescence intensity.

The ability of the excited state ZnPP to inject its electrons into the conduction band of TiO$_2$ is determined by energy difference between the conduction band of TiO$_2$ and oxidation potential of excited state ZnPP. According to equation $E_{s^*/s^+} = E_{s/s^+} - E_s$, the oxidation potential of excited state ZnPP is -1.24 eV versus SCE, where E_{s/s^+} is the oxidation potential of ZnPP, (0.87 eV) versus SCE [17] and E_s is the excited state energy of ZnPP, 2.11 eV excited state energy of the ZnPP calculated from the fluorescence maximum based on the reported method [18]. The conduction band potential of TiO$_2$ is -0.1 eV versus SCE [19]. Scheme 3 suggested that electron transfer from excited state ZnPP to the conduction band of TiO$_2$ is energetically favorable.

Therefore, we conclude that the fluorescence quenching shown in Figure 3 is caused by electron transfer.

3.2. Calculation of Free Energy Changes (ΔG_{et}) for the Electron Transfer Reactions.

The nature of the electron transfer pathway (i.e., oxidative or reductive quenching) can be understood by examining the free energy of the corresponding reactions. Thermodynamics of electron transfer from
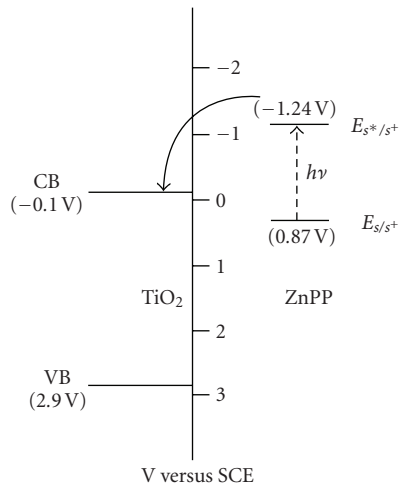
SCHEME 3: Schematic energy level diagram showing electron transfer process.

TABLE 1: Photophysical properties of ZnPP.

| S. no	Parameters	ZnPP
1	E_{ox} versus SCE (eV)	0.87
2	E_S (eV)	2.05
3	ΔG_{et} (eV)	-1.08

the sensitizer to the quencher can be calculated by the well-known Rehm-Weller equation [20]

$$\Delta G_{et} = E^{(ox)}_{1/2} - E^{(red)}_{1/2} - E_S + C, \qquad (3)$$

where $E^{(ox)}_{1/2}$ is the oxidation potential of the donor, $E^{(red)}_{1/2}$ the reduction potential of the acceptor, E_S the singlet state energy of the sensitizer, and C is the coulombic term. Since one of the species is neutral and the solvent used is polar in nature, the coulombic term in the above expression is neglected [21]. The oxidation potential, excited singlet state energy (E_S) and the calculated ΔG_{et} value for the ZnPP are shown in Table 1. The conduction band potential of TiO$_2$ is -0.1 V versus SCE [22]. By using Rehm-Weller equation negative value of ΔG_{et} was obtained. The absence of any overlap between the emission spectra of the ZnPP and the absorption spectrum of TiO$_2$ (Figure 5) and the well established electron accepting nature of e^-_{cb} of TiO$_2$ in presence of excited electron donors, namely, the dyes [23] coupled with the above observation support that the quenching mechanism in this work involves electron transfer (i.e., electron transfer from excited ZnPP to TiO$_2$) and hence there is no energy transfer.

3.3. Schematic Diagram Describing the Electron Transfer Quenching Process. Upon excitation of ZnPP, it goes to excited state, and an electron transfer from excited ZnPP to conduction band of TiO$_2$ occurs.

$$(4)$$
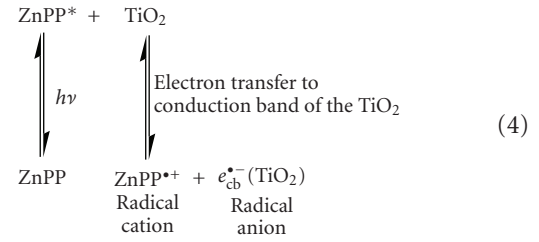
4. Conclusions

Based on the above results, the electron transfer mechanism was proposed for the fluorescence quenching of ZnPP by TiO$_2$. ZnPP serves as electron donor and TiO$_2$ as electron acceptor. Quenching follows static mechanism through ground complex formation which is confirmed by the curvature of Stern-Volmer plot.

Acknowledgments

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