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EPR Investigation of the Free Radicals Generated during the Photosensitization of TiO_2 Colloid by Hypocrellin B

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The cation radical of dye produced from the interfacial electron transfer from a surface chelated dye to the conduction band of the colloidal TiO_2 was studied by laser flash photolysis and electron paramagnetic resonance (EPR) techniques. The study employed hypocrellin B (HB), a natural photodynamic pigment with strong absorption over the visible light region, as a sensitizer and titanium dioxide as a colloid semiconductor. HB formed a chelate with this colloid semiconductor and exhibited a red-shifted and strongly enhanced absorption in the visible spectrum. Laser photolysis indicated that the electron excitation in the visible absorption band of the chelate resulted in extremely rapid and efficient electron injection from the excited triplet state of the dye into the conduction band of the semiconductor. A transient absorption of cation radical of HB at 570 nm was observed. The appearance of cation radical of HB was characterized by EPR spectrometry: the photoinduced EPR signal was not quenched by oxygen and its intensity decreased in the presence of NaI, a typical hole scavenger. The generation of conduction band electrons in HB-sensitized TiO_2 system was also verified by the spin elimination of a stable cyclic nitroxide, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and by the reduction of methyl viologen (MV^{2+}) to its radical $MV^{+\bullet}$.

Keywords: Natural pigment, titanium dioxide colloid, electron injection, cation radical, spin elimination

INTRODUCTION

Photosensitization of a stable, large-bandgap semiconductor has important applications in photoelectrochemical conversion of solar energy and light-induced decomposition of organic pollutants.[1] This phenomenon often serves the purpose of selectively extending the absorptive range of the semiconductor materials. Advances have recently been made by employing modified sensitizer systems such as antenna-sensitizer molecular devices.[2] The dye sensitization of a coupled semiconductor system could extend the photoresponse further into the red and improve the efficiency of the net charge-transfer process. Yet so far, the sensitizers used were practically synthetic dyes[3–5] and little effort

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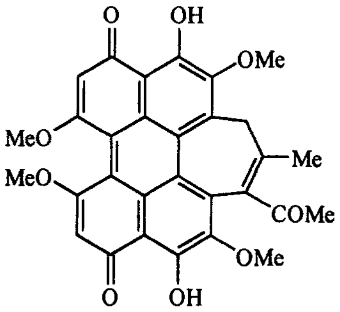
has been made to elucidate the role of the triplet excited state as the donor in the dye sensitization process. Hypocrellin B (HB), a natural photodynamic pigment with strong absorption in the visible region, high intersystem crossing quantum yield ($\phi_T = 0.76$), long excited triplet lifetime[6] and extremely high photostability,[7] has been employed as an ideal sensitizer for this purpose. Its energetics (the standard oxidation potential of the excited triplet HB is −0.62 V vs NHE) is thermodynamically favorable for injecting charge from its excited triplet state into the conduction band of TiO_2.



HB

Several researchers have investigated charge injection from excited dye into semiconductor particles by employing various fast kinetic spectroscopic techniques including emission,[4] nanosecond[3] and picosecond[8] laser flash photolysis, Raman resonance,[9] microwave absorption[10] and internal reflection flash photolysis.[11]

Electron paramagnetic resonance (EPR) coupled with spin trapping and spin elimination are versatile techniques for studying short-lived free radicals.[12] Yet until now they have not been widely used to investigate the formation of free radicals photoinduced in the dye coupled semiconductor systems. In this article, we evaluate by EPR method the transient products (cation radical of dye and conduction band electrons of the semiconductor) generated in HB photosensitization process.

MATERIALS AND METHODS

Materials

Hypocrellin B was obtained by dehydration of hypocrellin A.[13] Hypocrellin A was isolated from the fungus sacs of *Hypocrella bambusae* and recrystallized twice from benzene-light petroleum (bp 30–60 °C) before use. The purity was confirmed as >97% by HPLC. TEMPO was purchased from Aldrich Chemical Company, USA. NaI and methyl viologen dichloride hydrate were purchased from Beijing Chemical Plant, Beijing, China, and used without further purification. All other chemicals were at least reagent grade and were used as received.

Alcoholic TiO_2 was prepared according to the procedure of Gratzel.[14] No protective agent was added, as the TiO_2 particles were very stable for at least months. Scanning transmission electron microscopy yielded a size range of 4–7 nm for the particles, the average diameter being 5 nm.

Apparatus

Ground-state absorption spectra were recorded using a Shimadzu UV 160A UV-VIS spectrophotometer. Fluorescence spectra were obtained with Perkin-Elmer LS-5 spectrometer. Fluorescence lifetime was determined using a HORIBN NAES-1100 single photon counting apparatus. Time resolved transient absorption spectra were measured with a Q-switched Nd: YAG nanosecond laser photolysis that employs the second harmonic (532 nm) laser with a pulse width of ca. 10 ns (10 mJ pulse^{-1}). EPR spectra were recorded using a Bruker Model ESP 300E spectrometer at room temperature (20–25 °C). Samples were introduced into the specially made quartz cup and illuminated directly inside the microwave cavity. All samples were purged with purified N_2 for 30 min in darkness and irradiated with a Q-switched Nd: YAG nanosecond laser apparatus (full width at half-maximum, 35 mJ pulse^{-1}; $\lambda = 532$ nm).

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RESULTS AND DISCUSSION

Absorption and Emission Characteristics of Hypocrellin B-TiO_2 chelate System

Hypocrellin B in ethanol solution was strongly adsorbed to the surface of TiO_2. Addition of TiO_2 colloid induced a striking change in the spectral features of the HB solution. The maximum was red-shifted from 462 nm to 507 nm, and the extinction coefficient increased from 1.37×10^7 to $3.0 \times 10^7\,cm^2/mol$ (Figure 1). According to the method of Benesi,[15] the apparent association constant was calculated from the following equation:

$$\frac{[HB]}{A} = \frac{1}{\varepsilon} + \frac{1}{K_{app}\varepsilon}[TiO_2]^{-1} \qquad (1)$$

where [HB] and $[TiO_2]$ were the concentration of hypocrellin B and colloid TiO_2 that was added, respectively; A and ε were the absorbance value and the extinction coefficient at given wavelength, respectively. Plot of $[HB]/A$ vs $1/[TiO_2]$ is shown in Figure 1 inset, exhibits good linear relation which allows the determination of K_{app} value as $8.0 \times 10^3\,M^{-1}$.

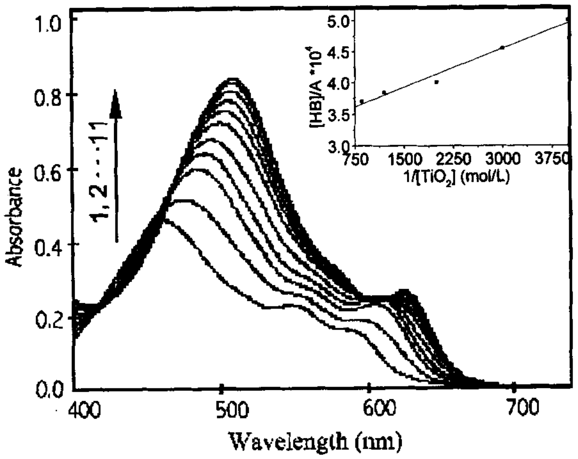

FIGURE 1 Absorption spectra of hypocrellin B (3.3×10^{-5}M) with different colloidal TiO_2 concentrations (1) 0; (2) 0.83×10^{-4}M; (3) 1.67×10^{-4}M; (4) 2.50×10^{-4}M; (5) 4.17×10^{-4}M; (6) 5.83×10^{-4}M; (7) 7.50×10^{-4}M; (8) 9.17×10^{-4}M; (9) 12.5×10^{-4}M; (10) 15.8×10^{-4}M; (11) 17.5×10^{-4}M. The inset shows the plot of $[HB]/A$ vs $1/[TiO_2]$, in which the absorbance wavelength is 507 nm.

The effect of colloid TiO_2 on the HB luminescence was also investigated. No change of the fluorescence lifetime of HB could be seen in TiO_2 suspension, so we can rule out the participation of the excited singlet state in the charge injection process.

Time-Resolved Transient Absorption Spectra of the Chelate

The transient difference absorption spectra recorded 3.9 μs after 532 nm laser pulse excitation are shown in Figure 2. In neat ethanol, a transient with a maximum absorption around 500 nm [$\tau = 6.17$ μs] arising as a result of triplet–triplet absorption[16] was seen (Figure 2a). However, Figure 2b showed three features in

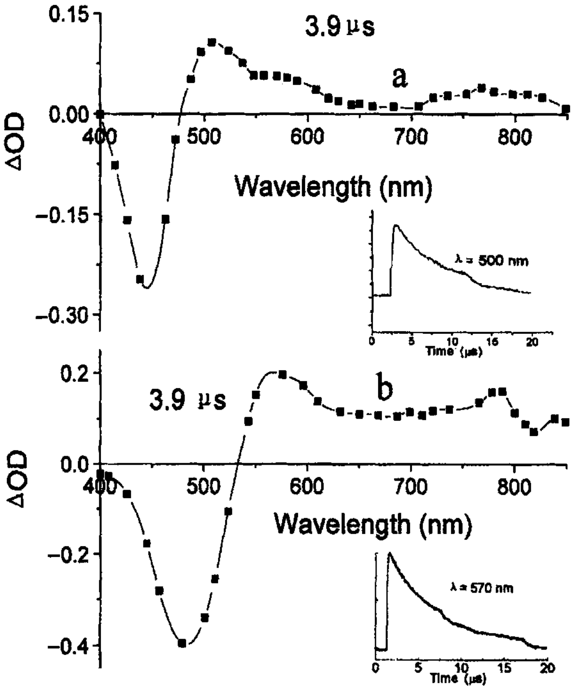

FIGURE 2 Transient difference absorption spectra recorded 3.9 μs following 532 nm laser pulse excitation (pulse duration 10 ns) of ethanolic solution containing (a) 1×10^{-4}M HB, (b) 1×10^{-4}M HB and 16.3×10^{-3}M colloidal TiO_2, inset shows the decay of transient absorption at 570 nm ($HB^{+\bullet}$).

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the transient absorption spectrum when HB was excited in TiO_2 suspensions: a bleaching signal at 477 nm and absorption peaks at 570 and above 700 nm, which were attributed to the cation radical absorption of HB and the TiO_2 conduction band electrons,[17] respectively. The transient absorption at 570 nm was composed of a short-lived component ($\tau = 0.7\,\mu s$) and a long-lived one ($\tau = 15.2\,\mu s$), which were resolved by the computer treatment of the decay curve, using the software *Origin 5.0* and the method of non-linear curve fit. The behavior of the short-lived transient is similar to that of triplet HB ($\lambda_{max} = 500\,nm$) because the lifetime of the transient absorption at 500 nm is also $0.7\,\mu s$. The long-lived transient ($\tau = 15.2\,\mu s$), was presumed as a cation radical of HB. The lifetime of triplet HB decreased from $6.17\,\mu s$ to $0.7\,\mu s$ in the absence and presence of TiO_2 colloid, indicating that the charge transfer occurs from the excited triplet state of HB into the conduction band of colloid TiO_2 (Equation 2).

$$^3HB^* + TiO_2 \xrightarrow{k_{inj}} HB^{+\bullet} + TiO_2(e^-_{cb}) \qquad (2)$$

The latter was known to exhibit a very broad absorption feature extending over the entire visible region into the near-infrared.[17] The electron injection rate constant k_{ET} was calculated by the following equation[18] to be $1.3 \times 10^6\,s^{-1}$.

$$k_{ET} = 1/\tau - 1/\tau^0 \qquad (3)$$

where τ^0, τ were the triplet lifetime of HB before and after the addition of TiO_2 colloid. By contrast, the recombination of the conduction band electron with the cation radical of HB was a much slower process. Like other dyes that sensitized electron injection in the colloidal semiconductor, the reverse electron transfer from the injected electron to $HB^{+\bullet}$ was reflected by the decay of transient absorption at 570 nm ($HB^{+\bullet}$).[19,20] The rate constant of reverse electron transfer $k_r = 1/\tau\ (HB^{+\bullet}) = 1/15.2\ \mu s = 6.5 \times 10^4\,s^{-1}$ was two orders of magnitude smaller than that of the forward electron injection.

To obtain further evidence for the efficient charge injection process, EPR spectrometry was employed.

EPR Measurements of Free Radical Produced during Anaerobic Photosensitization of the Chelate

Identification of the Photoinduced Semiquinone Cation Radical of HB

Illumination of HB in deoxygenated TiO_2 colloid generated the EPR spectrum shown in Figure 3b (Figure 3a displays the spectrum before irradiation). The spectrum exhibits poorly resolved hyperfine structure with $g = 2.0045$. In order to interpret this EPR signal, the following experiments were carried out.

(1) Illumination of HB in neat ethanol generated no EPR spectrum (not shown), indicating that the self-electron transfer[21] between the excited and ground state of HB (Equation 4) could not take place in ethanol.

$$HB + HB^* \longrightarrow HB^{+\bullet} + HB^{-\bullet} \qquad (4)$$

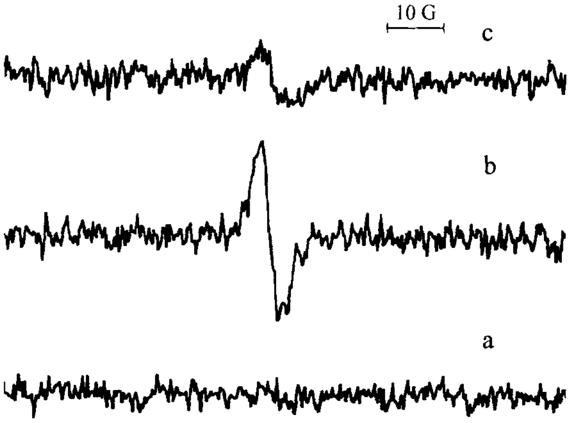

FIGURE 3 Photoinduced EPR spectra of deoxygenated ethanol solution containing HB (1×10^{-4} M) and TiO_2 (16.3×10^{-3} M) colloid with a Nd: YAG pulsed laser ($\lambda_{ex} = 532\,nm$). (a) Before irradiation; (b) Irradiation for 40 seconds; (c) As in (b) but in the presence of NaI (50 mM). Spectrometer settings: microwave power, 5 mW; modulation amplitude, 1.944 G; time constant, 20.5 ms; sweep width, 200 G; sweep time, 41.9 s; relative gain: 1.0×10^5.

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So neither semiquinone anion radical nor cation radical of HB could be produced according to the above way.

(2) NaI (50 mM), a typical hole scavenger, was added to the deoxygenated TiO_2 suspensions containing HB (1×10^{-4} M) irradiated under laser ($\lambda = 532$ nm). The presence of NaI decreased the EPR signal significantly, indicating the EPR signal in Figure 3b was cationic characteristics of the radical.

(3) The photoinduced EPR spectrum of radical shown in Figure 3b was not changed in the presence of oxygen (not shown), suggesting that the radical was not anionic and therefore can not be quenched by dissolved oxygen.

In accordance with the above results, the EPR spectrum in Figure 3b can be safely assigned to the cation radical of HB ($HB^{+\bullet}$). Normally it is very difficult to detect the cation radicals because their lifetimes are relatively shorter. In this system, due to the efficient charge injection into the conduction band electrons of TiO_2 colloid, the lifetime of cation radical from HB was prolonged greatly and it became more stable.[19] This allowed us to detect the cation radical from HB by EPR for the first time.

Indirect Evidence of the Existence of Conduction Band Electrons

The conduction band electrons of TiO_2 colloid generated from the charge injection can't be detected directly by EPR. Here the electron acceptor MV^{2+} was introduced, and the spin elimination of a stable cyclic nitroxide-TEMPO was studied.

When MV^{2+} (2×10^{-3} M) was added to the deoxygenated chelate under irradiation, the EPR signal of HB cation radical appeared first (Figure 4); then the typical EPR spectrum of $MV^{+\bullet}$ appeared[22] gradually and the intensity of the signal increased with the irradiation time. The color of the sample changed from red to blue (which is the color of $MV^{+\bullet}$ and could be observed even by steady state absorption spectrum at 630 nm). A composite EPR spectrum was observed at the end. Control experiment showed that illumination of neat HB ethanol in the presence of MV^{2+} does not generate any EPR spectra, indicating that no electron transfer occurs between HB and MV^{2+}. The appearance of the EPR spectrum of $MV^{+\bullet}$ (seen in Figure 4) was attributed to the electron transfer reaction (Equation (5)).

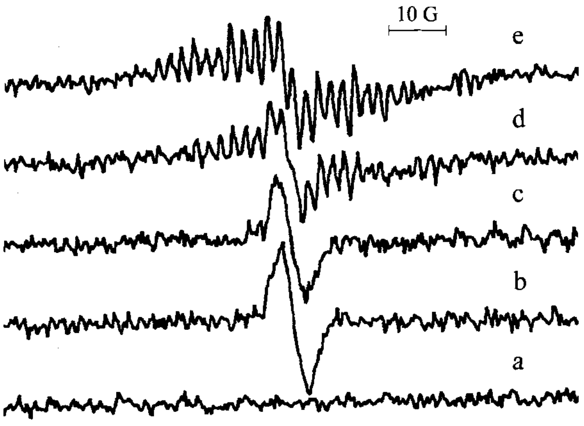
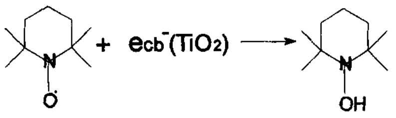


FIGURE 4 Photoinduced EPR spectra of the semiquinone cation radical at different irradiation times in the presence of MV^{2+} (2×10^{-3} M) with a Nd: YAG pulsed laser ($\lambda_{ex} = 532$ nm). (a) 0 s; (b) 40 s; (c) 80 s; (d) 120 s; (e) 160 s. Spectrometer settings as in Figure 3.

$$e_{cb}^{-}(TiO_2) + MV^{2+} \longrightarrow MV^{+\bullet} \qquad (5)$$

Previously, Moan has developed a method to detect indirectly porphyrin anion radicals, which is based on the fact that under anaerobic conditions the porphyrin anion radical reduces TEMPO.[23] The reaction leads to an elimination of the spin of TEMPO under anaerobic conditions (Equation 6). We employed this method to determine the formation of conduction band electrons.



(6)

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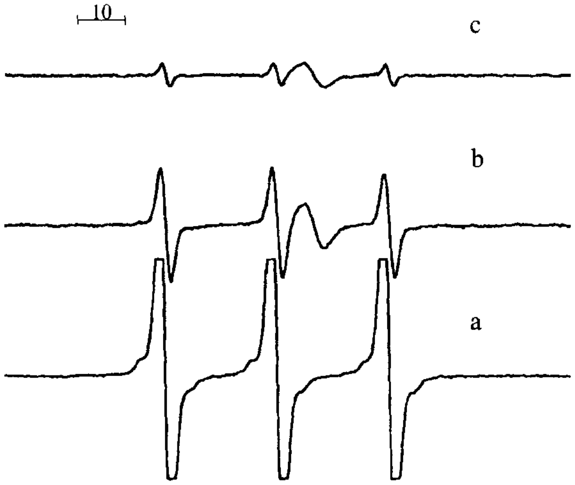

FIGURE 5 Photoinduced loss of intensity EPR spectra of the TEMPO radical at different irradiation times in the HB (1×10^{-4} M) and TiO_2 colloid (16.3×10^{-3} M) with a Nd: YAG pulsed laser ($\lambda_{ex} = 532$ nm). (a) 0 s; (b) 80 s; (c) 440 s. Spectrometer settings as in Figure 3. [TEMPO] = 20 μM.

When the deoxygenated HB-TiO_2 colloid and TEMPO (20 μM) were irradiated, the intensity of the signal of TEMPO decreased exponentially with the irradiation time (Figure 5), the EPR signal of cation radical of HB appeared at the same time and its intensity was not changed during the process. As no semiquinone anion radical of HB was observed, we couldn't detect any spin elimination of TEMPO in HB solution. These results suggested that conduction band electrons were produced in the photosensitization of TiO_2 colloid. There is an additional proof that the presence of oxygen inhibited the spin elimination of TEMPO since oxygen can accept the conduction band electrons.

CONCLUSION

Illumination of HB in the deoxygenated TiO_2 colloid generated a strong EPR signal. This EPR signal was identified by the addition of hole scavenger and ascribed to the cation radical of HB ($HB^{+\bullet}$) rather than other species for the first time.

The generations of conduction band electrons in the process of charge injection, which can't be directly detected by EPR method, were detected by the spin elimination of TEMPO and the addition of MV^{2+}, confirming that charge injection does occur from the excited state of HB into the conduction band electrons of TiO_2 colloid. EPR is, by no means, able to provide us with a better understanding of the photosensitization process involved in the semiconductor systems.

Acknowledgements

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