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Journal of Photochemistry and Photobiology A: Chemistry 137 (2000) 191–196
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.nl/locate/jphotochem

Photosensitization of TiO_2 colloid by hypocrellin B in ethanol

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Received 21 April 2000; received in revised form 26 July 2000; accepted 31 August 2000

Abstract

Hypocrellin B (HB), a natural pigment, when adsorbed on colloidal TiO_2 can participate in the sensitization process by injecting electrons from its excited singlet and triplet states into the conduction band of the semiconductor. Upon excitation in its absorption band, 80% of the fluorescence emission of HB could be quenched by colloidal TiO_2. Lifetime measurements and time-resolved absorption spectra gave the rate constant for the electron injection process from the excited singlet and triplet states of HB into the conduction band of the semiconductor as 6×10^8 and $1.3 \times 10^6\,s^{-1}$, respectively. Analysis of the electron paramagnetic resonance spectra confirmed the generation of the cation radical of HB. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: TiO_2 colloid; Hypocrellin B; Photoinduced electron transfer; Excited singlet and triplet states; Rate constant; EPR spectra

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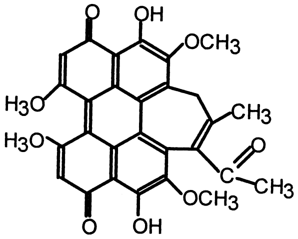
1. Introduction

The photosensitization of electron transfer across the semiconductor solution interface is the subject of an intensive investigation, mainly due to its importance for solar energy conversion [1,2], silver halide photography [3] and electrophotography [4]. Efforts in this area have concentrated on improving the visible light response of wide-bandgap semiconductors such as ZnO and TiO_2. Sensitization is achieved by adsorption of dye molecules at the semiconductor surface which, upon excitation, inject an electron into its conduction band. The first successful experiment of this type was described by Putzeiko and Terenin [5], who found that the Dember effect of ZnO powder in visible light was sensitized by xanthene and cyanine dyes. The photosensitization of TiO_2 combined with its ability to effectively and quickly separate charge, makes it a potentially attractive material for solar energy cells.

While much important knowledge has been gathered over the years on the overall performance of dye-sensitized semiconductor systems, more information about the details of the electron-injection process is urgently required. The rapid nature of these reactions requires application of fast kinetic techniques, which in the case of solid electrodes or powders is very difficult. On the other hand, semiconductor particles of colloidal dimensions are sufficiently small to yield transparent solutions, allowing for direct analysis of interfacial charge-transfer processes by a laser photolysis technique [6].

The present study employs hypocrellin B (HB)



as a sensitizer to study electron injection in colloidal TiO_2 particles. HB, a natural photodynamic pigment with strong absorption in the visible region, high intersystem crossing quantum yield ($\Phi_{ISC} = 0.76$) due to the small gap between the singlet excited state and the triplet excited state of HB, long excited triplet lifetime [7] and extremely high photostability [8], has been employed as an ideal sensitizer for this purpose. HB would keep unaltered in ethanol for half of a month and 10 h in the daylight and sodium lamp, respectively. Its energetics (the standard oxidation potential of the excited singlet and triplet states of HB is at −0.68, −0.62 V vs. NHE, respectively) is thermodynamically favorable [9] for injecting charge from both of its excited singlet and triplet states into the conduction band of TiO_2 (Scheme 1).

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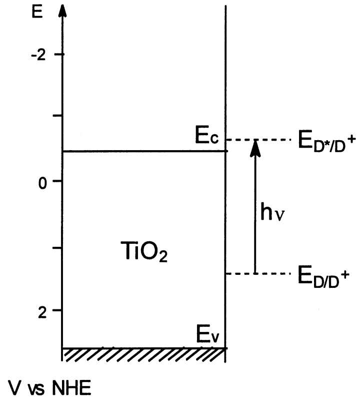
PII: S1010-6030(00)00366-X



Scheme 1. Schematic diagram describing the conduction and valence bands for TiO_2 and the electron-donating energy levels for HB.

2. Experimental section

2.1. Materials

The alcoholic TiO_2 was prepared according to the procedure of Gratzel and coworkers [10]. No protective agent was added, as the TiO_2 particles were very stable for at least a few months. Scanning transmission electron microscopy yielded a size range of 40–70 Å for the particles, the average diameter being 50 Å.

HB was obtained by dehydration of hypocrellin A [11]. Hypocrellin A was isolated from the fungus sacs of *Hypocrella bambusae* and recrystallized twice from benzene-light petroleum (b.p. 30–60°C) before use. The purity was confirmed as >97% by HPLC. NaI was 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.

2.2. Apparatus

Ground-state absorption spectra were recorded with a Shimadzu UV 160A UV–Vis spectrophotometer. Fluorescence spectra were obtained with Perkin-Elmer LS-5 spectrometer. Fluorescence lifetime was determined using an Horibn Naes-1100 single photon counting apparatus. Time resolved transient absorption spectra were measured with a Q-switched Nd:YAG nanosecond laser photolysis that employed the second harmonic (532 nm) laser with a pulse width of ca. 5 ns (10 mJ per pulse). Electron paramagnetic resonance (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 directly in the cavity of the EPR spectrometer with a Q-switched Nd:YAG nanosecond laser apparatus (the pulse width was ca. 15 ns, the energy delivered was 35 mJ per pulse; $\lambda = 532$ nm).

3. Results and discussion

3.1. Absorption characteristics

A 3.3×10^{-5} M solution of HB in ethanol has a light-red color. Fig. 1 showed an absorption maximum of HB at 462 nm ($\varepsilon = 1.37 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$). Addition of TiO_2 colloid induced a striking change in the spectral features of the HB solution. The maximum was red-shifted so as to 507 nm until the concentration of TiO_2 was up to 140 mg/l and the extinction coefficient was increased to $2.5 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$. The solution color was turned to purple red after TiO_2 addition

$$\mathrm{HB} + \mathrm{TiO_2} \rightleftarrows \mathrm{HB{-}TiO_2} \qquad (1)$$

According to the method of Benesi and Hildebrand [12], the apparent association constant was deduced from the following equation:

$$\frac{[\mathrm{HB}]}{A} = \frac{1}{\varepsilon} + \frac{1}{K_{\mathrm{app}}\varepsilon}[\mathrm{TiO_2}]^{-1} \qquad (2)$$

where [HB] and [TiO_2] were the concentration of HB and colloid TiO_2 added, respectively, A and ε were the absorbance and the extinction coefficient of HB–TiO_2 at given wavelength, which was 640 nm in our study, respectively. At this wavelength the absorbance of HB was zero. From Fig. 1, the good liner relation gave out the K_{app} value as $5.0 \times 10^3\ \mathrm{M^{-1}}$. The large value of K_{app} indicated a strong association between HB and TiO_2 colloid, which was an essential requisite to observe the heterogeneous charge-transfer process at the semiconductor–sensitizer interface.

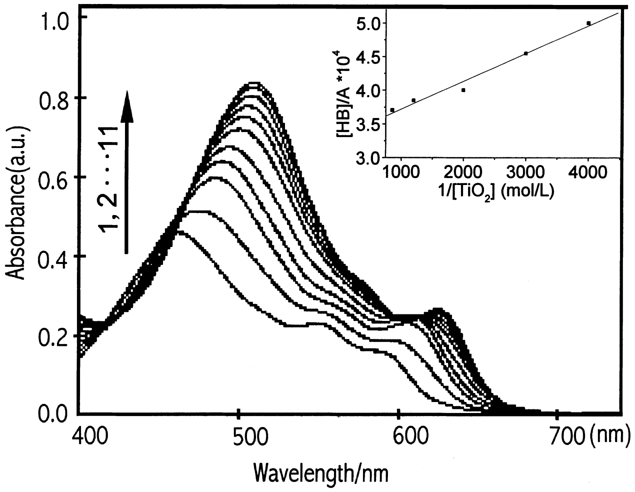


Fig. 1. Absorption spectra of HB (3.3×10^{-5} M) at various colloidal TiO_2 concentrations: (1) 0 mM; (2) 6.6 mg/l; (3) 13.4 mg/l; (4) 20 mg/l; (5) 33.4 mg/l; (6) 46.6 mg/l; (7) 60 mg/l; (8) 73.3 mg/l; (9) 100 mg/l; (10) 126 mg/l; (11) 140 mg/l. The inset showed the plot of [HB]/A vs. 1/[TiO_2].

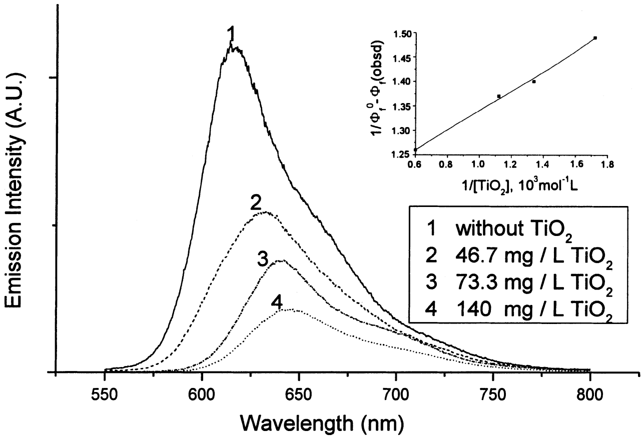


Fig. 2. Fluorescence quenching of 3.3×10^{-5} M HB at various TiO_2 concentrations ($\lambda_{ex} = 470$ nm). The inset showed the plot of $1/[\Phi_f^0 - \Phi_{f(obsd)}]$ vs. $1/[TiO_2]$.

3.2. Emission characteristics

The effect of colloidal TiO_2 on the luminescence of HB was investigated and the results were shown in Fig. 2. The emission maximum of HB in neat ethanol was located at 612 nm and the observed fluorescence quantum yield was 0.09. The fluorescence yield decreased upon successive addition of colloidal TiO_2 to a solution of 3.3×10^{-5} M HB. Addition of colloidal TiO_2 (46.7 mg/l) led to a pronounced decrease in the luminescence yield (Φ_f) and to a red shift in the emission maximum (λ_{max}). When 140 mg/l of TiO_2 was present, Φ_f dropped to 20% of its initial value and λ_{max} is ca. 645 nm. At this TiO_2 concentration Φ_f reached a minimum. Further increase in TiO_2 concentration did not change the fluorescence spectra of HB any more. The ability of TiO_2 to quench the fluorescence of HB suggested interception of the excited state on the TiO_2 surface.

According to the following equation [15] the apparent association constant was calculated to be 5.4×10^3 M, which was in quite accordance with that obtained from the absorption spectra:

$$\frac{1}{\Phi_f^0 - \Phi_{f(obsd)}} = \frac{1}{\Phi_f^0 - \Phi_f'} + \frac{1}{K_{app}(\Phi_f^0 - \Phi_f')[TiO_2]} \tag{3}$$

where $\Phi_{f(obsd)}$ was the fluorescence quantum yield of HB observed in the colloidal TiO_2, Φ_f^0 and Φ_f' were the fluorescence quantum yields of HB before and after the addition of colloidal TiO_2, respectively.

Since at a TiO_2 concentration of 140 mg/l HB was quantitatively associated with the colloidal particles, the emission with λ_{max} at 645 nm can be attributed to the adsorbed state of the dye. Red shifts in the emission were due to hydrogen-bond formation with surface hydroxyl groups. The displacement of the maximum was related to the polarizability and electronegativity of the metal cation. Similar phenomena were also observed in the case of fluorescein, when adsorbed onto $Zn(OH)_2$ and AlOOH, $\Delta\lambda_{max}$ was 150 and 30 nm, respectively [13].

The marked decrease in the fluorescence yield was due to the quenching of the excited singlet state of HB by TiO_2 colloid. It could be attributed to the electron transfer to the semiconductor TiO_2 colloid. Similar qualitative aspects of fluorescence quenching had been discussed earlier for TiO_2–erythrosin B system [14].

3.3. Fluorescence lifetime measurement

To probe the mechanism of fluorescence quenching of HB by TiO_2 colloid, we further measured the fluorescence lifetimes of HB in the absence and presence of TiO_2 colloid.

The experimentally observed fluorescence lifetimes of HB were 1.2 ns in neat ethanol and 0.7 ns in colloidal TiO_2. The observed decrease in the singlet lifetime of HB when adsorbed on colloidal TiO_2 parallels the fluorescence quenching experiments described earlier and supports the involvement of the charge-transfer step (K_{ET}) in the quenching process:

$$\text{HB–TiO}_2\ (S_0) \xrightarrow{h\nu} \text{HB}^*\text{–TiO}_2\ (S_1) \tag{4}$$

$$\text{HB}^*\text{–TiO}_2\ (S_1) \xrightarrow{K_{ET}} \text{HB}^{+\bullet} + \text{TiO}_2\ (e_{cb}{}^-) \tag{5}$$

Then the rate constant of electron transfer from the excited singlet state of HB would be given by Kamat [15]

$$K_{ET} = \frac{1}{\tau_{ads}} - \frac{1}{\tau} \tag{6}$$

The value of K_{ET} obtained upon the substitution of the values of τ and τ_{ads} in Eq. (6) was $6\times10^8\ s^{-1}$. The value of K_{ET} reported by Moser and Gratzel [16] for eosin Y–colloidal TiO_2 in water was $8.5 \times 10^8\ s^{-1}$ which was determined by making use of the fluorescence lifetime of the sensitizer. The variation in the environment and the energetics of the excited sensitizer systems was expected to influence the charge injection process at the semiconductor–sensitizer interface.

3.4. Laser photolysis studies of sensitized electron injection

Since the energy gap between the excited singlet and triplet states of HB was very little and the intersystem crossing yield was relatively high ($\Phi_{ISC} = 0.76$), it was also possible that electron injection occurs from the excited triplet state of HB into the TiO_2 colloid conduction band. Therefore the laser flash technique was employed in our study.

The transient difference absorption spectrum of deaerated HB ethanol solution after the laser pulse ($\lambda_{ex} = 532$ nm) were shown in Fig. 3. The absorption maximum at 510 nm with a lifetime $\tau = 6.17\ \mu s$ can be ascribed to the triplet–triplet absorption of the dyes, which is almost identical with that of HB in n-hexane reported earlier [17]. It was also confirmed by T–T energy transfer to β-carotene, whose

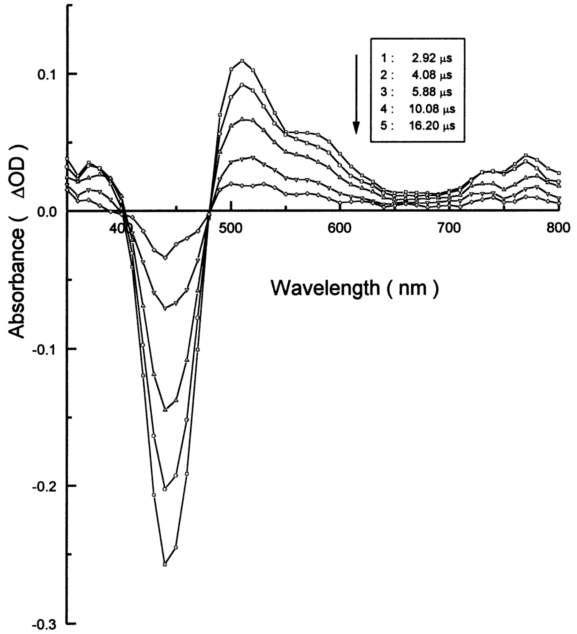


Fig. 3. Transient difference absorption spectra recorded at different delay times obtained from a deaerated solution of HB (1.67×10^{-4} M) in ethanol ($\lambda_{ex} = 532$ nm).

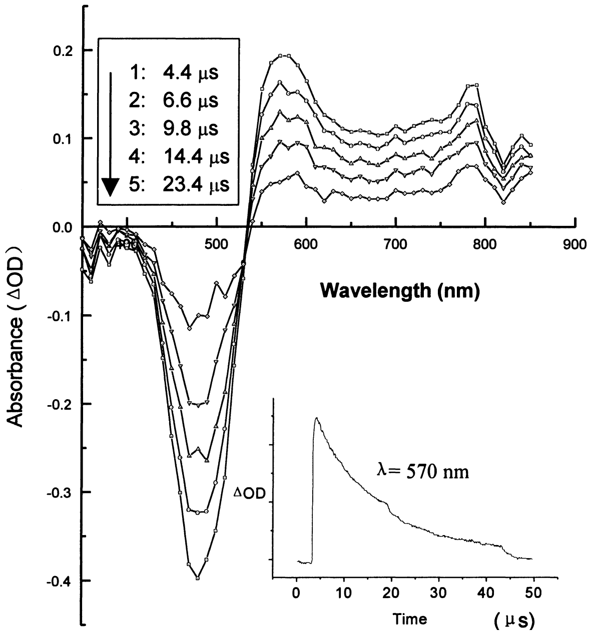


Fig. 5. Transient difference absorption spectra recorded at different delay times obtained from a deaerated solution of HB (1.67×10^{-4} M) in the presence of 1.3 g/l TiO_2 in ethanol ($\lambda_{ex} = 532$ nm), inset showed the decay of transient absorption at 570 nm ($HB^{+\bullet}$).

intersystem crossing yield was zero. The time-resolved absorption spectra recorded after 532 nm laser photolysis of an ethanol solution containing 4.5×10^{-4} M β-carotene and 1.67×10^{-4} M dye was obtained (Fig. 4). Upon excitation of HB by laser pulse the photobleaching of HB decayed quickly, and the absorption at 520 nm enhanced so as to the maximum until the time delay was 6.76 μs. Fig. 4 showed the decay of the photobleaching of HB was much faster than that showed in Fig. 3, which indicated that the energy transfer occurred between HB and β-carotene [18]. Control experiments showed in the absence of hypocrellins, no β-carotene T–T absorption was observed.

The transient absorption observed upon excitation of HB in 1.3 g/l colloid TiO_2 was shown in Fig. 5. The inset in Fig. 5 was a typical decay of the 570 nm absorption profile that showed the contribution from a short-lived and a long-lived transients. The behavior of the short-lived transient was similar to that of triplet HB ($\tau = 0.7$ μs) because the lifetime of the transient absorption at 510 nm was also 0.7 μs. The lifetime of the long-lived transient, presumably a cation radical of HB, can be derived as 15.20 μs. In addition to a prominent peak at 570 nm, the corrected transient spectra were distinguished by a broad absorption about 780 nm with a lifetime of 26.20 μs. It was attributed to conduction band electrons formed via charge injection as followed. Therefore electron injection did occur from the excited triplet state HB into the conduction band of colloidal TiO_2:

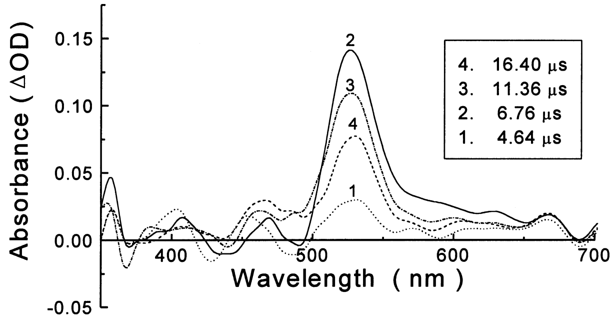


Fig. 4. Transient difference absorption spectra recorded at different delay times obtained from a deaerated solution of HB (1.67×10^{-4} M) in the presence of 4.5×10^{-4} M β-carotene in ethanol ($\lambda_{ex} = 532$ nm).

$$HB^*\text{–}TiO_2\,(S_1) \overset{K_{ISC}}{\rightarrow} HB^*\text{–}TiO_2\,(T_1) \tag{7}$$

$$HB^*\text{–}TiO_2\,(T_1) \overset{K_{ET}}{\rightarrow} HB^{+\bullet} + TiO_2\,(e_{cb}{}^-) \tag{8}$$

From the change of triplet lifetime of HB before and after the addition of TiO_2 colloid, the electron injection rate constant K_{ET} from excited triplet state of HB was calculated to be $1.3 \times 10^6\,s^{-1}$.

After all, a question may be arisen that the decrease in fluorescence of the dye adsorbed on TiO_2 colloid was due to enhanced intersystem crossing efficiency. This possibility was evaluated by monitoring the triplet yield observed on the direct excitation (532 nm) of dye samples containing different concentrations of the TiO_2 colloid (Fig. 6). No increase in the triplet yield could be seen when monitored at the T–T absorption (510 nm). Instead, a decrease in the triplet yield was observed. This ruled out the increase of intersystem crossing (S_1–T_1) as the primary deactivation route of singlet state.

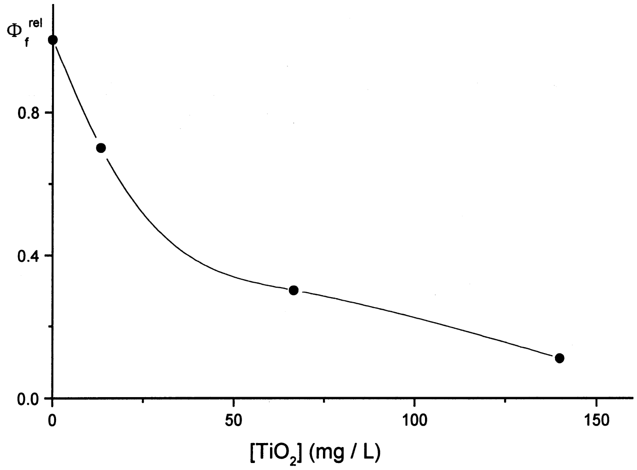


Fig. 6. Effect of TiO_2 concentration on the triplet state quantum yield of HB. Φ_f for HB in neat ethanol is normalized to unity.

Reverse electron transfer has been found to be an important factor controlling the net charge-transfer efficiency in the photosensitization process. Like other dyes [19,20] that sensitized electron injection in the colloidal semiconductor, the reverse electron transfer between $HB^{+\bullet}$ and the injected electron was monitored from the decay of the transient absorption at 570 nm ($HB^{+\bullet}$). Therefore the rate constant of reverse electron transfer $K_r = 1/\tau = (1/15.2)\ \mu s = 6.5 \times 10^4\ s^{-1}$. The lower value of the rate constant was an indication of the weak interaction between the cation radical of the sensitizer and TiO_2 colloid:

$$HB^{+\bullet} + TiO_2\ (e_{cb}{}^{-}) \rightarrow HB\text{–}TiO \qquad (9)$$

3.5. *Identification of the photoinduced cation radical of HB*

Illumination of HB in deoxygenated TiO_2 colloid generated the EPR spectrum shown in Fig. 7b (Fig. 7a showed the spectrum before irradiation). The spectrum showed poorly resolved hyperfine structure with $g = 2.0045$. In order to identify 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 (Eq. (10)) could not take place in ethanol:

   $$HB + HB^{*} \rightarrow HB^{+\bullet} + HB^{-\bullet} \qquad (10)$$

   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 Fig. 7b has cationic characteristics of the radical.

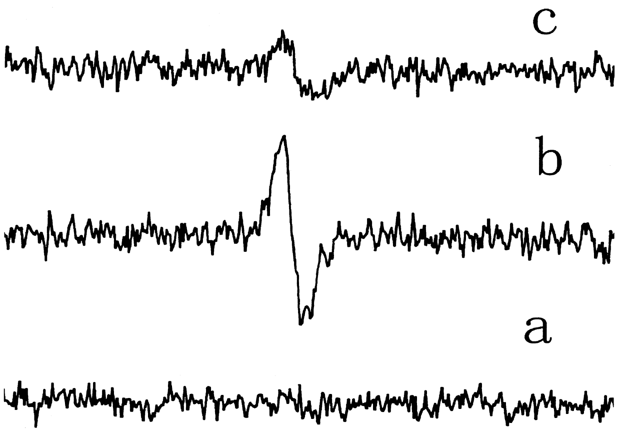


Fig. 7. Photoinduced EPR spectra of deoxygenated ethanol solution containing HB (1.67×10^{-4} M) and TiO_2 (1.3 g/l) colloid with a Nd:YAG pulsed laser ($\lambda_{ex} = 532$ nm): (a) before irradiation; (b) irradiation for 40 s; (c) as in (b) but in the presence of NaI (50 mM). Spectrometer settings: microwave power, 5 mW; modulation amplitude, 1.944 G; time constant, 20.48 ms; sweep width, 200 G; sweep time, 41.9 s; relative gain, 1.0×10^5.

3. The addition of oxygen did not decay the EPR signal of the cationic radical, while the $HB^{-\bullet}$ would be decayed sharply in the present of oxygen.

In accordance with the above results, the EPR spectrum in Fig. 7b 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 and they are easy to be protonated. 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 for the first time to detect the cation radical from HB by EPR method.

4. Conclusion

HB has been successfully used to photosensitize the semiconductor TiO_2 colloidal particles in nonaqueous medium. Strong association between the sensitizer and the semiconductor is the essential feature to observe the photosensitization process. Measurements of fluorescence lifetime and time-resolved absorption spectra have been employed to determine the rate constant for the light-induced charge injection process (useful experimental data had been summarized in Table 1). The feasibility of employing an EPR technique in probing the interfacial process in a semiconductor particulate system has been demonstrated. The production of the cation radical $HB^{+\bullet}$ confirmed that the photosensitization process involved charge-transfer at the semiconductor–sensitizer interface. As Gratzel and coworkers [16] and Kamat and Fox [14] reported, a lot of dyes could inject electrons either from its singlet excited state or triplet excited state to the colloidal TiO_2. Seldom dyes could inject electrons from both excited

Table 1
Excited-state properties of HB

	In ethanol	In colloidal TiO_2 suspension[a]
Absorption maximum (nm)	462	507
Fluorescence emission maximum (nm)	612	645
Fluorescence quantum yield[b]	0.09	0.02
Fluorescence lifetime (ns)	1.2	0.7
K_{ET}^{S} (s^{-1})		6×10^{8}
Triplet absorption maximum	510	510
Triplet lifetime (μs)	6.17	0.7
K_{ET}^{T} (s^{-1})		1.3×10^{6}

[a] 0.14 g/l colloidal TiO_2 in ethanol.
[b] HB in ethanol ($\Phi_f = 0.09$) was used as a standard.

state, while HB could inject electron to colloidal TiO_2 from both singlet excited state and triplet excited state.

Acknowledgements

This research is supported by the Chinese National Science Foundation (No. 29872038, 29772035).

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