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Photosensitization of a colloidal TiO_2 semiconductor system with hypocrellin B

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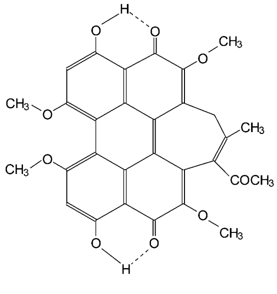
Abstract

The adsorption of hypocrellin B (HB) on the surface of TiO_2 colloidal particles and the electron transfer process from its singlet excited state to the conduction band of TiO_2 were examined by absorption, fluorescence quenching, fluorescence lifetime measurements, laser flash photolysis and pulse radiolysis techniques. Adsorption of HB onto the surface of colloidal TiO_2 particle led to red-shifted absorption, and the apparent association constant (K_{app}) was 3145 $(mol/l)^{-1}$ from fluorescence quenching. Exciting HB with visible light could induce electron transfer from its singlet excited state into conduction band of TiO_2 ($K_{et}= 4.93\times10^9$ s^{-1}). Laser flash photolysis and pulse radiolysis studies demonstrated the formation of radical cation of HB . © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hypocrellin B (HB); Colloidal TiO_2 semiconductor; Photosensitization; Electron transfer

1. Introduction

The photosensitization of a stable, large-band-gap semiconductor such as TiO_2 by organic dyes is an interesting and useful phenomenon that was used to extend its absorptive range and, thus carry out photoelectrochemical reactions under irradiation [1–4]. In this system, a dye acting as an electron donor adsorbs directly onto the surface of semiconductor particle and can transfer an electron from its singlet excited state into the conduction band of the semiconductor particle.


HB

Hypocrellin B (HB) is obtained from *Hypocrella bambusae* (B. et. Br) Sacc, a Chinese herb that grows most abundantly in the southwestern part of China. It has been shown that HB is not only an effective photo-therapeutic agent but also a good photo-sensitizer [5,6]. Recently the chemistry,

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photochemistry and photophysics of HB have been studied and reviewed [7–9], but photosensitization of semiconductors with HB by the injection of electrons from its singlet excited state in aqueous solution is little studied.

In the present work, HB was employed to investigate the adsorption behaviors of HB onto the surface of TiO_2 particles and the mechanism of the interfacial electron transfer process from the excited singlet state of HB to the conduction band of colloidal TiO_2 particles. The change in the molecular extinction coefficient and displacement of maximum absorption of HB in the presence of the TiO_2 colloid confirmed the occurrence of interaction between the sensitizer and the particle surface. Fluorescence quenching and the fluorescence lifetime measurements afforded useful information concerning the process of electron injection from singlet excited state of HB to the conduction band of TiO_2. Time-resolved transient absorption spectra (laser flash photolysis and pulse radiolysis) demonstrated formation of the radical cation $HB^{\cdot +}$ on electron injection, providing confirming evidences for the occurrence of such electron transfer processes from the excited state of the sensitizer. In this case, the back-electron transfer from the semiconductor particle to the radical cation $HB^{\cdot +}$ occurred with a rate that was four orders of magnitude slower than that of the forward injection. This further demonstrates that HB is a good photosensitization agent for TiO_2 and that it can improve the photoreduction efficiency of TiO_2 semiconductor.

2. Experimental

2.1. Materials

Hypocrellin B (HB) was obtained from the Microbiology Institute of Yunnan Province, P.R. China, and the purity of HB is above 98%. HB was dissolved in ethanol. $TiCl_4$ (AR grade) was used without further purification.

2.2. Preparation of TiO_2 colloidal semiconductor

The transparent dispension of colloidal TiO_2 was prepared by hydrolysis of $TiCl_4$ at 0 °C [10–12]. The stock dispersion was 6.00×10^{-3} mol/l in colloidal TiO_2 stabilized by poly(vinyl alcohol; PVA, 0.1%). PVA was treated with UV light to remove impurity that could absorb 337 nm laser-light [12]. The average particle diameter, as measured by transmission electron microscopy, was about 6 nm. The freshly prepared colloidal TiO_2 dispersion was diluted with distilled water to obtain the desired concentration of TiO_2 in the sample. Control experiments showed that traces of PVA had no effect on the characteristics of the sensitized photochemistry.

2.3. Apparatus

The radius of the particles was measured using a JEM-100CX transmission electron microscopy. Absorption spectra were recorded using a Hitachi U-3200 spectrophotometer. Emission spectra were recorded using a Hitachi F-4500 fluorescence photometer at 20 ± 2 °C.

The picosecond laser system utilized a Spectra Physics M3800 CW Nd: YAG Laser coupled to a Spectra Physics M3500 Ultrashort Pulse Dye Laser (rhodamine 6G) and Spectra Physics M3295 Cavity Dumper, operated at 800 KHz. The dye laser was operated at 580 nm. The fluorescence lifetime measurements were carried out on a time-correlated single-photon-counting spectrofluoremeter system (EG&G) and detected by a Hamamatsu E3059-00 microchannel plate photomultiplier.

Laser flash photolysis studies were performed using an excimer laser that provided a 337 nm pulse with a 20-ns duration. The maximum energy was 3 mJ per pulse. The analyzing light source was a 500-W xenon lamp, the intensity of which was increased about 100 times during the detection of transient absorption. The laser light beam and the xenon light beam passed perpendicularly through a quartz cell with an optical path length of 10 mm. The transmitted light entered a monochromator that was equipped with an R955 photomultiplier. The resultant signals were collected using a HP54510B digital oscilloscope processed by a Sun 586 personal computer.

Pulse radiolysis experiments were conducted by use of a linear accelerator, providing an 8 MeV electron beam pulse with a duration of 8 ns. The dosimetry of the electron beam pulse was determined by use of a thiocyanate dosimeter containing 10 mmol/l KSCN aqueous solution saturated with air. The detailed description of set-up for pulse radiolysis and the attendant experimental conditions have been given elsewhere [13] .

All the solutions were prepared just before experiments at room temperature.

3. Results and discussion

3.1. Absorption characteristics of the HB–TiO_2 system

In an aqueous suspension, the polar surface of TiO_2 resulting from the protonation equilibria facilitate adsorption of polar species in solution, and such interactions can lead to absorption spectra changes of these molecules [14–16]. Similiarly, HB can associate with TiO_2 through its polar groups such as OH or/and C=O, and this association will lead to a change of π-electron distribution in HB molecule. As a result, an increase in the molar absorbancy and an extended absorption of HB into the visible region were observed as the colloidal TiO_2 was added (Fig. 1), which were similar to the changes observed elsewhere [14–17]. This made HB bound to TiO_2 as a good candidate for the purpose of modification.

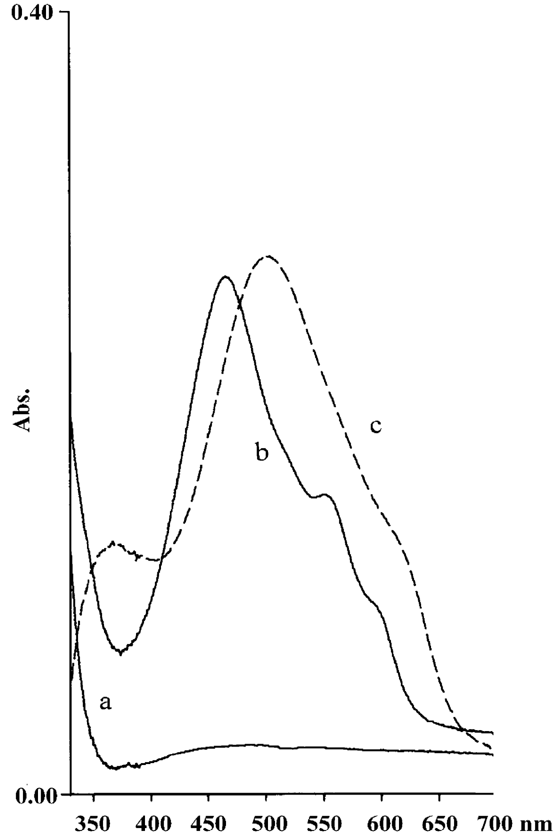

Fig. 1. Absorption spectra in (CH_3CH_2OH: H_2O (V/V) = 1:100) solution: (a) 9.00×10^{-4} mol/l colloidal TiO_2. (b) 1.20×10^{-5} mol/l HB, and (c) 1.20×10^{-5} mol/l HB + 9.00×10^{-4} mol/l TiO_2. Dimension of sample cuvette is 1.0 cm long and 0.5 cm wide.

3.2. Fluorescence quenching by colloidal TiO_2

The fluorescence emission of HB was quenched upon successive addition of TiO_2 to a solution of 3.50×10^{-5} mol/l HB (Fig. 2). The decrease in the fluorescence emission could be attributed to interfacial electron transfer, the concentration quenching among the adsorbed sensitizer molecules [11] or energy transfer between the sensitizer and the colloidal TiO_2. The bandgap energy of TiO_2 semiconductor is greater than that of the sensitizer, (it can be deduced from the position of their absorption bands in Fig. 1). Thus, energy transfer from the singlet state of the sensitizer to the TiO_2 colloidal is impossible. Therefore, it can be concluded that the fluorescence quenching shown in Fig. 2 should not be caused by energy transfer. At relatively high TiO_2 concentrations, the fluorescence emission decreased continuously with increasing amount of colloidal TiO_2, indicating a negligible contribution from concentration quenching to the observed fluorescence quenching of HB. The oxidation potential of $^1HB^*$, which is −1.55 V (vs. NHE) measured by cyclic voltammogram, and the energy level of the conduction band of TiO_2, which lies around −0.40 V (vs. NHE, pH 4.0) [12], provide favorable energy for such an interfacial electron transfer process. This quenching behavior is similar to the previously reported fluorescence quenching of chlorophyllin [14], anthracene-9-carboxylic acid (9AC) [15], and erythrosin B [16], etc., which was caused by the electron injection from the singlet excited state of sinsitizer to the conduction band of colloidal TiO_2 semiconductor (Reaction 1).

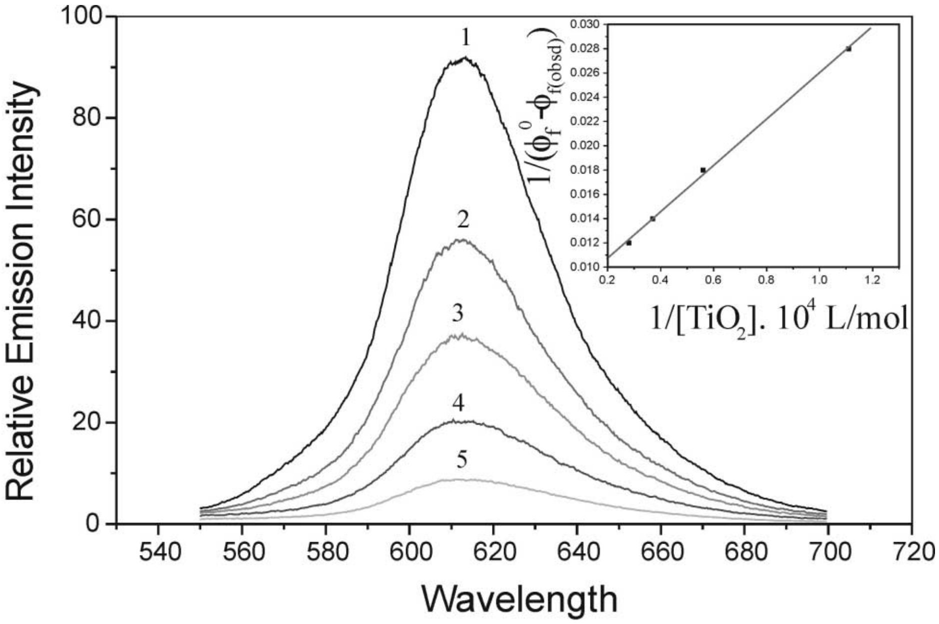

Fig. 2. Fluorescence emission spectra of 3.50×10^{-5} mol/l HB in aqueous solution at various concentrations of TiO_2: (1) 0 mol/l, (2) 9.00×10^{-6} mol/l, (3) 1.80×10^{-5} mol/l, (4) 2.70×10^{-4} mol/l, (5) 3.60×10^{-4} mol/l. The excitation wavelength was at 465 nm. The insert showed the dependence of $(\phi_f^0 - \phi_{f(obsd)})^{-1}$ on the reciprocal concentration of TiO_2.

$$ {}^1HB^* \cdots TiO_2 \rightarrow HB^{\cdot+} \cdots TiO_2(e) \tag{1} $$

The apparent association constant K_{app} between HB and the TiO_2 semiconductor could be determined by study of the slowly fluorescence quenching behavior, (Reaction 2).

$$ HB + TiO_2 \overset{K_{app}}{\rightleftarrows} [HB \cdots TiO_2] \tag{2} $$

At relatively high TiO_2 concentration, if the quenching was due to the association of HB with TiO_2, one would expect a linear dependence of $1/(\phi_f^0 - \phi_{f(obsd)})$ on the reciprocal concentration of TiO_2 with an intercept equal to $1/(\phi_f^0 - \phi_f')$ and a slope equal to $1/((\phi_f^0 - \phi_f')\ K_{app})$ [15]:

$$ \left(\phi_f^0 - \phi_{f(obsd)}\right)^{-1} = \left(\phi_f^0 - \phi_f'\right)^{-1} + \left\{K_{app}\left(\phi_f^0 - \phi_f'\right)[TiO_2]\right\}^{-1} \tag{3} $$

Here, $\phi_{f(obsd)}$ is the observed quantum yield of the sensitizer in TiO_2 suspension, ϕ_f^0 and ϕ_f' are fluorescence yields of unadsorbed and adsorbed molecules of the sensitizer, respectively.

The straight plot described in the insert of Fig. 2 supported the assumption above. By Eq. (3), the value of K_{app}, as determined from this plot, was 3145 $(mol/l)^{-1}$. This suggests that there was a complex associated between HB and TiO_2 semiconductor, which is necessary for observing the heterogeneous charge-transfer process at the interface of the dye–semiconductor.

3.3. Fluorescence lifetime measurements

It has been shown earlier [15] that sensitizer molecules adsorbed on the TiO_2 surface have a significantly shorter excited lifetime than those in homogeneous solution. This decrease in lifetime can be correlated with the electron transfer process. In the absence of TiO_2, the fluorescence of HB has a single exponential decay with lifetime of 0.928 ns. However, addition of colloidal TiO_2 make the fluorescence emission of HB fit to a two-exponential decay, with shorter-lived (0.165 ns) and longer-lived (0.883 ns) components. The longer lifetime was similar to that of HB itself, and the shorter one was much smaller than that of HB alone. The two components with different lifetimes could be attributed to the molecules of HB that are adsorbed on the surface of TiO_2 colloid and the molecules that are unabsorbed. The fluorescence decay for HB in TiO_2 colloidal system was as shown in Fig. 3.

If it is assumed that the observed decrease in fluorescence lifetime is entirely due to the electron transfer process (Reaction 1) and the other radiation and nonradiative decay processes of HB associated with TiO_2 colloid, occurred at the same rates as in neat solvent, one could correlate the observed lifetimes by Eq. (4) [15],

$$1/\tau_{\mathrm{ads}} = 1/\tau + K_{\mathrm{et}} \tag{4}$$

Here, τ and τ_{ads} are the lifetime of the sensitizer in aqueous solution and adsorbed on the TiO_2 surface and K_{et} is the specific rate of the electron transfer process from excited singlet state of HB to conduction band of TiO_2 semiconductor. The value of K_{et} calculated upon substitution of the values of τ and τ_{ads} in Eq. (4) was 4.93×10^{9} s^{-1}. This means that the electron transfer from singlet state of HB to the conduction band of TiO_2 takes place efficiently.

3.4. Laser flash photolysis studies to probe the electron transfer process

Time-resolved laser flash photolysis is very useful in the investigation of the interfacial electron-transfer processes in a colloidal semiconductor system [10,11,14]. If electron injection from the excited state of HB to the conduction band of the semiconductor occurs, the radical cation $HB^{\cdot+}$ should be detected.

The transient absorption spectra, observed in the 337 nm laser photolysis of HB with the presence of TiO_2 suspension in deaerated solution, are shown in Fig. 4. A new transient species with a maximum absorption around 680 nm was generated (Fig. 4). In control experiments, the HB in the absence of TiO_2 had no transient absorption band in this region, under the same conditions. Thus, the species that produce the absorption at around 680 nm,

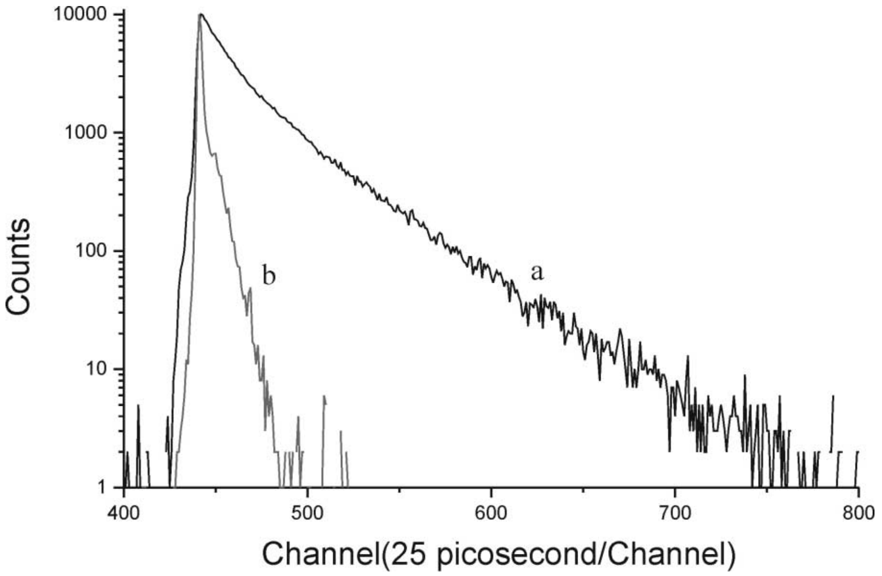

Fig. 3. Fluorescence decay curve of 2.00×10^{-5} mol/l HB in 4.00×10^{-4} mol/l colloidal TiO_2 solution. Curve a is a calculated fluorescence decay curve derived from nonlinear least-squares fit to a two-exponential decay law with the following parameters: $A_1 = 73.94\%$, $\tau_1 = 0.165$ ns; $A_2 = 26.06\%$, $\tau_2 = 0.883$ ns, $\chi^2 = 1.515$. A_1, A_2 are the percentages of components with the defined fluorescence lifetime. Time scale: 25 picosecond per channel. Excitation was at 580 nm, and the emission was recorded at 600 nm. Curve b is the measured instrumental response curve.

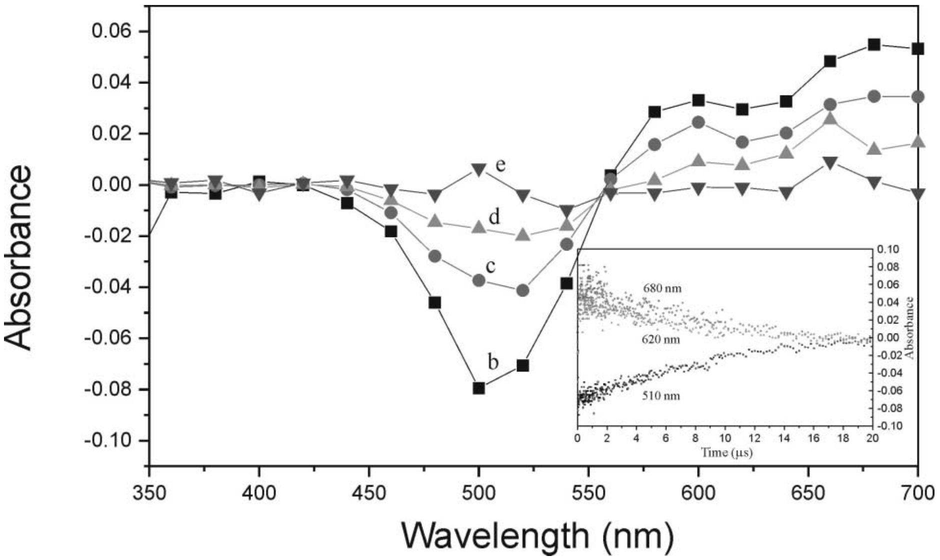

Fig. 4. Transient absorption spectra from photolysis of 8.00×10^{-5} mol/l HB (CH_3CH_2OH:H_2O (V/V) = 1:100) solution and 1.00×10^{-3} mol/l TiO_2 suspension deoxygenated with N_2 at 0.1 μs (a), 5.0 μs (b), 10 μs (c), 20 μs (d) after 337 nm laser pulsing. Inset: the traces recorded at 680, 620, and 510 nm.

shown in Fig. 4, may be assigned to $HB^{\cdot+}\ldots TiO_2$. This point was confirmed in carrying out the following pulse photolysis experiment with the same characteristic absorption spectra. The formation mechanism of $HB^{\cdot+}\ldots TiO_2$ can be illustrated as follows:

$$HB + TiO_2 \rightarrow HB\cdots TiO_2 \xrightarrow{hv} {}^1HB^*\cdots TiO_2 \quad (5)$$

$$\begin{aligned} {}^1HB^*\cdots TiO_2 &\rightarrow HB^{\cdot+}\cdots TiO_2(e) \xrightarrow{HB\cdots TiO_2} \\ &HB^{\cdot+}\cdots TiO_2 + HB\cdots TiO_2(e) \end{aligned} \quad (6)$$

Recombination between the injected charge and the cation radical of the sensitizer often limits the efficiency of sensitization. As shown in the insert in Fig. 4, the decay profile at 680 nm was a lifetime of about 8.0 μs, for the cation radical of HB. The corresponding rate constant for the recombination process (K_r) was 1.25×10^5 s^{-1}, was four orders of magnitude slower than the rate constant of electron transfer from the singlet HB to TiO_2 colloidal semiconductor ($K_{et} = 4.93\times10^9$ s^{-1}). This further demonstrates that HB is a good photosensitizer for the TiO_2 semiconductor. This favorable charge separation in the sensitization of oxide semiconductors can be used in conversion of light to electricity under visible light irradiation [4].

3.5. Pulse radiolysis studies

Fig. 5 shows the transient absorption spectra obtained from the pulse radiolysis of aqueous solutions containing 6.00×10^{-5} mol/l HB, 7.00×10^{-4} mol/l TiO_2, 1.30×10^{-2} mol/l $K_2S_2O_8$ and 0.06 ml *tetra*-butanol, saturated with N_2 recorded at 0.1 μs, 1.0 μs, 5.0 μs, 20 μs, 50 μs after beam pulse. Accompanying the decay of the species with maximum absorption at 340 nm, a new transient species, with a maximum absorption peak at 680 nm, appears subsequently. Since the optical absorption maximum of $SO_4^{\cdot-}$ is around 340 nm [18], the transient spectrum with an absorption peak at 680 nm, as shown in Fig. 5, is assigned to $HB^{\cdot+}\ldots TiO_2$, as $HB\ldots TiO_2$ was oxidized by $SO_4^{\cdot-}$ which was generated according to Reactions (7)–(9). The generation process of the $HB^{\cdot+}\ldots TiO_2$ radical can be expressed as:

$$H_2O \rightarrow e_{aq}^- + {}^\cdot OH + {}^\cdot H \quad (7)$$

$$\begin{aligned} t\text{-BuOH} + {}^\cdot OH({}^\cdot H) &\rightarrow {}^\cdot CH_2(CH_3)_2COH \\ &+ H_2O(H_2) \end{aligned} \quad (8)$$

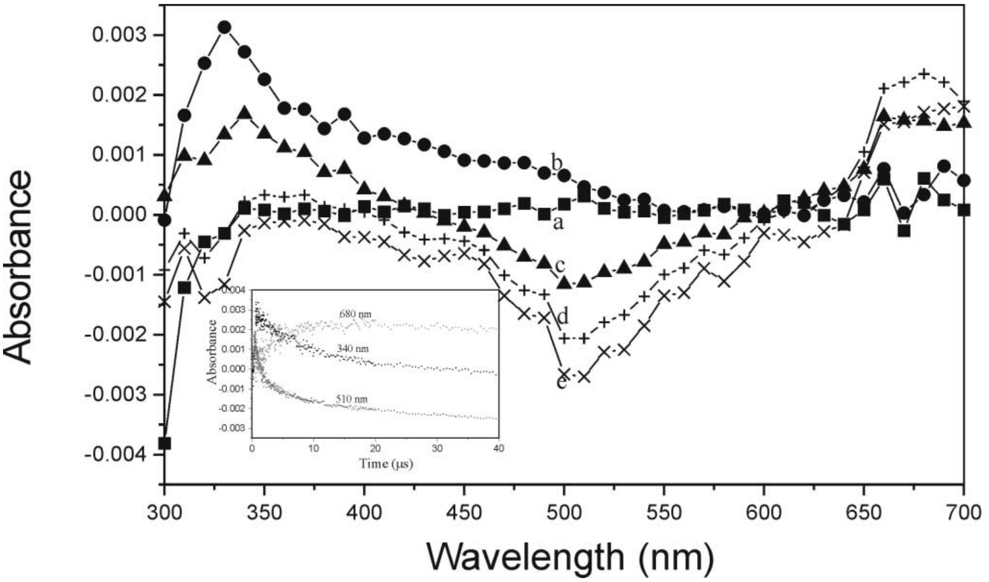

Fig. 5. Transient absorption spectra obtained from pulse radiolysis of 6.00×10^{-5} mol/l HB and 7.00×10^{-4} mol/l TiO_2 suspension, 1.30×10^{-2} mol/l $K_2S_2O_8$, 0.06 ml *t*-BuOH saturated with N_2 recorded at 0.1 μs (a), 1.0 μs (b), 5.0 μs (c), 20 μs (d), 50 μs (e). Inset: the traces recorded at 340, 510, and 680 nm.

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{\cdot-} + SO_4^{2-} \quad (9)$$

$$HB \cdots TiO_2 + SO_4^{\cdot-} \rightarrow HB^{\cdot+} \cdots TiO_2 + SO_4^{2-} \quad (10)$$

In this solution, the ˙OH and ˙H radicals that were generated were rapidly scavenged by *tetra*-butanol, leading to the formation of the rather unreactive *tetra*-butanol radical (Reaction 8) [19]. e^-_{aq} reacted with $S_2O_8^{2-}$ to produce $SO_4^{\cdot-}$ (around 340 nm in Fig. 5) by reaction (9). $SO_4^{\cdot-}$ was then used to oxidize HB...TiO_2 to produce $HB^{\cdot+}\ldots TiO_2$ (around 680 nm in Fig. 5) and SO_4^{2-} (Reaction 10).

This result is in very good agreement with that obtained using the laser flash photolysis depicted in Fig. 4 and it could be used as an evidence for the formation of $HB^{\cdot+}$ ...TiO_2 via electron transfer, with maximum absorption at 680 nm.

The bleaching position as represented by the band at 510 nm (Figs. 4 and 5) was from HB...TiO_2. $HB^{\cdot+}$ on the surface of the TiO_2 is unstable. Therefore could be decomposed into smaller molecules, as a result, absorption at 510 nm in Fig. 5 finally showed the permanent decrease.

4. Conclusion

HB can be adsorbed on the surface of TiO_2 colloidal semiconductor particle with an apparent association constant of 3145 $(mol/l)^{-1}$; the rate constant for the electron transfer process from excited singlet state of HB into the conduction band of TiO_2 semiconductor (K_{et}) was 4.93×10^9 s^{-1}; the lifetime of $HB^{\cdot+}$ on the surface on TiO_2 colloid was 8.0 μs, and the rate constant of the recombination process between the injected charge and the cation radical of the HB (K_r) was 1.25×10^5 s^{-1}, which was four orders of magnitude slower than the rate constant of electron transfer from the singlet HB to TiO_2 colloidal semiconductor (K_{et}). This demonstrated that HB was a good photosensitizer for TiO_2 semiconductor under visible light.

Acknowledgements

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References

[1] Hoffmann MR, Martin ST, Choi WY, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chem Rev 1995;95:69–96.

[2] O'Regan B, Graetzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature 1991;353:737–40.

[3] Xu HJ, Li HW, Liu K. Synthesis of novel amphiphilic zinc phthalocyanines and fabrication of zinc phthalocyanine-titanium oxide multilayers. Dyes and Pigments 2001;49:9–14.

[4] Hagfeldt A, Graetzel M. Light-induced redox reactions in nanocrystalline systems. Chem Rev 1995;95:49–68.

[5] Wang NH, Zhang ZY. Relationship between photosensitizating activities and chemical structure of hypocrellin A and B. J Photochem Photobiol B: Biol 1992;14: 207–17.

[6] Liang RY, Mei GD, Zhou WY. 62 cases with hypertrophic scars treated with hypocrellin photochemotherapy. Chin J Derma 1982;15:87–8.

[7] Zhang ZY, Wang NH, Wan Q, Li MF. EPR study of singlet oxygen ($^1O_2$) and free radicals ($O_2^{\cdot -}$, $^{\cdot}OH$, $HB^{\cdot -}$) generated during photosensitization of hypocrellin B. 1993; 14: 1–9.

[8] Diwu ZJ, Lown JW. Photosensitization by anticancer agents 12. Perylene quinonoid pigments, a novel type of singlet oxygen sensitizer. J Photochem Photobiol A: Chem 1992;64:273–87.

[9] He YY, Liu HY, An JY, Han R, Jiang LJ. Photodynamic action of hypocrellin dyes: structure-activity relationships. Dyes and Pigments 2000;44:63–7.

[10] Moser J, Graetzel M. Photosensitized electron injection in colloidal semiconductors. J Am Chem Soc 1984;106:6557–64.

[11] Kalyanasundaram K, Vlachopoulos N, Krishnan V, Monnier A, Graetzel M. Sensitization of TiO_2 in the visible light region using Zinc Porphyrins. J Phys Chem 1987;91:2342–7.

[12] Moser J, Graetzal M. Light-induced electron transfer in colloidal semiconductor dispersions: single vs. dielectronic reduction of acceptors by conduction-band electrons. J Am Chem Soc 1983;105:6547–55.

[13] Yao SD, Sheng SG, Cai JH, Zhang JS, Lin NY. Nanosecond pulse radiolysis studies in China. Radiat Phys Chem 1995;46:105.

[14] Kamat PV, Chauvet JP, Fessenden RW. Photoelectrochemistry in particulate systems. 4. Photosensitization of a TiO_2 semiconductor with a chlorophyll analogue. J Phys Chem 1986;90:1389–94.

[15] Kamat PV. Photoelectrochemistry in particulate systems. 9. Photosensitized reduction in a colloidal TiO_2 system using anthracene-9-carboxylic acid as the sensitizer. J Phys Chem 1989;93:859–64.

[16] Kamat PV, Fox MA. Photosensitization of TiO_2 colloids by Erythrosin B in acetonitrile. Chem Phys Lett 1983;102: 379–84.

[17] Hilgendorff M, Sundstrom V. Dynamics of electron injection and recombination of dye-sensitized TiO_2 particles. J Phem Chem B 1998;102:10505–14.

[18] Ma JH, Qian SP, Lin WZ, Yao SD. Fast electron transfer repair of oxidizing OH adduct of dGMP by chlorogenic acid. Science in China 1998;41(5):556–60.

[19] Lu CY, Yao SD, Wang WF, Tong YP, Lin WZ, Rong TW, Lin NY. Laser flash photolysis of fullerols of C_{60} and of C_{70} in aqueous solutions. Science in China (series B) 1998;41(3):259–65.