Electron transfer in colloidal TiO$_2$ semiconductors sensitized by hypocrellin A

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Abstract

The electron transfer from singlet states of hypocrellin A (HA) to colloidal TiO$_2$ nanometer-sized particles has been examined by absorption, fluorescence quenching, fluorescence lifetime measurements, laser flash photolysis and pulse radiolysis techniques. Adsorption of HA onto the surface of TiO$_2$ particles extended its absorption spectrum further into the visible region, and the apparent association constant (K_{app}) for the association between HA and colloidal TiO$_2$ was $3600 \, (mol/l)^{-1}$ determined by fluorescence quenching method. Fluorescence lifetime measurement was used to elucidate the process of electron transfer from the singlet state of HA to conduction band of TiO$_2$ ($K_{et} = 4.26 \times 10^9 \, s^{-1}$). Laser flash photolysis and pulse radiolysis studies demonstrated formation of the radical cation of HA. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hypocrellin A (HA); Colloidal TiO$_2$ semiconductor; Photosensitization; Electron transfer; Singlet state

1. Introduction

Semiconductor materials such as TiO$_2$ have been widely used as photocatalysts for solar energy conversion (Kamat, 1993), chemical transformation (Pichat, 1985) and for the photodegradation of organic pollutants (Hoffmann et al., 1995). However, the photoactivities of many metal oxide semiconductors are limited to the UV region. Therefore, photoactive dyes such as erythrosine B (Kamat and Fox, 1983), eosin (Moser and Graetzal, 1984), chlorophyllin (Kamat et al., 1986), phthalocyanines (Fan and Bard, 1979), Ru(bpy)$_3^{2+}$ (Kiwi, 1981), and anthracene-9-carboxylic acid (Kamat, 1989) etc., with high extinction coefficients in the visible region, are often employed in photosensitization of stable, large-bandgap semiconductor electrodes and particles.
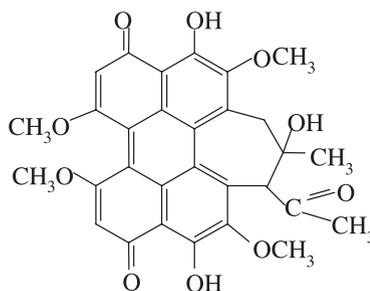
HA

Hypocrellin A (HA) is obtained from *Hypocrella bambusae* (B. et. Br) Sacc, a Chinese herb which grows most abundantly in the southwestern part of China (An et al., 1985). It has been shown that HA is not only an effective photo-therapeutic agent but also a good photosensitizer (Ma et al., 1989). Although the photochemical and photophysical properties of HA have been reported (Diwu and Lown, 1992a, b), photosensitization of semiconductor with HA is little reported.

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The present study employed HA as sensitizer to investigate the adsorption details on the surface of the TiO_2 particles and the mechanism of the interfacial electron-transfer process from singlet state of HA to conduction band of colloidal TiO_2 particles in aqueous solution. The increases in the extinction coefficient and the red-shift of the absorption maxima in the absorption spectra of HA in the presence of TiO_2 colloids demonstrated the occurrence of surface interactions between the sensitizer and the particle surface. Quenching of the fluorescence emission and changes in the fluorescence lifetime of the sensitizer afforded useful information of the process of electron injection from singlet excited state of HA to the conduction band of TiO_2. Furthermore, time-resolved transient absorption spectra (laser flash photolysis and pulse radiolysis) of HA radical cation provided confirming evidence for the occurrence of electron transfer from the excited state of the sensitizer to the conduction band of the semiconductor.

2. Materials and methods

2.1. Materials

HA was obtained from the Microbiology Institute of Yunnan Province, People's Republic of China. It was purified by HPLC with an ultrasphere column (Beckman, Palo Alto, CA) and eluted in chloroform-methanol (80:20, v/v), the purity of HA is above 98%. HA was dissolved in ethanol. $TiCl_4$ (AR grade) was used without further purification.

2.2. Preparation of TiO_2 colloidal semiconductor

The transparent solution of TiO_2 colloidal was prepared by hydrolysis of $TiCl_4$ at $0°C$ according to Moser and Graetzal (1983, 1984), Michael et al. (1983). A volume of 0.043 ml of $TiCl_4$ (AR grade, colorless liquid, FW: 189.72, d: 1.76 g/ml) pre-chilled to $-20°C$ was added slowly to 50 ml of vigorously stirred deionized water at $0°C$. So the concentration of TiO_2 molecules in 50 ml colloidal TiO_2 solution was 0.64 g/l or 8.00×10^{-3} mol/l. Poly(vinyl alcohol) (PVA, 0.1%) was used in this case to stabilize the colloidal particles. PVA was treated with UV light to remove impurity before used (Moser and Graetzal, 1983, 1984). The average particle diameter, as measured by transmission electron microscopy, was 6 nm. The freshly prepared colloidal TiO_2 solution 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 sensitized photochemistry.

2.3. Apparatus

The radius of particle was measured with JEM-100CX transmission electron microscopy. Absorption spectra were recorded with a Hitachi U-3200 spectrophotometer, and emission spectra were recorded with a Hitachi F-4500 fluorescence photometer at $20 \pm 2°C$.

The picosecond laser system utilized a Spectra Physics M3800 CW Nd:YAG Laser with 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 spectrofluorometer system (EG&G) detected by a Hamamatsu E3059-00 microchannel plate photomultiplier.

The laser flash photolysis was performed with 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 and xenon light beams passed perpendicularly through a quartz cell with an optical path length of 10 mm. The transmitted light entered a monochromator equipped with an R955 photomultiplier. The resultant signals were collected using a HP54510B digital oscilloscope processed with 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 electron beam pulse was determined by thiocyanate dosimeter containing 10 mmol/l KSCN aqueous solution saturated with air. Detailed description of set-up of pulse radiolysis equipment and experimental conditions have been given elsewhere (Yao et al., 1995).

All solution was prepared just before experiments at room temperature.

3. Results and discussion

3.1. Absorption characteristics of the HA-TiO_2 system

In an aqueous solution, the colloidal TiO_2 can be assumed to have predominantly Ti-OH groups at its surface, and through which polar species in solution can strongly interact with the particles (Fox, 1985; Graetzel, 1983). As shown earlier (Kamat and Fox, 1983; Kamat et al., 1986; Kamat and Ford, 1987; Kamat, 1989), such interactions can lead to absorption spectra changes of sensitizers. Similarly, HA 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 the π-electron distribution in HA molecule. As a result, as shown in Fig. 1, an increase in the molar absorbancy
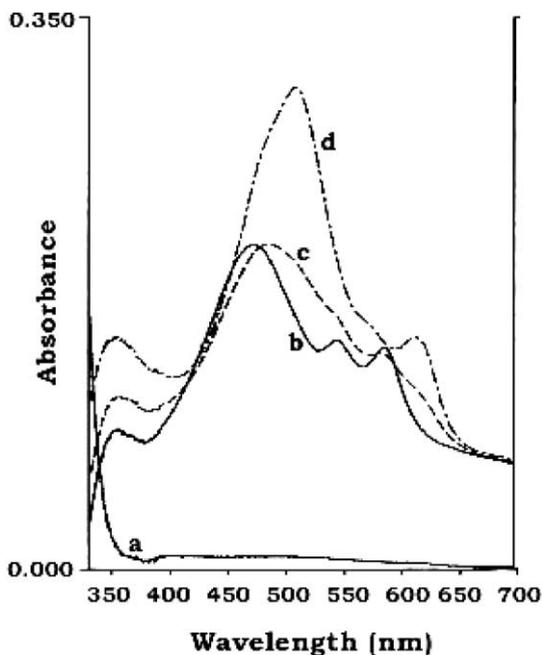
Fig. 1. Absorption spectra in $(CH_3CH_2OH:H_2O$ (v/v) = 1:100) solution: (a) 239.70 mg/l colloidal TiO_2, (b) 5.00×10^{-5} mol/l HA, and (c) 5.00×10^{-5} mol/l HA + 7.99 mg/l TiO_2, (d) 5.00×10^{-5} mol/l HA + 239.70 mg/l TiO_2. Pathlong: 0.5 cm.

and an extended absorption of HA into the visible region were observed as the concentration of TiO_2 was increased, which were similar to the changes observed elsewhere (Kamat and Fox, 1983; Kamat et al., 1986; Kamat and Ford, 1987; Kamat, 1989). This made HA bound to TiO_2 as a good candidate for the purpose of photo-sensitization.

3.2. Fluorescence quenching by TiO_2 colloidal semiconductor

The fluorescence emission of HA was quenched upon successive addition of TiO_2 to a solution of 5.00×10^{-5} mol/l HA (Fig. 2). This quenching behavior was similar to the previously reported fluorescence quenching of erythrosin B (Kamat and Fox, 1983), and anthracene-9-carboxylic acid (9AC) (Kamat, 1989), which were caused by the electron injection from the singlet excited state of sensitizers to the conduction band of colloidal TiO_2 semiconductor (reaction (1)).

$$^1HA^* \cdots TiO_2 \rightarrow HA^+ \cdots TiO_2(e). \tag{1}$$

The oxidation potential of $^1HA^*$, which is -1.56 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) (Moser and Graetzal, 1983), provide favorable energy for such an electron-transfer process.

The participation of TiO_2 in the quenching process was further analyzed by considering the equilibrium between adsorbed and unabsorbed molecules of the sensitizer with an apparent association constant K_{app} (reaction (2)).

$$HA + TiO_2 \underset{K_{app}}{\rightleftharpoons} HA \cdots TiO_2. \tag{2}$$
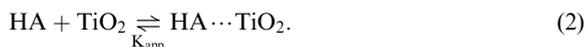
At relatively high TiO_2 concentration, if the quenching was due to the association of HA with TiO_2, one would expect a linear dependence of $1/(\phi_f^0 - \phi_{f(obsd)})$ on the reciprocal concentration of TiO_2 with an intercept equal to $1/(\phi_f^0 - \phi_f')$ and a slope equal to $1/((\phi_f^0 - \phi_f')K_{app})$ (Kamat, 1989):

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

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

The straight line shown in the insert of Fig. 2 supported the assumption above. It also meant that the process of electron transfer was preferable to the scattering of light by the added colloidal TiO_2. By Eq. (3), the value of K_{app} as determined from this plot was 3600 (mol/l). This suggested that there was a complex associated between HA and TiO_2 semiconductor, which was necessary for observing the heterogeneous electron-transfer process at the interface of sensitizer-semiconductor.

3.3. Fluorescence lifetime measurements

In order to analyze the fluorescence quenching process further, fluorescence lifetime measurements were performed. Molecule adsorbed on a colloidal semiconductor particle surface typically displayed significantly shorter fluorescence lifetime than unadsorbed molecule. This decrease in lifetime could be correlated with the interfacial electron-transfer process (Kamat, 1989). In the absence of TiO_2, the fluorescence lifetime of HA exhibited a single-exponential decay $(F(t) = A\exp(-t/\tau))$ with lifetime of 1.07 ns. However, in the presence of colloidal TiO_2, the fluorescence emission of HA followed a two-exponential decay $(F(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2))$. The fluorescence decay for HA in 7.99 mg/l TiO_2 suspension was shown in Fig. 3 (curve b). There was an obvious component with much shorter lifetime. A component with lifetime similar to that of HA alone was also observed. Computer analysis of the decay gave a lifetime of 0.186 ns for the shorter-lived component, which was assumed to be due to the adsorbed dye. The lifetime of the longer-lived component was 0.893 ns, which was close to the lifetime of HA in TiO_2 free solution (1.07 ns).
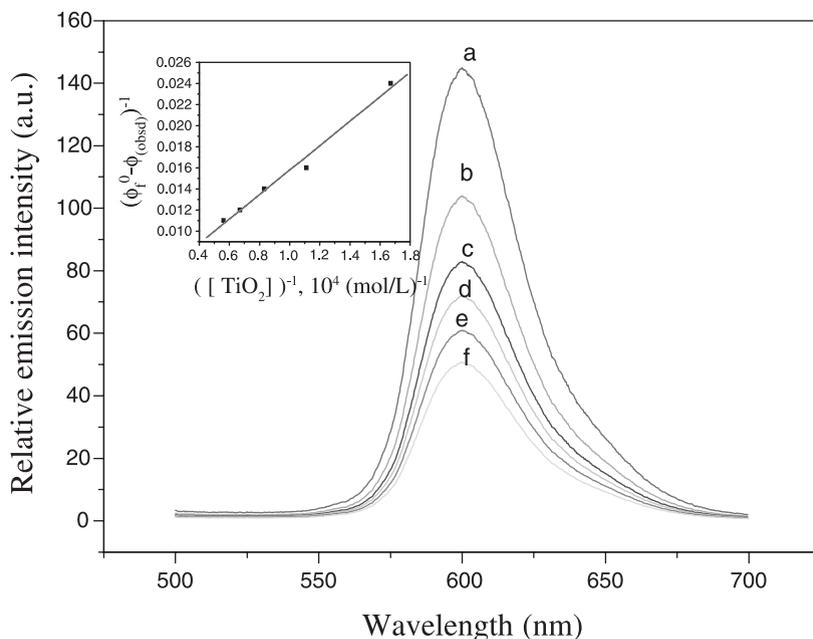
Fig. 2. Fluorescence emission spectra of 5.00×10^{-5} mol/l HA in $(CH_3CH_2OH:H_2O$ $(v/v) = 1:100)$ solution at various concentrations of TiO_2: (a) 0 mg/l, (b) 4.79 mg/l, (c) 7.19 mg/l, (d) 9.59 mg/l, (e) 11.99 mg/l, (f) 14.38 mg/l. The excitation wavelength was at 470 nm. The insert shows the dependence of $(\phi_f^0 - \phi_{f(obsd)})^{-1}$ on the reciprocal concentration of TiO_2 molecule.
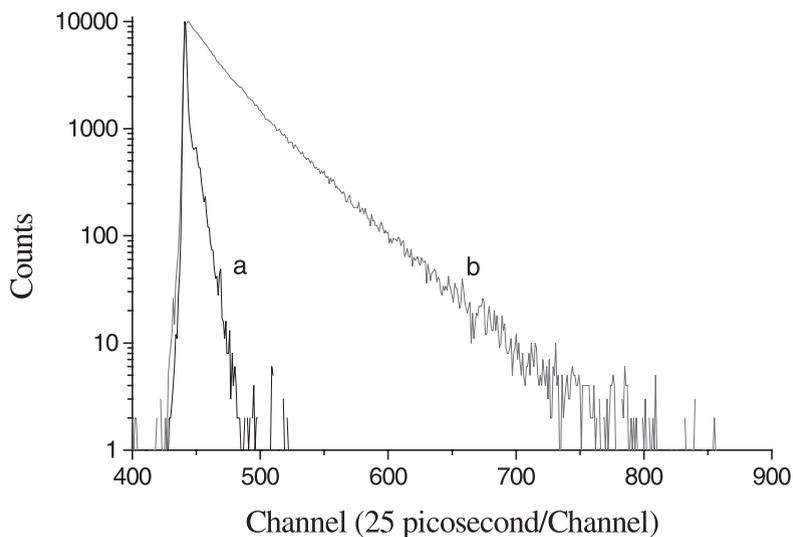

Fig. 3. Fluorescence decay curve of 2.00×10^{-5} mol/l HA in 7.99 mg/l TiO_2 colloidal solution. Curve a is the measured instrumental response curve. Curve b is the fluorescence decay curve fit to a two-exponential decay law with the following parameters: $A_1 = 55.51\%$, $\tau_1 = 0.186$ ns; $A_2 = 44.49\%$, $\tau_2 = 0.893$ ns, $\chi^2 = 1.390$. A_1, A_2 are the percentages of components with the defined fluorescence lifetime. Time scale: 25 ps per channel. Excitation was at 580 nm, and the emission was recorded at 600 nm.

If the observed decrease in fluorescence lifetime was entirely due to the electron-transfer process (reaction (1)) and the other radiation and nonradiative decay processes of HA associated with TiO_2 colloid occurred at the same rates as in neat solvent, one would correlate the observed lifetime by the following expression

(Kamat, 1989).

$$1/\tau_{ads} = 1/\tau + K_{et}, \qquad (4)$$

where τ and τ_{ads} were the lifetimes of the sensitizer in aqueous solution and adsorbed on the TiO_2 surface and K_{et} was the specific rate of the electron-transfer process
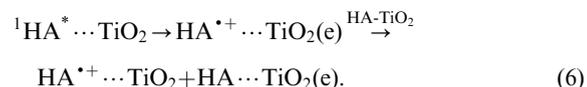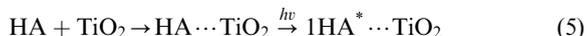
from excited singlet state of HA to conduction band of TiO$_2$ semiconductor. The value of K_{et} calculated upon substitution of the values of τ and τ_{ads} in Eq. (4) was $4.26 \times 10^9 \, \text{s}^{-1}$, it was an order of magnitude faster than the rate of intersystem crossing from S_1 to T_1 for HA ($K_{isc} \approx 10^8 \, \text{s}^{-1}$ (Zhang et al., 1996)). This meant that the electron transfer from singlet state of HA to the conduction band of TiO$_2$ semiconductor performed much more efficiently than intersystem crossing.

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 colloidal semiconductor system (Moser and Graetzal, 1984; Kamat et al., 1986; Kalyanasundaram et al., 1987). If electron injection from the excited state of HA to the conduction band of the semiconductor occurred, the radical cation HA$^{\bullet +}$ should be detected.

The transient absorption spectra observed in 337 nm laser photolysis of HA in the presence of TiO$_2$ suspension in deaerated solution were shown in Fig. 4. A new transient species with maximum absorption around 680 nm generated (Fig. 4). In control experiments (TiO$_2$ free), the HA had no transient absorption band in this region under the same conditions. So the species shown in Fig. 4 should be assigned to the HA$^{\bullet +} \cdots$TiO$_2$ intermediate, which could be confirmed

by pulse photolysis experiment which show the same characteristic absorption spectrum. The absorption around 620 nm might be due to HA$^{\bullet +}$-TiO$_2$(e) which had the same lifetime as that of HA$^{\bullet +}$-TiO$_2$ (Fig. 4.). The formation mechanism of HA$^{\bullet +} \cdots$TiO$_2$ can be illustrated as following:

$$\text{HA} + \text{TiO}_2 \rightarrow \text{HA} \cdots \text{TiO}_2 \xrightarrow{hv} {}^1\text{HA}^* \cdots \text{TiO}_2 \qquad (5)$$

$${}^1\text{HA}^* \cdots \text{TiO}_2 \rightarrow \text{HA}^{\bullet +} \cdots \text{TiO}_2(\text{e}) \xrightarrow{\text{HA-TiO}_2}$$

$$\text{HA}^{\bullet +} \cdots \text{TiO}_2 + \text{HA} \cdots \text{TiO}_2(\text{e}). \qquad (6)$$

The interaction between the semiconductor and sensitizer and their energetics are two important factors that control the course of a charge injection process (Patrick and Kamat, 1992). As shown in Fig. 5, compared to ${}^1\text{HA}^*$, there was less driving force for ${}^3\text{HA}^*$ (Diwu and Lown, 1992a, b) to inject an electron into the conduction band of the semiconductor. In addition, the electron transfer from singlet state of HA (K_{et}) to TiO$_2$ semiconductor performed much more efficiently than intersystem crossing (K_{isc}). Thus, at relatively high TiO$_2$ concentration, the electron injection mainly came from the singlet state of HA adsorbed on the surface of TiO$_2$, and just only a little part of the triplet state of HA which survived for a longer time of ($\tau_{(T)} \approx 4.0 \, \mu\text{s}$) (Zhang et al., 1996) would participate in diffusion-controlled interfacial electron-transfer process.

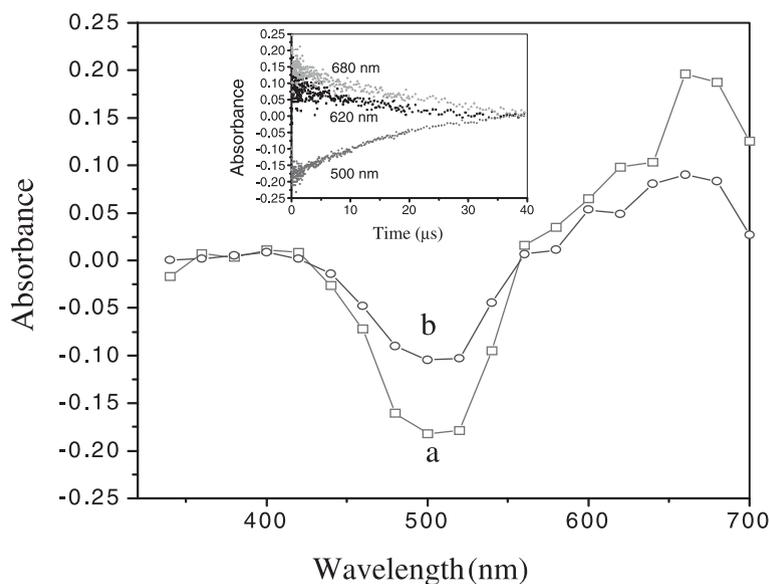An important aspect of the sensitization process is the recombination between the injected charge and the

Fig. 4. Transient absorption spectra from photolysis of 5.00×10^{-5} mol/l HA (CH$_3$CH$_2$OH:H$_2$O (v/v) = 1:100) solution and 79.90 mg/l TiO$_2$ suspension deoxygenated with N$_2$ at 0.1 μs (a), 10 μs (b), after 337 nm laser pulsing. Inset: the traces recorded at 500, 620, and 680 nm.
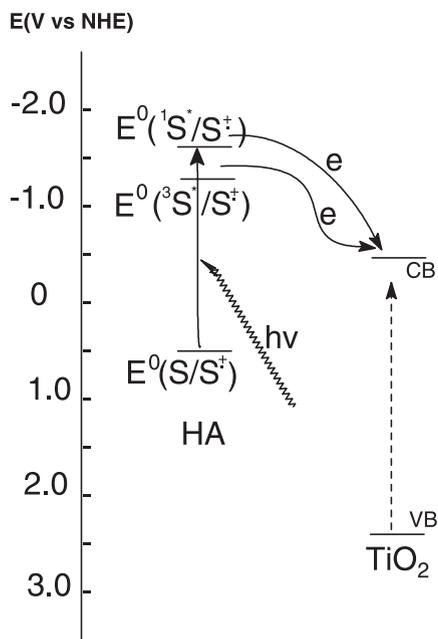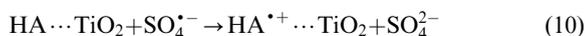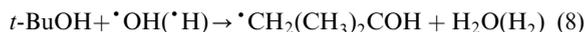
E(V vs NHE)

Fig. 5. Mechanism diagram describing the photosensitized electron-transfer process in the HA-TiO$_2$ system. Schematic diagram describing the conduction and valence band energy levels for TiO$_2$ and electron-donating levels for HA.

cation radical of the sensitizer, which often limits the efficiency of sensitization. As shown in insert in Fig. 4, the decay profile at 680 nm referred a lifetime of about 16.0 μs for the cation radical of HA, and the rate constant of recombination process (K_r) is $6.25 \times 10^4\,\mathrm{s}^{-1}$, which was five orders of magnitude slower than the value observed in the sensitization of TiO$_2$ colloidal semiconductor by singlet HA ($K_{et} = 4.26 \times 10^9\,\mathrm{s}^{-1}$). This further demonstrated that HA was a good photosensitizer for TiO$_2$ semiconductor.

3.5. Pulse radiolysis studies

Fig. 6 shows the transient absorption spectra obtained from pulse radiolysis of aqueous solution containing 8.00×10^{-5} mol/l HA, 55.93 mg/l TiO$_2$, 1.30×10^{-2} mol/l K$_2$S$_2$O$_8$ and 0.318 mol/l *tert*-butanol (*t*-BuOH) saturated with N$_2$ recorded at 0.5 and 15 μs after beam pulse. Accompanying the decay of the species with maximum absorption at 340 nm, a new transient species with maximum absorption peak at 680 nm appeared subsequently. Since the optical absorption maximum of SO$_4^{\bullet-}$ was around 340 nm (Ma et al., 1998), the transient spectrum with an absorption peak at 680 nm, as shown in Fig. 6, was assigned to HA$^{\bullet+}\cdots$TiO$_2$ as HA$\cdots$TiO$_2$ was oxidized by SO$_4^{\bullet-}$ that generated according to the reactions (7)–(9). Therefore, the generation process of

the HA$^{\bullet+}\cdots$TiO$_2$ radical can be expressed as

$$H_2O \rightarrow e_{aq}^- + {}^{\bullet}OH + {}^{\bullet}H \tag{7}$$

$$t\text{-BuOH} + {}^{\bullet}OH({}^{\bullet}H) \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O(H_2) \tag{8}$$

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \tag{9}$$

$$HA\cdots TiO_2 + SO_4^{\bullet-} \rightarrow HA^{\bullet+}\cdots TiO_2 + SO_4^{2-} \tag{10}$$

In this solution, the $^{\bullet}$OH and $^{\bullet}$H atoms generated were rapidly scavenged by tert-butanol leading to the formation of the rather unreactive tert-butanol radical (reaction (8)) (Buxton et al., 1988), while e_{aq}^- reacted with S$_2$O$_8^{2-}$ to produce SO$_4^{\bullet-}$ (around 340 nm in Fig. 6) by reaction (9). SO$_4^{\bullet-}$ was then used to oxidize HA$\cdots$TiO$_2$ (around 500 nm in Fig. 6) to produce HA$^{\bullet+}\cdots$TiO$_2$ (around 680 nm in Fig. 6) and SO$_4^{2-}$ (reaction (10)).

The result was in very good agreement with that obtained in laser flash photolysis in Fig. 4 and it could be used as an evidence for the formation of HA$^{\bullet+}$ $\cdots$TiO$_2$ with maximum absorption at 680 nm generated via electron transfer from excited states of HA to TiO$_2$.

It was found that the radical cation of HA was stable for 40 μs as shown by the laser photolysis in Fig. 4, whereas it was very unstable for 5 μs as observed pulse radiolysis as shown in Fig. 6. This results led to the conclusion that the recombination reaction between HA$^{\bullet+}$ (TiO$_2$) and TiO$_2$(e) was much slower than reactions of HA$^{\bullet+}$ (TiO$_2$) with radiolytic transient species e.g. $^{\bullet}$CH$_2$(CH$_2$)$_2$OH.

The bleaching at 500 nm (in Figs. 4 and 6) was from HA$\cdots$TiO$_2$. Because HA$^{\bullet+}$ on the surface of TiO$_2$ was unstable, it could be decomposed into smaller molecules at last, as a result, absorption at 500 nm in Fig. 6 showed a permanent decrease.

Because of the restriction of absorption, a large bandgap semiconductor cannot utilize sunlight efficiently. However, with the addition of appropriate photosensitizer, the situation will be improved. It will be feasible that HA$\cdots$TiO$_2$ complex can utilize visible sunlight more efficiently than pure TiO$_2$ as HA has high extinction coefficients in visible light range and intensively improve the photoelectrochemical efficiency of TiO$_2$.

4. Conclusion

The absorption spectrum gave an evidence of the strong association between HA and TiO$_2$ and the apparent association constant (K_{app}) determined by fluorescence quenching was 3600 (mol/l). The electron could be injected from singlet excited states of HA to conduction band of TiO$_2$ colloidal semiconductor. Fluorescence lifetime measurement was used to
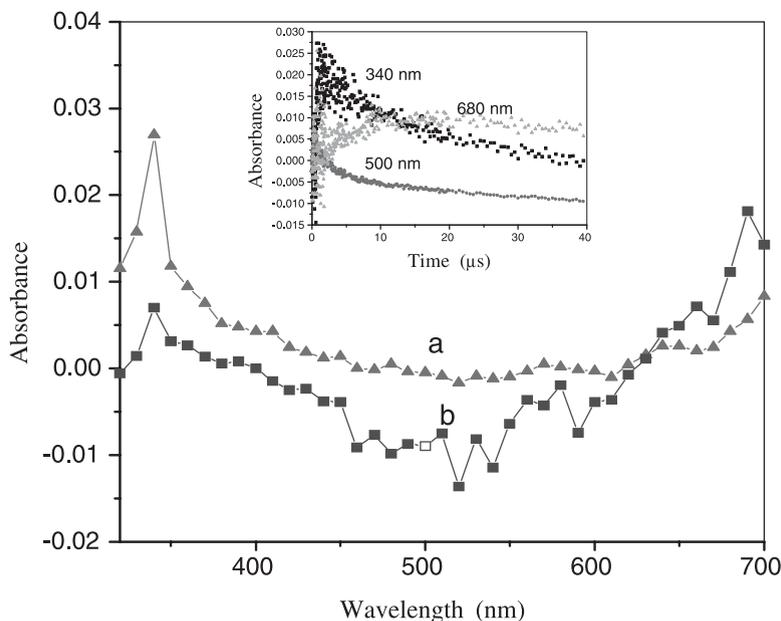
Fig. 6. Transient absorption spectra obtained from pulse radiolysis of 8.00×10^{-5} mol/l HA and 55.93 mg/l TiO_2 suspension, 1.30×10^{-2} mol/l $K_2S_2O_8$, 0.318 mol/l t-BuOH saturated with N_2 recorded at 0.5 μs (a), 15 μs (b). Inset: the traces recorded at 340, 680, and 500 nm.

elucidate the process of electron transfer from the singlet state of HA to conduction band of TiO_2 ($K_{et} = 4.26 \times 10^9 \, \text{s}^{-1}$). With laser flash photolysis and pulse radiolysis techniques, a direct evidence for the process of electron injection was obtained.

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