

*Communications*

## Photoinduced charge injection from excited triplet hypocrellin B into TiO<sub>2</sub> colloid in ethanol

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Photosensitization of TiO<sub>2</sub> colloid by hypocrellin B (HB), a natural photodynamic pigment with extremely high photostability, has been studied by surface enhanced Raman spectroscopy (SERS), laser flash photolysis and electron paramagnetic resonance (EPR) techniques. The photosensitization of TiO<sub>2</sub> occurred practically from the excited triplet dye and the electron injection rate constant is  $1.3 \times 10^6 \text{ s}^{-1}$ . The influences of donor and acceptor on the electron injection were investigated.

**Keywords** Hypocrellin B, TiO<sub>2</sub>, photosensitization, electron injection

Photosensitization of a stable large-bandgap semiconductor TiO<sub>2</sub> has important application in solar energy conversion and light-induced decomposition of organic pollutants.<sup>1</sup> So far, the sensitizers used were practically synthetic dyes<sup>2-4</sup> and little effort 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, long excited triplet lifetime (the standard oxidation potential of the excited triplet HB is at  $-0.62 \text{ V vs. NHE}$ ) and extremely high photostability,<sup>5</sup> has been employed as an ideal sensitizer of injecting charge to TiO<sub>2</sub> from triplet state of the dye. The sensitization process is studied here using surface enhanced Raman spectroscopy (SERS), nanosecond laser flash photolysis and EPR techniques.

TiO<sub>2</sub> was prepared according to the procedure of

Gratzel.<sup>6</sup> Application of scanning transmission electron microscopy yields an average radius of 5 nm. Addition of TiO<sub>2</sub> (2 g/L) induces a striking change in the absorption spectrum of the HB ethanol solution. The maximum is red-shifted from 467 to 507 nm, the extinction coefficient is increased 1.26 fold to  $2.53 \times 10^7 \text{ cm}^2 \cdot \text{mol}^{-1}$  and the calculated apparent association constant is  $8.0 \times 10^3 (\text{mol/L})^{-1}$ . SERS verified that there are strong transitions at 1058, 1335 and 1609  $\text{cm}^{-1}$  in the chelate compared with the pure HB in ethanol, which are the C—O and C=O characteristic frequencies of the perylenequinones of HB (Fig. 1A). A proposition for the structure of the chelate present at the surface of the TiO<sub>2</sub> particles in ethanol is given in Fig. 1B. Formation of an adduct of the HB with a surface titanium cation is assumed. The fluorescence lifetime of HB at various concentration of TiO<sub>2</sub> was the same with that of HB in the absence of TiO<sub>2</sub>, suggesting that electron injection in the conduction band of TiO<sub>2</sub> can not take place from excited singlet state of HB. Laser flash photolysis experiments were carried out by employing a 532-nm Nd:YAG laser (laser pulse width was 5 ns). Fig. 2(a) shows three features in the transient absorption spectrum: a bleaching signal at 477 nm and absorption peaks at 570 nm and above 700 nm which are attributed to the cation radical absorption of HB ( $\tau = 15.46 \mu\text{s}$ ) and the TiO<sub>2</sub> conduction band electrons<sup>7</sup> ( $\tau = 26.2 \mu\text{s}$ ), respectively. This indicates that the electron injection from the excited triplet state of HB in the conduction band of colloidal TiO<sub>2</sub> occurs during and within the laser pulse.

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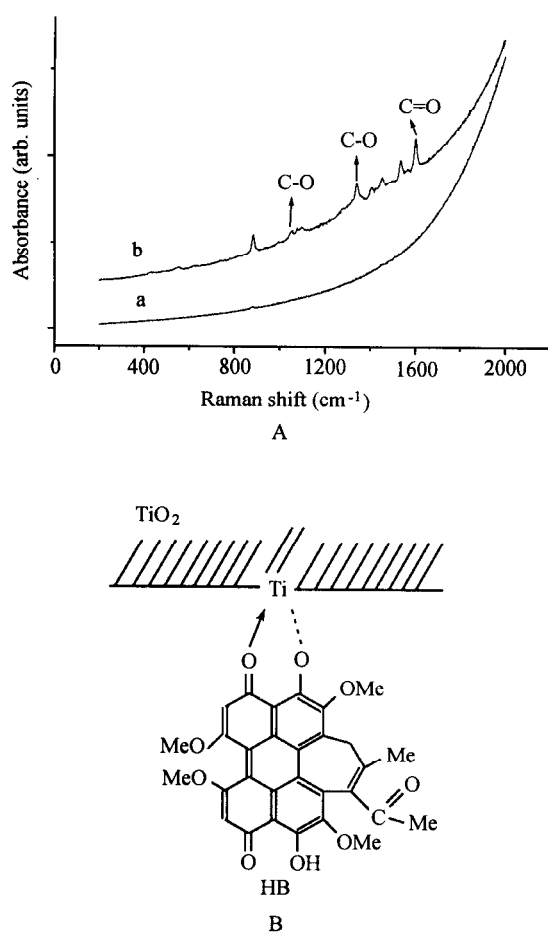
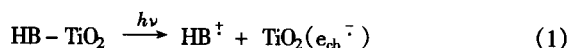


Fig. 1 A: SERS spectra of HB in ethanol in the absence of  $\text{TiO}_2$  (a) and in the presence of  $\text{TiO}_2$  (2 g/L) (b).

B: Schematic illustration of the structure of the surface chelate of HB with  $\text{TiO}_2$ .



In addition, double exponential analysis was used to fit the decay kinetics of 570 nm, finding that except the slow components with  $\tau = 15.46 \mu\text{s}$  (assigned to  $\text{HB}^\dagger$ ). The fast component with  $\tau = 0.7 \mu\text{s}$  is assigned to the quenched triplet absorption of HB because the absorption at 510 nm has a lifetime as  $\tau = 0.7 \mu\text{s}$ . Therefore, the electron injection rate constant is  $K_{\text{ET}} = 1.3 \times 10^6 \text{ s}^{-1}$ .<sup>8,9</sup> The transient absorption of the chelate in the presence of electron acceptor or donor was also examined. The reduction of methylviologen ( $\text{MV}^{2+}$ ) by conduction band electrons of colloidal  $\text{TiO}_2$  has previously been examined

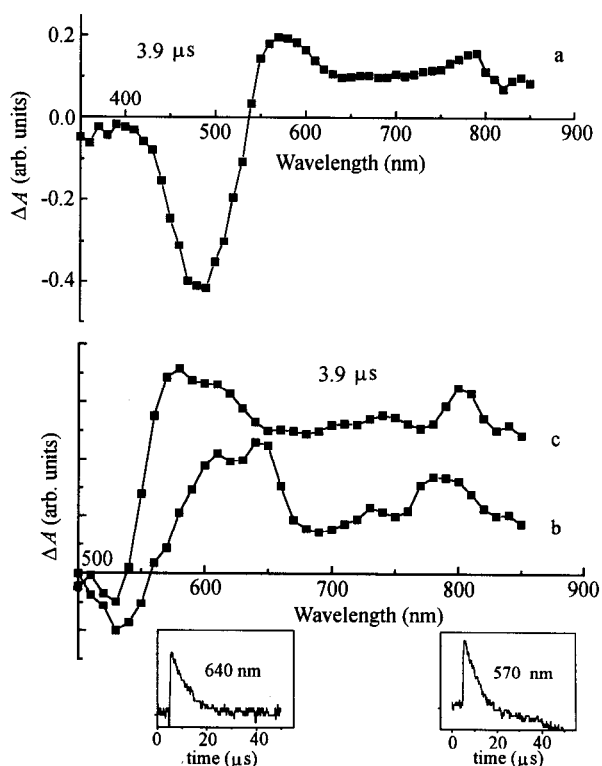
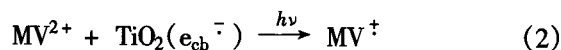
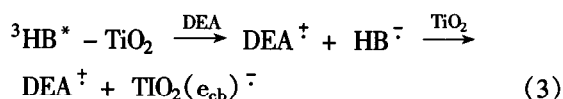
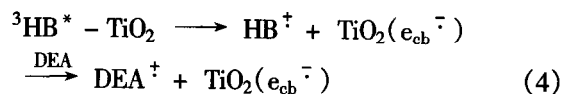


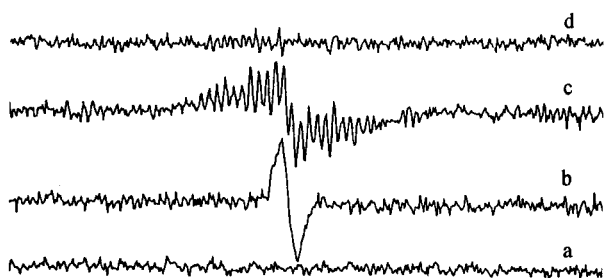
Fig. 2 (a) Transient absorption spectrum upon laser pulse excitation of  $1 \times 10^{-4} \text{ mol/L}$  HB in the presence of  $\text{TiO}_2$  (2 g/L) in ethanol. (b) Be the same with (a) and in the presence of  $\text{MV}^{2+}$  ( $2 \times 10^{-3} \text{ mol/L}$ ) (insert left is a decay file of the transient at 640 nm). (c) Be the same with (a) and in the presence of DEA ( $6 \times 10^{-2} \text{ mol/L}$ ) (insert right is a decay file of the transient at 570 nm).

in great detail.<sup>10</sup> Fig. 2(b) shows the  $\text{MV}^\dagger$  absorption at 640 nm when  $\text{MV}^{2+}$  is added to the chelate in ethanol. Its decay is biphasic: a fast initial component with lifetime of  $9.0 \mu\text{s}$  is followed by a slower decrease with lifetime of  $26.01 \mu\text{s}$ . The former is attributed to  $\text{MV}^\dagger$  and the latter is the cation radical of HB. Due to the existence of reaction (2), the recombination of the conduction band electron with the oxidized chelate is a much slower process, and the lifetime of the cation radical of HB is prolonged. *N,N*-diethylaniline (DEA) acts as an electron donor in the photosensitization process and there exists two possible pathways of electron transfer when DEA is involved in.





Because the products of (3) and (4) are the same, the behavior of the transient absorption should have no difference, as indeed is observed. In Fig. 2(c), the 570-nm absorption decayed rapidly due to the existence of DEA ( $\tau = 6.32 \mu\text{s}$ ); the 780-nm decay is much slower, which could not be observed over the scope of the experimental conditions.



**Fig. 3** EPR spectra of HB/TiO<sub>2</sub> chelate in deaerated ethanol (a) No irradiation; (b) Under laser irradiation at  $\lambda = 532 \text{ nm}$ ; (c) Be the same with (b) and in the presence of  $\text{MV}^{2+}$  ( $2 \times 10^{-3} \text{ mol/L}$ ); (d) Be the same with (b) and in the presence of NaI ( $0.4 \text{ mol/L}$ ). (EPR spectra are recorded using a Bruker Model ESP 300E spectrometer at room temperature ( $20\text{--}25^\circ\text{C}$ ). 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:  $1.0 \times 10^5$ ).

EPR experiments were carried out as a supplementary proof. The EPR signal ofcation radical of HB was observed (Fig. 3b) in the anaerobic chelate under laser irradiation ( $\lambda = 532 \text{ nm}$ ) and it was decreased significantly

with the addition of NaI (Fig. 3d) which is a hole scavenger. In the presence of  $\text{MV}^{2+}$ , the EPR signal intensity of  $\text{HB}^\dagger$  was not changed and along with the irradiation, the EPR signal of  $\text{MV}^+$  was appeared (Fig. 3c).

In addition, self-sensitized photooxidation experiment shows that the photostability of the chelate is even higher than that of the pure HB in ethanol. Together with the discussions above, these results should be important for the chelate in the application of photosensitization and photocatalysis.

## References and notes

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