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Photophysical and photochemical events during the photosensitization of Hypocrellin A on a colloidal CdS semiconductor

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Abstract

UV–visible spectroscopy, fluorescence quenching measurements, and single-photon counting have been employed to study electron transfer from excited Hypocrellin A (HA) into the conduction band of a colloidal CdS semiconductor. It has been determined that HA dye adsorbed on colloidal CdS with an apparent association constant of 940 $(\text{mol/l})^{-1}$, and fluorescence lifetime measurements gave a rate constant of $5.16\times10^{9}\ \text{s}^{-1}$ for the electron transfer process. The transferred electrons could be used to reduce the substrate 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO). In this regard electron paramagnetic resonance spectroscopy was used to study the photoreduction of TEMPO by electrons in the CdS semiconductor. The results suggested that CdS photoreduction efficiency was enhanced by photosensitization of HA in visible region. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hypocrellin A; CdS colloidal semiconductor; Fluorescence quenching; Fluorescence lifetime; EPR; TEMPO; Electron transfer

1. Introduction

During the past two decades, considerable attention has been given to nanometer-sized semiconductor particles [1–5]. Such ultrasmall particles possess a unique catalytic behavior and exhibit size quantization effects, non-linear optical properties and unusual luminescence [6–8]. These properties have been widely employed in light energy conversion [9], chemical transformation [10], and the light-induced decomposition of organic pollutants [11].

It is well known that the energy level of the excited state of a semiconductor increases with a decrease in particle size, leading to a blue shift in the absorption spectrum of the particle. In addition, the separated electron can easily recombine with a hole in the semiconductor to release heat or light before reaching the particle surface. Therefore, efforts have been made to extend the photoresponse of the semiconductor particle across the entire visible spectrum, to retard the recombination of holes and electrons within the semiconductor particle, and to promote heterogeneous electron transfer at the semiconductor surface. These efforts have included surface modification of the semiconductor with organic dyes such as

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Chlorophyll [2], Erythrosin B [12], Eosin [12], phthalocyanines [13], $Ru(bpy)_3^{2-}$ [14], and oxazines [15]. In these systems, dyes adsorbed on semiconductors can transfer electrons into the conduction bands of semiconductors upon absorption of visible light. Dye-induced photosensitization of semiconductors has been the subject of many investigations because of its wide application in electrochemistry and photography [16,17].

The present study utilises the dye Hypocrellin A (HA) [18] as a sensitizer, to investigate the electron transfer from excited HA into the conduction band of a colloid CdS semiconductor. In these experiments, the fluorescence lifetime of the sensitizer HA was varied, as part of an approach to enhancing our understanding of the photosensitization process. In order to demonstrate the feasibility of using the electron transfer process to reduce another substrate, EPR measurements were used to probe the reduction of TEMPO in colloidal CdS.

2. Experimental

2.1. Materials

$CdCl_2$, Na_2S and hexametaphosphate (HMP) were analytical grade reagents. 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) was obtained from Aldrich Chemical Company and Triton X-100 was purchased from FARCO Chemical Company. Both were used without further purification. Redistilled water was used in all experiments.

HA was obtained from the Microbiology Institute of Yunnan Province, People's Republic of China. It was purified by HPLC on an ultrasphere column (Beckman, Palo Alto, CA), eluting with chloroform–methanol (80:20, vol/vol). The purity of HA was >98%. HA was also recrystallized twice from acetone before use, then dispersed in water using Triton X-100 to give a dye to dispersant ratio of 1:1.

2.2. Preparation of colloidal CdS semiconductor

Using vigorous stirring, $CdCl_2$ (3.0 ml, 1.00×10^{-2} M) was added rapidly to a solution (23.5 ml) containing Na_2S (3.0×10^{-5} mol) and HMP stabilizer (5.0×10^{-6} mol), at 0 °C. The average diameter was ~15 nm, the absorption onset for CdS was 510 nm, and the solution pH was 7.0.

2.3. Measurements

Particle size measurements were made using a JEM-100CX transmission electron microscope. Absorption spectra were recorded on a Hitachi U-3200 spectrophotometer, and emission spectra were recorded on a Hitachi F-4500 fluorescence photometer at 20±2 °C. The picosecond laser experiments utilized a Spectra Physics M3800 CW Nd: YAG Laser equipped 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 spectrofluorimeter (EG&G). The photons were detected by a Hamamatsu E3059-00 microchannel plate photomultiplier.

EPR spectra were obtained using a Varian E-109 spectrometer. After purging with purified N_2 for 20 min prior to light exposures, samples were transferred to quartz capillaries for EPR analysis. The EPR spectra were obtained at room temperature (20±2 °C), using a microfrequency of 10 GHz (X-band), and a modulation frequency of 100 kHz. All samples were continuously irradiated.

A 1000 W Br–W lamp was used as the light source in the visible region. The light was passed through a filter containing cooling water to remove UV and infra-red irradiation, then through a lens, and was focused on the sample in a quartz capillary. An irradiation intensity of 400 W/m^2 was measured using a BTY-820 radiometer, and the irradiation time was controlled by an automatic-timing exposure apparatus (Zhujiang-9, Guangzhou Automatic Instrument Factory, China).

3. Results and discussion

3.1. Fluorescence quenching by colloidal CdS

The results in Fig. 1 show the effects of increasing the concentration of CdS colloids on the fluorescence emission spectrum of dye HA. It

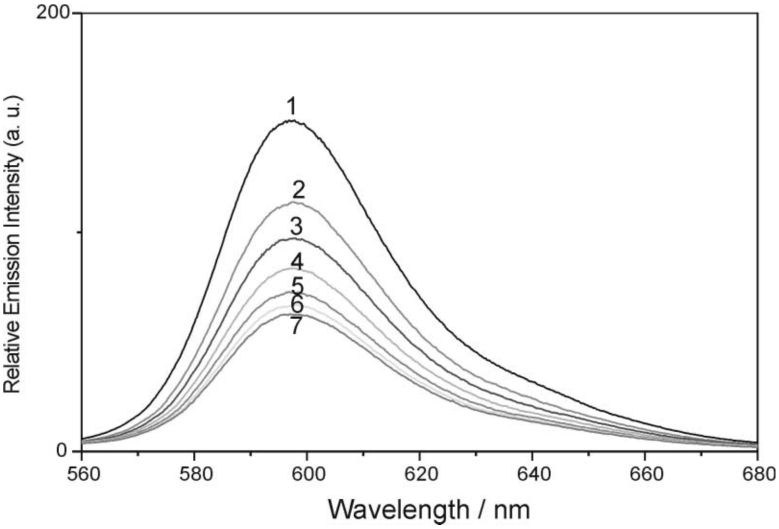

Fig. 1. Fluorescence emission spectra for 1.5×10^{-5} M HA in aqueous solution at CdS concentrations of (1) 0 M, (2) 2.88×10^{-4} M, (3) 4.80×10^{-4} M, (4) 6.72×10^{-4} M, (5) 8.64×10^{-4} M, (6) 10.08×10^{-4} M, (7) 11.04×10^{-4} M. $\lambda_{ex}=470$ nm.

is clear that the addition of CdS quenched the fluorescence of HA. This type of quenching behavior is similar to that of other organic dyes used for the sensitization of large-bandgap semiconductors [12], and is attributed to electron transfer from the excited singlet state of the dye to the conduction band of CdS. The oxidation potential for HA*(S1), which is −1.55 V [versus normal hydrogen electrode (NHE)] [19], and the energy level of the CdS conduction band, which is near −1.00 V (versus NHE) [20], provide favorable conditions for charge transfer.

The participation of CdS in the quenching process was further analyzed by considering the equilibrium between adsorbed and unabsorbed sensitizer molecules with an apparent association constant of K_{app} [Eq. (1)]:

$$\mathrm{HA} + \mathrm{CdS} \overset{K_{app}}{\leftrightarrow} [\mathrm{HA} \ldots \mathrm{CdS}] \tag{1}$$

In this regard, the observed quantum yield, $\phi_{f(obsd)}$, for the sensitizer in a colloidal CdS suspension can be related to the fluorescence yields of unabsorbed (ϕ_f^0) and adsorbed sensitizer molecules (ϕ_f') by Eq. (2) [3,4]. Here, α is the association degree of sensitizer on the surface of CdS. At relatively high CdS concentrations, α corresponds to $[K_{app}[\mathrm{CdS}]/(1+K_{app}[\mathrm{CdS}])]$ and Eq. (2) can be simplified to give Eq. (3).

$$\phi_{f(obsd)} = (1-\alpha)\phi_f^0 + \alpha\phi_f' \tag{2}$$

$$\frac{1}{\phi_f^0 - \phi_{f(obsd)}} = \frac{1}{\phi_f^0 - \phi_f'} + \frac{1}{(\phi_f^0 - \phi_f')K_{app}[\mathrm{CdS}]} \tag{3}$$

If the observed quenching were due to the association of the dye with colloidal CdS, one would expect a linear dependence of $1/(\phi_f^0 - \phi_{f(obsd)})$ on the reciprocal of the CdS colloid concentration, with an intercept of $1/(\phi_f^0 - \phi_f')$ and a slope of $1/(\phi_f^0 - \phi_f')K_{app}$. Indeed, the linearity of the double-reciprocal plot shown in Fig. 2 confirmed this behavior. The value of K_{app} determined from this plot was 940 $(\mathrm{mol/l})^{-1}$, suggesting that there was a complex interaction between HA and CdS.

3.2. Fluorescence lifetime measurements

To further analyse the fluorescence quenching process, fluorescence lifetime measurements were made. In this regard, results of prior studies have shown that sensitizer molecules had a significantly shorter singlet state lifetime when adsorbed on a TiO_2 surface than in homogeneous solution, and this decrease in lifetime was associated with a

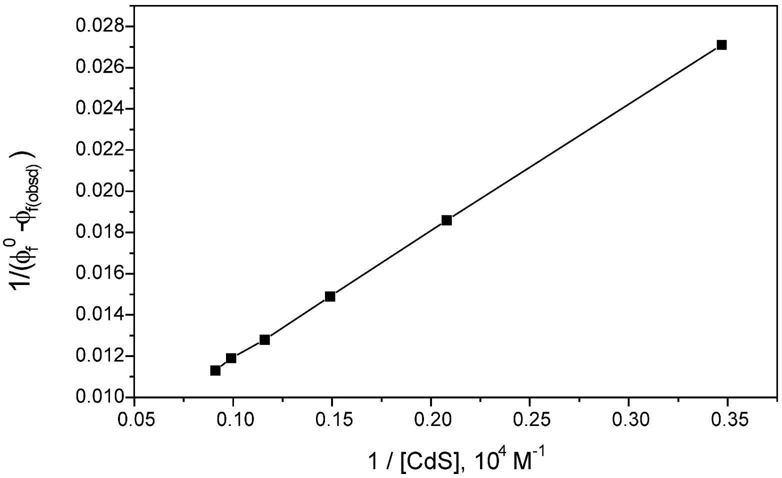

Fig. 2. Dependence of $(\phi_f^0 - \phi_{f(obsd)})^{-1}$ on the reciprocal concentration of CdS.

charge transfer process [3,4,21]. In the absence of CdS, the fluorescence behavior of HA was characterised by single-exponential decay, where $(F(t) = A \exp(-t/\tau))$, with a lifetime of 1.07 ns. However, in a CdS suspension, the fluorescence emission of HA was characterised by double-exponential decay, where $(F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2))$. The fluorescence decay behavior for HA in a 5.20×10^{-5} M CdS suspension is shown in Fig. 3 (curve a). The graph shows a transient species with a much shorter lifetime and one with a lifetime similar to that of HA alone. Computerised analysis of the decay data gave a lifetime of 0.159 ns for the shorter-lived species, which was assigned to the adsorbed dye. The lifetime of the longer-lived species was 0.886 ns, which was close to the lifetime of HA in CdS-free solution (1.07 ns).

As discussed in previous work [3,4,21], if the observed decrease in fluorescence lifetime were due entirely to the electron transfer process and other radiation and nonradiation decay processes arise from HA on colloidal CdS occurred at the same

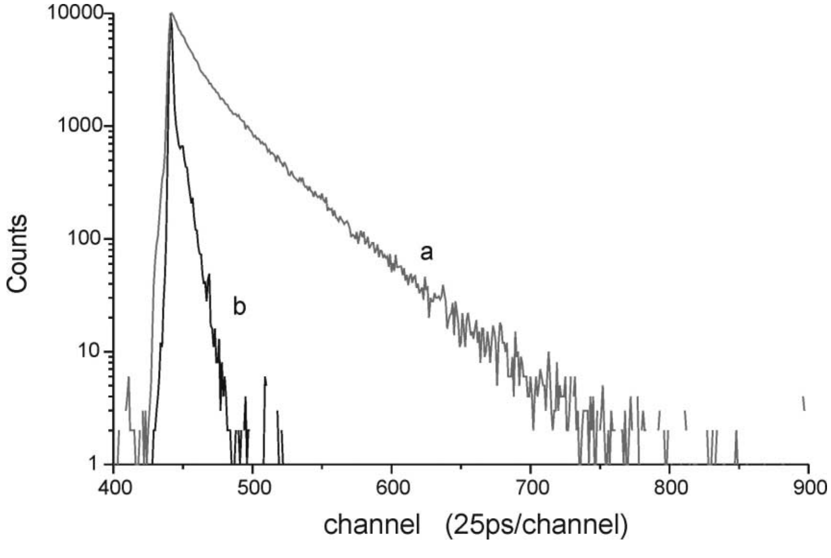

Fig. 3. Fluorescence decay and instrument response curves for 2.00×10^{-5} M HA in 5.20×10^{-5} M CdS/H_2O suspension. $\lambda_{ex} = 580$ nm and $\lambda_{emis} = 600$ nm. Exponential decay parameters: $A_1 = 0.743$, $\tau_1 = 0.159$ ns, $A_2 = 0.257$, $\tau_2 = 0.886$ ns, and reduced $\chi^2 = 1.313$.

rates as in neat solvent, the observed lifetimes can be expressed as Eq. (4) [3,4,21].

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

where τ and τ_{ads} are the lifetimes for the sensitizer in aqueous solution and adsorbed on the CdS surface, and K_{et} is the specific rate for the charge transfer process from the excited singlet state of HA to conduction band of the CdS semiconductor. The results obtained from the use of this equation are summarized in Table 1.

3.3. The sensitized photoreduction of TEMPO

TEMPO, a stable free radical, was used to probe the interfacial charge-transfer process in our colloidal semiconductor system because it can be reduced after accepting a proton and an electron [22]. The reduction product from TEMPO cannot be detected via EPR because it does not have an unpaired electron. The concentration of TEMPO is direct proportion to the intensity of the middle peak of its EPR spectra. As shown in Fig. 4, the relative intensity of the EPR signal of TEMPO changed with irradiation time. The rate of decrease in the intensity of TEMPO in an HA–CdS system (line 3) was faster than that in CdS alone (line 2); however, in the absence of CdS, HA (3.20×10^{-6} M) did not cause a reduction of TEMPO (line 1). It is clear that in the presence of visible light, the sensitization of HA improved the reduction efficiency of CdS.

The mechanism for the sensitized reduction of TEMPO can be explained with the aid of the energy diagram in Fig. 5. The absorption of CdS sol is limited in the visible region, and only a small percentage of electrons required to reduce TEMPO in the conduction band could come from the valance band of CdS following excitation (line 2, in Fig. 4). However, when the excited HA species is efficiently connected to CdS particles, it is able to transfer electrons to the conduction band of the colloidal semiconductor, increasing the electron concentration in the conduction band of the CdS semiconductor and improving the reduction efficiency of CdS (line 3, Fig. 4).

Table 1
Data from fluorescence lifetime measurements at [HA] = 2.0×10^{-5} M, [CdS] = 5.2×10^{-5} M^{a}

Samples	τ_1 (ns)	A_1	τ_2 (ns)	A_2	χ^2	K_{et} (s^{-1})
HA	1.07	1			1.250	
HA–CdS	0.159	0.743	0.886	0.257	1.313	5.16×Á10^9

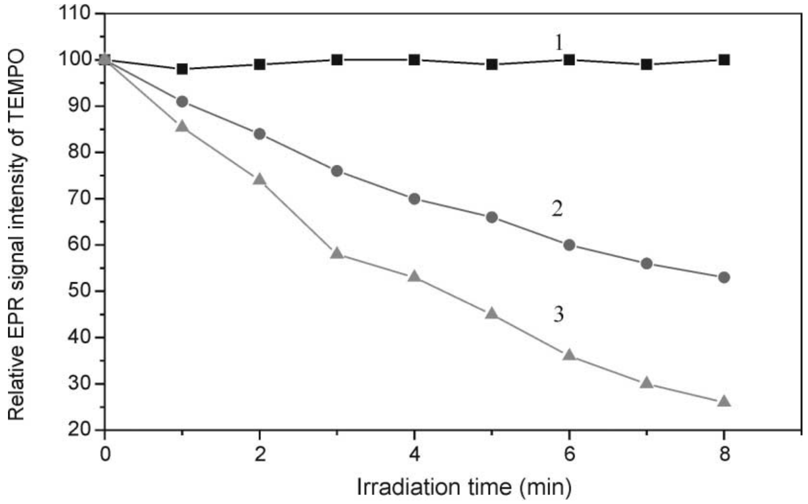

Fig. 4. The relative EPR signal intensity of TEMPO vs. irradiation time. 1: [CdS] = 0 M, [HA] = 3.20×10^{-6} M; 2: [CdS] = 4.00×10^{-4} M, [HA] = 0 M; 3: [CdS] = 4.00×10^{-4} M, [HA] = 3.20×10^{-6} M. Inset: EPR spectrum for TEMPO (α_N = 16.3G, g = 2.0056). A 1000 W Br–W lamp was used as the light source.

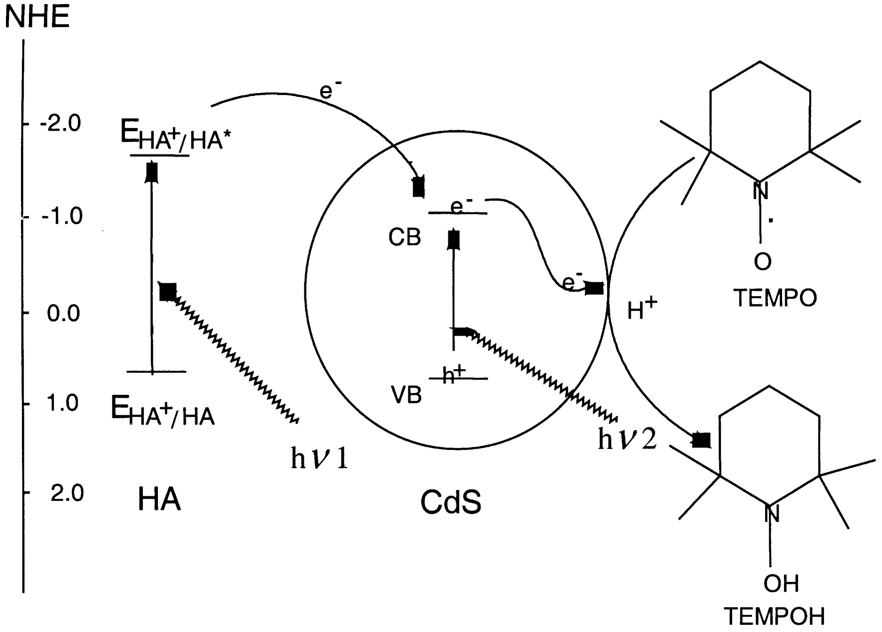

Fig. 5. The possible pathway for the light-induced electron transfer process, and schematic diagram describing the CB and VB levels for CdS and electron donating energy levels for HA.

4. Conclusions

The fluorescence emission of the sensitising dye HA can be efficiently quenched by CdS colloids, owing to electron transfer from the excited singlet state of HA to the conduction band of colloidal CdS. Fluorescence lifetime measurements can be used to determine the electron transfer rate constant (K_{et}) for this process, and EPR measurements proved useful in confirming an electron transfer mechanism.

Acknowledgements

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