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The photoinduced electron transfer between hypocrellins and colloidal semiconductors

1. Kinetics of photosensitized reduction in a colloidal CdS system with Hypocrellin A as a sensitizer

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Abstract

The apparent association constant (k_{app}) between Hypocrellin A(HA) and CdS sol was determined by the fluorescence quenching method to be 1400 M^{-1}. TEMPO (2,2,6,6-tetramethyl-1-piperdinyloxy), a stable free radical, was used in the kinetic study of the reduction reaction taking place on the surface of a CdS colloidal semiconductor because after TEMPO accepts an electron and a proton, its signal would be lost. Kinetics of the reaction was determined by the electron paramagnetic resonance (EPR) method. The reaction order of TEMPO is different from that of the spin elimination reaction in a hematoporphyrin (HP) and HA system and the difference may be due to the adsorption effect of colloidal particles. When HA was added, the rate of EPR increased greatly. By comparing rate constants, the HA–CdS system was revealed to be 350 times more efficient than CdS sol in the photoreduction of TEMPO under visible light. It suggests that HA can be used as an efficient sensitizer of a colloidal semiconductor in the application of solar energy.

Keywords: Colloidal semiconductor; CdS; Hypocrellin A; TEMPO; K_{app}; rate constant; EPR

1. Introduction

When a semiconductor absorbs light with energy equal to or greater than its bandgap, electron–hole pairs are generated; the photo electron can transfer to an adsorbed species on the surface without recombining with the hole. The colloidal semiconductor has characteristics both of the semiconductor and of the colloid. As a colloid, it is a diffused heterogeneous material. Its surface/volume ratio lies between that of a bulk semiconductor and that of a molecule. Compared to the bulk semiconductor, it can more efficiently absorb light and avoid electron–hole recombination [1]. Therefore, colloidal semiconductors have been widely investigated in the conversion of solar energy [2] and environmental clean up [3]. Although numerous investigations have been conducted on photophysical and photochemical properties of semiconductor sols [4], the kinetic equation of the reaction taken place on their surface has not been reported. We established such an equation using the electron paramagnetic resonance (EPR) method and revealed its special features.

EPR is a favorable method in the study of kinetics because the EPR can measure the concentration change of spin materials at any time without interfering with the reaction. So when an appropriate spin material is selected, the photoelectrochemistry reaction of colloidal semiconductor can be investigated conveniently. Most colloidal semiconductors cannot carry out a photoelectrochemical reaction efficiently in visible light because of their large bandgap. The investigation of extending the colloidal semiconductor's absorption range to visible light has been carried out intensively [5]. One of the attractive techniques is attachment of photoactive molecules with high extinction coefficients to the semiconductor surface [6]. By comparing rate constants of a CdS sol and CdS–HA (HA, Hypocrellin A) complex, we proved HA, a kind of photosensitizer with a broad absorption in visible light, can improve photochemical efficiency of CdS in visible light intensively.

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2. Experimental details

2.1. Materials

$CdCl_2$, Na_2S, and hexametaphosphate (HMP) were of analytical grades. 2,2,6,6-Tetramethyl-1-piperdinyloxy (TEMPO) was obtained from Aldrich Chemical Company. Triton X-100 was purchased from FARCO Chemical Company. They are all 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 recrystallized twice in acetone and dispersed in water using Triton X-100; occupancy number, 1:1

2.2. Preparation of CdS sols

1.5 ml of 1.00×10^{-2} M $CdCl_2$ solution was added rapidly under vigorous stirring to 23.5 ml solution containing 1.50×10^{-5} mol Na_2S and 2.50×10^{-6} mol HMP as the stabilizer of sol. Both solutions were at 0 °C. The absorption onset of CdS was 510 nm and particles' mean diameter was 6 nm, pH 7.0

2.3. Spectra and irradiation

The EPR spectrum was obtained using a Varian E-109 spectrometer operating at room temperature (22 ± 1 °C) (X-band, microfrequency, 9.5 GHz, modulation frequency 100 KHz). Samples were injected into quartz capillaries for EPR analysis. When necessary, samples were placed in front of a visible light source (1000 W Br–W lamp) which was filtered by UV and IR filters and focused by a light-convergent lens by illumination outside the microwave cavity (about 400 W m^{-2}).

The fluorescence intensities were measured with a Hitachi-850 fluorometer at 22 ± 1 °C.

3. Results and discussions

3.1. Fluorescence quenching by colloidal CdS

Addition of CdS to a solution of HA resulted in the quenching of its fluorescence emission. Fig. 1 shows the effects of increasing the concentration of CdS colloids on the fluorescence emission of HA. This quenching behavior is attributed to the electron injection from excited HA to the conductor band (CB) of CdS (reaction (1)), as previously reported on the fluorescence quenching of dyes such as erythrosin and Chlorophyllin by TiO_2 [7].

$$HA^*(s1) + CdS \rightarrow HA^+ + {}^{\cdot}CdS(e) \qquad (1)$$

The oxidation potential of $HA^*(s1)$ is −1.56 V (vs. NHE) (unpublished result) and the energy level of CB of CdS lies around −1.0 V [8] (vs. NHE). This provides favorable energetics for such a charge injection process.

The apparent association constant (k_{app}) between CdS particles and HA can be determined by the fluorescence quenching behavior. We assume there is a equilibrium between adsorbed and unadsorbed HA:

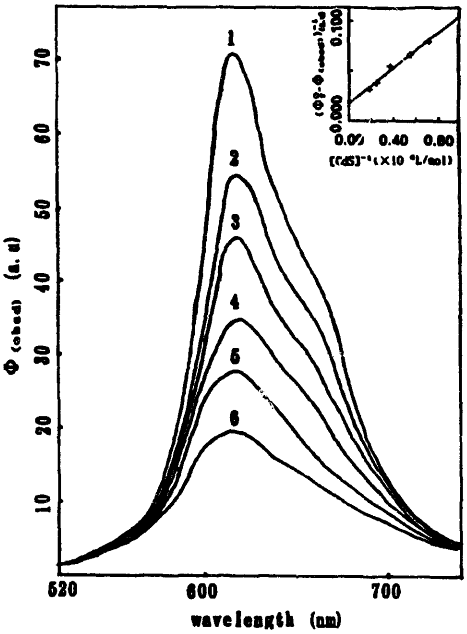
$$CdS + HA \overset{k_{app}}{\rightleftarrows} CdS - HA \qquad (2)$$

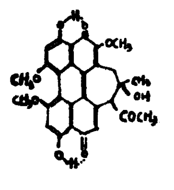
At relatively high CdS concentration, if the quenching is due to the association of CdS with HA, the observed quantum $\Phi_{(obsd)}$ of the sensitizer in a colloidal CdS suspension can be expressed as [6]:

$$(\Phi^0_f - \Phi_{(obsd)})^{-1} = (\Phi^0_f - \Phi'_f)^{-1} + \{k_{app}(\Phi^0_f - \Phi'_f)[CdS]\}^{-1} \qquad (3)$$

where Φ^0_f and Φ'_f are fluorescence yields of unadsorbed and adsorbed molecules of the sensitizer, respectively.

There will be a linear dependence of $(\Phi^0_f - \Phi_{(obsd)})^{-1}$ on $1/[CdS]$ if the assumption above is correct. This is confirmed by the inset of Fig. 1. By Eq. (3), the values of k_{app} can be determined to be 1400 M^{-1}. It should be noticed that the right part of Eq. (2) is not a simple complex made up of HA and CdS but a complex in which the HA can transfer its electron from an excited singlet state to CdS. The k_{app} between HA and CdS is lower than that between 9 AC and TiO_2 (6400 M^{-1}) [6]. There are several reasons: TiO_2 can absorb solute through oxygen atom on its surface [9] while CdS does not have this advantage; HA is coated by Triton X-100 and the hydrophilic groups of HA are the only parts of molecule





HA

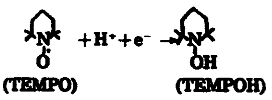
Fig. 1. Fluorescence emission spectra of 2.00×10^{-5} mol l^{-1} HA in aqeous solution at various concentrations of CdS: (1) 0 mol l^{-1}, (2) 1.40×10^{-4} mol l^{-1}; (3) 1.82×10^{-4} mol l^{-1}; (4) 2.73×10^{-4} mol l^{-1}; (5) 4.15×10^{-4} mol l^{-1}; (6) 5.45×10^{-4} mol l^{-1}. The excitation wavelength was at 470 nm. The inset shows the dependences of $(\Phi^0_f - \Phi_{(obsd)})^{-1}$ on the reciprocal concentration of CdS.

which can associate with CdS, limiting the possibility of electron transfer between the associated excited HA and CdS. These factors contribute to the low k_{app} between CdS and HA.

The absorption spectrum of HA did not change after CdS was added. This is different from the reported results that the spectra of the sensitizer were changed by added colloidal semiconductors. The reason for this may be the existence of a quick equilibrium in the association between coated HA and CdS particles.

3.2. The kinetics equation of photoreduction

TEMPO is a stable free radical which can be degraded after accepting a proton and an electron [10] (Eq. (4)).



(4)

The production of TEMPO cannot be detected in EPR because it does not have an unpaired electron. The concentration of TEMPO is in direct proportion to the height of the middle peak of its EPR spectra. The initial rate of reaction can be expressed as:

$$V_o = -d[TEMPO]/dt = k[CdS]^m[TEMPO]^n \qquad (5)$$

where k is the rate constant, and m and n are reaction orders. When keeping [CdS] constant, one would expect a linear dependence of $\lg(V_o)$ on lg[TEMPO] and the slope is n, and vice versa. This was confirmed by the plots in Fig. 2(a) and Fig. 2(b). We can determine $m = k = 1.006 \approx 1$ and $n = k_2 = 0.03 \approx 0$. Besides this, we should expect a linear dependence of $\lg(t_{1/2})$ on lg[TEMPO]. This is confirmed by Fig. 2(c) and the slope is $1-n$. The plot's slope is 1.02 then $n = -0.02 \approx 0$

The change in trend of C/C_o depending on $\lg(t)$ of some common reaction orders was plotted [11] as a Powell plot in Fig. 2(d). In a plot of C/C_o vs. lg$t$, any reaction of the same order is of the same figure but different A value. A plot of $[TEMPO]/[TEMPO]_0$ versus lg$t$ was made (Fig. 2(e)). Superimposing Fig. 2(e) on a Powell plot and letting their abscissae lie in the same line, we will find the plot b fits curve a on the Powell plot perfectly. This means the reaction order of TEMPO is zero.

When HA was added, n in Eq. (5) did not change. By the initial-rate method (line 2 of Fig. 2(a)), $n = 0$, and by the half-life method (Fig. 2(c), line 2), $n = 0$. Plot a fits curve a on the Powell plot, meaning $n = 0$.

In one word, the degradation of spin is a zero-order reaction for TEMPO and a first-order reaction for CdS or a CdS–HA complex, although the complex is in fast equilibrium.

So when HA is added, the photodegradation of TEMPO can be expressed as:

$$\begin{aligned} V &= -d[TEMPO]/dt \\ &= \mathrm{k}_1([CdS] - [CdS-HA]) + k_2[CdS-HA] \qquad (6) \end{aligned}$$

where k_1 and k_2 are the rate constants of CdS and CdS–HA, respectively. Because the reaction order of TEMPO is zero, [TEMPO] is omitted. At relatively high CdS concentration and low k_{app}, [CdS–HA] can be equated to k_{app}[CdS][HA], and Eq. (6) can be derived,

$$V = k_1[CdS] + (k_2 - k_1)K_{app}[CdS][HA] \qquad (7)$$

If the assumption is correct, one would expect a linear dependence of V on the [CdS] (or [HA]) when [HA] (or [CdS]) was kept unchanged. Indeed the linearities of V versus [HA] of the inset of Fig. 3 and V versus [CdS] in Fig. 4 confirm Eq. (7).

Based on the kinetics equation determined, we can conclude that the control factor of the reaction is how fast CdS or the CdS–HA complex can offer electrons to TEMPO. There is always enough TEMPO available to be reduced on the particles' surface. But in the degradation of TEMPO in hematoporphyrin (HP) [12] and HA [10] systems, there are first-order reactions for TEMPO even if it is in the same range or of higher concentration. That is to say, when [TEMPO] was reduced, the reaction rate of the HP or HA system would slow down for the limitation of TEMPO. While in a colloidal system, particles can adsorb some TEMPO on its surface because of the large interface between the particles and solution, so when the concentration of TEMPO changed within a range the reaction rate would not drop. But the adsorption effect of a colloidal particle is not very tight and, because particles move fast in the solution, TEMPO's reduced production can be exchanged by TEMPO quickly, and the reaction would not be deactivated like most of the reactions on a semiconductor electrode.

Due to this colloid character, the reaction taking place on the surface of the colloid can be more quick and thorough. In our experiment, the spin degradation rate almost does not change when [TEMPO] was reduced from 2.22×10^{-5} M to 3.00×10^{-6} M.

3.3. The kinetics rate constant

According to Eq. (7), in the absence of HA there will be linear dependence of V on [CdS] and the slope is k_1. This is confirmed by straight line b of Fig. 4. The k_1 determined by the method is $2.40 \pm 0.27 \times 10^{-4}$ s^{-1}.

When [CdS] was kept constant, the degradation of TEMPO became faster. When [HA] was increased (Fig. 3), although HA did not cause the degradation alone in this experiment conditions. According to Eq. (7) the degradation rate will linearly depend on [HA] with the slope equal to $(k_2 - k_1)k_{app}$[CdS] and the intercept equals k_1 [CdS]. The linearity is confirmed by the inset of Fig. 3. Values of k_2 and k_1 determined from this plot were 8.30×10^{-2} s^{-1} and 2.10×10^{-4} s^{-1} respectively. The k_1 matched well with the value of $2.40 \pm 0.27 \times 10^{-4}$ s^{-1} determined independently.

When [HA] was kept constant (Fig. 4, plot a), TEMPO's degradation rate linearly depended on [CdS] and this straight line's slope is 1.01×10^{-3} s^{-1}. This linearity matched with

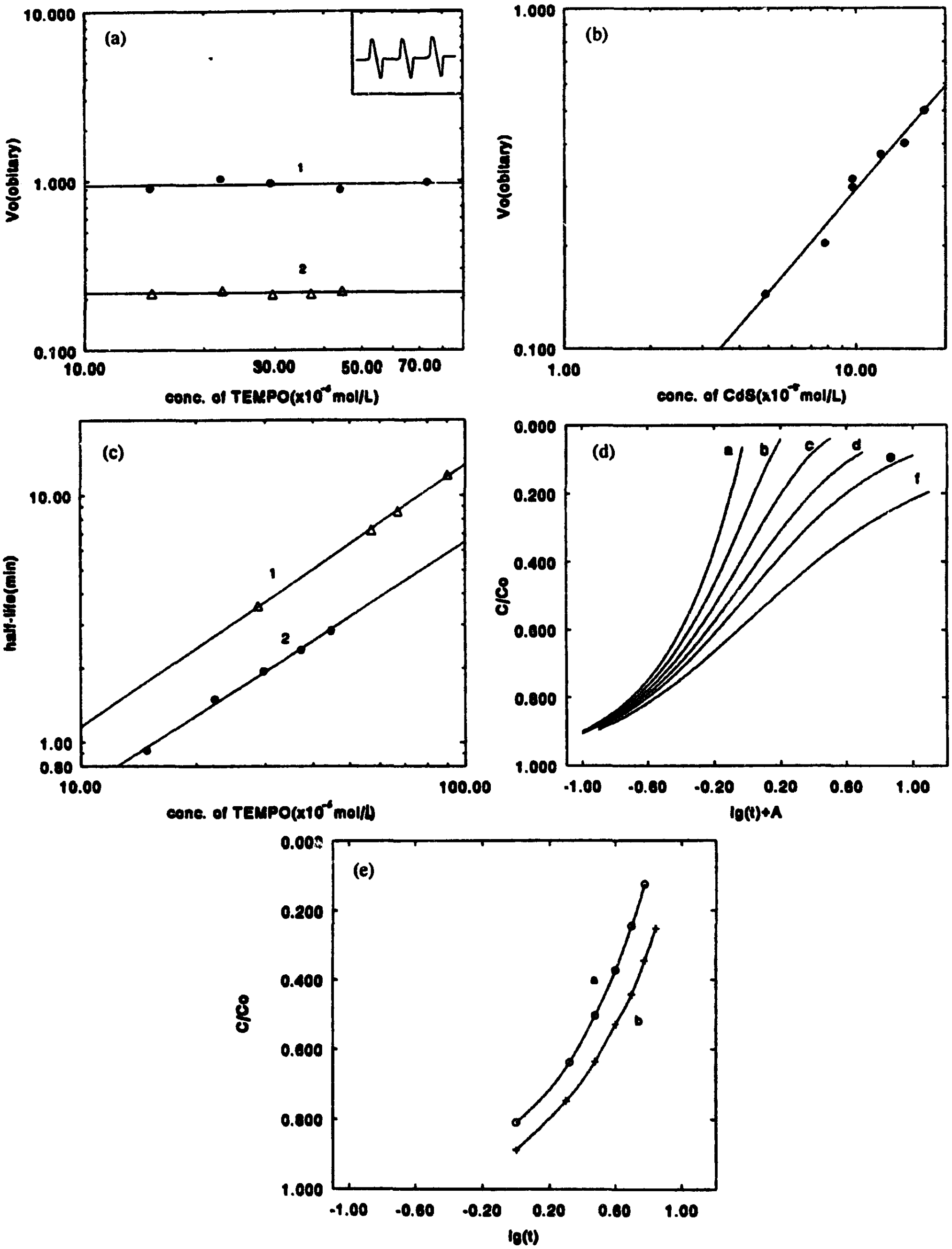


Fig. 2. Initial rate (V_0) of degradation of TEMPO vs. the concentration of TEMPO: (a-1) [CdS] 9.76×10^{-5} mol l^{-1}, [HA] 7.32×10^{-6} mol l^{-1}; (a-2) [CdS] 1.45×10^{-4} mol l^{-1}. Inset: a typical EPR spctrum of TEMPO ($a_N = 16.3$ G; $g = 2.0056$). Spectrometer settings: microwave power, 5 mW; modulation amplitude, 10 G; time constant, 0.128 s; scan rate, 4 min. (b) The initial rate of degradation vs. the concentration of CdS. Initial concentration of TEMPO is 2.22×10^{-5} mol l^{-1}. (c) Dependence of half-life on the concentration of TEMPO: (c-1) [CdS] 9.76×10^{-5} mol l^{-1}; (c-2) [CdS] 9.76×10^{-5} mol l^{-1}, [HA] 2.20×10^{-6} mol l^{-1}. See the text for details. (d) Powell plot dependence of C/C_0 on $\lg(t)+A$. C/C_0 is how many portions of reactant is left, C_0 is the reactant's initial concentration, $\lg(t)$ is the logarithm of reaction time, A is a constant for each reaction. Curves a–f represent the dependence of C/C_0 on $\lg(t)$ of some common orders of reaction: a, zero order; b, one-half order; c, first order; d, 3/2 order; e, second order; f, third order. (e) C/C_0 of TEMPO vs. $\lg(t)$. C/C_0, how many portions of TEMPO was left; t, the irridation time (min). See text for details.

Eq. (7), and according to this equation the slope is $k_1+(k_2-k_1)k_{app}[\mathrm{HA}]$. Based on values determined above, the slope was calculated to be 1.09×10^{-3} s^{-1} which matched well with the value measured. The lines' intercept is zero, this confirms that HA will not reduce TEMPO in this condition without CdS.

Because TEMPO's degradation rate depends on how fast CdS or the CdS–HA complex can offer electrons, we found

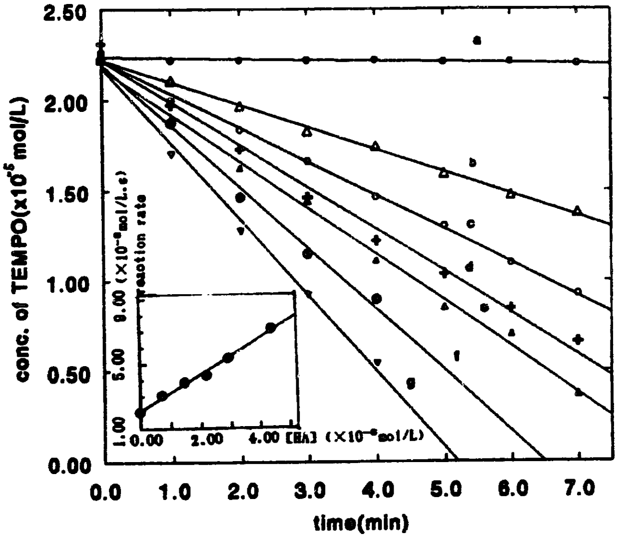


Fig. 3. Concentration of TEMPO vs. irridation time. [CdS]: a, 0 mol l^{-1}; b–g, 9.76 × 10^{-5} mol l^{-1}. [HA]: a, 4.39 × 10^{-6} mol l^{-1}; b, 0 mol l^{-1}; c, 7.32 × 10^{-7} mol l^{-1}; d, 1.46 × 10^{-6} mol l^{-1}; e, 2.20 × 10^{-6} mol l^{-1}; f, 2.93 × 10^{-4} mol l^{-1}; g, 4.39 × 10^{-6} mol l^{-1}. Inset: the relationship between degradation rate and concentration of HA, when [CdS] is 9.76 × 10^{-4} mol l^{-1}.

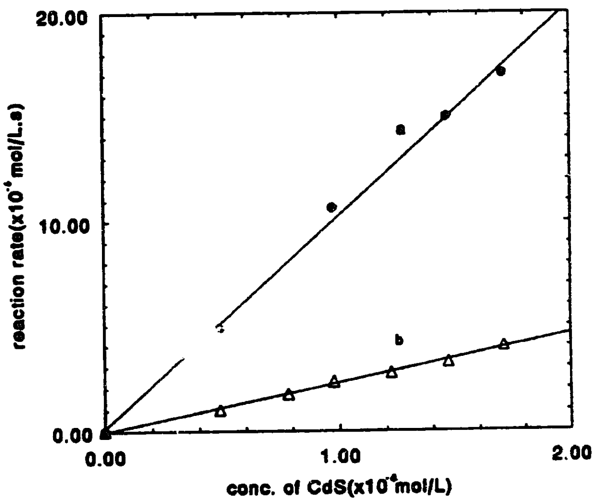


Fig. 4. Dependence of degradation rate on the concentration of CdS. The initial concentration of TEMPO is 2.22 × 10^{-5} mol l^{-1}. a, [HA] 7.32 × 10^{-6} mol l^{-1}; b, without HA.

the CdS–HA complex is at about 350 times more efficient in offering electrons than the CdS colloid based on k_2 and k_1 determined above.

The irradiation we used was only visible light but the absorption of CdS in this range is limited and it has no absorption above 510 nm (Fig. 5). Because HA has high extinction coefficients in visible light and high quantum efficiency, the CdS–HA complex can utilize more light and more efficiently. Besides this, almost all electron–hole pairs are generated in the bulk of particles, some separated electrons may recombine with holes to release heat or light before reaching the surface. But electrons which transfer from excited HA do not need such a journey. So HA may be more efficient than the CdS–HA complex in offering electrons.

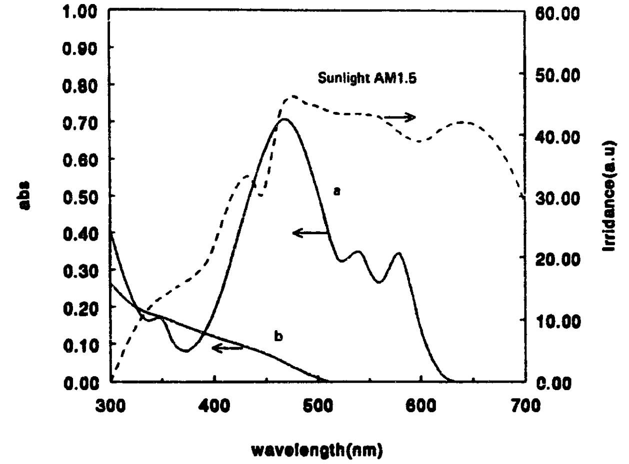


Fig. 5. The solar irridation spectrum and absorption spectra of HA and CdS. a, 3.00 × 10^{-5} mol l^{-1} HA, (reference water) dispersed in aqueous by Triton X-100 occupancy number 1:1. b, 3.00 × 10^{-4} mol l^{-1} CdS colloid, stablized by HMP 5.00 × 10^{-5} mol l^{-1} (reference 0.50 × 10^{-5} mol l^{-1} HMP solution).

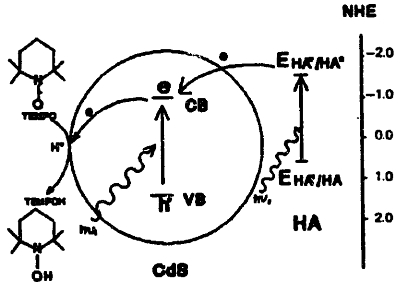


Fig. 6. The possible pathway of photoinduced electron transfer with a schematic diagram describing the CB and VB levels for CdS and electron donating energy levels for HA. See text for details.

The possible pathway of electron transfer from HA to CdS is shown in Fig. 6. When HA was excited, it reached s1*. If the excited HA connects CdS particles efficiently, the electron can transfer to the conductor band (CB) of the colloidal semiconductor. A small percentage of electrons in the CB came from the VB (valance band) of CdS when CdS was excited. The electrons in CB can reduce TEMPO adsorbed by CdS particles.

Most of the solar irradiation is in the visible light range (Fig. 5). Because of the restriction of absorption, a large bandgap semiconductor cannot utilize sunlight efficiently. But when an appropriate sensitizer is used, the situation would improve. The sensitizer's concentration can be very low (10^{-6} M in this article); in such a low concentration, HA could not reduce TEMPO directly, but HA can improve the photo-reduction efficiency of CdS greatly. This implies this is an economic association to make highly efficient photochemical materials.

4. Conclusion

In this article, EPR was used to determine the kinetics equation of degradation of TEMPO on the surface of colloidal semiconductors. A new kind of sensitizer (HA) which can assist CdS sol to utilize visible light more efficiently was reported and their k_{app} was determined for the first time. We established a method to measure the rate constants of reaction taking place on the surface of colloidal particles of a semiconductor–sensitizer complex and determined the latter is more photoreduction active in visible light.

References

[1] Arnim Henglein, *Top. Curr. Chem.*, *143* (1988) 113.

[2] Prashant V. Kamat and Nada M. Dimitrijevic, *Sol. Energy*, *44* (2) (1990) 83.

[3] (a) Amy L. Linsebigler, Guangquan Lu and John T. Yates, Jr., *Chem. Rev.*, *95* (1995) 735. (b) K. Tennakone, C.T.K. Tilakaratne and I.R.M. Kottegoda, *J. Photochem. Photobiol. A: Chem.*, *87* (1995) 177.

[4] Anders Hangfedlt and Michael Grätzel, *Chem. Rev.*, *95* (1995) 49, and references cited therein.

[5] A.J. McEvoy and M. Gratzel, *Solar Energy Mater. Solid Cells*, *32* (1994) 221.

[6] Prshamt V. Kamat, *J. Phys. Chem.*, *93* (1989) 859.

[7] (a) Prshamt V. Kamat and Marye Anne Fox, *Chem. Phys. Lett.*, *102* (1983) 379. (b) Prshamt V. Kamat, Jean-Paul Chavuet and Richard W. Fessenden, *J. Phys. Chem.*, *90* (1986) 1389.

[8] R. Rossetti and L. Brus, *J. Phys. Chem.*, *86* (1982) 4470.

[9] J.H. Fendler, *J. Phys. Chem.*, *89* (1985) 2730.

[10] Wang Nenghui and Zhang Zhiyi, *J. Photochem. Photobiol. B: Biol.*, *14* (1992) 207

[11] Ira N. Leveine, *Physical Chemistry*, 2nd edn., McGraw-Hill, New York, 1983.

[12] J. Moan, *Acta Chem. Scand. B*, *34* (1980) 519.