Photosensitization of TiO_2 semiconductor with porphyrin

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Abstract

Zn-tetrasulfophenylporphyin (ZnTSPP), stable colloidal TiO_2 and a transparent microporous TiO_2 electrode have been prepared. The interaction of ZnTSPP with colloidal TiO_2 was studied by absorption and fluorescence spectroscopy, the apparent association constant for the association between ZnTSPP and TiO_2 nanoparticles is about 1.6×10^4 M^{-1}. ZnTSPP adsorbed on colloidal TiO_2 can participate in the sensitization process by injecting electrons from its excited states into the conduction band of TiO_2. Upon excitation of its absorption band, 90% of the fluorescence emission of ZnTSPP could be quenched by colloidal TiO_2, and the maximum of incident photon to current efficiency is 51.3% at 427 nm with a 10 μm thick TiO_2 film sensitised by ZnTSPP.　　© 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Sensitization of large band-gap semiconductor electrode with organic dye molecules has been a field of extensive research over past decades due to its potential applications in solar energy conversion [1,2]. In the configuration, organic dyes deposited on a semiconductor electrode surface was used to absorb incident light. Light absorption of the dye was followed by an electron injection from the excited state of the dye into the conduction band of the semiconductor. The remaining positive hole was scavenged by a redox couple in solution. As long as less than a monolayer of dye molecules were coated on the surface, high quantum yields for electron transfer process was observed. If the degree of coating was increased, the quantum yields decreased because a large fraction of the dye molecules have no direct contact with the substrate [3]. Therefore, only one layer organic dye was used to sensitize semiconductor electrode in most of the previous work.

2. Experimental

ZnTSPP was synthesised by Institute of Photographic Chemistry, Academia Sinica, whose molecular structure is shown in Fig. 1.

The absorption and fluorescence spectra were performed at room temperature in quartz cells (1 cm optical pathlength). In a typical experiment, small aliquots of 1×10^{-2} M TiO_2 colloidal solution was added with a micropipette to 2 ml of a 1.3×10^{-6} M solution of ZnTSPP.

TiO_2 colloidal solution and TiO_2, ZnTSPP/TiO_2 electrode were prepared by a similar procedure to that described in paper [4,5]. The diameter of TiO_2 particles on the TiO_2 electrode surface is about 50 nm and the morphology of ZnTSPP/TiO_2 electrode is similar with TiO_2 electrode. A two-electrode photoelectro-chemical (PEC) cell was used in the photovoltaic study which is composed of a working electrode and a platinum electrode separated by an electrolyte containing 0.1 M KI, 0.01 M I_2 and 0.001 M $HClO_4$.

Absorption spectra were recorded on a Hitachi-557 spectrometer. Fluorescence spectra were determined on Perkin-
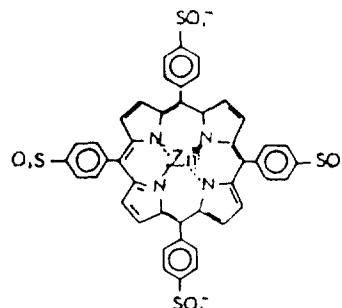

Fig. 1. The structure of ZnTSPP.

Elmer LS-5 spectrofluorometer with a Model 3600 data station. The morphology of the TiO_2 electrode was examined with an atomic force microscope (DI, NanoScope III). Redox potential was recorded by a Par 276 potentiostat.

3. Results and discussion

Fig. 2 shows the spectral changes of a solution of ZnTSPP in DMF upon titration with a solution of TiO_2 colloidal. We can see ZnTSPP monomer exhibits three peaks at 427, 562 and 598 nm in DMF. Upon addition of TiO_2 colloidal, the absorption of ZnTSPP decreases with four isobestic points at 398, 431,569 and 608 nm respectively. On the same time, the absorption red shift of ZnTSPP occurs. Especially in the 420–440 nm region, red shift about 10 nm. There are three new bands at 437, 570, 606 nm for ZnTSPP adsorbed on TiO_2 nanoparticle. Earlier studies suggest this red shift is caused by aggregation of porphyrin [6,7]. In this system ZnTSPP exists in two forms, unadsorbed ZnTSPP monomer and adsorbed ZnTSPP$\cdots TiO_2$. Upon titration with a solution of colloidal TiO_2, the concentration of ZnTSPP$\cdots TiO_2$ is increased, but the density of ZnTSPP on colloidal TiO_2 surface is not increased. When enough TiO_2 colloid is added, the density of ZnTSPP on the TiO_2 colloidal surface is decreased, the possibility of aggregation of ZnTSPP is decreased also. If the red shift is caused by the aggregation of ZnTSPP, blue shift would occur in this time. In our experiment, we do not find the absorption spectrum changing.

On the other hand, ZnTSPP is adsorbed on the TiO_2 colloid by electrostatic interaction. So the electron density of ZnTSPP is changed after it is adsorbed on the TiO_2 colloid surface, and this is the reason for red shift of absorption spectrum.

We can express the adsorbed and unadsorbed molecules of ZnTSPP by Eq. (1):

$$ZnTSPP + TiO_2 = ZnTSPP\cdots TiO_2 \qquad (1)$$
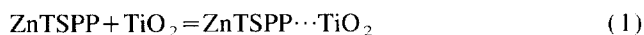
$$K_a = [ZnTSPP\cdots TiO_2]/[ZnTSPP]\cdot[TiO_2] \qquad (2)$$

By the Benesi and Hildebrand method [8], we can get Eq. (3) from Eqs. (1) and (2),

$$\frac{[ZnTSPP]_0}{D} = \frac{1}{\varepsilon} + \frac{1}{[TiO_2]_0 K_a \varepsilon} \qquad (3)$$

In Eq. (3), $[ZnTSPP]_0$, $[TiO_2]_0$ refer to the total concentration of ZnTSPP and TiO_2. D refers the absorption of ZnTSPP$\cdots TiO_2$ band, and ε is the molar extinction coefficient.

Due to Eq. (3), we obtain a linear dependence of $[ZnTSPP]/D$ on the reciprocal concentration of TiO_2 colloid with an intercept equal to $1/\varepsilon$ and the slope equal to $1/K_a\varepsilon$. Indeed, the straight line plot was observed in the inserted figure of Fig. 2. The apparent association constant K_a calculated from the straight line is 1.7×10^4 M^{-1}.
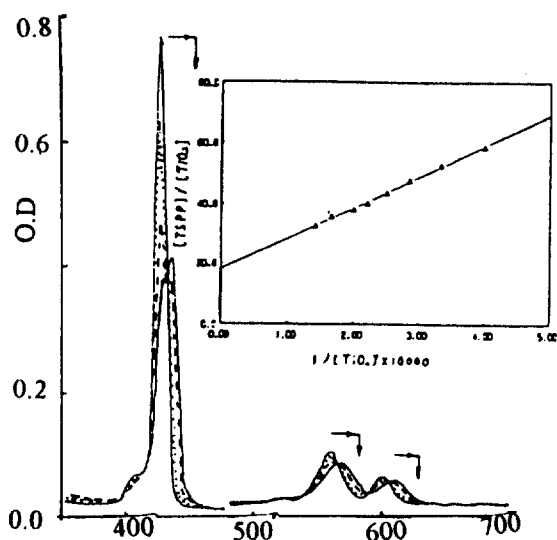

Fig. 2. The absorption spectrum change of ZnTSPP (1.3×10^{-6} M) solution in DMF upon titration with a TiO_2 colloidal solution (0.0–5.0×10^{-4} M). The insert is the straight line dependence of [ZnTSPP]$/D$ on the reciprocal concentration of TiO_2 colloid.

The fluorescence emission spectrum of ZnTSPP exhibited two bands at 610 nm and 660 nm, the observed fluorescence quantum yield was 0.038. the fluorescence yield decreased upon successive addition of colloidal TiO_2 to a solution of 1.3×10^{-6} M ZnTSPP (see Fig. 3). The marked decrease in the fluorescence yield was due to the quenching of excited singlet state of ZnTSPP by TiO_2 colloidal. The standard oxidation potential of the excited singlet ZnTSPP is at -0.96 V vs. NHE and the conduction band of colloidal TiO_2 is around -0.5 V vs. NHE. So the observed quenching of the excited singlet of ZnTSPP could be attributed to the electron transfer to the semiconductor TiO_2 colloid. The relation between the electron-donating energy level of ZnTSPP with the conduction and valence bands of TiO_2 is shown in Fig. 4.

The apparent association constant K_f can be deduced from the fluorescence quenching data by the method of Ref. [9].

The observed fluorescence quantum yield ($\varphi_{f(obsd)}$) of the ZnTSPP in the colloidal TiO_2 suspension is related to the
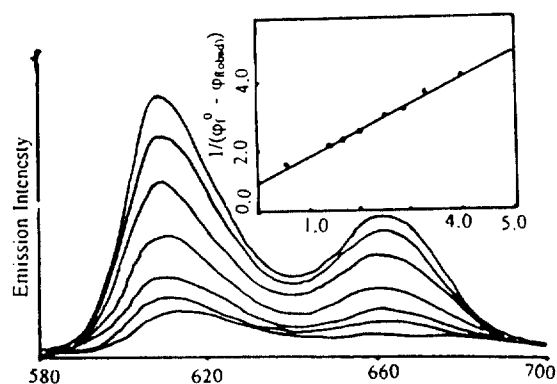

Fig. 3. Fluorescence emission spectrum of ZnTSPP (1.3×10^{-6} M) solution in DMF upon titration with a TiO_2 colloid solution (0.0–5.0×10^{-4} M). The insert is the relation of $1/(\varphi_f^0 - \varphi_{f(obsd)})$ with $1/TiO_2$.
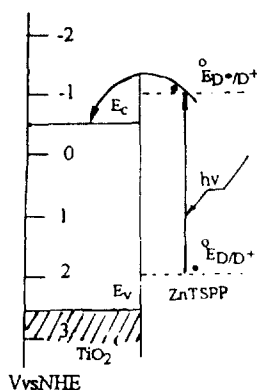
Fig. 4. Schematic diagram describing the conduction and valence bands for TiO₂ and the electron-donating energy levels for ZnTSPP.

fluorescence yields of the unadsorbed (φ_f^0) and the adsorbed (φ_f') molecules of the sensitizer by the equation:

$$\varphi_{f(obsd)} = (1-\alpha)\varphi_f^0 + \alpha\varphi_f' \tag{4}$$

where α is the fraction of adsorbed ZnTSPP.

$$\varphi_f^0 - \varphi_{f(obsd)} = \alpha(\varphi_f^0 - \varphi_f') \tag{5}$$

when $[TiO_2] \gg [ZnTSPP]$

$$\alpha = K_{app}[TiO_2]/(1/K_{app}[TiO_2]) \tag{6}$$

Upon substituting the value of α in Eq. (5) can obtain

$$1/(\varphi_f^0 - \varphi_{f(obsd)}) = 1/(\varphi_f^0 - \varphi_f') + 1/K_{app}(\varphi_f^0 - \varphi_f')[TiO_2] \tag{7}$$

From Eq. (7) we can get a straight line (see the inserted figure in Fig. 3) of $1/(\varphi_f^0 - \varphi_{f(obsd)})$ on $1/TiO_2$ and the K_{app} determined from the slope is 1.5×10^4 M^{-1}. This result is agreement with the result obtained from absorption method. φ_f' is very small, so ZnTSPP adsorbed on TiO₂ colloid has no fluorescence.

Fig. 5 shows the absorption spectrum of the TiO₂ electrode and a ZnTSPP coated TiO₂ electrode. A TiO₂ electrode is used as reference in the measurement for ZnTSPP/TiO₂ electrode. The ZnTSPP/TiO₂ electrode exhibits the characteristic absorption of monomer ZnTSPP around 435 nm, which corresponds to the B band of ZnTSPP molecule, but the B band of ZnTSPP red shift about 8 nm. This change is similar with ZnTSPP adsorbed on TiO₂ colloid. Comparing with the absorption of TiO₂ electrode, ZnTSPP/TiO₂ extends the optical absorption spectrum into visible region, so higher solar energy conversion efficiency could be obtained.

The TiO₂ and ZnTSPP/TiO₂ electrodes have been further examined by measuring the photocurrent action spectra. The incident-photon-to-current-conversion efficiency (IPCE) [4] as a function of wavelength of these two electrodes is also given in Fig. 5. IPCE can be calculated by Eq. (8):

$$IPCE = (1240 \times I_{sc}/\lambda \times P)100\% \tag{8}$$

In Eq. (8), I_{sc} is the short-circuit current, λ is the wavelength of incident light, P is the power of the incident light.
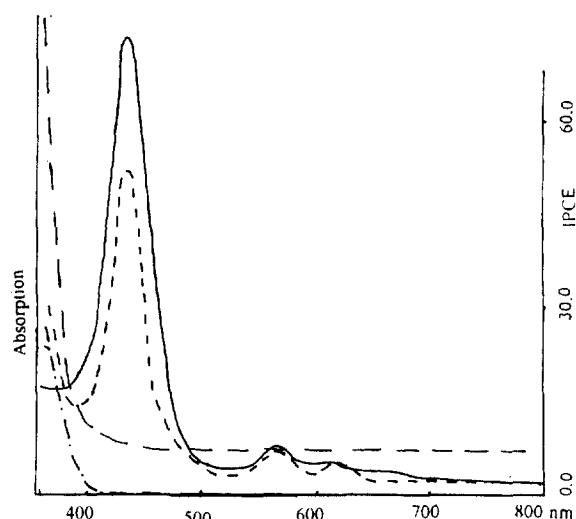

Fig. 5. The absorption of TiO₂ electrode (———) and ZnTSPP/TiO₂ electrode (———); photocurrent spectrum of TiO₂ electrode (– · –) and ZnTSPP/TiO₂ electrode (– – –).

The result shows the photocurrent response of TiO₂ can reach 20% in the ultraviolet region, but it is very poor in the visible region. When the TiO₂ electrode sensitized by ZnTSPP, the response is extended to the visible region, and the IPCE is improved significantly. The maximum IPCE reaches 51.3% at 437 nm for ZnTSPP/TiO₂ electrode. Considering 20% incident light has been absorbed and reflected by TiO₂ electrode, so the quantum efficiency of photons absorbed by ZnTSPP at 437 nm attains 64%. The photocurrent action spectrum of ZnTSPP/TiO₂ electrode shows peaks corresponding to the absorption spectrum of ZnTSPP/TiO₂ electrode. Compared with the absorption of ZnTSPP in the DMF, the photocurrent action band has broadened with a red-shift about 10 nm. This phenomenon agrees well with the absorption spectrum change of ZnTSPP adsorbed on TiO₂ colloid. The reason of this change is the electrostatic interaction between the anionic ZnTSPP with the protonated TiO₂ electrode.

The largest short circuit current density has been determined is 0.21 mA and the related open circuit voltage is 0.24 V for the ZnTSPP/TiO₂ electrode, the active surface area is 0.8 cm² and the incident light intensity is 60 mW/cm². So the total photon–electron conversion efficiency of ZnTSPP/TiO₂ electrode is about 1%.

4. Conclusion

The interaction of ZnTSPP with colloidal TiO₂ was studied by absorption and fluorescence spectroscopy. The result shows ZnTSPP can be strongly adsorbed onto a TiO₂ colloid surface, and participate in the sensitization process by injection of electrons from its excited states into the conduction band of TiO₂. The maximum of IPCE is 51.3% at 437 nm and photon–current transfer efficiency is about 1% for a TiO₂ electrode sensitized by ZnTSPP.

Acknowledgements

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