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Effect of functional group on photochemical properties and photosensitization of TiO_2 electrode sensitized by porphyrin derivatives

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Abstract

A series of porphyrin derivatives containing carboxylic-, sulfo- and hydro- groups, 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TCPP), 5,10,15,20-tetrakis(4-sulfophenyl)porphyrin (TSPP) and 5,10,15,20-tetraphenyl-porphyrin (TPP), were examined as sensitizers for porous nanocrystalline TiO_2. The difference in the adsorption behavior on the TiO_2 electrode surface was discussed. The interaction between the porphyrins and the TiO_2 surface was determined and compared using UV–Vis spectra and X-ray photoelectron spectroscopy (XPS). The luminescence spectra of the porphyrins in DMF solution and adsorbed onto TiO_2 electrodes were measured. The ionization potentials of the porphyrins in the solid state and adsorbed onto TiO_2 electrodes were determined by a new approach using an apparatus for measuring the emission yield under atmospheric conditions. The importance of the binding states between the dye and TiO_2 surface was discussed by comparison of the energy conversion efficiency in a dye-sensitized solar cell. The results indicate that the binding state and the amount of adsorbed dye are important factors affecting the properties of the dye-sensitized solar cell.

Keywords: Photoelectrochemical properties; Nanocrystalline TiO_2; Porphyrin derivatives; Functional group; Dye-sensitized solar cell

1. Introduction

Studies on the fundamental properties of organic semiconductors toward application in photovoltaic solar cells have been carried out for several decades. However, the energy conversion efficiencies are limited to about 1% [1]. Recently, a new type of solar cell based on dye-sensitized nanocrystalline titanium dioxide has been developed by Grätzel and coworkers. Using the ruthenium bipyridyl complex as a sensitizer, high quantum efficiencies have been obtained and overall energy conversion efficiencies have increased to 11% [2,3]. Some of the dyes, except for the ruthenium complexes, have also been used as sensitizers. Porphyrin species, such as the chlorophyll derivatives and zinc porphyrin complex, have been investigated [4,5]. These dyes show an efficient sensitive effect due to their strong absorption in the visible region. We have developed a free-base porphyrin with carboxyl group, 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TCPP), as a sensitizer. Photosensitization of the nanocrystalline TiO_2 electrode by this porphyrin shows high incident photon-to-current conversion efficiency (IPCE: 42% at 420 nm), and the all energy conversion efficiency is 0.65% (100 mW/cm^2) without optimization of the cell [6,7]. In a recent report, the conversion efficiency has been improved due to optimization of the cell and the addition of a coadsorbent (IPCE: 55%, η: 3.5%, 1.4 mW/cm^2) [8].

Although many studies concerning the fundamental understanding of the dye-sensitized solar cells have been carried out, a systematic study of the effect of different functional groups of the dye on the photochemical properties and the energy conversion efficiency of the TiO_2 electrode sensitized with the dye has not been reported. Various spectroscopies are important to understand these properties, such as interaction at the interface, surface composition, coordination geometry and distribution of the energy level. In this paper, we present a comparison of the photochemical properties and photosensitization for three free-base porphyrins, TCPP, 5,10,15,20-tetrakis(4-sulfophenyl)porphyrin (TSPP) and 5,10,15,20-tetraphenyl-porphyrin (TPP), containing different functional groups (Fig. 1). The results of the spectral measurements are quite different, and suggest that the binding state between the dye and semiconductor is an important factor in the dye-sensitized solar cell.

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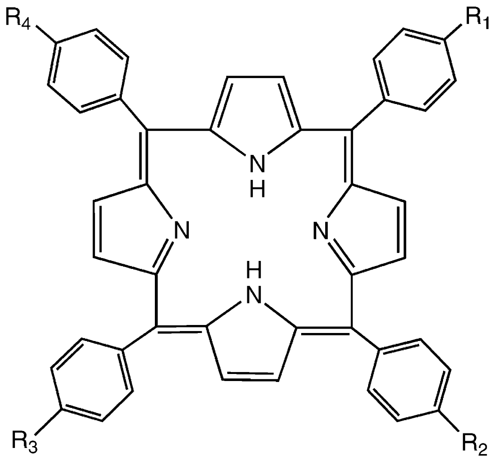

$R_1 = R_2 = R_3 = R_4 = COOH$, TCPP;
$R_1 = R_2 = R_3 = R_4 = SO_3^-$, TSPP;
$R_1 = R_2 = R_3 = R_4 = H$, TPP

Fig. 1. Structure of the porphyrin derivatives.

2. Experimental section

2.1. Preparation of porous TiO_2 film

Colloidal paste was prepared according to the procedure described in the literature [3]. P-25 TiO_2 powder (6 g) in a mortar with 6 ml of distilled water, 0.2 ml acetylacetone, and 0.2 ml Triton X-100 were ground for 1.5 h, then the obtained paste was spread onto a conducting glass support TCO electrode (Asahi Glass; fluorine-doped SnO_2 overlayer; sheet resistance: 10 Ω/sq). After drying in air, the electrode was sintered for 30 min at 450 °C. The resulting film thickness was ca. 10 μm. The surface morphology of the TiO_2 electrode was observed using SEM. The highly porous nature of the film was confirmed.

2.2. Adsorption of a dye onto TiO_2 electrode

The TiO_2 electrodes obtained above were reheated at 450 °C for 30 min, and then cooled to 80 °C. Plunged into 3×10^{-4} mol/l DMF solutions of TCPP, TSPP and TPP, which are the electrodes were allowed to set overnight in the solution at room temperature. The TiO_2 electrodes coated with the porphyrins were withdrawn from the solution and dried.

2.3. Photoeletrochemical characterization of sensitized films

Action spectra were obtained by scanning a wavelength of a monochromator with a step of 10 nm during the measurements of photocurrent, using a three-electrode cell consisting of the dye-sensitized TiO_2 working electrode, a platinum wire counter electrode, and a calomel reference electrode. Current–voltage curves were obtained by scanning a bias voltage while measuring photocurrents or dark currents under white light (100 mW/cm^2) irradiation, using a sandwich solar cell constructed of the dye-sensitized TiO_2 electrode and a thin layer platinum sputtered on conducting glass. The electrolyte solution was composed of 0.5 mol/l of potassium iodide and 0.05 mol/l of iodine in ethylene carbonate and propylene carbonate (75:25, v/v). The dye-coated TiO_2 films were illuminated through the conductive glass support using a Xe lamp as the light source. The intensity of the illumination source was measured using a power meter (OPHIR, NOVA-51545).

2.4. Spectroscopic and analytical methods

UV–Vis transmission and reflectance spectra were taken on a JASCO V-550 using an integrating sphere setup. The solution spectra were referenced against the appropriate solvent. X-ray photoelectron spectra (XPS) were measured using a JASCO X-700 spectrometer equipped with two ultrahigh-vacuum chambers, and an Al Kα X-ray source was used. The reference energies used for the calibration were the C(1s) signal. Fluorescence spectra were obtained on a JASCO FP-750 spectrofluorometer. The photoemission yield measurements were carried out using a surface apparatus, AC-1, manufactured by Riken Keiki. The measurements were carried out at 25 °C under atmospheric conditions. The UV light source was a 150 W xenon lamp; the energy range of the monochromatized incident UV light was from 3.4 to 6.8 eV. In order to avoid the influence of water and the residual solvent, and charge that stems from evaporation of the solvent, the powder and the films were dried under vacuum for 6 h.

3. Results and discussion

3.1. UV–Vis spectroscopy

The absorption spectrum of TCPP in DMF (Fig. 2, thick line) shows a strong peak at about 418 nm (Soret band) and four smaller peaks at 515, 549, 591 and 646 nm (Q bands). The ratio between the Soret and the Q band intensities is approximately 20. In contrast, the intensity in the Soret band for the TiO_2 film coated with TCPP remarkably decreased and the ratio is reduced to ca. 1.5 (Fig. 2, thin line). The reduction of the intensity at wavelengths below about 500 nm is explained by the effect of the extreme light scattering [8]. For TSPP and TPP, a similar phenomenon was also observed.

The absorption data for the porphyrins in DMF solution and coated TiO_2 film are shown in Table 1, and the shift values between the two conditions are also given. It is clear that the degree of the shift decreased in the order TCPP > TSPP > TPP. The larger red shift for TCPP/TiO_2 can be attributed to a strong interaction between the TCPP and cationic TiO_2 surface and to the delocalized π^* state

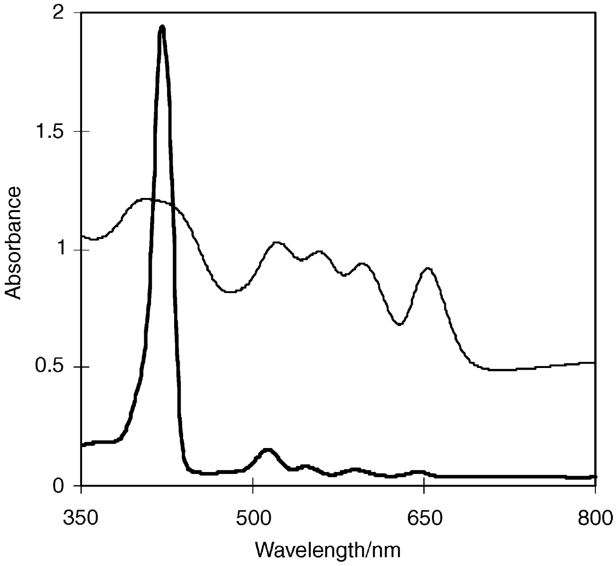

Fig. 2. UV–Vis spectra of TCPP in DMF solution (thick line) and TCPP adsorbed onto the TiO_2 film (thin line).

of the porphyrin derivative into the TiO_2 conduction band, in the same manner as the Ru complex [9]. This strong interaction is accomplished through a chemical linkage between the dye molecules and the semiconductors surface. We have measured the IR spectra and the results reveal that TCPP is combining to the TiO_2 surface by the bridging or bidentate chelate coordination. The detailed discussion will be described in a separate paper. For TSPP/TiO_2, however, slight red shifts of UV–Vis data were observed, which indicated the occurrence of a weak interaction between TSPP and the TiO_2 surface, dependent on an electrostatic force of attraction. Moreover, the film of TPP/TiO_2 shows a weaker interaction than the two dyes above, so it is considered that the dye is absorbed only by physical absorption.

The TiO_2 electrode coated with TCPP gives a dark red appearance due to a strong adsorption. On the other hand, the TSPP/TiO_2 and TPP/TiO_2 electrodes only show a light red color and almost no color. The amounts of the three porphyrins adsorbed on the TiO_2 films were determined by spectroscopic measurement of the dye desorbed from the TiO_2 surface in a NaOH (0.1 M) containing DMF, to be 4.3×10^{-8}, 6.2×10^{-9} and 5.1×10^{-10} mol/cm^2, respectively. The result indicates that the amount of adsorbed dye is markedly different, though almost the same thickness of the TiO_2 film and the same concentration of the dye for soaking were used. These differences are considered to be due to the difference in the adsorption state of the porphyrin on the TiO_2 film, i.e., chemical adsorption and physical adsorption. These results show that the functional groups of the porphyrins have an extremely important effect on their adsorption behavior.

3.2. XPS spectra

It is known that XPS is a highly surface-selective technique. The shifts for the O(1s) and Ti(2p3/2) peaks of TiO_2 upon the adsorption of TCPP have been observed [8]. Under the same conditions, the XPS spectra for the TiO_2 films adsorbed by TSPP and TPP were measured. The survey spectrum of TPP/TiO_2 and the spectra of the O(1s) regions for TCPP/TiO_2, TSPP/TiO_2 and TPP/TiO_2 are shown in Fig. 3. They are compared with those of TCPP/TiO_2 and a blank TiO_2 electrode. For the films coated with TSPP and TPP, a slight shift and no shift of the peaks were observed, in contrast to the substantial shifts for TCPP/TiO_2. In the Ti(2p) regions, similar phenomenons were also observed. These results suggest that the interaction between TSPP and/or TPP and TiO_2 are weaker than that of TCPP, and the strength of interaction is in the order TCPP > TSPP > TPP. These results are consistent with those observed in the UV–Vis spectra. The shifts can be interpreted in terms of an increase in the delocalization of the π orbital of the porphyrin upon adsorption. The interaction between the carboxyl groups and the surface Ti ions is formed through C–O–Ti bonds, as discussed in IR spectra. Therefore, the carboxylate serves as an interlocking group by enhancing electronic coupling between the π^* orbitals of the porphyrin and the Ti(3d) orbital manifold of TiO_2. This coupling leads to increase delocalization of the π^* level of the porphyrin. The energy of the π^* level of the porphyrin is decreased by this delocalization, which explains the observed shift of the peaks.

3.3. Emission spectroscopy

The three kinds of porphyrins in DMF solution and adsorbed on the TiO_2 film show a distinct fluorescence at room temperature. In all the cases, the authenticity of the emission has been verified from the excitation spectrum. In DMF solution, the emission spectra for the three porphyrins were found to be quite similar, as would be expected, since they differ only in the *para* subsitituent on the *meso* phenyl group in the porphyrin skeleton. For the three TiO_2 electrodes coated with the porphyrins the fluorescence intensity decreased in the order of TCPP/TiO_2 > TSPP/TiO_2 > TPP/TiO_2, it can be attributed to the difference in the amount

Table 1
UV–Vis data of the porphyrins in solution and adsorbed onto the TiO_2 films

Dye	TPP (nm)	TSPP (nm)	TCPP (nm)
Solution (in DMF)	415, 514, 549, 590, 646	418, 515, 550, 592, 647	418, 515, 549, 591, 646
TiO_2/dye film	418, 518, 551, 592, 649	422, 521, 555, 596, 654	422, 523, 559, 596, 653
Shift (average value)	3	5	8

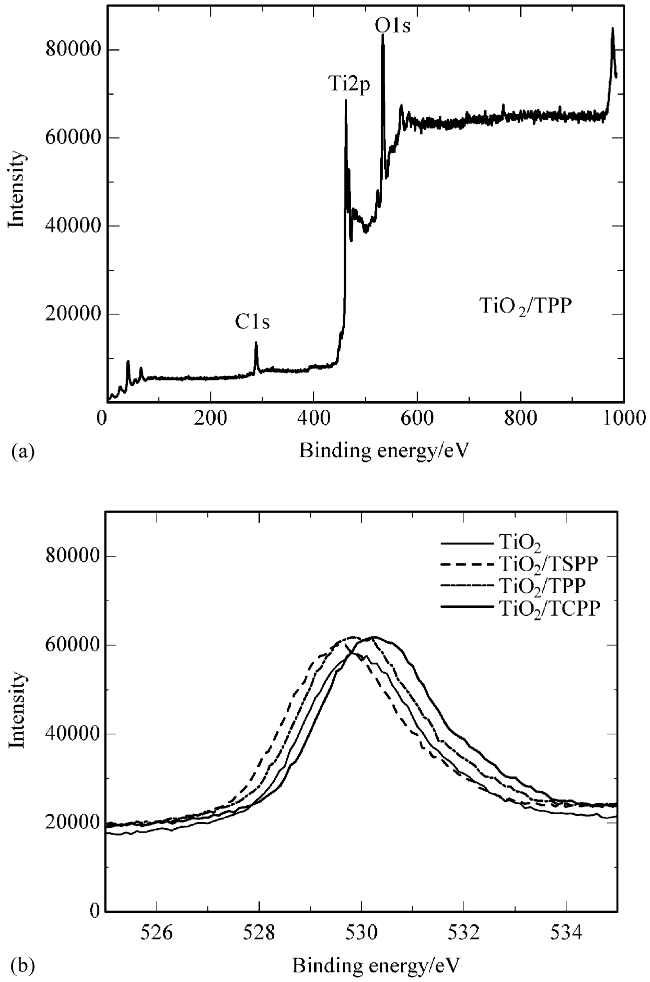

Fig. 3. XPS spectra: (a) the survey spectrum of TPP adsorbed onto a TiO_2 film; (b) the O(1s) region for TCPP, TSPP and TPP adsorbed onto the TiO_2 films.

of the adsorbed dye. Furthermore, it is known that the fluorescence lifetimes and quantum yields for TCPP, TSPP and TPP are very similar from the results of early studies [10]. These results suggest that the difference in the functional groups has very little influence on the formation and decay of the singlet and triplet excited states. However, after adsorption on the TiO_2 electrode, it is estimated that the electron injection efficiency from excited dye molecules into the conduction band of the TiO_2 may be different depending on the binding state at the surface, because it is known that the state of interaction, such as electrostatic, hydrophobic, and chemical interaction between the TiO_2 surface and dye molecules is a dominant factor in the electron transfer mechanism and electron transfer rate [11,12].

3.4. *Ionization potential (IP)*

In order to determine the IP of the dye adsorbed on the TiO_2 electrode, a new approach was used, i.e., using a surface analyzer apparatus to measure the emission yield under atmospheric conditions and then to determine the IP by the least squares method. In general, two methods are used to determine the IP of organic compound, namely measuring oxidation potential with electrochemical method and measuring the energy level by UV photoemission spectroscopy. However, the energy levels measured for dissolved dye in solvent or under high vacuum condition cannot really reflect the relative level of the dye adsorbed on the TiO_2 electrode under working condition in the dye-sensitized solar cell, because the potential is changed upon adsorption, the detail will be described in a separate paper. Therefore, we used an open counter to measure the photoemission yield of the porphyrins adsorbed on the TiO_2 electrodes under atmospheric conditions for the determination of the IP. It is well known in the case of semiconductors and molecular crystals that the quantum yield of photoemitted electrons, $Y(h\nu)^{1/n}$, is proportional to $(h\nu - E_{\mathrm{th}})$, where $h\nu$ is the incident photon energy, E_{th} the threshold energy of photoemission and it corresponds to IPs and the relative HOMO level [13,14]. For some organic molecules, e.g. phthalocynine, the square root law is adopted to determine the threshold energy [15]. This method has been successfully used to determine the ionization energy levels of semiconductor and organic electroluminescent materials [16,17].

The photoemission yields for the TCPP, TSPP and TPP powders were measured and the results are given in Fig. 4(a). The threshold energy, namely IP, was determined, and the IP for TPP, TSPP and TCPP are 5.54, 5.59 and 5.66 eV, respectively. The difference of IP observed among the TCPP, TSPP and TPP systems are considered resulting from the substituent effect. Although the phenyl substituent with functional group is in the vertical position of porphyrin ring, the electronic effect of substitute is smaller than that of the Ru-bipyridyl complex [18], but a change of π electron distribution of the porphyrin is also caused by introducing the four negatively charged functional groups, these influences likely change the height of HOMO level. This is supported by the results reported on characterizations of a series of push–pull porphyrins [19].

Fig. 4(b) shows the photoemission yield curves of the dyes adsorbed onto the TiO_2 electrode. The IP determined for TPP, TSPP and TCPP are 5.52, 5.57 and 5.56 eV. After the adsorption, a shift to lower energy for TCPP was clearly observed. For TSPP and TPP, however, the shifts in the HOMO levels were in experimental error and no definite change. The main reason for this shift is considered due to the strong interaction between TCPP and TiO_2, i.e., the formation of the chemical bonding causes a change of the electron density of π orbital. This is in agreement with the result for Ru complex [9]. Another reason is considered to attribute to the formation of an electronic dipole layer at the interface [20].

3.5. *Photocurrent action spectra*

The photocurrent action spectra for the TiO_2 films sensitized by TCPP, TSPP and TPP are shown in Fig. 5. The spectra were uncorrected for the absorption and scattering

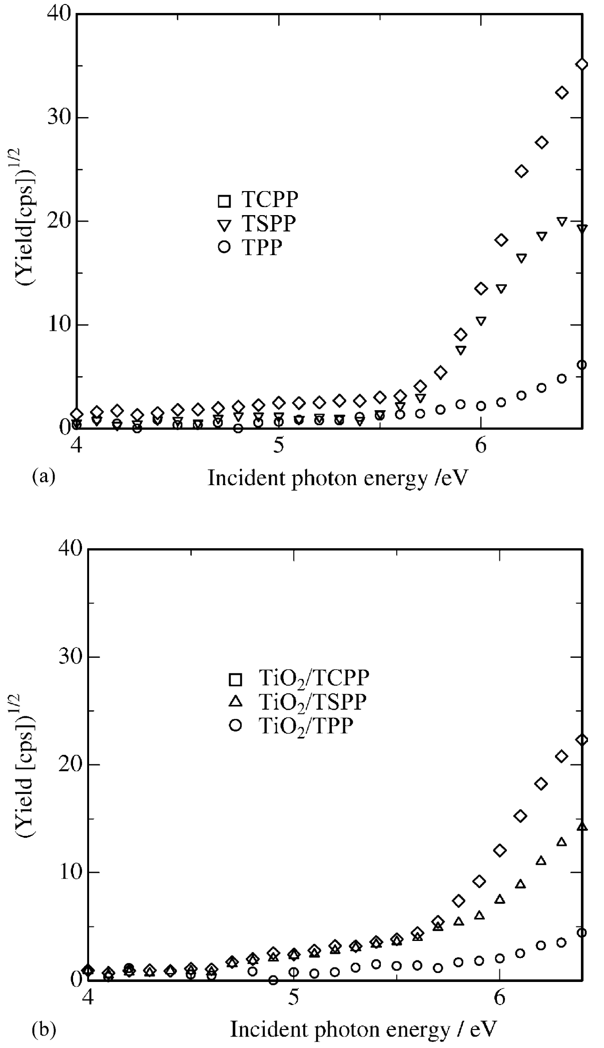

Fig. 4. Photoemission yield curves of the porphyrin derivatives: (a) in the solid state; (b) adsorbed onto the TiO_2 films.

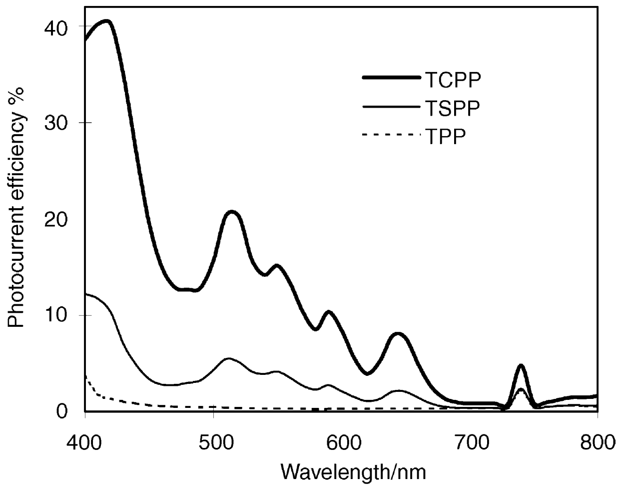

Fig. 5. Action spectra of the porphyrins adsorbed onto the TiO_2 films.

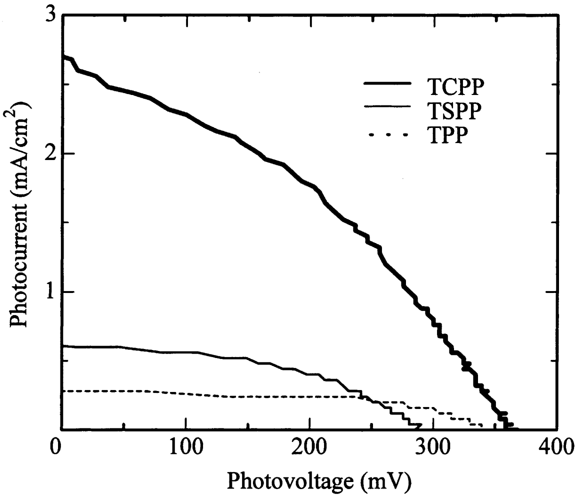

Fig. 6. Current–voltage curves of the porphyrin-sensitized TiO_2 cells.

of incident light by both the glass and the redox electrolyte. As shown in Fig. 5, the maximum IPCE of TCPP is about 40% at 420 nm. This value is higher than that obtained in our previous study, which was 32%, without the addition of P-25 and polyethylene glycol to the colloidal solution prepared by the hydrolysis of tetrabutyl titanate [6]. IPCE can be improved by adding deoxycholic acid to avoid dye aggregation and minimize the back-electron transfers by coating the otherwise uncovered areas of the TiO_2 surface [8].

For the TiO_2 electrode sensitized by TSPP and TPP, on the other hand, the monochromatic photocurrent remarkably decreased. The absorbance of the Soret band only generates a photocurrent with a maximum IPCE of 10 and 2% at about 420 nm for TSPP and TPP, respectively. These results suggest that the amount of adsorbed dye and the binding state between the porphyrins and the semiconductor are important factors in determining the photocurrent efficiency. The shape of the action spectra for the three kinds of porphyrins used in this experiment is slightly broader, but clearly, it is similar to the shape of the absorption spectrum of the porphyrins absorbed on the TiO_2. For all of the electrodes, weak peaks were observed in the region of 730–760 nm. This is considered to be due to the absorption of the aggregate of porphyrins molecules onto the TiO_2 surface. The aggregate phenomenon has been observed for the free-base porphyrins in earlier studies [10,21].

3.6. *Current–voltage curves*

Fig. 6 shows the current–voltage curves obtained for the sandwich-type cells under illumination by white light (100 mW/cm^2). The performance characteristics of the cells are summarized in Table 2. It is known that the short-circuit photocurrent (I_{sc}) and the solar-to-electric energy conversion efficiency (η) can be improved by various kinds of treatments and optimization of the cells. In order to avoid

Table 2
Performance characteristics of the porphyrins-sensitized TiO_2 cells

Dye	IPCE (%)	V_{oc} (mV)	I_{sc} (μA)	Fill factor (%)	η (%)
TCPP	40	360	2700	37	0.36
TSPP	10	290	630	44	0.04
TPP	2	340	320	5.1	0.006

the influence of other factors, neither treatment nor optimization of the cells was done in this experiment. As shown in Fig. 6 and Table 2, the characteristics for the cells are quite different. Especially, the conversion efficiency for TCPP is about nine times higher than that of TSPP, and 60 times higher than that of TPP. As shown in Fig. 6, no large difference in the open-circuit photovoltage V_{oc} for the cells by the three porphyrins sensitized was observed, however, the short-circuit photocurrent density I_{sc} showed an remarkable difference. Although the density of photocurrent depend on the amount of adsorbed dye, it is also influenced by many other factors, such as the electron injection efficiency, the electron back-transfer, the location of the conduction band potential, and the dye potential, which are strongly related to the linkage situation between the dye and the semiconductor. In our studies, the linkage situation is considered to be an important factor, because it directly influences the electron injection efficiency. The electron of the dye can transfer to the semiconductor conduction band through space and a conjugated linkage; the latter route may be more advantageous than that of the former [22]. For SnO_2 electrodes sensitized with perylene derivatives, it has been demonstrated that the dye with a conjugated linkage was more efficient than that with nonconjugated [23]. Therefore, we concluded that the binding state is very important for the performance of the cell.

4. Conclusion

A systematic study on the functional groups of porphyrin derivatives was carried out by various spectroscopic measurements to reveal the effects of these groups on the photochemical properties and conversion efficiency. The adsorption behaviors of three kinds of porphyrins are different on the surface of the TiO_2 electrode. An interaction between the porphyrin and the TiO_2 surface was observed, and their strengths were quite different and decreased in the order TCPP > TSPP > TPP. The IPs of the porphyrins in the bulk and adsorbed onto the TiO_2 electrode were determined, and a shift in the IP between the two states was found. This approach provides a method to determine the energy level for a semiconductor sensitized by dye under the working conditions. The photocurrent and the conversion efficiency are significantly influenced by the type of the functional groups on the dye. These results indicate that the binding state between the dye and semiconductor is an important factor affecting the properties of the dye-sensitized solar cell.

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References

[1] J. Wienke, T.J. Schaafsma, J. Phys. Chem. B 103 (1999) 2702.
[2] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
[3] A. Kay, M. Grätzel, J. Phys. Chem. 97 (1993) 6272.
[4] A. Kay, R. Humphry-Baker, M. Grätzel, J. Phys. Chem. 98 (1994) 952.
[5] K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier, M. Grätzel, J. Phys. Chem. 91 (1987) 2342.
[6] T. Ma, K. Inoue, H. Noma, K. Yao, E. Abe, S. Yamada, The Abstract of the 78th National Meeting of the Chemical Society of Japan, 2000, p. 92.
[7] T. Ma, E. Abe, Recent advances in research and development for dye-sensitized solar cell, CMC of Japan, 2001, p. 169.
[8] S. Cherian, C. Wamser, J. Phys. Chem. B 104 (2000) 3624.
[9] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
[10] K. Kalyanasundaram, M. Neumann-Spallart, J. Phys. Chem. 86 (1982) 5163.
[11] G.K. Boschloo, A. Goossens, J. Phys. Chem. 100 (1996) 19489.
[12] Y. Hou, P. Xie, B. Zhang, Y. Cao, X. Xiao, W. Wang, Inorg. Chem. 38 (1999) 6320.
[13] M. Cardona, L. Ley (Eds.), Photoemission in Solid I, Springer, Berlin, 1978, p. 22.
[14] M. Pope, C.E. Swenberg, Electronic Processes in Organic Crystals, Oxford University Press, New York, 1982, p. 519.
[15] K. Yanagita, O. Okada, K. Oka, Jpn. J. Appl. Phys. 32 (1993) 5603.
[16] H. Kirihata, M. Uda, Rev. Sci. Instr. 52 (1981) 68.
[17] (a) E. Yamakuti, Y. Yamakuti, M. Yokoyama, Denshishasingakaishi 22 (1989) 364;
(b) Y. Nagashima, Shishozai 5 (1996) 37.
[18] V. Skarda, M.J. Cook, A.P. Lewis, G.G. McAuliffe, A.J. Thomson, D.J. Robbins, J. Chem. Soc., Perkin Trans. II (1984) 1309.
[19] C. Chen, S. Hsieh, J. Chin. Chem. Soc. 44 (1997) 23.
[20] D. Cahen, G. Hodes, M. Grätzel, J.F. Guillemoles, I. Riess, J. Phys. Chem. B. 104 (2000) 2053.
[21] H. Deng, Z. Lu, H. Mao, Y. Shen, J. Chem. Soc., Faraday Trans. 94 (5) (1998) 659.
[22] K. Sayama, H. Sugihara, H. Arakawa, Chem. Mater. 10 (1998) 3825.
[23] S. Ferrere, A. Zaban, B.A. Gregg, J. Phys. Chem. B 101 (1997) 4490.