Significant effects of the distance between the cyanine dye skeleton and the semiconductor surface on the photoelectrochemical properties of dye-sensitized porous semiconductor electrodes

Letter

Kazuhiro Sayama,[a] Kohjiro Hara,[a] Yasuyo Ohga,[b] Akira Shinpou,[b] Sadaharu Suga[b] and Hironori Arakawa*[a]

[a] *National Institute of Materials and Chemical Research (NIMC), Higashi 1-1, Tsukuba, Ibaraki 350-8565, Japan. E-mail: h.arakawa@home.nimc.go.jp*
[b] *Hayashibara Biochemical Laboratories, Inc, Fujita 564-176, Okayama 701-0221, Japan*

Received (in Montpellier, France) 26th September 2000, Accepted 31st October 2000
First published as an Advance Article on the web 18th January 2001

The incident photon-to-current conversion efficiency (IPCE) of a porous TiO_2 electrode sensitized by cyanine dyes increased with decreasing distance between the skeleton of the dye and the TiO_2 surface. The photocurrent of oxide semiconductor electrodes sensitized by a cyanine dye increased with the positive shift of the conduction band potential of the oxide semiconductor in the following order: $Nb_2O_5 < TiO_2 < ZnO < SnO_2$. The SnO_2 semiconductor cell showed the best light-to-electric conversion efficiency among the four semiconductors.

There is much intense research being carried out on solar light-to-electrical energy conversion using porous oxide semiconductor electrodes combined with charge transfer sensitizers such as Ru polypyridyl complexes.[1,2] The sensitizer is directly attached onto the semiconductor surface using anchoring groups such as carboxyl, and the dye sensitizer, excited by a photon, injects an electron into the conduction band of the semiconductor. Therefore, in order to improve the photocurrent efficiency, studies of the interface linkage between dye sensitizer and semiconductor surface are very important. Meyer *et al.* reported[3,4] that an intimate electronic coupling between dye sensitizer and semiconductor was not essential, and that the photocurrent efficiency of the $Ru(bpy)_2bpy$–COOH complex (bpy: bipyridyl) was higher than that of the $Ru(bpy)_2bpy–(CH_2)_3$–COOH complex. The position of the carboxyl group of the bipyridyl ligands also affects the photocurrent efficiency.[5] On the other hand, in the case of a porphyrin sensitizer on a gold electrode without a semiconductor oxide layer, a study of the effect of chain length between the dye sensitizer and the electrode carried out systematically found that the photocurrent decreased with decreasing chain length because of quenching of the excited sensitizer by the electrode.[6] However, a systematic study of the effect of interfacial structure on the photoelectrochemical properties is not sufficient in the case of semiconductor electrodes sensitized by various dye sensitizers. Recently, some organic dye sensitizers, as well as metal complexes, on porous semiconductor electrodes have been extensively studied, and it was reported that some dyes such as merocyanine showed an excellent efficiency.[7] A number of merocyanine and cyanine dyes have been employed for photographic sensitization. In order to find a guiding principle for designing an efficient sensitizer, we have systematically investigated the photoelectrochemical properties of porous oxide semiconductor electrodes sensitized by various cyanine dyes that have different anchoring groups. Here, we report the significant influence of the distance between the skeleton of the cyanine and the semiconductor surface on the photocurrent efficiency.

Table 1 shows the photoelectrochemical properties of porous TiO_2 electrodes sensitized by indolenine-type cyanines, a typical cyanine dye. The C1′ dye containing no carboxyl group could hardly adsorb onto TiO_2 and the cell efficiency was quite low. All other dyes adsorbed strongly onto the TiO_2 surface due to the presence of anchoring groups. Therefore, it is suggested that the presence of a carboxyl group to fix dyes onto the semiconductor surface is essential for efficient dye sensitization. Fig. 1 shows the absorption spectra of C*n*-D ($n = 0$–3) dyes in ethanol solution. The light absorption peak shifts to longer wavelength by *ca.* 100 nm with each increase of one in *n* (increasing length of the conjugated methine chain). It was reported that some cyanine dyes formed J-aggregates, showing a sharp and strong absorption in the longer wavelength region on Ag halide or ZnO surfaces.[8,9] In our experiments, the typical absorption of J-aggregates was not observed; however, a slight red shift of the absorption threshold as well as a broadening of the absorption spectra were observed when the dye was adsorbed on a TiO_2 surface, as shown in Fig. 2. It is speculated that an interesting interaction occurs between the dye and the TiO_2 surface or between adjacent dye molecules, just like aggregates.

The best incident photon-to-current conversion efficiency (IPCE = 11.8%) was observed on the TiO_2 electrode with cyanine dye C1-D ($n = 1$), and the efficiency dramatically decreased for $n \geqslant 2$. The dyes of the C*n*-N series also showed the same behavior. The light absorption regions of both C0-D dye and I_3^- in the electrolyte overlapped, therefore, the IPCE of C0-D was lower than that of C1-D. The low IPCE for $n \geqslant 2$ is ascribed to a positive shift of the redox potential of the excited dyes with the increase in *n*. The dye potentials in

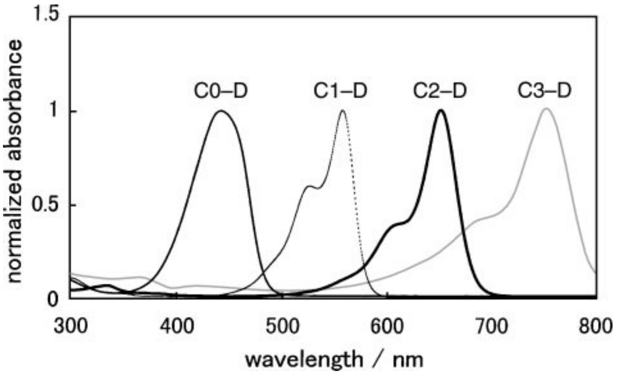
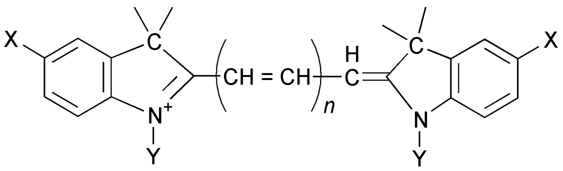


Fig. 1 Absorption spectra of C*n*-D ($n = 0$–3) dyes in ethanol solution.

Table 1 Photoelectrochemical properties of a porous TiO_2 solar cell sensitized with various cyanine dyes



	Dye structure								
Dye	n	X	Y	λ_{max}[a] /nm	$\lambda_{threshold}$[a] /nm	IPCE[b] (%)	J_{sc}[c] /mA cm^{-2}	V_{oc}[c] /V	fill factor[c] (%)
C0-D	0	COOH	CH_3	440 (470)	500 (530)	4.1	0.23	0.52	72
C1-D	1	COOH	CH_3	560 (570)	600 (630)	11.8	0.97	0.59	71
C2-D	2	COOH	CH_3	650 (660)	720 (>700)	0.4	0.09	0.50	62
C3-D	3	COOH	CH_3	750 (>750)		<0.1	0.06	0.34	48
C1-N	1	H	C_2H_4COOH	550 (580)	590 (630)	6.5	0.57	0.75	72
C2-N	2	H	C_2H_4COOH	650 (650)	700 (>700)	0.2	0.03	0.47	53
C3-N	3	H	C_2H_4COOH	750 (>750)		<0.1	<0.01	0.37	57
C1′	1	H	CH_3	550 (540)	590 (570)	<0.1	0.02	0.48	68
C1-D#	1	CH_2COOH	CH_3	560 (570)	600 (630)	5.7	0.55	0.67	70
C2-Ns	2	H	CH_2COOH	650 (650)	700 (>700)	0.7	0.14	0.56	62
C2-ND	2	COOH	C_2H_4COOH	620 (620)	700 (>700)	1.2	0.15	0.45	68

[a] In ethanol. Values in parentheses were measured on TiO_2. [b] IPCE was measured by monochromatic light near λ_{max} using a bandpass filter. [c] Under white light from a Xe lamp (>420 nm, 80 mW cm^{-2}).

the excited state were roughly estimated by measuring the redox potential of the dye and the excitation energy; the estimated dye potential in the excited state shifted positively with increasing n. For example, the excited state oxidation potentials of C0-D, C1-D, C2-D and C3-D were estimated to be −1.58, −1.39, −1.14 and −1.02 V (*vs.* NHE), respectively, by theoretical calculations.

Moreover, we investigated the photoelectrochemical properties of various semiconductor electrodes, as shown in Table 2. The open-circuit potential (V_{oc}) is expressed as the difference between the I^-/I_3^- redox potential and the flat band potential close to the n-type semiconductor conduction band. The conduction band potential of these electrodes was estimated to lie in the following order: $TiO_2 < ZnO < SnO_2$. Therefore, the conduction band of single crystal SnO_2 lies approximately 0.3 V to more positive values than that of TiO_2.[10] Generally, the conduction band potential of Nb_2O_5 is more negative than that of TiO_2,[11] however, the V_{oc} of the Nb_2O_5 cell was smaller than that of the TiO_2 cell because the photocurrent of the Nb_2O_5 cell was significantly smaller than that of the other semiconductor cells. The order of the conduction band potentials was experimentally estimated by the dark current-potential curve to be as follows: $Nb_2O_5 < TiO_2 < ZnO < SnO_2$. The photocurrent increased in the same order, consistent with that of the conduction band potentials.

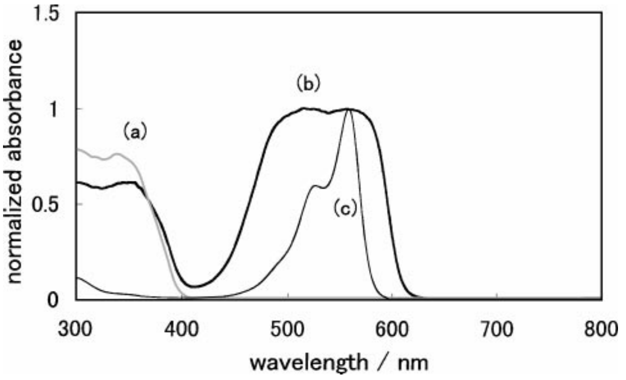


Fig. 2 Absorption spectra of (a) TiO_2 electrode without dye, (b) C1-D dye on TiO_2 electrode and (c) C1-D dye in ethanol solution. The spectra of electrode films were converted from reflection to absorbance by the Kubelka–Munk method.

The IPCE value of a TiO_2 (or Nb_2O_5) electrode sensitized by C2-D was one order of magnitude lower than that of an electrode sensitized by C1-D, while the difference of the IPCE between C1-D and C2-D was not so large on the SnO_2 and ZnO electrodes. Therefore, it is suggested for cyanine dyes that the photocurrent is governed by the relationship of the potential level between the excited dye and the conduction band of the semiconductor electrode; it is also suggested that the positive shift of dye potential in the excited state with increasing n is the main reason for the decrease in the IPCE. Similar behavior was also reported in the case of Ru complexes on TiO_2 and SnO_2.[10] From a comparison of the light-to-electric energy conversion efficiency in Table 2, SnO_2 is the

Table 2 Photoelectrochemical properties of cyanine dyes on several porous semiconductor electrodes

Dye	Semiconductor	IPCE (%)	J_{sc}/mA cm^{-2}	V_{oc}/V	fill factor (%)	η[a] (%)
C1-D	Nb_2O_5	6.2	0.27	0.49	53	<0.1
	TiO_2	11.8	0.97	0.59	71	0.5
	ZnO	14.0	1.22	0.49	59	0.4
	SnO_2	35.5	2.67	0.39	52	0.7
C2-D	Nb_2O_5	<0.1	0.02	0.31	43	<0.1
	TiO_2	0.4	0.09	0.50	62	<0.1
	ZnO	3.8	0.54	0.43	55	0.2
	SnO_2	17.6	1.85	0.36	43	0.4

[a] The light-to-electric energy conversion efficiency.

best semiconductor for the C1-D and C2-D dyes, due to the contribution of the large photocurrent.

The fluorescence of C1-D on various semiconductors and on SiO_2 as a typical insulator was measured. C1-D on a SiO_2 film had a strong fluorescence at 580 nm. The intensity of the fluorescence on Nb_2O_5, TiO_2, ZnO and SnO_2 was significantly smaller than that on SiO_2, and in particular the fluorescence of the dye on SnO_2 was completely quenched. It is suggested that the fluorescence of the excited dye is quenched by electron injection into the conduction band of the semiconductors, and that the quenching of fluorescence takes place effectively on the SnO_2 semiconductor electrode due to the positive potential of the SnO_2 conduction band. The SnO_2 electrode in this experiment is not completely optimized, therefore the efficiency will be increased by improving the preparation of the SnO_2 film.

In the series of C1 dyes, which have similar absorption spectra, the IPCE of a TiO_2 electrode sensitized by C1-D was about twice as large as those sensitized by C1-N and C1-D#, in which the carboxyl anchoring group is connected to a non-conjugated $-CH_2-$ chain. The higher efficiency of C1-D can be explained on the basis of two factors: (*i*) the shorter distance from the dye to the TiO_2 surface and (*ii*) the presence of the conjugated linkage with carboxyl group directly connected to the dye skeleton. From the comparison of photoelectrochemical properties between C2-N and C2-Ns, the current efficiency increased with a decrease of the $-CH_2-$ chain length between the dye skeleton and the carboxyl group. The C2-ND dye containing four carboxyl groups showed a higher IPCE than those of C2-D, C2-N and C2-Ns containing two carboxyl groups. It is speculated that the distance between the TiO_2 semiconductor surface and the skeleton of the C2-ND dye is very short when the dye is anchored by three or four carboxyl groups, because the plane of the dye frame is supposed to lie parallel to the TiO_2 surface. We have also investigated other semiconductor electrodes (ZnO, Nb_2O_5 and SnO_2), and the behavior of the IPCE of the cyanine dyes on these semiconductors were generally similar to that on TiO_2.

Therefore, from all the results obtained here, an intimate electronic coupling between sensitizer and semiconductor by a conjugated linkage is not essential, as pointed out by Meyer and co-workers,[3,4] but it is concluded that the photocurrent increases with decreasing distance between the skeleton of the dye and semiconductor due to an efficient charge transfer through a short distance. These conclusions on the cyanine/semiconductor electrode are consistent with the results on the Ru complex/TiO_2 electrode;[3] however, they are not consistent with the results of the sensitizer/metal electrode in which backward electron transfer caused quenching of the excited sensitizer.[6] It is speculated that the semiconductor surface plays an important role in preventing backward electron transfer. In the case of Ru complexes on TiO_2 electrodes, it is reported that the backward reaction, the electron transfer from the conduction band to the oxidized dye sensitizer, was very slow compared to electron injection into the conduction band.[12] Kinetic studies for the cyanine dyes on semiconductors are now in progress.

Experimental

All dyes were synthesized by Hayashibara Biochemical Laboratories Inc. The preparation of the porous semiconductor film electrode (*ca.* 7 μm thickness) on a conducting glass support (F-SnO_2, 10 Ω sq^{-1}), with a slurry of semiconductor powder (TiO_2: Nihon Aerosil P-25, N_2O_5: Central Glass Co., ZnO and SnO_2: Kanto Chemical), was carried out according to the published procedure.[2,11] The thickness and area of the semiconductor film are *ca.* 7 μm and 1 cm^2, respectively. Adsorption of dye on the semiconductor surface was carried out by soaking the semiconductor electrode in a dry ethanol solution of the dye (220 mg dm^{-3}) at 80 °C for 1 h; the electrode was then washed with sufficient ethanol to remove excess dye. The light source was a 500 W Xe lamp (USHIO Denki Co.). Appropriate band pass filters (3–4 mW cm^{-2}) near the absorption peak were used for the IPCE measurements. A UV cutoff filter was used for white light irradiation (>420 nm, 80 mW cm^{-2}). The electrolyte solution was a mixture of tetrapropylammonium iodide (0.5 M) and iodine (0.05 M) in ethylene carbonate–dry acetonitrile (60 : 40 v/v).

References

1 B. O'Regan and M. Grätzel, *Nature* (*London*), 1991, **353**, 737.
2 M. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry–Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
3 T. Heimer, S. D'Arcangelis, F. Farzad, J. Stipkala and G. Meyer, *Inorg. Chem.*, 1996, **35**, 5319.
4 R. Argazzi, C. Bignozzi, T. Heimer and G. Meyer, *Inorg. Chem.*, 1997, **36**, 2.
5 Y. Hou, P. Xie, B. Zhang, Y. Cao, X. Xiao and W. Wang, *Inorg. Chem.*, 1999, **38**, 6320.
6 H. Imahori, H. Norieda, S. Ozawa, K. Ushida, H. Yamada, T. Azuma, K. Tamaki and Y. Sakata, *Langmuir*, 1998, **14**, 5335.
7 K. Sayama, K. Hara, S. Tuskagoshi, Y. Abe, N. Mori, M. Satsuski, S. Suga, H. Sugihara and H. Arakawa, *Chem. Commun.*, 2000, 1173.
8 H. Hada, Y. Yonezawa and H. Inaba, *Ber. Bunsen-Ges. Phys. Chem.*, 1981, **85**, 425.
9 C. Reich, W. Pandolfe and G. Bird, *Photogr. Sci. Eng.*, 1973, **17**, 334.
10 T. Heimer, E. Heilweil, C. Bignozzi and G. Meyer, *J. Phys. Chem.*, A, 2000, **104**, 4256.
11 K. Sayama, H. Sugihara and H. Arakawa, *Chem. Mater.*, 1998, **10**, 3825.
12 S. Haque, Y. Tachibana, R. Willis, J. Moser, M. Grätzel, D. Kung and J. Durrant, *J. Phys. Chem.*, B, 2000, **104**, 538; P. Kamat, I. Bedja, S. Hotchandani and L. Patterson, *J. Phys. Chem.*, 1996, **100**, 4900.