Improved Solid-State Dye Solar Cells with Polypyrrole using a Carbon-Based Counter Electrode

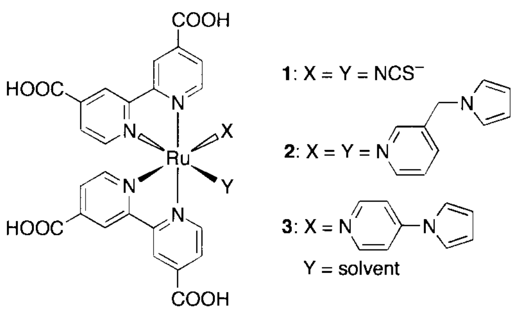
Takayuki Kitamura, Masato Maitani, Mizuho Matsuda, Yuji Wada, and Shozo Yanagida*
Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871

(Received July 25, 2001; CL-010700)

Solid state dye-sensitized solar cell using polypyrrole as a hole transport layer was improved. Carbon-based counter electrode gave a good electric contact with the hole transport layer of polypyrrole to give higher cell performance compared to the cell with gold or platinum counter electrode.

Dye-sensitized solar cells (DSC) have attracted much attention because of the respectable conversion efficiency, and low cost materials and production.[1] Solidification of the liquid electrolyte phase of DCS is an important research subject for long-term stability. Some approaches[2–6] have been done for the solidification of DSCs, but the performance of solid-state cells usually became lower than the liquid cells particularly under high light intensity like AM 1.5 conditions. The lack of complete penetration of solid hole-transport materials in the void of the mesoporous TiO_2 phase may lead to poor electronic contact between dye molecules and the hole transport materials. Only the performance of the quasi-solid state cells using low molecular weight gelators was reported comparable to the liquid cells even under high irradiance conditions.[6] Thermal reversibility of gel-to-fluid transition of the gel electrolytes made them possible to penetrate into the void at higher than the transition temperature.

In order to fabricate the perfect solid-state DSC, we proposed in situ photo-electrochemical polymerization of pyrrole (PPy) as a hole transport phase in the void of the *cis*-$Ru^{II}(dcbpy)_2(NCS^-)_2$ (**1**: dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid; Scheme 1)-adsorbed mesoporous TiO_2 films and vacuum deposited gold as a counter electrode, and also achieved the solid-state DSC using a Ru dye with pyrrole group, *cis*-$Ru^{II}(dcbpy)_2(pmp)_2$ (**2**: pmp = 3-(1-pyrrolylmethyl)-pyridine).[3] However, the fill factor (*ff*) and the resulting conversion efficiency (η) was still low (ca. 0.4 and ca. 0.1% at 22 $mW{\cdot}cm^{-2}$), and the reproducibility of the efficiency was poor as far as vacuum deposition was employed for making the counter electrode. Thus the molecular level wiring of PPy to the dye molecules and of PPy to the counter electrode should play a decisive role in the high conversion efficiency.[3b] In the present letter, we report that use of carbon-based electrode as a counter electrode improves the performance of the solid-state DSC using PPy as a hole transport layer.



Scheme 1. Chemical structure of dyes.

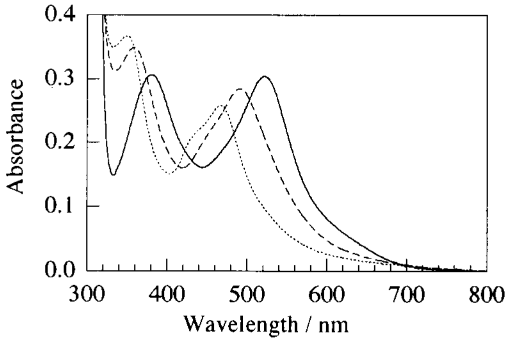


Figure 1. Absorption spectra of dyes in ethanol (3×10^{-5} $mol{\cdot}dm^{-3}$); **1** (——), **2** (·····) and **3** (-----).

A novel dye, *cis*-$Ru^{II}(dcbpy)_2(pp)(solvent)$[7] (**3**: pp = 4-(1-pyrrolyl)pyridine) was synthesized by the similar procedure to that of **2**,[3b] where an aqueous solution of *cis*-$Ru^{II}(dcbpy)_2Cl_2$ and pp was refluxed for 24 h under nitrogen atmosphere in the dark. The role of pyrrole group in the dye **3** was expected comparable to that in dye **2**. However, ES-MS and NMR analyses revealed that dye **3** had only one pp group in one molecule. The absorption spectra of these dyes are shown in Figure 1. The absorption showed blue shift in the order of **1** > **3** > **2** according to the number of pyridine ligand substitution. This fact may be explained as due to the strong ligand field of pyridine stabilized t_{2g} orbital of the dyes.

Mesoporous TiO_2 film with 10–12 μm of thickness was prepared on an optically transparent F doped SnO_2 conducting glass (OTE; 10 Ω/□ (represents sheet resistance ρ_s), Nippon Sheet Glass) using an aqueous TiO_2 paste composed of P25, acetylacetone, and Triton X-100. PPy was introduced into the void of the dyed TiO_2 films by photoelectrochemical polymerization on the dyed films under potentiostatic conditions as reported.[3] The potential (0 to –300 mV) of the dyed films dipped in an acetonitrile solution ($LiClO_4$: 1.0 M, pyrrole: 0.1 M) were maintained by Ag/Ag^+ ($AgNO_3$: 0.01 M) reference electrode and then irradiated by a 500-W Xe lamp (22 $mW{\cdot}cm^{-2}$; 400–800 nm). Total charge of anodic photopolymerization was 40 $mC{\cdot}cm^{-2}$. TiO_2/Dye/PPy films were doped by immersion in an acetonitrile solution of $LiClO_4$ (1.0 M) for 100 h, and then washed with acetonitrile and dried. As a counter electrode, platinum sputtered OTE (Pt/OTE) was used, because of the difficulty in making gold counter electrodes.

Table 1 lists the performance of solid cells fabricated using dyes **1**, **2** and **3** under 10 $mW{\cdot}cm^{-2}$ irradiance (500-W Xe lamp, 400–800 nm). The amount of adsorbed dye was in the same order of 10^{-8} $mol{\cdot}cm^{-2}$. Highest η for each dye was obtained in the polymerization potential of ca. –200 mV. Despite the blue shifted absorption bands, the cell fabricated using **2** as a dye

Table 1. Cell performance of the solid-state dye-sensitized solar cells with platinum sputtered F:SnO_2 counter electrode[a]

Dye	A_{dye}[b] / 10^{-8} mol·cm^{-2}	E[c] / mV	V_{oc}[d] / V	J_{sc}[e] / µAcm^{-2}	ff[f]	η[g] / %
1	7.5	–300	0.73	54.0	0.43	0.17
		–200	0.75	62.9	0.38	0.18
		–100	0.72	65.0	0.32	0.14
		0	0.73	51.6	0.30	0.11
2	6.1	–300	0.77	94.7	0.28	0.20
		–200	0.78	82.9	0.31	0.20
		–100	0.73	67.7	0.37	0.18
		0	0.73	44.3	0.44	0.14
3	6.7	–300	0.72	52.5	0.37	0.14
		–200	0.75	76.7	0.31	0.18
		–100	0.76	57.6	0.37	0.16
		0	0.71	48.7	0.30	0.10

[a] 10 mW·cm^{-2} irradiance (500-W Xe lamp, 400–800 nm). [b] Amount of adsorved dye per projection unit area. [c] Applied potential for photoelectrochemical polymerization of pyrrole. [d] Open circuit voltage. [e] Short circuit photocurrent density. [f] Fill factor. [g] Photon-to-current conversion efficiency.

was the best. The importance of direct connection between dye and hole transport layer was confirmed here again. Open circuit voltage (V_{oc}) and short circuit photocurrent density (J_{sc}) were improved, but ff of the cells was still low, provably due to the poor electric connectivity between PPy and Pt/OTE.

To improve the connectivity, highly conductive carbon-based materials were introduced between PPy and Pt/OTE, where dye **2** was employed as sensitizing dye. A carbon-based paste was prepared by mixing carbon black (Ketjenblack; LION) with an aqueous poly(diallyldimethylammonium chloride) (PDDAC, 20 wt% in water, M_w = 400000–500000, Aldrich) solution of 1:6 weight ratio, being spread on the doped TiO_2/Dye/PPy film. A Pt/OTE electrode was placed on the TiO_2/Dye/PPy/Carbon film, and they were pinched by a clip. The resulting cell was dried *in vacuo* for 24 h at r.t. Figure 2 shows the best result of the dark and photo I–V curves of the solid cells with the carbon-based electrode under 10 mW·cm^{-2} irradiance. Figure 2 also shows the photo I–V curve of the solid cell only with Pt/OTE as a counter electrode (Table 1: Dye **2**, E = –300 mV). The cell with carbon-based electrode showed η of 0.62%, J_{sc} of 104 µA·cm^{-2}, V_{oc} of 716 mV, and ff of 0.78. The η value was six and three times higher than that of the cell with gold[3b] and Pt/OTE counter electrodes, respectively. The viscous carbon-based paste on the TiO_2/Dye/PPy film gave a homogeneous filling in the void of PPy, leading to the improvement of electric connectivity through increased interface of conductive carbon and PPy. Relatively high cathodic dark current of the cell might be explained as direct electron transfer from OTE to PPy to induce de-doping of PPy.

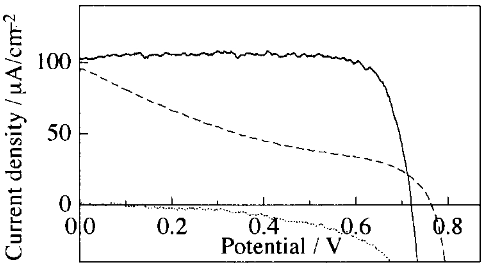


Figure 2. The cell performance of the solid-state dye(**2**)-sensitized solar cells with polypyrrole as a hole transport layer under 10 mW·cm^{-2} irradiance (500-W Xe lamp, 400–800 nm): photo (——) and dark (·····) I–V curves for the cell with carbon-based counter electrode (PPy polymerized at E = –250 mV), and photo I–V (----) curve for the cell with Pt/OTE counter electrode (PPy polymerized at E = –300 mV).

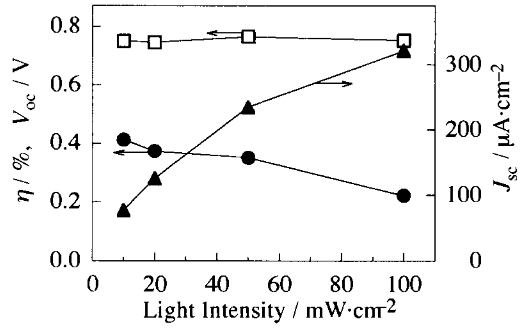


Figure 3. The irradiation light intensity dependent cell performance of the solid-state dye-sensitized solar cell with polypyrrole as a hole transport layer and carbon-based counter electrode: dye was **2**, PPy was polymerized at E = –250 mV, conversion efficiency (●), V_{oc} (□), J_{sc} (▲).

Figure 3 shows light intensity dependent change of the cell performance up to 1 sun conditions (100 mW·cm^{-2}). V_{oc} was independent of the light intensity, but J_{sc} did not increase linearly with the increase of the light intensity, resulting in decrease of η. This tendency might be due to the low conductivity of PPy.

Higher performance of the solid-state dye-sensitized solar cell with polypyrrole as a hole transport layer was successfully obtained by using carbon-based counter electrode. The molecular level electric connectivity could also be improved between polypyrrole and the PDDAC-containing carbon-based counter electrode. The test of the long-term stability of the solid cells is in progress.

ES-MS measurements were supported by Prof. Ryuichi Arakawa, Kansai University. This work was partially supported by Grant-in-Aid for Scientific Research (A) (No. 11358006), and by Millennium Project (No. 12310) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Note

1 a) B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991). b) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc.*, **115**, 6382 (1993).
2 a) M. Matsumoto, H. Miyazaki, K. Matsuhiro, Y. Kumashiro, and Y. Takaoka, *Solid State Ionics*, **89**, 263 (1996). b) M. Matsumoto, Y. Wada, T. Kitamura, K. Shigaki, T. Inoue, M. Ikeda, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, **74**, 387 (2001).
3 a) K. Murakoshi, R. Kogure, Y. Wada, and S. Yanagida, *Chem. Lett.*, **1997**, 471. b) K. Murakoshi, R. Kogure, Y. Wada, and S. Yanagida, *Sol. Energy Mater. Sol. Cells*, **55**, 113 (1998).
4 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel, *Nature*, **395**, 583 (1998).
5 K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda, V. P. S. Perera, and P. S. R. S. Weerasundara, *J. Photochem. Photobiol. A*, **117**, 137 (1998).
6 W. Kubo, K. Murakoshi, T. Kitamura, Y. Wada, K. Hanabusa, H. Shirai, and S. Yanagida, *Chem. Lett.*, **1998**, 1241.
7 Dye **3** (solvent = EtOH) was isolated as a monohydrated bisperchlorate salt. ^{1}H NMR (0.05 M NaOD in D_2O, δ_{HDO} = 4.67) δ = 9.01 (d, J = 5.73 Hz, 1H), 8.97 (d, J = 5.73, 1H), 8.59 (m, 2H), 8.50 (m, 2H), 7.88 (d, 2H), 7.84 (d, J = 5.95, 2H), 7.65 (m, 2H), 7.57 (d, J = 7.06, 2H), 7.41 (m, 2H), 6.31 (d, J = 7.06, 2H), 6.14 (d, J = 7.06, 2H). Anal. Found: C, 42.39; H, 3.33; N, 8.78%. Calcd for $C_{35}H_{32}Cl_2N_6O_{18}Ru$: C, 42.18, H, 3.24, N, 8.43%. ES-MS, Found: *m/z* 390.1. Calcd for $C_{35}H_{30}N_6O_9Ru$: 390.0.