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High-efficiency (7.2%) flexible dye-sensitized solar cells with Ti-metal substrate for nanocrystalline-TiO_2 photoanode

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High-efficiency flexible dye-sensitized solar cells were fabricated with a Ti-metal foil substrate for photo anode and using a Pt-electrodeposited counter electrode on ITO/polyethylene naphthalate (ITO/PEN); these devices were characterized by incident photon-to-current efficiency (IPCE), optical transmittance and electrical impedance spectroscopy.

Investigation of lightweight and flexible solar cells is important because of their advantages for transportation and photovoltaic power-supply systems equipment. New designs and applications for supplying mobile electricity for lap-top computers, mobile phones, watches, *etc.* are possible. Moreover, replacing a rigid substrate by a flexible material allows a low-cost fabrication by roll-to-roll mass production. Therefore, applying flexible-device technologies to dye-sensitized solar cells (DSCs),[1] a prospective cost-effective photovoltaic-generating system, is very significant.

In the past, different methods have been applied to fabricate nanocrystalline-TiO_2 layers on top of polymer films, such as ITO-coated poly(ethylene terephthalate) (ITO/PET) for DSCs.[2–4] The coating and surface activation of TiO_2-electrodes on ITO/PET are crucial. Previously, the TiO_2-layers were deposited on ITO/PET by using doctor-blade coating,[2] electrophoretic deposition[3] and spray coating.[4] In flexible ZnO electrode DSCs, electrochemical deposition has been performed.[5] The surface activation methods reported were low-temperature heating,[2a,c,3c,5] compression,[2b,f,3d] microwave irradiation,[3a,4] hydrothermal crystallization,[2d] electron-beam annealing[2e] and chemical-vapor deposition with UV irradiation.[3b] In a rare case where no activation was applied and the films were simply dried at room temperature, 1.2% efficiency was achieved.[2g] The highest efficiency of flexible DSCs under 100 mW/cm^2 (AM 1.5) with low-temperature sintering (150 °C) on polymer films was 4.1% fabricated with electrophoretic deposition followed by additional TiO_2-particle impregnation.[3c] However, the efficiencies of the flexible DSCs on polymer films were lower than the efficiencies of DSCs on FTO (F-doped tin oxide)/glass substrates sintered at high-temperature, because of the poor connection between TiO_2 particles due to the low-temperature sintering.[6] In order to enhance the activity of the TiO_2 layer, a lift-off and transfer method has been proposed after sintering at 450 °C on Au/glass as supporting substrate, resulting in the highest efficiency of flexible DSC (5.8%) under AM 1.5.[7] But this procedure may not be suitable for practical applications, due to the complications in transferring a nanocrystalline-TiO_2 layer from Au/glass to ITO/PET.

In order to use high-temperature TiO_2 sintering, a cell configuration using a metal substrate for the nanocrystalline-TiO_2 layer requiring illumination of the dye-sensitized film through the counter electrode (back illumination, Fig. 1) has been proposed.[8] Promising substrates are Ti, stainless steel, W and Zn. An efficiency of 4.2% under 100 mW/cm^2 incident power has been reported recently with nanocrystalline-TiO_2 film on ITO/SiO_2/stainless steel.[9]

In this report, the thickness of the nanocrystalline-TiO_2 layer has been optimized for high-efficiency flexible DSC using a titanium metal substrate and high-temperature sintering at 500 °C to produce a device yielding a conversion efficiency under standard global AM 1.5 solar light of 7.2%. The differences between the photovoltaic characteristics of flexible and glass DSCs are discussed by comparison of incident photon-to-current efficiencies (IPCE) and electrical impedance spectroscopy.

TiO_2 nanoparticles (d = 42 nm, calculated from BET data) were synthesized by hydrothermal crystallization in basic solution with $N(CH_3)_4OH$,[10] and converted to a TiO_2 screen-printing paste,[11] giving semi-opaque TiO_2 films. The syntheses of *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4-carboxylic acid-4′-tetrabutylammonium carboxylate)ruthenium(II) (N-719) and butylmethylimidazolium iodide (BMII) were reported in our previous papers.[12,13] The chromatographic purification of N-719 was carried out three times on a column of Sephadex LH-20.[14] Fig. 1 shows the structure of a typical DSC. To prepare the DSC working electrodes, the Ti foil (0.2 mm thickness) was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. After treatment in a UV–O_3 cleaning system for 18 min, the Ti foil was immersed in a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. A layer of the paste was coated on the Ti foil by screen printing (90 T mesh), kept in a clean box for 3 min so that the paste could relax to reduce the surface irregularity and then

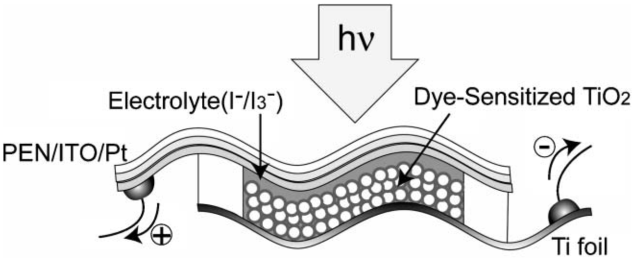

Fig. 1 Configuration of a flexible dye-sensitized solar cell irradiated through Pt-counter electrode (back illumination).

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dried for 3 min at 125 °C. This screen-printing procedure (coating, storing and drying) was repeated to change the thickness of the working electrode from 3 to 21 μm. The electrodes coated with the TiO_2 pastes were gradually heated under air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and 500 °C for 15 min. After sintering, the surface area of the TiO_2 electrodes was measured precisely by a scanner followed by integration of the resulting image.[14] After the size measurement, the TiO_2 film was treated with 40 mM $TiCl_4$ solution as described above, rinsed with water and ethanol and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 electrode was immersed in a 0.5 mM N-719 dye solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio: 1 : 1) and kept at room temperature for 20–24 h to complete the sensitizer uptake. To prepare the counter electrode, a Pt catalyst was coated on the ITO/PEN (7 ohm γ^{-1}, Tobi, Japan) by electrochemical deposition with a two-electrode system (electrolyte: 5 mM H_2PtCl_6 aqueous solution; counter electrode: glass/FTO/Pt(heat-deposited); distance between electrodes: 4 mm; applied voltage: 1.8 V; deposition time: 15 s). The DSCs on glass/FTO substrate (Nippon Sheet Glass, Japan) were prepared by using the same TiO_2 paste with the flexible DSC applying published procedures ("glass DSCs" below).[14] The results were used for TiO_2-thickness optimization of photovoltaic performances and for comparison with the flexible DSCs.

The dye-covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell (Fig. 1) and sealed with a hot-melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (DuPont). A drop of the electrolyte, a solution of 0.60 M BMII, 0.03 M I_2, 0.10 M guanidinium thiocyanate and 0.50 M 4-*tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio: 85 : 15) was put on the hole in the back of the working electrode. The electrolyte was introduced into the cell *via* vacuum backfilling. The hole was sealed with a Surlyn layer. Light reflection losses were eliminated using a self-adhesive fluorinated polymer film (ARKTOP, Asahi Glass) that served at the same time as a 380 nm UV cut-off filter. Masks made of black plastic tape were attached to the ARKTOP filter to reduce scattered light.[14] Photovoltaic measurements employed an AM 1.5 solar simulator (100 mW cm^{-2}) by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter.

Fig. 2 shows the conversion efficiency of glass substrate DSC as a function of the TiO_2-layers thickness, for front/back-side illuminations. The front-side illumination efficiency (9.9%) of glass/FTO/TiO_2 electrode made by the basic-solution procedure was close to the efficiency (10.2%)[14] of transparent (d = 20 nm, acidic preparation) and scattering (d = 400 nm, CCIC, Japan) TiO_2 double layer systems. In both cases the efficiencies of front/back-side illuminations display a maximum at the same thickness of 14 μm. The difference of efficiency between front-side and back-side illuminations is constant, *i.e. ca.* 4%. The thickness of the nanocrystalline-TiO_2 layer was fixed at 14 μm for the flexible DSC.

Fig. 3 shows I–V curves of flexible and glass DSCs with back-side and front-side illuminations, respectively. The photovoltaic characteristics of flexible DSCs with back-side illumination were V_{OC}, 0.78 V; J_{SC}, 13.6 mA cm^{-2}; FF, 0.68 and Eff. 7.2%. Those of glass DSCs with front-side illumination were V_{OC}, 0.79 V; J_{SC}, 16.9 mA cm^{-2}; FF, 0.74; Eff. 9.9%. In this case, the difference of V_{OC}s was small. On the other hand, J_{SC} and FF of flexible DSC were significantly smaller than those of glass DSC. The reasons for the low J_{SC} and FF were characterized by using IPCE and electrical impedance measurements.

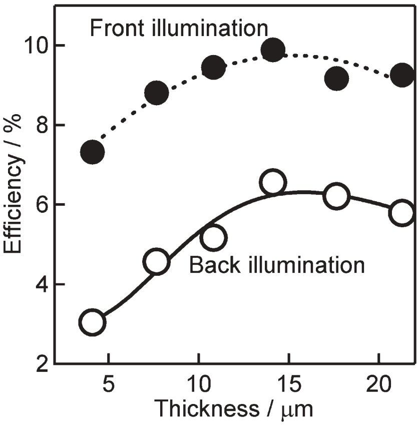

Fig. 2 Conversion–efficiency relationships of glass DSCs between the front (TiO_2/dye) and back (Pt/electrolyte) side illuminations.

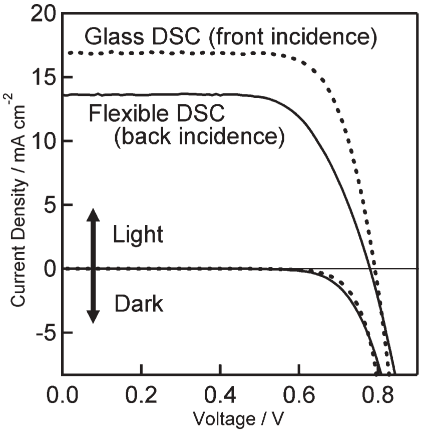

Fig. 3 I–V characteristics of a flexible and a glass DSC. The irradiation was AM 1.5 (100 mW cm^{-2}).

Fig. 4 shows IPCE spectra of flexible and glass DSCs and the transmittance spectra of some of the DSC components. The anti-reflecting film (ARKTOP) cuts off the incident UV-light below 380 nm for both DSCs. The onset is around 415 nm. It is noticeable that the IPCE of flexible DSC from 400 nm to 680 nm is lower than that of the glass DSC, resulting in the difference of J_{SC}s (Fig. 3). The I_3^- electrolyte cuts the incident light significantly (from 400 nm to 600 nm) in the flexible DSC because of the back-side illumination (Fig. 1). Although the absorbance of Pt was 2–3%, the transmittance difference between FTO and PEN/ITO/Pt had some influence on the IPCEs from 540 nm to 680 nm. Above 680 nm wavelength, the IPCEs are very close due to the lower influences of electrolyte and the transparent-conducting materials.

Fig. 5 shows the electrical impedance spectra of flexible and glass DSCs. The small peaks on the left express the Pt/redox-(I^-/I_3^-) interface charge transfer and the large peaks on the right express dye-sensitized TiO_2/redox(I^-/I_3^-) interface charge transfer. The reaction resistance of the counter electrode was analyzed by software (Z-view) using an equivalent circuit containing a constant phase element (CPE) and resistances (R) (Fig. 5, inset).[15] The series

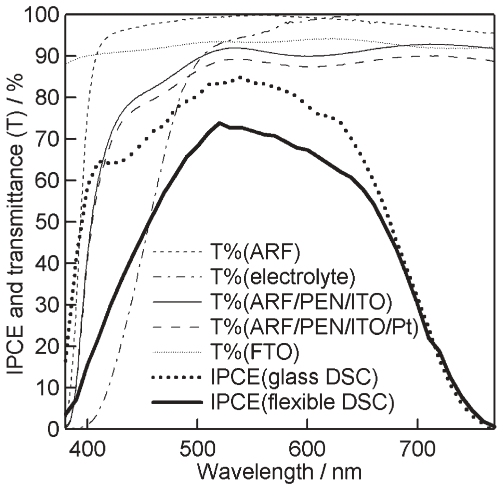

Fig. 4 IPCE spectra of a flexible and a glass DSC and transmittance (T) spectra of anti-reflecting film (ARF), electrolyte, flexible substrate (PEN/ITO) with/without Pt and conductive glass substrate (glass/FTO). The optical pathlength of the electrolyte was 25 μm. The spectrum of FTO was obtained using a 〈glass/FTO/butoxyacetonitrile/glass〉 configuration and a background of 〈glass/butoxyacetonitrile/glass〉.

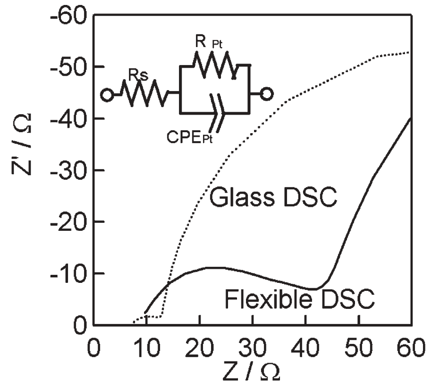

Fig. 5 Electrical impedance spectra of a flexible and a glass DSC in the dark at a forward bias of 0.76 V. The inset shows the equivalent circuit used to analyse the small peaks.

resistance (R_S) was 7–8 ohm in each cell. Hence, the difference of R_Ss (FTO/glass: 10 ohm γ^{-1}, ITO/PEN: 7 ohm γ^{-1}) did not cause the difference in the fill factors. On the other hand, the interface resistance of Pt/electrolyte (R_{Pt}) was 7.2 ohm (heat-activated Pt on FTO/glass) and 31 ohm (electrodeposited Pt on ITO/PEN). Therefore, the low *FF* of flexible DSC is due to the lower activity of electrodeposited Pt catalyst at the counter electrode.

In summary, we have obtained a 7.2% flexible DSC with 14 μm thickness porous-TiO_2 electrode. The electrolyte employed does contain acetonitrile which may escape across the PEN film under prolonged heat stress. For the application, therefore, further investigation is required concerning the stability. The lower conversion efficiency of the flexible device, when compared to a glass device, is due to the decrease in the J_{SC} and *FF*. The lower J_{SC} and *FF* were due to the absorption by the I_3^- electrolyte and the PEN/ITO/Pt electrode as well as the resistance of the Pt/electrolyte interface.

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Notes and references

1 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; M. Grätzel, *Nature*, 2001, **414**, 338.
2 (*a*) F. Pichot, J. R. Pitts and B. A. Gregg, *Langmuir*, 2000, **16**, 5626; (*b*) H. Lindström, A. Holmberg, E. Magnusson, S.-E. Lindquist, L. Malmqvist and A. Hagfeldt, *Nano Lett.*, 2001, **1**, 97; (*c*) C. Longo, A. F. Nogueira, M.-A. De Paoli and H. Cachet, *J. Phys. Chem. B*, 2002, **106**, 5925; (*d*) D. Zhang, T. Toshida and H. Minoura, *Adv. Mater.*, 2003, **15**, 814; (*e*) T. Kado, M. Yamaguchi, Y. Yamada and S. Hayase, *Chem. Lett.*, 2003, **32**, 1056; (*f*) S. A. Haque, E. Palomares, H. M. Upadhyaya, L. Otley, R. J. Potter, A. B. Holmes and J. R. Durrant, *Chem. Commun.*, 2003, 3523; (*g*) S.-S. Kim, J.-H. Yum and Y.-E. Sung, *J. Photochem. Photobiol., A*, 2005, **171**, 269.
3 (*a*) T. Miyasaka, Y. Kijitori, T. N. Murakami, M. Kimura and S. Uegusa, *Chem. Lett.*, 2002, **31**, 1250; (*b*) N. Murakami Takurou, Y. Kijitori, N. Kawashima and T. Miyasaka, *Chem. Lett.*, 2003, **32**, 1076; (*c*) T. Miyasaka and Y. Kijitori, *J. Electrochem. Soc.*, 2004, **151**, A1767; (*d*) J.-H. Yum, S.-S. Kim, D.-Y. Kim and Y.-E. Sung, *J. Photochem. Photobiol., A*, 2005, **173**, 1.
4 S. Uchida, M. Tomiha, H. Takizawa and M. Kawaraya, *J. Photochem. Photobiol., A*, 2004, **164**, 93.
5 T. Yoshida, T. Oekermann, K. Okabe, D. Schlettwein, K. Funabiki and H. Minoura, *Electrochemistry*, 2002, **70**, 470.
6 S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori and S. Yanagida, *J. Phys. Chem. B*, 2002, **106**, 10004.
7 M. Dürr, A. Schmid, M. Obermaier, S. Rosselli, A. Yasuda and G. Nelles, *Nat. Mater.*, 2005, **4**, 607.
8 M. G. Kang, N.-G. Park, K. S. Ryu, S. H. Chang and K.-J. Kim, *Chem. Lett.*, 2005, **34**, 804.
9 M. G. Kang, N.-G. Park, K. S. Ryu, S. H. Chang and K.-J. Kim, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 574.
10 S. D. Burnside, V. Shklover, C. Barbé, P. Comte, F. Arendse, K. Brooks and M. Grätzel, *Chem. Mater.*, 1998, **10**, 2419.
11 P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B*, 2003, **107**, 14336.
12 M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C. Fischer and M. Grätzel, *Inorg. Chem.*, 1999, **38**, 6298.
13 P. Bonhôte, A. P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.
14 S. Ito, M. K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, S. M. Zakeeruddin and M. Grätzel, *Prog. Photovoltaics*, in press (available on web).
15 Q. Wang, J.-E. Moser and M. Grätzel, *J. Phys. Chem. B*, 2005, **109**, 14945.