Electron Transport in Nanocrystalline TiO_2 Films Sensitized with $[NBu_4]_2[\textit{cis}\text{-}Ru(Hdcbpy)_2(NCS)_2]$ (N719; $[NBu_4]^+$ = Tetrabutyl Ammonium Cation; H_2dcbpy = 4,4′-Dicarboxy-2,2′-bipyridine) and $[NBu_4]_2[Ru(Htcterpy)(NCS)_3]$ (B-dye; $H_3tcterpy$ = 4,4′,4″-Tricarboxy-2,2′:6′,2″-terpyridine)

Koji Miyamoto,[1] Masatoshi Yanagida,*[2] Kazuhiro Sayama,[2] Hideki Sugihara,[2] and Yoshimoto Abe[1]
[1]*Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510*
[2]*Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, AIST-Tsukuba Central 5, Tsukuba 305-8565*

(Received December 28, 2005; CL-051579; E-mail: m.yanagida@aist.go.jp)

We compared electron transport in nanocrystalline TiO_2 films sensitized with $[NBu_4]_2[\textit{cis}\text{-}Ru(Hdcbpy)_2(NCS)_2]$ (**N719**; $[NBu_4]^+$ = tetrabutylammonium cation; H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) and with $[NBu_4]_2[Ru(Htcterpy)(NCS)_3]$ (**B-dye**; $H_3tcterpy$ = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine). The electron diffusion coefficient (D) and the electron lifetime (τ) of the **N719**-sensitized TiO_2 were comparable to those of **B-dye**-sensitized TiO_2, although the open circuit photovoltage (V_{oc}) of the solar cells based on **N719**-sensitized TiO_2 was ca. 60 mV larger than that of the solar cells based on **B-dye**-sensitized TiO_2. We concluded that the energy of the conduction band edge (E_{cb}) of TiO_2 sensitized with **N719** was ca. 50 mV more negative than that of TiO_2 sensitized with **B-dye**.

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 sensitized with **N719** or **B-dye** exhibit solar conversion efficiencies of about 10%. **B-dye** cells have large short-circuit photocurrent densities (J_{sc}), because the dye absorbs over a wide range of wavelength. The open circuit photovoltage (V_{oc}) of **B-dye** cells is smaller than that of **N719** cells.[1,2] In this letter, we report on the influence of electron transport processes in **N719**- and **B-dye**-sensitized TiO_2 on the photovoltaic performance of DSSCs.

TiO_2 nanoparticles were prepared as described previously.[3] A nanoporous TiO_2 photoelectrode (area, 0.25 cm^2; thickness (d), 3 μm) was prepared by a screen-printing technique. After annealing at 450 °C, the TiO_2 thin films were immersed in ethanolic dye solution at a concentration of 0.2 mM and then kept at 25 °C for at least 16 h. Solar cells were assembled with the photoelectrode placed on the platinum counter electrode. The two electrodes were separated by a thermal adhesive film and sealed by heating of the film. The electrolyte solution, which consisted of 0.5 M 4-*tert*-butylpyridine (tBP), 0.6 M (1,2-dimethyl-3-propyl)imidazolium iodide, 0.05 M I_2, and 0.1 M LiI in acetonitrile, was introduced between the Pt electrode and the photoelectrode. The photovoltaic performance of the solar cells was measured with a source meter and an AM 1.5 G solar simulator (100 $mW\,cm^{-2}$). The intensity-modulated photocurrent spectra (IMPS) at short circuit and the intensity-modulated photovoltage spectra (IMVS) at open circuit were measured with an impedance analyzer under irradiation with modulated laser light (532 nm) and bias light (Xe lamp).[3–7]

Figure 1 shows the typical current–voltage curve obtained for **N719** cells and **B-dye** cells. The J_{sc} and V_{oc} values for **N719** cells were higher than those for **B-dye** cells. The maximum incident photon-to-current conversion efficiency (IPCE) of **B-dye** cells was 40% less than that of **N719** cells (Figure 1 inset).

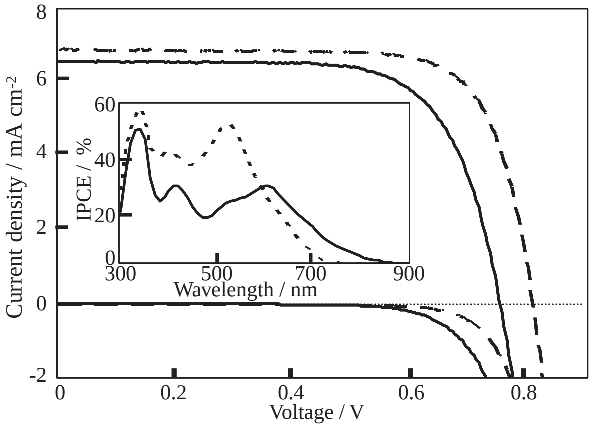

Figure 1. Photocurrent density–voltage curves of **N719** (- - -) and **B-dye** (—) cells under AM 1.5 irradiation (100 $mW\,cm^{-2}$). The onset of the dark current densities of the **N719** cell (- - -) and the **B-dye** cell (—) are also shown. (Inset) IPCE spectra of the **N719** (- - -) and the **B-dye** (—) cells.

Figure 2 shows D and τ values determined by measuring IMPS at short circuit and IMVS at open circuit, respectively. J_{sc} was linearly related to the bias light intensity, so J_{sc} was used to represent the light intensity and the electron density (n) in TiO_2. Figure 2 also shows that the electron diffusion coefficient (D) increased and the electron lifetime (τ) decreased as the bias light intensity was increased. When the trap sites at deeper energies were filled under higher bias light intensities, the diffusion of trapped and detrapped electrons became faster.[5] The τ value decreased when the bias light intensity increased because charge recombination is second order in n.[5] Figure 2 shows that there were no differences in the electron transport properties, such as D and τ, between **N719** cells and **B-dye** cells.

At short circuit, the diffusion length ($L = \sqrt{D\tau} \times 10^4$) was calculated to be 54 μm at $J_{sc} = 1\ mA\,cm^{-2}$, and this L value was much longer than d (3 μm). When $L \gg d$, J_{sc} is given by eq 1:[8]

$$J_{sc}(\lambda) = q\Phi \mathrm{LHE}(\lambda)\mathrm{APCE}(\lambda) \qquad (1)$$

where q is the quantity of charge on the electron (C), λ is the wavelength (nm), Φ is the incident light intensity (photons $s^{-1}\,cm^{-2}$), APCE is the absorbed photon-to-current conversion efficiency, and LHE is the light-harvesting efficiency, given by

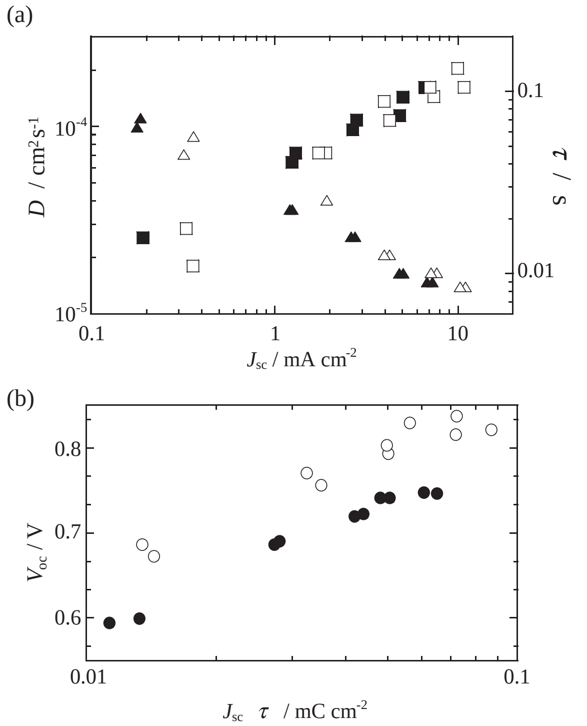

Figure 2. (a) Electron diffusion coefficient (D) vs. short-circuit photocurrent (J_{sc}) for an **N719** cell (□) and a **B-dye** cell (■), and electron lifetime (τ) vs. J_{sc} for a **N719** cell (△) and a **B-dye** cell (▲). J_{sc} values varied with bias light intensity. (b) Plots of V_{oc} vs. $J_{sc}\tau$ for an **N719** cell (○) and a **B-dye** cell (●).

LHE(λ) = 1–$10^{(-\varepsilon\Gamma 1000)}$, where ε and Γ are the molar absorption coefficient ($M^{-1}cm^{-1}$) and the amount of dye absorbed on TiO_2 (mole cm^{-2}), respectively. The LHE values for **N719** and **B-dye** cells were 0.70 at 520 nm and 0.41 at 600 nm, respectively. The APCE value is given by eq 2:[8]

$$\mathrm{APCE}(\lambda) = \frac{\eta_{\mathrm{inj}}}{1 - \left(\frac{1}{L^2 d^2}\right)} \tag{2}$$

where η_{inj} is the electron injection yield from the dye to TiO_2. The APCE values of **N719** and **B-dye** cells were 75% at 520 nm and 70% at 600 nm, respectively. Because the L value for **B-dye** cells was the same as that for **N719** cells, the η_{inj} value for **B-dye** cells was also comparable to that for **N719** cells. This fact means that J_{sc} depended mainly on LHE and on the wavelength range of absorption. For thin films ($d = 3\,\mu$m), the J_{sc} value of **N719** cells was higher than that of **B-dye** cells, because of the large difference in the LHE values of the two types of cells. For thicker films (LHE = 1), the J_{sc} value of **B-dye** cells was larger than that of **N719** cells (data not shown), because of the difference in the absorption wavelength range.

The relationship between V_{oc} and τ is given by eq 3:[8]

$$V_{oc} = \frac{kTm}{q} ln\left(\frac{10 J_{sc}\tau}{q n_0 d} + 1\right) \approx \frac{kTm}{q} ln\left(\frac{10 J_{sc}\tau}{q n_0 d}\right) \tag{3}$$

where k is Boltzmann's constant (JK^{-1}), T is absolute temperature (K), m is the ideal factor, and n_0 is the electron density (cm^{-3}) in the dark. The τ values in TiO_2 sensitized with **B-dye** were close to the values for **N719** (Figure 2), although the V_{oc} value for **B-dye** cells was 60 mV smaller than that for **N719** cells. Plots of $J_{sc}\tau$ vs. V_{oc} for **B-dye** and **N719** cells are shown in Figure 2. The slope of the curve for **B-dye** cells was comparable to that for **N719** cells. However, the intercept for **N719** cells was ca. 50 mV larger than that for **B-dye** cells. The onset of dark current density for **B-dye** cells shifted to a value that was 40 mV more positive than the value for **N719** cells (Figure 1). According to eq 3, these results show that the n_0 value for TiO_2 sensitized with **B-dye** was larger than that for TiO_2 sensitized with **N719**. The value of n_0 is given by Eq 4:[5]

$$n_0 = N_c \exp\left(\frac{E_{cb} - E_{redox}}{kT}\right) \tag{4}$$

where N_c is the density of states in the conduction band (cm^{-3}), and E_{redox} is the redox potential of I_3^-/I^-. Assuming that N_c does not depend on which dye was used, the energy of the conduction band edge (E_{cb}) for **B-dye** cells shifted to a value ca. 50 mV more positive than the energy for **N719** cells. We propose two possible explanations for the difference between the E_{cb} values for **B-dye** sensitized TiO_2 and **N719** sensitized TiO_2. One explanation is the degree of the interaction between the additives and TiO_2. Additives such as tBP, Li^+, and NBu_4^+ in the electrolyte cause a shift in the E_{cb} value.[9,10] These additive effects may vary with the structure of the dye on TiO_2. The other possible explanation is the interaction between the dye and TiO_2. The E_{cb} value may depend on the electric charge and polarity of the dye. Distinguishing between these two possibilities will require further investigation.

References

1 C. J. Baré, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, *J. Am. Ceram. Soc.* **1997**, *80*, 3157.
2 Md. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* **2001**, *123*, 1613.
3 M. Yanagida, K. Miyamoto, K. Sayama, K. Kasuga, M. Kurashige, Y. Abe, H. Sugihara, *Electrochim. Acta.*, in press.
4 L. Dloczik, O. Ileperuma, I. Lauermann, L. M. Peter, E. A. Ponomarev, G. Redmond, N. J. Shaw, I. Uhlendorf, *J. Phys. Chem. B* **1997**, *101*, 10281.
5 G. Franco, J. Gehring, L. M. Peter, E. A. Ponomarev, I. Uhlendorf, *J. Phys. Chem. B* **1999**, *103*, 692.
6 L. M. Peter, E. A. Ponomarev, G. Franco, N. J. Shaw, *Electrochim. Acta* **1999**, *45*, 549.
7 G. Schlichthörl, N. G. Park, A. J. Frank, *J. Phys. Chem. B* **1999**, *103*, 782.
8 S. Södergren, A. Hagfeldt, J. Olsson, S.-E. Lindquist, *J. Phys. Chem.* **1994**, *98*, 5552.
9 G. Schlichthörl, S. Y. Huang, J. Sprague, A. J. Frank, *J. Phys. Chem. B* **1997**, *101*, 8141.
10 S. Nakade, T. Kanzaki, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **2005**, *109*, 3480.

Published on the web (Advance View) February 22, 2006; DOI 10.1246/cl.2006.336