

Electron Transport in Coumarin-Dye-Sensitized Nanocrystalline TiO<sub>2</sub> ElectrodesKohjiro Hara,<sup>\*,†</sup> Koji Miyamoto,<sup>‡</sup> Yoshimoto Abe,<sup>‡</sup> and Masatoshi Yanagida<sup>\*,†</sup>

National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

Received: September 30, 2005

We investigated electron transport kinetics in terms of electron diffusion coefficient ( $D$ ) and electron lifetime ( $\tau$ ) in coumarin-dye-sensitized nanocrystalline TiO<sub>2</sub> electrodes by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS). We found that the values of  $\tau$  for coumarin-dye-sensitized TiO<sub>2</sub> electrodes were much shorter than that for an electrode coated with a Ru complex (N719 dye), suggesting that the back-electron-transfer process corresponding to recombination between conduction-band electrons in the TiO<sub>2</sub> and I<sub>3</sub><sup>−</sup> ions in the electrolyte occurs more easily in coumarin-dye-sensitized solar cells. In addition, the values of  $\tau$  depended on the kind of coumarin dye, each of which has a different number of thiophene moieties, suggesting that the molecular structure of the adsorbed dyes also affects the kinetics of electron transport in the TiO<sub>2</sub> electrodes.

Over the past decade, there has been a considerable increase in interest in dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO<sub>2</sub> electrodes, because these nonconventional solar cells exhibit high performance and have the potential for low-cost production.<sup>1–5</sup> Many researchers have been focusing on the process of electron transport in the nanocrystalline TiO<sub>2</sub> electrodes to understand the underlying mechanisms of DSSCs. In DSSCs, the electron transport process is important for high solar-cell performance, because this process is competitive between charge recombination with the dye cations and charge recombination with redox ions (I<sub>3</sub><sup>−</sup>). For the photogenerated electrons to be collected, electron transport in the TiO<sub>2</sub> electrode must be predominant against the charge recombination processes. The electron transport kinetics in nanocrystalline TiO<sub>2</sub> electrodes have been investigated in terms of electron diffusion coefficient ( $D$ ) and electron lifetime ( $\tau$ ) by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS).<sup>6–13</sup>

Ru–polypyridyl complexes, e.g., *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II), [Ru(dcbpH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>] (called N3 dye), and (Bu<sub>4</sub>N)<sub>2</sub>[Ru(dcbpyH)<sub>2</sub>(NCS)<sub>2</sub>] (N719 dye) developed by Grätzel and co-workers,<sup>2,3</sup> have usually been employed as the photosensitizers in DSSCs. The electron transport kinetics in nanocrystalline TiO<sub>2</sub> electrodes sensitized by N3 dye (or N719 dye) has been also investigated.<sup>14</sup> In comparison to a bare TiO<sub>2</sub> electrode, adsorption of N719 dye increases  $D$ , suggesting that the electron transport kinetics in the TiO<sub>2</sub> electrodes is affected by the dye adsorbed onto the surface.<sup>14</sup>

In addition to Ru complexes, organic dyes have also been utilized as photosensitizers in DSSCs. Coumarin derivatives,<sup>15,16</sup>

merocyanine derivatives,<sup>17</sup> and polyene dyes<sup>18,19</sup> have been designed successfully as organic-dye photosensitizers in DSSCs, and high solar energy to electricity conversion efficiencies of up to 8% under AM 1.5 G irradiation have been attained. However, the performances of DSSCs based on organic dyes have not yet exceeded the performances of those based on Ru complexes. We consider that the lower performance of DSSCs based on organic dyes compared to those based on Ru complexes is probably due to the lower open-circuit voltage ( $V_{oc}$ ) that is generated in the DSSCs based on organic dyes, rather than the performance of the short-circuit photocurrent density ( $J_{sc}$ ), which is almost the same. To obtain a high  $V_{oc}$ , for example, a higher concentration of 4-*tert*-butylpyridine (TBP), which suppresses the charge recombination between the electrons and I<sub>3</sub><sup>−</sup> ions (back-electron-transfer process), was required for DSSCs based on a coumarin dye than was required for DSSCs based on Ru complexes.<sup>20</sup> This suggests that the back-electron-transfer process occurs more easily in DSSCs based on a coumarin dye than in DSSCs based on Ru complexes.

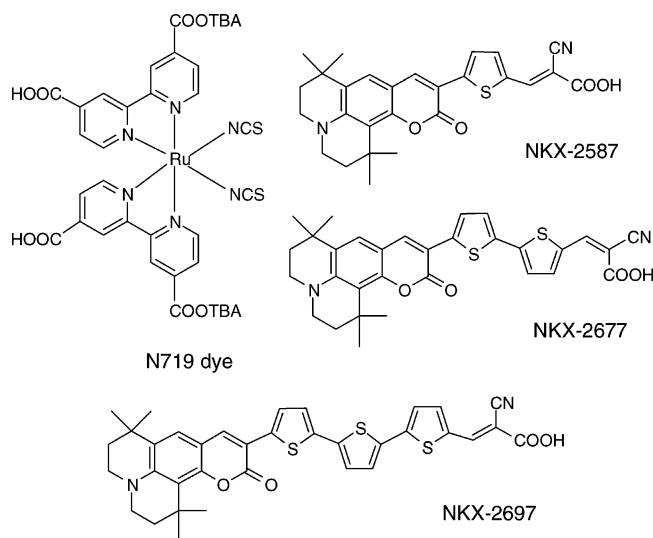
To clarify the differences between behaviors in DSSCs based on a Ru complex and those based on organic dyes, we used IMPS and IMVS to investigate the electron transport kinetics in coumarin-dye-sensitized nanocrystalline TiO<sub>2</sub> electrodes. We found that electron transport kinetics depended markedly on the kind of adsorbed dye. In this letter, we report that the electron transport kinetics in organic-dye-sensitized nanocrystalline TiO<sub>2</sub> electrodes was quite different from the electron transport kinetics in electrodes coated with a Ru complex.

Nanocrystalline TiO<sub>2</sub> photoelectrodes were prepared by a screen-printing technique. TiO<sub>2</sub> nanoparticles and an organic TiO<sub>2</sub> paste were prepared by the methods reported by Grätzel and co-workers.<sup>21</sup> The TiO<sub>2</sub> paste was then screen-printed onto a glass substrate coated with transparent conducting oxide (TCO, F-doped SnO<sub>2</sub>) and sintered at 500 °C in air for 1 h. The

\* To whom correspondence should be addressed. Tel: +81-29-861-3474. Fax: +81-29-861-3475. E-mail: k-hara@aist.go.jp.

<sup>†</sup> National Institute of Advanced Industrial Science and Technology.

<sup>‡</sup> Tokyo University of Science.

**CHART 1: Molecular Structures of N719 Dye (TBA: tetra-*n*-butylammonium cation), NKX-2587, NKX-2677, and NKX-2697**

thickness of the TiO<sub>2</sub> electrode was 3  $\mu$ m. In this study, we used N719 dye (Solaronix) and coumarin dyes, NKX-2587, NKX-2677, and NKX-2697 (Chart 1), as photosensitizers. Detailed procedures for the synthesis of the coumarin dyes are described elsewhere.<sup>16</sup> The dyes were dissolved at a concentration of 0.3 mM in a mixed solvent of 50:50 (vol %) *tert*-butyl alcohol and acetonitrile (AN). The TiO<sub>2</sub> films were immersed in the dye solutions and then kept at 25 °C for more than 12 h to allow the dye to adsorb onto the TiO<sub>2</sub> surface.

The electrochemical cell (two-electrode type) used for photovoltaic measurements consisted of a dye-sensitized TiO<sub>2</sub> electrode, a counter electrode, a film spacer (30- $\mu$ m thick), and an organic electrolyte; the cell was sealed. The counter electrode was a Pt film (ca. 200 nm thick) sputtered onto a TCO-coated glass plate. The electrolyte was 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI)/0.1 M LiI/0.05 M I<sub>2</sub>/0.5 M TBP in AN. The apparent surface area of the TiO<sub>2</sub> film electrode, measured by an optical microscope equipped with a digital camera, was 0.25–0.26 cm<sup>2</sup>. The photovoltaic performance of each solar cell was measured with a source meter and an AM 1.5 G solar simulator as the light source. The incident light intensity was calibrated by using a standard crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving a photoresponse range of an amorphous silicon solar cell.

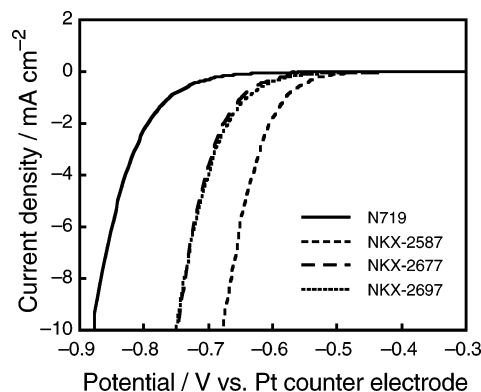
IMPS and IMVS measurements were carried out with a combination of constant-bias light irradiation (90% intensity) and low-intensity modulated illumination (10% intensity) from a green diode laser (532 nm, 50 mW), attenuated as necessary with a neutral density filter. The laser irradiation was modulated by an acousto-optic modulator. For IMPS and IMVS measurements, we used an impedance/gain-phase analyzer to drive the laser and to measure the photocurrent and photovoltage response. Electron lifetime ( $\tau$ ) was obtained from the frequency giving the minimum value for the imaginary part ( $\omega_{\min}$ ) by using the relation of  $\tau = 1/\omega_{\min}$ .<sup>7,8</sup> Detailed characterizations of  $D$  and  $\tau$  are given in the Supporting Information.

The light-harvesting efficiencies (LHEs) and photovoltaic performances of the DSSCs based on each of the dyes are summarized in Table 1. The LHE for the DSSC based on N719 dye is below unity (0.6) because of using a thin TiO<sub>2</sub> electrode (3  $\mu$ m), whereas the LHEs for the DSSCs based on coumarin

**TABLE 1: Photovoltaic Performance of DSSCs Based on Several Dyes**

dye	LHE <sup>a</sup> at $\lambda_{\max}$	$J_{sc}/\text{mA cm}^{-2}$	$V_{oc}/\text{V}$	fill factor	$\eta/\%$
N719	0.6 <sup>b</sup>	7.0	0.83	0.76	4.4
NKX-2587	1.0	9.4	0.64	0.76	4.6
NKX-2677	1.0	11.3	0.72	0.75	6.1
NKX-2697	1.0	11.6	0.68	0.67	5.3

<sup>a</sup> Light-harvesting efficiency. <sup>b</sup> LHE at 530 nm. Conditions: irradiated light, AM 1.5 G (100 mW cm<sup>-2</sup>); photoelectrode, TiO<sub>2</sub> (3- $\mu$ m thickness and 0.25–0.26 cm<sup>2</sup>); electrolyte, 0.6 M DMPImI/0.1 M LiI/0.05 M I<sub>2</sub>/0.5 M TBP in AN.

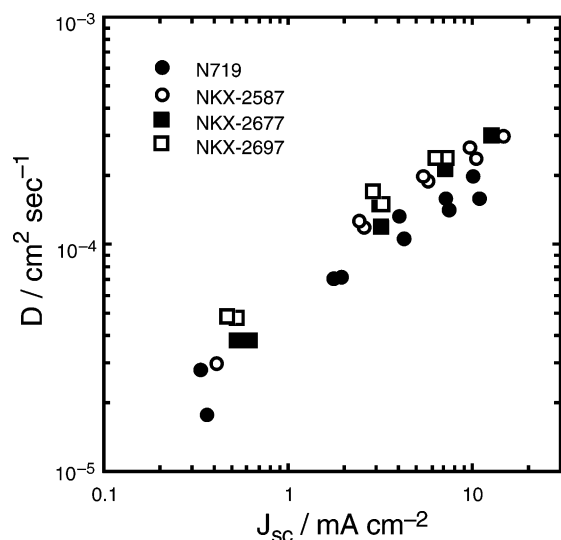


**Figure 1.** Current density vs potential (vs Pt counter electrode) curves obtained with DSSCs based on N719 dye and coumarin dyes under dark conditions: (—) N719 dye, (---) NKX-2587, (- - -) NKX-2677, (.....) NKX-2697.

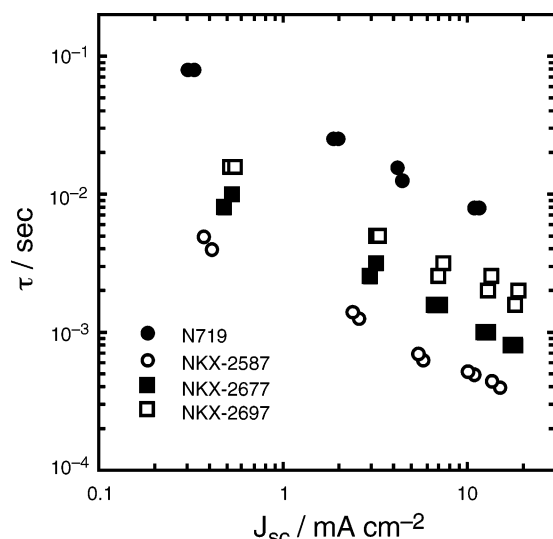
dyes are unity because of the large absorption coefficients of the coumarin dyes.<sup>16</sup> The  $V_{oc}$  for the DSSC based on N719 dye was much higher than for the DSSCs based on coumarin dyes NKX-2587, NKX-2677, and NKX-2697 (Table 1). The current–voltage curves obtained under dark conditions showed onsets that were obviously more positive for the DSSCs based on coumarin dyes than for the DSSC based on N719 dye (Figure 1). This indicates that the back-electron-transfer process corresponding to the reaction between the conduction-band electrons in the TiO<sub>2</sub> and I<sub>3</sub><sup>-</sup> ion in the electrolyte under dark condition occurs more easily in DSSCs based on coumarin dyes than in the DSSC based on N719 dye. A predominant back-electron-transfer process would directly act to lower the  $V_{oc}$  of DSSCs based on coumarin dyes, compared to DSSCs based on N719 dye: the mechanism of the back-electron-transfer process under irradiation should also be considered in addition to the process under the dark condition.

No large difference between the electron diffusion coefficients ( $D$ ) for the DSSCs based on coumarin dyes and N719 dye was observed (Figure 2). Nakade et al. previously observed that adsorption of N719 dye onto a TiO<sub>2</sub> electrode increases the  $D$  value compared to a bare TiO<sub>2</sub> electrode, and they interpreted this increased  $D$  as being caused by a decrease in the number of trap sites on the TiO<sub>2</sub> surface due to adsorption of the dye.<sup>14</sup> Our result suggests that the  $D$  value does not depend on the kind of dye.

The electron lifetimes ( $\tau$ ) were much shorter for the DSSCs based on the coumarin dyes than for the DSSC based on N719 dye (Figure 3). From these results, it can be seen that the electron diffusion length,  $L (= (D\tau)^{0.5})$ , would be affected more markedly by changing the value of  $\tau$ , rather than changing the value of  $D$ . The details of the mechanism underlying the different values of  $\tau$  for N719 dye and coumarin dyes are unclear at present. Nakade et al. reported that  $\tau$  for a DSSC with an electrolyte containing tetra-*n*-butylammonium (TBA) cation was



**Figure 2.** Electron diffusion coefficient ( $D$ ) obtained with DSSCs based on N719 dye and coumarin dyes as a function of the short-circuit photocurrent density ( $J_{sc}$ ): (●) N719 dye, (○) NKX-2587, (■) NKX-2677, (□) NKX-2697.



**Figure 3.** Electron lifetime ( $\tau$ ) obtained with DSSCs based on N719 dye and coumarin dyes as a function of the short-circuit photocurrent density ( $J_{sc}$ ): (●) N719 dye, (○) NKX-2587, (■) NKX-2677, (□) NKX-2697.

longer than that of those in DSSCs based on electrolytes of Li and 1,2-dimethyl-3-*n*-propylimidazolium (DMPIIm) cations.<sup>13</sup> Nakade et al. concluded that adsorption of TBA cations, which are more bulky than Li and DMPIIm cations and form a thicker double layer on the TiO<sub>2</sub> surface, decreased the concentration of I<sub>3</sub><sup>−</sup> ions near the surface, and consequently decreased the back-electron-transfer process.<sup>13</sup> With these points taken into consideration, the different values of  $\tau$  for N719 dye and coumarin dyes might be caused by the different molecular size and structure of these dyes.

The  $\tau$  for the DSSCs based on coumarin dyes increased as the number of thiophene moieties increased (Figure 3). The amount of NKX-2587 adsorbed onto the TiO<sub>2</sub> film (3  $\mu$ m thickness) was much less than the amount of NKX-2697:  $1.7 \times 10^{-8}$  mol cm<sup>−2</sup> for NKX-2587 and  $8.3 \times 10^{-8}$  mol cm<sup>−2</sup> for NKX-2697. This is probably caused by intermolecular  $\pi$ – $\pi$  stacking interactions due to the thiophene moieties, as has been observed in substituted oligothiophenes.<sup>22,23</sup> The larger molecular size of NKX-2697, which has the largest number of

thiophene moieties, together with the larger amounts adsorbed onto the TiO<sub>2</sub> electrode, might prevent the back-electron-transfer process because of a steric effect.

At the present, we can conclude that the lower voltages in DSSCs based on organic dyes as compared to those based on Ru complexes are due to shorter  $\tau$  values in the system, resulting in shorter  $L$ . We are now further investigating the detailed mechanisms.

**Acknowledgment.** This work was supported by Japan's Ministry of Education, Culture, Sports, Science, and Technology, Center of Excellence Development (COE).

**Supporting Information Available:** Detailed characterizations of  $D$  and  $\tau$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- O'Regan, B.; Grätzel, M. *Nature (London)* **1991**, 353, 737–739.
- Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, 115, 6382–6390.
- Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fishcer, C.-H.; Grätzel, M. *Inorg. Chem.* **1999**, 38, 6298–6305.
- Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, 33, 269–277.
- Grätzel, M. *J. Photochem. Photobiol., A* **2004**, 164, 3–14.
- Cao, F.; Oskam, G.; Meyer, G. J.; Searson, P. C. *J. Phys. Chem.* **1996**, 100, 17021–17027.
- Schlichthörl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J. *J. Phys. Chem. B* **1997**, 101, 8141–8155.
- Dloczik, L.; Ieperuma, O.; Lauermann, I.; Peter, L. M.; Ponomarev, E. A.; Redmond, G.; Shaw, N. J.; Uhlendorf, I. *J. Phys. Chem. B* **1997**, 101, 10281–10289.
- Peter, L. M.; Wijayantha, K. G. U. *Electrochem. Commun.* **1999**, 1, 576–580.
- Nakade, S.; Matsuda, M.; Kambe, S.; Saito, Y.; Kitamura, T.; Sakata, T.; Wada, Y.; Mori, H.; Yanagida, S. *J. Phys. Chem. B* **2002**, 106, 10004–10010.
- Bisquert, J.; Vikhrenko, V. S. *J. Phys. Chem. B* **2004**, 108, 2313–2322.
- Oekermann, T.; Yoshida, T.; Minoura, H.; Wijayantha, K. G. U.; Peter, L. M. *J. Phys. Chem. B* **2004**, 108, 8364–8370.
- Nakade, S.; Kanzaki, T.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2005**, 109, 3480–3487.
- Nakade, S.; Saito, Y.; Kubo, W.; Kanzaki, T.; Kitamura, T.; Wada, Y.; Yanagida, S. *Electrochem. Commun.* **2003**, 5, 804–808.
- Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, 107, 597–606.
- Hara, K.; Wang, Z.-S.; Sato, T.; Furube, A.; Katoh, R.; Sugihara, H.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S. *J. Phys. Chem. B* **2005**, 109, 15476–15482.
- Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, 126, 12218–12219.
- Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, 16, 1806–1812.
- Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Yoshihara, T.; Murai, M.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Arakawa, H. *Adv. Funct. Mater.* **2005**, 15, 246–252.
- Hara, K.; Dan-oh, Y.; Kasada, C.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Langmuir* **2004**, 20, 4205–4210.
- Wang, P.; Zakeeruddin, S. M.; Comte, P.; Charvet, R.; Humphry-Baker, R.; Grätzel, M. *J. Phys. Chem. B* **2003**, 107, 14336–14341.
- Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, 115, 8716–8721.
- Stecher, R.; Gompf, B.; Münter, J. S. R.; Effenberger, F. *Adv. Mater.* **1999**, 11, 927–931.