Transactions of the Materials Research Society of Japan 33[1] 161-164 (2008)

Interfacial electron transfer mechanisms in bithiophene sensitized TiO_2 based solar cells

Yasuhiro Tachibana,* Yasuhide Otsuka, Kazuya Umekita, and Susumu Kuwabata
Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan
Fax: 81-6-6879-7374, e-mail: y.tachibana@chem.eng.osaka-u.ac.jp

Kinetic studies at TiO_2/bithiophene/electrolyte interfaces were conducted, and their parameters to the solar cell functions were related. The solar cell based upon the bithiophene sensitised TiO_2 films resulted in the maximum IPCE of approximately 25 % at 400 nm. Comparison of emission studies between the bithiophene adsorbed TiO_2 and Al_2O_3 revealed the electron injection from the excited bithiophene into the TiO_2 with the efficiency of nearly 100 %. The charge recombination between the bithiophene cation and the electron in the TiO_2 appeared to be fast with a half decay time of 70 μs in comparison to the ruthenium dye sensitized TiO_2 film (~1 ms). The bithiophene regeneration rate with the half time of 20 μs was slightly faster, clarifying the inferior photocurrent performance.
Key words: Thiophene, TiO_2, nanohybrid, solar cells, electrolyte

1. INTRODUCTION

Conducting polymer/metal oxide nanohybrid films have received considerable interests for their applications to electronic devices.[1-4] Conducting polymers have been studied for a wide variety of electronic devices, e.g. display devices,[5], lasers,[6], FETs,[7] and photovoltaics[8] owing to economical viability and easy processability. Metal oxides also possess attractive properties such as environmental viability and excellent stability, having been applied for transparent electrodes,[9] photocatalysis[10] and solar cells.[11] Combination of these materials with nanometer size control leads to introduction of further novel functions in addition to their individual attractive properties.

As a novel fabrication process of polymer/metal oxide nanohybrid films, we have recently introduced photoinduced polymerization of thiophene inside the TiO_2 nanoporous film.[12] Initially, thiophene monomers possessing a carboxyl group, 2,2'-bithiophene-5-carboxylic acid (BTC), were adsorbed on the TiO_2 surface, and a selective excitation of the BTC led to the thiophene photo-polymerization inside the TiO_2 pore. Thus, this method has thoroughly provided nanohybridization and electronic connection within TiO_2. The resultant nanohybrid films were readily applied as working electrodes in sensitized-type solar cells. This experimentation was devised to substantiate if this nanohybrid fabrication method can directly be employed for device applications. However, their solar cell performance resulted to be low in comparison to the Ru dye sensitized solar cells.[12] The origin could be explained by the following factors; (i) less accessibility of the redox electrolyte (I_3^-/I^-) inside pores, (ii) slow re-reduction of the surface attached polythiophene due to the negative potential shift of the polythiophene, (iii) accelerated charge recombination rate between the oxidized polymer and the electron in the TiO_2. These factors correlate to interfacial charge transfer processes in the solar cell, and thus it is important to elucidate parameters controlling the charge transfer rates.

In this paper, we focused on kinetic studies at TiO_2/BTC/electrolyte interfaces. The BTC adsorbed TiO_2 films rather than the polymer/TiO_2 nanohybrid films were employed to exclude the point (i), and thus the electrolyte can penetrate inside the pore. The origin of the inferior performance obtained for the nanohybrid films in relation to the point (iii) is particularly discussed.

2. EXPERIMENTAL

2.1 Samples

TiO_2 nanocrystalline films, thickness 4~7 μm, were prepared on a slide glass or a fluorine doped tin oxide glass, FTO, (Asahi glass, type-U, 10 Ω/square) as previously described.[12] The TiO_2 paste (Ti-Nanoxide HT/SP, 15 nm in diameter) was purchased from Solaronix SA. The printed film was calcined at 500 °C for 1 h in air. Al_2O_3 (Degussa Aluminum Oxide, Alu C, particle diameter 13 nm) nanoporous films, thickness: 4 μm, were prepared following the reported method.[12] Sensitization of a TiO_2 or Al_2O_3 film by 2,2'-bithiophene-5- carboxylic acid, BTC, (Maybridge, 97%) was conducted by immersion

into the 10 mM BTC ethanol solution for 10 min. at room temperature.

2.2 Optical experiments

Absorption and emission spectra were measured by a UV/Vis absorption spectrometer (JASCO, V-670) and an emission spectrometer (Horiba, FluoroLog-3), respectively.

Microsecond to millisecond transient absorption studies were conducted with a Nd/YAG laser (Spectra Physics, Quanta-Ray GCR-11) pumped dye laser (Usho Optical Systems, DL-100, ~10 ns pulse duration) as a pump source, a 100 W tungsten lamp as a probe source, and a photodiode-based detection system (Costronics Electronics) with a TDS-2022 Tektronix oscilloscope. Details of the laser system will be described elsewhere. The BTC sensitized TiO_2 (BTC/TiO_2) film was immersed in an optical cuvette filled with approximately 4 ml propylene carbonate solution containing 0.1 M LiI or $LiClO_4$. The Li^+ concentration was adjusted to 0.1 M, so that the TiO_2 conduction band energy level remained constant.[13-15] Transient data were obtained by employing a low excitation density ~0.13 mJ/cm^2 with 425 nm excitation at 1 Hz. This excitation density corresponds to ~1.0 excited BTC per TiO_2 nanoparticle.

2.3 Photoelectrochemical solar cells

Sandwich type solar cells were fabricated by binding a redox electrolyte with the nanohybrid electrode and the Pt counter electrode.[16] Prior to the BTC adsorption on the TiO_2, the film was treated with titanium tetrachloride aqueous solution to coat the surface with a thin TiO_2 layer. The electrolyte was prepared by dissolving 0.6 M dimethyl propyl imidazolium iodide (Tomiyama Pure Chemical), 0.05 M iodine (99.8%, Wako), 0.1 M lithium iodide (99.995 %, Wako) and 0.5 M *tert*-butylpyridine (99%, Aldrich) in dried acetonitrile (99%, Wako). A Xe lamp with a monochromator (Bunko Keiki, SM-25) was used for IPCE measurements. An I-V curve was observed by an AM1.5 solar simulator (100 mW/cm^2, Yamashita Denso, YSS-50A).

3. RESULTS AND DISCUSSION

Bithiophene is known to possess an absorption band in a UV region, and as shown in Fig. 1, an absorption spectrum of 100 μM BTC in ethanol exhibits light absorption at <380 nm. However, the TiO_2 film turned yellow, when the BTC is adsorbed on the TiO_2. Fig. 1 also compares an absorption spectrum and a photograph of the BTC/TiO_2 with those of a TiO_2 film alone. The yellow coloration may originate from a BTC-TiO_2 charge transfer (CT) state (from BTC HOMO to Ti^{4+}) following the tight adsorption of the BTC molecules to the TiO_2 surface. Appearance of similar absorption bands were previously reported,[17, 18] and were assigned to CT absorption bands.

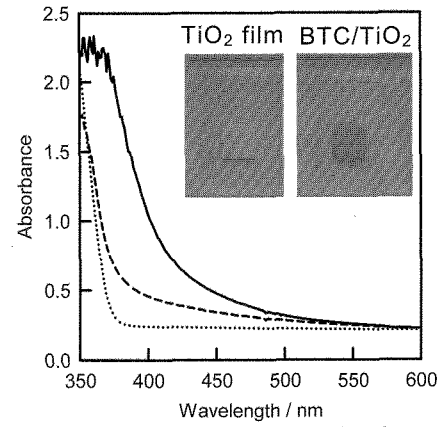


Fig. 1. Absorption spectra and photographs (inset) of the TiO_2 film (– – –) and BTC/TiO_2 (——). The paste containing large TiO_2 particles (diameter: ~50 nm) was used for the photographs. An absorption spectrum of 100 μM BTC in ethanol (·····) is also shown as comparison.

The BTC/TiO_2 was readily applied as a working electrode in a sensitized-type solar cell. Fig. 2 shows IPCE spectra obtained for the cells based on the BTC/TiO_2 film and the unsensitised TiO_2 film. The BTC/TiO_2 film clearly exhibits enhanced photocurrent response in a wavelength range of 400~650 nm, with the maximum IPCE of 25% at 400 nm, in comparison to the unsensitised TiO_2 film. I-V characteristics of the BTC/TiO_2 solar cell are presented in the inset of Fig. 2. The short circuit photocurrent density, J_{sc}, the open circuit photovoltage, V_{oc}, the fill factor, FF, and the solar-to-electric conversion efficiency, η, are 0.70 mA/cm^2, 0.39 V, 0.53 and 0.14 %, respectively. On comparison with the absorbance of the film shown in Fig. 1, the electron transfer yield is low compared to the ruthenium dye sensitized solar cells.[16, 19]

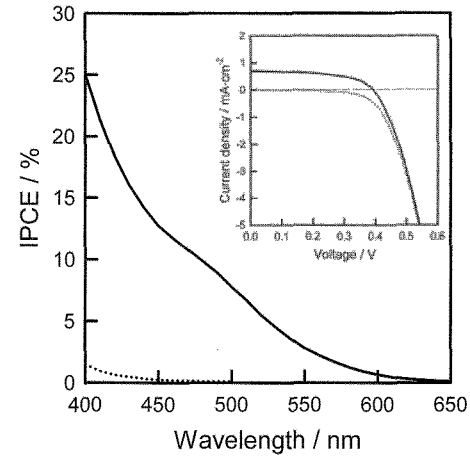
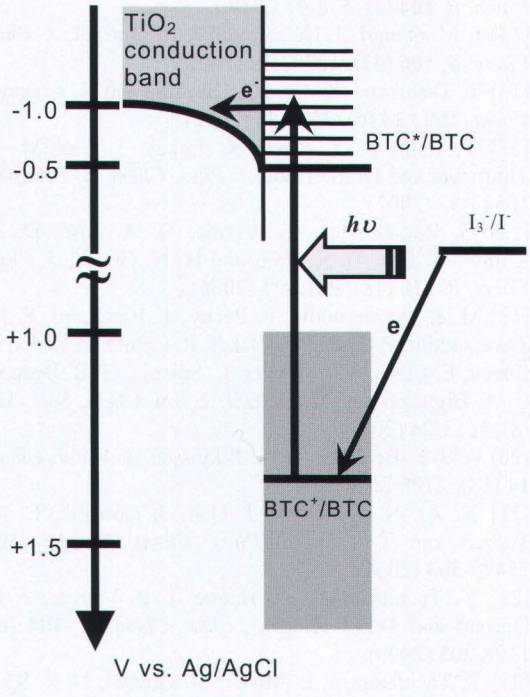


Fig. 2. IPCE spectra observed for the BTC sensitized solar cell (——).The IPCE obtained for the TiO_2 alone is also shown (·····). The inset shows I-V curves in dark (·····) and under AM1.5 light with the light power of 100 mW/cm^2 (—).

The potential energy diagram for the TiO_2 conduction band, the BTC and the I_3^-/I^- redox potentials are summarized in Scheme 1. The TiO_2 conduction band edge and the BTC redox potential were determined experimentally in the previous study.[12] Interestingly, the BTC indicates a wide distribution of redox potentials when adsorbed on the TiO_2 surface, probably owing to local electric fields. Due to this potential distribution, there is much difficulty in determining the LUMO potential. Nevertheless, if the HOMO-LUMO energy difference of the BTC is assumed to 2.3 eV, deduced from the absorption onset (at 540 nm), the LUMO level can provisionally be calculated to ~-0.5 V. Comparing the potential energy levels between the TiO_2 conduction band and the BTC excited state potentials, an efficient electron injection from the BTC into the TiO_2 can be expected. The BTC cation state, following the injection process, can readily be re-reduced by the I_3^-/I^- electrolyte.

The electron injection efficiency was estimated by emission spectra of the BTC adsorbed on the TiO_2 and the Al_2O_3. Since Al_2O_3 is known as an insulator, no electron acceptor state is available for the BTC. Fig. 3 shows the absorption and emission spectra. The BTC/Al_2O_3 indicates an absorption maximum at approximately 320 nm, and the strong emission with a peak at 425 nm was observed. In contrast, the emission for the BTC/TiO_2 was completely quenched, suggesting the efficient injection from the BTC to the TiO_2.



Scheme 1. Potential energy diagram of the TiO_2 electronic states, the adsorbed BTC and the I_3^-/I^- electrolyte. The distribution of the BTC redox potentials is shown according to our recent published results.[12]

Excitation at 290, 400, 425 and 450 nm also results in complete emission quenching, implying that the TiO_2 excitation at <400 nm does not influence the quenching. The electron injection yield is estimated to be >99 % by calculation from these quenching data, in accordance with the previous reports.[20, 21] Following the BTC excitation, the electron injection from the BTC to the TiO_2 conduction band is expected to occur on femtosecond or picosecond time scales. This speculation can be justified by the report published by Janssen et al.[20] that the electron transfer from the terthiophene attached TiO_2 nanoparticle was <4 ps. The electron injection from a dye to a semiconductor is reported to occur on femtosecond and picosecond time scales.[22] These ultrafast electron injection studies are in sound agreement with the emission quenching data shown in Fig. 3.

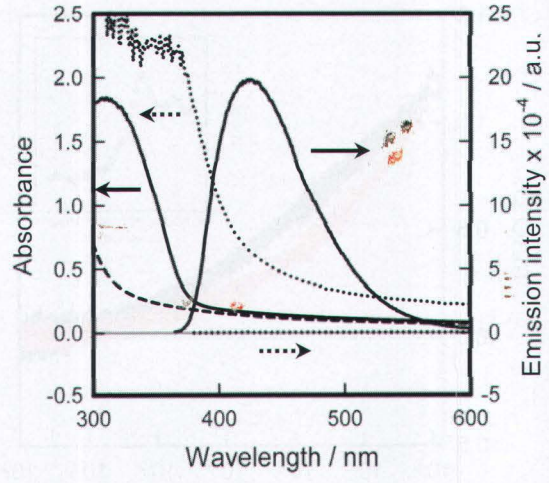


Fig. 3. Absorption and emission spectra for BTC adsorbed Al_2O_3 (——) and TiO_2 films (·····). Both films were excited at 355 nm for the emission data. An absorption spectrum of an Al_2O_3 film (– – –) is also shown as comparison.

The BTC regeneration process was observed using a transient absorption spectrometer. Following the excitation, an instrument response limited absorption spectrum was appeared with a peak at 670 nm (see the inset in Fig. 4). This absorption is provisionally attributed to the BTC cation band since the injected electrons have low absorption coefficients in the range of visible to near infra-red wavelengths.[15] Fig. 4 compares the cation absorption decays of the BTC/TiO_2 films in the presence and the absence of I^-. The BTC/TiO_2 in the $LiClO_4$ solution indicates charge recombination reactions between the BTC cation and the electron in the TiO_2, being attributed to a geminate recombination reaction.[14] The observed recombination with a decay half time of 70 μs is faster than the ruthenium dye/TiO_2 (~1 ms).[14, 23] In contrast, slight acceleration of the decay profile was observed for the BTC/TiO_2 film in the LiI solution with a half time of 20 μs. This acceleration probably results from the re-reduction of the BTC by I^-, competing with the

charge recombination process. These similar time scales of the BTC regeneration and the charge recombination rate clarify the origin of the lower IPCEs observed as in Fig. 2. Palomares reported[24] that the distance between the dye and the TiO_2 largely influences charge recombination rates for the dye sensitized TiO_2 films; the shorter the distance, the faster the charge recombination rate. A bithiophene unit is directly linked to the TiO_2 through the carboxylic moiety, indicating that the relatively fast charge recombination rate is expected. This study therefore reinforces the importance of the distance control between the chromophore and the TiO_2 surface, probably being the key parameter determining the performance of the solar cells based upon the polythiophene/TiO_2 nanohybrid films.

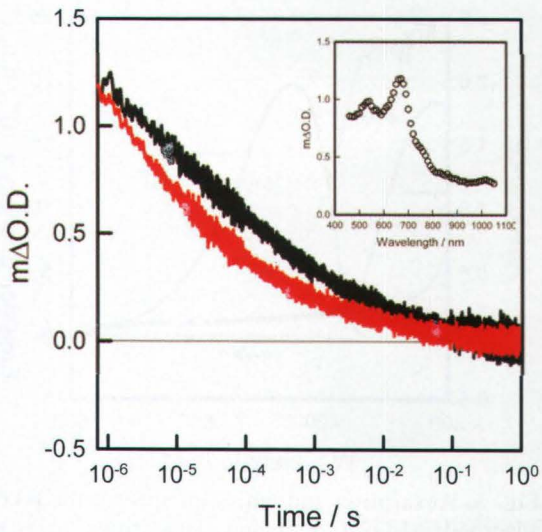


Fig. 4. Transient absorption decays of the BTC cation states at 650 nm, obtained for the BTC/TiO_2 film in the presence of 0.1 M $LiClO_4$ (black line) and 0.1 M LiI (red line) in the solvent with the light excitation at 425 nm. The absorption decay half times are 70 and 20 μs for 0.1 M $LiClO_4$ and 0.1 M LiI, respectively. A transient spectrum of the charge separated state (BTC^+ and $e^-(TiO_2)$) at 1 μs after the excitation is shown in the inset.

We acknowledge Professors Hikaru Kobayashi and Masao Takahashi from the Institute of Scientific and Industrial Research in Osaka University for using AM1.5 solar simulator. We also thank Dr. Norio Nagayama from Osaka University for the emission measurements. This work was financially supported by Grant-in-Aid for Scientific Research, 18201022 and 18685002, from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and TEPCO Research Foundation. The Association for the Progress of New Chemistry, Japan, and the Venture Business Laboratory in Osaka University are also acknowledged for the financial support.

References

[1] K. Tajima, L.-S. Li and S. I. Stupp, *J. Am. Chem. Soc.,* **128** (16), 5488-95 (2006).
[2] Y. Liu, M. A. Summers, C. Edder, J. M. J. Frechet and M. D. McGehee, *Adv. Mater.,* **17** (24), 2960-64 (2005).
[3] W. J. E. Beek, M. M. Wienk and R. A. J. Janssen, *Adv. Funct. Mater.,* **16** (8), 1112-16 (2006).
[4] P. Ravirajan, S. A. Haque, J. R. Durrant, D. Poplavskyy, D. D. C. Bradley and J. Nelson, *J. Appl. Phys.,* **95** (3), 1473-80 (2004).
[5] Y. Cao, I. D. Parker, G. Yu, C. Zhang and A. J. Heeger, *Nature (London),* **397** (6718), 414-17 (1999).
[6] N. Tessler, G. J. Denton and R. H. Friend, *Nature (London),* **382** (6593), 695-97 (1996).
[7] N. Stutzmann, R. H. Friend and H. Sirringhaus, *Science (Washington),* **299** (5614), 1881-85 (2003).
[8] L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science (Washington),* **293** (5532), 1119-22 (2001).
[9] H. Kawazoe, M. Yasukawa, H. Kyodo, M. Kurita, H. Yanagi and H. Hosono, *Nature (London),* **389** (6654), 939-42 (1997).
[10] A. Fujishima and K. Honda, *Nature (London),* **238** (5358), 37-8 (1972).
[11] B. O' Regan and M. Grätzel, *Nature,* **353** 737-39 (1991).
[12] Y. Otsuka, Y. Okamoto, H. Y. Akiyama, K. Umekita, Y. Tachibana and S. Kuwabata, *J. Phys. Chem. C, in press* (2008).
[13] G. Redmond and D. Fitzmaurice, *J. Phys. Chem.,* **97** (7), 1426-30 (1993).
[14] S. A. Haque, Y. Tachibana, R. L. Willis, J. E. Moser, M. Grätzel, D. R. Klug and J. R. Durrant, *J. Phys. Chem. B,* **104** (3), 538-47 (2000).
[15] I. Montanari, J. Nelson and J. R. Durrant, *J. Phys. Chem. B,* **106** (47), 12203-10 (2002).
[16] Y. Tachibana, K. Hara, K. Sayama and H. Arakawa, *Chem. Mat.,* **14** (6), 2527-35 (2002).
[17] T. Rajh, L. X. Chen, K. Lukas, T. Liu, M. C. Thurnauer and D. M. Tiede, *J. Phys. Chem. B,* **106** (41), 10543-52 (2002).
[18] G. Ramakrishna, S. Verma, D. A. Jose, D. K. Kumar, A. Das, D. K. Palit and H. N. Ghosh, *J. Phys. Chem. B,* **110** (18), 9012-21 (2006).
[19] M. 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 and M. Grätzel, *J. Am. Chem. Soc.,* **123** (8), 1613-24 (2001).
[20] W. J. E. Beek and R. A. J. Janssen, *J. Mater. Chem.,* **14** (18), 2795-800 (2004).
[21] X. Ai, N. Anderson, J. Guo, J. Kowalik, L. M. Tolbert and T. Lian, *J. Phys. Chem. B,* **110** (50), 25496-503 (2006).
[22] Y. Tachibana, S. A. Haque, I. P. Mercer, J. R. Durrant and D. R. Klug, *J. Phys. Chem. B,* **104** (6), 1198-205 (2000).
[23] Y. Tachibana, J. E. Moser, M. Grätzel, D. R. Klug and J. R. Durrant, *J. Phys. Chem.,* **100** (51), 20056-62 (1996).
[24] E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz and J. R. Durrant, *J. Am. Chem. Soc.,* **125** (2), 475-82 (2003).

(Received December 31, 2007;Accepted Febrary 13, 2008)