Enhanced Photocurrent in Nanocomposite of Dye-doped Titania Gel and Carbon Nanotubes

Hiroyuki Itai,[1] Hiromasa Nishikiori,*[1] Nobuaki Tanaka,[1] Morinobu Endo,[2] and Tsuneo Fujii[1]
[1]*Department of Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553*
[2]*Department of Electrical and Electronic Engineering, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553*

(Received June 2, 2008; CL-080551; E-mail: nishiki@shinshu-u.ac.jp)

A photocurrent was observed in a nanocomposite electrode consisting of an unheated dye-doped titania gel and carbon nanotubes. The electrode was prepared by the electrophoresis of carbon nanotubes and a simple dip-coating with a titanium isopropoxide sol containing fluorescein on ITO–glass plates at room temperature. The shape of the photocurrent action spectra was similar to that of the absorption spectrum of fluorescein. The photocurrent was generated by excitation of the dye and was enhanced by the carbon nanotubes.

Fine functional materials are required for the development of high-quality electronic devices. Dye-sensitized solar cells based on titania have been paid significant attention as new energy generators.[1] Carbon nanotubes (CNTs) and nanofibers are promising materials having quantum characteristics.[2–4] The composition of these materials provides very interesting characteristics for producing new and excellent devices.[5–9] We previously investigated a photocurrent of an unheated titania gel containing dispersed dye.[10] In this study, a nanocomposite consisting of such a dye-doped titania gel and CNTs has been prepared by a simple low-temperature process, and its photoelectric properties have been measured by simple techniques.

Glass plates coated with an ITO transparent electrode (AGC Fabritech) were soaked in hydrochloric acid ($1.0\,\mathrm{mol\,dm^{-3}}$) for 1 h and then rinsed with pure water. The electrolyte for the electrical measurement consisted of a diethylene glycol solution of iodine ($5.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) and lithium iodide ($0.50\,\mathrm{mol\,dm^{-3}}$).

The multiwalled CNTs (95% purity, Ilijin Nanotech) have a diameter of 10–30 nm and a length of 10–20 μm. In order to increase their dispersibility into matrices, the CNTs were treated with a concentrated H_2SO_4/HNO_3 mixture (3/1 in volume) at 313 K for 24 h and then rinsed with a copious amount of water.[11]

The sol–gel reaction system was prepared by mixing $5.0\,\mathrm{cm^3}$ of titanium tetraisopropoxide, $25.0\,\mathrm{cm^3}$ of ethanol, $0.21\,\mathrm{cm^3}$ of water, and $0.21\,\mathrm{cm^3}$ of concentrated nitric acid as the catalyst for the sol–gel reaction. Fluorescein was dissolved in the sol–gel system in which the concentration of fluorescein was $1.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ (dye/Ti $= 1/60$). The dip-coated thin films were made from the sol–gel systems reacting for one day to prepare the electrodes in this study.

The acid-treated CNTs were deposited onto the ITO–glass plates by electrophoresis at 5.0 V for 1 min in *N*,*N*-dimethylformamide to form blackish transparent thin film (50–100 nm). The dye-containing sol–gel reaction system was applied three times (ca. 200 nm) on the CNT-coated and CNT-free ITO-glass plates. The former is the nanocomposite of dye-doped titania gel and CNTs.

The UV–vis absorption spectra of the prepared electrode samples were observed in transmission using a spectrophotometer (Shimadzu UV-2500). The iodine-based electrolyte was allowed to soak into the space between the electrode sample and the counter Pt electrode. Visible light of wavelengths longer than 400 nm obtained from a fluorescence spectrophotometer (Shimazdu RF-5300) with a 150-W Xe short arc lamp (Ushio) was irradiated on the electrodes for the spectroscopy. Under light irradiation, the short circuit currents of the electrodes were measured by an electrometer (Keithley model 617). The *I*–*V* curves of the electrodes were measured by a potentiostat (Hokuto Denko HSV-100).

Figure 1 shows a comparison of the visible absorption and photocurrent spectra of the fluorescein-doped titania gel and the composite of it and the CNTs. The spectra of these films were observed around 400–550 nm. A higher absorbance (ca. 1.3 times) was observed over the range from 300 to 600 nm in the spectrum of the composite due to the CNT absorption. The photocurrent spectra of both films have a shape similar to the broad absorption spectrum of fluorescein. The photocurrent values are triply enhanced by the presence of the CNT films. Their peaks at 490–500 nm are assigned to the mixture of the anion and dianion

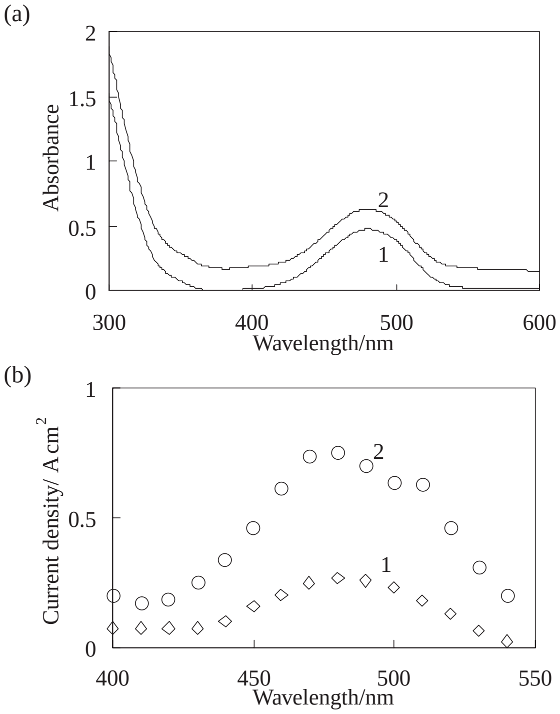

Figure 1. (a) UV–vis absorption and (b) photocurrent spectra of (1) the fluorescein-doped titania gel and (2) the composite of it and CNTs.

species of fluorescein, based on the spectra observed in water.[10,12] This correspondence indicates that the current electrons were produced by a process consisting of the light absorption of fluorescein and electron transfer from its excited states to the titania gel. The enhanced photocurrent is not due to only the CNT absorption because only a weak photocurrent was observed in the composite of the dye-free titania gel and CNTs similar to its dark current. It is noted that a photocurrent should be generated even in the unheated dye-doped titania gel as reported in a previous paper.[10] It is possible that the conduction band-like states are formed in the titania gel, which has an incomplete structure of titanium dioxide containing many defects.

We theorize that the dye-doped titania gel consists of amorphous, nanosized, and particle-like units having a semiconductor-like band structure and that the quasi-conduction band accepts an electron from the excited dye molecule. The electron transfer efficiently occurs because the dye molecules are highly dispersed into the titania gel network at a molecular level. However, the electron must travel in the amorphous titanium gel layer, which has low conductivity, in order to reach the ITO electrode. The CNTs are coated with the dye-doped titania gel layer in the composite, and the electron is easily injected into the ITO electrode via the CNTs because of the excellent bridge and interconnection between the titania gel and the ITO electrode.[5,6,8,10]

Figure 2 shows the I–V curves of the dye-doped titania gel and the composite of it and the CNTs. They were observed during visible light irradiation (>400 nm, 2.0 W cm^{-2}). The photoelectric conversion parameters are shown in Table 1. The short circuit photocurrent density (J_{SC}) values of the composite are remarkably higher than those of the dye-doped titania gel relating the higher values of its photocurrent spectrum shown in Figure 1. The open circuit voltage (V_{OC}) of the composite, however, is lower than the CNT-free film. This is due to the charge recombination at the interface between the titania gel and the CNTs.[5a] The short circuit between the CNTs and the electrolyte also causes a decrease in V_{OC} value, accompanied by a decrease in the fill factor (FF). The enhancement of the photocurrent due to the presence of the CNTs improved the maximum power (P_{max}) and quantum efficiency (QE) of the cell by nearly seven and three times, respectively. Even though these values are very low for use in a solar cell, a further improvement is expected after crystallization of the titania gel by treatment at low temperature, such as steam treatment.[10,13]

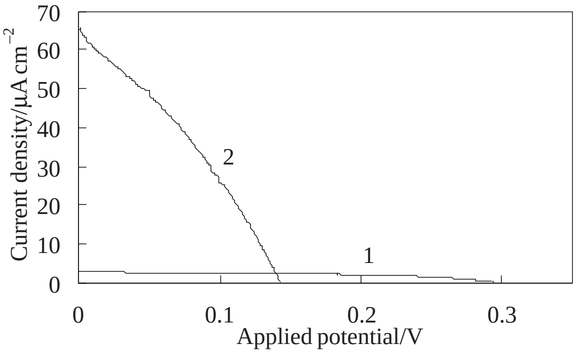

Figure 2. I–V curves of (1) the fluorescein-doped titania gel and (2) the composite of it and CNTs.

Table 1. Photoelectric conversion properties of (1) the fluorescein-doped titania gel and (2) the composite of it and CNTs

Sample	J_{SC} /μA cm^{-2}	V_{OC}/V	FF	P_{max} /μW cm^{-2}	QE/%
1	2.8	0.30	0.51	0.43	0.095
2	65.4	0.14	0.32	2.91	0.033

In conclusion, a photocurrent was observed in a nanocomposite electrode consisting of unheated dye-doped titania gel and CNTs. The photocurrent was generated by excitation of the dye and was enhanced by the CNTs.

This study was supported by a Sasagawa Scientific Research Grant from the Japan Science Society and a Research Grant from the Thermal & Electric Energy Technology Foundation. This study was also supported by the CLUSTER and the Grant-in-Aid for Young Scientists (B) (No. 20750104) of the Ministry of Education, Culture, Sports, Science and Technology.

References

1 a) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737. b) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müeller, P. Liska, N. Vlachopoulos, M. Grätzel, *J. Am. Chem. Soc.* **1993**, *115*, 6382. c) M. Grätzel, *J. Photochem. Photobiol., C* **2003**, *4*, 145.

2 a) A. Oberlin, M. Endo, T. Koyama, *J. Cryst. Growth* **1976**, *32*, 335. b) M. Endo, *CHEMTECH* **1988**, *18*, 568. c) M. Endo, Y. A. Kim, T. Hayashi, K. Nishimura, T. Matsushita, M. S. Dresselhaus, *Carbon* **2001**, *39*, 1287.

3 a) S. Iijima, *Nature* **1991**, *354*, 56. b) S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603.

4 a) P. Jarillo-Herrero, J. A. van Dam, L. P. Kouwenhoven, *Nature* **2006**, *439*, 953. b) Y. He, C. Zhang, C. Cao, H.-P. Cheng, *Phys. Rev. B* **2007**, *75*, 235429. c) E. Vogel, *Nat. Nanotechnol.* **2007**, *2*, 25.

5 a) K. Jung, J. S. Hong, R. Vittal, K.-J. Kim, *Chem. Lett.* **2002**, 864. b) S. L. Kim, S.-R. Jang, R. Vittal, J. Lee, K.-J. Kim, *J. Appl. Electrochem.* **2006**, *36*, 1433.

6 H. Yu, X. Quan, S. Chen, H. Zhao, *J. Phys. Chem. C* **2007**, *111*, 12987.

7 N. Ikeda, T. Miyasaka, *Chem. Lett.* **2007**, *36*, 466.

8 T. Y. Lee, P. S. Alegaonkar, J.-B. Yoo, *Thin Solid Films* **2007**, *515*, 5131.

9 S. H. Kang, J.-Y. Kim, Y.-K. Kim, Y.-E. Sung, *J. Photochem. Photobiol., A* **2007**, *186*, 234.

10 a) H. Nishikiori, N. Tanaka, T. Kitsui, T. Fujii, *J. Photochem. Photobiol., A* **2006**, *179*, 125. b) T. Kitsui, H. Nishikiori, N. Tanaka, T. Fujii, *J. Photochem. Photobiol., A* **2007**, *192*, 220.

11 a) S. Kubota, H. Nishikiori, N. Tanaka, M. Endo, T. Fujii, *J. Phys. Chem. B* **2005**, *109*, 23170. b) T. Tanigaki, H. Nishikiori, S. Kubota, N. Tanaka, M. Endo, T. Fujii, *Chem. Phys. Lett.* **2007**, *448*, 218. c) H. Nishikiori, N. Tanaka, T. Tanigaki, M. Endo, T. Fujii, *J. Photochem. Photobiol., A* **2008**, *193*, 161.

12 T. Fujii, A. Ishii, N. Takusagawa, M. Anpo, *Res. Chem. Intermed.* **1992**, *17*, 1.

13 H. Nishikiori, W. Qian, M. A. El-Sayed, N. Tanaka, T. Fujii, *J. Phys. Chem. C* **2007**, *111*, 9008.