Enhanced Photocurrent of Dye-Sensitized Solar Cells by Modification of TiO_2 with Carbon Nanotubes

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The effect of incorporating single-wall carbon nanotubes in TiO_2 film electrodes on the properties of dye-sensitized solar cells was studied. Compared with an unmodified solar cell, it is observed that the short-circuit photocurrent (J_{sc}) of the modified solar cells increases while the open-circuit photovoltage decreases slightly. The enhanced J_{sc} is correlated with increased electrical conductivity, light scattering and concentration of free conduction band electrons.

Recent interests in the novel dye-sensitized solar cells stem from their high solar conversion efficiency.[1] One of the strategies to further improve the efficiency is to promote the electron transfer through film electrodes and block the interface states lying below the conduction band edge. The interface states facilitate recombination of injected conduction band electrons with I_3^- ions. Efforts have been made to improve the conversion efficiency by modifying TiO_2 film with pyridine derivatives,[2,3] cholic acid,[4,5] polymers,[6] larger TiO_2 particles[7] and colloidal nanoparticles of TiO_2/SnO_2, WO_3/TiO_2, CdS/ZnO and CdS/TiO_2.[8–11]

In this letter, the effect of incorporating single-wall carbon nanotubes (CNTs, Carbon Nanotechnologies Inc.) in TiO_2 (Degussa, P25) film on photocurrent-voltage (*J-V*) characteristics is reported, intending to improve the solar conversion efficiency. It is expected that the incorporation of CNTs promote the electron transfer through the TiO_2 film, according to a recent report that doping of an insulating polymer with CNTs has increased conductivity by several orders.[12]

CNTs were purified with a concentrated acid mixture of $H_2SO_4 : HNO_3 = 3 : 1$ by vol. The purity of the nanotubes was evidenced in the Raman spectrum using a Jasco NR 1100 Raman spectrophotometer by the enhancement of the G-line at $1581\,cm^{-1}$ relative to the D-line at $1350\,cm^{-1}$.[13] Typical diameter of the long tubes was estimated to be about 10 nm from an SEM image. A small amount of purified CNTs dispersed in N,N-dimethylformamide was mixed with P25 for preparing TiO_2 electrodes. Transparent film electrodes were obtained by spin coating the colloidal mixture on $SnO_2 : F$ conducting glasses (Libbey-Owen-Ford Co.), using a spin coater from Laurell Technologies Corporation WS-200-4NPP. The resulting film was annealed at 450 °C for 30 min in air. Thickness of the film was estimated to be about 4 μm. The TiO_2 film electrode thus obtained was coated with $[RuL_2(NCS)_2]\cdot 2H_2O$ (where $L = 2,2'$-bipyridine-4,4′-dicarboxylic acid) in 3 mM absolute ethanol for 12 h at room temperature.

Short-circuit photocurrent and open-circuit voltage were measured using a Keithley Model M236 source measure unit. A 250-W tungsten-halogen lamp (Oriel) was used to illuminate an area of 3 mm in diameter of the working electrode, and its light intensity was adjusted to approximately $50\,mW/cm^2$, using an Si solar cell. The other side of the working electrode was in contact with the electrolyte containing 60 mM LiI and 3 mM I_2 in acetonitrile. Pt gauze was used as a counter electrode.

An $Ag|Ag^+$ (0.1 M $AgNO_3$ in CH_3CN) reference electrode was used in 1.0 M $LiClO_4$ propylene carbonate for determining free electron concentration in the conduction band of TiO_2 by absorption spectrophotometry.[14] An HP 8453A diode array spectrophotometer was used for obtaining absorption spectra. The surface morphology and thickness of the films were obtained using a Hitachi S-4300 FE-SEM. Scattering intensity of the film was measured by utilizing an Aminco-Bomam series-2 luminescence spectrometer with a solid film holder.

Figure 1 shows the cross-sectional view SEM image of a TiO_2 film incorporated with CNTs and annealed at 450 °C (hereafter denoted by CNT/TiO_2). It can be seen that the CNTs adhere well to the TiO_2 particles suggesting that there appears to be no loss of interconnectivity among the TiO_2 particles. Furthermore, TiO_2 particles tend to aggregate around CNTs to produce TiO_2 aggregates of several hundred nanometers. Measurements of light scattering by the films listed in Table 1 reveals that the CNT/TiO_2 films scattered more light over 300–800 nm region at three different angles than a P25 film, supporting the TiO_2 aggregation.

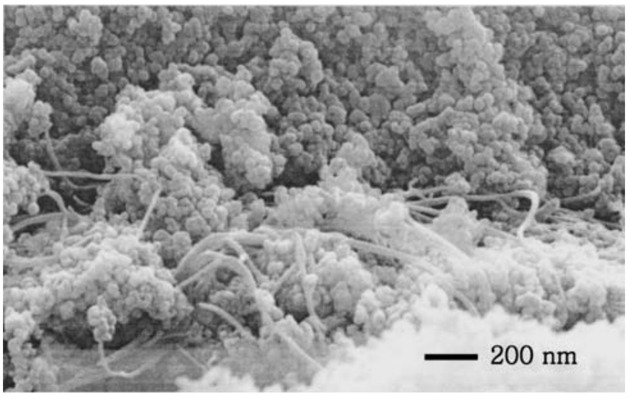

Figure 1. Cross-sectional view of the SEM image of a CNT/TiO_2 film.

Figure 2 shows the *J-V* characteristics in the dark and under illumination for dye-sensitized solar cells as a function of weight fraction *f* of CNTs with respect to TiO_2 in CNT/TiO_2 film electrodes. It can be seen that when the *f* increases to 0.0055, the short-circuit photocurrent density (J_{sc}) increases by as much as 50%, while the open-circuit photovoltage (V_{oc}) and fill factor decrease by 20 mV and 4%, respectively.

Table 1. Relative scattering intensities by TiO_2 particles in CNT/TiO_2 and TiO_2 films as a function of wavelength

	TiO_2			CNT/TiO_2[a]		
λ/nm	scattering angle					
	10°	20°	−10°	10°	20°	−10°
300	1.00	0.41	1.21	1.62	0.62	1.87
400	1.00	0.68	0.89	2.25	1.50	2.04
500	1.00	0.67	0.69	2.33	1.50	1.83
600	1.00	0.56	0.61	2.22	1.20	1.59
700	1.00	0.71	0.69	1.71	1.00	1.21
800	1.00	0.86	0.80	1.40	1.00	1.10

[a] The weight fraction of CNTs $f = 0.0055$.

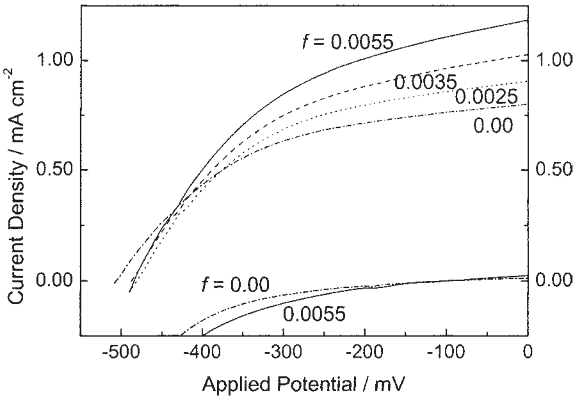

Figure 2. *J-V* curves for dye-sensitized solar cells prepared with CNT/TiO_2 films, as a function of weight fraction f of CNTs under illumination and in the dark.

One explanation for the J_{sc} behavior may lie in the increased electrical conductivity of the film. Four-probe analysis indeed indicates that the electrical conductance of the CNT/TiO_2 film at room temperature increases to $3.5 \times 10^{-5}\,\Omega^{-1}cm^{-1}$ and $6.1 \times 10^{-5}\,\Omega^{-1}cm^{-1}$ for $f = 0.0025$ and $f = 0.0055$ respectively, compared to $1.7 \times 10^{-5}\,\Omega^{-1}cm^{-1}$ for a P25 film. Increased electrical conductivity of CNT/TiO_2 film manifests itself by an increased slope near V_{oc}.[15] Similar result is reported in case of an insulating polymer incorporated with CNTs.[12] Furthermore, Figure 3 shows that the absorbance at 800 nm arising from Li^+ ions intercalation into TiO_2 for a CNT/TiO_2 film electrode in a solution of $LiClO_4$ increases as a function of applied potential, which indicates that the CNT incorporation has increased concentration of free electrons in the conduction band of TiO_2.[14] Such behavior suggests that the incorporation of CNTs may promote forward electron transfer through the CNT/TiO_2 film, most likely due to the introduction of conducting paths in TiO_2. In addition, the aggregates of TiO_2 particles around CNTs (Figure 1) increase light-harvesting efficiency due to the increased light scattering, enhancing the J_{sc}.[7] However, the amount of dye that desorbs from the surface of films is found to decrease with the incorporation of CNTs, resulting in an offset of the J_{sc} increase.

Contrary to the strong dependence of J_{sc} on f, the V_{oc} shows only a slight decrease irrespective of f (Figure 2). With the CNT incorporation, the surface recombination sites are reduced owing to the good adherence of CNTs to TiO_2, leading to an increase of V_{oc}.[2] However, the effect of recombination on the photovoltage is apparently more than offset by an increase in dark current. The combination of both effects likely results in a small decrease of V_{oc} with the incorporation of CNTs. The V_{oc} decrease is supported by a positive shift of onset potential with the CNT incorporation (Figure 3).

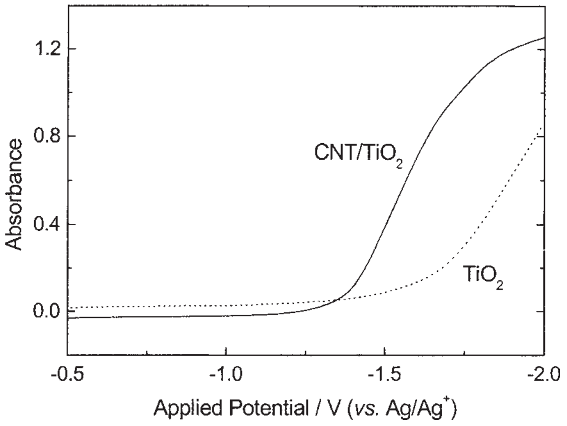

Figure 3. Comparison of absorbance at 800 nm vs applied potential for CNT/TiO_2 and TiO_2 electrodes in acetonitrile containing 0.2 M TBAP and 0.1 M $LiClO_4$.

The slight decrease of the fill factor for the CNT/TiO_2 electrode in Figure 2 appears to correlate mainly with the increased slope near the short-circuit potential. Increase in the slope reflects decrease in the parallel resistance of the cell, which facilitates back electron transfer to the electrolyte.[15] Figure 2 provides the evidence for this, in which the CNT/TiO_2 electrode shows an increase in the dark current. The increase in the dark current indicates an increase in the back electron transfer to I_3^- ions.[16]

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References

1 B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991).
2 G. Schlichthörl, S. Y. Huang, J. Sprague, and A. J. Frank, *J. Phys. Chem. B*, **101**, 8141 (1997).
3 S. Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel, and A. J. Frank, *J. Phys. Chem. B*, **101**, 2576 (1997).
4 A. Kay and M. Grätzel, *J. Phys. Chem.*, **97**, 6272 (1993).
5 K. Hara, H. Sugihara, Y. Tachibana, A. Islam, M. Yanagida, K. Sayama, H. Arakawa, G. Fujihashi, T. Horiguchi, and T. Kinoshita, *Langmuir*, **17**, 5992 (2001).
6 B. A. Gregg, F. Pichot, S. Ferrere, and C. L. Fields, *J. Phys. Chem. B*, **105**, 1442 (2001).
7 J. Ferber and J. Luther, *Sol. Energy Mater. Sol. Cells*, **54**, 265 (1998).
8 D. Liu and P. V. Kamat, *J. Phys. Chem.*, **97**, 10769 (1993).
9 K. Vinodgopal and P. V. Kamat, *Environ. Sci. Technol.*, **29**, 841 (1992).
10 S. Hotchandani and P. V. Kamat, *Chem. Phys. Lett.*, **191**, 320 (1992).
11 I. Shiyanovskaya and M. Hepel, *J. Electrochem. Soc.*, **145**, 3981 (1998).
12 E. Kymakis, I. Alexandou, and G. A. J. Amaratunga, *Synth. Met.*, **127**, 59 (2002).
13 J. M. Holden, P. Zhou, X.-X. Bi, P. C. Eklund, S. Bandow, R. A. Jishi, K. D. Chowdhury, G. Dresslhaus, and M. S. Desselhaus, *Chem. Phys. Lett.*, **220**, 186 (1994).
14 Z.-S. Wang, C.-H. Huang, Y.-Y. Huang, Y.-J. Hou, P.-H. Xie, B.-W. Zhang, and H.-M. Cheng, *Chem. Mater.*, **13**, 678 (2001).
15 M. Matsumoto, Y. Wada, T. Kitamura, K. Shigaki, T. Inoue, M. Ikeda, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, **74**, 387 (2001).
16 H. Lindström, H. Rensmo, S. Södergren, A. Solbrand, and S. Lindquist, *J. Phys. Chem.*, **100**, 3084 (1996).