

Incorporation of Functionalized Single-Wall Carbon Nanotubes in Dye-Sensitized TiO₂ Solar Cells

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Effects of incorporation of acid-treated single-wall carbon nanotubes (*a*-SWCNs) in TiO₂ film and of anchorage of dye-linked, *a*-SWCNs (hereafter dye-SWCNs) to the TiO₂/electrolyte interface on photocurrent–voltage characteristics of dye-sensitized solar cells were studied. Compared with an unmodified cell, the modified cell with the *a*-SWCNs in TiO₂ film showed a 25% increase in short-circuit photocurrent (J_{sc}). The J_{sc} increase is correlated with improved connectivity between the *a*-SWCNs and the TiO₂ particles and with enhanced light scattering by TiO₂ clusters formed in the presence of the *a*-SWCNs. In the case of anchoring dye-SWCNs to the TiO₂/electrolyte interface, the open-circuit voltage (V_{oc}) increased by as much as 0.1 V, possibly due to the basicity of the TiO₂ surface from NH groups of ethylenediamine moieties of the anchored dye-SWCNs.

Introduction

Recent research activity for novel dye-sensitized solar cells (DSSCs) can be ascribed to their high solar conversion efficiency.¹ Strategies to enhance efficiency include the promotion of electron transfer through film electrodes and the blockage of interface states lying below the conduction band edge. Interface states facilitate recombination of injected conduction band electrons with I₃[−] ions. Efforts have been made to improve the conversion efficiency by modifying TiO₂ film with pyridine derivatives,^{2,3} cholic acid,^{4,5} polymers,⁶ larger TiO₂ particles,⁷ and colloidal nanoparticles of TiO₂/SnO₂, WO₃/TiO₂, CdS/ZnO, and CdS/TiO₂.^{8–11}

Reports over the past decade have shown that incorporation of carbon nanotubes in poly(3-octylthiophene)^{12,13} or poly(methyl methacrylate) polymer film¹⁴ enhanced the electrical conductivity of the composite film. Carbon nanotubes also conferred electrical conductivity to metal–oxide nanocomposites.¹⁵ A composite of poly(*p*-phenylene vinylene) with carbon nanotubes in a photovoltaic device

showed good quantum efficiency, owing to the formation of a complex interpenetrating network with the polymer chains.¹⁶ However, no reports have been found in the literature where carbon nanotubes were used in TiO₂ films of DSSCs, despite their expected potential to enhance solar energy conversion efficiency due to favorable electrical conductivity. We have recently reported that incorporation of untreated single-wall carbon nanotubes (SWCNs) in TiO₂ films increased the short-circuit photocurrent of DSSCs.^{17,18} However, scanning electron microscopy (SEM) analyses in these cases have indicated that SWCNs were not uniformly distributed in the TiO₂ films and that some portions of the SWCNs were not attached to the nanocrystalline TiO₂ particles. We have also verified that dye molecules do not adsorb to SWCNs. For these reasons, it is assumed that the SWCNs incorporation reduces the amount of adsorbed dye in a TiO₂ film layer compared with the case without SWCNs. It has been reported that treating SWCNs with a concentrated acid mixture of H₂SO₄ and HNO₃ results in introducing carboxylic acid groups to the nanotubes.^{19–21} In analogy to the fact that carboxylic acid groups of Ru(II)-based dye molecules bond covalently to TiO₂ in DSSCs, it is assumed that acid-treated single-wall carbon nanotubes (*a*-SWCNs) can adhere better to TiO₂ particles than untreated SWCNs. In addition, the acid treatment shortens the chain lengths of SWCNs, thereby enabling them to embed easily in a thin TiO₂ film. However, detailed reports on characterization of the *a*-SWCNs are lacking.

Two types of investigations are presented in this paper. First, *a*-SWCNs were incorporated in TiO₂ films to improve charge transfer in DSSCs. We treated SWCNs with a H₂SO₄–HNO₃ mixture prior to the incorporation. The effect of the incorporation on photocurrent–voltage (J – V) characteristics of DSSCs was studied. Second, *a*-SWCNs

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(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(2) Schlichthörl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 8141.

(3) Huang, S. Y.; Schlichthörl, G.; Nozik, A. J.; Grätzel, M.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 2576.

(4) Kay, A.; Grätzel, M. *J. Phys. Chem.* **1993**, *97*, 6272.

(5) Hara, K.; Sugihara, H.; Tachibana, Y.; Islam, A.; Yanagida, M.; Sayama, K.; Arakawa, H.; Fujihashi, G.; Horiguchi, T.; Kinoshita, T. *Langmuir* **2001**, *17*, 5992.

(6) Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L. *J. Phys. Chem. B* **2001**, *105*, 1442.

(7) Ferber, J.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 265.

(8) Liu, D.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 10769.

(9) Vinodgopal, K.; Kamat, P. V. *Environ. Sci. Technol.* **1992**, *29*, 841.

(10) Hotchandani, S.; Kamat, P. V. *Chem. Phys. Lett.* **1992**, *191*, 320.

(11) Shiyonovskaya, I.; Hepel, M. *J. Electrochem. Soc.* **1998**, *145*, 3981.

(12) Kymakis, E.; Alexandou, I.; Amaratunga, G. A. J. *Synth. Met.* **2002**, *127*, 59.

(13) Musa, I.; Baxendale, M.; Amaratunga, G. A. J.; Eccleston, W. *Synth. Met.* **1999**, *102*, 1250.

(14) Haggemueller, R.; Gommans, H. H.; Rinzler, A. G.; Fischer, J. E.; Winey, K. I. *Chem. Phys. Lett.* **2000**, *330*, 219.

(15) Flahaut, E.; Peigney, A.; Laurent, Ch.; Marlière, Ch.; Chastel, F.; Rousset, A. *Acta Mater.* **2000**, *48*, 3803.

(16) Ago, H.; Petrisch, K.; Shaffer, M. S. P.; Windle, A. H.; Friend, R. H. *Adv. Mater.* **1999**, *11*, 1281.

(17) Jung, K.-H.; Hong, J. S.; Vittal, R.; Kim, K.-J. *Chem. Lett.* **2002**, *31*, 864.

(18) Jung, K.-H.; Jang, S.-R.; Vittal, R.; Kim, D.; Kim, K.-J. *Bull. Korean Chem. Soc.* **2003**, *24*, 1501.

(19) Liu, Z.; Shen, Z.; Zhu, T.; Hou, S.; Ying, L.; Shi, Z.; Gu, Z. *Langmuir* **2000**, *16*, 3569.

(20) Nan, X.; Gu, Z.; Liu, Z. *J. Colloid Interface Sci.* **2002**, *245*, 311.

(21) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.

were covalently attached with $[\text{RuL}_2(\text{NCS})_2] \cdot 2\text{H}_2\text{O}$ (hereafter Ru(II), which is commonly used in DSSCs, where $L = 2,2'$ -bipyridine-4,4'-dicarboxylic acid) by a synthetic route.^{19–21} The resulting product, dye-SWCN, was anchored to the TiO_2 /electrolyte interface for improving the $J-V$ characteristics. The basis for this anchorage of dye-linked SWCNs was a recent report that a 400-nm TiO_2 particle layer on nanocrystalline TiO_2 thin films could act as a light scattering layer,²² resulting in an increased incident photon-to-current conversion efficiency at 700 nm. The SWCN part of the dye-linked SWCNs was considered to be large enough to scatter light at the TiO_2 /electrolyte interface.

Experimental Section

SWCNs (Iljin Nanotech, 90% purity) were oxidized in a concentrated acid mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3 = 3:1$ by volume under ultrasonication for 24 h at 50–60 °C, to produce shortened SWCNs with terminal COOH groups.^{19–21} The resulting solution was filtered by a poly(tetrafluoroethylene) membrane with a 200-nm pore size. The filtrate was washed thoroughly with water by decantation to remove any remaining acid, followed by drying in an oven at 100 °C. Raman, Fourier transform infrared (FTIR), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) characterized the *a*-SWCNs. Raman spectra and FTIR spectra were obtained using a Jasco NR 1100 Raman spectrophotometer and a Bowman & Braun MB-series, respectively, to identify the formation of carboxylic acid groups on SWCNs. XPS spectra were obtained by an SSI 2803-S X-ray photoelectron spectrometer. TEM micrographs were measured by a JEOL, 1200EX, and high-resolution transmission electron microscopy (HRTEM) micrographs were measured by a JEOL, JEM-4010.

It is emphasized that these *a*-SWCNs were used in both investigations, that is, modification of TiO_2 film and anchorage of dye-SWCNs to the TiO_2 /electrolyte interface. In the first investigation, a small amount of *a*-SWCNs was mixed with P25 (Degussa) for preparing the TiO_2 colloidal mixture. Transparent films were obtained by spin-coating three times the colloidal mixture on F-doped SnO_2 (FTO) conducting glass (Libbey-Owens-Ford Co.), using a WS-200-4NPP spin coater from Laurell Technologies Corp., followed by annealing at 450 °C for 30 min in air. Thickness of the film was estimated to be about 2.4–2.7 μm using a Hitachi S-4300 field-emission scanning electron microscope. Scattering intensity of the film was measured by utilizing an Aminco-Bowman series-2 luminescence spectrometer with a solid film holder. The TiO_2 film thus obtained was coated with dye in absolute ethanol containing 0.3 mM Ru(II) for 24 h at room temperature.

In the second investigation, we covalently attached Ru(II) to *a*-SWNTs as follows.^{23,24} Ten milligrams of *a*-SWNTs was sonicated in 0.25 mL of *N,N*-dimethylformamide (DMF) for 10 s, and then 5 mL of thionyl chloride was added. The mixture was refluxed for 24 h, filtered, and washed with tetrahydrofuran to remove any unreacted SOCl_2 . The filtrate was stirred in 5 mL of ethylenediamine for 3 days and filtered, using a 200-nm membrane. To produce dye-SWCNs, the product formed was treated with a 0.3 mM Ru(II) ethanol solution for 1 day. Dye-SWCNs were then attached to the TiO_2 surface by immersing TiO_2 films in 3.5 mL of ethanol solutions containing both 0.3 mM Ru(II) and varying amounts of dye-SWCNs for 24 h at room temperature. This gives TiO_2 working electrodes with different amounts of dye-SWCNs. FTIR and XPS characterized the reaction products. An HP 8453A diode array spectrophotometer was used for obtaining absorption spectra of dye-SWCNs.

$J-V$ characteristics in both investigations were measured in an ordinary electrochemical cell (not the usual thin cells), using a Keithley model M236 source measure unit under 100 mW/cm^2 illumination. The cell consisted of one of the two types of TiO_2

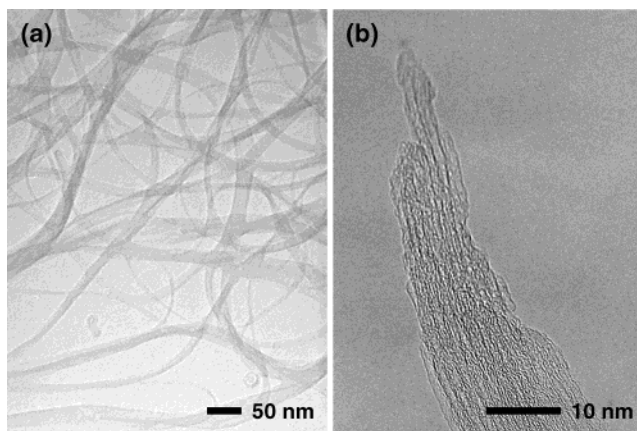


Figure 1. (a) TEM image of untreated bundles of SWCNs and (b) HRTEM image of a single fragmented bundle of *a*-SWCNs.

working electrodes, one incorporated by SWCNs and the other attached by dye-SWCNs, and a platinum gauge counter electrode in acetonitrile with 0.8 M LiI and 0.05 M I_2 . A 250-W tungsten-halogen lamp (Oriel) was used to back-illuminate an area of 3 mm in diameter of the working electrode, and its light intensity was adjusted by using a Si solar cell.

Results and Discussion

Incorporation of *a*-SWCNs in TiO_2 Film. TEM, XPS, Raman, and FTIR characterized *a*-SWCNs. Figure 1b shows the HRTEM image of a fragment of a bundle of *a*-SWCNs, in contrast to the untreated ones (TEM image in Figure 1a). We have observed in different TEM images that the length of shortened bundles of *a*-SWCNs varies over the range of 0.5–3.5 μm , whereas untreated SWCNs consist of 10–20- μm long straight chains and 10–15-nm-thick bundles. The diameter of nanotubes in both the cases is 1–1.3 nm. The tube diameter of SWCNs is calculated according to the equation $d = 234/\nu$, where ν is the wavenumber of the A_{1g} peak of the SWCN at 180 cm^{-1} in the Raman spectrum. The oxidation of SWCNs is evident by the weakening of their characteristic line intensities at both 1581 and 180 cm^{-1} in the Raman spectrum. Furthermore, the formation of carboxylic acid groups is confirmed by FTIR and XPS. FTIR spectra show a peak at 1716 cm^{-1} and a broad OH vibration peak over 2400–3400 cm^{-1} . XPS data show that the relative area of the peak at 289.0 eV containing the contribution of carboxylic acid groups is enhanced compared with that of untreated SWCNs. Analysis of XPS also indicated that the ratio of the atomic concentrations of O(1s) to C(1s) had increased considerably by the oxidation. On the basis of these results, the presence of carboxylic acid groups is confirmed in the *a*-SWCNs. As a result of the presence of COOH groups, *a*-SWCNs were well dispersed in water. Their good miscibility with water is beneficial for the fabrication of TiO_2 film; otherwise SWCNs need to be dispersed in an organic solvent such as DMF or *N*-methylpyrrolidine before being mixed with an aqueous TiO_2 colloidal solution.¹⁷ Other TEM images also revealed that carboxylic acid groups lead to firm adherence of TiO_2 particles to the *a*-SWCNs. However, our energy-dispersive X-ray (EDX) results showed that the *a*-SWCNs adsorb neither the redox couple, I^- and I_3^- in acetonitrile, nor the Ru(II) dye from the ethanol solution.

Analyses of SEM indicate that incorporation of the *a*-SWCNs up to 0.01 wt % into the TiO_2 film followed by annealing at 450 °C for 30 min essentially yields a uniform TiO_2 film thickness and surface morphology. Figure 2a shows a plain-view SEM image of the resulting TiO_2 film

(22) Nazeeruddin, M. K.; Splivallo, R.; Liska, P.; Comte, P.; Grätzel, M. *Chem. Commun.* **2003**, 1456.

(23) Baker, S. E.; Cai, W.; Lasseter, T. L.; Weidkamo, K. P.; Hamers, R. J. *Nano Lett.* **2002**, *2*, 1413.

(24) Pompeo, F.; Resasco, D. E. *Nano Lett.* **2002**, *2*, 369.

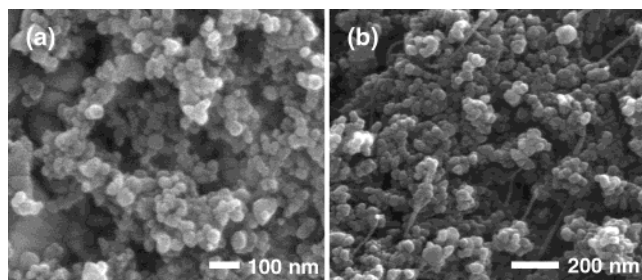


Figure 2. Field-emission SEM images of TiO₂ films incorporated with (a) *a*-SWCNs and (b) untreated SWCNs.

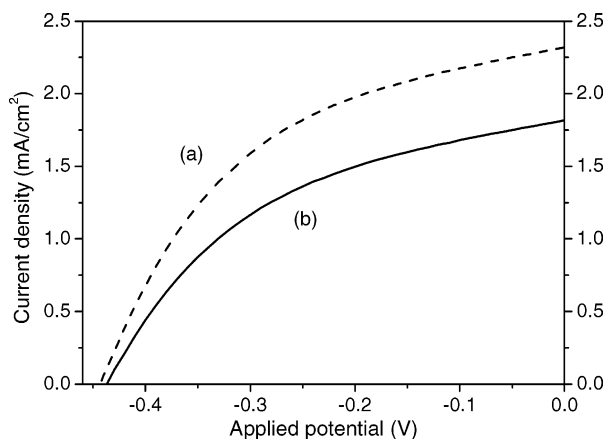


Figure 3. *J*-*V* curves of DSSCs prepared (a) with and (b) without *a*-SWCNs in the TiO₂ films (film thickness $\approx 2.4 \mu\text{m}$).

with a heart-shaped cluster that is entirely surrounded by TiO₂ particles, indicating improved connectivity between the *a*-SWCNs and the TiO₂ particles in the film, compared with the poor connectivity between untreated SWCNs and TiO₂ particles as can be seen in Figure 2b. As emphasized by the all-encompassing nature of the TiO₂ particles around the SWCNs, a physical appearance of SWCNs cannot be expected in Figure 2a. We have observed that the TiO₂ films with *a*-SWCN scatter more light intensity over 400–800-nm region than a P25 film by 10 and 13% at angles of 10 and 20°, respectively. This can be a consequence of the cluster formation.

The effect of the modification of the TiO₂ film with 0.01 wt % *a*-SWCN on *J*-*V* curves of the DSSCs is shown in Figure 3. Compared with the unmodified cell, the modified cell shows higher average J_{sc} by about 25%, but V_{oc} remains nearly the same. The J_{sc} increase of the modified cell likely arises from the enhanced light scattering over the visible region by the film having clusters formed in the presence of SWCNs, compared with the case of a P25 film as mentioned above (Figure 2). Furthermore, the J_{sc} behavior can be related to the increased electrical conductivity of the film coming from improved interconnectivity between TiO₂ particles and SWCNs, based on the recent reports that carbon nanotubes increase electrical conductivity of an insulating polymer and a TiO₂ film by several orders^{12,13} and about 2–3 times,¹⁷ respectively. We also have recently verified the fact, through electrochemical impedance spectroscopic data, optimized by fitting to an equivalent circuit, using Z View software, that resistance of the SWCN/TiO₂ film decreases conspicuously by a factor of 3 compared with that of the TiO₂ film.¹⁸ However, the amounts of the adsorbed dye molecules are considered not to affect J_{sc} behavior, because they were found to be almost the same regardless of incorporation of *a*-SWCNs in the TiO₂ electrodes up to 2%. This was confirmed by the

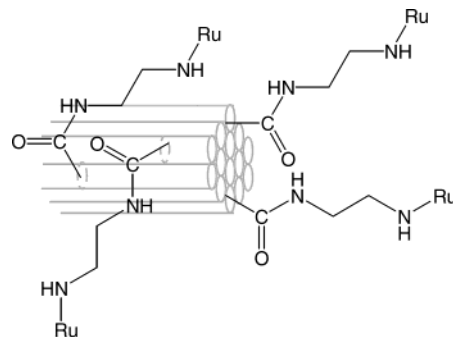


Figure 4. Schematic representation of dye-SWCNs, where Ru denotes Ru(II) linked through an amide bond with one of the four carboxylic acid groups.

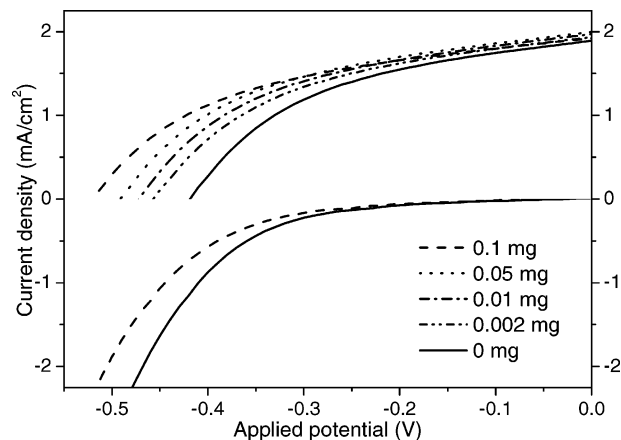


Figure 5. (Top) *J*-*V* curves of DSSCs prepared with varying amounts of dye-SWCN. (Bottom) Dark currents of DSSCs prepared with and without 0.1 mg of dye-SWCN (TiO₂ film thickness $\approx 2.7 \mu\text{m}$).

absorbance measurements of the desorbed Ru(II) from TiO₂ in 1 mM KOH.

Anchorage of Dye-SWCNs to the TiO₂/Electrolyte Interface. Recently, a 400-nm TiO₂ particle layer on the nanocrystalline TiO₂ thin film was reported to act as a light scattering layer, resulting in an increased incident photon-to-current conversion efficiency at 700 nm.²² It was considered that *a*-SWCNs are large enough to scatter light at the interface. To utilize *a*-SWCNs as light scattering particles, Ru(II) was covalently attached to the *a*-SWCNs according to a published procedure^{23,24} and as described in the experimental section. The product, dye-SWCN, was effectively anchored to the TiO₂/electrolyte interface, when a working electrode containing it was put in contact with the electrolyte. The dye portion of dye-SWCN has carboxylic acid groups (Figure 4), through which they can adsorb to TiO₂ particles. FTIR characterized the dye-SWCN by identifying the appearance of CN and NCS groups at 1390 and 2110 cm⁻¹, respectively, in the product. The attachment of dye-SWCNs on the TiO₂ surface was confirmed by the significant enhancement of carbon peak intensity in EDX of the TiO₂ film surface, compared with the intensity in the case of the TiO₂ film surface adsorbed with Ru(II) dye only.

Figure 5 shows dependence of *J*-*V* curves of DSSC on the amounts of dye-SWCN added to 3.5 mL of Ru(II) ethanol solutions. It is expected that the more the dye-SWCNs, over the range of amounts used in this study, the wider the anchorage of them at the TiO₂/electrolyte interface. The curves on the top show that V_{oc} increases with increasing amounts of dye-SWCNs in the dyeing solution, whereas J_{sc} remains essentially the same. The

V_{oc} increases as much as 0.1 V with a TiO_2 film anchored with 0.1 mg of dye-SWCN. This J - V behavior is contrasted with the case of incorporation of the a -SWCNs into TiO_2 films, where J_{sc} increases with a constant V_{oc} (Figure 3). The differences in the relative values of V_{oc} and J_{sc} between Figure 3 and Figure 5 arise from differences in respective TiO_2 film thicknesses. The V_{oc} increase is consistent with the dark current decrease, which is also shown in the bottom of Figure 5 for a TiO_2 film electrode anchored with 0.1 mg of dye-SWCN. It is envisaged that the dye part of dye-SWCN is attached to a TiO_2 particle whereas the SWCN part protrudes out toward the electrolyte solution because of the large size of the SWCN part (Figure 1b). This alignment of dye-SWCNs at the TiO_2 /electrolyte interface can increase the basicity of the TiO_2 surface by attachment and presence of the NH groups of ethylenediamine moieties of dye-SWCN to and near the TiO_2 surface and retard the movement of triiodide ions into and out of the film. The increase in the surface basicity leads to a negative shift of flat band potential of TiO_2 , which in turn results in a V_{oc} increase. This result is in agreement with V_{oc} increases upon addition of pyridine derivatives.^{3,25,26} In addition, positively charged ions may have a tendency to be attached to NH and possibly CO groups of dye-SWCNs and, thus, can be forced away from the TiO_2 surface. The removal of positive ions from the TiO_2 /electrolyte interface can also lead to a negative shift of the TiO_2 flat band potential. As a consequence of the negative shift of the conduction band, the dark current decreases as a result of an increased potential barrier. Replenishment of triiodide ions can be retarded in the presence of dye-SWCNs at the TiO_2 /electrolyte interface. This can reduce the I_3^- concentration in the film and can also be a reason for the dark current decrease. In contrast to expectations, the J_{sc} increase is, however, not appreciable as can be seen in Figure 5, indicating that light scattering by the large SWCN part of the anchored dye-SWCNs at the TiO_2 /electrolyte interface appears to have negligible influence on J_{sc} .

The average molecular weight of a -SWCN per mole of carboxylic acid (M_w) was estimated by utilizing ethanol solutions of dye-SWCN by absorption spectrometry. Figure 6 compares the absorption spectra of Ru(II), a mixture of Ru(II) and 0.1 mg of a -SWCN, and a mixture of Ru(II) and 0.1 mg of dye-SWCN. The same concentration of Ru(II), 5×10^{-5} M, and 3.5 mL of ethanol solutions were used in the three cases. Curve b is necessary to compensate for the scattering by a -SWCNs, which are still large enough to scatter the light. The absorbance difference between curve b and curve c corresponds to the concentration of Ru(II) in dye-SWCN. It is found that M_w is about 6800, assuming that all carboxylic acid groups are connected to Ru(II) and that the molar absorptivity of dye-SWCN is the same as that of Ru(II) at each maximum around 530 nm. In view of the reduced size of a -SWCN bundles, a large number of carboxylic acid groups appear to have been attached to them.

(25) Nazeeruddin, M. K.; Kay, A.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

(26) Hong, J. S.; Joo, M.; Vittal, R.; Kim, K.-J. *J. Electrochem. Soc.* **2002**, *149*, E493.

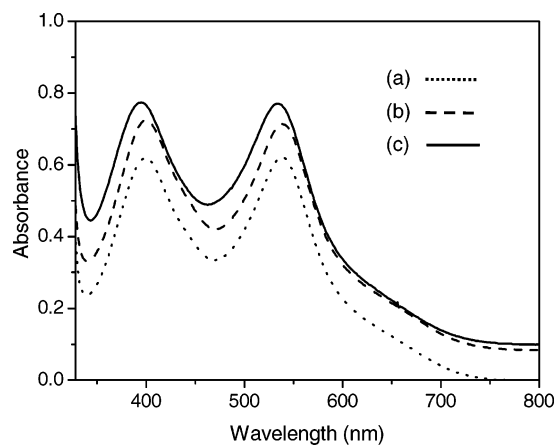


Figure 6. Absorption spectra of (a) Ru(II) dye (dotted line), (b) Ru(II) dye in the presence of a -SWCNs (broken line), and (c) Ru(II) dye in the presence of dye-SWCNs in ethanol (solid line).

It is to be emphasized here that J_{sc} and V_{oc} are not optimized in absolute terms for film thickness, electrolyte type and concentration, and cell dimension and configuration, in view of the comparative nature of this study regarding the influence of a -SWCNs in the TiO_2 film or at the TiO_2 /electrolyte interface on photovoltaic properties. A very thin layer of TiO_2 film of about 2.4–2.7 μm was used in this study, compared with about 10 μm in the usual DSSCs, to avoid needless dark films in the presence of a -SWCNs.

Conclusions

Beneficial influences of incorporation of a -SWCNs in the TiO_2 film and anchorage of Ru(II)-linked, a -SWCNs (dye-SWCNs) to the TiO_2 /electrolyte interface on the photocurrent–voltage characteristics of DSSC were studied. The acid treatment shortened the chain length of SWCNs, caused the formation of carboxylic acid groups attached to them, as evident by TEM, XPS, FTIR, and Raman spectra, and improved miscibility with water. Compared with an unmodified cell, the a -SWCN-incorporated cell showed a 25% increase in J_{sc} with essentially no change in V_{oc} . The enhanced J_{sc} is correlated with an improved interconnectivity between the TiO_2 particles and the fragmented a -SWCNs in the TiO_2 film electrode and an enhanced light scattering by TiO_2 clusters formed in the presence of a -SWCNs. It is emphasized that incorporation of the a -SWCNs in the TiO_2 film provides more efficient electron transfer through the film in DSSCs. In another investigation, anchorage of dye-SWCNs to the TiO_2 /electrolyte interface resulted in an increase of V_{oc} by as much as 0.1 V with hardly any change in J_{sc} . The V_{oc} increase can be attributed to the negative shift of the conduction band edge owing to the basicity of the TiO_2 surface caused by the NH groups of ethylenediamine moieties of dye-SWCNs.

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