

Stacked-Cup Carbon Nanotubes for Photoelectrochemical Solar Cells**

Taku Hasobe, Shunichi Fukuzumi,* and Prashant V. Kamat*

The usefulness of carbon nanotubes in optical, electronic, and catalytic applications has prompted researchers to synthesize carbon nanostructures of different shapes and sizes.^[1–4] Stacked-cup carbon nanotubes consisting of truncated conical graphene layers are of particular interest because whereas conventional carbon nanotubes are made up of seamless cylinders of hexagonal carbon networks, the stacked-cup structure provides a hollow tubular morphology.^[5] This truncated-cone morphology provides a large portion of exposed and reactive edges in the outer and inner surfaces of the hollow tubes. The availability of the inner and outer edges of these stacked-cups to chemical functionalization or surface modification opens up new avenues in electronic and catalytic applications.^[6] The longer stacked cups are broken into smaller units by ball milling, and thus the number of accessible active sites is increased.^[7] These smaller stacked cup units are also referred to as nanobarrels. The increased active area along the tubular surface facilitates impregnation of metal nanoparticles quite effectively. By making use of this

added feature, carbon stacked cups have been successfully used as supports in fuel cells.^[8]

An interesting property of carbon nanostructures is their optical response, and their utilization in light energy conversion devices. Fullerenes, for example, exhibit rich photochemistry and act as electron shuttles in photochemical solar cells.^[9] They also play an important role in improving the performance of organic photovoltaic cells. On the other hand, the semiconducting carbon nanotubes undergo charge separation when subjected to bandgap excitation. The exciton annihilation and charge-separation processes have been characterized by transient absorption and emission measurements.^[4,10,11] Efforts have also been made to modify the carbon nanotubes with semiconductors for use in photocurrent generation.^[12,13] Herein we present the optical properties of stacked-cup carbon nanotubes, and the effectiveness of their semiconducting properties to generate photocurrent in a photoelectrochemical cell with high photoconversion efficiency (Figure 1).

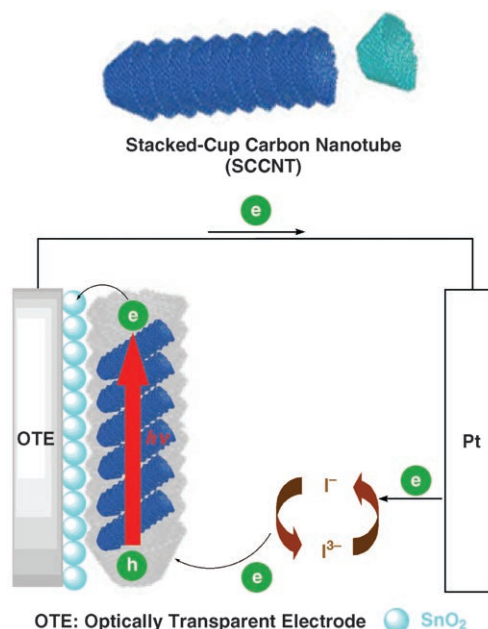


Figure 1. Light-induced charge separation in a photoelectrochemical cell based on stacked-cup carbon nanotubes (SCCNTs).

The ball-milled sample of stacked-cup carbon nanotubes (referred to as SCCNTs or carbon nanobarrels) in the tubular form was a gift from GSI Creos corporation, Japan. These nanotubes can be readily suspended in organic solvents, such as THF, by sonication for 30–60 minutes, and remain in suspension for more than 24 h. The absorption spectrum of the suspension in THF showed broad absorption with no specific absorption peaks (spectrum a in Figure 2 A). The ease of solubilization of these stacked cups allowed us to carry out transient absorption spectroscopy measurements (see below).

We adopted an electrophoretic deposition method to cast the films of SCCNTs onto conducting glass electrodes. The procedure was similar to that employed in assembling films of

[*] Dr. T. Hasobe,^[†] Prof. Dr. P. V. Kamat
Radiation Laboratory
Department of Chemistry & Biochemistry and
Department of Chemical & Biomolecular Engineering
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 574-631-8068
E-mail: pkamat@nd.edu
Dr. T. Hasobe,^[†] Prof. Dr. S. Fukuzumi
Department of Material and Life Science
Graduate School of Engineering
Osaka University, SORST
Japan Science and Technology Agency
2-1 Yamada-oka, Suita, Osaka 565-0871 (Japan)

[†] Current address:
School of Materials Science
Japan Advanced Institute of Science and Technology
Ishikawa, 923-1292, Japan

[**] We would like to thank GSI Creos Corporation, Japan for providing the sample of stacked-cup carbon nanotubes, and Tim Hall for his assistance in SEM characterization. This work was partially supported by Grant-in-Aid (No. 16205020) and by the COE program of Osaka University (Integrated Ecochemistry) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. T.H. acknowledges the support of Research Fellowships from the Japan Society for the Promotion of Science (JSPS) for Young Scientists. P.V.K. acknowledges support from the Office of Basic Energy Science of the U.S. Department of the Energy. This is contribution No. NDRL 4623 from the Notre Dame Radiation Laboratory and from Osaka University.

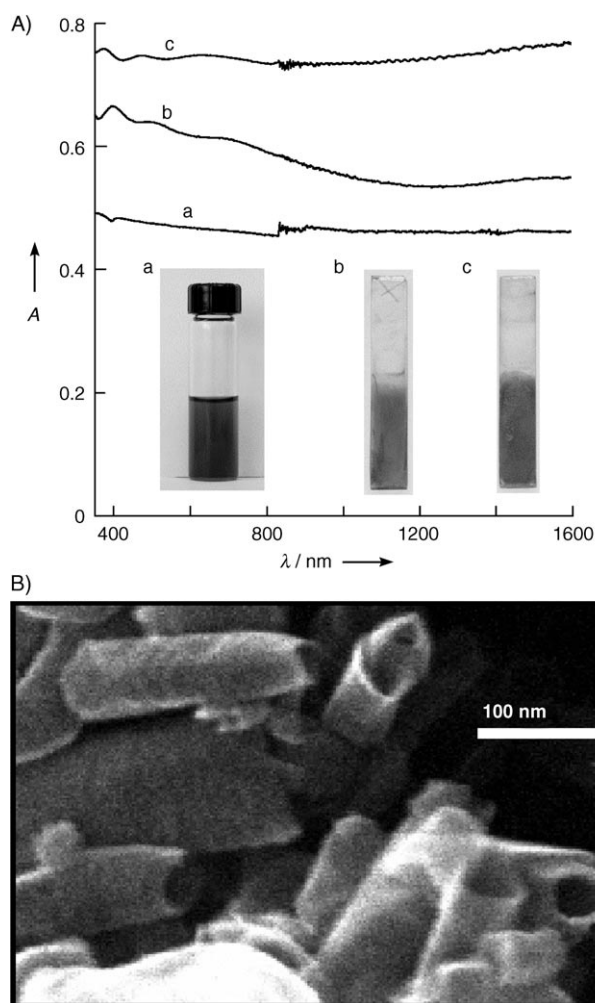


Figure 2. A) Absorption spectra of: a) a suspension of SCCNTs in THF, b) OTE/SCCNT, and c) OTE/SnO₂/SCCNT. B) Transmission electron microscope (TEM) image of SCCNTs.

carbon nanotubes and C₆₀ clusters on electrode surfaces.^[14,15] A suspension of SCCNTs (3 mL) in THF was transferred to a 1-cm cuvette. Two optically transparent electrodes (OTE) cut from conducting glass were inserted and a dc field (200 V cm⁻¹) was applied. Within one minute, the SCCNTs were driven to the positive electrode surface and a robust film was deposited (referred to as OTE/SCCNT). A similar procedure was also adopted to deposit SCCNTs onto OTE/SnO₂ and OTE/TiO₂ electrodes (referred to as OTE/SnO₂/SCCNT and OTE/TiO₂/SCCNT, respectively). The absorption spectra and photographs of these two electrodes are shown in Figure 2A. The scanning electron micrograph of these films shows a closed packed assembly of SCCNTs (Figure 2B). The hollow tubes are approximately 50 nm in diameter and 0.2–0.3 μ m in length. The assembly of SCCNTs onto the electrode surface provides a porous morphology to the film. The ball-milled samples produce relatively short-length stacked-cup tubes, as expected.^[7] Another interesting aspect is that these individual stacked tubes remain separated and are not bundled as we usually see with single-wall or multi-wall carbon nanotubes. Previous studies^[5,6] have shown that these hollow tubes possess a significantly higher propor-

tion of exposed outer edges which in turn minimizes van der Waals interactions between the tubes.

To probe the optical activity of these stacked cups we subjected the OTE/SCCNT electrode to laser pulse (387 nm) excitation in a femtosecond transient absorption spectrometer. The transient spectra recorded at different times are shown in Figure 3A. A broad bleaching in the red region was seen immediately following the laser pulse excitation. The bleaching recovers within 2 ps, thus illustrating the reversibility of the system to optical excitation. The reproducibility of the transient recovery at 760 nm is confirmed by the forward and reverse delay scans (Figure 3B). The transient bleaching and its recovery observed in these experiments parallels the behavior of single-wall carbon nanotubes (SWCNTs).^[11] The ultra-bandgap excitation of SCCNTs with a laser pulse at 387 nm produces excitons in the C₂-V₂

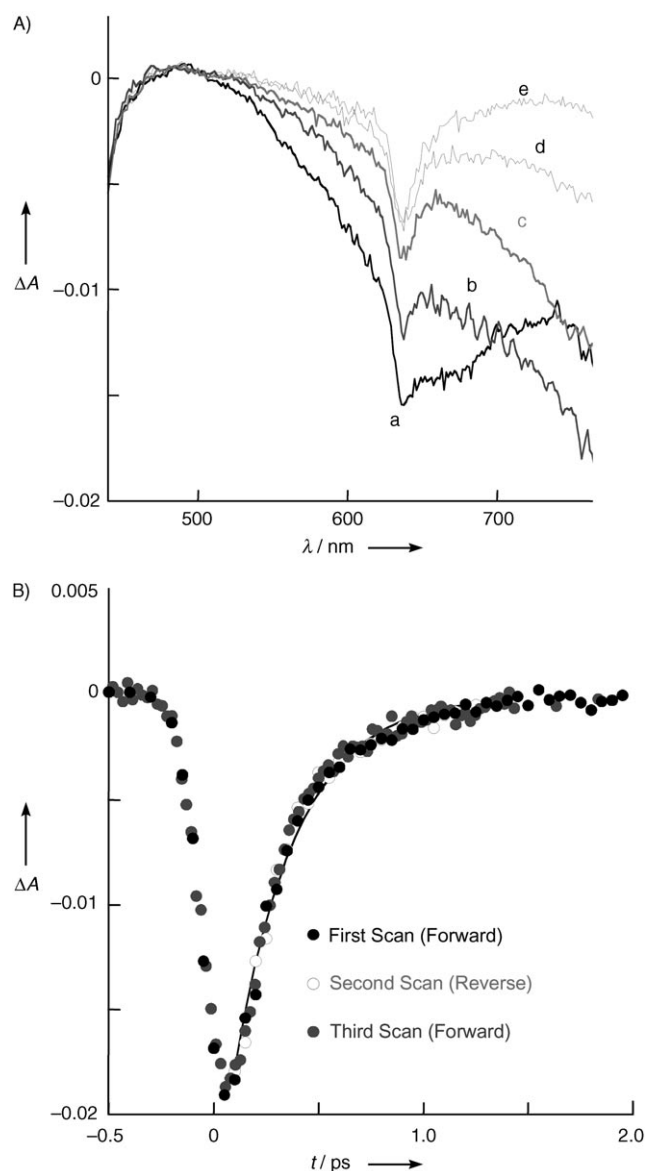


Figure 3. A) Time-resolved transient absorption spectra of OTE/SCCNT recorded using a laser pulse of 387 nm: a) 0 ps, b) 0.1 ps, c) 0.3 ps, d) 0.5 ps, and e) 1.0 ps. B) Time profiles of absorption at 760 nm after first (forward), second (reverse), and third scans (forward).

level. These excitons quickly migrate to the C_1-V_1 level and undergo deactivation by exciton annihilation. A small fraction of these excitons dissociate to produce a charge-separated state. By comparing these results with those of SWCNTs,^[11,15,16] one can conclude that SCCNTs exhibit optical transitions similar to those of SWCNTs, and provide the basis for exploring other semiconducting properties of these materials.

If the optical transitions we observe in Figure 3 were indeed responsible for charge separation, we should be able to harvest these charge carriers for generating photocurrent in a photovoltaic or photoelectrochemical cell. A photoelectrochemical cell consisting of an OTE/SnO₂/SCCNT electrode and a Pt counterelectrode was constructed and the generation of photovoltage and photocurrent, in the presence of the I₃⁻/I⁻ redox couple, were recorded (Figure 4). Visible light ($\lambda > 400$ nm) was obtained from a 450 W Xenon lamp filtered using a Corning 3-73 filter. When the OTE/SnO₂/SCCNT

electrode was subjected to excitation with visible light we observed a rapid generation of photocurrent. The photo-generated electrons in the SCCNTs are collected by the SnO₂ nanocrystallites to generate anodic current. Thus, a steady photocurrent can be delivered using SCCNT-based photoelectrochemical cells. The on-off cycles of illumination confirmed the reproducibility and stability of the photocurrent response of the SCCNT film (Figure 4B).

We recorded the photocurrent action spectrum by employing a monochromatic excitation source. The IPCE (incident photon to charge carrier generation efficiency) response at different excitation wavelengths (trace a in Figure 4A) shows a maximum efficiency value of 4%. These IPCE values are nearly an order of magnitude greater than those obtained for SWCNT electrodes (OTE/SnO₂/SWCNT: trace b in Figure 4A) under similar experimental conditions.^[15]

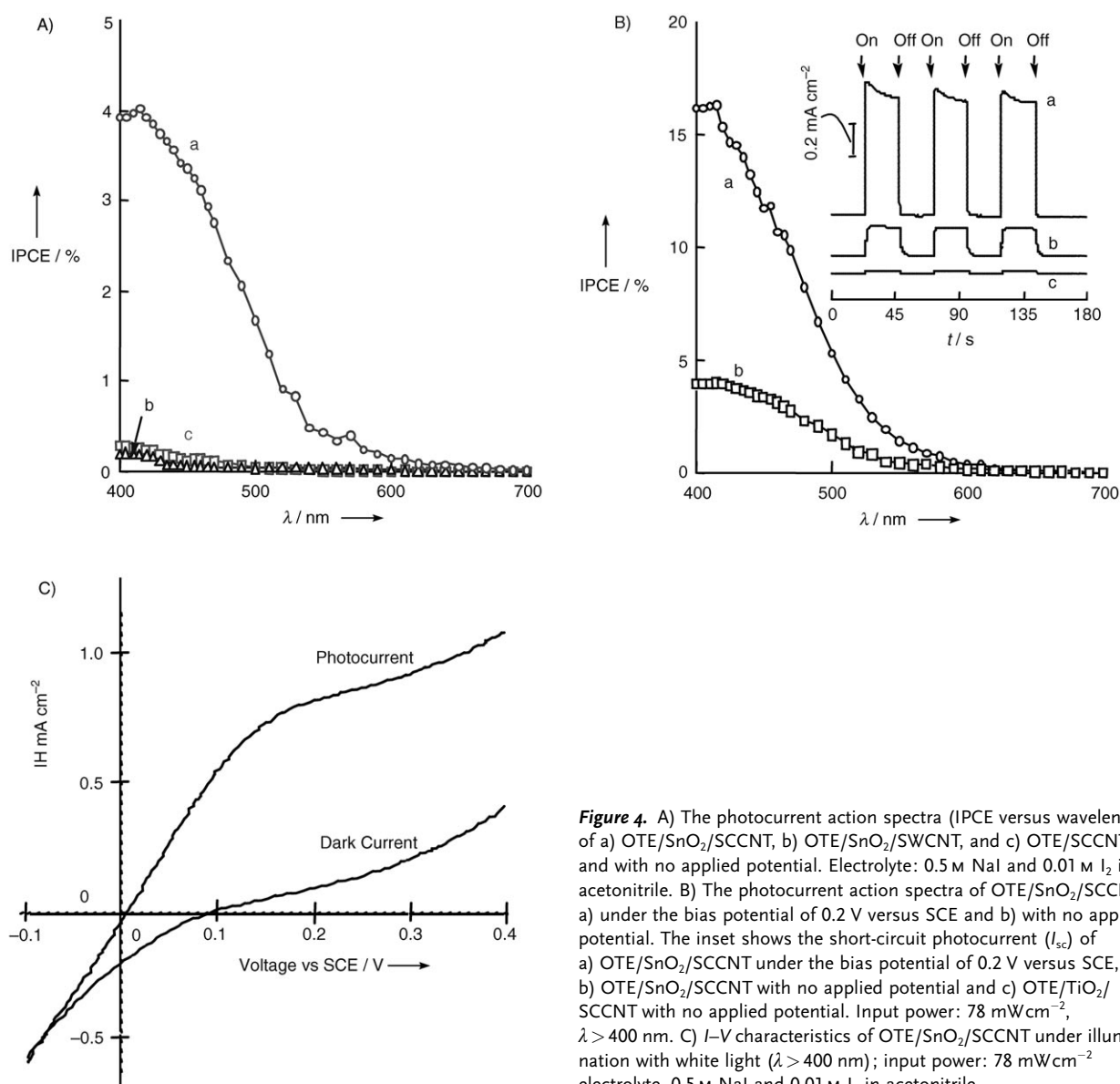


Figure 4. A) The photocurrent action spectra (IPCE versus wavelength) of a) OTE/SnO₂/SCCNT, b) OTE/SnO₂/SWCNT, and c) OTE/SCCNT and with no applied potential. Electrolyte: 0.5 M NaI and 0.01 M I₂ in acetonitrile. B) The photocurrent action spectra of OTE/SnO₂/SCCNT a) under the bias potential of 0.2 V versus SCE and b) with no applied potential. The inset shows the short-circuit photocurrent (I_{sc}) of a) OTE/SnO₂/SCCNT under the bias potential of 0.2 V versus SCE, b) OTE/SnO₂/SCCNT with no applied potential and c) OTE/TiO₂/SCCNT with no applied potential. Input power: 78 mWcm⁻², $\lambda > 400$ nm. C) I-V characteristics of OTE/SnO₂/SCCNT under illumination with white light ($\lambda > 400$ nm); input power: 78 mWcm⁻² electrolyte, 0.5 M NaI and 0.01 M I₂ in acetonitrile.

The SnO_2 films cast on OTE do not exhibit any photocurrent at wavelengths greater than 350 nm. The presence of SnO_2 nanocrystallites increases the surface area and maximizes the charge collection from excited SCCNTs. Indeed, the increased IPCE of OTE/ SnO_2 /SCCNT electrodes relative to the OTE/SCCNT electrode (trace c in Figure 4A) confirms the role of SnO_2 nanocrystallites as charge collectors. Further improvements in the efficiency of charge collection can be achieved by applying an external electrochemical bias. Figure 4B compares the performance of the SCCNT electrodes under no bias with those under +0.2 V versus the standard calomel electrode (SCE) bias. A maximum IPCE of 17%, recorded at +0.2 V, is the highest efficiency ever reported for pristine carbon nanostructures. Previous studies, which report the photoelectrochemical effect of carbon nanostructures, do not show photocurrent efficiencies of similar magnitude. For example, C_{60} films exhibit a maximum IPCE value of less than 5%^[14,17] and SWCNT films^[15] exhibit a maximum IPCE value of less than 0.2%. Furthermore, the photoconversion efficiency of SCCNT films are comparable to those obtained with pristine nanostructured semiconductor films (TiO_2 , ZnO , CdS),^[18,19] thereby suggesting the effectiveness of SCCNTs to undergo equally efficient charge separation under excitation with visible light.

The short circuit photocurrent (I_{sc}) measurements carried out with the OTE/ SnO_2 /SCCNT electrode, with and without anodic bias, and the OTE/ TiO_2 /SCCNT electrode without bias are compared in the inset of Figure 4B. The photocurrent response is sensitive to illumination by visible light and can be reproduced during on-off cycles. Interestingly, the I_{sc} value of OTE/ TiO_2 /SCCNT (trace c) is much smaller than that of OTE/ SnO_2 /SCCNT (traces a and b). This result suggests that the electron transfer from excited SCCNTs to SnO_2 nanocrystallites is exergonic, while that from excited SCCNTs to TiO_2 nanocrystallites is endergonic (see below).

The I - V characteristics of the OTE/ SnO_2 /SCCNT electrode are shown in Figure 4C. The increased photocurrent generation at anodic potentials shows that the SCCNT films possess n-type semiconducting behavior, which delivers a maximum photocurrent of about 1 mA cm^{-2} under anodic bias. Another interesting feature of the I - V characteristics is the zero current potential which in the present case is close to 0 V versus the SCE. As shown in earlier studies,^[20] this value represents the apparent flat band potential as the photo-generated charge carriers recombine at this potential without producing net current. As a result of the n-type behavior seen in SCCNT films, effective charge separation is observed at potentials greater than 0 V versus the SCE.

The mechanism of photocurrent generation (Figure 1) shows photoinduced charge separation within SCCNTs as the primary step, followed by hole transfer to the I_3^-/I^- redox couple in solution, and transfer of electrons to the collecting electrode. If this semiconducting property of SCCNTs is indeed responsible for the generation of photocurrent, we should be able to observe the photovoltage generation even in the absence of the I_3^-/I^- redox couple. The accumulated charges during excitation with visible light will cause a change in the open circuit voltage. Spectra a-c (Figure 5) show the generation of photovoltage with time for OTE/ SnO_2 /SCCNT

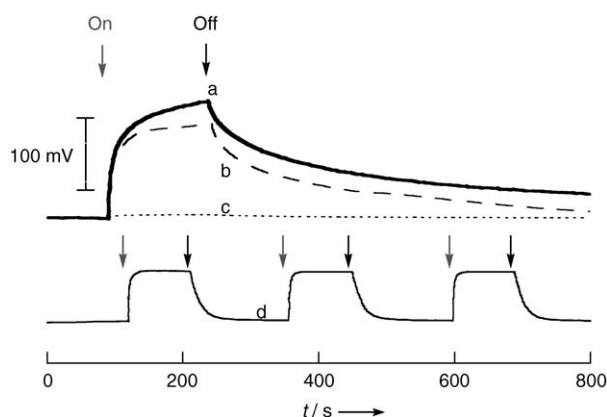


Figure 5. Photovoltage responses of OTE/ SnO_2 /SCCNT in an acetonitrile solution containing 0.1 M *n*-tetrabutylammonium perchlorate (TBAP) under a) deaerated and b) air-saturated conditions. c) Photovoltage response of OTE/ SnO_2 in an acetonitrile solution containing 0.1 M TBAP under deaerated condition (blank experiment). d) Photovoltage response of OTE/ SnO_2 /SCCNT in acetonitrile solution containing 0.5 M I_3^- and 0.01 M I^- ; input power: 78 mW cm^{-2} .

and OTE/ TiO_2 /SCCNT electrodes in an acetonitrile solution (0.1 M *n*-tetrabutylammonium perchlorate as the electrolyte). Care was taken to prevent excitation below wavelengths of 400 nm, and photovoltage observed with blank OTE/ SnO_2 and OTE/ TiO_2 electrodes was negligible under these conditions.

The rise in the photovoltage is seen only when SCCNT was deposited on the SnO_2 support. The photovoltage observed with OTE/ TiO_2 /SCCNT was negligibly small. The reason behind this discrepancy is the conduction band energy of the two supports (E_{CB} for SnO_2 and TiO_2 are 0 and -0.5 V (versus the normal hydrogen electrode (NHE)) respectively). The ability of excited SCCNTs to transfer electrons only to SnO_2 and not TiO_2 shows that the conduction band of the SCCNTs lies between 0 and -0.5 V (versus NHE). This estimate is also in close agreement with the I - V characteristics (Figure 4C), which exhibit anodic photocurrents at potentials greater than 0 V. The photovoltage response in the presence of a redox couple I_3^-/I^- (spectrum d, Figure 5) was also rapid, but decayed faster when the illumination was turned off. The electrode quickly attains equilibration in the presence of a redox couple by transferring access charge to the I_3^-/I^- couple.

To date, SWCNTs and MWCNTs (multi-wall carbon nanotubes) have not been fully explored for use in photovoltaic applications because of their poor charge separation efficiency. Superior performance observed in the present study with SCCNTs highlights the usefulness of carbon nanostructures for applications in the conversion of light energy. Our study explores, for the first time, the semiconducting property of SCCNTs and its efficient utilization in the photoelectrochemical conversion of light energy into electricity. We conclude on the basis of the results presented in this study that the SCCNTs exhibit photocurrents two orders of magnitude greater than SWCNTs. It should be noted that the observed maximum photoconversion efficiency (IPCE) of about 17% is lower than the one observed with

dye-sensitized solar cells (80–90 %).^[21] On the other hand, the efficiencies of SCCNT based cells are comparable to the efficiency (5–15 %) of photoelectrochemical cells based on nanostructured semiconductor films (TiO₂, ZnO, CdS etc).^[18,19] Modification of SCCNT films with sensitizers or organic semiconductors may provide new avenues to further improve the photoconversion efficiency. Efforts are currently underway to employ SCCNTs in organic solar cells based on polyphenylene vinylene (PPV).

Received: August 9, 2005

Published online: December 21, 2005

Keywords: charge separation · nanotubes · photochemistry · solar cells

-
- [1] H. J. Dai, *Acc. Chem. Res.* **2002**, 35, 1035.
 - [2] O. Zhou, H. Shimoda, B. Gao, S. J. Oh, L. Fleming, G. Z. Yue, *Acc. Chem. Res.* **2002**, 35, 1045.
 - [3] P. Serp, M. Corrias, P. Kalck, *Appl. Catal. A* **2003**, 253, 337.
 - [4] A. Jorio, R. Saito, T. Hertel, R. B. Weisman, G. Dresselhaus, M. S. Dresselhaus, *MRS Bull.* **2004**, 29, 276.
 - [5] M. Endo, Y. A. Kim, T. Hayashi, Y. Fukai, K. Oshida, M. Terrones, T. Yanagisawa, S. Higaki, M. S. Dresselhaus, *Appl. Phys. Lett.* **2002**, 80, 1267.
 - [6] C. Kim, Y. J. Kim, Y. A. Kim, T. Yanagisawa, K. C. Park, M. Endo, M. S. Dresselhaus, *J. Appl. Phys.* **2004**, 96, 5903.
 - [7] Y. A. Kim, T. Hayashi, Y. Fukai, M. Endo, T. Yanagisawa, M. S. Dresselhaus, *Chem. Phys. Lett.* **2002**, 355, 279.
 - [8] M. Endo, Y. A. Kim, M. Ezaka, K. Osada, T. Yanagisawa, T. Hayashi, M. Terrones, M. S. Dresselhaus, *Nano Lett.* **2003**, 3, 723.
 - [9] P. V. Kamat, M. Haria, S. Hotchandani, *J. Phys. Chem. B* **2004**, 108, 5166.
 - [10] M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. P. Ma, R. H. Hauge, R. B. Weisman, R. E. Smalley, *Science* **2002**, 297, 593.
 - [11] Y. Z. Ma, J. Stenger, J. Zimmermann, S. M. Bachilo, R. E. Smalley, R. B. Weisman, G. R. Fleming, *J. Chem. Phys.* **2004**, 120, 3368.
 - [12] L. Sheeney-Haj-Khia, B. Basnar, I. Willner, *Angew. Chem.* **2005**, 117, 78; *Angew. Chem. Int. Ed.* **2005**, 44, 78.
 - [13] I. Robel, B. Bunker, P. V. Kamat, *Adv. Mater.* **2005**, 17, 2458.
 - [14] P. V. Kamat, S. Barazzouk, K. G. Thomas, S. Hotchandani, *J. Phys. Chem. B* **2000**, 104, 4014.
 - [15] S. Barazzouk, S. Hotchandani, K. Vinodgopal, P. V. Kamat, *J. Phys. Chem. B* **2004**, 108, 17015.
 - [16] Y. Z. Ma, L. Valkunas, S. M. Bachilo, G. R. Fleming, *J. Phys. Chem. B* **2005**, 109, 15671.
 - [17] T. Hasobe, H. Imahori, S. Fukuzumi, P. V. Kamat, *J. Phys. Chem. B* **2003**, 107, 12105.
 - [18] S. Hotchandani, P. V. Kamat, *J. Phys. Chem.* **1992**, 96, 6834.
 - [19] V. Subramanian, E. Wolf, P. V. Kamat, *J. Phys. Chem. B* **2001**, 105, 11439.
 - [20] V. Subramanian, E. E. Wolf, P. V. Kamat, *J. Am. Chem. Soc.* **2004**, 126, 4943.
 - [21] M. K. Nazeeruddin, A. Kay, I. Rodicio, B. R. Humphry, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, *J. Am. Chem. Soc.* **1993**, 115, 6382.
-