

Single-Wall Carbon Nanotube Films for Photocurrent Generation. A Prompt Response to Visible-Light Irradiation

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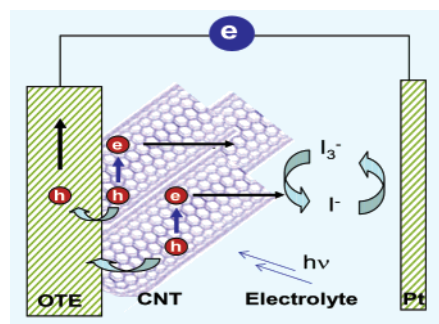
Electrophoretically deposited single-wall carbon nanotube (SWCNT) films on optically transparent electrodes are photoelectrochemically active and generate photocurrent upon visible excitation. A low photon-to-current conversion efficiency of 0.15% suggests that most of the photogenerated charge carriers are lost in the recombination process. Time-resolved transient absorption experiments confirm the charge separation following the laser-pulse excitation of SWCNTs. Relaxation of photogenerated charge carriers in the SWCNT to the lowest energy gap occurs in ~ 1 ps.

Carbon nanotubes (CNTs) are gaining prominence in a variety of disciplines.¹ They are potential components in electronic devices and catalytic applications.^{2–5} The photoresponse of carbon nanotubes filaments has been demonstrated by demonstrating the elastic response of the aligned bundles between two metal electrodes.⁶ Avouris et al.⁷ monitored hot carrier luminescence from ambipolar CNT field-effect transistors. The holes and electrons injected via external circuit produced emission resulting from electron–hole ($e-h$) recombination. The recent report of band-gap fluorescence from a semiconducting single-wall carbon nanotube (SWCNT) sample rich in individual nanotubes has made it possible to correlate optical properties with individual tube species as a result of their well-defined optical transitions.^{8,9} Spectroscopic studies have demonstrated that the relaxation of electrons and holes to the fundamental band edge occurs within 100 fs after photoexcitation of the second van Hove singularity of a specific tube structure.¹⁰

Spatial confinement of these charge carriers within the nanotubes leads to the Coulombic coupling of excited electrons and holes to create strongly bound excitons.^{11–13} Spataru et al.¹⁴ used an *ab initio* many-electron Greene's function approach to determine the $e-h$ interaction effects on the optical spectra of small-diameter nanotubes. Based on these calculations, they predict that the excitons are bound by ~ 1 eV in the semiconducting tubes and by ~ 100 meV in the metallic tubes. These excitons decay via radiative relaxation or by creating $e-h$ pairs within the band structure. Based on the difference between the intensity dependence of emission decay and transient absorption recovery, Ma et al.¹⁰ concluded that a branching of emission and charge separation/trapping follows the photoexcitation. The obvious question is whether one can suitably collect these photoinduced charge carriers for photocurrent generation, similar to the photovoltaic application of other semiconductors (see Scheme 1).

We recently reported the assembly of solubilized CNTs into linear bundles at high dc field (>200 V/cm) and their deposition as a film at lower dc field (~ 100 V/cm).¹⁵ We now report here an important photovoltaic property that characterizes the p -type

SCHEME 1. SWCNT-Based Photoelectrochemical Cell



semiconducting nature of carbon nanotubes. The photoelectrochemical effect described here involves photoinduced charge separation and collection of charges at the conducting electrode surface to generate photocurrent.

Purified SWCNTs prepared by the electric arc method (from SES Research) were solubilized by mixing with tetraoctylammonium bromide (TOAB) in tetrahydrofuran (THF) (10 mg of CNTs and 0.13 g of TOAB in 25 mL of THF). Sonication of the mixture for 20–30 min yields a stable dark suspension. This suspension was washed with THF, using several cycles of centrifugation and resuspension. Electrophoretic deposition was performed by subjecting the solubilized CNT suspension in THF to a dc electric field.¹⁵ Two conducting glass electrodes were kept ~ 5 mm apart in a quartz cuvette and a dc field of 100 V/cm was applied. (Note that, at higher applied voltages, the CNTs assemble into linear bundles that extend across the space between the two electrodes.) The two stages of solubilization and electrophoretic deposition of CNTs on a conducting glass electrode (referenced as the optically transparent electrode, OTE) are illustrated in Figure 1. The movie included in the Supporting Information shows a real-time deposition of solubilized CNTs from solution onto a positively charged electrode. The time scale and the movement of SWCNT toward the positive electrode can be visualized through this movie. It is important to keep the applied field at <100 V/cm. At higher fields, the SWCNT align themselves parallel to the field instead of electrodeposition.

The transmission electron microscopy (TEM) micrograph shows that the solubilized SWCNTs are still in the form of bundles with a diameter of ~ 50 nm. We expect them to be in the aggregated form when they are assembled as a film on the

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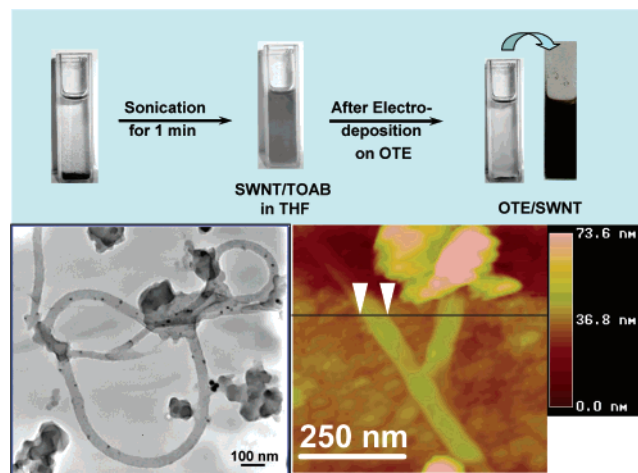


Figure 1. (Top) Solubilization and electrophoretic deposition steps involved for casting single-wall carbon nanotube (SWCNT) films on an optically transparent electrode (OTE). The panel in the bottom left-hand corner is a transmission electron microscopy (TEM) image of tetraoctylammonium bromide (TOAB)-capped SWCNT in tetrahydrofuran (THF), whereas that in the bottom right is an atomic force microscopy (AFM) image of a selected SWCNT bundle of electrodeposited film on the OTE/SnO₂.

OTE. The electrophoretically deposited SWCNT films were robust and can be washed with solvent. They are suitable for electrical or electrochemical measurements. The absorption spectrum of the CNT suspension in THF shows the typical broad featureless absorption in the UV extending into the near-IR region. The same absorption features are retained in the CNT film cast on a conducting glass surface or on a nanostructured SnO₂ surface (Figure 2, inset).

Figures 2 and 3 show the photoresponse of CNT film in a photoelectrochemical cell. After excitation using visible light ($\lambda > 400$ nm), we observe a prompt generation of photocurrent. The maximum photocurrent and photovoltage observed in these experiments were 8 $\mu\text{A}/\text{cm}^2$ and 12 mV, respectively. The maximum incident photon conversion efficiency (IPCE) is only $\sim 0.15\%$ at 400 nm. Although these values are small, compared to many nanostructured semiconductor films, the photoelectrochemical effects are reproducible and stable currents can be drawn in the presence of a redox couple (e.g., I^-/I_3^-). The photoresponse extends up to the red region and follows the broad absorption trend.

In Figure 2, we also compare the incident photon to photocurrent efficiency (IPCE) of CNT films cast on plain OTE and OTE films modified with SnO₂ colloids. Casting a layer of SnO₂ on an OTE increases the surface area for collecting photogenerated charges at the electrode surface. As a result of

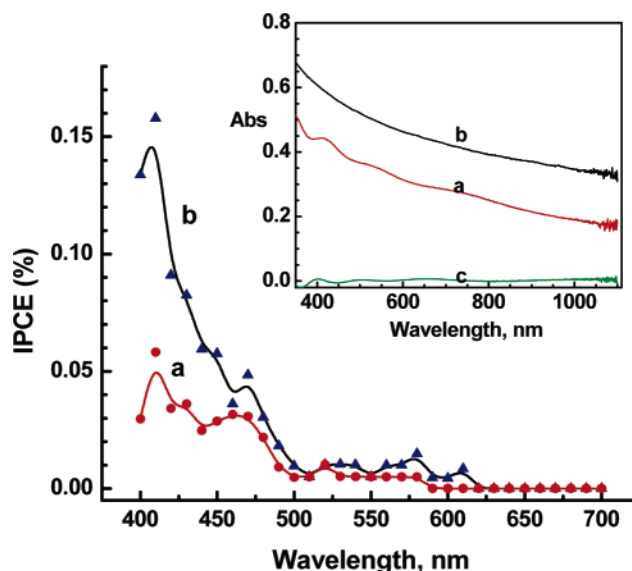


Figure 2. Photocurrent action spectra of (a) OTE/SWNT and (b) OTE/SnO₂/SWCNT electrodes showing the incident photon to photocurrent efficiency (IPCE) at different excitation wavelengths. The counter electrode is platinum gauze, and the electrolyte is 0.5 M LiI and 0.01 M I₂ in acetonitrile. Inset shows the absorption spectra of SWNT film cast by electrodeposition (50 Vdc) on an OTE electrode (curve a), OTE/SnO₂ electrodes (curve b), and the OTE reference electrode (curve c).

the increased electrode surface area, we see an enhancement of a factor of ~ 3 in the photocurrent. Direct interaction between SnO₂ and the SWCNT could also be a factor for driving away the charge carriers to the collecting surface. We are currently investigating the interaction between SWCNTs and various semiconductor systems.

The cathodic current generation at a CNT film is indicative of the mechanism that the photogenerated holes are collected at the OTE surface and transported to the counter electrode via an external circuit. The regenerative I_3^-/I^- redox couple facilitates the scavenging of charges at the electrode surfaces and thus enables the delivery of steady photocurrent. The observation of cathodic photocurrent further supports the notion that CNTs possess *p*-type semiconducting properties. The energetics of the conduction and valence bands, as illustrated by the van Hove singularities, is shown in Figure 4.¹⁶ The transition energies corresponding to the $\text{C}_1\text{--V}_1$ and $\text{C}_2\text{--V}_2$ transitions appear in the near-IR and red region, respectively.

Photoexcitation of the nanotubes generates $e\text{--}h$ pairs within this band structure. Columbic interaction between spatially confined charge carriers results in the formation of strongly bound excitons. These excitons eventually relax via intraband

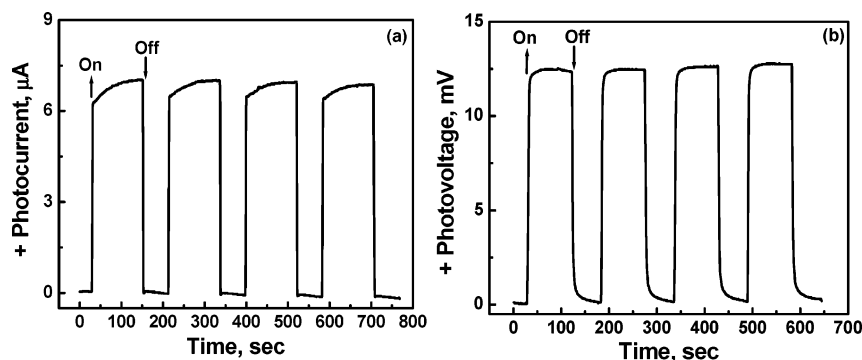


Figure 3. (a) Photocurrent and (b) photovoltage on-off cycles of OTE/SWNT excited with visible light ($\lambda > 400$ nm, $P \approx 100$ mW/cm²). The electrolyte is 0.5 M LiI and 0.01M I₂ in acetonitrile, and the counter electrode (CE) is platinum gauze.

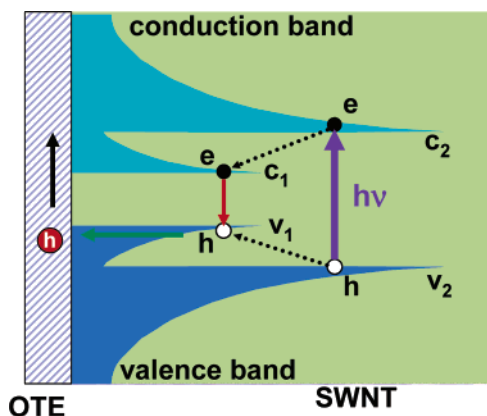
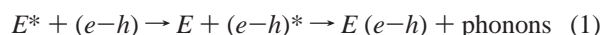


Figure 4. Schematic diagram illustrating the density of states of a single carbon nanotube. Photogenerated holes are captured at the collecting electrode surface, resulting in current generation in a photoelectrochemical cell.

transitions to the low-lying C_1 and V_1 level of the fundamental gap to produce a second sub-band-gap exciton or unbound $e-h$ pairs (reaction 1):¹⁰



where E represents excitons, the asterisk (*) denotes the excited species, and e and h respectively are electrons and holes that create the charge-separated state. The ionization of excitons to create the charge-separated state becomes an important process to tap into photocurrent generation. As the holes are driven away to the collecting electrode surface, the electrons are scavenged by the redox couple, thus producing the cathodic current.

We further probed the charge separation in these nanotubes by subjecting the TOAB-capped SWCNT suspension in THF to 387-nm laser pulse excitation using a Clark model MXR-2010 laser system and an Ultrafast Systems detection setup. The representative transient absorption spectra and the kinetic trace at 700 nm are shown in Figure 5. The photoexcitation of the laser pulse results in the bleaching of SWCNT in the red region. The broad band of bleaching essentially arises from the diversity

of tube diameters, chiral angle, and aggregation of nanotubes. Similar bleaching and recovery kinetics have also been observed for the SWCNT films cast on OTE.

The bleaching in the visible region, which corresponds to the C_2-V_2 transition, recovers in ~ 1 ps as the bound $e-h$ pairs or excitons are relaxed to the low-lying C_1-V_1 state. The dynamics of the transient bleaching recovery and the decay of the emission in the infrared arising from the charge recombination in the fundamental gap have been studied recently by Ma et al.¹⁰ They observed that the $e-h$ pairs accumulate in the fundamental gap (C_1-V_1) and their lifetime (10–100 ps) is dependent on the excitation intensity. Based on the difference between the emission decay and transient absorption recovery, these researchers noted the involvement of charge trap states as the additional contributing factors responsible for electronic transitions. Presence of such surface states are likely to stabilize the photogenerated charge carriers and contribute to the overall photocurrent generation. Such longer charge separation is crucial for increasing the probability of charge collection at the electrode surface. The fact that the photopotential continues to exhibit a slow increase for several seconds further supports the involvement of trap sites.

Note that most of the CNTs exist as bundles in the film. No doubt such bundling phenomenon is expected to decrease the lifetime of excitons. The fact that we observe transient bleaching and a recovery under laser-pulse excitation that is comparable to that observed in THF suspension shows that there is a significant fraction of the nanotubes with minimal intertube interactions in the excited state. Previous observation of photoconductivity and photoinduced alignment of nanotube bundles also support the ability to undergo photoinduced charge separation.

In summary, we have shown that electrophoretically deposited SWCNT films are photoactive and generate photocurrent under excitation by visible light. Ultrafast transient absorption studies confirm the charge separation in CNTs upon optical excitation. By minimizing the intertube interactions, it should be possible to improve the photoelectrochemical performance. Furthermore, CNTs should also serve as a support to anchor other semicon-

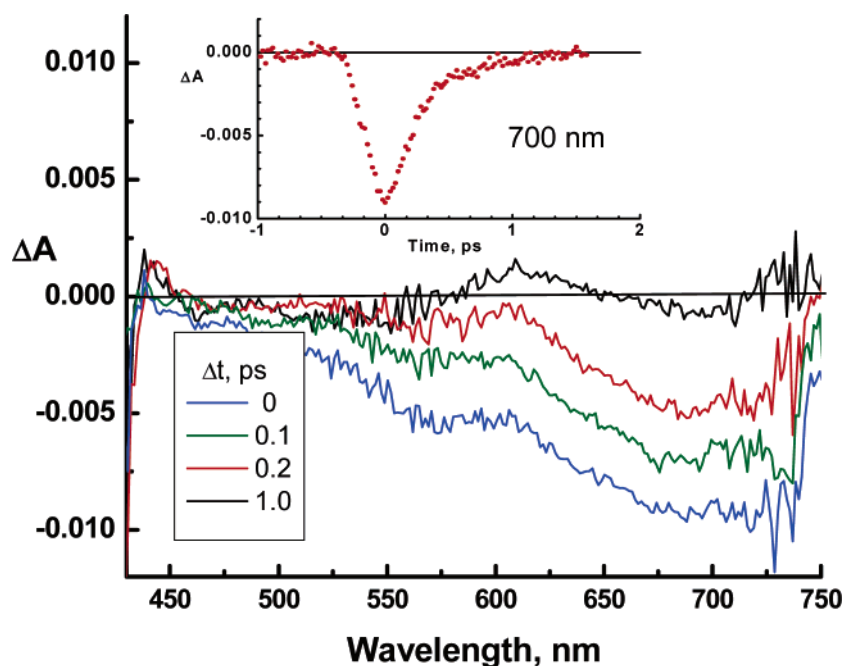


Figure 5. Time-resolved transient absorption spectra of a TOAB-capped SWCNT suspension in THF (flow cell) recorded using a 387-nm laser pulse. (Pulse width of 150 fs; $\Delta t = 0$ corresponds to the end of the pulse.) Inset shows the bleaching recovery at 700 nm.

ductor nanomaterials (e.g., CdS and CdSe) and facilitate photoinduced charge separation and charge transport in the composite film.

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Supporting Information Available: The movie shows an electrophoretic deposition process for casting SWCNT film on a conducting glass electrode. As the SWCNT from the suspension is driven to the positive electrode, the solution between the two electrodes becomes transparent. Transient absorption-time profiles obtained following the laser-pulse excitation of the SWCNT film is also included. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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