Photocurrent generation in random networks of multiwall-carbon-nanotubes grown by an "all-laser" process

M. A. El Khakani,[1,a)] V. Le Borgne,[1] B. Aïssa,[1] F. Rosei,[1] C. Scilletta,[2] E. Speiser,[2] M. Scarselli,[2] P. Castrucci,[2] and M. De Crescenzi[2]

[1]*Institut National de la Recherche Scientifique, INRS-Énergie, Matériaux et Télécommunications, 1650, Blvd. Lionel–Boulet, C.P. 1020, Varennes, Québec J3X-1S2, Canada*
[2]*Dipartimento di Fisica, Unità CNISM, Università di Roma "Tor Vergata," 00133 Roma, Italy*

We report photocurrent generation in entangled networks of multiwall-carbon nanotubes (MWCNTs) grown on TiN/Si substrates by an *all-laser* process. By integrating these MWCNTs into planar devices, we demonstrate that they generate photocurrent over all the visible and near-ultraviolet range, with maximum efficiency around 420 nm. Photocurrent is obtained even at zero applied voltage, pointing to a true photovoltaic (PV) effect. The extracted photocurrent as a function of applied voltage exhibits nonlinear behavior for voltages ≥2 V, suggesting that the devices do not behave as pure photoresistances. Other mechanisms (e.g., Schottky barriers imbalance) are invoked to describe current flow in these PV devices. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3211958]

Carbon nanotubes (CNTs) exhibit the surprising property of generating a photocurrent under illumination from visible and near ultraviolet (UV) energy.[1–5] This behavior paves the way for their use in optoelectronic and photovoltaic devices. Both single-walled CNT (SWCNT) and multiwalled CNTs (MWCNT) generate a sizeable photocurrent in electrochemical solar cells when exposed to UV-visible light.[3,4] The basic mechanism invoked for this photocurrent generation relies on the electronic transitions between van Hove singularities in their electronic density of states, which leads to exciton creation upon illumination. The electrolyte scavenges the electrons (/holes) and favors, through a redox reaction, the current flowing in the electrochemical cell. On the other hand, in solid state devices (without electrolytes), extensive studies carried out on the creation of electron-hole pairs in an individual SWCNT and their subsequent transport along the nanotube revealed the importance of the Schottky junctions formed between metallic electrodes and SWCNTs.[6,7] Here we show that a random network of MWCNTs collectively exhibit photocurrent generation properties similar to those reported for an isolated SWCNT. This behavior is interpreted as due to the presence of a high density of local unconventional Schottky barriers formed between the nanotubes in the MWCNTs network and/or inside the MWCNTs because of different chiralities, defects, kinks, twisting, and bending.

The MWCNTs were directly grown on TiN (~100 nm thick) coated Si(100) substrates by our *all-laser* synthesis process.[8] In this two-step process, the same KrF excimer laser (λ=248 nm) is used, first, to deposit Co/Ni catalyst nanoparticles (NPs), onto the TiN/Si substrates, through the laser ablation of a Co/Ni target in a controlled atmosphere (300 mTorr of He). In the second step, the TiN/Si substrates decorated with Co/Ni NPs were placed in a furnace-based-reactor where they were exposed to the carbon species produced from 100 laser ablation shots of a pure graphite target by the same KrF laser (under 5 Torr of argon at ~1000 °C). The amount of Co/Ni NPs is negligible compared to that of

CNTs (Co/Ni NPs cover only ~0.2% of the surface of the substrate onto which a highly dense and entangled three-dimensional network of CNTs is grown). The as-grown samples were characterized by scanning electron microscopy (SEM). The high-resolution transmission electron microscopy (HRTEM) [Jeol JEM-2100 F FEG-TEM (200 kV) microscope] was also used to examine the CNTs nanostructure.

Figure 1(a) shows a typical SEM micrograph of the samples where a highly dense network of entangled CNTs completely covers the TiN surface. (Their aspect ratio can be as high as ≥1000.) TEM analyses reveal that these CNTs are mainly multiwalled, as illustrated by the HRTEM image of Fig. 1(b). These MWCNTs are highly pure since no contaminants were found either inside or outside the tubes. Their length is of several micrometers while their inner and outer diameters are between 3.6 and 8 nm and between 4.8 and 20 nm, respectively. They consist of 2 up to 17 walls with a high crystalline quality, as shown in Fig. 1(c).

As the presence of amorphous and/or disordered carbon (*a*-C) cannot be excluded in the case of as-grown deposits [their Raman spectra (not shown) feature a D-band], the as-grown deposits were systematically annealed under oxygen (500 °C for 30 min.) to burn out any *a*-C. Then, metallic electrodes were deposited on the random network of MWCNTs (at a distance of ~6 mm from each other) to obtain a planar device, where the photocurrent laterally flows between the electrodes through the MWCNT entangled network. Unlike vertically designed devices where nanotubes form *p-n* junctions with the doped Si substrates,[9] our geometry ensures that all the observed effects are exclusively due to the nanotubes (no CNTs/Si junctions are probed here). Photocurrent spectra were collected, with and without biasing voltages, as a function of the incident photon wavelength using a focused beam from a xenon lamp (spot size ~2 × 3 mm²) coupled with a monochromator. By positioning the spotlight at increasing distances from the metal contacts, we find the highest value of the photocurrent near the ungrounded electrode; its value decreases when moving the illuminating spot toward the ground electrode. By inverting

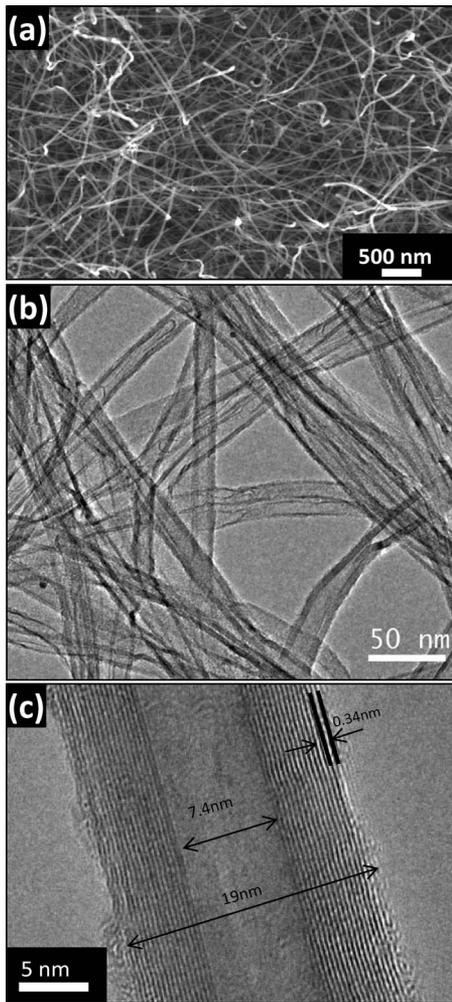a)Electronic mail: elkhakani@emt.inrs.ca.

FIG. 1. (a) Typical SEM micrograph of randomly entangled MWCNTs network; (b) Typical TEM image of the MWCNTs; and (c) high-resolution TEM image of an individual MWCNT with 17 walls.
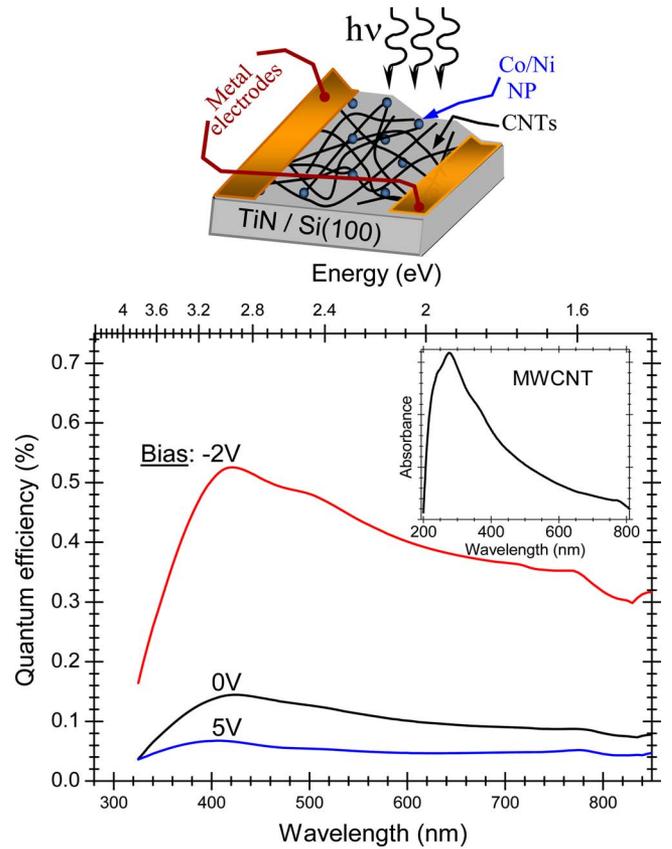

FIG. 2. (Color online) Quantum efficiency spectra obtained by illuminating the MWCNTs planar device next to the ungrounded electrode for different applied voltages (-2, 0, and 5 V). The inset shows the optical absorbance of MWCNTs scratched out from the TiN/Si substrate and appropriately deposited on quartz. A schematic layout of our MWCNTs-based planar devices is shown on the top of the figure.

the ground position, we measured the same behavior with the photocurrent changing sign, indicating that the carriers involved in the photogeneration process are always the same regardless of the polarity of the electrodes. This confirms the symmetric nature of our two-electrode planar devices and the arbitrary sign of the current. Thus, regardless of the polarity of the electrodes, the absolute value of the photocurrent is given by the relative difference between the currents measured under dark and illumination. No measurable current was recorded from the bare TiN substrate (with or without Co/Ni NPs) either before or after annealing (at 1000 °C under 5 Torr of argon to simulate the CNTs growth process). Thus, the observed photocurrent generation is exclusively associated with the presence of the MWCNTs.

The quantum efficiency (QE) was evaluated in terms of the number N_{e-h} of *e-h* pairs normalized to the number of incident photons $N_{ph} = \lambda P(\lambda)/hc$, where $P(\lambda)$ is the measured power density of the Xe lamp so that QE $= 100 \ N_{e-h}/N_{ph} = 100 \ I_{sample} \ hc/[P(\lambda) \cdot \lambda \cdot e]$. For each wavelength, N_{e-h} was deduced from the photocurrent extracted by the lock-in amplifier following sample exposure to alternating dark and light cycles. Figure 2 shows the measured QE as a function of the incident photon wavelength for different applied voltages. The QE strongly depends on the applied voltage, but does not vanish at zero bias, pointing to a true

photovoltaic effect. The QE curves show a general trend with a maximum around 400 nm (as high as 0.54% for the -2 V biased devices) and a slight decrease toward infrared wavelengths. This photoresponse behavior is even more pronounced for the -2 V biased devices and strongly resembles that of the optical absorbance[10] of MWCNTs (inset of Fig. 2). In fact, the QE curve of the nanotubes is expected to be proportional to their associated optical absorbance. In the present case, while both curves exhibit similar trends as a function of the wavelength, the maximum of the optical absorbance curve is blueshifted in comparison to that of the QE curve. Such a behavior has been also observed for MWCNTs on SiO_2/Si measured by using a photoelectrochemical cell,[11] and could be due to the rather important difference in the thicknesses involved in both QE and optical transmission measurements.[12] Fig. 3 shows the dark current (dark open circles) measured on the sample and the photocurrent (blue filled circles) measured as a function of the applied voltage (with an illumination at $\lambda = 504$ nm). The dark current data lie on a straight line,[13] following an Ohmic behavior, suggesting that the current in the device mainly flows through a percolated "metalliclike" pathway in the nanotube network. From the slope of this curve, the resistance of the device is estimated to 1388 Ω. By alternating illumination and dark cycles, the lock-in-measured photocurrent (at a given voltage) switches between ON and OFF states, respectively, at the frequency of the light chopper (lower-right inset of Fig. 3). Upon illumination, the I_{light}-V curve of the MWCNTs
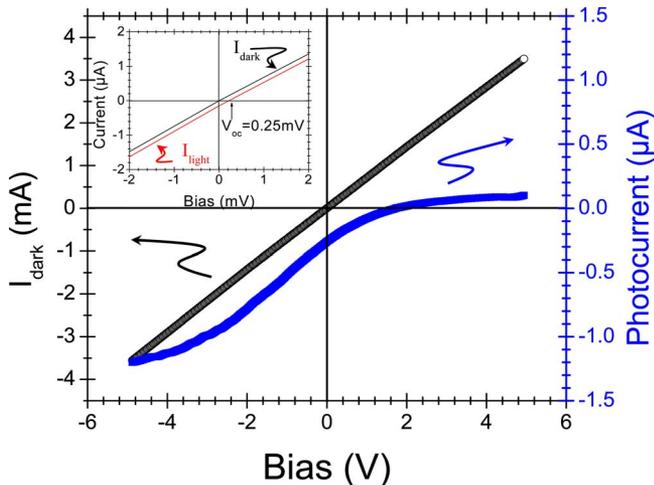
FIG. 3. (Color online) Dark current and photocurrent as a function of the applied voltage *V*. The upper inset shows the *I-V* curves under light (I_{light}; in red) and in darkness (I_{dark}, in black). The lower inset shows the photocurrent modulation by the illumination cycles monitored by the light chopper frequency at *V*=0 V. The ON-OFF cycles due to the chopper frequency are well reproduced even at zero bias, providing thereby another indication of the occurrence of a true photovoltaic effect.

device is still linear particularly at low voltages. A closeup of the two *I-V* curves (upper-left inset of Fig. 3) permits to determine the offset photovoltage, which is found to be of V_{oc}=0.38 mV. The extracted photocurrent[14] does not exhibit a linear behavior and saturates for voltages ≥ 2 V (Fig. 3). This may indicate that the effective separation of the photo-generated charges is reached at 2 V and above. These results show that MWCNTs based devices are not a pure photore-sistance but other mechanisms of current generation occur and depend on the applied voltage. Such a behavior has been already reported in the case of an individual metallic SWCNT connected through two metal electrodes.[13] We therefore suggest that the photocurrent produced by the ran-dom network of MWCNTs is highly likely similar to that exhibited by an individual metallic SWCNT. In the latter case, the current flow upon illumination was ascribed to the imbalance of the two Schottky barriers formed at the elec-trodes and supported by the presence of a photovoltage.[7] In our case, this imbalance could be even more enhanced be-cause of the inhomogeneity and complexity of the nanotube network underneath the metallic contacts. The presence of two asymmetric Schottky barriers gives rise to an electric field that separates the *e-h* pairs formed inside the nanotubes upon illumination, even without external bias. The excitons ionize when experiencing an electric field that separates the pairs. In the randomly entangled network of MWCNTs, the electric field could result from a variety of local Schottky junctions including those forming either within the same tube, or at the local interfaces between semiconducting and metallic nanotubes.[15] In particular, for the former effect, metal-semiconductor junctions along an individual nanotube occur when the tube is bent, twisted[16] or doped.[17] Finally, the flux of photogenerated charges is found to flow more easily to the ungrounded electrode than to the grounded one. This reflects the overall asymmetry between the two CNTs/metal-electrode Schottky barriers, believed to be responsible for charge transport in our devices.[7,18]

In summary, we demonstrated that a random network of all-laser grown MWCNTs exhibits a true photovoltaic effect, generating photocurrent even at zero bias. As a function of the applied voltage, the photoresponse of the MWCNTs is very similar to that exhibited by an individual SWCNT sus-pended between two metallic electrodes. This implies that the underlying physical mechanisms are very similar and re-lated to the presence of asymmetric Schottky junctions be-tween the metallic contacts and the nanotube network. Our device is certainly more complex than a single suspended tube and we have to invoke the formation of a high density of local unconventional Schottky junctions inside each tube and/or between adjacent tubes in the entangled network. The charges created at each of these local junctions by the im-pinging photons, their subsequent separation and transport leads to the overall photocurrent flowing between device electrodes. Finally, the efficiency of these devices (up to 0.54% around 400 nm at −2 V bias) could be further en-hanced by at least one order of magnitude by decorating the MWCNTs with metal nanodots[11] or semiconducting NPs.[19] Work is in progress to investigate the photocurrent genera-tion of CNTs/NPs nanocomposites.

[1] A. Mohite, S. Chakraborty, P. Gopinath, G. U. Sumanasekera, and B. W. Alphenaar, Appl. Phys. Lett. **86**, 061114 (2005).
[2] A. Mohite, G. U. Sumanasekera, K. Hirahara, S. Bandow, S. Iijima, and B. W. Alphenaar, Chem. Phys. Lett. **412**, 190 (2005).
[3] S. Barazzouk, S. Hotchandani, K. Vinodgopal, and P. V. Kamat, J. Phys. Chem. B **108**, 17015 (2004).
[4] P. Castrucci, F. Tombolini, M. Scarselli, E. Speiser, W. Richter, M. De Crescenzi, M. Diociaiuti, E. Gatto, and M. Venanzi, Appl. Phys. Lett. **89**, 253107 (2006).
[5] M. Passacantando, F. Bussolotti, V. Grossi, S. Santucci, A. Ambrosio, M. Ambrosio, G. Ambrosone, V. Carillo, P. Maddalena, E. Perillo, and A. Raulo, Appl. Phys. Lett. **93**, 051911 (2008).
[6] M. Freitag, Y. Martin, J. A. Misewich, R. Martel, and Ph. Avouris, Nano Lett. **3**, 1067 (2003).
[7] N. Peng, Q. Zhang, O. K. Tan, and N. Marzari, Nanotechnology **19**, 465201 (2008).
[8] M. A. El Khakani and J.-H. Yi, Nanotechnology **15**, S534 (2004).
[9] J. Wei, Y. Jia, Q. Shu, Z. Gu, K. Wang, D. Zhuang, G. Zhang, Z. Wang, J. Luo, A. Cao, and D. Wu, Nano Lett. **7**, 2317 (2007).
[10] The optical absorbance of the MWCNTs was measured after their scratch-ing from the TiN/Si substrate, dispersion in isopropanol, and drop casting on a quartz substrate.
[11] M. Scarselli, C. Scilletta, F. Tombolini, P. Castrucci, M. Diociaiuti, S. Casciardi, E. Gatto, M. Venanzi, and M. De Crescenzi, J. Phys. Chem. C **113**, 5860 (2009).
[12] The optical absorbance is defined as $1-R(\lambda)-T(\lambda)$, where $R(\lambda)$ and $T(\lambda)$ are the reflectance and transmittance which strongly depend on both light wavelength and sample thickness. The MWCNTs film formed on the quartz substrate is much thinner than that used in the PC measurements.
[13] K. Balasubramanian, M. Burghard, K. Kern, M. Scolari, and A. Mews, Nano Lett. **5**, 507 (2005).
[14] As the value of the photocurrent is much smaller than that of the dark current (μA versus mA), the use of a lock-in amplifier is highly recom-mended to extract the photocurrent.
[15] M. S. Fuhrer, J. Nygård, L. Shih, M. Forero, Y.-G. Yoon, M. S. C. Maz-zoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zettl, and P. L. McEuen, Science **288**, 494 (2000).
[16] P. Castrucci, M. Scarselli, M. De Crescenzi, M. A. El Khakani, F. Rosei, N. Braidy, and J.-H. Yi, Appl. Phys. Lett. **85**, 3857 (2004).
[17] D. A. Stewart and F. Leonard, Phys. Rev. Lett. **93**, 107401 (2004), and references therein.
[18] J. U. A. Lee, Appl. Phys. Lett. **87**, 073101 (2005).
[19] F. Vietmeyer, B. Seger, and P. V. Kamat, Adv. Mater. **19**, 2935 (2007).