

# Electrochemical gating of individual single-wall carbon nanotubes observed by electron transport measurements and resonant Raman spectroscopy

S. B. Cronin,<sup>a)</sup> R. Barnett, and M. Tinkham

*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*

S. G. Chou, O. Rabin, and M. S. Dresselhaus

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

A. K. Swan, M. S. Ünlü, and B. B. Goldberg

*Department of Electrical and Computer Engineering and Department of Physics, Boston University, Boston, Massachusetts 02215*

(Received 29 September 2003; accepted 8 January 2004)

Metal electrodes patterned lithographically on top of individual single-wall carbon nanotubes are used to gate the nanotubes with respect to a reference electrode in an electrolyte drop. The gating is found to have a dramatic effect on both the Raman spectra and electron transport of the nanotubes. Current through metallic nanotubes is found to increase sharply with electrochemical gate voltage, indicating that the Fermi energy reaches valence and conduction band van Hove singularities. Using resonant confocal micro-Raman spectroscopy, we observe a  $9 \text{ cm}^{-1}$  upshift of the tangential mode vibrational frequency, as well as a 90% decrease in intensity, by applying 1 V between an individual nanotube and a silver reference electrode in a dilute  $\text{H}_2\text{SO}_4$  solution. The mechanisms for the shifts of the Raman mode frequencies are discussed on the basis of changes in the lattice constant of heavily charged nanotubes. © 2004 American Institute of Physics. [DOI: 10.1063/1.1666997]

Electrical gating and charge transfer in carbon nanotubes are important for both fundamental physics and device applications.<sup>1,2</sup> The ability to change the resistivity of a semiconducting single-wall carbon nanotube (SWNT) by many orders of magnitude by electrostatic gating and also by gas adsorption has a potential for many practical applications, such as SWNT-FETs<sup>3</sup> and electrochemical sensors.<sup>4</sup> Because of their large surface-to-volume ratio, nanotubes are very sensitive to the presence of chemical species on their surface. By applying a voltage between a nanotube and a reference electrode in an electrochemical solution, the Fermi energy of a nanotube can be changed, as ions from the solution accumulate on the surface of the nanotube and act as a close-spaced gate. This is illustrated schematically in Fig. 1. Electrochemical gating of nanotubes has been shown previously to effectively shift the Fermi energy of semiconducting SWNTs resulting in large changes in resistivity and transistor-like behavior.<sup>5,6</sup>

In a resonant Raman process, the laser energy is in resonance with an electronic transition from the valence to the conduction band. In nanotubes, this resonance is enhanced because of the sharp van Hove singularities that occur in the density of states in one-dimensional systems. Consequently, when a nanotube is in resonance with the laser energy, we can observe the Raman spectrum from a single SWNT.<sup>7</sup> Electrochemical gating of nanotubes has been shown previously to produce observable effects on the Raman spectra of nanotubes.<sup>8–12</sup> However, in the present work, the geometry of the nanotube and gate are much different from prior reports. In previous work, large ensembles of tubes and bundles were deposited on conducting substrates, all gated

and measured simultaneously, resulting in Raman spectra summed over many different nanotubes. In the present work, a single tube is measured that is resting on an insulating substrate with electrodes on the ends of the nanotube away from the area viewed by the Raman microprobe. In this geometry, we can ensure from the atomic force microscope topography that only one SWNT contributes to the Raman signal.

In this work we report Raman measurements of electrochemically gated isolated SWNTs. We also show the first electron transport measurement of a metallic single SWNT

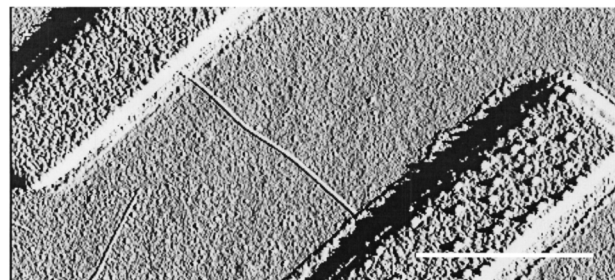
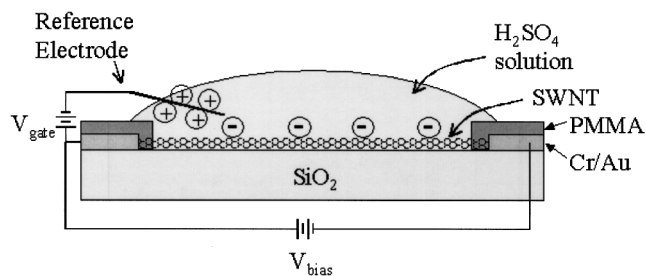


FIG. 1. Schematic diagram of electrochemical gating of ions in solution on one SWNT (upper panel). Atomic force microscope image of metal electrodes on a SWNT (lower panel). The scale bar indicates  $1 \mu\text{m}$ .

<sup>a)</sup>Electronic mail: steve@rsj.harvard.edu

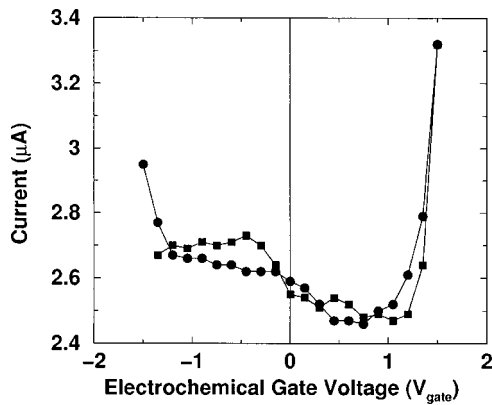


FIG. 2. Current vs electrochemical gate voltage for a nanotube with a fixed 0.5 V bias voltage. The gate voltage is first swept up (circles) from  $-1.5$  V to  $+1.5$  V and then down (squares).

demonstrating effective electrochemical gating. By measuring both Raman and electron transport as a function of electrochemical gating, we demonstrate that both the vibrational and electronic properties of SWNTs can be appreciably changed.

Samples were prepared by depositing SWNTs from a sonicated suspension in dichloroethane on a doped Si substrate with  $1 \mu\text{m}$  of insulating  $\text{SiO}_2$ . Metal electrodes of Cr–Au were then patterned on top of a single nanotube, as shown in Fig. 1, using electron beam lithography. We then lithographically pattern an insulating layer of PMMA (polymethyl-methacrylate) over the electrodes, so that the PMMA electrically insulates the electrodes from the solution and prevents shorting. In this configuration only the nanotube and not the leads are exposed to the electrolytic solution. Finally, Raman spectra are taken with a Renishaw Raman microprobe RM1000B with a 514 nm Ar ion laser and a beam size of  $1\text{--}2 \mu\text{m}$  in diameter.

The measured current dependence on the electrochemical gate voltage is shown in Fig. 2. The current through the nanotube is first measured while the sample is dry, and then again after a drop of  $1 \text{ mM H}_2\text{SO}_4$  solution is deposited on the surface. The SWNT current is found to remain unchanged by the presence of the solution, indicating that all the current is going through the nanotube and not the solution. During the  $I\text{--}V_{\text{gate}}$  measurement, the leakage current through the gate was monitored and found never to exceed  $1 \mu\text{A}$  in absolute value. Any contribution to the measured nanotube current from the gate leakage current would result in a monotonic dependence, which is not observed. We therefore can neglect both current introduced by gate leakage and shorting of the nanotube's electrodes through the solution. The  $I\text{--}V_{\text{gate}}$  measurement was done with a constant bias voltage of  $V_{\text{bias}}=0.5 \text{ V}$ , as depicted in Fig. 1. Due to rapid corrosion of the sample in the acidic electrolyte, we were able to make measurements at only one bias voltage.

In Fig. 2 we see a sharp increase in current for large negative and positive electrochemical gate voltages and a roughly constant current of  $\sim 2.6 \mu\text{A}$  for intermediate gate voltages. The behavior of the current through the SWNT is reversible with electrochemical gate voltage. We believe that the sharp increases in current for large positive and negative gate voltages are evidence of carrier occupation of the con-

duction and valence subbands. Due to the large amount of charge induced by the electrochemical gate, we expect a large increase in the number of free carriers when a van Hove singularity is reached. The onset of this increase in current is observed for electrochemical gate voltages of  $\pm 1.2 \text{ V}$ . The symmetry of this  $I\text{--}V_{\text{gate}}$  curve indicates that the Fermi energy at zero applied gate voltage is in the middle of the conduction and valence subbands. From atomic force microscopy measurements, we approximate the diameter of this tube to be  $2.0 \pm 0.5 \text{ nm}$ . Although this is a crude measurement of the diameter, we can estimate the energy separation of the first valence and conduction subbands of this metallic SWNT as  $1.35 \pm 0.35 \text{ eV}$ , using a tight binding calculation with an overlap integral value of  $2.9 \text{ eV}$ .<sup>13</sup> We therefore estimate the proportionality constant between the change in the Fermi energy and the electrochemical gate voltage to be between 0.4 and 0.7.

Raman spectra were taken on samples similar to that of Fig. 2 for which a resonance was found between a SWNT electronic transition and the incident laser energy. The specific nanotube that was used in the electron transport measurement could not be measured by Raman spectroscopy because it was not resonant with the incident laser energy of  $2.41 \text{ eV}$ , but could in principle be measured using another laser energy. As with the electron transport measurement discussed earlier, we first measure the Raman spectrum of a dry individual SWNT with metal electrodes. After adding a drop of  $1 \text{ mM H}_2\text{SO}_4$  with no voltage applied, we see no change in the position of the tangential phonon mode. This indicates that there is no significant spontaneous charge transfer due to the presence of the electrolyte. By applying a gate voltage between an individual nanotube and a  $25 \mu\text{m}$ -diam silver wire reference electrode in the dilute  $\text{H}_2\text{SO}_4$  solution, as shown in the schematic diagram of Fig. 1, we observe dramatic changes in the tangential mode (TM) Raman spectra of the nanotube. No bias voltage was applied in the Raman measurements, since an electric current is not expected to affect the phonon spectrum, but may induce a nonuniform potential along the nanotube. The TM Raman spectra of the gated nanotube are plotted in Fig. 3 for positive and negative gate voltages. For large positive applied voltages, the intensity of the TM is found to decrease by almost 90% of the peak intensity at zero applied voltage. However, for negative applied electrochemical gate voltages, the intensity of this peak only decreases by approximately 60%. In addition to this large drop in intensity, we observe a significant upshift of the peak position for positive and negative applied voltages. A  $9 \text{ cm}^{-1}$  upshift of the peak position is observed for this sample with electrochemical gating of  $+0.95 \text{ V}$  and a  $4.5 \text{ cm}^{-1}$  upshift is observed with electrochemical gating of  $-0.95 \text{ V}$ . Both the change in peak intensity and the change in peak position were found to be reversible with electrochemical gate voltage. The upshift and drop in intensity are more pronounced for positive applied voltages than negative. For another nanotube studied (not shown), we observed similar unequal decreases in intensity for positive and negative applied voltages. However, for this second SWNT, we only observed an upshift in the TM frequency for positive voltages and no frequency shift for negative voltages.

As was the case in the  $I\text{--}V_{\text{gate}}$  measurement, rapid

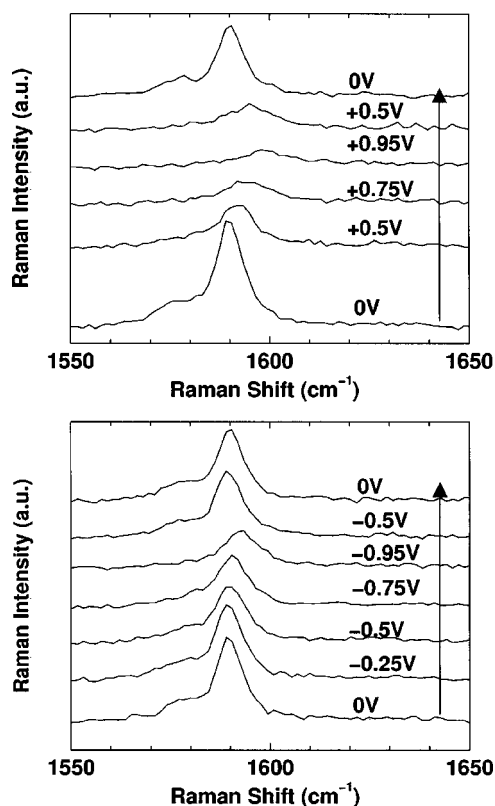


FIG. 3. Tangential mode Raman spectra of an individual SWNT for various applied positive (upper panel) and negative (lower panel) electrochemical gate voltages. The arrows indicate the sequence in which data were taken.  $E_{\text{laser}} = 2.41$  eV (514 nm).

corrosion of the sample in the  $\text{H}_2\text{SO}_4$  electrolyte, even for zero applied voltage, limits the sample life and limits the maximum gate voltage that can be applied. Data must therefore be taken quickly before irreversible sample degradation destroys the signal. For this reason we only study the TM.

The upshift observed for positive applied voltages is understood by analogy to acceptor doped nanotubes and graphite. The accumulation of negatively charged sulfate ions on the surface of the nanotube causes a depletion of the free electrons in the nanotube. This results in a slight contraction of the graphitic hexagons on the surface of the SWNT causing an upshift of the TM frequencies. The upshift in the TM frequency observed for negative applied voltage is not understood on the basis of such simple arguments. However, a nonmonotonic doping dependence of the TM frequency has been observed previously.<sup>14</sup> The slight distortion of the lattice vector of the nanotube is also expected to shift the position of the van Hove singularities in the density of states. In a resonant Raman process, the very sharp van Hove singularities are in resonance with the laser energy. Therefore, any shift in their position due to a distortion of the lattice will spoil the resonance condition and lead to a large decrease in Raman intensity, as observed.

Electrochemical gating of macroscopic quantities of nanotubes show significant upshifts in the TM frequency for positive applied potentials in various electrolytes, such as  $\text{H}_2\text{SO}_4$ ,<sup>8,9</sup>  $\text{NaCl}$ ,<sup>10,11</sup>  $\text{KCl}$ ,<sup>11</sup> and  $\text{LiClO}_4$ .<sup>12</sup> However, little or no shift for negative applied voltages has been observed. This is consistent with our findings, where we also observe asymmetric shifts of the TM for positive and negative gate voltages.

Raman measurements on doped NTs show downshifts of the TM frequencies for donors (K, Rb, Li) and upshifts for acceptors ( $\text{Br}_2$ , polyiodide chain intercalation), suggesting a monotonic dependence of the TM on charge.<sup>14,15</sup> However, Bendiab *et al.*<sup>15</sup> have shown significant upshifts in the TM mode frequency for donor doping with Li and Rb. While charge transfer to the nanotubes is expected to be the main mechanism in both doping and gating experiments, a direct comparison of the two is not straightforward, since there may be other effects associated with the presence of the electrolytic solution or dopant atoms that contribute to the upshift in TM frequency observed for negative applied gate voltages.

In conclusion, by applying a voltage between an individual SWNT and a reference electrode in an electrolyte, we observe significant changes in the electronic transport properties and phonon spectra of nanotubes. Sharp increases in current through metallic nanotubes gated electrochemically indicate that the Fermi energy reaches valence and conduction band van Hove singularities. We also observe a large decrease in the intensity of the tangential phonon mode of a SWNT and a significant upshift in frequency for positive and negative applied electrochemical gate voltages. For positive gate voltages, the upshift of the TM frequency and strong decrease in Raman intensity are understood on the basis of changes in the lattice constant and the vibrational force constant caused by charge transfer. However, the mechanism responsible for the upshift in TM frequency observed for negative applied voltages is not yet understood.

The authors thank Dr. Gene Dresselhaus for helpful discussions. This research was supported by NSF Grant Nos. DMR-01-16042, DMR-02-44441, and NITRT-0210752 NSEC Grant No. PHY-01-17795, and the Dupont-MIT Alliance.

<sup>1</sup>J. Nygard, D. H. Cobden, M. Bockrath, P. L. McEuen, and P. E. Lindelof, *Appl. Phys. A: Mater. Sci. Process.* **69**, 297 (1999).

<sup>2</sup>M. Freitag, A. T. Johnson, S. V. Kalinin, and D. A. Bonnell, *Phys. Rev. Lett.* **89**, 216801 (2002).

<sup>3</sup>S. J. Tans, A. R. M. Verschueren, and C. Dekker, *Nature (London)* **393**, 49 (1998).

<sup>4</sup>A. Modi, N. Koratkar, E. Lass, B. Wei, and P. M. Ajayan, *Nature (London)* **424**, 171 (2003).

<sup>5</sup>S. Rosenblatt, Y. Yaish, J. Park, J. Gore, V. Sazonova, and P. L. McEuen, *Nano Lett.* **2**, 869 (2002).

<sup>6</sup>M. Kruger, M. R. Buitelaar, T. Nussbaumer, C. Schonenberger, and L. Forro, *Appl. Phys. Lett.* **78**, 1291 (2001).

<sup>7</sup>A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. Lett.* **86**, 1118 (2001).

<sup>8</sup>G. U. Sumanasekera, J. L. Allen, S. L. Fang, A. L. Loper, A. M. Rao, and P. C. Eklund, *J. Phys. Chem. B* **103**, 4292 (1999).

<sup>9</sup>P. Corio, P. S. Santos, V. W. Brar, Ge. G. Samsonidze, S. G. Chou, and M. S. Dresselhaus, *Chem. Phys. Lett.* **370**, 675 (2003).

<sup>10</sup>M. Stoll, P. M. Rafailov, W. Frenzel, and C. Thomsen, *Chem. Phys. Lett.* **375**, 625 (2003).

<sup>11</sup>L. Kavan, P. Rapta, and L. Dunsch, *Chem. Phys. Lett.* **328**, 363 (2000).

<sup>12</sup>L. Kavan, P. Rapta, L. Dunsch, M. J. Bronikowski, P. Willis, and R. E. Smalley, *J. Phys. Chem. B* **105**, 10764 (2001).

<sup>13</sup>R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).

<sup>14</sup>A. Claye, S. Rahman, J. E. Fischer, A. Sirenko, G. U. Sumanasekera, and P. C. Eklund, *Chem. Phys. Lett.* **333**, 16 (2001).

<sup>15</sup>N. Bendiab, E. Anglaret, J.-L. Bantignies, A. Zahab, J. L. Sauvajol, P. Petit, C. Mathis, and S. Lefrant, *Phys. Rev. B* **64**, 245424 (2001).