

## Probing the Reversibility of Sidewall Functionalization Using Carbon Nanotube Transistors

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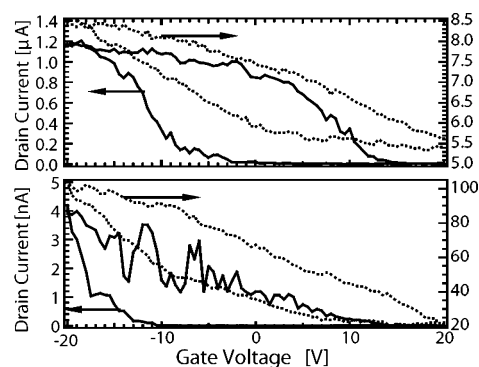
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Covalent functionalization of single-wall carbon nanotubes (SWNTs) is currently developing as one of the most powerful tools enabling their processing, manipulation, and assembly from solution.<sup>1</sup> SWNTs are rather inert, and only harsh chemical or mechanical treatments can activate the highly conjugated C–C bonds. Moreover, the functionalization introduces disorder that disrupts the electrical and optical properties of SWNTs. Thus, the covalent SWNT chemistry presents important issues, and more sensitive methods are required in order to gain a better understanding of the reactions. For example, oxidation processes involving hard sonication and strong acids were among the first approaches to functionalize the SWNT sidewalls,<sup>2</sup> but they are known to introduce irreversible damage.<sup>1b,3</sup> Recently, new functionalization reactions using radical addition, such as the diazonium, fluorination, and peroxide reactions, have been developed in order to avoid permanent damage. The diazonium reaction, for instance, provides an effective path to anchor new groups onto the sidewalls,<sup>4</sup> and a large variety of functionalities can then be attached.<sup>5</sup> This approach is particularly interesting because it is general. Raman studies have also shown evidence that the reaction is reversible. However, the Raman signature is difficult to interpret due to stringent selection rules and complications associated with resonance enhancement process.<sup>6</sup>

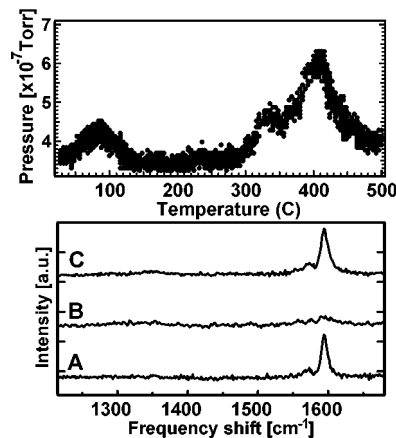
Here we present a general and sensitive method to probe the reversibility of SWNT sidewall reactions. The approach is to combine Raman spectroscopy and conductance measurements from a large ensemble of nanotube field-effect transistors (SWNT FET). The data are taken during several functionalization/defunctionalization cycles and then used to build a good statistic on the evolution of the reactions. We present here the case of the diazonium reaction. The study reveals for the first time that the reaction is partially reversible and leads to a small accumulation of defects onto the SWNT sidewall. The reaction rate is also much faster for the metallic SWNT species.

We fully characterized 22 p-type SWNT FETs during several cycles of functionalization (f-SWNT) and defunctionalization (d-SWNT) reactions. The SWNT FETs are about 0.5  $\mu\text{m}$  long and consist of 1–3 bundles of 1.5–5 nm of height, as determined by AFM imaging. We functionalized the SWNT FETs using a solvent-free diazotization and coupling procedure.<sup>7</sup> The defunctionalization was conducted by annealing the devices at 500  $^{\circ}\text{C}$  for 1 h under vacuum ( $4 \times 10^{-5}$  mbar). A TGA and a thermodesorption analysis confirm that these conditions ensure a complete defunctionalization. A typical desorption spectra is shown in Figure 2 with three main peaks at 100, 330, and 430  $^{\circ}\text{C}$ . The first is simply water desorption, while the peaks at 330–410  $^{\circ}\text{C}$  are associated with the removal of the iodophenyl from the sidewall of the SWNTs. No other desorption was observed at a temperature up to 650  $^{\circ}\text{C}$ .

Typical transfer characteristics of SWNT devices taken before and after reactions are shown in Figure 1. We observe two types



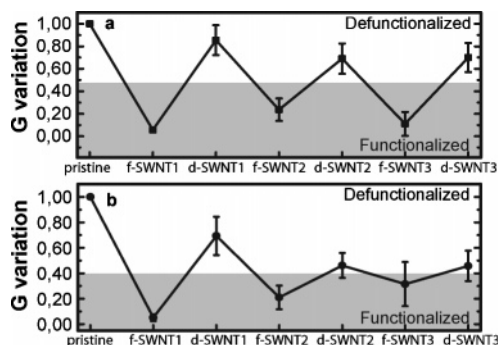
**Figure 1.** Transfer characteristics of typical nanotube field-effect transistors taken before (pristine SWNT, top) and after (f-SWNT, bottom) the diazonium reaction. The  $I$ – $V$  curves of two SWNT FETs are displayed, one by a solid line and the other by a dotted line.



**Figure 2.** Top: Typical thermodesorption spectrum of functionalized SWNTs deposited on Si substrate (heating rate 2  $^{\circ}\text{C}/\text{s}$ ). Bottom: Raman spectra ( $\lambda = 514.5$  nm) of the (A) pristine SWNT, (B) functionalized SWNT, and (C) defunctionalized SWNT.

of devices: one is composed of semiconducting SWNTs and presents no current in the OFF state, while the other cannot be turned off completely. Such a leaky OFF state is indicative that metallic nanotubes are also present in the bundle. In this case, the conductance in the OFF state probes mainly the metallic SWNTs, while both kinds of SWNTs are probed using the ON state conductance. In all cases, we observe that the conductance of the SWNTs decreases significantly upon functionalization in both the ON and the OFF states. Sampling of the devices in both regions ensures that semiconducting and metallic SWNTs are being probed and allows us to identify possible differences between the two species.

To ensure that the electrical behavior is directly linked to the functionalization, we took Raman spectra at different device



**Figure 3.** Conductance variations of SWNT transistors during reaction/annealing cycles in the ON (a) and in the OFF states (b). A voltage of 1 V was applied between the source and the drain.

locations with a wavelengths of 514.5 nm, which enhances the signal of the semiconducting SWNTs. Examples are presented in Figure 2a–c for pristine SWNT, f-SWNT, and d-SWNT devices. Two main features, the D-band at around  $1350\text{ cm}^{-1}$  and the G-band at around  $1590\text{ cm}^{-1}$ , are observed. Their total intensity decreases upon functionalization.<sup>8</sup> This indicates a partial loss of the resonance process, which is a clear indication that the reaction took place. Either a loss of resonance due to charge transfer doping or a broadening of the nanotube Van Hove singularity induced by disorder can explain the change in intensity. In fact, the D- and G-bands are difficult to probe for individual f-SWNT. The increase of the D-band/G-band ratio upon the reaction was further confirmed by taking bulk measurements using a large ensemble of nanotubes (see Supporting Information). Because the D-band is mainly related to lattice defects, the changes in the Raman spectra are induced by the presence of functional groups covalently attached to the nanotube sidewall.<sup>6,8</sup> Upon thermal treatments, the spectral characteristics return to the original spectral features and intensity.

Statistics have been generated from the transfer characteristics of the SWNT FETs for every step during the functionalization/defunctionalization cycles. We present in Figure 3a and 3b the conductance values taken at  $V_D = 1\text{ V}$  in the ON and OFF states, respectively. Each point is an average of the conductance normalized by their respective starting values (i.e., pristine SWNT). Several observations can be made: First, the conductance significantly decreases after the first reaction down to about 7 and 5% for the ON and OFF states. Second, the conductance recovers only partially from its initial value after the thermal defunctionalization. The statistics show that the conductance degrades significantly after each reaction/annealing cycle. The final ON and OFF conductances are, respectively, at about 70 and 50% of the initial value after three cycles. Last, the OFF state data indicate that the efficiency of the reaction is maximal on the pristine SWNTs and decreases upon cycling. This damping effect is also visible in the ON state, but to a much lower extent.

Schottky barriers at the nanotube–electrode contacts dominate the device characteristics,<sup>9</sup> and this may complicate the interpretation. However, this effect can be neglected here given the large increase of resistance in Figure 1. The changes are therefore only linked to the presence of functional groups. Similar changes have already been observed elsewhere,<sup>10</sup> and theoretical studies have ascribed this effect to an increase of backscattering by quasibound

states<sup>11</sup> leading, at high concentration, to Anderson localization.<sup>12</sup> Since only part of the initial conductance was restored after each reaction cycle, it appears that the diazonium reaction cycles follow two different pathways. The main is fully reversible and helps to recover the nanotube conductance, while the other leads to permanent damages of the sidewall and contributes to the residual resistance of the nanotubes. In fact, we can also infer from the data that the permanent defects thus produced lead to a significant decrease of the reactional sites for subsequent reactions. Moreover, it seems that the effect is more accentuated in the OFF state of the device, which is consistent with the recent claims that the metallic SWNTs are more reactive<sup>10</sup> and therefore more prone to irreversible damage. This can be rationalized by the first step of the diazonium reaction, which is to extract an electron from the SWNT structure. As metallic SWNTs have higher electron densities near the Fermi level, they should be more reactive.<sup>13</sup> The higher defects density for the metallic SWNT brought on the reaction cycles could therefore come from a faster reaction mechanism leading to a higher degree of functionalization.

In summary, this paper presents conductance measurements that reveal strong evidence that the diazonium functionalization is not fully reversible. The fast degradation of the characteristics in the OFF state is explained in terms of the different reactivity between the semiconducting and metallic SWNTs and of defect accumulation on the nanotube sidewall.

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**Supporting Information Available:** Devices fabrication, functionalization procedure, thermodesorption, and Raman spectra taken on bulk samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Klinke, C.; Hannon, J.; Afzali, A.; Avouris, Ph. *Nano Lett.* **2006**, *6*, 906. (b) Banerjee, S.; Hemraj-Benny, T.; Wong, S. *Adv. Mater.* **2005**, *17*, 17.
- (2) Chen, J.; Hamon, M.; Hu, H.; Chen, Y.; Rao, A.; Eklund, P.; Haddon, R. *Science* **1998**, *282*, 95.
- (3) Hirsch, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853.
- (4) Bahr, J.; Tour, J. *Chem. Mater.* **2001**, *13*, 3823.
- (5) (a) Buffa, F.; Hu, H.; Resasco, D. *Macromolecules* **2005**, *38*, 8258. (b) Dyke, C.; Tour, J. *Chem.—Eur. J.* **2004**, *10*, 812. (c) Li, H.; Cheng, F.; Duff, A.; Adronov, A. *J. Am. Chem. Soc.* **2005**, *127*, 14518.
- (6) Dresselhaus, M.; Dresselhaus, G.; Saito, R.; Jorio, A. *Phys. Rep.* **2005**, *409*, 47.
- (7) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 1156.
- (8) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M.; Smalley, R.; Tour, J. *J. Am. Chem. Soc.* **2001**, *123*, 6536.
- (9) Heinze, S.; Tersoff, J.; Martel, R.; Derycke, V.; Appenzeller, J.; Avouris, P. *Phys. Rev. Lett.* **2002**, *89*, 106801.
- (10) (a) An, L.; Fu, Q.; Lu, C.; Liu, J. *J. Am. Chem. Soc.* **2004**, *126*, 10520. (b) Wang, C.; Cao, Q.; Ozel, T.; Gaur, A.; Rogers, J.; Shim, M. *J. Am. Chem. Soc.* **2005**, *127*, 11460.
- (11) Choi, H.; Ihm, J.; Louie, S.; Cohen, M. *Phys. Rev. Lett.* **2000**, *84*, 2917.
- (12) Biel, B.; Garcia-Vidal, F.; Rubio, A.; Flores, F. *Phys. Rev. Lett.* **2005**, *95*, 266801.
- (13) Strano, M.; Dyke, C.; Usrey, M.; Barone, P.; Allen, M.; Shan, H.; Kittrell, C.; Hauge, R.; Tour, J.; Smalley, R. *Science* **2003**, *301*, 1519.

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