

## A Simple Chemical Route To Selectively Eliminate Metallic Carbon Nanotubes in Nanotube Network Devices

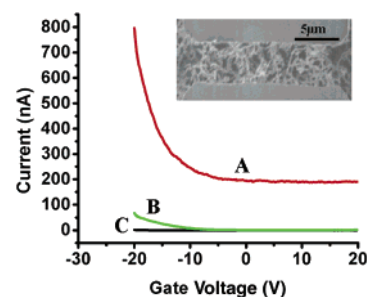
Lei An, Qiang Fu, Chenguang Lu, and Jie Liu\*

Department of Chemistry, Duke University, Durham, North Carolina 27708

Received June 14, 2004; E-mail: j.liu@duke.edu

Although research based on carbon nanotubes blossomed over the past decade, there are still some obstacles remaining that hamper further progress in the application of this unique material. Among them, separating metallic and semiconducting carbon nanotubes has been the central issue in terms of effective fabrication of high-performance electronic devices based on carbon nanotubes, such as field effect transistors (FETs) and sensors. It is well-known that single-walled carbon nanotubes (SWNTs) can be either semiconducting or metallic depending on their helicities.<sup>1</sup> Up to now, the synthesis of SWNTs yields a mixture of semiconducting and metallic carbon nanotubes, which significantly restricts the application of carbon nanotubes as the building block for molecular electronics because semiconducting and metallic materials have very different functions in electronic devices. For example, metallic SWNTs are usually undesired because only semiconducting SWNTs have a significant electrical response to electric field gating effect and chemical doping effect that are essential for the functions of FETs and chemical sensors. Extensive efforts have been made to separate those two kinds of SWNTs.<sup>2–8</sup> However, most of these approaches developed were only applicable to suspended nanotubes in solvents. Only two reported approaches can selectively remove metallic nanotubes from existing nanotube devices composed of multiple nanotubes between metal electrodes. The approach developed by the IBM group<sup>3</sup> requires the application of gate voltage on the device before passing a large current to selectively “burn” away the metallic nanotubes, while a recent electrochemical approach by Balasubramanian et al.<sup>9</sup> needs to precondition each device before electrochemical removal of the metallic nanotubes. Both approaches cannot be easily scaled up to a full wafer scale for selective removal of metallic nanotubes. In this communication, we demonstrate that by using a simple chemical reaction developed recently,<sup>5</sup> which used diazonium reagents to selectively react with metallic nanotubes, high-performance FETs containing only semiconducting SWNTs can be easily obtained without gating or preconditioning. This new technique will greatly speed up the process to build SWNT-based devices into real application in nanoscale electronics. In addition, the experiments have shown that the concentration of diazonium reagents plays a key role in the selectivity of the reaction, meaning that the excessive diazonium salts do not have the desired selectivity and will react with both kinds of nanotubes.

The SWNT devices were prepared using the standard chemical vapor deposition system, composed of a heated 1 in. quartz tube and a gas handling system,<sup>10,11</sup> and a two-step photolithography process. First, the catalyst islands were lithographically patterned on silicon substrates with 1- $\mu\text{m}$  thick thermally grown oxide<sup>12,13</sup> using PMMA or Photoresist 1813 from Shipley. Aqueous suspension of 0.05 mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.15 mmol  $\text{MoO}_2(\text{acac})_2$ , and 15 mg of alumina powder per 15 mL of water were used to deposit catalyst islands. The catalysts were annealed at 500 °C in air for 5 min and reduced at 800 °C in  $\text{H}_2$  (200 sccm) for 5 min before

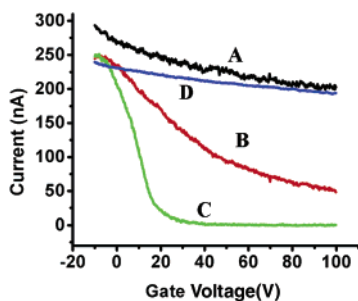


**Figure 1.** Gate dependence curves of the device. (A) Before the diazonium reaction. (B) After the reaction with the diazonium reagent (3.7 mM). (C) After further reactions (3.7 mM). The inset is an SEM image of a typical SWNT network device. The bias was 100 mV. The doped Si substrate was used as back gate in all measurements.

being exposed to ethanol carried by Ar (1000 sccm) for 10 min to grow SWNTs. Then the electrodes were patterned on the top of the catalyst islands, followed by metal evaporation (5-nm Cr and 30-nm Au) and liftoff. The gap between the electrodes is about 5  $\mu\text{m}$ . The devices were annealed at 300 °C in Ar atmosphere for 30 min before the electrical measurements and chemical modification.

The diazonium reaction we have used to selectively eliminate metallic SWNTs was derived from a previous publication.<sup>5</sup> It is believed that the reaction selectivity comes from the difference between the electronic band structures of metallic SWNTs and semiconducting SWNTs. In other words, metallic SWNTs, contrary to semiconducting SWNTs, have finite electron density of states at their Fermi levels, meaning that there are electrons available to stabilize the charge-transfer complex presumably formed by the diazonium reagent at the nanotube surface, which is suggested to facilitate the reaction.<sup>5</sup> On the other hand, the absence of the electrons near the Fermi level makes semiconducting nanotubes less likely to react with the diazonium reagent. However, semiconducting nanotubes are not absolutely inert to this reaction.

In our initial experiments, the nanotube devices were simply immersed in 3.7 mM 4-bromobenzenediazonium tetrafluoroborate aqueous solution (pH = 10).<sup>5</sup> The mixture was stirred for various period times, ranging from 10 min to 24 h. The devices were rinsed thoroughly with water after the reaction and baked at 100 °C for 2 min to remove water molecules absorbed on the devices before the electrical measurements were carried out. Typically, the on-state conductance for the p-type device dropped dramatically (90% in this case) as seen from Figure 1. Further repeating of the reaction on the same sample would totally destroy the device as the conductance diminished to zero. Even though the results clearly showed that nanotubes reacted with the diazonium reagent, the selectivity of the reaction is not clear since too many semiconducting nanotubes were sacrificed in this process as suggested by the significant decrease in the on-state conductance after the reaction in Figure 1. Apparently, selectivity was not achieved under this kind of reaction condition, and the performance of the device after

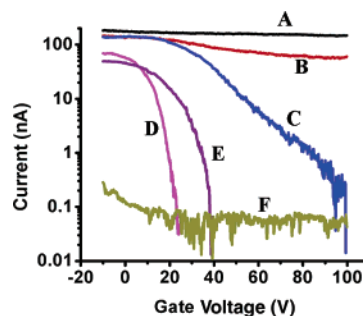


**Figure 2.** Gate dependence curves of the device. (A) Before the diazonium reaction. (B) After the first reaction with the diazonium reagent ( $5.3 \times 10^{-7} \mu\text{M}$ ). (C) After a second reaction ( $5.3 \times 10^{-7} \mu\text{M}$ ). (D) After annealing. The bias was 100 mV.

the reaction was far worse than that before the reaction, which is not desirable for in situ fabrication of semiconducting-only nanotube devices. Similar results were also observed by Balasubramanian et al.<sup>9</sup> in their control experiments.

To improve the selectivity of the chemical reaction, we took careful control of the concentration of the diazonium reagent that was used for every reaction. In a typical experiment, we first roughly estimated the total number of nanotubes in the device from an SEM picture, as shown by the inset of Figure 1. Then we carefully conducted the reaction with the specific concentration of the diazonium reagent so that only a small portion of carbon atoms would be reacted, for example, 10 to 20 carbons out of 1000 carbons as suggested by a previous report.<sup>5</sup> The concentrations of the diazonium reagent varied with different samples, but we usually started by putting a drop of  $5.3 \times 10^{-7} \mu\text{M}$  aqueous solution of the diazonium reagent on the top of the device, and the reaction time was normally 10 min.<sup>14</sup> As Figure 2 shows, after the first reaction, the off-state current decreased about 74% while the on-state current decreased only about 15%, a clear indication that most of the metallic nanotubes were eliminated and the semiconducting ones were almost intact. A second reaction was carried out on the same sample, and afterward the device was completely turned off at positive gate voltage while the on-state current was left almost unaffected. Evidently, the selectivity of this diazonium reaction has been successfully achieved. Finally, the sample was annealed at 300 °C in Ar for 30 min, the aryl functional groups on the nanotubes underwent cleavage in the inert gas atmosphere,<sup>5</sup> and the device recovered back to a level close to that before the reactions.

A different set of measurements was illustrated in Figure 3 with the current plotted in log scale showing the importance of the diazonium reagent concentration. The off-state conductance dropped about 59% while the on-state current only decreased about 18% after the first reaction. A second reaction kept the on-state current the same and only saw the total elimination of metallic nanotubes as indicated by the infinitesimal current at the turn-off state. The ON and OFF current ratio is approaching  $10^5$ , and it is limited by the instruments (2400 Keithley sourcemeters), which have a resolution of more than 10 pA. To elaborate the importance of controlling the concentration of the diazonium reagent, we increased the concentration of the diazonium reagent to 3.7 mM and kept the reaction time the same. As a result, the on-state conductance slumped about 50%, indicating that a considerable portion of semiconducting nanotubes had been reacted. Further reaction with the excessive amount of the diazonium reagent reduced another 30% of the on-state current. Finally, the device became insulating



**Figure 3.** Gate dependence curves of the device. (A) Before the diazonium reaction. (B) After the first reaction with the diazonium salts ( $5.3 \times 10^{-7} \mu\text{M}$ ). (C) After a second reaction ( $5.3 \times 10^{-7} \mu\text{M}$ ). (D) After annealing (3.7 mM diazonium salts). (E) After another reaction (3.7 mM). (F) After further reactions (3.7 mM). The bias was 100 mV.

after successive reactions when all the semiconducting nanotubes were reacted. These data clearly demonstrate that the selectivity of the reaction between the diazonium reagent and carbon nanotubes can only be achieved by controlling the concentration of the diazonium reagent being used. It is also possible, however, that the observed selectivity might be because the metallic nanotubes are more sensitive to the small number of defects introduced by the reaction than semiconducting ones. Further experiments on individual nanotube devices may give a clear answer.

In summary, we demonstrated in this communication a simple method for in situ fabrication of high-performance semiconducting-only SWNT network FETs by selectively eliminating metallic nanotubes in the devices. We have found that the concentration of the diazonium reagent is a critical factor to achieve selective reaction of metallic nanotubes. Unlike the previous reported methods, no gating or preconditioning is needed in this approach, which makes it applicable for a full wafer scale treatment of nanotube networks. This method will certainly give us more control over the process to produce nanotube-based electronic devices, making nanotubes a more promising building block for future nanoscale electronics.

**Acknowledgment.** The project was supported by NSF Grant CCR-0326157 and the Duke University Common Fund. J.L. also acknowledges DuPont for a 2002 Young Professor Award.

## References

- (1) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998.
- (2) Krupke, R.; Henrich, F.; Lohneisen, H.; Kappes, M. M. *Science* **2003**, *301*, 344.
- (3) Collins, P. G.; Arnold, M. S.; Avouris, P. *Science* **2001**, *292*, 706.
- (4) Chattopadhyay, D.; Galeska, I.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2003**, *125*, 3370.
- (5) Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. *Science* **2003**, *301*, 1519.
- (6) Kamaras, K.; Itkis, M. E.; Hu, H.; Zhao, B.; Haddon, R. C. *Science* **2003**, *301*, 1501.
- (7) Banerjee, S.; Wong, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 2073.
- (8) Chen, Z.; Du, X.; Rancken, C. D.; Cheng, H.; Rinzler, A. G. *Nano Lett.* **2003**, *3*, 1245.
- (9) Balasubramanian, K.; Sordan, R.; Burghard, M.; Kern, K. *Nano Lett.* **2004**, *4*, 827.
- (10) Zheng, B.; Lu, C.; Gu, G.; Makarovski, A.; Finkelstein, G.; Liu, J. *Nano Lett.* **2002**, *2*, 895.
- (11) An, L.; Owens, J. M.; McNeil, L. E.; Liu, J. *J. Am. Chem. Soc.* **2002**, *124*, 13688.
- (12) Huang, S. M.; Maynor, B.; Cai, X. Y.; Liu, J. *Adv. Mater.* **2003**, *15*, 1651.
- (13) Huang, S. M.; Cai, X. Y.; Liu, J. *J. Am. Chem. Soc.* **2003**, *125*, 5636.
- (14) Dyke, C. A.; Tour, J. M. *Nano Lett.* **2003**, *3*, 1215.

JA046482M