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Selective Suppression of Conductance in Metallic Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) are being intensively studied for various applications owing to their unique physical and chemical properties.[1] In particular, semiconducting SWNTs have huge potential as future nanoelectronic device elements because of their excellent hole mobility (can exceed ~100 000 cm^2/Vs)[2] and high current modulation on/off ratios. However, SWNTs with a uniform electronic structure (i.e., uniform chirality) have yet to be fabricated, which represents a barrier to the realization of SWNT-based electronic devices. Various approaches have been used in efforts to separate metallic nanotubes from semiconducting ones, including dielectrophoresis,[3] DNA wrapping,[4] electrical breakdown of metallic nanotubes,[5] and chemical functionalization using various compounds.[6−8] Recently, it was found that diazonium compounds and nitronium ions showed better reactivity toward metallic SWNTs and that this chemical functionalization approach could easily be adapted to large-scale device-level electronic structure control.[9] It has been suggested that nitronium ions and diazonium compounds selectively attack metallic SWNTs owing to the finite electron density at the Fermi level. In light of these findings, it is worthwhile to explore whether other electrophilic (electron-accepting) molecules can play a similar role and how they differ in terms of their selective affinity toward metallic SWNTs.

In the present study, we investigated the electrical transport properties and AFM topography of SWNT field-effect transistors (SWNT-FETs) reacted with four electrophilic molecules, specifically 4-bromobenzene diazonium tetrafluoroborate (4-BBDT), nitronium tetrafluoroborate ($NO_2^+BF_4^-$), 2,4,6-triphenylpyrylium tetrafluoroborate (2,4,6-TPPT), and 1,3-benzodithiolylium tetrafluoroborate (1,3-BDYT).

The SWNT-FETs were prepared using the patterned catalyst growth technique and a typical microfabrication process. The detailed sample fabrication process can be found elsewhere.[10] The electrical characteristics ($I-V_{sd}$, $I-V_{bg}$) of the bare nanotube devices were recorded first, and then the samples were allowed to react with solutions of electrophilic molecules. For chemical functionalization, the devices were stirred in a ~3 mM solution of electrophilic molecules in tetramethyl sulfone (TMS)/chloroform ($CHCl_3$) for various times, ranging from 20 min to 24 h. The devices were then rinsed thoroughly with TMS/$CHCl_3$ solution, followed by rinsing with deionized water. The electrical characteristics of the functionalized SWNT-FETs were measured, along with AFM topographic images. After these measurements had been conducted, the samples were annealed at 300 °C in an Ar atmosphere for 10 min to confirm recovery of the original nonfunctionalized SWNT-FETs. After this process, AFM topographic images and electrical measurements were again recorded to measure any change that might have occurred during the process.

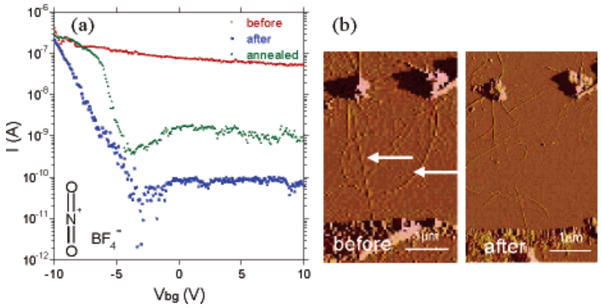

Figure 1. (a) Gate voltage dependence curve of the SWNT-FET before and after reaction with $NO_2^+BF_4^-$ for 20 min. The bias voltage was 100 mV. The inset shows the molecular structure of $NO_2^+BF_4^-$. (b) AFM images of the device before and after the reaction.

Figure 1a shows the electrical transfer characteristics of the SWNT-FET before and after the reaction with $NO_2^+BF_{4-}^-$ for 20 min. The pristine sample had a conductance that could only be partially modulated by the gate voltage. After the $NO_2^+BF_4^-$ treatment, by contrast, the device showed a large gate modulation with an on/off ratio in excess of 10^4 and complete depletion of conduction from the device. Moreover, the metallic conduction (current that cannot be modulated by the gate bias voltage) was not recovered even after annealing. The AFM images (Figure 1b) indicate that some of the nanotubes were broken during the $NO_2^+BF_4^-$ treatment. The heights of the destroyed nanotubes were 0.2 nm, compared to 1.8 nm before $NO_2^+BF_4^-$ treatment (see Supporting Information, Figure S1). The present findings are consistent with the strong adsorption of nitronium ions onto metallic nanotubes and further disintegration of the nanotube sidewalls, as was reported by An et al.[8] As a control, we performed the same experiment with TMS/$CHCl_3$ solution, and no dramatic changes in electrical characteristics or AFM images were observed in this case (Supporting Information, Figure S2).

Similar trends were observed for the SWNT-FETs treated with 2,4,6-TPPT or 1,3-BDYT. After the 2,4,6-TPPT treatment, metallic conductance disappeared and a significant decrease of the on state current was observed (Figure 2a). Unlike the case of $NO_2^+BF_4^-$ treatments, which destroyed some of the metallic nanotubes completely, no changes were apparent in the AFM image following 2,4,6-TPPT treatment or after annealing (Supporting Information, Figure S3). Nevertheless, metallic conductance did not return, even after annealing. 1,3-BDYT treatment also irreversibly modified the SWNT-FET (Figure 2b). To investigate the effects of 2,4,6-TPPT and 1,3-BDYT on the SWNTs, we performed a Raman spectrum analysis on the functionalized devices using Nanofinder 30 (Figure S4). In the case of 1,3-BDYT, a highly enhanced D-band is observed. The D-band, which is characteristic of amorphous carbon or defects, increased following treatment with molecules that can covalently bind with SWNTs. The observation of such an enhanced

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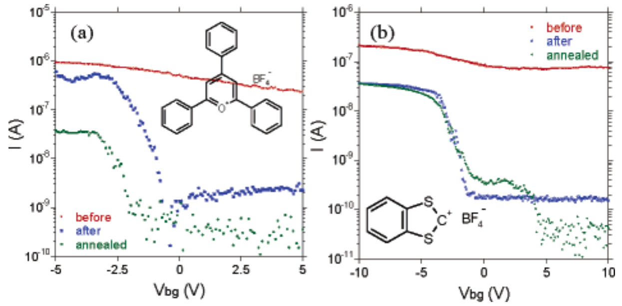

Figure 2. Gate voltage dependence curve of the (a) 2,4,6-TPPT functionalized SWNT-FET and (b) 1,3-BDYT functionalized SWNT-FET. The insets show the molecular structure of these molecules.

disorder for the 1,3-BDYT functionalized device can be attributed to the fact that 1,3-BDYT is the strongest electrophile among the four molecules studied. In contrast, almost no changes of disorder peak appeared following the treatment with 2,4,6-TPPT. We confirmed this by taking Raman spectra from nanotube films before and after the reaction as well (Figure S5). Unlike other molecules that form covalent sp^3 bonds with SWNTs, 2,4,6-TPPT is expected to engage in strong noncovalent π-stacking interactions. Recently, Lu et al.[11] and O'Connel et al.[12] showed that aromatic molecules with strong charge-transfer character can have chiral selectivity, especially when they make effective contact with SWNTs.[11]

We also measured the electrical transport characteristics and AFM images of the 4-BBDT-treated SWNT-FET (Supporting Information, Figure S6). Unlike the devices treated with 2,4,6-TPPT or 1,3-BDYT, the conductance of the 4-BBDT-treated device returned to its original value after thermal annealing, consistent with previous findings.[6,9] The difference in behavior between 4-BBDT and other electrophiles we studied might be due to our molecules having a higher binding energy compared with 4-BBDT, but a more systematic examination of the interaction between electrophilic molecules and SWNTs would be required to confirm this hypothesis.

In the case of SWNT-FETs exhibiting single semiconducting nanotube behavior (depletable samples, D), all four of the electrophilic molecules considered here had a similar effect. Specially, only minor changes were observed in the electrical transport characteristics or AFM images following reaction with these molecules (see Figure S7). However, a noticeable shift of gate threshold voltage was observed in some cases, which might be due to the binding of electrophiles at the defect site of nanotubes. This result provides further confirmation that these molecules interact selectively with metallic SWNTs rather than semiconducting SWNTs. The statistics of the functionalized devices are summarized in Table 1. About 30% of the devices that contain both metallic and semiconducting SWNTs (nondepletable sample, ND) show highly improved performance following reaction with electrophilic molecules, while depletable devices (D) retain their characteristics in most cases. An apparent structural change was confirmed by AFM analysis and observed only with $NO_2^+BF_4^-$. Among the four electrophiles we studied, only 4-BBDT recovers metallic conduction after thermal annealing.

Table 1. Summary of Devices Functionalized with Four Electrophilic Molecules

		$NO_2^+BF_4^-$	2,4,6-TPPT	4-BBDT	1,3-BDYT
percentage[13]	(ND → D)	8/27 (29.6%)	6/17 (35.2%)	3/9 (33.3%)	4/13 (30.7%)
	(D → D)	14/14 (100%)	3/3 (100%)	3/3 (100%)	9/9 (100%)
structural deformation		broken	none	none	none
recovery		no	no	yes	no

In summary, we have demonstrated that electrophilic molecules such as 2,4,6-TPPT and 1,3-BDYT preferentially react with metallic SWNTs through noncovalent and covalent binding, respectively. Although the highest yield at the moment is about ~35%, we believe that the performance can be greatly improved by narrowing down the diameter distribution of nanotubes to 1~2 nm, where strain-related nonspecific reactivity can be lifted.[8]

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Supporting Information Available: Complete ref 7; AFM image and height scan of the $NO_2^+BF_4^-$-treated SWNT-FET; control experiment for solvent effect; AFM images of the 2,4,6-TPPT- and 1,3-BDYT-treated SWNT-FETs; Raman spectra of the 2,4,6-TPPT- and 1,3-BDYT-treated SWNT-FETs and SWNT-films; electrical measurements and AFM images of the 4-BBDT-treated SWNT-FET; electrical responses of semiconducting SWNT-FETs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) It shows percentage of devices turned into depletable devices from nondepletable ones (ND → D) and percentage of depletable devices that showed minor changes upon reaction (D → D).

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