Tuning Chirality of Single-Wall Carbon Nanotubes by Selective Etching with Carbon Dioxide

Kwayong Seo,† Changwook Kim,†§ Yong Soo Choi,‡ Kyung Ah Park,‡ Young Hee Lee,*‡ and Bongsoo Kim*†

Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea, and Center for Nanotubes and Nanostructured Composites, Institute of Basic Science, Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea

Received March 20, 2003; E-mail: bongsoo@kaist.ac.kr; leeyoung@sskku.ac.kr

Application of carbon nanotubes (CNTs) to various electronic devices such as field emission displays, gas sensors, and nanotransistors have been hampered by the difficulties in control of the electronic properties that are determined by the chirality1 and diameter of carbon nanotubes. One way to overcome these difficulties is to modify the electronic properties of CNTs by posttreatment after synthesis. Functionalization of a single-wall carbon nanotube (SWNT) wall by atomic hydrogen6 transforms metallic tubes to semiconducting ones,3 and fluorination of the SWNT walls can also alter the electronic structures significantly.4 These approaches, however, often degrade the atomic structures of SWNTs.3 A selective etching process may become another alternative to select nanotubes that have appropriate electronic properties. While oxidative etching of CNT edge can be utilized for purification of CNTs from other carbonaceous particles,6 selection of CNTs with appropriate electronic properties by this method is difficult because of similar etching rates for nanotubes with different chiralities.

In this communication we propose that selective etching with CO2 may provide a route to SWNTs of specific chirality. Theoretical calculations were done on the supercells of (5,5) and (10,0) nanotubes, using a self-consistent charge-density-functional-based tight-binding (SCC-DFTB) method7 and local atomic orbital basis DF calculations within local-density-approximation (LDA) and generalized gradient approximation (GGA), as implemented in DMol3 code.8 Ten and eight carbon layers along the tube axis (z-direction) were used for armchair and zigzag tubes, respectively. Open-ended edges were chosen to see the adsorption effect, and the bottom dangling bonds were saturated by hydrogen atoms to minimize the edge effect.9 We define the adsorption energy of molecules as $E_{\text{ad}} = E_{\text{tot}}(\text{gas + CNT}) - E_{\text{tot}}(\text{gas}) - E_{\text{tot}}(\text{CNT})$, where $E_{\text{tot}}$ is the total energy of a given system. Atoms were fully relaxed by the conjugate gradient method in the SCC-DFTB calculations except for the bottom two carbon layers and a hydrogen layer. More accurate calculations were done with the LDA and GGA when necessary.

We investigated adsorption of CO2 molecules at various sites in armchair and zigzag tube edges. Only one weakly bound state of CO2 molecule was found at the seat site of an armchair edge despite the presence of triple bonds,10 as shown in Figure 1a. The π states at the armchair edge do not interact with the molecular states of CO2, resulting in physisorption with an adsorption energy of $-0.02 (-0.33$; $-0.01)$ eV from SCC-DFTB (LDA-GGA) calculations. The adsorption of CO2 at a zigzag tube edge is much stronger than at an armchair edge with an adsorption energy of $-3.51 (-5.82$; $4.82)$ eV, as shown in Figure 1b. Two carbon atoms at the zigzag edge are stabilized by saturating the dangling bonds. The carbon atom of the adsorbent CO2 becomes less positive in Mulliken excess charge (+0.58) than that of an ambient CO2 (+0.74) molecule. This carbon atom forms a strong bond with the carbon atom at the tube edge. The adsorbed CO2 molecule forms a pentagon at the seat site, minimizing its distortion energy. Note that one of the CO bond length is 1.52 Å, which is longer than the other one (1.19 Å) and therefore expected to be a route for CO desorption which will be discussed later. We also find another stable configuration at a zigzag tube edge, where the carbon atom in CO2 adsorbent is located upward, as shown in Figure 1c. Two dangling bonds were saturated by two oxygen atoms symmetrically by forming a hexagon. The small Mulliken excess charge (+0.05) of the carbon atom at the adsorbent CO2 indicates that the exposed carbon atom at the top possesses unpaired electrons, that is it holds almost four electrons.

Figure 1. Adsorption of a CO2 molecule on (a) armchair edge and (b,c) zigzag edge. The dark and gray balls indicate the oxygen and carbon atoms, respectively. All bond lengths are in units of Å. The Mulliken excess charges of the oxygen and carbon atoms are shown in parentheses in units of electron. The adsorption energies are shown in the figure from SCC-DFTB (LDA-GGA).

1 Korea Advanced Institute of Science and Technology.
2 Sungkyunkwan University.
3 Also with Technology division, Samsung SDF Company, Limited, Suwon, 442-390, Korea.

10.1021/ja035262q CCC: $25.00 © 2003 American Chemical Society
atom in the CO$_2$ adsorbent$^{11}$ and the weak CO bond is placed parallel to the tube edge plane (x-direction) with a bond length of 1.52 Å, we first took a desorption pathway along the x-direction. We moved the carbon atom in CO$_2$ adsorbent to the wall carbon nanotubes. CO$_2$ molecule physisorbs on an armchair tube edge, whereas it chemisorbs strongly on a zigzag tube edge, resulting in no etching process. NO molecule chemisorbs on both tube edges with relatively large adsorption energies, and no physisorption is observed.

The oxygen atom which is left after CO desorption is strongly bound to the carbon atom at the tube edge. This configuration is similar to that of zigzag tubes,$^{12}$ we expect that adsorption and desorption behaviors of these chiral tubes would not be much different from those of zigzag tubes. Similar oxidizing reaction by CO$_2$ is observed in the reverse Boudouard reaction, C(s) + CO$_2$ (g) $\rightarrow$ 2CO(g).$^{13}$ The heat-treatment temperature is estimated to be 937 K for this etching process from the Readhead equation.$^{14}$ The distinctive selectivity observed in the adsorption of CO$_2$ on SWNTs is rarely seen in adsorptions of other molecules containing oxygen atoms such as O$_2$,$^{15}$ CO, NO, NO$_2$.$^{16,17}$

In summary, the result from density functional calculations provides a clue to the control of the electronic properties of single-wall carbon nanotubes. CO$_2$ molecule physisorbs on an armchair tube edge, whereas it chemisorbs strongly on a zigzag tube edge with large adsorption energy of $\sim$4.82 eV (GGA). We propose that annealing with ambient CO$_2$ gas can lead to selective etching with initial CO desorption, followed by subsequent CO desorption from the tube edge. Using this process we can obtain only armchair tubes.

Acknowledgment. We thank MOST for National R&D Project for Nanoscience & Tech. and Program for NT-IT Fusion Strategy of Adv. Tech. and NRL, KOSEF through CNNC and BK21.

Supporting Information Available: Figure S1: Local charge densities of (a) HOMO and (b) LUMO. The (10,0) nanotube when CO$_2$ is adsorbed as in Figure 1b (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

8. (The forces on each atom to be converged during each relaxation are less than $10^{-3}$ au. DMol$^3$ is a registered software product of Molecular Simulations Inc. (a) Delley, B. J. Chem. Phys. 1990, 92, 508. (b) Delley, B. J. Phys. Chem. 1996, 100, 6107.
11. (To the forces on each atom to be converged during each relaxation are less than $10^{-3}$ au. DMol$^3$ is a registered software product of Molecular Simulations Inc. (a) Delley, B. J. Chem. Phys. 1990, 92, 508. (b) Delley, B. J. Phys. Chem. 1996, 100, 6107.
14. (The forces on each atom to be converged during each relaxation are less than $10^{-3}$ au. DMol$^3$ is a registered software product of Molecular Simulations Inc. (a) Delley, B. J. Chem. Phys. 1990, 92, 508. (b) Delley, B. J. Phys. Chem. 1996, 100, 6107.
18. (The forces on each atom to be converged during each relaxation are less than $10^{-3}$ au. DMol$^3$ is a registered software product of Molecular Simulations Inc. (a) Delley, B. J. Chem. Phys. 1990, 92, 508. (b) Delley, B. J. Phys. Chem. 1996, 100, 6107.