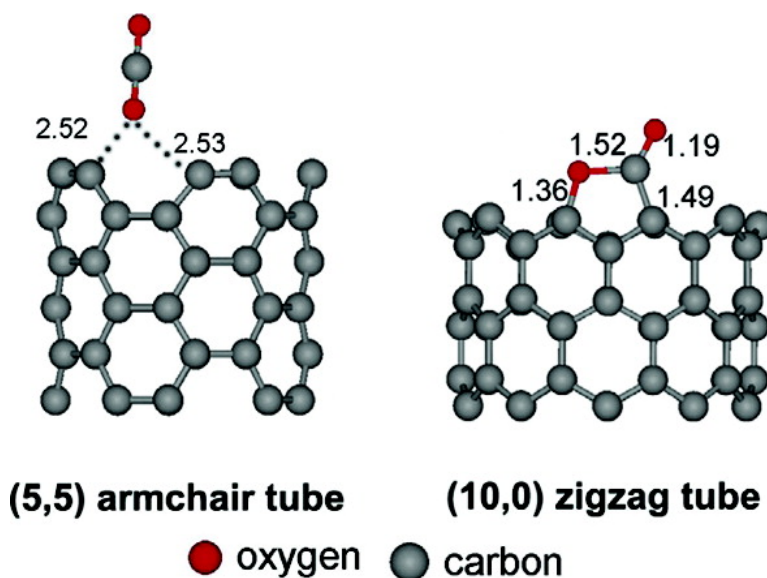


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Tuning Chirality of Single-Wall Carbon Nanotubes by Selective Etching with Carbon Dioxide

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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 hydrogen² 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.⁵ 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 $E_{ad} = E_{tot}(\text{gas} + \text{CNT}) - E_{tot}(\text{gas}) - E_{tot}(\text{CNT})$, where E_{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 that at an armchair edge with an adsorption energy of -3.51 (-5.82 – $-$

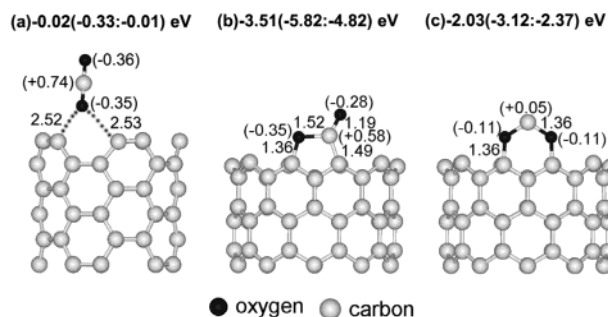


Figure 1. Adsorption of a CO₂ molecule on (a) armchair edge and (b,c) zigzag edge. The dark and gray balls indicate the oxygen and carbon atoms, respectively. All bond lengths are in units of Å. The Mulliken excess charges of the oxygen and carbon atoms are shown in parentheses in units of electron.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

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. The adsorption energy in this case becomes -2.03 (-3.12 – -2.37) eV, which is smaller than those in the previous case (Figure 1b). From these calculations, we clearly see that adsorption of CO₂ molecules on zigzag and armchair tube edges is highly selective.

The high selectivity in the adsorption of CO₂ molecule on tube edges of different structures can be used to control the electronic properties of SWNTs. When the SWNT powder containing both armchair and zigzag nanotubes is exposed to CO₂ gas, chemisorption occurs preferentially on zigzag tube edges. Heat treatment of SWNT powder under CO₂ ambient at an appropriate temperature could lead to selective etching of zigzag tubes. To understand the desorption process more clearly, we calculated a concerted desorption pathway, as shown in Figure 2. We started from the most stable configuration as shown in Figure 1b. Considering that the lowest unoccupied molecular orbital (LUMO) was located on the carbon

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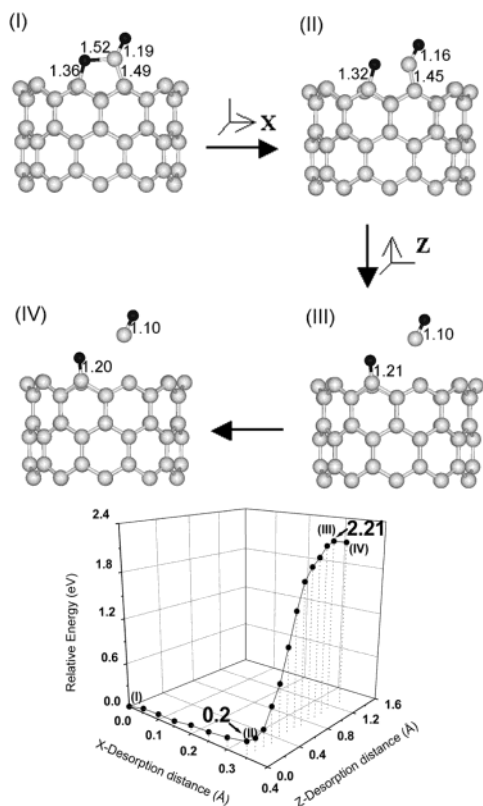


Figure 2. Desorption pathway of the C–O pair from (I) to (IV) and desorption energy barrier of CO from given pathway. All other notations are the same as Figure 1.

atom in the CO₂ adsorbent¹¹ 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 CO₂ adsorbent to the *x*-direction by 0.05 Å, followed by a full relaxation of all other atoms except the chosen carbon atom. Moving the carbon atom from step (I) to step (II) extends the CO bond length to 1.85 Å, which requires an energy of 0.2 eV. The next step is to move the CO pair upward along the tube axis (*z*-direction). After the CO pair was moved upward slightly, all the atoms except the chosen carbon atom are fully relaxed again. This procedure involves a complete dissociation of C–C bond, which requires a large energy of 2.01 eV. The energy is little bit lowered in step (IV) by a small modification of the tube edge structure. The complete desorption pathway, then, has an activation barrier of 2.21 eV. When the CO pair in the adsorbent was moved along *xz*-direction, an activation barrier of similar size was obtained.

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 O₂ adsorption on a zigzag tube edge.⁶ The activation barrier for the desorption of this second CO pair from the tube edge would be similar to the value in case of O₂ adsorption, 2.44 eV,⁶ which is not much larger than that of the first CO desorption in CO₂ adsorbent. Thus, the desorption rate for this first and second CO pairs would be similar and repetition of this desorption procedure eventually leads to selective etching of zigzag tube edges. Since the edge shape of tubes with chiral angles ranging 3–12° 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 CO₂ is observed in the reverse Boudouard reaction, C(s) + CO₂(g) → 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 CO₂ on SWNTs is rarely seen in adsorptions of other molecules containing oxygen atoms such as O₂,¹⁵ CO, NO, NO₂.^{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. CO₂ molecule physisorbs on an armchair tube edge, whereas it chemisorbs strongly on a zigzag tube edge with large adsorption energy of –4.82 eV (GGA). We propose that annealing with ambient CO₂ 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.

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Supporting Information Available: Figure S1: Local charge densities of (a) HOMO and (b) LUMO. The (10,0) nanotube when CO₂ is adsorbed as in Figure 1b (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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