Band-gap sensitive adsorption of fluorine molecules on sidewalls of carbon nanotubes: an ab initio study

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Abstract
We report from ab initio calculations that the band-gap sensitive side-wall functionalization of a carbon nanotube is feasible with the fluorine molecule (F₂), which can provide a route to the extraction of semiconducting nanotubes by etching away metallic ones. In the small diameter cases like (11, 0) and (12, 0), the nanotubes are easily functionalized with F₂ regardless of their electronic properties. As the diameter becomes larger, however, the fluorination is favoured on metallic CNTs with smaller activation barriers than those of semiconducting ones. Our results suggest that low-temperature exposure to F₂ molecules in the gas phase can make a dominant portion of fluorinated metallic nanotubes and unfluorinated semiconducting ones. This is consistent with recent experimental reports.

1. Introduction
The carbon nanotube (CNT), a tubular form of graphite, is one of the promising candidate materials for future nanoscale electronic devices such as chemical sensors and field emitters. In most applications proposed to date, the selective use of either metallic or semiconducting CNTs has been highly desirable and this is posing a main hurdle for further progress towards technological application of CNTs. Therefore it is important to find a way to obtain CNTs with a specific electronic property. Recently, several experimental trials, mostly post-processing techniques, have reported various degrees of separation of metallic and semiconducting CNTs from their mixtures: dielectrophoresis, the selective interaction of DNA, porphyrin, and bromine with CNTs, to name a few [1–4]. However, a method achieving both high yields and high separation degrees is yet to be developed.

The main difference between metallic and semiconducting CNTs lies in their electronic density of states at the Fermi level. The chemical interactions involving large charge transfer should be sensitive to the energy gap of the CNT and therefore can be used for discriminating between semiconducting and metallic CNTs [5]. In this sense, the halogen elements, strong electron attractors, are elements worth a detailed investigation. In a previous calculation, we showed that the binding energies of Br atoms or molecules depend on the radius of the CNT as well as the density of states at the Fermi level, and the experimental observation of selective sedimentation was attributed to an extrinsic effect [6]. On the other hand, it is expected that fluorine atoms or molecules will be more sensitive to the energy gap of CNTs. Recently, a selective etching of metallic nanotubes was achieved with a gas phase
the tube–tube separation is larger than 7 ˚A. We define the adsorption energy of the F2 molecule as 

\[ E_{ad} = E_{tot}(F_2 + CNT) - E_{tot}(F_2) - E_{tot}(CNT) \]

Thus the ionic interaction dominates the adsorption energy in \( R_1 \) and \( A_1 \). In \( R_2 \) and \( A_2 \), the F2 molecule is dissociated as the covalent bonds are formed between one or both F atoms and nearby C atoms. Regarding \( A_2 \), we investigate various nearest-neighbour pairs of C atoms bonded to F atoms and find that A2 is most stable among them. It is interesting that \( E_{ad} \) of R2 is comparable to A1 and R1 although the covalent C–F(1) bond (see figure 1) is formed. This is because the F(2) atom becomes unstable with the F–F bond broken. The final product, A2, is very stable with \( E_{ad} \) less than −2 eV, indicating that F atoms are hardly detached, once A2 is formed (figure 1(d)).

3. Results and discussions

We investigate various types of F2 adsorption on the sidewall of the zigzag nanotube and find that four distinct geometries are locally stable in the configuration space, as shown in figure 1. In \( R_1 \) and \( R_2 \), the F2 molecule is pointing to the radial (R) direction of the CNT while \( A_1 \) and \( A_2 \) represent a situation where F–F direction lies in parallel with the axial (A) direction of the CNT.

The computational data on binding geometries and adsorption energies are compiled in table 1. In \( R_1 \) and \( A_1 \), the molecular form of the F2 molecule is more or less maintained with the bond length increased by ~0.3 ˚A compared with that of the isolated molecule (1.43 ˚A). This should be caused by the electronic charge transfer from the CNT to the F2 molecule. We estimate the charge transfer by integrating excess electrons \( \Delta \rho = \rho(F_2 + CNT) - \rho(F_2) - \rho(CNT) \) in the region around the F2. In spite of a large distance (~3 ˚A), the transferred charge is as much as 0.4–0.6e, due to the large electron affinity of the F2 molecule (see figure 2). In fact, when the isolated F2 molecule is charged with these amounts of fractional charges, we find that the F–F distance becomes longer, similar to those found in table 1. Thus the ionic interaction dominates the adsorption energy in \( R_1 \) and \( A_1 \). In \( R_2 \) and \( A_2 \), the F2 molecule is dissociated as the covalent bonds are formed between one or both F atoms and nearby C atoms. Regarding \( A_2 \), we investigate various nearest-neighbour pairs of C atoms bonded to F atoms and find that A2 is most stable among them. It is interesting that \( E_{ad} \) of R2 is comparable to A1 and R1 although the covalent C–F(1) bond (see figure 1) is formed. This is because the F(2) atom becomes unstable with the F–F bond broken. The final product, A2, is very stable with \( E_{ad} \) less than −2 eV, indicating that F atoms are hardly detached, once A2 is formed (figure 1(d)).

Table 1 reveals the interplay between the curvature effect stabilizing the binding to smaller-radius nanotubes (\( R_2 \) and \( A_2 \)) and the band-gap effect favouring the metallic nanotubes (\( R_1 \) and \( A_1 \)). In short, the ionic-binding states (\( R_1 \) or \( A_1 \)) show the band-gap sensitive binding while the chemisorption states (\( A_2 \) or \( R_2 \)) are largely influenced by the curvature effect that depends only on the diameter. Therefore, it is important to utilize the ionic-binding states before the final chemisorption state for the selective adsorption of F2 molecules.

The actual reaction rate from the precursor states (\( R_1 \), \( R_2 \), and \( A_1 \)) to the chemisorption state (\( A_2 \)) depends on the minimum energy barrier along the reaction pathway. We calculate the activation barriers (\( E_a \)) along the minimum energy path (MEP) between locally stable configurations by using the nudged elastic band method [11] implemented within the code. \( R_1 \) and \( A_1 \) are regarded as reactants and five replicas...
For the metallic (18, 0) CNT with a similar diameter a lower reaction rate for the A fluorinated regardless of the band gap and the larger-radius CNTs is expected. We would like to mention that the fluorination hinges on the energy barrier along the reaction path, rather than binding energies of the final states. SWNTs functionalization for larger-radius CNTs. The selective fluorination of metallic CNTs is fluorinated 2 gases are supplied at 100 K, for instance, the (18, 0) CNT will be fluorinated 2 reactant, which requires a relatively large $E_a (0.08 \text{ eV})$. For the small radius CNTs such as (11, 0) and (12, 0), barriers are negligible because the curvature effect stabilize $R_2$. This means that the small-radius carbon nanotubes are easily fluorinated regardless of whether they are metallic or semiconducting. As the diameter becomes larger, however, different magnitudes of the activation barriers appear between metallic and semiconducting CNTs. In the case of the (17, 0) CNT, the $R_2$ precursor state is unstable because the charge transfer to stabilize the $F(2)$ atom (see figure 2(a)) does not readily happen due to the absence of electronic states at the Fermi level. Therefore the MEP is directly from $R_1$ precursor to $A_2$ reactant, which requires a relatively large $E_a$ of 0.18 eV. For the metallic (18, 0) CNT with a similar diameter a lower $E_a (0.08 \text{ eV})$ occurs starting from the $R_2$ configuration.

The above results on reaction barriers indicate that all small-radius SWNTs (diameter <1 nm) will be easily fluorinated regardless of the band gap and the larger-radius SWNTs can be selectively fluorinated. The ratio of the reaction rate for the $A_2$ state between (17, 0) and (18, 0) CNTs is $\exp(-\Delta E_a/kT)$, where $\Delta E_a$ is the difference in energy barriers between (17, 0) and (18, 0) CNTs. If $F_2$ gases are supplied at 100 K, for instance, the (18, 0) CNT will be fluorinated $2.2 \times 10^{14}$ times faster than the (17, 0) CNT. For lower temperatures, we expect an enhanced rate difference. We would like to mention that the fluorination is a strongly exothermic process, and delicate control of the temperature and $F_2$ dose will be important for the experimental realization of the observed selective fluorination. Once metallic CNTs are fluorinated, one could separate semiconducting CNTs by etching metallic components away at elevated temperatures [12]. Or, one can exploit the solubility difference between fluorinated and pristine CNTs in various alcohol solvents [13]. Our results are in good comparison with a recent experiment where metallic CNTs were found to be more vulnerable to fluorine gas [7]. In this work, it was found that CNTs with radii between 0.9 and 1.1 nm were preferentially etched, while our work predicts selectivity can be achieved for CNTs with radii larger than ~1.3 nm. We note that the experiment was carried out at room temperature, and lowering the reaction temperature may give rise to selective functionalization for larger-radius CNTs.

### 4. Conclusion

In summary, our ab initio study demonstrates the feasibility of selectively fluorinating metallic SWNTs. The selective fluorination hinges on the energy barrier along the reaction path, rather than binding energies of the final states. SWNTs with diameters <1 nm are easily functionalized with the $F_2$ molecule regardless of their energy gaps. As the diameter becomes larger, fluorination is favoured for metallic SWNTs because of (i) larger ionic binding energies and (ii) smaller activation barriers to chemisorption of the $F_2$ molecule in metallic SWNTs.

### Acknowledgment

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### References


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**Table 1.** Detailed information of various adsorption configurations of fluorine molecule. The minus sign in the adsorption energy means that the binding is stable. C–F distance means the shortest one between the nanotube and F atom. The equilibrium distance of the $F_2$ molecule is 1.43 Å.

<table>
<thead>
<tr>
<th>Diameter (Å)</th>
<th>(11, 0)</th>
<th>(12, 0)</th>
<th>(13, 0)</th>
<th>(17, 0)</th>
<th>(18, 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{app}$ (eV)</td>
<td>8.77</td>
<td>9.48</td>
<td>10.14</td>
<td>13.34</td>
<td>14.20</td>
</tr>
<tr>
<td>$R_1$ $E_{ad}$ (eV)</td>
<td>0.93</td>
<td>0.06</td>
<td>0.61</td>
<td>0.59</td>
<td>0.04</td>
</tr>
<tr>
<td>C–F/F–F (Å) Unstable ($→ R_2$)</td>
<td>−0.61</td>
<td>−0.39</td>
<td>−0.48</td>
<td>−0.57</td>
<td></td>
</tr>
<tr>
<td>$R_2$ $E_{ad}$ (eV)</td>
<td>−0.58</td>
<td>−0.76</td>
<td>−0.49</td>
<td>Unstable ($→ R_2$)</td>
<td>−0.57</td>
</tr>
<tr>
<td>C–F/F–F (Å) 1.49/2.45</td>
<td>1.49/2.56</td>
<td>1.52/2.28</td>
<td></td>
<td>1.51/2.45</td>
<td></td>
</tr>
<tr>
<td>$A_1$ $E_{ad}$ (eV)</td>
<td>−0.40</td>
<td>−0.59</td>
<td>−0.39</td>
<td>−0.42</td>
<td>−0.53</td>
</tr>
<tr>
<td>C–F/F–F (Å) 3.14/1.65</td>
<td>2.97/1.72</td>
<td>3.14/1.64</td>
<td>3.09/1.66</td>
<td>2.92/1.71</td>
<td></td>
</tr>
<tr>
<td>$A_2$ $E_{ad}$ (eV)</td>
<td>−2.90</td>
<td>−2.88</td>
<td>−2.52</td>
<td>−2.34</td>
<td>−2.35</td>
</tr>
<tr>
<td>C–F/F–F (Å) 1.44/2.40</td>
<td>1.44/2.40</td>
<td>1.45/2.40</td>
<td>1.45/2.38</td>
<td>1.46/2.38</td>
<td></td>
</tr>
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</table>

**Table 2.** Minimum energy path and the activation energy barriers ($E_a$) from the reactant ($R_1$) to the product ($A_2$) are shown for various radii of nanotubes.

<table>
<thead>
<tr>
<th>Minimum energy path</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(11, 0) $R_1 \rightarrow R_2 \rightarrow A_2$</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>(12, 0) $R_1 \rightarrow R_2 \rightarrow A_2$</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>(13, 0) $R_1 \rightarrow R_2 \rightarrow A_2$</td>
<td>0.09</td>
</tr>
<tr>
<td>(17, 0) $R_1 \rightarrow A_2$</td>
<td>0.18</td>
</tr>
<tr>
<td>(18, 0) $R_1 \rightarrow R_2 \rightarrow A_2$</td>
<td>0.08</td>
</tr>
</tbody>
</table>
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