

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 (F_2), 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 F_2 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 F_2 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

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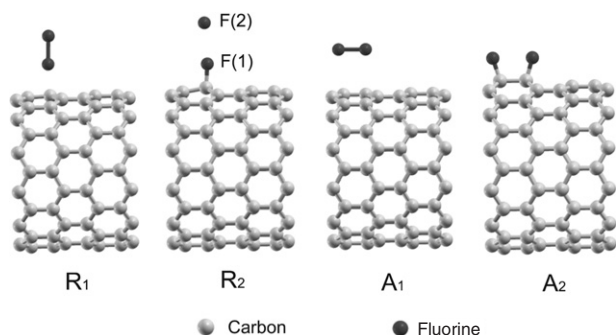


Figure 1. Various adsorption configurations of a F_2 molecule on a $(12, 0)$ CNT. The grey and black spheres indicate the carbon and the fluorine atoms, respectively. R_1 : The F–F bond is aligned in the radial direction of the nanotube. R_2 : The F–F bond is broken to form the F–C bond. A_1 : The F–F bond is aligned along the axial direction of the nanotube. A_2 : The final product where two covalent F–C bonds are formed.

reaction using fluorine molecules, (F_2) [7]. However, the microscopic mechanism has not yet been revealed.

In this work, we find from density functional calculations that the band-gap sensitive side-wall functionalization of a single-walled carbon nanotube (SWNT) is feasible with the fluorine molecule, which can provide a route to the extraction of semiconducting SWNTs by etching away metallic ones.

2. Computational methods

The computations are carried out using the generalized gradient approximation (GGA) [8] within the pseudopotential framework. We employ the plane-wave basis method [9] in conjunction with the ultrasoft pseudopotential [10] to reduce the energy cutoff of the basis to 35 Ryd. The atomic positions are relaxed until atomic forces are less than $0.01 \text{ eV } \text{Å}^{-1}$.

To reduce the effect of supercell length on the computational results, we choose zigzag-type $(n, 0)$ nanotubes for studying the interaction between nanotubes and F_2 molecules. Nanotubes with various diameters ($n = 11, 12, 13, 17,$ and 18) are investigated to discriminate the size (diameter) effect and the band-gap effect. Two unit cells of the pristine zigzag nanotube are taken along the tube axis (8.52 Å) and the tube–tube separation is larger than 7 Å . We define the adsorption energy of the F_2 molecule as $E_{\text{ad}} = E_{\text{tot}}(F_2 + \text{CNT}) - E_{\text{tot}}(F_2) - E_{\text{tot}}(\text{CNT})$, where E_{tot} indicates the total energy of the given system.

3. Results and discussions

We investigate various types of F_2 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 F_2 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 F_2 molecule is more or less maintained

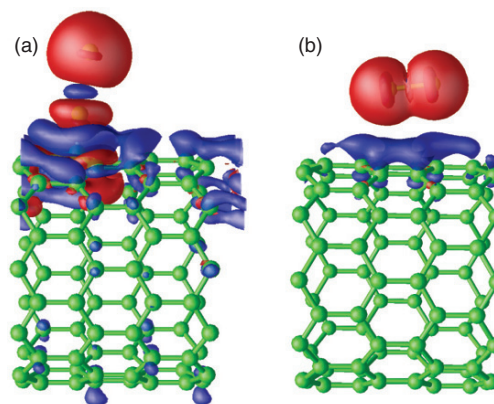


Figure 2. Isosurface plot of the electron transfer between the $(11, 0)$ CNT and the F_2 molecule. (a) and (b) correspond to R_2 and A_1 configurations, respectively. Light-grey (red) and dark-grey (blue) surfaces indicate regions where electrons are in excess or deficient, respectively.

(This figure is in colour only in the electronic version)

with the bond length increased by $\sim 0.3 \text{ Å}$ compared with that of the isolated molecule (1.43 Å). This should be caused by the electronic charge transfer from the CNT to the F_2 molecule. We estimate the charge transfer by integrating excess electrons $\Delta\rho = \rho(F_2 + \text{CNT}) - \rho(F_2) - \rho(\text{CNT})$ in the region around the F_2 . In spite of a large distance ($\sim 3 \text{ Å}$), the transferred charge is as much as $0.4\text{--}0.6e$, due to the large electron affinity of the F_2 molecule (see figure 2). In fact, when the isolated F_2 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 F_2 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 A_2 is most stable among them. It is interesting that E_{ad} of R_2 is comparable to A_1 and R_1 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, A_2 , is very stable with E_{ad} less than -2 eV , indicating that F atoms are hardly detached, once A_2 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 F_2 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

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 F₂ molecule is 1.43 Å.

	(11, 0)	(12, 0)	(13, 0)	(17, 0)	(18, 0)
Diameter (Å)	8.77	9.48	10.14	13.34	14.20
E_{gap} (eV)	0.93	0.06	0.61	0.59	0.04
R_1 E_{ad} (eV)	Unstable ($\rightarrow R_2$)	-0.61	-0.39	-0.48	-0.57
C–F/F–F (Å)		2.00/1.78	2.04/1.72	2.17/1.69	2.22/1.71
R_2 E_{ad} (eV)	-0.58	-0.76	-0.49	Unstable ($\rightarrow R_1$)	-0.57
C–F/F–F (Å)	1.49/2.45	1.49/2.56	1.52/2.28		1.51/2.45
A_1 E_{ad} (eV)	-0.40	-0.59	-0.39	-0.42	-0.53
C–F/F–F (Å)	3.14/1.65	2.97/1.72	3.14/1.64	3.09/1.66	2.92/1.71
A_2 E_{ad} (eV)	-2.90	-2.88	-2.52	-2.34	-2.35
C–F/F–F (Å)	1.44/2.40	1.44/2.40	1.45/2.40	1.45/2.38	1.46/2.38

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.

	Minimum energy path	E_a (eV)
(11, 0)	$R_1 \rightarrow R_2 \rightarrow A_2$	<0.01
(12, 0)	$R_1 \rightarrow R_2 \rightarrow A_2$	<0.01
(13, 0)	$R_1 \rightarrow R_2 \rightarrow A_2$	0.09
(17, 0)	$R_1 \rightarrow A_2$	0.18
(18, 0)	$R_1 \rightarrow R_2 \rightarrow A_2$	0.08

are chosen to represent the paths from these states to A_2 , the final product. The MEPs thus found are summarized in table 2. The E_a from A_1 to A_2 is usually 0.2–0.4 eV and that from R_1 to R_2 is always less than 0.01 eV when applicable. Much lower values of E_a are found for $R_2 \rightarrow A_2$ than those for direct paths $R_1 \rightarrow A_2$. This is consistent with the weakened F–F bond as found in the above. 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 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 ΔE_a is the difference in energy barriers between (17, 0) and (18, 0) CNTs. If F₂ gases are supplied at 100 K, for instance, the (18, 0) CNT will be fluorinated 2.2×10^4 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 F₂ 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 F₂ 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 F₂ molecule in metallic SWNTs.

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