Theoretical Study of Chemisorption of Hydrogen and Fluorine Atoms on the Sidewalls Armchair Single-walled Carbon Nanotubes with Two Carbon Ad-dimer Defects

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Abstract. Single-walled carbon nanotubes with two carbon ad-dimer defect and the chemisorption of hydrogen and fluorine on the surface of these nanotubes were studied through density functional theory method. The results indicate that nanotubes with two carbon ad-dimers defect exhibit a higher reactivity than perfect ones. Moreover, side-wall reactions of H₂ and F₂ are thermodynamically feasible. The reaction energy for per F₂ chemisorption is more exothermic than for per H₂ chemisorption.

Introduction

Single-walled carbon nanotubes (SWCNTs) have been the focus of numerous theoretical and experimental investigations since their discovery in 1991 [1]. This activity is due to its unusual structural and electronic properties, which make it a promising candidate for use in hydrogen storage [2], chemical sensors [3], and nanobioelectronics [4], etc.

The experimentally available SWCNTs are not perfect. The defects are formed inevitably during the growth of SWCNTs. The most common types of stable point defects observed in SWCNTs include Stone-Wales (SW) defects, vacancies, dopants, and heptagons [5, 6]. The SW defects are formed by rotating a C-C bond by 90° about its center, leading to the formation of a 5-7-7-5 topological defect. Vacancies are created by the removal of a single carbon atom. Based on molecular dynamics, the introduction of the 7-5-5-7 topological defect by adsorption of a carbon dimer was proposed [7]. This carbon ad-dimer defect is quite stable, and the activation barrier of 7-5-5-7 defect is much smaller than that of 5-7-7-5 defect [8]. It is known that defects can change the physical and chemical properties of SWCNTs significantly. Therefore, investigations of properties of SWCNTs with defects are of great interest.

Several theoretical studies have been performed regarding the carbon ad-dimer in SWCNTs. Wang et al. investigated the structural and electronic properties of armchair (n, n) and zigzag (m, 0) SWCNTs with a carbon ad-dimer defect, indicating that the chemisorption of two hydrogen atoms on the surface of these nanotubes are thermodynamically more stable than the pristine nanotubes [9]. Ghafouri et al. studied the exohedrally functionalized a carbon ad-dimer defective SWCNTs through the [2+3] cycloaddition reactions of 1,3 dipoles [10]. Wang et al. used first-principle calculations to study the chemical modification on the stability and electronic properties of multiple carbon ad-dimer defects in SWCNT [11]. The 7-5-5-7 defective SWCNTs would be unstable, since each contains pentagon-pentagon fusion. The nanotube with 7-5-5-7 defect might be more favorable for subsequent chemical reactions. However, there is limited information on two carbon ad-dimer defective SWCNTs. SWCNTs are considered as promising hydrogen storage media. Chemisorption of hydrogen atoms on the exterior surface of defect-free SWCNTs has been extensively investigated [12, 13]. In the paper, the structural and electronic properties of armchair with two carbon ad-dimer defect and the chemisorption of hydrogen and fluorine on the surface of these nanotubes were studied through density functional theory method.
Calculation Methods

Finite-length models of perfect armchair (4, 4), (5, 5), (6, 6), (7, 7) and (8, 8) SWCNTs, including seven carbon layers, were constructed and terminated by hydrogen atoms as the initial structure models. The perfect carbon nanotube structures contain 56, 70, 84, 98, and 112 carbon atoms for seven layers (4, 4), (5, 5), (6, 6), (7, 7) and (8, 8) tubes, respectively. Two carbon ad-dimer defective tubes were created by the adsorption of two C₂ dimers on hexagonal rings. The pentagon-pentagon fusion vertexes (PPFVs) are believed to be the most active sites of the fullerene and carbon nanotube [14, 15]. Here, the hydrogen and fluorine atoms were attached to the PPFV for each of the above defective SWCNTs. The geometries of all the structures presented in the present work were fully optimized with hybrid density functional theory (DFT) at the B3LYP/6-31G* level [16, 17]. Frequency calculations were carried out for all the systems at the same level of theory, and real frequencies were obtained. All calculations were done using the Gaussian 03 program package. The reaction energies of per H₂/F₂ adsorbed were calculated according to the expression:

\[
E_r = \frac{1}{2} \left( E(\text{SWCNT-H}_2/\text{F}_2) - E(\text{SWCNT}) - 2E(\text{H}_2/\text{F}_2) \right)
\]

where \( E(\text{SWCNT-H}_2/\text{F}_2) \), \( E(\text{SWCNT}) \) and \( E(\text{H}_2/\text{F}_2) \) denote the total energy of hydrogenated or fluorinated nanotube, defective nanotube, and \( \text{H}_2/\text{F}_2 \), respectively.

Results and Discussions

Defect-free and two carbon ad-dimer defective armchair (n, n) (n=4-8) SWCNT nanotubes were first optimized. The optimized geometrical structures are shown in Figs 1 and 2, respectively. For the perfect SWCNTs, the obtained structural parameters are consistent with the literature, for example, C-C bond lengths in the middle of the tube are predicted to be 1.446-1.458 Å which can be compared to the previously reported values (1.458Å) [18]. For two carbon ad-dimer defective SWCNTs, the C-C bond lengths at the pentagon-pentagon fusion are found to be 1.491-1.398 Å, which are in agreement with those reported for a carbon ad-dimer defective SWCNTs [11]. The properties of the electronic structure of the perfect and defective SWCNTs calculated at the B3LYP/6-31G* level are shown in Table 1. The finite-length perfect armchair (n, n) SWCNTs have larger HOMO-LUMO gaps. The HOMO-LUMO gaps of the perfect armchair (4,4), (5,5), (6,6), (7,7), and (8,8) are 2.03, 2.21, 2.24, 2.45, and 2.52 eV, respectively. Two carbon ad-dimer defects reduce the HOMO-LUMO gaps of (n, n) SWCNTs. The HOMO-LUMO gap decreases to 0.73-1.77 eV, about 71-31% lower than that of the corresponding perfect SWCNT.

![Figure 1. Optimized structures of finite-length perfect armchair (n,n) SWCNT models.](image1)

![Figure 2. Optimized structures of two ad-adimer defective (colored yellow) armchair CNT models.](image2)

The pentagon-pentagon fusion vertexes (PPFVs) are believed to be the most active sites of the fullerene and carbon nanotube [15,31]. The PPFVs in SWCNT were considered for the adsorption of hydrogen and fluorine atoms. The optimized structures of hydrogenated or fluorinated two carbon
ad-dimer defective SWCNT models are shown in Figure 3. The properties of the electronic structure of hydrogenated and fluorinated SWCNTs calculated at the B3LYP/6-31G* level are shown in Table 2. The HOMO-LUMO gaps of hydrogenated (4,4), (5,5), (6,6), (7,7), and (8,8) are 2.88, 2.87, 2.85, 2.79, and 2.72 eV, respectively; fluorinated (4,4), (5,5), (6,6) (7,7), and (8,8) are 2.76, 2.80, 2.81, 2.77, and 2.67 eV, respectively. The HOMO-LUMO gaps of the H-, F-modified SWCNTs are larger than that of defective SWCNTs, implying that the chemical derivating on the active sites could enhance the stability of defective SWCNTs. Note that tube diameter has very slight effect on the HOMO-LUMO gap of hydrogenated or fluorinated defective SWCNTs.

Table 1. HOMO, LUMO, and HOMO-LUMO energy gap (ΔE) values obtained at the B3LYP/6-31G* level for perfect and two ad-dimer defective SWCNTs (All energies in eV).

| Structure | HOMO | LUMO | ΔE  | HOMO | LUMO | ΔE  |
|-----------|------|------|-----|------|------|-----|
| (4,4)     | -4.35| -2.32| 2.03| -4.12| -3.08| 1.04|
| (5,5)     | -4.51| -2.30| 2.21| -3.97| -3.12| 0.85|
| (6,6)     | -4.51| -2.27| 2.24| -3.90| -3.12| 0.78|
| (7,7)     | -4.70| -2.25| 2.45| -4.42| -2.65| 1.77|
| (8,8)     | -4.75| -2.24| 2.52| -3.83| -3.11| 0.73|

Figure 3. The schematic structures of the hydrogenated and fluorinated SWCNTs with two ad-dimer defects. The green balls represent the exohedral H and F atoms.

Table 2. HOMO, LUMO, and HOMO-LUMO energy gap (ΔE) values obtained at the B3LYP/6-31G* level for hydrogenated and fluorinated defective SWCNTs (All energies in eV).

| Structure | Hydrogenated tube | Fluorinated tube |
|-----------|-------------------|------------------|
|           | HOMO | LUMO | ΔE | HOMO | LUMO | ΔE |
| (4,4)     | -4.66| -1.78| 2.88| -5.09| -2.33| 2.76|
| (5,5)     | -4.73| -1.86| 2.87| -5.10| -2.29| 2.80|
| (6,6)     | -4.78| -1.94| 2.85| -5.10| -2.28| 2.81|
| (7,7)     | -4.82| -2.03| 2.79| -5.09| -2.32| 2.77|
| (8,8)     | -4.81| -2.09| 2.72| -5.03| -2.36| 2.67|

Table 3. Total energies (Etot, au) and reaction energies per H2, F2 (E_r, kcal/mol) computed at the B3LYP/6-31G* level of theory for two ad-dimer defective and hydrogenated and fluorinated SWCNTs.

| Structure | Defective tube | Hydrogenated tube | Fluorinated tube |
|-----------|----------------|-------------------|------------------|
|           | E_tot | E_tot | E_r/H2  | E_tot | E_tot | E_r/F2  |
| (4,4)     | -2295.79170| -2298.34917| -64.8| -2695.26566| -149.8|
| (5,5)     | -2831.82663| -2834.37691| -62.5| -3231.29518| -148.1|
| (6,6)     | -3367.85413| -3370.39876| -60.8| -3767.31828| -146.7|
| (7,7)     | -3903.91739| -3906.41649| -46.5| -4303.33672| -132.6|
| (8,8)     | -4439.89214| -4442.43014| -58.7| -4839.35081| -145.0|

The hydrogenation and fluorination reaction energies computed at the B3LYP/6-31G* level of theory for two carbon ad-dimers defective armchair CNTs are present in Table 3. It can be seen that the reaction energies per H2 and F2 additions are all negative value, indicating that the absorption reactions are exothermic. The hydrogenation/fluorination reaction energies (per H2/F2) are -64.8/-149.8, -62.5/-148.1, -60.8/-146.7, -46.5/-132.6, and -58.7/-145.0 kcal/mol for two carbon
ad-dimer defective (4,4), (5,5), (6,6), (7,7) and (8,8) SWCNTs, respectively. The energy of chemisorption decreases as the diameter of the armchair nanotube increase except (7,7) SWCNT. The reaction energy for per F$_2$ chemisorption is more exothermic than for per H$_2$ chemisorption. The energy differences between the fluorinated and hydrogenated SWCNTs are 85.0-86.3 kcal/mol.

Summary
In summary, armchair (4, 4), (5, 5), (6, 6), (7, 7) and (8, 8) SWCNTs with two carbon ad-dimer defect and the chemisorption of hydrogen and fluorine on the surface of these nanotubes were studied at the B3LYP/6-31G* level. The calculated energy gaps indicate that the LUMO-HOMO gaps of defective SWCNTs are smaller than those of perfect ones, and the LUMO-HOMO gaps of the H-, F-modified SWCNTs larger than those the corresponding defective ones. The chemisorptions of hydrogen and fluorine atoms on the defective SWCNTs are exothermic processes. The side-wall reactions of H$_2$ and F$_2$ are thermodynamically feasible.

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