The stability of multiple carbon ad-dimer defects in single-walled carbon nanotubes as a function of its distance from the nanotube end

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Abstract. Single-walled carbon nanotubes (SWCNTs) are considered as one of the most promising materials for a diverse range of applications. The multiple carbon ad-dimer defects in SWCNTs are particularly attractive structures. By using density functional theory calculations, the structural and electronic properties of a (4, 4) SWCNT with the positions of the defect states induced by multiple carbon ad-dimmers and the chemisorption of hydrogen and fluorine on the surface of these nanotubes were studied. The results indicate that nanotubes with multiple carbon ad-dimers defect exhibit a higher reactivity than perfect ones. The chemisorptions of hydrogen and fluorine atoms can enhance the stability of defective SWCNTs. The reaction energy of chemisorption of hydrogen and fluorine atoms is almost independent of the positions of the defect states.

1. Introduction
Single-walled carbon nanotubes (SWCNTs), known as a perfect graphene sheet wrapped up into a cylinder, have unique structural, mechanical, and electrical properties [1, 2]. These materials are potentially useful for hydrogen storage, chemical sensors, and nanobioelectronics [3, 4], etc. The experimentally available SWCNTs are not perfect. The defects such as vacancies, pentagons, heptagons, dopants, and Stone-Wales defects, are formed inevitably during the growth of SWCNTs [5, 6]. These defects can have a positive impact on the electrical, chemical, and mechanical properties. Therefore, investigations of properties of SWCNTs with defects in their structures are of great interest.

Based on molecular dynamics, another topological defects resulted from the addition of a carbon dimer to the graphene lattice are proposed by Sternberg et al [7]. A properly placed carbon ad-dimer results in the 7-5-5-7 topological defect (two pentagons connected by a pair of heptagons). This carbon ad-dimer defect associated activation barrier is much smaller than that of Stone-Wales defect. In particular, the ordered defect structure of ad-dimer rings is an appealing configuration. Novel structures of nanotubes lead to increase in nanotube diameter. This increase allows the single walled nanotubes to act as a novel type of molecular container. In a previous publication, Wang et al. investigated the structural and electronic properties of armchair (n, n) SWCNTs with multiple carbon ad-dimer defect and the chemisorption of hydrogenation, fluorination, and chlorination atoms on the surface of these nanotubes [8], but it is only one of several possibilities for ad-dimer geometries is discussed.

In the present paper, the structural and electronic properties of a (4, 4) SWCNT with the positions of the defect states induced by multiple carbon ad-dimers, the chemisorption of hydrogen and fluorine on the surface of these nanotubes were studied through density functional theory method.
2. Calculation methods

A finite-length cluster of perfect armchair (4, 4) SWCNT containing 104 carbon atoms terminated by hydrogen atoms were constructed as the initial structure models. The multiple carbon ad-dimers defective (4, 4) tubes were constructed by inserting symmetrically 4 C₂ around the circumference as a function of their distance from the open end of the nanotube. The pentagon-pentagon fusion vertexs are believed to be the most active sites of the fullerene and carbon nanotube⁹,¹⁰. Here, the hydrogen, and fluorine atoms were attached to the pentagon-pentagon fusion vertexs for each of the defective SWCNTs. The geometries of all the structures presented in the present work were fully optimized with hybrid density functional theory at the B3LYP/6-31G* level¹¹,¹². All calculations were done using the Gaussian 03 program package. The reaction energies of per H₂/F₂ adsorbed were calculated according to the expression:

\[ E_r = \frac{E(\text{SWCNT}-\text{H}_2/\text{F}_2) - E(\text{SWCNT}) - 4E(\text{H}_2/\text{F}_2)}{4} \]  

where E(SWCNT-H₂/F₂), E(SWCNT) and E(H₂/F₂) refer as the total energy of hydrogenated or fluorinated nanotube, defective nanotube, and H₂/F₂, respectively.

3. Results and Discussion

The optimized structure of perfect armchair (4, 4) SWCNT is shown in Figure 1. For the (4, 4) SWCNT, the calculated bond lengths fall into 1.54 Å (for single bond) and 1.34 Å (for double bonds), and the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energy gap (LUMO-HOMO energy difference, ΔE) value is 1.18 eV, which are in good agreement with the reported values from the literature⁸.

![Figure 1. Optimized structure of perfect armchair (4, 4) SWCNT.](image)

Four multiple carbon ad-dimer defects close to the open end of the (4, 4) SWCNT were created by inserting symmetrically 4 C₂ around the circumference. The optimized geometrical structures are shown in Figure 2. The calculated bond lengths at the pentagon-pentagon fusion have almost the same bond length (1.400-1.405 Å), which can be compared to the previously reported values (1.402-1.408 Å)⁸. The HOMO-LUMO gaps of four defective isomers are 0.95, 0.89, 0.92, and 1.02 eV, respectively. Multiple carbon ad-dimer defects reduce the HOMO-LUMO gaps of (4, 4) SWCNT compared to the corresponding perfect SWCNT.

![Figure 2. Optimized structure of armchair (4, 4) SWCNT with multiple carbon ad-dimer defect (colored yellow) at different positions.](image)

The pentagon-pentagon fusion vertexes are believed to be the most active sites of the fullerene and carbon nanotube⁹,¹⁰. Here the pentagon-pentagon fusion vertexes were considered for the adsorption of hydrogen and fluorine atoms. The optimized structures of hydrogenated or fluorinated defective (4, 4) SWCNTs 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 1. With the introduction of multiple ad-dimers defects in SWCNTs, the HOMO energy increases and the LUMO
energy decreases, resulting in lower gaps. The HOMO-LUMO gaps of four hydrogenated (4,4) SWCNTs are 1.96, 1.40, 1.95, and 2.45 eV, respectively; fluorinated SWCNT are 1.91, 1.36, 1.89, and 2.35 eV, respectively. The HOMO-LUMO gaps of the H- or F-modified SWCNTs are large than that of defective SWCNTs, implying the enhanced the stability of defective SWCNTs. Note that the defective position has very slight effect on the HOMO-LUMO gap of hydrogenated or fluorinated defective SWCNTs. The hydrogenation reaction energies (per H2) are -53.3, -53.1, -52.9, -53.1 kcal/mol, the fluorination reaction energies (per /F2) are -138.4, -138.4, -138.0, -138.2 kcal/mol for defective (4,4)-a, (4,4)-b, (4,4)-c, and (4,4)-d SWCNTs, respectively. The results indicate that the positions of the defect states have very slight effect on the reaction energy.

Figure 3. Optimized structures of four hydrogenated (1a, 1b, 1c, and 1d, respectively) and fluorinated (2a, 2b, 2c, and 2d, respectively) defective (colored yellow) (4,4) SWCNTs.

Table 1. The HOMO-LUMO energy gaps (ΔE, eV) and reaction energies per H2, F2 (E, kcal/mol) obtained at the B3LYP/6-31G* level for four defective (4,4) SWCNTs.

| Structure | Symm | ΔE | Hydrogenated tube | Fluorinated tube |
|-----------|------|----|-------------------|------------------|
| a         | C4v  | 0.95 | 1.96 | -53.3 | 1.91 | -138.4 |
| b         | C4v  | 0.89 | 1.40 | -53.1 | 1.36 | -138.4 |
| c         | C4v  | 0.92 | 1.95 | -52.9 | 1.89 | -138.0 |
| d         | D4h  | 1.02 | 2.45 | -53.1 | 2.35 | -138.2 |

4. Conclusions
This study presents a (4, 4) SWCNT with multiple carbon ad-dimers defect at different positions, the chemisorption of hydrogen and fluorine on the surface of these nanotubes by means of the density functional method at the B3LYP/6-31G* level. The calculated LUMO-HOMO gaps of defective SWCNTs are much lower than that of perfect ones, which means that the defective nanotubes exhibit a higher reactivity than perfect ones. The LUMO-HOMO gaps of the hydrogenated and fluorinated SWCNTs are larger than those the corresponding defective ones. Moreover, the reaction energies of the hydrogenated and fluorinated SWCNTs are strongly exothermic reactions. The calculations suggest that that the H-, F-modified SWCNTs are stable, being similar to perfect ones in terms of thermodynamic stability.

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