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RESEARCH ARTICLE

Sidewall fluorination and hydrogenation of single-walled carbon nanotubes: a density functional theory study

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The fluorination and hydrogenation reactions on (6, 6) and (10, 0) single-walled carbon nanotubes (SWCNTs) have been examined via computing the reaction energy for the chemisorption. The examined nanotubes have comparable lengths and diameters, with or without Stone–Wales defects on the sidewall. The two fluorine or hydrogen atoms are anchored to the external walls of the SWCNTs. The computed chemisorption energies of these virtual reactions reveal that the fluorination and hydrogenation of the nanotubes are moderately sensitive to the nanotube chirality and the sidewall topology, and the (10, 0) SWCNT with Stone–Wales defect can be easily fluorinated and hydrogenated.

Keywords carbon nanotube, first-principle calculation, fluorination, hydrogenation, Stone–Wales defect

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Carbon nanotubes (CNTs), discovered in 1991 [1], have been widely regarded as candidate materials for future technologies [2] because of their outstanding physical, chemical, and mechanical properties. Due to the inter-tube van der Waals attractive force, the as-prepared CNTs tend to exist as bundled structures and have poor dispersion in polymers [3, 4]. Functionalization of CNTs has drawn much attention in the past decade because the modified CNTs can breach the limitation of their structures and are of potential applications in catalysis, nano-device, and other high-tech fields.

The electronic structure of a single-walled carbon nanotube (SWCNT) is governed by its chiral index (n, m). When $n - m = 3k$, where k is an integer, the nanotube becomes metallic; otherwise, it would be semiconducting [5]. It is therefore necessary and desirable to find out an approach to prepare SWCNTs with specific electronic properties. For this purpose, one of the strategies is to functionalize the sidewall surface of nanotubes and consequently tune their physical/chemical properties [6–10]. It has been shown, both experimentally [2, 11–14] and theoretically [15–23], that covalent sidewall functionalization can effectively modify the structural and electronic properties of CNTs. For example, metallic SWCNTs were transformed to semiconducting ones by functionalizing the sidewalls of SWCNTs using fluorine and hydrogen atoms [24, 25]. Meanwhile, the atomic structures of the nanotube sidewall were modified by the newly formed strong covalent bonds that often lead to deformation of the local atomic structures of nanotubes [26] and sometimes result in destruction of the tubular structures [27].

Stone–Wales (SW) defect is a typical style of topological defect in the nanotubes, which consists of two pairs of five-membered and seven-membered rings. It was suggested that the SW defects could act as nucleation centers for forming dislocations in the originally ideal graphic network and initiate plastic deformation of

the CNTs [28, 29]. Due to deviation from the perfect network by six-membered rings, the SW defect sites on the sidewall of carbon nanotubes would be more favorable for subsequent reactions.

Previously, there have been some theoretical efforts on the fluorination and hydrogenation of the SWCNTs. For instance, Zhou *et al.* reported a systematic first-principles investigation of the charging effect on hydrogen molecule chemisorption on (3, 3), (5, 5), (5, 0), and (8, 0) carbon nanotubes [30]. They found that the influence of injected charge on the chemisorption energy barriers is sensitive to the nanotube diameter and chirality. From the PBE/3-21G calculations on a series of armchair F-SWCNTs of C_2F stoichiometry with periodic boundary condition [31], Bettinger *et al.* discovered that the thermodynamic stability of these F-SWCNTs as well as the average C–F bond energy decrease with increasing tube diameter. Bauschlicher [32] investigated the addition of several fluorine atoms on a H-terminated short zigzag (10, 0) SWCNT by means of the ONIOM approach and found that the F atoms tend to bond next to existing F atoms. Gregory *et al.* investigated the chemical addition patterns governing the fluorination of single-walled carbon nanotubes via Monte Carlo simulation; they found that fluorination is stabilized in a band-like pattern on the bond network topology of nanotube due to electronic confinement effects [33].

Despite of the above theoretical works, the correlation between the fluorination/hydrogenation reactivity and the structural factors (such as chirality and sidewall topology) of carbon nanotubes is still largely unknown. In this work, we report a first-principle study of the chemisorption of hydrogen and fluorine molecules on CNTs with perfect sidewall topology or containing Stone–Wales defects. The chemisorption energies on CNTs with different sidewall geometries will be compared to reveal the difference in reactivity.

All-electron density functional theory (DFT) calculations were carried out using the DMol^3 program [34, 35]. We adopted the generalized gradient approximation (GGA) with PW91 parameterization for exchange-correlation interaction. The double numerical plus (p, d) polarization (DNP) basis set was used. We chose two model CNT systems with comparable diameter/length but different chirality, i.e., finite (6, 6) and (10, 0) SWC-NTs with hydrogen atoms terminated on the two ends. The tube diameter is 8.446 Å for the (6, 6) SWNT and 7.930 Å for the (10, 0) SWCNT, respectively. The finite

(6, 6) tube of 16.612 Å length contains six and half unit cells (156 carbon atoms and 24 hydrogen atoms); the finite (10, 0) SWCNT of 17.816 Å length contains four unit cells (160 carbon atoms and 20 hydrogen atoms). In addition to perfect SWCNTs, one Stone–Wales defect was created at the middle of finite tubes to investigate the effects of topological defects.

To simulate the reactivity of the tube sidewall, we considered two virtual reactions, that is, the fluorination and hydrogenation of the CNTs, which is schematically shown in Fig. 1. The reaction of F_2 (H_2) chemisorption on SWCNT involves the dissociation of F_2 or H_2 molecule into two individual F or H atoms and then the attachment of the two F or H atoms to the tube
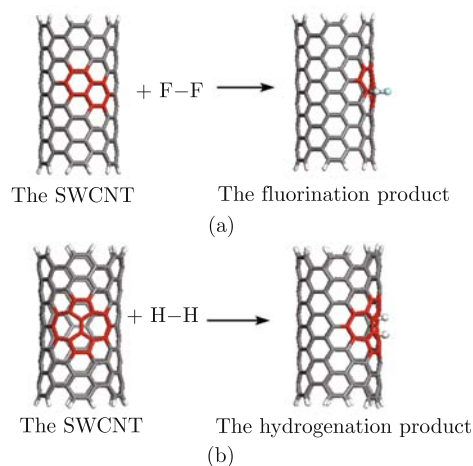

Fig. 1 A virtual reaction system for the fluorination **(a)** and hydrogenation **(b)** of SWCNTs.

sidewall via covalent bonds. The local geometries of the adsorption sites in the middle of finite (6, 6) and (10, 0) SWCNTs are shown in Fig. 2. For the fluorinalized and hydrogenated SWCNTs, the first fluorine or hydrogen atom is anchored to the O site on the tube wall. For the second F or H atom, there are many possible adsorption sites for the sidewall functionalization. Here, we primarily considered those nearby the O site attached with the first F or H atom, since that our test calculations show that these nearby sites are more reactive than the other sites. For the perfect (6, 6) and (10, 0) SWCNTs, six adsorptions sites (A, B, C, D, E, and F) were considered, which are shown in Fig. 2(a) and (b), respectively. In the case of the (6, 6) [Fig. 2(c)] and (10, 0) SWCNT [Fig. 2(d)] with Stone–Wales defect, the possible sites neighbouring to the O site are A, B, C, D, E, F, and G, respectively.
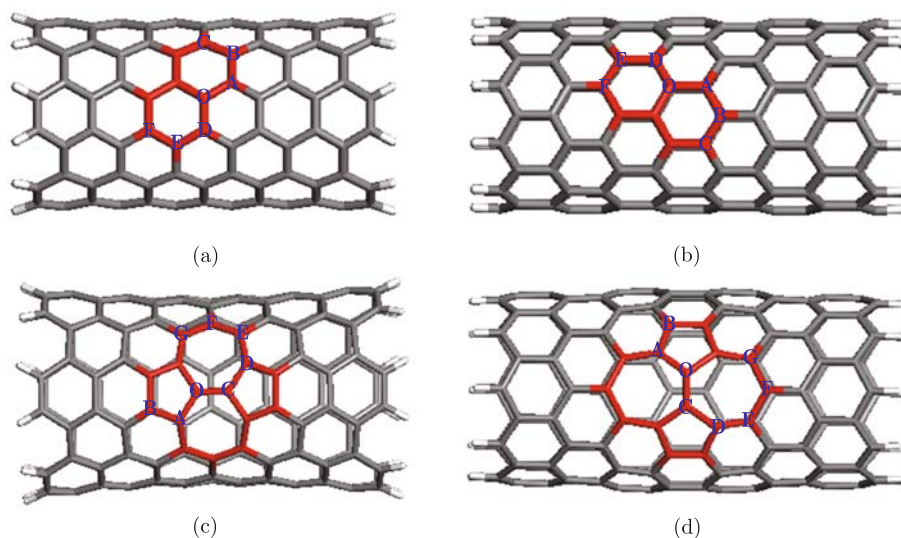
Fig. 2 The chemisorption sites for a fluorine and hydrogen molecule on the pristine SWCNT (6, 6) **(a)**, the pristine SWCNT (10, 0) **(b)**, the SWCNT (6, 6) with Stone–Wales defect and **(c)** the SWCNT (10, 0) with Stone–Wales defect **(d)**.

The thermodynamics of these virtual fluorination and hydrogenation reactions can be characterized by the heat of reaction computed by the difference of total energies of the reactants (SWCNT and F_2/H_2) and the products (SWCNT + 2F/2H):

$$E_{react} = E_{tot}(SWCNT+2F/2H) - E_{tot}(SWCNT)$$
$$- E_{tot}(F_2/H_2) \qquad (1)$$

where a positive (negative) E_{react} refers to an endothermic (exothermic) reaction.

The computed chemisorption energies for all the adsorption sites are summarized in Fig. 3, where the geometry configurations of all reactants and products were fully optimized. For the perfect (6, 6) SWCNT, the fluorination energies of the A, B, C, D, E, and F adsorption site are −61.100, −49.809, −64.976, −64.378, −50.055, and −61.324 kcal/mol, respectively, while the hydrogenation energies of the A, B, C, D, E, and F adsorption site are 16.317, 41.031, 16.921, 14.354, 40.647,

and 20.829 kcal/mol, respectively. In the case of the perfect (10, 0) SWCNT, the fluorination energies of the A, B, C, D, E, and F adsorption site are −68.319, −54.793, −64.269, −62.648, −52.269, and −67.272 kcal/mol, respectively; the hydrogenation energies of the A, B, C, D, E, and F adsorption site are 8.912, 32.722, 16.999, 13.195, 36.111, and 11.093 kcal/mol, respectively. From these results, one can clearly see that the fluorination process is exothermic, while the hydrogenation is endothermic. Moreover, the fluorination is not very sensitive to the tube chirality.

For the SWCNTs with SW defects, the fluorination reaction is still exothermic. In contrast, the hydrogenation on the defective (6, 6) SWCNT is endothermic, but it can be either exothermic or endothermic on the defective (10, 0) SWCNT. Again, these results indicate that the fluorination reaction on the SWCNTs is easier than the hydrogenation, in agreement with experimental observations [36].
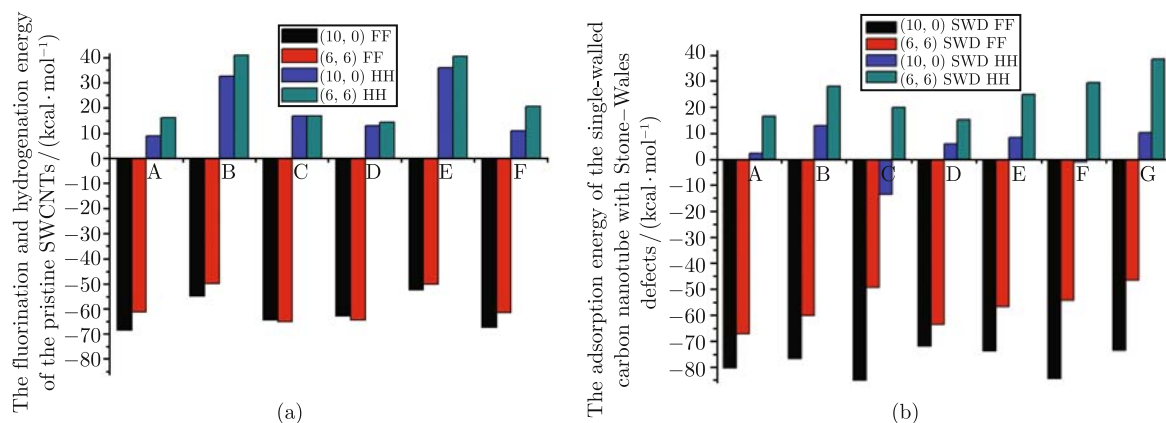

Fig. 3 The reaction energy for fluorination and hydrogenation at different chemisorption sites of the pristine SWCNTs **(a)** and the defective SWCNTs **(b)**.

Table 1 The minimum adsorption energy E_{ad}, F–C or H–C bond length, and on-site charge on F or H atom for the virtual reactions of F_2/H_2 chemisorption on different kinds of SWCNT.

SWCNT	F_2			H_2		
	$E_{ad}/(\text{kcal}\cdot\text{mol}^{-1})$	$d/\text{Å}$	$Q(e)$	$E_{ad}/(\text{kcal}\cdot\text{mol}^{-1})$	$d/\text{Å}$	$Q(e)$
(6, 6)	−64.976	1.454	−0.327	14.354	1.104	0.134
		1.457	−0.328		1.104	0.135
(10, 0)	−68.321	1.424	−0.313	8.912	1.102	0.131
		1.424	−0.313		1.102	0.131
Stone–Wales	−67.182	1.475	−0.334	15.253	1.114	0.147
Defect (6, 6)		1.422	−0.316		1.107	0.133
Stone–Wales	−84.970	1.417	−0.305	−13.475	1.104	0.144
Defect (10, 0)		1.418	−0.305		1.104	0.145

To further discuss the relationship between the functionalized group, sidewall topology and tube chirality, we selected the minimum adsorption energy E_{ad} for each virtual reaction system and the results are summarized in Table 1. The bond length between the attached F or H atom and the nearest carbon atom on the nanotube as well as the charge transfer between the SWCNT to the F or H atoms are also presented. We found that both the F–C and H–C bond lengths and the charge transferred from CNT to F and H atoms are not very sensitive to the details of the tube chirality and sidewall topology. For all types of nanotubes studied, carbon atoms donate about 0.3 electrons to each F atom, while the CNT receives about 0.1 electrons from each H atom. The typical lengths for the F–C and H–C bonds are about 1.42 Å and 1.1 Å, respectively.

However, the reaction energy for the chemisorption of F_2 and H_2 molecules on the SWCNT still rely on the detailed geometry structure of the nanotubes. When a SW type 5-7-7-5 defect appears on the sidewall of a (6, 6) SWCNT, the E_{ad} of fluorination changes from −64.976 to −67.182 kcal/mol and the E_{ad} of hydrogenation changes from 14.354 to 15.253 kcal/mol. Meanwhile, the presence of a Stone–Wales defect on the (10, 0) SWCNT reduces the fluorination energy from −68.321 to −84.970 kcal/mol and the hydrogenation energy from 8.912 to −13.475 kcal/mol. In other words, the SW defect on the (6, 6) SWCNT has only weak effect on the fluorine and hydrogen chemisorption, but SW defect on the SWCNT (10, 0) significantly increases the reaction energies for fluorination and hydrogenation by about 20 kcal/mol, making these reactions more easier.

To summarize, the fluorination and hydrogenation of the SWCNTs were studied by DFT calculations of the chemisorption energy of several target reaction systems. It was found that fluorination and hydrogenation of the SWCNTs are only moderately sensitive to the chirality and sidewall topology of the SWCNTs. The (10, 0) SWCNT with SW defect is more easily fluorinated and hydrogenated. These simulation results may help to explore new chemical methods to tune the structures and electronic properties of CNTs.

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