

Fluorination of BC₃ nanotubes: DFT studies

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Received: 24 April 2013 / Accepted: 23 June 2013 / Published online: 7 July 2013
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Abstract We have studied the adsorption of atomic and molecular fluorines on a BC₃ nanotube by using density functional calculations. It was found that the adsorption of atomic fluorine on a C atom of the tube surface is energetically more favorable than that on a B atom by about 0.97 eV. The adsorption of atomic fluorine on both C and B atoms significantly affects the electronic properties of the BC₃ tube. The HOMO-LUMO energy gap is considerably reduced from 2.37 to 1.50 and 1.14 eV upon atomic F adsorption on B and C atoms, respectively. Molecular fluorine energetically tends to be dissociated on B atoms of the tube surface. The associative and dissociative adsorption energies of F₂ were calculated to be about -0.42 and -4.79 eV, respectively. Electron emission density from BC₃ nanotube surface will be increased upon both atomic and molecular fluorine adsorptions due to work function decrement.

Keywords Boron carbide nanotube · DFT · F₂ · Nanostructure

Introduction

Due to their excellent electrical, thermal and mechanical properties, carbon nanotubes (CNTs) are potential candidates for several applications [1–5]. In addition, their peculiar property, a high surface area, makes CNTs suitable electrode materials in energy-storage supercapacitors. In addition to CNT, there are other nanotubes which are found

experimentally such as BN nanotube (BNNT), AlN nanotube (AlNNT), SiC nanotube (SiCNT), etc. [6–8]. The BC₃ and B₂C nanotubes were also theoretically proposed, among which the BC₃ nanotubes (BC₃NTs) have been experimentally realized [9, 10]. The CNTs could be either metallic or semiconducting depending on their radii and chiralities. BNNTs are predicted to be semiconductors regardless of their diameters, chiralities, or number of walls of the tube. Intuitively, the properties of BC₃NTs may be intermediate between those of CNTs and BNNTs [11].

Engineering the electronic properties of nanotubes is very important and if their band gap could be controlled like a normal semiconductor through a regular mechanism, their ranges of application would be greatly extended particularly in sensors and nanoelectronics [12]. Doping or functionalizing through chemical binding of atoms, molecules, or molecular groups is viewed as a viable approach to tailoring electronic properties of nanotubes [13]. Among covalent functionalization of CNTs, fluorination is one of the most studied and important ways. It is a good starting point for further covalent sidewall modification of CNTs (alkylation, hydroxylation, amino-functionalization, etc.) [14, 15]. Fluorinated CNTs themselves also exhibit a large range of possible applications. Fluorination allows dispersion of CNTs in alcoholic solvents [16], and potential applications of F-CNTs include electric storage as cathodes in lithium batteries, in supercapacitor electrodes, sensors, and solid lubricants [17].

Fluorination can also increase the solubility of nanotubes and it can offer intermediates for further chemical modifications [18]. Experimental and theoretical studies indicate that the electronic properties of BNNTs can be controlled by F doping, involving both substitution and addition [19]. Furthermore, ab initio calculations by Liew et al. showed that chemisorption of the F atom on the Si atom induces a push down of the Fermi level of SiCNTs, whereas the Fermi level is lifted up when the F atom is attached to the C site [20]. In the current work, the interaction of atomic (F) and molecular

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fluorines (F_2) with BC_3NT will be theoretically investigated based on analyses of structure, energies, electronic properties, stability, etc.

Computational methods

We selected a (8, 0) zigzag BC_3NT consisted of 72 C and 24 B atoms, in which the end atoms have been saturated with hydrogen atoms to reduce the boundary effects. A partial structure was shown in Fig. 1. Geometry optimizations, energy calculations, and density of states (DOS) analysis were performed on the pristine and fluorinated nanotubes using B3LYP functional with 6–31G(d) basis set as implemented in GAMESS suite of program [21]. The B3LYP has been demonstrated to be reliable and commonly used in the study of different nanostructures [22–26]. The length and diameter of the optimized BC_3NT were computed to be about 11.92 and 6.86 Å, respectively. We have defined adsorption energy in the usual way as:

$$E_{ad} = E(F \text{ or } F_2/BC_3NT) - E(BC_3NT) - E(F \text{ or } F_2), \quad (1)$$

where $E(F \text{ or } F_2/BC_3NT)$ corresponds to the energy of the BC_3NT in which the atomic or molecular fluorine has been adsorbed on the outer wall, $E(BC_3NT)$ is the energy of the isolated tube, $E(F \text{ or } F_2)$ is the energy of a single F atom or F_2 molecule. Basis set superposition error was corrected for weak interactions. Charge of all systems was set to be zero. Spin multiplicity was set to be singlet and doublet for the closed and open shell systems, respectively. The canonical assumption for Fermi level (E_F) is that in a molecule (at $T=0$ K) it lies approximately in the middle of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy gap (E_g). It is noteworthy to mention that, in fact, what lies in the middle of the E_g is the chemical potential, and since the chemical potential of a free gas of electrons is equal to its Fermi level as traditionally defined, herein, the Fermi level of the considered systems is at the center of the E_g .

Results and discussion

In Fig. 1, we have shown partial structure of the optimized BC_3NT . Two types of B–C bonds can be identified, one with the bond length of 1.57 Å and in parallel with the tube axis, and another with the bond length of 1.56 Å, but not in parallel with the tube axis (diagonal). Also, two types of C–C bonds exist in the tube wall, namely parallel and diagonal, with bond lengths of 1.41 and 1.42 Å, respectively. Molecular electrostatic potential surface (MEP, Fig. 1)

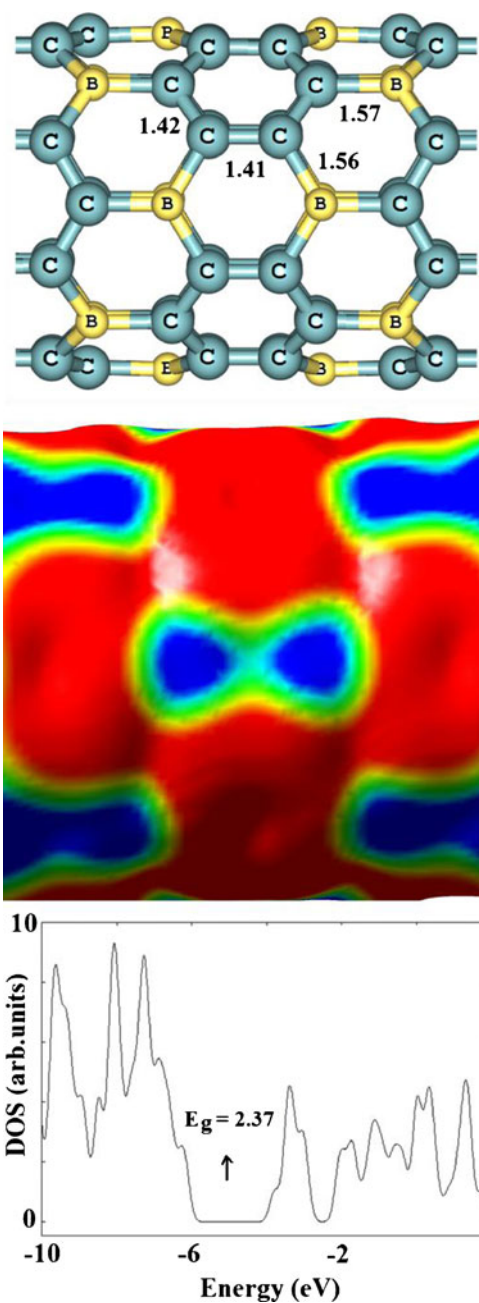


Fig. 1 Geometrical parameters of the optimized BC_3NT and its density of states (DOS) and MEP plots. The surfaces are defined by the 0.0004 electrons/ b^3 contour of the electronic density. Color ranges, in a.u.: blue, more positive than 0.004; green, between 0.004 and -0.004 ; yellow, between 0 and -0.004 ; red, more negative than -0.004 . Bonds are in Å

indicates that C and B atoms have negative (red regions) and positive (blue regions) charges, respectively. To find the adsorption behavior of an F atom on the tube, we have tested all possible adsorption configurations. To this end, an F atom was located on the top of B and C atoms, separately or on the center of hexagonal rings and on the bridge sites of the bonds. Finally, only two local minima were obtained upon

the optimization process as shown in Fig. 2. More detailed information from the simulation of the different F/BC₃NT complexes, including values of E_{ad} , electronic properties and the charge transfer (Q_{T}) is listed in Table 1. Configuration **A** stands for the interaction between the F atom and the C atom of the nanotube with distance of 1.49 Å and its corresponding calculated E_{ad} value is about -2.03 eV.

As shown in Fig. 2b, the most stable configuration of the F-BC₃NT system (**B**) is that in which the F atom is attached to a boron atom of the tube surface ($E_{\text{ad}} = -3.00$ eV). Formation of strong B–F bond, probably like B–F in F-doped BNNTs [27], may be due to an ionic-covalent resonance bond strengthening (i.e., either a double bond between two ions (C^+ and F^-) or a single bond between B and F atoms). In this configuration, the length of the newly formed F–B is about 1.41 Å and a charge of $0.284 e$ is transferred from the tube to the atom, indicating that the interaction is very strong. The MEP plot for configuration **B** (Fig. 3) clearly indicates that electronic charge plots of F and the BC₃NT are strongly overlapped, leading to more orbital mixing in which the BC₃NT acts as an electron donor.

Further indication of the deformation degree in the geometry of the nanotube caused by the adsorption process is given by the bond reorganization energy (E_{br}) which is calculated as the energy difference between the geometry of the tube before and after the adsorption. In other words, to calculate E_{br} we have removed F atom(s) from the surface of

the functionalized tube and obtained total energy of the bare tube by performing a single point calculation. The energy difference between this bare tube and the pristine tube gives E_{br} . For configuration **B** the E_{br} is about 2.78 eV, confirming the strong nature of the interaction. The NBO analysis shows that the hybridization of adsorbing B atom changes from $\text{sp}^{1.97}$ in the free tube to $\text{sp}^{2.91}$ in the form of BC₃NT-F. It is found that the E_{ad} for the most favorable fluorine chemisorption on the BC₃NT may be more negative than that of F attached to the C atom of the (10,0) CNT (-0.93 eV) and Si atom of the (8,0) SiCNT (-2.73 eV) which was obtained with generalized-gradient approximation with the Perdew-Burke-Ernzerhof correction [17, 20]. As shown in Fig. 2, the adsorbing B atom is pulled outward from the tube wall, in which the length of parallel and diagonal B–C bonds is increased from 1.57 to 1.56 Å of the pristine tube to 1.61 and 1.68 Å, respectively.

Next, we studied the influence of the F adsorption on the electronic properties of the nanotube. The DOS plots for the F-adsorbed BC₃NTs are shown in Fig. 2. For the bare BC₃NT from Fig. 1 and Table 1, it can be seen that it is a semi-conducting material with a difference in the energies between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO), E_{g} , about 2.37 eV. It should be noted that the E_{g} also stands for singly occupied molecular orbital (SOMO)/LUMO energy gaps for open shell systems. The adsorption of a single F on

Fig. 2 Models for stable adsorption of atomic F on BC₃NT and their density of states (DOS) plots. Bonds are in Å

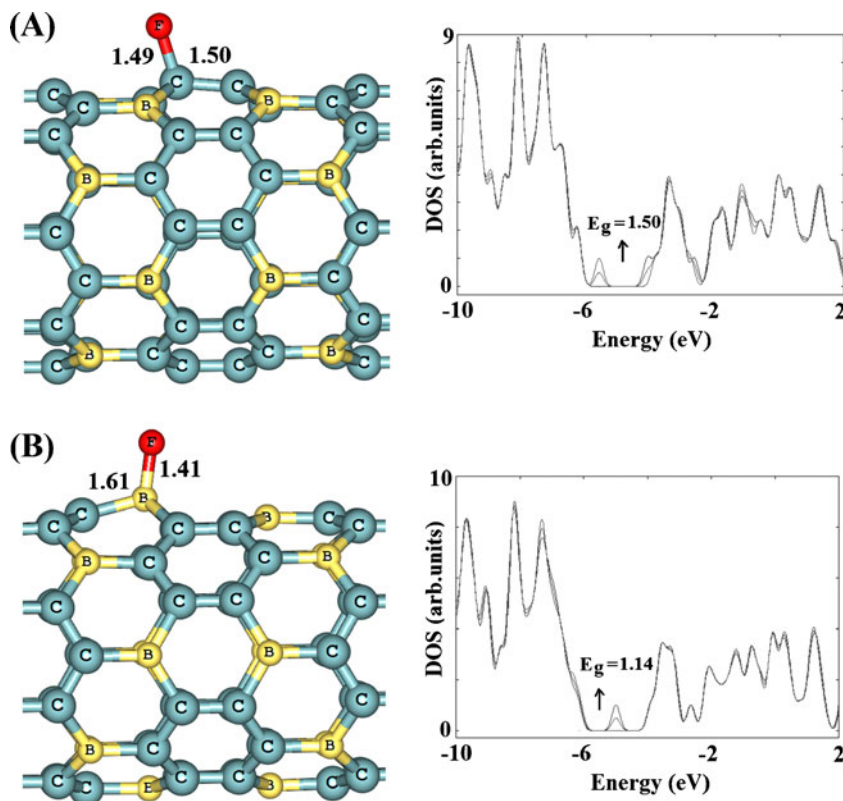


Table 1 Calculated adsorption (E_{ad} in eV) and bond reorganization (E_{br} in eV) energies of F, dipole moment (μ , Debye), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO-LUMO energy gap (E_{g}), Fermi level (E_{F}) and effective work function (Φ_{eff}) of systems (Figs. 1 and 2) in eV

Configuration	E_{ad}	E_{br}	μ	${}^{\text{a}}Q_{\text{T}}$ (e)	E_{HOMO}	E_{F}	E_{LUMO}	E_{g}	Φ_{eff}	${}^{\text{b}}\Delta E_{\text{g}}$ (%)
BC ₃ NT	–	–	0.00	–	–6.15	–4.96	–3.78	2.37	1.18	–
(A) BC ₃ NT-F	–2.03	1.66	1.52	–0.341	–5.60	–4.85	–4.10	1.50	0.75	36.7
(B) BC ₃ NT-F	–3.00	2.78	3.93	–0.284	–6.12	–5.55	–4.98	1.14	0.57	51.7

^a Q_{T} is defined as the total Mulliken charge on the F atom

^b Change of E_{g} of BC₃NT after F adsorption

the top of B and C atoms of the nanotube moves the Fermi energy to lower energies. In configurations **A** and **B** (Fig. 2), the E_{g} of the BC₃NT is drastically decreased from 2.37 eV to 1.50 and 1.14 eV, respectively. Largest change in DOS plot of BC₃NT was occurred after the adsorption of F atom top of C atom, so HOMO energy almost remains constant but LUMO energy significantly decreases from –3.78 eV in the bare nanotube to –4.98 eV in fluorinated form. As a result, smaller values of E_{g} at a given temperature lead to larger electric conductivity of the tube. When F atom is added to the BC₃NT, dipole moment of the tube is significantly increased from 0.00 Debye in the pristine form to 1.52 and 3.93 Debye for **A** and **B** configurations, respectively. Electric dipole moment is one of the properties which are traditionally used to discuss and rationalize the structure and reactivity of many chemical systems [28, 29].

Subsequently, we investigated the adsorption of molecular fluorine (F₂) on the BC₃NT. In order to find minimum adsorption configurations of BC₃NT/F₂, the F₂ molecule was initially placed at different positions above the tube with different orientations, including linear F₂ molecule located on the top of B–C and C–C bonds, both of the F atoms close to two B atoms or C atoms of nanotube, and the F–F bond

being vertical to each atom of the tube. After geometrical full optimization without any constraints, two stable configurations were found (Fig. 4). The E_{ad} obtained for these structures depends on the orientation and location of the F₂ outside the tube (Table 2). Accordingly, we have divided the interactions into two categories including (i) associative adsorption: in which an insignificant change occurs in the geometrical parameters after adsorption (configuration **P**) and (ii) dissociation: very strong interaction that largely deforms the structure of the tube with bond cleavage and formation (configuration **Q**). In configuration **P**, a bond is formed between one of the F atoms of F₂ molecule and a boron atom of BC₃NT with distance of 1.52 Å, and its corresponding calculated E_{ad} value is about –0.42 eV.

An interesting adsorption case is the dissociation of F₂ molecule through 1, 4 addition of the molecule to the tube surface (Fig. 4q). E_{ad} of this process (–4.79 eV) is more negative than that on configuration **P** with rather a significant Mulliken charge transfer from the tube to the F atoms. Based on the natural bond orbitals (NBO) analysis, both of B atoms move outward from tube's surface and two new bonds are formed, namely B–F with bond lengths of 1.42 Å. It suggests that this bond cleavage may be activated by using substrate of BC₃NT. DOS plots for two adsorption models of **P** and **Q** have been shown in Fig. 4, indicating that in configuration **P**, the electronic properties of the BC₃NT have been significantly changed, so the DOS near the conduction level has a distinct change compared to that of the pristine tube, and as a result, an impurity electron state appears at energy level of –4.98 eV after the F₂ adsorption which would result in the E_{g} reduction from 2.37 to 1.26 eV. It shows a considerable change of E_{g} about 1.11 eV (46.8 %), indicating that the electronic properties of the tube are very sensitive to the adsorption of F₂ molecule.

Theoretical investigations have shown that introducing adsorbates on nanotubes might effectively modify the field emission properties [30], which is necessary to estimate the potential for designing efficient field emission display. Thus, we analyze the modifications of the effective work function (Φ_{eff}) due to fluorination of BC₃NT. It should be noted that Φ_{eff} is defined as the energy difference between the Fermi level and the LUMO. The results of Tables 1 and 2 reveal that

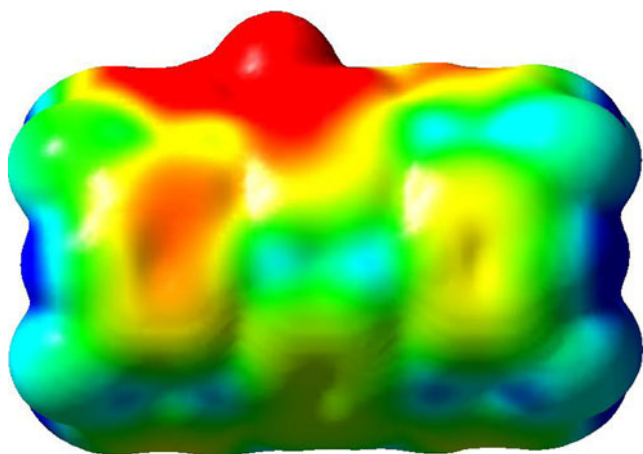
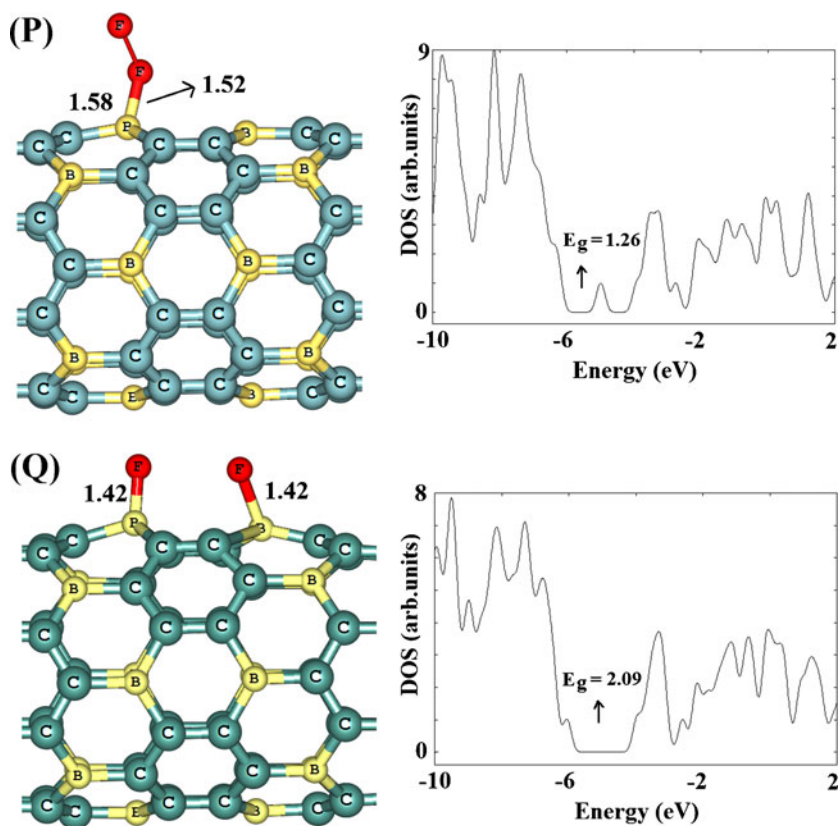


Fig. 3 The MEP of F-BC₃NT for configuration **B**. The surfaces are defined by the 0.0004 electrons/b³ contour of the electronic density. Color ranges, in a.u.: *blue*, more positive than 0.004; *green*, between 0.004 and –0.004; *yellow*, between 0 and –0.004; *red*, more negative than –0.004

Fig. 4 Models for stable adsorption of molecular F_2 on BC_3NT and their density of states (DOS) plots. Bonds are in Å



calculated Φ_{eff} of the pristine BC_3NT is about 1.18 eV which significantly decreased upon the atomic and molecular fluorine adsorption. For example, the Φ_{eff} of BC_3NT is obviously decreased from 1.18 to 0.57 eV ($\Delta\Phi_{eff} = -0.61$ eV, F adsorption in configuration **B**) and 0.63 eV ($\Delta\Phi_{eff} = -0.55$ eV, F_2 adsorption in configuration **P**). The decrement in the work function indicates that the field emission properties of the BC_3NT s are facilitated upon the adsorption of mentioned adsorbates. Furthermore, this results in reduced potential barrier of the electron emission for the nanotube, facilitating the electron emission from the BC_3NT surface. These changes can lead researchers to design new and different BC_3NT s which have unique surface properties and make them suitable for microelectronics technology.

Conclusions

The adsorption of atomic and molecular fluorine on a BC_3NT was studied using DFT calculations. The results showed that atomic F atom prefers to be adsorbed on the top of B and C atoms of the tube surface with E_{ad} of -2.03 and -3.00 eV, respectively. Also, our results indicate that the attachment of the F atom on the walls of BC_3NT gives rise to significant changes in the electronic properties of nanotube and its conductivity increases after fluorination. F_2 molecule is strongly adsorbed on the tube via two mechanisms including chemisorption and dissociation with E_{ad} of -0.42 to -4.79 eV, respectively. These processes also significantly change the electronic properties of BC_3NT by decreasing

Table 2 Calculated adsorption (E_{ad} in eV) and bond reorganization (E_{br} in eV) energies of F, dipole moment (μ , Debye), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO-LUMO energy gap (E_g), Fermi level (E_F) and effective work function (Φ_{eff}) of systems (Fig. 4) in eV

Configuration	E_{ad}	E_{br}	μ	aQ_T (e)	E_{HOMO}	E_F	E_{LUMO}	E_g	Φ_{eff}	${}^b\Delta E_g$ (%)
BC_3NT	–	–	0.00	–	–6.15	–4.96	–3.78	2.37	1.18	–
(P) BC_3NT-F_2	–0.42	–1.74	3.81	0.292	–6.24	–5.61	–4.98	1.26	0.63	46.6
(Q) BC_3NT-F_2	–4.79	–6.87	5.08	0.559	–6.05	–5.00	–3.96	2.09	1.04	11.8

^a Q_T is defined as the total Mulliken charge on the F_2 molecule

^bChange of E_g of BC_3NT after F_2 adsorption

its E_g and decreasing the work function. The decrement in the work function indicates that the field emission properties of the BC₃NTs are facilitated upon the fluorination.

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