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Fluorination of BCN nanostructures: A first principles study

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ABSTRACT

Spin polarized density functional theory has been used to investigate energetics and electronic properties that BC_2N nanostructures (tubes and layers) exhibit after fluorine is adsorbed. The calculated adsorption energies show that fluorine atoms are exothermically and preferentially adsorbed on top of boron atoms. The electronic properties show that fluorinated nanostructures can exhibit acceptor properties or deep electronic levels inside the band gap, depending on whether the fluorine atoms are adsorbed on top of boron or carbon atoms. In addition, we observe that fluorinated nanostructures have non-zero spin magnetic moments.

1. Introduction

Nanostructured materials have a large surface to volume ratio compared to conventional bulk material. This large surface area allows for the development of functionalized materials, which are suitable for nanoelectronics, optical devices and biomedicine. The most versatile way to obtain functionalized nanomaterials is through the chemical binding of atoms, molecules or molecular groups. The adsorption of fluorine on graphene [1], carbon nanotubes (CNTs) [2] and boron nitride nanotubes (BN NTs) [3] has already been obtained through experimental assays, resulting in "fluoronanotubes", which are more soluble and reactive than the pristine form and can be cut by pyrolysis [4,5]. Furthermore, the fluoronanotubes can be solvated in alcohol via ultrasonication [6], producing functionalized nano-materials.

First principles calculations have been performed on fluorinated nanostructures to support experimental findings. The calculations predicted that the fluorination of graphene (F-G) would be an exothermic reaction and fluorination would open the band gap [1,7,8]. Similar calculations showed that the thermodynamic stability of fluorinated NTs is inversely dependent on tube diameter [9]. Quantum chemistry calculations based on the density functional theory (DFT) and the B3LYP functional found that the zigzag Single Walled CNTs are more stable than the armchair ones [10].

The F-CNTs are shown to exhibit interesting electronic properties. Kudin et al. observed that either metallic or semiconductor F-CNTs could be obtained depending on the fluorine pattern [11]. However, a tube deformation occurred in heavy doping nanotubes (more than 50% surface coverage). It was also observed that the density of states (DOS) near the Fermi energy decreases after the F adsorption [12,13].

Ab initio calculations were also performed on BN nanostructures (tubes and layers). The calculations showed that fluorine adsorption is highly exothermic and F atoms preferentially adsorb on top of B atoms. The fluorine single walled BN NTs (F-BNNTs) exhibited a p-type semiconductor character at low F coverage. At high F coverage, the number of acceptor levels increase and a band-like p-type conductor structure is obtained [14,15]. Multi-walled BN NTs presented different interwall interactions after the adsorption of one unique F atom in the interstitial region, which leads the system to exhibit different structural and electronic properties [16] when compared to the pristine system. Magnetic properties were theoretically predicted after the adsorption of F atoms on BN single-layers [17].

Mixed $B_xC_yN_z$ compounds (x, y and z indicate stoichiometry) are stable in hexagonal structures and are predicted to form one and bi-dimensional (1D and 2D) nanostructures [18,19]. Theoretical investigations have shown that BC_2N stoichiometry is one of the most stable forms of ternary BCN nanostructures (layers and nanotubes) and there exist three different types, namely type-I, type-II and type-III. The three types differ on the type and number of bonds between the three atomic chemical species involved [20]. According to previous DFT calculations [21], type-II BC_2N NTs were shown to be the most stable, a result that may be attributed to the large number of stable C – C and B – N bonds. Two different carbon atoms (C_I and C_{II}) can be identified in type-II BC_2N compounds. The C_I bonds with a boron atom while the C_{II} bonds with a nitrogen atom. These calculations also showed that type-II BC_2N NTs are semiconductor with a band gap of about 1.6 eV, which present a slight dependence on tube diameter and chirality.

The bonds of the atoms in the surface of the BCN nanostructures have an ionic character, which is similar to that of BN nanostructures and different from structures composed strictly of carbon atoms. This ionic character favors the adsorption of atoms and molecules. Studies of carbon doped BN NTs have shown an increase in surface reactivity

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due the doping, which favors the chemical adsorption of important molecules like O_2, H_2, CO and NO [22–24]. Recent studies on the adsorption of H_2 and O_2 on pristine BC_2N NTs have shown that the surface of these specific NTs is more reactive than that of CNTs and BN NTs, enabling the possibility to functionalize the BCN nanostructures through the adsorption of atoms and molecules on their surfaces.

Contrary to CNTs and BN NTs, the presence of defects in BCN nanostructure has been scarcely studied [21,25–28]. In particular, fluorinated BCN NTs and layers have yet to be studied. In an attempt to investigate the main features of fluorinated BCN nanostructures, we used first principles calculations to study the energetic and electronic properties of fluorinated type-II BC_2N nanostructures. Although BCN nanostructures with BC_2N stoichiometry have yet to be produced on a large scale, our calculations demonstrate important properties of fluorinated nanocompounds based on carbon and BN (C/BN nanostructures), which can be produced using different methods.

The applied methodology will be described in the next section, the results will be provided and discussed in section three, and the conclusions will be presented in the final section. We use two NTs with small diameters, the (3,3) armchair and the (5,0) zigzag in order to investigate chirality effects. The results show that F atoms are preferentially adsorbed on B atoms and the BCN nanostructures exhibit a p-type semiconductor character. We also notice that the adsorption of F atoms leads the system to show non-zero magnetic moments.

2. Methodology

Our calculations are based on the spin-polarized density functional theory (SP-DFT) within the generalized gradient approximation (GGA) for the exchange–correlation term, as proposed by Perdew et al. [29] and implemented in the SIESTA code [30]. The SIESTA performs a fully self-consistent (SCF) calculation by solving the standard Kohn–Sham (KS) equations. We expand KS orbitals using a linear combination of numerical pseudoatomic orbitals, similar to the ones proposed by Sankey and Niklewski [31]. A split-valence double-zeta quality basis set enhanced with polarization functions and an energy shift of 0.10 eV is used in all our calculations to determine the radius cutoff of the pseudoatomic orbitals. In order to guarantee a precise description of the charge density, we utilize a cutoff of 100 Ry for the grid integration to project the charge density in real space and calculate the self-consistent Hamiltonian matrix elements. We modulate the ion–electron interaction by ab initio norm-conserving fully separable Troullier–Martins pseudopotentials [32]. We use the special point procedure within the Monkhorst–Pack scheme [33] to represent the Brillouin Zone (B.Z.) and to calculate the average of the periodic functions in the **k**-space. For semiconductor NT systems we observe that three special **k**-points obtained using the $1 \times 1 \times 5$ grid are enough to give the correct geometry and electronic properties. However, for a metallic system we need to increase the number of special **k**-points. For NTs when a metallic character is present we use 11 **k**-points to calculate the equilibrium geometry and the electronic properties. For the single-layer when the smaller supercell is used the number of special **k**-points is increased to 18 points to describe the correct metallic character of the system.

We utilize two NTs, the (3,3) armchair and the (5,0) zigzag, to investigate the influence of the chirality of the NTs on the structural and electronic properties. These NTs have small diameter, 8.35 and 8.17 Å, respectively. We should bear in mind that the lattice parameter of hexagonal BC_2N has a lattice parameter (a), which is approximately twice of the corresponding graphite or hexagonal BN and the basic unit cell for the BC_2N NTs has four atoms while for graphite and BN the basic unit cell has only two atoms. Thus, the (n,n) and (n,0) BC_2N NTs have a diameter that is approximately twice the correspondent diameter of C or BN NTs with the same chirality. In order to minimize the non-realistic effects due to “periodic” doping, we use supercells to describe fluorinated NTs and single-layer. The supercell for the fluorinated (3,3) and (5,0) NTs has three (144 atoms) and two (160 atoms) basic BC_2N units plus the F adsorbed atoms, in respective order. We use two supercells with different planar dimensions (32 atoms and 128 atoms) to study different fluorine coverages in the single-layer. We utilize a vacuum region of about 10 Å to ensure a negligible interaction between images, in the supercell approach. The positions of all atoms of the freestanding NTs, the single-layer and the adsorbed fluorine atoms are relaxed using the conjugated gradient algorithm. The system is considered optimized when all the force components are smaller than 0.05 eV/Å.

We calculate the adsorption energy for each adsorbed fluorine atom using total energy calculations, according to the equation:

$$E_{ads}[F]/n = \{E_T[\text{pristine}] + n\mu_F - E_T[nF]\}. \quad (1)$$

In Eq. (1), $E_T[nF]$ is the total energy of the supercell with n adsorbed F atoms, $E_T[\text{pristine}]$ is the total energy of the pristine system, and μ_F is the atomic chemical potential of the F atom, which is calculated as the total energy per F atom in the F_2 molecule. Positive values of E_{ads} indicate that F atoms are readily adsorbed (an exothermic process).

3. Results and discussion

Firstly, we consider the low concentration of F atoms; that is, there is only one F atom present per unit cell. Then we study the adsorption of an F atom on the armchair (3,3) NT and zigzag (5,0) NT, and the single-layer of the type-II BC_2N nanostructure. Based upon the studies of F adsorption on carbon and BN nanostructures, we determine that F adsorption must occur on top of an atom of an adsorbed system (tube or layer). For the NTs, we study the adsorption of F atoms in the inner side and in the outer side of the tubes' surfaces. The outer side is more stable by approximately 1 eV for both of the tubes. There are four possible sites for each nanostructure: on top of the B atom, on top of the N atom and on the top of the two nonequivalent C atoms (C_I and C_{II}). Table 1 shows the calculated adsorption energy in eV per adsorbed F atom (eV/F). The F atom is preferentially adsorbed on top of a B atom. The second most reactive site for the F atom is on top of a C_{II} atom. The adsorption on top of the N atom is unstable (our SCF calculations using the CG algorithm show that the F atom migrates to a nearby site). The adsorption of the F atom on top of a C_I is also unstable in the single-layer.

The preference of the F atom to be adsorbed on top of a B atom is in accordance with the results of the F adsorption on BN nanostructures [14–17]. The F atom bonds preferentially with the least electronegative atom (the B atom). Table 1 shows that the F adsorption is more stable for tubes than for layers. The F atom has a stronger bond with NT atoms than with single-layer atoms due to the curvature effects present in the NTs. The curvature of the NTs induces a small sp^3 character in the bonds, increasing the NTs' reactivity. We obtain similar curvature effects for F adsorption than the ones obtained for Carbon [9] and BN [16] NTs. We show that the F – C and F – B bonds are stronger for NTs with smaller diameters.

The electronegativity of the nearest neighbor atom must be analyzed to be able to understand the F atoms' preference to be adsorbed on top of a C_{II} atom instead of a C_I atom. The C_I atom bonds with two C_{II} atoms and one B atom, while the C_{II} atom bonds with two C_I atoms and one N

Table 1
Adsorption energies (E_{ads}) in eV/F for one single F atom adsorbed per supercell on top of four nonequivalent atoms of the BC_2N nanostructures.

Formation energy			
Configuration/system	NT (3,3)	NT (5,0)	Single-layer
F – B	2.70	2.77	2.21
F – N	Unstable	Unstable	Unstable
F – C_I	1.05	1.20	Unstable
F – C_{II}	1.25	1.49	0.70