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First-principles study of the adsorption of atomic and molecular hydrogen on BC_2N nanotubes

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The adsorption of atomic and molecular hydrogen on armchair and zigzag boron carbonitride nanotubes is investigated within the *ab initio* density functional theory. The adsorption of atomic H on the BC_2N nanotubes presents properties which are promising for nanoelectronic applications. Depending on the adsorption site for the H, the Fermi energy moves toward the bottom of the conduction band or toward the top of the valence band, leading the system to exhibit donor or acceptor characteristics, respectively. The H_2 molecules are physisorbed on the BC_2N surface for both chiralities. The binding energies for the H_2 molecules are slightly dependent on the adsorption site, and they are near to the range to work as a hydrogen storage medium.

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I. INTRODUCTION

Recently, quasi-one-dimensional materials have been the focus of intensive research, especially the materials that are in the nanotube structures. Among these materials, carbon nanotubes (CNTs)[1] and boron-nitride nanotubes (BNNTs)[2] have shown great potential for nanotechnology applications, such as electronic devices, optical devices, sensor, etc. More recently, the ternary compound $B_xC_yN_z$ nanotubes have been synthesized using chemical vapor deposition,[3–6] arc-discharge,[7–9] and pyrolysis[10] techniques. The hexagonal-nanotubes BC_2N stoichiometry is shown as the most stable one.[11] These nanotubes can be obtained by rolling the hexagonal BC_2N sheet, and three configurations labeled as type I, type II, and type III can be obtained,[12] whereas type II is the most stable one owing to the fact that this configuration maximizes the number of B–N and C–C bonds. These nanotubes (type II) are always semiconductor and the band gap presents a slightly dependence with the tube chirality.[13–15]

Chemical doping,[16,17] atoms and molecules bonded to nanotubes,[18] is an important mechanism to functionalize nanotubes. The adsorption of atomic hydrogen on the top of a carbon atom in semiconductor (8,0) pristine CNTs introduces a donor level in the band gap.[19] Whereas for BNNTs, acceptor and donor electronic states appear, depending on whether the H atom is adsorbed on the cation or on the anion atom, respectively.[20] Interesting electronic properties are expected when hydrogen is adsorbed on the ternary BC_2N nanotubes.

Besides the great interest of these materials for the electronic applications, nowadays, one challenge that has received special attention of the scientific community is the pursuit of new materials that present high hydrogen storage capacity. The nanotube, due to the high surface-to-bulk ratio, is a class of materials that presents a great potential for this clean energy alternative. The hydrogen storage capacity in CNTs is about 0.2 wt %,[21] while in BNNTs, the capacity reaches up to 3 wt %.[22] BNNTs are, in some aspects, similar to CNTs, but the difference between them seems to favor the use of BNNTs for hydrogen storage. For BNNTs, it was suggested that moderate substitutional doping in materials could enhance the binding energies of H_2 to values suitable for hydrogen storage.[20]

In this work, we have done a systematic study of the interaction of atomic (H) and molecular (H_2) hydrogen on type-II BC_2N nanotubes. The calculations were carried out using an *ab initio* method based on the density functional theory (DFT) on armchair (3,3) and zigzag (4,0) and (5,0) BC_2N nanotubes. Our results show that the atomic hydrogens are adsorbed preferentially on top of carbon atoms, and the Fermi energy moves to the top of the valence band or to the bottom of the conduction band, depending on the site where the H is adsorbed. For molecular hydrogen, only a physisorption is observed with a range of the H_2 binding energy from 50 to 100 meV.

II. METHODOLOGY

The calculations are based on the spin-polarized DFT implemented within the SIESTA code,[23] which performs a fully self-consistent calculations by solving the standard Kohn-Shan (KS) equations. The KS orbitals are expanded using a linear combination of numerical pseudoatomic orbitals, similar to the ones proposed by Sankey and Niklewski.[24] In all calculations, we have used a split-valence double-zeta quality basis set enhanced with polarization function. To guarantee a good description of the charge density, a cutoff of 100 Ry for the grid integration was utilized to project the charge density in the real space and calculated the self consistent Hamiltonian matrix elements. The ion-electron interaction is modulated by the *ab initio* norm-conserving fully

TABLE I. Calculated binding energies (in eV), distance (in Å) between the H and the hydrogenated atom (d_H), and the outward relaxation (in Å) of the hydrogenated atom from the tube surface (d_{tube}), for atomic H adsorbed on armchair (3,3) and zigzag (4,0) BC_2N nanotubes. The values in parenthesis are the binding energies for the zigzag (5,0) nanotube.

	Symmetry	E_b	d_H	d_{tube}
Tube+H-B	Armchair	−1.33	1.26	0.45
Tube+H-B	Zigzag	−1.34 (−1.17)	1.26	0.38
Tube+H-N	Armchair	−0.39	1.04	0.31
Tube+H-N	Zigzag	−0.99 (−0.44)	1.04	0.27
Tube+H-C_I	Armchair	−1.63	1.13	0.37
Tube+H-C_I	Zigzag	−1.95 (−1.52)	1.13	0.24
Tube+H-C_{II}	Armchair	−1.53	1.13	0.31
Tube+H-C_{II}	Zigzag	−1.51 (−1.39)	1.13	0.44

separable Troullier-Martins[25] pseudopotentials in the Kleinman-Bylander form.[26] To sampling the Brillouin zone, a set of two Monkhorst-Pack special k points[27] along the tube axis has been used. We check the electronic and structural properties for the freestanding nanotube and when H atoms are adsorbed on the nanotube surface, considering up to four k points. Our results do not show any significant variation in the properties with respect to the two k point calculation. For the exchange correlation, we have used the generalized gradient approximation (GGA) as proposed by Perdew *et al.*[28]

Hydrogen adsorption is studied into two types of BC_2N nanotubes, the armchair (3,3) and the zigzag (4,0) and (5,0), which have 8.34, 6.54, and 8.10 Å in diameter, respectively. The choice of these tubes permits us to investigate the influence of the chirality and the curvature, as well the interaction between distinct adsorbed hydrogens on the same nanotube. The (3,3) and (4.0) nanotubes were described with supercells containing two basic BC_2N units, 96 and 128 atoms, respectively. For the (5,0) nanotube, we use one unit cell with 80 atoms. To ensure negligible interaction between the tube images in the supercell approach, we consider a vacuum region of about 9 Å. The positions of all atoms of the freestanding nanotubes as well the adatom nanotubes were relaxed using the conjugated gradient algorithm until the force components become smaller than 0.05 eV/Å. The binding energy ($E_b[X]$) is calculated using total energy, according to the equation,

$$E_b[X] = E_T[\text{tube}+X] - (E_T[\text{tube}] - E_T[X]), \qquad (1)$$

where $E_T[\text{tube}+X]$, $E_T[\text{tube}]$, and $E_T[X]$ are the tube total energy with an adsorbed X atom or molecule, the tube total energy, and the total energy of the adsorbed species, respectively.

III. RESULTS AND DISCUSSION

A. Adsorption of atomic hydrogen

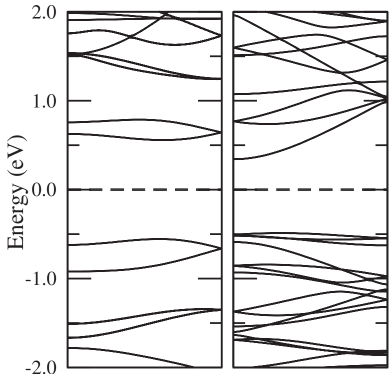

FIG. 1. Band structure of the armchair (3,3) and zigzag (4,0) BC_2N nanotubes, respectively.

We study the adsorption of a H atom in the inner side and in the outer side of the tube surface. The outer side is more stable by ≈0.1 eV, depending on the tube diameter and on the particular site for the H adsorption. In the case of the H atom adsorbed on the outer side, we study the H adsorption on the top site of B (H-B) atom, on the top site of N atom (H-N), and on the top site of two nonequivalent carbon atoms, H-C_I and H-C_{II}. We denote C_I as the carbon atom that is bounded to two other carbon atoms and a boron atom. C_{II} is the carbon atom that is bounded to two other carbon atoms and a nitrogen atom. Table I summarizes the results for the binding energy, the distance between the adsorbed H atom and its nearest neighbor, and the outward relaxation of the hydrogenated atom from the tube surface. From the results shown in this table, we observe that the atomic hydrogen prefers to adsorb on top of carbon atoms for both zigzag and

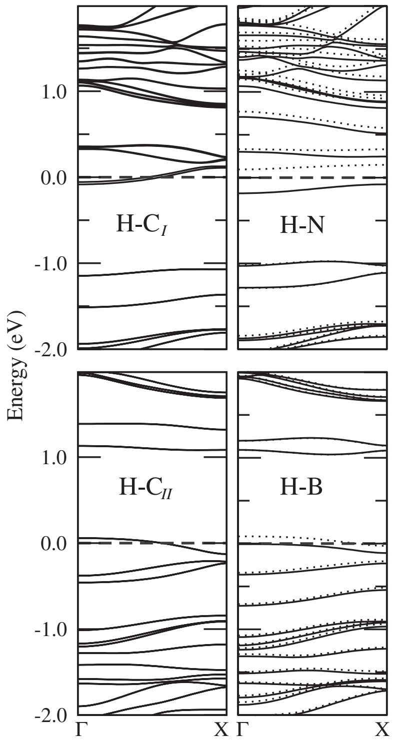

FIG. 2. Band structure of the armchair (3,3) BC_2N nanotube when a H atom is adsorbed on the C_I, C_{II}, N, and B sites. The Fermi energy represented by the dashed line is always set on the zero energy. The solid lines correspond to spin up bands, and the dotted lines the spin down bands.

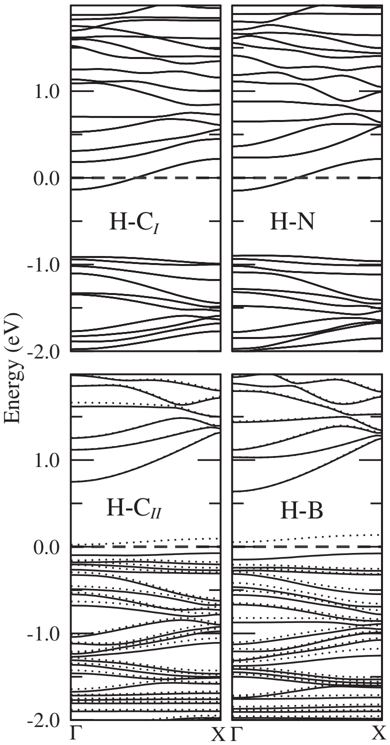

FIG. 3. Band structure of the zigzag (4,0) BC_2N nanotube when a H atom is adsorbed on the C_I, C_{II}, N, and B sites. The Fermi energy represented by the dashed line is always set on the zero energy. The solid lines correspond to spin up bands, and the dotted lines the spin down bands.

armchair BC_2N nanotubes. Also, we observe that, in general, the H atoms are stronger bonded to the (4,0) than to the (3,3) BC2N nanotube. Two effects contribute for this finding: (i) the unit length for the (4,0) is greater than that of the (3,3) (interaction between the H atoms), and (ii) the (4,0) has a smaller diameter (curvature effect). To investigate the chirality effects, we have performed calculations for H adsorption on the (5,0) type-II BC_2N nanotube, which have a diameter (8.10 Å) similar to that of the (3,3) nanotube. The binding energies (in parenthesis in Table I) are very similar to those of the armchair (3,3) nanotube, showing that chirality effects are minimum for these nanotubes. The binding energies of the H with C atoms are always higher than those with N atoms. This result can be understood by the fact that C atoms when bounded to H atoms are more stable when fourfold coordinated, while N prefer to be threefold coordinated. For example, this is the case of the CH_4 and NH_3 compounds. Although the smaller binding energies (less stable configurations) are obtained when the H atoms are bounded to N atoms, these configurations present the smaller bond lengths between the H atoms and the host N atoms (see fourth column of Table I). The last column of Table I shows the relative displacement of the host hydrogenated atom before and after the H adsorption. For all configurations, the hydrogenated atoms relax outward from the tube surface. It is interesting to know that for the most stable site of the atomic H [H on the top of C_I atom in the (4,0) nanotube], the hydrogenated C_I atom presents the lowest relaxation.

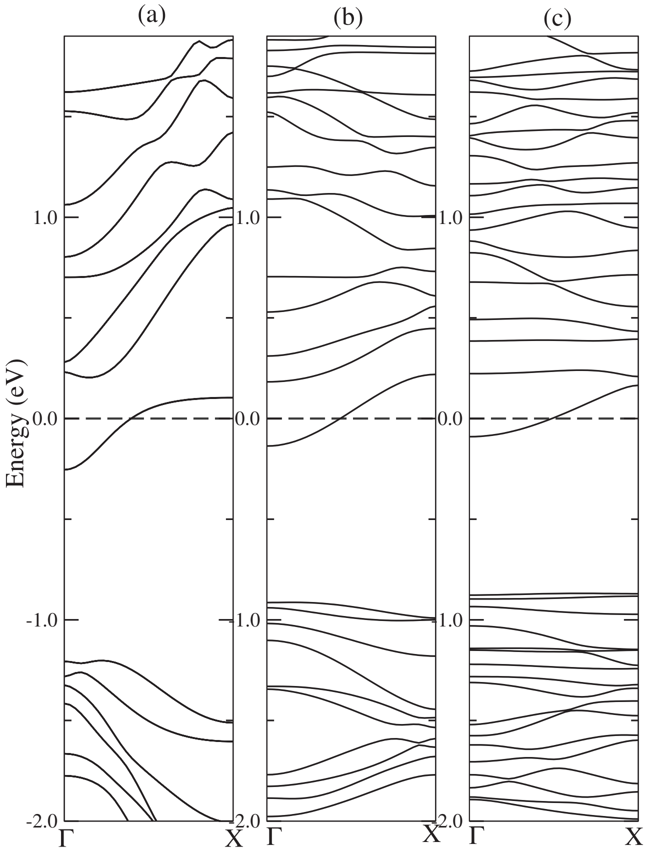

FIG. 4. Band structure of the zigzag (4,0) BC_2N nanotube when a H atom is adsorbed on C_I sites for nanotubes lengths of 8.74, 17.49, and 26.23 Å. The dotted line represents the Fermi energy.

Theoretical calculations show that all type-II BC_2N nanotubes are semiconductors.[13,15] Our calculated band structure (Fig. 1) shows that the band gaps for the armchair (3,3) and the zigzag (4,0) BC_2N nanotubes are 1.1 and 0.8 eV, respectively. The adsorption of an atomic hydrogen on top site of C_I and N of the armchair (3,3) and zigzag (4,0) nanotubes moves the Fermi energy to the conduction band minimum (CBM), and the adsorption of the H atom on top site of the C_{II} and B atoms moves the Fermi energy to the valence band maximum (VBM). These results are showed in Figs. 2 and 3. It is important to stress that the roles played by the C_I and C_{II} are quiet different. The C_I behaves like an anion site and the C_{II} like a cation site. In particular, the H-C_I system acts as donor and H-C_{II} as acceptor. In fact, the most stable adsorption site for the atomic hydrogen, H-C_I site for both chiralities, presents a metallic behavior. This metallic behavior was obtained for H concentrations of 1.56%, 0.78%, and 0.52% (corresponding to H-H distances of 8.74, 17.49, and 26.23 Å, respectively). As observed in Fig. 4, a semioccupied energy band around the CBM is kept even for a H-H distance of 26.23 Å. With respect to the polarization of the spin, it is interesting to observe that for metallic systems the spin is quenched, as is the case of H-C_I and H-C_{II} of the armchair nanotube and the H-C_I and H-N of the zigzag nanotube. By increasing the distance between the adsorbed H, the metallization and the spin paired are preserved (see Fig. 4). These results are similar to those obtained by Duplock *et*

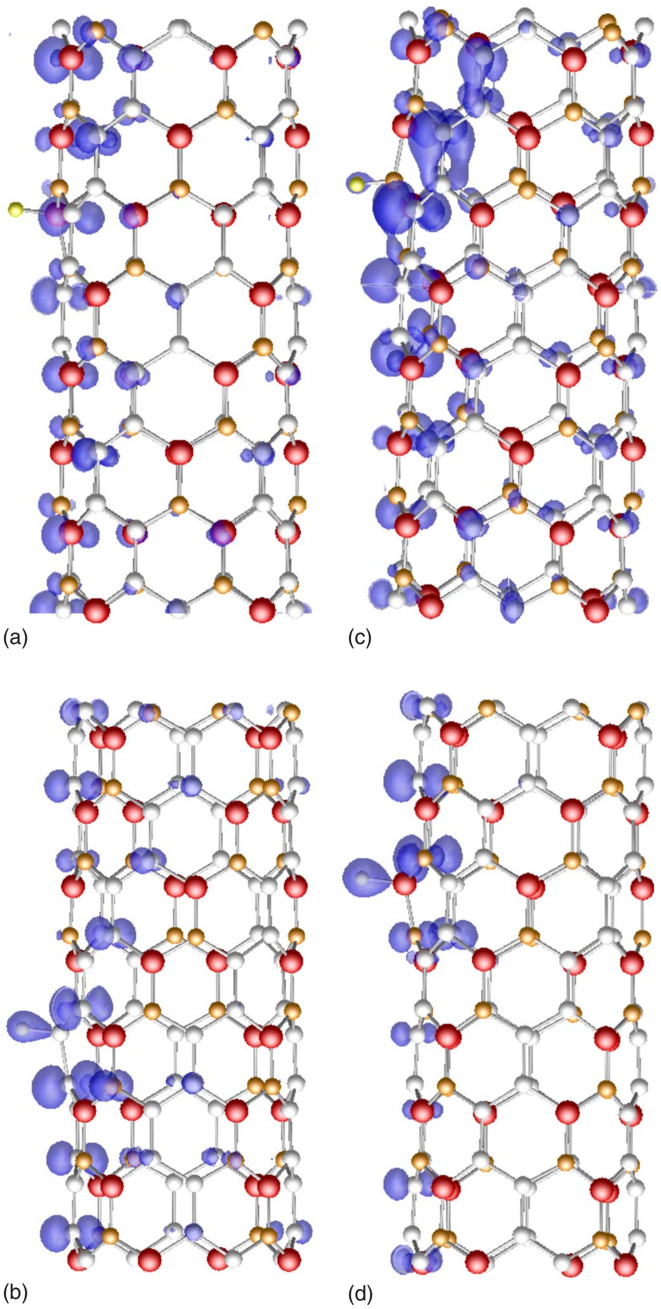

FIG. 5. (Color online) Highest occupied molecular orbital (HOMO) for the (4,0) BC_2N nanotube when a hydrogen is adsorbed on the C_I (top-left), C_{II} (top-right), N (bottom-left), and B (bottom-right) sites, respectively. The bigger (red), the medium (white), the small (orange), and the smaller one (yellow) balls represent the B, C, N, and the H atoms, respectively.

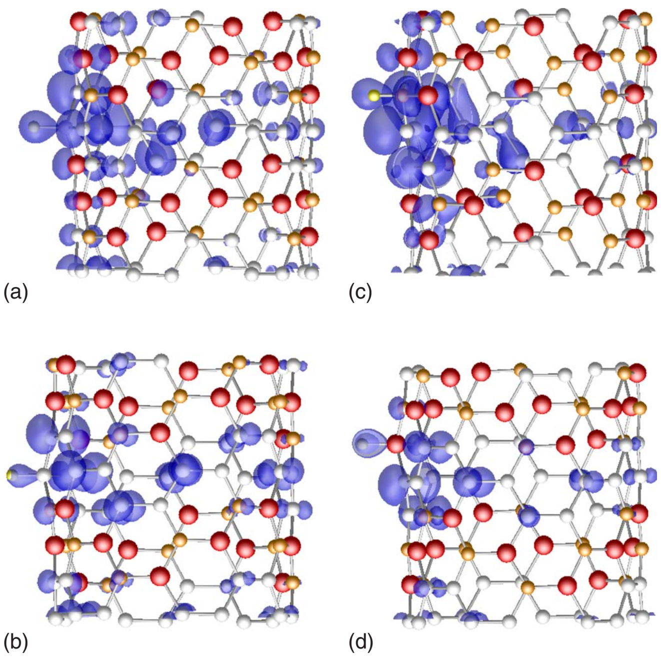

FIG. 6. (Color online) HOMO for the (3,3) BC_2N nanotube when a hydrogen is adsorbed on the C_I (top-left), C_{II} (top-right), N (bottom-left), and B (bottom-right) sites, respectively. The bigger (red), the medium (white), the small (orange), and the smaller one (yellow) balls represent the B, C, N, and the H atoms, respectively.

al.[29] for atomic hydrogen adsorbed on graphene with a Stone-Wales defect, where the metallization has been observed to quench the spin.

To understand the electronic properties played by the H adsorption, we have to look at the band structure of the pristine BC_2N nanotubes. As already described,[13–15] the states at the VBM come mainly from C_I atoms and the states at the CBM come from C_{II} atoms for both chiralities. However, the CBM of the zigzag nanotube has a large energy dispersion as compared to that of the armchair nanotube. Consequently, the H adsorbed on C_I and N atoms induces a semioccupied energy band with a large delocalized charge distribution, as shown in Fig. 5. On the other hand, for the H adsorbed on C_{II} and B atoms of the zigzag nanotube as well on the top sites of the armchair tube, the charge density of the semioccupied energy bands is more localized, as shown in Figs. 5 and 6.

In order to understand the H adsorption evolution, we added a second H atom in a neighboring site on the surface of the nanotubes, in such way that the H atoms are on adjacent sites or second neighbors. The adsorption of two H atoms is a favorable process for most of the configurations. The configuration with two H atoms bounded to adjacent carbon atoms ($H\text{-}C_I$+$H\text{-}C_{II}$) is the most stable one for both chiralities (see Table II). By comparing two H atoms bounded to C_I nearest neighboring sites with respect to two H atoms bounded to C_I sites far from each other, the binding energy is higher for the later by ≈0.18 and 0.14 eV for the (3,3) and (4,0) nanotubes, respectively. When two H atoms are bounded on the nanotube surface, we have electronically three different configurations: nonactive center, when the band gap is free of levels, similar to that of the freestanding nanotube (na); *n* type, when the Fermi energy is around the CBM; and *p* type, when the Fermi energy is around the VBM. The character is indicated in the last column of Table II. The most stable sites for two adsorbed atomic H are those electronically nonactive centers.

B. Adsorption of H_2 molecule

In the case of the H_2 molecule on the surface of armchair (3,3) and zigzag (4,0) BC_2N nanotubes, we focus on the

TABLE II. Calculated binding energies per H atom (in eV) when two adjacent atomic H are adsorbed on the armchair (3,3) and on the zigzag (4,0) BC_2N tube surfaces. The last column represents the electronic character of the system (see text). The values in parenthesis are the binding energies per H adsorbed on the same configuration, however, in sites far from each other.

	E_b		Character
	(3,3)	(4,0)	
Tube+2H-C_I	−1.45 (−1.63)	−1.81 (−1.95)	*n*
Tube+2H-C_{II}	−1.39 (−1.53)	−1.50 (−1.51)	*p*
Tube+H-C_I+H-C_{II}	−2.31 (−1.58)	−2.35 (−1.73)	na
Tube+H-C_I+H-B	−2.19 (−1.48)	−2.19 (−1.65)	na
Tube+H-C_I+H-N	−1.04 (−1.01)	−1.35 (−1.47)	*n*
Tube+H-C_{II}+H-B	−1.50 (−1.43)	−1.42 (−1.43)	*p*
Tube+H-C_{II}+H-N	−1.68 (−0.96)	−1.80 (−1.25)	na
Tube+H-B+HN	−1.61 (−0.86)	−1.94 (−1.17)	na

TABLE III. Calculated binding energies (in meV) for H_2 adsorbed on the BC_2N nanotube surface and distances (in Å) between the tube and the closest H atom of the H_2 molecule.

	Symmetry	E_b	$d_{\text{tube-H}}$
Tube+H_2-B	Zigzag	−70	2.82
Tube+H_2-B	Armchair	−69	2.95
Tube+H_2-N	Zigzag	−62	2.64
Tube+H_2-N	Armchair	−53	2.79
Tube+H_2-C_I	Zigzag	−98	2.58
Tube+H_2-C_I	Armchair	−102	2.76
Tube+H_2-C_{II}	Zigzag	−85	2.93
Tube+H_2-C_{II}	Armchair	−84	2.86
Tube+H_2-hex	Zigzag	−95	2.52
Tube+H_2-hex	Armchair	−95	2.56

energetic properties. The most stable position for the H_2 is on the top site of C_I atoms. Different from the atomic H, here we have a new site for the H_2 molecule, which is on the center of a hexagon. The H_2 adsorbed on this site is the second more stable one. In Table III, we present the results for the binding energy for several configurations. It is important to observe that all configurations for the H_2 molecule on the tube surface present binding energies from 50 to 100 meV. The H_2 molecule is physisorbed on the BC_2N nanobute surface.

As it is known, the GGA approximation, which we have used in these calculations, underestimates binding energies. In this way, we expect, experimentally, greater binding energies than those presented in Table III, in such way that the binding energies for the H_2 molecule adsorbed on the BC_2N nanotube can be in the range to work as a hydrogen storage medium.[30–32]

We can see from Table III that, although the distances between the H_2 molecule and the nanotube surface (last column of Table III) are changed from 2.52 to 2.95 Å, the binding energies are little changed. These differences on the tube-molecule distances are related with the ionicity of the different sites of the tube surface. The small difference among the binding energies for the different sites is typical for physisorbed processes, where the potential energy curves for the H_2 molecule approaching to the BC_2N surface are very smooth, as also observed for H_2 on BN and C doped BN nanotubes.[20]

We analyze the possibility of the H_2 molecule to be dissociated when it approaches to the BC_2N nanotube surface. Using the same calculation procedure, we evaluate the binding energy of an isolated H_2 molecule, obtaining a value of −4.34 eV. To dissociate a H_2 molecule, the energy gain of two isolated H atoms adsorbed on the tube surface must be greater than the H_2 binding energy plus the binding energy of the H_2 on the tube surface (≈4.44 eV), not considering kinetic and thermal energies. By looking the binding energies shown in Table II, we observe that only the H-C_I+H-C_{II} configuration has binding energies (−2.31 and −2.35 eV per H) in the range to break the H_2 molecule in the conditions described above. The energy differences between the adsorbed H_2 molecule on the most stable (C_I site) and the adsorption of two H atoms on the C_I and C_{II} sites are 0.19 and 0.27 eV for the armchair (3,3) and zigzag (4,0), respectively. For all other configurations, the H_2 molecule should not be dissociated.

IV. CONCLUSION

In summary, our first-principles calculations show that atomic hydrogen adsorbed on the (3,3) armchair and (4,0) zigzag BC_2N nanotubes induces the system to exhibit acceptor or donor characteristic depending on which site the hydrogen is adsorbed. The H atoms are preferentially adsorbed on the top of two nonequivalent C atoms that behave like an anion or a cation site. The adsorption of two adjacent H atoms is a favorable process, being the most stable configuration where both H atoms are adsorbed on the two nonequivalent nearest neighbor C atoms (H-C_I+H-C_{II}). For both chiralities, the H_2 molecules are physisorbed on the nanotube surface. The binding energies present a small dependence on the tube surface site, and these energies are near to the range to work as a hydrogen storage medium. Our results show that there is one conformation where the H_2 molecule can be dissociated.

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