ORIGINAL PAPER

NH_3 on a BC_3 nanotube: effect of doping and decoration of aluminum

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Abstract The adsorption of the NH_3 molecule was investigated on pristine, Al-doped and Al-decorated BC_3 nanotubes (BC_3NT) using density functional theory calculations. It was found that NH_3 prefers to be adsorbed on a B atom of the tube wall, releasing energy of 1.02 eV. Al-doping increases the acidity of the tube surface and, therefore, its reactivity toward NH_3 so that the released energy in this case is about 1.62 eV, while decorating the BC_3NT with Al atom decreases the acidity and reactivity. Although Al-doping has no significant effect on the electronic properties of the BC_3NT, Al-decoration significantly reduces its HOMO/LUMO energy gap from 2.37 to 1.16 eV so that the tube becomes an *n*-type semiconductor. However, we believe that the acidity of the BC_3NTs may be controlled by doping or decoration of Al atoms.

Keywords Boron carbide nanotube · Density functional theory · Computational study · Band gap

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], much research has focused on these new nanoscale tubular materials because of their great potential in technological applications [2–7]. It was postulated that other compounds that form laminar graphite-like structures could also form nanotubes. Nanotubes of BN, AlN and SiC have been synthesized successfully [8–10]. Theoretical studies have shown that CNTs could be either metallic or semiconducting, depending on radii and chirality. However, BN nanotubes combine both ultimate strength and stable dielectric properties. They are predicted to be semiconductors regardless of their diameter, chirality, or the number of walls of the tube. Substituting CNTs with other elements like B or N can tune their electronic properties efficiently and lead to novel applications [11, 12]. B-doped CNT or composite boron–carbon nanotubes of different B/C ratio have been synthesized [13, 14]. For higher levels of boron doping, the boron carbide nanotube with the particular stoichiometry of BC_3 is feasible [15]. Just like CNTs, BC_3 nanotubes (BC_3NTs) can be structurally formed by rolling a BC_3 sheet along the chiral vector. On the BC_3 sheet and, thus, on the BC_3NTs, there are only B–C and C–C chemical bonds; the less stable B–B bonds are excluded [16, 17]. BC_3NTs have been synthesized [18], and the electronic structures have also been investigated theoretically [19].

The reactivity of these nanotubes is often adjusted by doping or decoration with other elements. It is important to understand and to be able to quantify modification of the surface properties by the addition of such elements. Surface acidity is an important property that is used frequently to characterize the reactivity of surfaces. Ammonia (NH_3) is used widely as the probe molecule in experimentally determining the Lewis and Brønsted acidity of surfaces, and the binding energy to a particular site on the surface serves as a measure of acid strength [20]. Most surfaces have several types of reactive sites and, with the addition of a dopant and decorant, the number of such sites can be additionally increased [21]. Theoretical methods are well suited to probing the strength of the binding of NH_3 for these numerous

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reactive sites numerically, thus providing rich information about the reactivity of the surface [22, 23].

In this work, the interaction of NH_3 with BC_3NTs will be investigated theoretically based on analyses of structure, energies, electronic properties, etc. The main purpose of this study is to gain fundamental insights into the influence of aluminum doping and decoration on the adsorption properties of the nanotube with NH_3, and how these effects could change the acidity of BC_3NTs.

Computational methods

We selected a (8, 0) zigzag BC_3NT consisting of 72 C and 24 B atoms, in which the end atoms have been saturated with hydrogen atoms to reduce boundary effects. This tube is a closed shell system in which all electrons are paired. Geometry optimizations, energy calculations, and density of states (DOS) analysis were performed on the nanotube and different NH_3/nanotube complexes using B3LYP functional with 6–31G (d) basis set as implemented in the GAMESS suite of program [24]. The DOS describes the number of states per interval of energy at each energy level that are available to be occupied by electrons, and was calculated using the GaussSum program [25].

The B3LYP has been demonstrated to be a reliable and commonly used level of theory in the study of different nanostructures [26–30]. Matsuda et al. [31] reported ab initio quantum mechanical calculations of band structures of single-walled carbon nanotubes using the B3LYP flavor of density functional theory (DFT). They found that B3LYP leads to very accurate E_g values compared to experimental results, suggesting its use in designing carbon nanotube devices. We defined adsorption energy in the usual way as:

$$E_{ad} = E\left(NH_3 \big/ nanotube\right) - E(nanotube) - E(NH_3) + E_{BSSE} \quad (1)$$

where E (NH_3/nanotube) corresponds to the energy of the nanotube in which a single NH_3 has been adsorbed on the inner and outer wall, E (nanotube) is the energy of the isolated tube, E (NH_3) is the energy of a single NH_3 molecule, and E_{BSSE} is the energy of the basis set superposition error. 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). Also, E_g designates the gap between singly occupied molecular orbital (SOMO) and LUMO in open shell systems. It is noteworthy 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, the Fermi level of the systems considered herein is at the center of the E_g.

Results and discussion

NH_3 adsorption on pure BC_3NT

Figure 1a shows a partial structure of a side view of the optimized BC_3NT. Two types of B–C bonds can be found: one with a bond length of 1.57 Å and in parallel with the tube axis, and another with bond length 1.56 Å, but not in parallel with the tube axis (diagonal). Two types of C–C bonds also exist in the tube, with the parallel bond having a bond length of 1.41 Å and other one 1.42 Å. There are two types of carbon atoms in BC_3NT; C_I is a carbon atom that is bonded to the B atom in parallel with the tube axis, while C_{II} is a carbon atom that is bonded to the B atom (diagonal B–C bond).

To obtain the most stable configuration of single NH_3 adsorbed on the BC_3NT, various possible initial adsorption geometries, including single (hydrogen or nitrogen) and double (N–H) bonded atoms to B and C atoms on different adsorption sites are considered. However, only one stable structure was obtained upon the relaxation process (Fig. 2). More detailed information from the simulation of different NH_3/BC_3NT systems, including values of E_{ad}, E_g and the charge transfer (Q_T) for this configuration is listed in Table 1. This configuration stands for the covalent bonding between the nitrogen atom of the NH_3 molecule and the boron atom of the nanotube with a distance of 1.68 Å. The adsorption of NH_3 on the B site in BC_3NT can be rationalized by molecular electrostatic potential (MEP) analysis. Based on Mulliken population analysis, the point charge of boron in BC_3NT is + 0.44 e, which is in agreement with our calculated MEP. As shown by the mapped MEP of BC_3NT in Fig. 1b, B atoms are positively charged (blue) while C atoms are negatively charged (red) in B–C bonding. As a result, ammonia adsorption (Lewis base that acts as a probe molecule in experimentally determining the acidity of surfaces) is adsorbed strongly on Lewis acid sites (B site). This configuration indicated that a net charge of about 0.240 electron transfers from the molecule to the tube and its corresponding calculated E_{ad} value (Table 1) is about −1.02 eV. The more negative E_{ad} of NH_3 on BC_3NT and the transferred charge between them reveal the chemical nature of the interaction, suggesting the high acidity behavior of BC_3NTs.

Next, we studied the influence of NH_3 adsorption on the electronic properties of the nanotube. For bare BC_3NT (Fig. 1a), it can be concluded that it is a semi-conducting material with an E_g of 2.37 eV. By referring to Fig. 2, both conduction and valence levels move to higher energies, so that the E_g of the tube decreased from 2.37 eV in the bare tube to 2.32 eV for the NH_3/BC_3NT complex. Also, the Fermi level of the tube (−4.96 eV) is shifted to a slightly higher energy value (−4.77 eV). However, this change in electronic properties is negligible, indicating that BC_3NT is still a semiconductor after NH_3 adsorption.

Fig. 1 **a** Partial structure of optimized BC$_3$NT and its density of states (DOS) plot. Bonds lengths are in Ångstroms. **b** Calculated molecular electrostatic potential (MEP) surface of BC$_3$NT. *Red* High electron density, *blue* positive sites
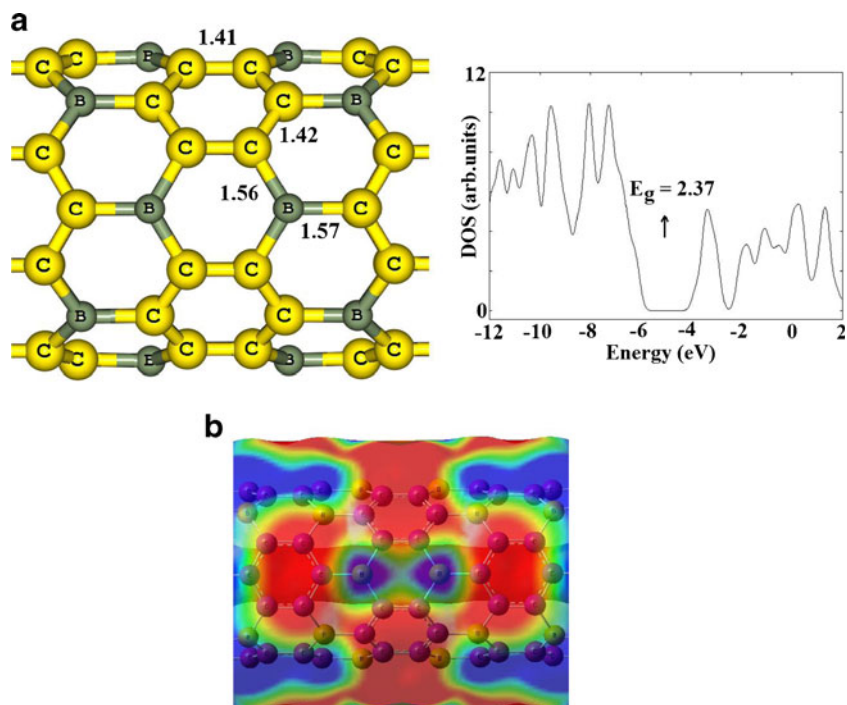
As a comparison, we investigated the adsorption of an NH$_3$ molecule on a BC$_3$ graphene-like sheet. To this end, a BC$_3$ sheet consisting of 102 C and 34 B atoms was selected, in which the end atoms were saturated with hydrogen atoms. In the optimized sheet, two types of B–C and C–C bonds can be identified, with corresponding lengths of 1.56, and 1.42 Å, respectively. The calculated E_g of this sheet is about 2.65 eV, which is smaller than that of the tube by about 0.28 eV. The trend of the NH$_3$ process on the sheet is similar to that on the tube, whereas the NH$_3$ molecule tends to attack a B atom of the sheet from its N atom, forming an N–B bond with length of 1.73 Å, which is longer than the N–B formed in the NH$_3$/tube complex. We calculated the E_{ad} value for the adsorption process on the sheet to be about 0.98 eV. The longer formed N–B bond and less negative E_{ad} value indicate that adsorption of NH$_3$ is weaker on the sheet than

in the tube. This may be due to the fact that the adsorbing B atom of the tube can be hybridized more easily to sp^3 than the adsorbing B atom of the sheet.

NH$_3$ adsorption on Al-doped BC$_3$NT

Furthermore, the effects of substituting the adsorbing B atom by an Al atom on the geometric structure and electronic properties of BC$_3$NT, and on the acidity of surface were investigated. Substituting the B atom with the impurity represented by Al, distorted the geometric structure of BC$_3$NT dramatically (Fig. 3). It should be noted that the Al-doped nanotube is an open shell system due to the existence of an unpaired electron in the SOMO. In the optimized Al-doped

Fig. 2 Model for stable adsorption of NH$_3$ on BC$_3$NT and its DOS plot. Bonds are in Ångstroms
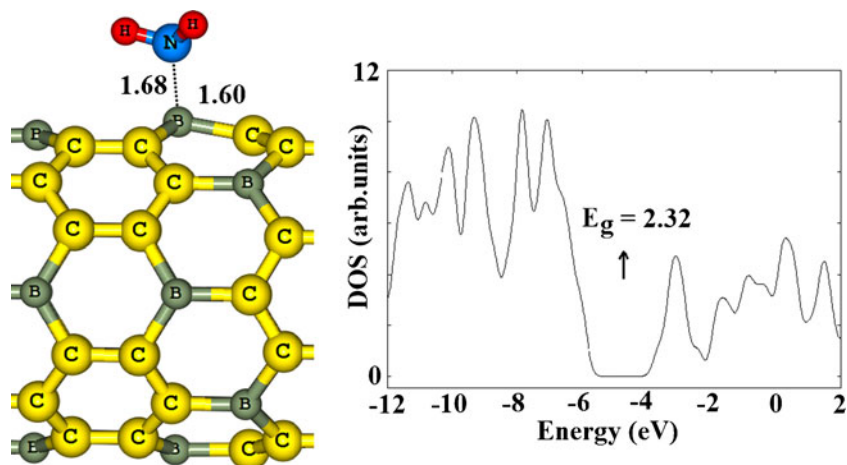
Table 1 Calculated adsorption energy of NH$_3$ (E_{ad}, eV), highest occupied molecular orbital (HOMO) energies (E_{HOMO}), lowest unoccupied molecular orbital (LUMO) energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Fermi level (E_F) of systems (Figs. 1–6) in eV

System	E_{ad}	Q_T (e) a	E_{HOMO}	E_F	E_{LUMO}	E_g
BC$_3$NT	–	–	−6.15	−4.96	−3.78	2.37
BC$_3$NT/NH$_3$	−1.02	0.240	−5.93	−4.77	−3.61	2.32
Al-doped BC$_3$NT	–	–	−6.13	−4.94	−376	2.37
Al-doped BC$_3$NT/NH$_3$	−1.62	0.286	−5.82	−4.68	−3.55	2.27
Al-decorated BC$_3$NT	–	–	−5.26	−4.68	−4.10	1.16
Al-decorated BC$_3$NT/NH$_3$	−0.66	0.250	−5.03	−4.44	−3.85	1.18

^{a} Q_T is defined as the total Mulliken charge on NH$_3$

tube, the Al atom impurity is projected out of the tube surface in order to reduce stress due to its larger size compared to the B atom. The calculated bond lengths are 1.88 and 1.90 Å for the C–Al bonds in the Al-doped BC$_3$NT, which are much longer than the corresponding B–C bonds in the pristine tube. Also, the Al–C–Al angles in the doped tube are 111° and 112°, i.e., smaller than the B–C–B angles in the pristine tube (117° and 120°).

Subsequently, we explored NH$_3$ adsorption on the Al-doped tube by locating the molecule above the Al atom with different initial orientations including the N or H atom of the molecule that is close to Al. After relax optimization of the initial structures, only one final stable structure was obtained (Fig. 4). Interestingly, during optimization, the NH$_3$ reoriented in such a way that its N atom moved closer to the Al site, with an E_{ad} of −1.62 eV. Also, the corresponding interaction distance between the Al atom of the doped-tube and the NH$_3$ is 2.00 Å. Larger charge transfer (0.286 e) and more negative E_{ad} between Al-doped BC$_3$NT and NH$_3$ indicated that doping of Al in BC$_3$NT can improve the acidity of the tube, which is in agreement with the usual mechanism proposed for such binding: the NH$_3$ binds at the exposed Al atom, which is electron-deficient and can receive electrons from the lone pair orbitals of nitrogen. Why is the reaction of NH$_3$ with the Al-doped tube more favorable than that with the pristine one? To answer this question, we performed natural bond orbital (NBO) analysis of the Al-doped BC$_3$NT. NBO analysis indicates that, unlike boron atoms, hybridization of the Al atom is approximately sp^3, and it can

have a coordination number of four. This site, which can accept electrons, is referred to as a "Lewis acid site" (and conversely, ammonia is termed a "Lewis base"). The calculated DOS of Al-doped BC$_3$NT is shown in Fig. 2a, indicating that its E_g value is similar to the pristine tube with E_g of 2.37 eV, revealing the semiconducting property of Al-doped BC$_3$NT. Figure 4 shows that NH$_3$ adsorption through this configuration has no detectable effect on the electronic properties of the tube, although that the E_g of the tube has slightly decreased from 2.37 to 2.27 eV. The calculated DOS values show that NH$_3$ adsorption on BC$_3$NT can be generally classified as a certain type of "electronically harmless modification". In other words, the electronic properties of BC$_3$NT are changed only negligibly by NH$_3$ adsorption.

NH$_3$ adsorption on Al-decorated BC$_3$NT

We first studied the bonding of a single Al atom to BC$_3$NT to form Al-decorated BC$_3$NT. In other words, in the decorated BC$_3$NT, an Al atom is adsorbed onto the surface of the tube. All systems containing the Al-decorated BC$_3$NT are open shell systems due to presence of an unpaired electron in the SOMO. With the optimized structures, the decoration energy (E_{dec}) of the Al on the pure nanotube is obtained using the following equation:

$$E_{dec} = E(Al-BC_3NT) - E(Al) - E(BC_3NT) \quad (2)$$

Fig. 3 Partial structure of optimized Al-doped BC$_3$NT and its DOS plot. Bonds are in Ångstroms
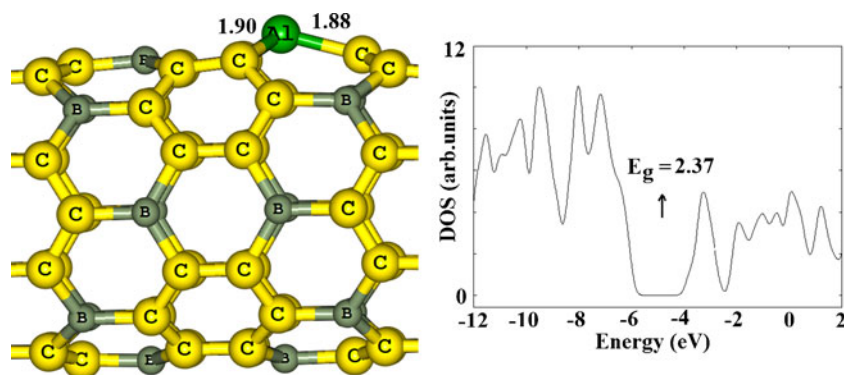
Fig. 4 Models for stable adsorption of NH₃ on the Al-doped BC₃NT and its DOS plot. Bonds are in Ångstroms
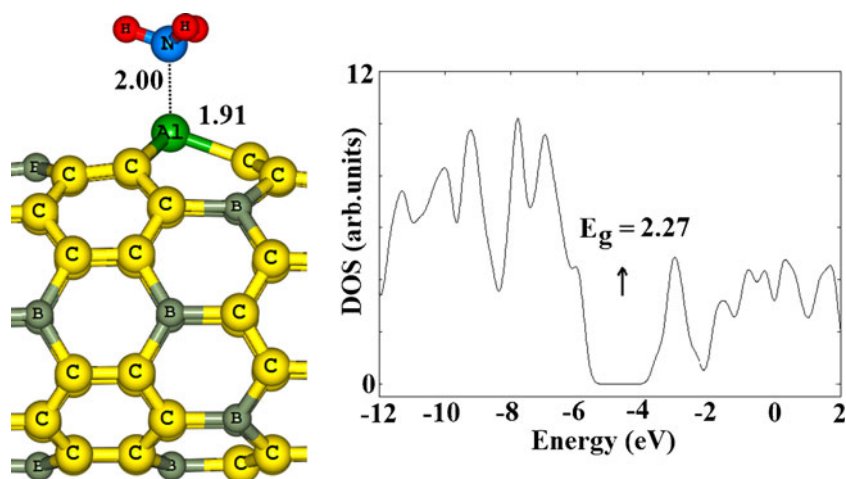
Fig. 5 Partial structure of optimized Al-decorated BC₃NT and its DOS plot. Bonds are in Ångstroms. As this system is open shell (with an unpaired electron) in its DOS plots, *red*, *green* and *blue* designate spin up, spin down and total DOS, respectively

Fig. 6 Model for the stable adsorption of NH₃ on Al-decorated BC₃NT and its DOS plot. Bonds are in Ångstroms. As this system is open shell (with an unpaired electron) in its DOS plots, *red*, *green* and *blue* designate spin up, spin down and total DOS, respectively
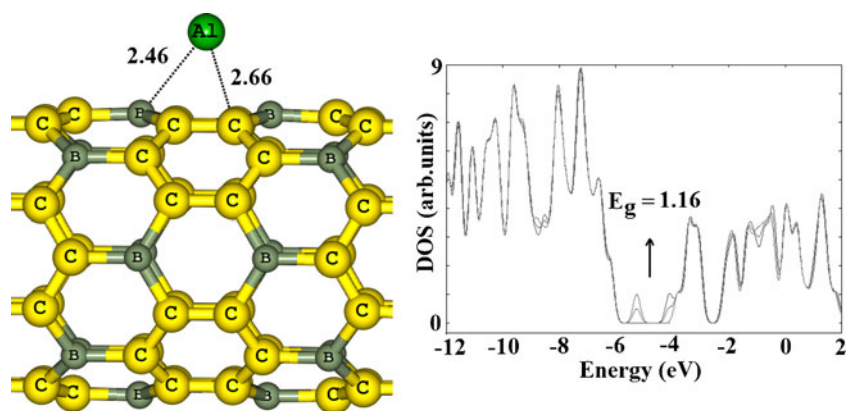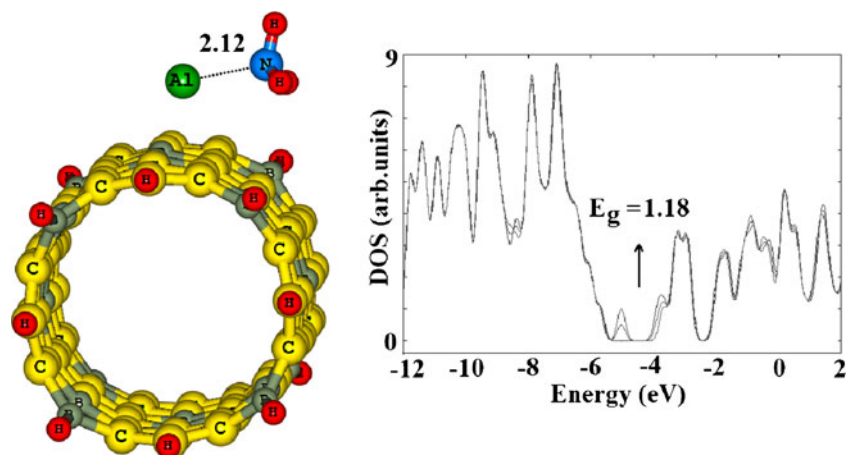
where E (Al–BC$_3$NT) is the total energy of Al decorated on the BC$_3$NT surface, and E (BC$_3$NT) and E (Al) are the total energies of the pristine BC$_3$NT and an Al atom, respectively. To find the minimum adsorption configurations for Al–BC$_3$NT complexes, Al was placed initially at different positions above the BC$_3$NT. Five possible adsorption sites on the BC$_3$NT, i.e., two top sites (C and B atoms), two bridge sites (B–C and C–C bonds) and two rings (C$_6$ and C$_4$B$_2$), were selected to examine the interaction between the tube and a single Al, and we found that the optimal position is over the H1 site of the BC$_3$NT (Fig. 5). The distance between Al and the tube surface is about 2.00 Å with an E_{dec} of −1.58 eV.

After investigating the stability of Al-decorated BC$_3$NT, we next studied the interaction between this complex and the NH$_3$ molecule. When one NH$_3$ molecule is adsorbed, the molecule is re-oriented to the side of the Al atom near to the BC$_3$NT surface. As shown in Fig. 6, the distance between the N atom of NH$_3$, and the decorated Al atom of the tube is 2.12 Å. The E_{ad} value for this configuration is about −0.66 eV with a charge transfer of about 0.250 e to the Al-decorated BC$_3$NT. In comparison, Al-decorated BC$_3$NT has a lower reactivity than pristine and Al-doped BC$_3$NT toward the NH$_3$ molecule. The nature of the nanotube's DOS near the Fermi level is critical to the understanding of electrical transport through these materials. Therefore, we have drawn DOS plots for the Al-decorated tube with and without NH$_3$. It should be noted that, herein, E_g stands for SOMO/LUMO energy gaps for open shell systems. The calculated DOS of Al-decorated BC$_3$NT is shown in Fig. 3a, indicating that HOMO and LUMO levels changed significantly, and its E_g value is reduced to 1.16 eV compared to the pristine BC$_3$NT. However, the Al-decorating forms a donor-like level, revealing that decorating semiconducting BC$_3$NTs with Al atom will create an n-type semiconducting material, resulting in increased conductivity. Table 1 and Fig. 6 show that the conduction, valence and Fermi levels of the tube shift simultaneously to higher energies upon the adsorption of NH$_3$ on Al-decorated BC$_3$NT, but cannot change the E_g of the tube. Thus, doping and decoration of Al can increase and decrease the Lewis acidity of the surface, respectively.

Conclusions

Surface acidity is an important property that is used frequently to characterize the reactivity of surfaces. The adsorption of ammonia at Lewis acid sites on the BC$_3$NT surface was investigated using DFT methods. It was found that NH$_3$ can be attached to the boron atom of the BC$_3$NT as Lewis acid sites. The relative magnetic order of the acidity for different surfaces is: Al-doped BC$_3$NT (E_{ad} of −1.6 eV)>BC$_3$NT (E_{ad} of −1.02 eV)>Al-decorated BC$_3$NT (E_{ad} of −0.66 eV), indicating that the acidity of BC$_3$NT can be controlled by doping or decorating the Al atom.

Although Al-doping has no significant effect on the electronic properties of the BC$_3$NT, the Al-decoration significantly reduces its E_g value from 2.37 to 1.16 eV.

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