Chemical Functionalization of Boron−Nitride Nanotubes with NH₃ and Amino Functional Groups

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Abstract: We have investigated properties of chemically modified boron nitride nanotubes (BNNTs) with NH₃ and four other amino functional groups (NH_2CH_3, $NH_2CH_2OCH_3$, NH_2CH_2COOH, and NH_2COOH) on the basis of density functional theory calculations. Unlike the case of carbon nanotubes, we found that NH₃ can be chemically adsorbed on top of the boron atom, with a charge transfer from NH₃ to the BNNT. The minimum-energy path calculation shows that a small energy barrier is encountered during the adsorption. Similarly, a small energy barrier (about 0.42 eV) is also involved in the desorption, suggesting that both adsorption and desorption can be realized even at room temperature. For chemically modified BNNTs with various amino functional groups, the adsorption energies are typically less than that of NH₃ on the BNNT. The trend of adsorption-energy change can be correlated with the trend of relative electron-withdrawing or -donating capability of the amino functional groups. Overall, the chemical modification of BNNTs with the amino groups results in little changes in the electronic properties of BNNTs. However, the chemical reactivity of the BNNTs can be enhanced by the chemical modification with the amino group containing −COOH.

Introduction

It is known that nanotubes tend to clump together into bundles due to intertube dispersion interactions. This tendency of tube association posts a hindrance for further purifying and processing of nanotubular materials. Chemical functionalization of nanotubes offers an effective route to enhance solubility of nanotubes in solvent, thereby deterring nanotubes from association. In addition to solubility enhancement, chemical functionalization through either covalent sidewall or noncovalent exohedral/endohedral functionalization can further expand potential applications of nanotubes when coupled with functionalities of the addends, for example in developing nanotube-based electronic devices, precursors, and sensors. Until now, much research efforts have been focused on chemical functionalization of carbon nanotubes (CNTs).[1−14] Experimentally, direct functionalization of the CNTs with various chemical functional groups has been reported, including covalent functionalization of the sidewall and the tip of CNTs,[1−9] as well as noncovalent functionalization of the sidewall.[10−11] Upon covalent functionalization, previous experiments have shown that the CNTs can be functionalized by using carboxylic acid[1,2] or fluorine,[3] followed by subsequent derivatization reactions with other functional groups, such as thionyl chloride,[1,2,6c] alkyllithium,[4] nitrenes,[5] amine,[1,2,6] diazonium reagents,[7] and azomethine ylides.[8] Upon noncovalent functionalization, CNTs can be coated with conjugated organic molecules[10] or biomolecules[11] through π-stacking interaction. On the theoretical side, chemical functionalization of the CNTs with several molecular functional groups has also been studied, from which insights into the CNT/

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addend interaction as well as the electronic properties modified by the addends have been attained.[12−14] The advances in both experiments and theories have prompted development of CNT-based polymeric compositions and biological sensors.

Similar to the CNTs, boron−nitride nanotubes (BNNTs) also possess many unique properties. In particular, BNNTs are semiconductors with a wide band gap ($\sim$5.5 eV) that is weakly dependent on the tube diameter, helicity, and the number of walls.[15−18] Compared with the CNTs, BNNTs not only have high thermal conductivity but also high oxidation resistivity as well as high thermal and chemical stability,[19−21] which render BNNTs a promising tubular material for developing nanotube-based electronic devices in certain hazardous and high-temperature environments. However, the tendency of tube association into bundles coupled with the insolubility of BNNTs in water and many other organic solvents has been a challenge for the applications of BNNTs as effective electronic devices or sensors. Recently, some experimental efforts have been made toward making soluble BNNTs through sidewall functionalization.[22−24] Xie et al. were the first to report the development of soluble BNNTs via functionalization of the tubes with amine-terminated oligomeric poly(ethylene glycol).[22] These researchers proposed a funcationalization mechanism based on interactions of amino functional groups with the boron atoms of the sidewall. Zhi et al. synthesized stearoyl chloride-functionalized BNNTs through the interaction of COCl group of stearoyl chloride and amino groups on the sidewall of BNNTs.[23] The functionalized BNNTs are shown to be soluble in many organic solvents. These researchers pointed out that the band structures of the BNNTs may be changed due to the functionalization.

Compared with the experimental progress, to our knowledge, no prior theoretical investigations have been reported for the effect of chemical modification on the electronic properties of
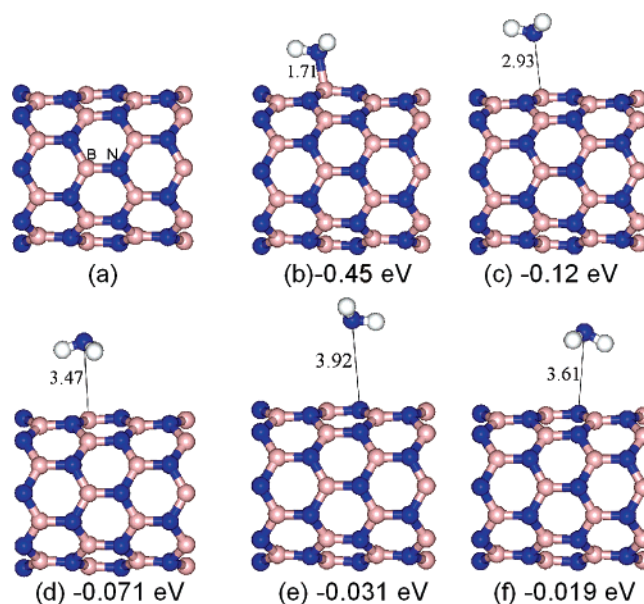
Figure 1. Optimized structures of (a) pristine BNNT, and (b−f) NH$_3$-modified BNNT with the adsorption energy given underneath. Various adsorption sites and NH$_3$ orientations were examined.

BNNTs, or on the chemical/physical nature of addend/BNNT interactions. In this paper, we report the first ab initio density-functional theory (DFT) study of BNNTs functionalized with NH$_3$ and four other amino functional groups, NH$_2$CH$_3$, NH$_2$-CH$_2$COOH, NH$_2$CH$_2$OCH$_3$, and NH$_2$COOH. We found that, although the adsorption energies can be dependent on the type of the functional groups, the chemically modified BNNTs are all semiconductors with band gaps similar to those of pristine BNNTs and that the electronic properties of BNNTs are generally preserved even with the chemical modification using NH$_3$ or amino functional groups.

Models and Methods

We carried out all-electron ab initio DFT calculations using double numerical basis sets with polarization function (the DNP basis set) implemented in the DMol3 package.[25] Spin-unrestricted DFT in the generalized-gradient approximation with the Perdew−Burke−Ernzerhof (PBE) functional[26] was used to obtain all the results given below. A zigzag (8,0) single-walled BNNT was chosen as the benchmark model system, and a tetragonal supercell of the size of 30 Å $\times$ 30 Å $\times$ 8.64 Å with the length of c equal to twice the periodicity of the (8,0) BNNT was set up for the calculation. The supercell includes totally 32 boron and 32 nitrogen atoms. The nearest distance between the BNNT and its periodic images is greater than 14.0 Å. The Brillouin zone is sampled by 1 $\times$ 1 $\times$ 3 special k-points using the Monkhorst−Pack scheme.[27] The binding (or adsorption) energy of the adsorbate with the BNNT is defined as $E_{ads} = E_{total}[\text{BNNT}+ \text{adsorbate}] - E_{total}[\text{BNNT}] - E_{total}[\text{adsorbate}]$, where E_{total} is the total energy of the system per supercell.

Results and Discussion

(1) Adsorption of NH$_3$. First, we searched for the most stable configuration of NH$_3$ on the sidewall of BNNT. The structure of a pristine (8,0) BNNT is shown in Figure 1a, where two types of B−N bonds can be identified, one with the bond length of 1.44 Å and in parallel with the tube axis, and another with

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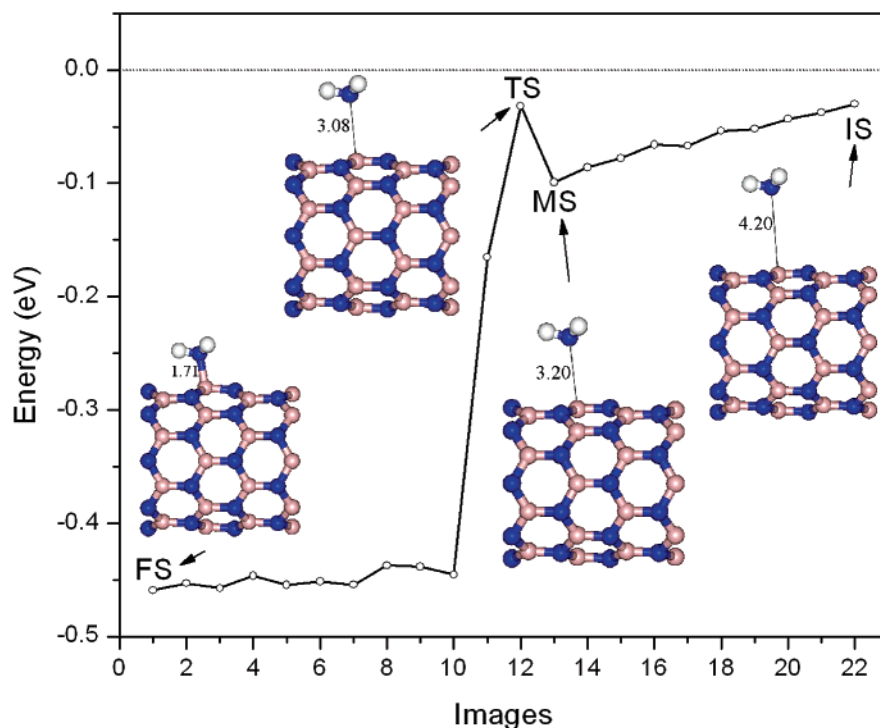
Figure 2. Calculated MEP for the chemical adsorption process of NH_3 on BNNT.

bond length of 1.46 Å, but not in parallel with the tube axis. The charge analysis using the Hirshfeld method indicates that about 0.21 *e* charges are transferred from the boron atom to its neighboring nitrogen atoms within the sidewall, that is, the B–N bonds of the sidewall are partially ionic.[28] Initially, a NH_3 molecule was placed on top of a sidewall boron or nitrogen atom. Full geometrical optimization was then performed with several different orientations of the NH_3 molecule. Structures b–f of Figure 1 display a side view of several stable (local-minimum) configurations of the NH_3 molecule on the BNNT. The NH_3 molecule can be adsorbed with two primary orientations with respect to the sidewall surface: (1) the hydrogen atoms are nearest to the surface, or (2) the nitrogen atom is nearest to the surface. The most stable configuration (Figure 1b) is such that the nitrogen atom of NH_3 is nearest to a sidewall boron atom with the distance between about 1.71 Å. At the most stable configuration, the adsorption energy is −0.45 eV, indicating that the adsorption process is chemical in nature although the formed B–N bond is not as strong as those within the BNNT. The negative value of the adsorption energy denotes exothermic adsorption. A locally structural deformation at the adsorption site can be observed due to the adsorption of the NH_3 molecule (Figure 1b), where the sidewall boron atom is slightly pulled out of the surface and the corresponding three B–N bonds within the side wall (with bond length about 1.50, 1.53, and 1.53 Å, respectively) are thus slightly elongated. This structural deformation can be attributed to the change in the local hybridization of the boron atom from sp^2 to sp^3 orbital, as the boron atom is bonded with the NH_3 molecule.

For other stable (local-minimum) configurations (Figure 1c–f), the NH_3 molecule is only *physically* (rather than chemically) adsorbed on the sidewall of BNNT with much weaker adsorption energy which ranges from a few tens to hundreds meV,

stemming from the van der Waals attraction. Note that DFT with GGA is not capable of describing physisorption. Thus, the calculated adsorption energy in the case of physisorption is only qualitative. The distance between the nitrogen of NH_3 and the nearest boron or nitrogen site of BNNT ranges from 2.7 to 3.9 Å, which is appreciably longer than that in the most stable configuration (Figure 1b). In general, the distance between the nitrogen of NH_3 and the BNNT sidewall is somewhat shorter if the NH_3 molecule is on top of the boron site rather than on nitrogen site. When NH_3 is physisorbed on the BNNT, no local structural deformation is observed on the sidewall of BNNT. As such, the NH_3 molecule can be easily removed from the sidewall of BNNT at room temperature.

As shown in Figure 1b, the NH_3 molecule can be only chemically adsorbed on the sidewall of BNNT through the formation of a covalent B–N bond with a sidewall boron atom.[16] To further understand this chemical adsorption (or chemical functionalization) process, we computed the minimum-energy path (MEP) for the adsorption reaction using the nudged elastic band (NEB) method.[29] In essence, the NEB method starts by inserting a series of image structures between the initial and final state of the reaction. Meanwhile, a fictitious spring force is introduced between all nearest-neighbor image structures. By optimizing these image structures simultaneously, the MEP of the reaction can be obtained since the real force on the image structures has a zero projection in the direction normal to the MEP. Here, we chose a weak physisorption configuration as the initial state (IS) and the chemisorption configuration as the final state (FS). In the initial state, the distance between nitrogen of the NH_3 molecule and the BNNT sidewall is 4.2 Å. To achieve sufficient accuracy for the MEP, 20 image structures are inserted between the initial and final state.

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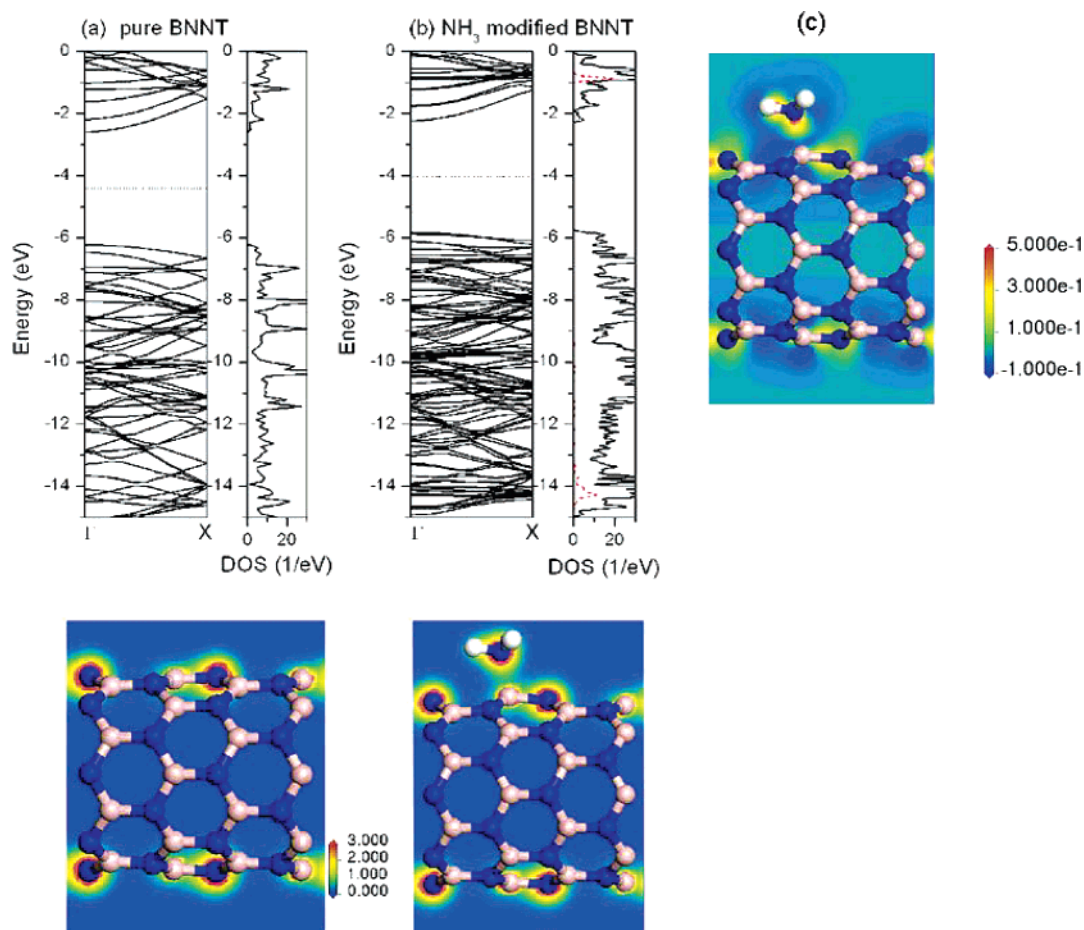
Figure 3. Band structures, density of states (DOS), and contour of total electronic density (in color) of (a) the pristine BNNT and (b) NH$_3$-modified BNNT. The Fermi level is plotted with black dotted line. The projected DOS of NH$_3$ is plotted with red dashed line in (b). (c) Contour plot of electronic deformation density of NH$_3$-modified BNNT. The contour plots are only shown for two opposing rows of sidewall atoms, in which one of the boron atoms is bonded with the nitrogen of NH$_3$ molecule.

Figure 2 displays a schematic representation of the calculated MEP for the entire reaction process. The zero energy corresponds to completely separated NH$_3$ molecule from the BNNT (two species are infinitely apart). The transition state and intermediate (stable) state are labeled as TS and MS, separately. Clearly, as shown in Figure 2, when moving toward the BNNT, the NH$_3$ molecule has to overcome a small energy barrier of ∼0.1 eV before being chemically adsorbed on the BNNT sidewall. In light of the small barrier to the adsorption, it is expected that the adsorption of NH$_3$ can be achieved quite easily even at room temperature. Conversely, to remove NH$_3$ from the BNNT sidewall, a small energy barrier of ∼0.42 eV should be overcome. Thus, it is also expected that the NH$_3$-modified BNNT can be repurified quite easily at room temperature.

Next, we studied the effect of chemical modification with NH$_3$ on the electronic properties of the BNNT. The changes in the band structures, the density of states, the total electronic density, and electronic deformation density are shown in Figure 3. The deformation density can be attained by subtracting the density of isolated atoms from the total electronic density (Figure 3c). From contours of both the total and deformation densities, it can be seen that certain amount of charge is transferred from NH$_3$ to the sidewall boron atom, concomitant with the formation of the B−N bond between NH$_3$ and BNNT. The charge population analysis with the Hirshfeld method indicates that the amount of the charge transferred is about 0.36 *e*. Upon the

chemical adsorption, the B−N bonds within the sidewall are slightly weakened. However, the electronic properties of the BNNT are little changed upon the chemical adsorption as shown by the band structures as well as the DOS of NH$_3$-modified BNNT (Figure 3b). In particular, the band gap and the band structures near the Fermi level are nearly unchanged upon the chemical modification, except that the band-structure symmetry of the pristine BNNT is broken. In summary, the chemically modified BNNT is still a semiconductor with a wide band gap. Moreover, the total DOS and projected DOS of the NH$_3$ molecule (red dashed line in Figure 3b) show that the electronic states contributed from the NH$_3$ molecule are far away from the Fermi level. This result is consistent with the above conclusion that the electronic properties of the BNNT are largely preserved even with the chemical modification. Thus, chemical modification of BNNT with NH$_3$ can be viewed as some kind of "harmless modification".

(2) Adsorption of Four Amino Functional Groups. As mentioned in the Introduction, previous experiments have shown that BNNTs can be chemically modified with amino functional groups, rather than NH$_3$ molecules. Therefore, in the second series of calculations, we studied properties of chemically modified BNNT with four amino functional groups, including NH$_2$CH$_3$, NH$_2$CH$_2$COOH, NH$_2$CH$_2$OCH$_3$, and NH$_2$COOH. The most stable structures are shown in Figure 4. We found that all the amino groups, except NH$_2$COOH, can be *chemically*
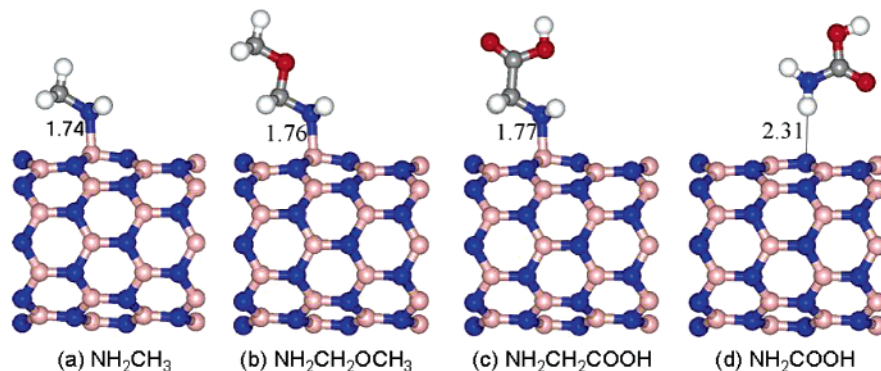
Figure 4. Most stable configurations of chemically modified BNNTs with the amino functional group (a) NH$_2$CH$_3$, (b) NH$_2$CH$_2$OCH$_3$, (c) NH$_2$CH$_2$COOH, and (d) NH$_2$COOH.
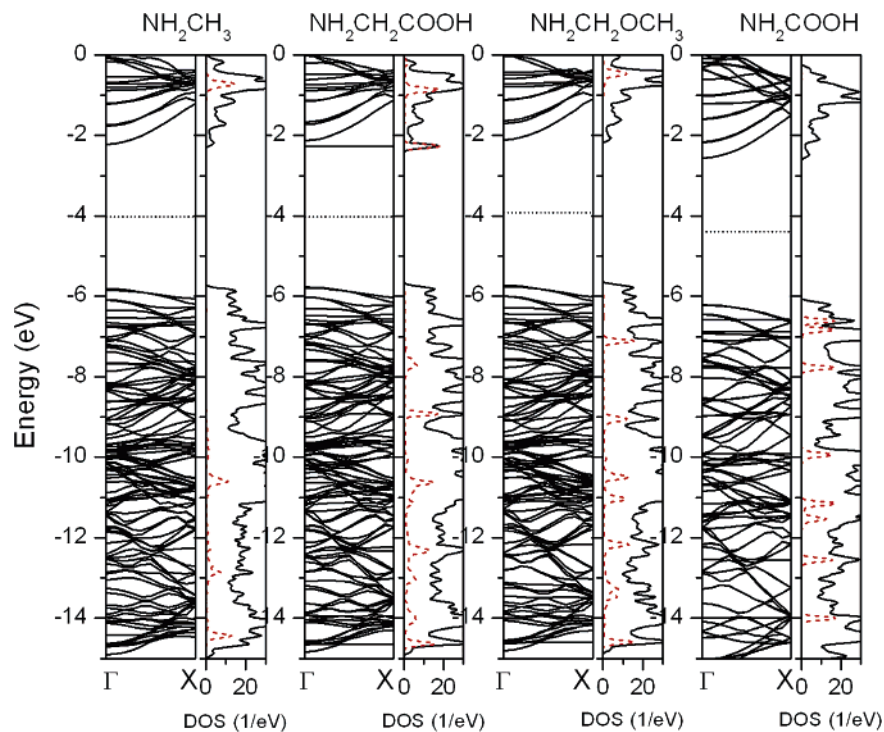
Figure 5. Band structures and DOS of amino functional group-modified BNNTs. The Fermi level is plotted with black dotted line. The projected DOS of the amino functional group is plotted with red dashed line.

adsorbed on the BNNT sidewall and covalently bonded with a boron atom, namely, forming a B−N bond. The B−N bond length ranges from 1.74 to 1.77 Å. For the NH$_2$COOH functional group, this molecule is only *physically* adsorbed on the BNNT with one N−H bond of NH$_2$COOH directing toward a sidewall nitrogen atom, as shown in Figure 4d. The corresponding adsorption energies and charge transfer from the five adsorbates to BNNT are listed in Table 1. The NH$_2$CH$_3$-modified BNNT shows nearly the same adsorption energy as NH$_3$ on BNNT, while the adsorption energies with other amino functional groups are typically smaller. Furthermore, the charge transfer from the amino functional group to the BNNT is slightly reduced with the larger functional group and becomes zero with the NH$_2$-COOH group. This trend of charge transfer and change of adsorption energy can be understood on the basis of relative electron-withdrawing or -donating capability of the added molecular groups. It is well-known that CH$_3$- has electron-donating capability similar to that of H-, while -COOH and -OCH$_3$ are relatively strong electron-withdrawing functional groups. Thus, by replacing H- with the -COOH or -OCH$_3$ groups

Table 1. Calculated Adsorption Energies (E_{ads}), B−N Bond Lengths ($B_{B−N}$), and Charge Transfer (C) from the Amino Functional Group to the BNNT

functional groups	E_{ads} (eV)	$B_{B−N}$ (Å)	C (e)
NH$_3$	0.45	1.71	0.36
NH$_2$CH$_3$	0.45	1.74	0.36
NH$_2$CH$_2$COOH	0.34	1.77	0.33
NH$_2$CH$_2$OCH$_3$	0.29	1.76	0.34
NH$_2$COOH	0.16	2.31[a]	0.0

[a] This value is the shortest distance between atoms of NH$_2$COOH and the sidewall nitrogen atom of the BNNT (Figure 4d).

the charge transfer to the BNNT should be reduced, thereby weakening the interaction between the amino functional group and the BNNT. This result reinforces our earlier explanation of the interaction between the BNNT and functional group, that is, the interaction is predominately induced by charge transfer from the functional group to the BNNT.

We also calculated the band structures and DOS of amino functional group-modified BNNTs, as shown in Figure 5. The band structures show that all the chemically modified BNNTs

are still semiconductors with a wide band gap close to that of the pristine BNNT. The DOS and projected DOS of the amino functional groups show that the contribution from the amino functional groups is largely away from the Fermi level. However, for the amino functional group containing an oxygen atom, the functional group does give some impurity states close to the conductive and valence band edges of the BNNT. Especially, the NH_2CH_2COOH group induces an unoccupied impurity state within the band gap of the BNNT and close to the conductive band edge. The orbital profile at the gamma (Γ) point shows that this impurity state is mainly contributed by the $-COOH$ subgroup of NH_2CH_2COOH, suggesting that some potentially new BNNT derivatives may be produced from the reaction of other chemical materials with the $-COOH$ subgroup. In other words, for chemically modified BNNTs with the amino group containing $-COOH$, the tube's chemical reactivity may be enhanced.

Conclusion

In conclusion, we have investigated, on the basis of density functional theory calculations, the structural and electronic properties of chemically modified BNNTs with NH_3 and four amino functional groups. We found that the NH_3 molecule can be chemically adsorbed on top of a sidewall boron atom along with a charge transfer from the adsorbate to the BNNT. The adsorption is *chemical* in nature with adsorption energy about -0.45 eV. In contrast, for CNTs, previous theoretical and experimental studies show that the adsorption of NH_3 on CNTs is only *physical* in nature with merely a weak charge transfer (about 0.03 *e*).[30−33]

With the amino functional groups, the adsorption energies, the distances between the functional groups and the BNNT sidewall, and the charge transfer from the functional groups to the BNNT are all dependent upon the chemical nature of the subgroups within the amino functional groups. The trend of charge transfer and change of adsorption energy can be correlated with the trend in relative electron-withdrawing or -donating capability of the subgroups. Subgroups with strong electron-withdrawing capability generally lead to less charge transfer and smaller adsorption energy. The calculated band structures and DOS show that the chemical modification of BNNTs with amino functional groups can be generally classified as certain type of "harmless modification". In other words, the electronic properties of the BNNT are little changed by the chemical modification. However, the amino functional groups containing $-COOH$ can give rise to an unoccupied impurity state close to the conductive edge within the band gap, suggesting that some new BNNT derivatives may be synthesized from reaction of the chemically modified BNNTs with other molecules.

Since the chemical modification of BNNTs with either NH_3 or amino functional groups results in little change in the electronic properties, more studies are needed to search for other ways of chemical modification to modify electronic properties of BNNTs by molecular design. On the other hand, the preservation of electronic properties of BNNTs coupled with the enhancement of solubility renders the chemical modification of BNNTs with either NH_3 or amino functional groups to be an effective way for the purification of BNNTs. The insight obtained from this ab initio study may also assist future development of BNNTs with targeted chemoselectivity through tactful chemical functionalization.

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