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RESEARCH ARTICLE

Functionalization of BN nanotubes with free radicals: electroaffinity-independent configuration and band structure engineering

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The preferable configuration and electronic structure of several types of free radical functionalized boron nitride nanotubes (BNNTs) were investigated by using density functional theory computations. All the free radicals have strong interaction with B atom in the tube, in spite of the electroaffinity of the radicals. However, though a large charge is transferred from tubes to NH_2, OH or CN radicals, little change happens to the electronic structure of BNNTs, while COOH and COCl radicals introduce half-filled impurity levels around the Fermi level. Higher functionalization concentration leads to multiple impurity states around the Fermi level, and makes BNNTs p-type semiconductors.

Keywords BN nanotubes, first-principles computations, functionalization, free radicals

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1 Introduction

Iijima's structural elucidation of carbon nanotubes in 1991 [1] has attracted a wide research interest in their analogous structures. Following carbon nanotubes, the nanotubes of another hexagonal compound, BN, were first theoretically proposed [2] and then successfully synthesized [3]. BN nanotubes (BNNTs) also possess excellent properties promising for various applications, such as high thermal conductivity, oxidation resistivity, and chemical stability. It is well known that the electronic properties of carbon nanotubes are sensitively dependent on its radius and chirality [4]. However, all BN nanotubes are semiconductors with a wide band gap (about 5.5 eV), which has little relationship with tube diameters, helicity and number of walls [5, 6]. The uniformity of electronic properties of BN nanotubes is the key advantage for their application to nanotechnology.

However, the large band gap and chemical inertness impose great restriction on the wider applications of BN nanotubes. Therefore, functionalization on the sidewalls of BN nanotubes may modify their properties. Experimentally, Xie *et al.* [7] first reported a successful attempt in the solubilization of BNNTs functionalized with oligomeric polyethyleneglycol bearing amino moieties. Zhi *et al.* [7] reported that BN nanotubes wrapped with a conjugated polymer were fully soluble in some organic solvents. Theoretically, Wu *et al.* [8] investigated the functionalization of BN nanotubes with NH_3 and other amino functional groups, and found that NH_3 can be strongly adsorbed on the sidewalls of BN nanotubes. However, we demonstrated that NH_3 adsorption does not significantly change the band structures of BN nanotubes, irrespective of NH_3 concentration [9]. Therefore, many recent studies have focused on functionalization of BN nanotubes with more reactive substances, such as H [10], F [11], Li [12], and CCl_2 [13]. Hydrogenation and fluorination can tune the electronic properties of BNNTs efficiently, but under high fluorine coverage, severe structural deformation was introduced to BN nanotubes. As for the CCl_2 attachment, the band structures of BN nanotubes do not change significantly, irrespective of the CCl_2 coverage [14].

In this work, density functional theory (DFT) studies were performed for the sidewall functionalization of single-walled BNNTs with amine group (NH_2), cyanogen group (CN), carboxylic group (COOH), hydroxyl group (OH), and acyl chloride group (COCl). Our results show that all the chosen radicals have strong interaction with BN nanotubes. The attachments of COOH and COCl have significant influence on the electronic properties of BN nanotubes. These radical-functionalized BN nanotubes may have potential applications in nanotechnology.

2 Computational methods

Spin-unrestricted all-electron DFT computations were performed by employing the generalized gradient approximation (GGA) with the PW91 [14] functional and the double numerical plus polarization (DNP) basic set as implemented in the DMol^3 package [15, 16]. Self-consistent field (SCF) calculations were conducted with convergence criteria of 10^{-6} a. u. for the total energy. Since BNNTs show a preferential zigzag orientation approved by experiments, only the models for zigzag tubes were considered here. For simulating infinite long (rather than truncated) nanotubes, we adopted the one-dimensional (1D) periodic boundary condition (PBC) along the tube axis. Our computational supercells include two unit cells of the (10, 0) BN nanotubes and the supercell length c is 8.64 Å. During the geometry optimization, the positions of all the atoms in the supercell were fully relaxed and 3 k points were used to sample the 1D Brillouin zone. Afterwards, band structures and electron density distribution were computed with 21 k points based on the equilibrium structures.

The radical binding energy (E_{b}) is defined as: $E_{\mathrm{b}} = (E_{\mathrm{BNNT}} + nE_{\mathrm{rad}} - E_{(\mathrm{BNNT}\text{–}n\mathrm{rad})})/n$, where $E_{(\mathrm{BNNT}\text{–}n\mathrm{rad})}$, E_{BNNT} and E_{rad} stand for the total energy of the radical attached BNNT, the pristine BNNT, and the individual radical, respectively, and n stands for the number of the radicals. In this definition, positive binding energy means exothermic reaction on the sidewalls of BN nanotubes.

3 Results and discussion

To investigate the interaction between radicals and BN nanotubes, we have considered all the possible sites for these radicals on the sidewall of (10, 0) BNNT, including the sites on top of B and N atoms, and at the bridge sites of B–N bonds. For special radicals, we investigated various possible attachment geometries. For example, for the COCl radical, we considered three configurations where the nanotube is close to the carbon, oxygen and chlorine atom, respectively. Our results show that the COCl radical prefers the pattern with the C atom attached to the B or N atom, probably due to the fact that the charge of COCl is mainly localized on the C atom. Also, we found that all the radicals studied in this work prefer the attachment on top of B atoms. In BNNTs, the electrons are mainly localized on N atoms, and B atoms are electron-deficient. Therefore, it is easy to understand that NH_2 and OH prefer the attachment to B atom since they are strong electron-donating groups. However, CN, COOH and COCl are all electron-withdrawing groups; why do they also prefer B sites? The reason is that there is more significant difference in electronegativity between B and C/O than that between N and C/O. In our previous study [11], we also found that the F atom also prefers to be attached on top of the B atom. This selectivity can be explained with frontier orbital theory; the highest occupied molecular orbital of radicals interacts with the lowest unoccupied states of BNNT which is contributed by the B atom [10]. Therefore, for the sidewall functionalization of BNNTs the B-preferable configuration is independent of the electroaffinity of the attached groups. All the systems involved in this study were determined to have a spin-unpolarized ground state, though the radicals all have an unpaired electron.

In Fig. 1 we show the most stable configurations of radical-attached BN nanotubes; the values of binding energies, equilibrium distances between radicals and BN nanotubes, and charge transfer, are listed in Table 1. All radicals introduce local structural deformation to BN nanotubes. The deformation may be due to the local sp^3 rehybridization of B atoms. As shown in Table 1, the radical-tube distances are in the range of 1.56−1.79 Å, indicating that new chemical bonds form between radicals and nanotubes. It is noted that in the NH_2-attached (10,0) BN nanotube, the length of the new B–N bond is 1.556 Å, and the B–N bond lengths in the BNNT wall involving the NH_2-attached B atom (1.534 Å, 1.547 Å and 1.547 Å) are close to those in the sp^3-hybridized cubic BN phase (1.57 Å) [17], but longer than those in the perfect BNNTs with sp^2 hybridization (1.44−1.45 Å). Similar results are also observed in other radical-attached BN nanotubes.

Table 1 Binding energy (E_{b}), equilibrium tube-radical distance (d), and charge transfer (Q) between radicals and tubes. The negative values mean that charges are transferred from nanotubes to radicals.

Radical	E_{b} / eV	d / Å	$Q(\lvert e\rvert)$
NH_2	1.60	1.556	−0.06
OH	1.77	1.481	−0.21
CN	2.05	1.619	−0.26
COOH	0.87	1.758	−0.09
COCl	0.45	1.785	−0.18

The largest binding energy is given by BNNT–CN, followed by BNNT–OH. There are 0.26 and 0.21 $|e|$ charges transferred from CN and OH radicals to (10,0) BN nanotubes, respectively. It is interesting to find that although NH_2 and OH are electron-donating groups, charges are also transferred from BN nanotubes to radicals, since N and O atoms have larger electronegativity than B atom. Also, we found that the binding energy is not proportional to the value of the transferred charge. For example, there are more charges transferred from nanotubes to COOH and COCl than to NH_2, but the binding energies of COOH and COCl on BNNTs are less than that of NH_2. We attribute it to the more significant structural deformation in COCl and COOH attached BN nanotubes.

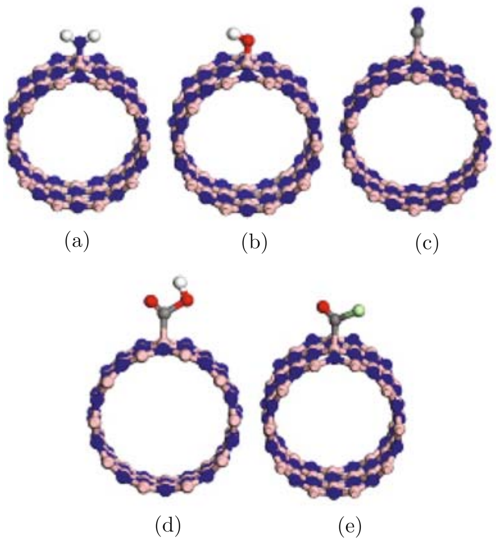


Fig. 1 Structural configurations of (10, 0) BN nanotube functionalized with **(a)** NH_2, **(b)** OH, **(c)** CN, **(d)** COOH, and **(e)** COCl. B, N, O, C, Cl and H atoms are denoted with orange, blue, red, grey, green, and white balls, respectively.

The electronic band structures of pristine and radical-attached (10, 0) BN nanotubes are presented in Fig. 2. For the pristine (10, 0) BNNT, it is a typical semiconductor with a wide band gap of 4.02 eV, reasonably consistent with previous theoretical studies [9, 11, 13]. It is well known that DFT usually underestimates the band gap. For the BN nanotubes attached with NH_2, OH, and CN groups, neither valence nor conduction bands are significantly changed. The wide-band-gap semiconductor feature of (10, 0) BN nanotubes is well kept. However, the attachment of these radicals leads to the appearance of impurity levels on top of valence band, and consequently reduces the band gap. Similar results have been found in NH_3 [9] and CCl_2 [13] functionalized BN nanotubes. In contrast, besides the flat impurity level in the bottom of the conduction band, the attachment of COOH and COCl also induces a half-filled level around the Fermi level, and makes the BNNTs p-type semiconductors. The functionalization of BNNTs with naphthoyl chloride ($C_{10}H_7COCl$), butyral chloride [$CH_3(CH_2)_2COCl$], and stearoyl chloride [$CH_3(CH_2)_{16}COCl$] has been investigated experimentally and theoretically, and similar results have been reported [13]. The appearance of the half-filled level in the gap region was also found in radical-functionalized carbon nanotubes [18, 19].

To clarify the origin of the impurity levels, we have computed the isosurfaces of charge density of impurity levels in the band structure of COCl-attached (10, 0) BNNT. The half-filled level is derived from the hybridization between COCl and (10, 0) BNNT (Fig. 3). In contrast, the flat level in the bottom of conduction bands is completely contributed by the molecular level of COCl.

Since COCl has significant effect on the electronic properties of BN nanotubes, it is interesting to study the functionalization of BN nanotubes with higher COCl coverage. Here we increase the number of COCl from 2 to 10 in the supercell of (10, 0) BN nanotubes. The COCl coverage is defined as the number of C atoms *vs.* the total number of B and N atoms in the sidewall of (10, 0) BN nanotubes. Therefore, within our computational supercell (40 B and 40 N atoms), one COCl corresponds to the coverage of 1.25%, while 10 COCl radicals correspond to the coverage of 12.5%. Initially, all COCl groups were put on top of the B atom, and the most stable configurations upon relaxation are presented in Fig. 4, along with the corresponding binding energies. Obviously, the binding energy decreases sharply with the increase of the COCl coverage. Even at the high coverage up to 12.5%, the binding energy is still as large as 0.39 eV, suggesting the possibility for further functionalization.

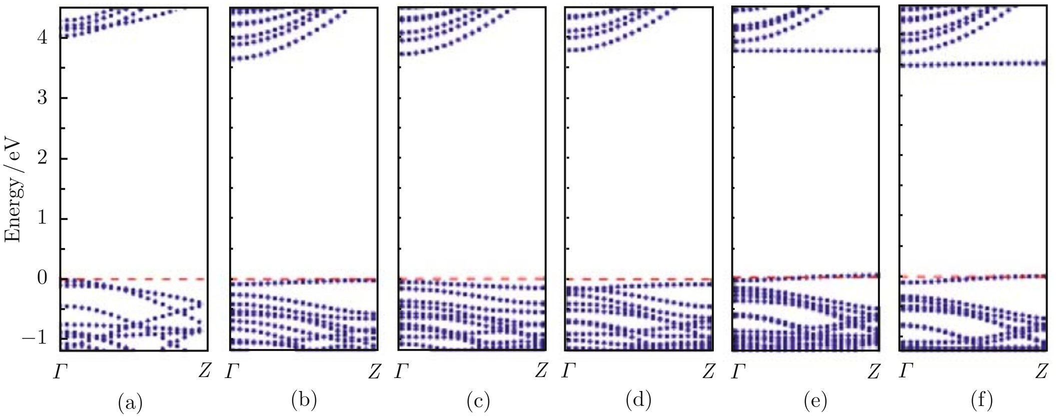


Fig. 2 Electronic band structure for **(a)** pristine (10, 0) BNNT, **(b)** (10, 0) BNNT–NH_2, **(c)** (10, 0) BNNT–OH, **(d)** (10, 0) BNNT–CN, **(e)** (10, 0) BNNT–COOH and **(f)** (10, 0) BNNT–COCl. The red dashed lines indicate the position of Fermi level.

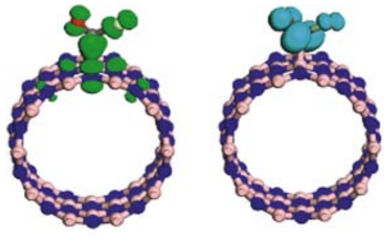

(a) (b)

Fig. 3 Charge densities of **(a)** the half-filled level and **(b)** the conduction band bottom in the band structure of COCl-attached (10, 0) BN nanotube.

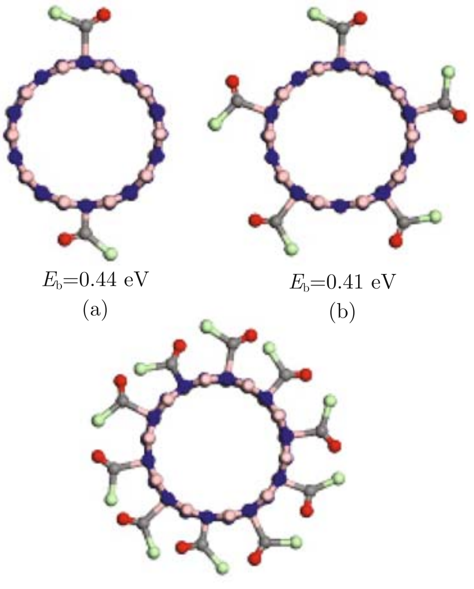
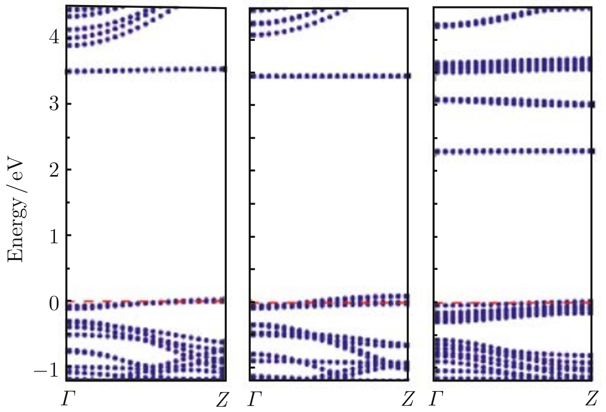

E_b=0.44 eV
(a)
E_b=0.41 eV
(b)
E_b=0.39 eV
(c)

Fig. 4 Structural configurations of COCl attached (10, 0) BNNTs with COCl coverage of **(a)** 1.25%, **(b)** 6.25%, and **(c)** 12.5 %. The corresponding binding energies are also given. See text for the definition of COCl coverage.



(a) (b) (c)

Fig. 5 Electronic band structures for (10, 0) BN nanotube with **(a)** 1.25%, **(b)** 6.25% and **(c)** 12.5% COCl coverage.

The electronic band structures for (10, 0) BN nanotubes with high COCl coverages are presented in Fig. 5. As the concentration of COCl increases, there are more and more impurity states appearing in the conduction bands and half-filled levels around the Fermi level. The band gap of BNNT has been decreased to 3.47, 3.29 and 2.90 eV for the 1.25%, 6.25% and 12.5% coverage, respectively. Therefore, functionalization of BN nanotubes with COCl could be a rather feasible way towards engineering their band structures.

4 Conclusion

To summarize, the structural and electronic properties of (10, 0) single-walled BN nanotubes functionalized with the NH_2, OH, CN, COOH and COCl radicals were studied by using DFT computations. The radicals studied in this work all have strong interactions with BN nanotubes, and they all prefer to be attached on top of the B atom, irrespective of the electronegativity of the group. The local structural deformation is induced to BN nanotubes due to the sp^3 rehybridization of B atoms. Whether electron-donating or electron-withdrawing radicals, charges are transferred from BN nanotubes to radicals. No apparent changes occur to the band structures of BNNTs upon the attachment of NH_2, OH, and CN radicals; however, the attachment of COOH and COCl introduces an impurity half-filled level around the Fermi level, which is originated from the hybridization of BNNTs and the attached radical. It is also flexible for the functionalization of BNNTs with higher COCl coverage, and the band gap can be significantly tuned and p-type semiconductors can be achieved with COCl functionalization.

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