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First-Principles Study of the Oxygenation of Carbon Nanotubes and Boron Nitride Nanotubes

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Using the first-principles method, we investigated the molecular and electronic structures of oxygenized carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs). This is done by considering (5,5) and (10,0) tubes, which have similar diameters. The reaction of CNTs with oxygen molecules is largely exothermic, particularly for (5,5) CNT. When the oxygen content is ∼5% in a (5,5) tube, oxygen atoms tend to form a contiguous row of ether along the tube axis, which can be understood in terms of a zipping mechanism. In (10,0) CNT, oxygen atoms tend to be uniformly distributed in pairs of ether on two opposite sides of the tube up to 10% oxygen content. Upon acid treatment of BNNTs, our data indicate that the oxygenation could occur in a chirality-specific way. Specifically, (5,5) BNNT is expected to favor the insertion of two oxygen atoms in the tube rather than the evaporation of an oxygen molecule, whereas (10,0) BNNT is not expected to do so.

1. Introduction

Carbon nanotubes (CNTs) have been considered one of the most promising materials in nanotechnology because of the diversity in their electronic properties depending upon tube chirality and the sensitivity of these properties to physisorption of small molecules or chemical modification.[1] Various synthetic methods have been developed for the controlled design of CNTs, i.e., arc discharge,[2] laser ablation,[3] and chemical vapor deposition (CVD) techniques.[4] However, as-grown CNTs contain significant amounts of impurities, including amorphous carbon, graphitic particles, and metal catalysis. Therefore, various purification methods have been developed involving oxidation and filtration.[5]

Boron nitride nanotubes (BNNTs) are an interesting CNT analog of III−V compounds. Their electronic structure is quite different from that of CNTs in that they are wide gap semiconductors regardless of tube diameter and chirality, serving as a perfect insulator.[6] There have been also various methods for the synthesis of BNNTs, including the arc discharge method[7] and CNT substitution reaction.[8] As in the case of CNTs, as-grown BNNTs are also subject to purification through oxidation.

Recently, Ogrin et al. showed that purification of CNTs can result in the epoxidation of the tubes up to 5% of oxygen content. In addition, treatment of CNTs with dioxirane and benzoic acid was found to enrich the oxygen content even up to the stoichiometry of C_5O.[9] Furthermore, acid purification and surface cleaning of CNTs leads to the enhancement of the surface area available for adsorption.[10] These findings raise an important question on the nature of CNTs used in physical devices and sensors, because those devices rely on purified CNTs. In this respect, a theoretical understanding of molecular and electronic structures of CNTs highly epoxidized is needed. However, theoretical calculation on the chemical oxidation of CNTs has been focused on the attachment of one oxygen atom or molecule as a whole.[11] Little investigation has been done on the oxygenations up to several percent oxygen atoms. To the best of our knowledge, Dag et al.'s theoretical exploration is the only

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work on the chemisorption of two oxygen atoms.[12] However, the work dealt with (8,0) CNT but not a CNT of other chirality. Namely, there has been no systematic understanding of the effect of chirality on the chemical oxygenation of the tubes. For example, Sorescu et al.[11(a)] and Froudakis et al.[11(b)] separately investigated the chemical oxygenation of zigzag and armchair CNTs by one oxygen atom. Even less is known about the similar reaction of boron nitride nanotubes (BNNTs) other than that BNNTs are chemically more inert than CNTs. In this respect, a systematic investigation on the relative tendency of oxygenation of BNNTs in comparison with that of CNTs is necessary. Our present work deals with these problems on the basis of first-principles calculation.

2. Theoretic Methods

Total energy calculations were performed using the Vienna ab initio simulation package (VASP).[13] Electron−ion interactions were described by the projected augmented wave (PAW) method,[14] which is basically a frozen-core all-electron calculation. Exchange-correlation effects were treated within the generalized gradient approximation presented by Perdew, Burke, and Ernzerhof (PBE).[15] The solution of the Kohn−Sham (KS) equation was obtained using the Davison blocked iteration scheme followed by the residual vector minimization method. We adopted a supercell geometry in which the *k*-space sampling was done from a one-dimensional Brillouin zone along the X axis. In doing this, we used large supercells that guaranteed that interatomic distances between neighboring cells along the *Y* and *Z* directions were greater than 7.00 Å. The cutoff energy was set high enough (400 eV) to ensure accurate results, and the conjugate gradient method was employed to optimize the geometry until Hellmann−Feynman force exerted on each atom was less than 0.03 eV/Å .

To investigate the effect of chirality on the oxygenation of CNTs and BNNTs, we studied the reaction of (5,5) and (10,0) tubes. From our calculation, primitive cells of (5,5) and (10,0) CNTs were found to have lattice constants 2.475 and 4.260 Å along the tube axis, in which 20 and 40 atoms were included, respectively. Similar parameters for BNNTs are 2.525 and 4.340 Å. These parameters were reoptimized for many of the oxygenated systems in order to reflect the change of bond lengths upon oxygenation. The oxygenation was investigated in a supercell of either CNT or BNNT, which consists of appropriate number of primitive cells. To investigate the effect of the diameter of the tube on the reaction, we have also made similar calculations for (6,6) and (8,0) tubes. (5,5) and (8,0) tubes have similar diameters (6.78 and 6.26 Å for CNTs, respectively). A similar argument holds for (6,6) and (10,0) CNTs, because their diameters are 8.14 and 7.83 Å, respectively.

Table 1. Energy of Oxygenation (E_i) for Various Isomers of Oxygenized CNTs[a]

chiral index	stoichiometry	isomer	E_i[b]	$l_{C=C}$[c]	l_{C-O}[d]	Lx[e]
(5,5)	$C_{80}O$ ($i = 1$)	e_1	−0.76(−0.75)	2.09	1.40	9.88(9.90)
		z_1	0.39(0.40)	1.51	1.46	9.88(9.90)
	$C_{80}O_2$ ($i = 2$)	a_2	−1.85(−1.83)	2.16, 2.16	1.40	9.88(9.90)
		b_2	−1.60(−1.57)	2.09, 2.09	1.40	9.86(9.90)
		c_2	(−1.37)	2.09, 2.09	1.40	(9.90)
	$C_{80}O_3$ ($i = 3$)	a_3	−2.79(−2.78)	2.12, 2.20	1.40	9.86(9.90)
		b_3	(−2.69)	2.08, 2.15	1.40	(9.90)
		c_3	(−2.43)	2.09, 2.16	1.40	(9.90)
	$C_{80}O_4$ ($i = 4$)	a_4	−3.56(−3.56)	2.13	1.40	9.88(9.90)
(6,6)	$C_{96}O_4$ ($i = 4$)	a_4	(−2.77)	2.15	1.40	(9.90)
(10,0)	$C_{80}O$ ($i = 1$)	z_1	0.05(0.10)	2.09	1.39	8.55(8.52)
		a_1	0.31(0.34)	1.48	1.47	8.55(8.52)
	$C_{80}O_2$ ($i = 2$)	a_2	−0.43(−0.35)	2.21, 2.21	1.39, 1.40	8.55(8.52)
		b_2	−0.41(−0.32)	2.20, 2.20	1.38, 1.40	8.59(8.52)
		c_2	(−0.15)	2.18, 2.18	1.36, 1.41	(8.52)
		d_2	(0.11)	1.47, 1.47	1.46, 1.47	(8.52)
		e_2	(0.13)	2.11, 2.11	1.39	(8.52)
		f_2	(0.38)	2.10, 1.63	1.39, 1.44	(8.52)
		g_2	(0.64)	1.55, 1.55	1.45, 1.45	(8.52)
		h_2	(0.72)	1.65, 1.48	1.43, 1.47	(8.52)
		i_2	(0.84)	1.49, 1.49	1.47	(8.52)
	$C_{80}O_3$ ($i = 3$)	a_3	−0.64(−0.49)	2.13, 2.22	1.39, 1.40	8.59(8.52)
		b_3	−0.45(−0.30)	2.14, 2.28	1.39, 1.40	8.59(8.52)
		c_3	−0.34	2.09, 2.20	1.39, 1.40	8.59
		d_3	(−0.01)	2.04, 2.20	1.39, 1.40	(8.52)
	$C_{80}O_4$ ($i = 4$)	a_4	−1.51(−1.26)	2.25, 2.26	1.39, 1.40	8.61(8.52)
		b_4	−1.10	2.17, 2.22	1.38, 1.40	8.61
		c_4	−0.83	2.19, 2.19	1.38, 1.40	8.61
		d_4	(−0.04)	2.10, 2.20	1.39, 1.40	(8.52)
(8,0)	$C_{64}O_4$ ($i = 4$)	a_4	(−2.40)	2.25, 2.25	1.38, 1.40	(8.52)

[a] The subscript "*i*" indicates the number of oxygen atoms in the four and two primitive cells of (*n*,*n*) and (*n*,0) tubes, respectively. Numbers in parentheses denote quantities obtained from the adoption of the fixed value of the lattice parameter (Lx) along the tube axis, which is the same as that for the pristine tube. On the other hand, numbers without parentheses were obtained from the use of the reoptimized lattice parameter shown in the last column. [b] Energy change of oxygenation with *i* oxygen atoms. See the text for more details. [c] Bond length of the C═C bond involved in the oxygenation. [d] Bond length of the C−O bond involved in the oxygenation. [e] Lattice parameter of one supercell along the tube axis, which includes four and two primitive cells for (*n*,*n*) and (*n*,0) tubes, respectively.

3. Results

A. Oxygenation of CNTs. First, we investigated the oxygenation of (5,5) CNT by relaxing the geometry of a supercell consisting of one oxygen atom on the surface of four primitive cells of the CNT. Two *k*-points were used for *k*-point sampling in the irreducible region of the first Brillouin zone. Calculation of the energy (E_1) of oxidation shows that it is much more favorable to oxidize an equatorial bond than a zigzag bond, which is evidenced by the values of E_1 (−0.76 and +0.39 eV, respectively) at the two bonds shown in Table 1. (Here, the energy of oxygenation (E_n) with (n/2) O_2 molecules is defined by the energy change of the process CNT + (n/2)O_2 (triplet) → CNT-nO. We note that the energy change was defined with respect to molecular oxygen and not with respect to atomic oxygen. Therefore, a negative value of E_n indicates that the system prefers the formation of n oxygen atoms chemically bonded to the CNT to the formation of (n/2) free oxygen molecules, regardless of the mechanism involved in the oxygenation. In relation to this definition, we want to point out that most other theoretical calculations rely on the definition of E_n based on the energy of n atomic oxygens. Indeed, the reaction is largely exothermic when an equatorial bond is involved. An equatorial bond is defined as the bond perpendicular to the tube axis, whereas a zigzag bond is positioned 30°from the axis (see Figure 1). The geometrical structure of the two different isomers of oxidized CNTs is also different. In the isomer (e_1) with the oxidation at an equatorial site, the C═C bond involved in the reaction becomes broken, as evidenced by the bond lengths (1.43 and 2.09 Å) before and after reaction. Two C−O single bonds (l(C−O) = 1.40 Å) are formed instead (See Figure 1a and Table 1). On the basis of these

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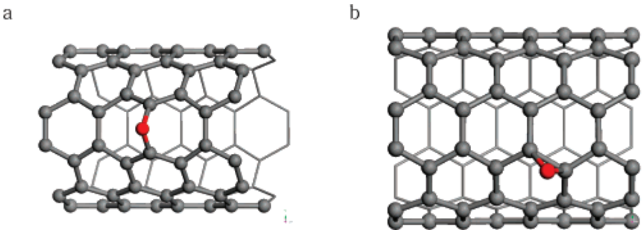

Figure 1. Oxygenation of (5,5) CNT at (a) equatorial and (b) zigzag bonds. Note that the C═C bond involved in the reaction is broken in the former, whereas it is not in the latter.

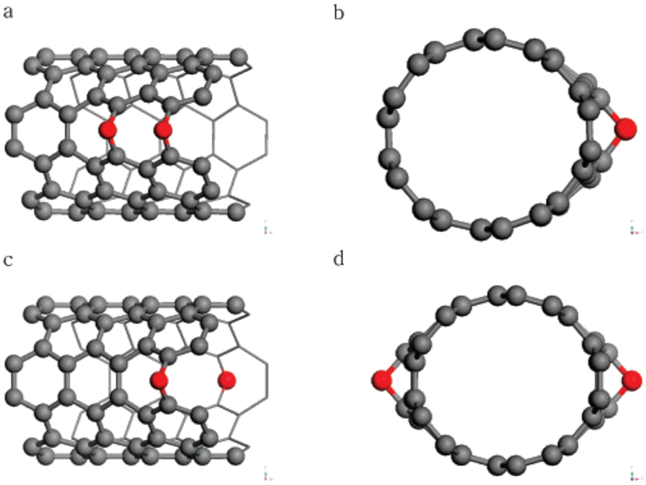

Figure 2. Two most stable isomers of (5,5) CNT oxygenized with two oxygen atoms: isomer a_2 and b_2 are shown in (a, b) and (c, d), respectively. For each isomer, two different views are shown.

data, the chemical structure of the isomer does not correspond to an epoxide but rather to that of an ether. In contrast to the equatorially oxidized CNT, the zigzag-functionalized CNT contains a three-membered epoxide ring, as shown by the bond lengths (1.51 and 1.46 Å, respectively) of the C−C and C−O bonds involved in the ring. Namely, the C−C bond is not broken but becomes a single bond (See Table 1 and Figure 1b).[16]

Next, we considered the oxygenation of (5,5) CNT with two oxygen atoms in the CNT, which also consists of four primitive cells. Among a large number of isomers, structures a and b in Figure 2 show that the most stable one (a_2) is characterized by the formation of two adjacent equatorial ether bonds that are parallel to each other. Its value (−1.85 eV) of $E_2(a_2)$ in comparison with $E_1(e_1)$ (−0.76 eV) suggests that it is easier to introduce the second oxygen atom at the adjacent equatorial bond once the first oxygen atom has been introduced at an equatorial bond of the CNT. The isomer is more stable than the second most stable isomer (b_2) by 0.25 eV. In isomer b_2, structures c and d in Figure 2 show that two oxygen atoms are introduced on two opposite sides of the CNT. Isomer a_2 is even more stable than isomer c_2, shown in Figure S1 in the Supporting Information, in which two oxygen atoms are located at right angles on the circumference of the tube. Therefore, we can expect that the majority of oxygen atoms will form a contiguous row of ether at equatorial bonds along the tube axis of an armchair CNT as more and more oxygen atoms are introduced. Although less pronounced, there will also be a tendency to align oxygen atoms in two rows on the opposite sides of the circumference of the tube. To confirm this, we made a further calculation on the introduction of three oxygen atoms in the tube. Our calculation of the oxygenation energy E_3 indicates that the most stable isomer a_3 has oxygenation at three consecutive equatorial C═C bonds, which is shown in structures a and b in Figure 3. Note the elliptic conformation of the system when viewed along the tube axis. The next stable isomer (b_3) has two oxygen atoms as in isomer a_2 with an additional oxygen atom on the opposite side of the circumference of the tube, which is more stable than isomer c_3, shown in Figure S2 of the Supporting Information. In short, oxygen atoms will tend to form a continuous row of equatorial ether bonds along the tube axis of an armchair tube. This structure represents the most stable isomer (a_4) among those with four oxygen atoms, i.e., those with an oxygen content of 5%, which is easily achieved in the purification of CNTs.[9] The stability of isomer b_3 also indicates that oxygen atoms will tend to align in two rows of ether bonds on the opposite sides of the circumference of the tube when the oxygen content reaches 10%.

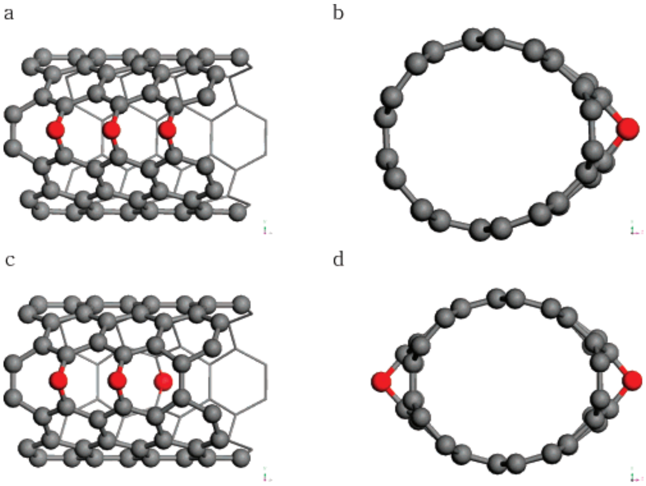

Figure 3. Two most stable isomers of (5,5) CNT oxygenized with three oxygen atoms: isomer a_3 and b_3 are shown in (a, b) and (c, d), respectively. For each isomer, two different views are shown.

With these studies in hand, we investigated the oxygenation of CNTs of other chirality. For this objective, we chose two primitive cells of (10,0) CNT as a supercell. Two *k*-points were used for *k*-point sampling in the irreducible region of the first Brillouin zone. An oxygen atom can bind to either an axial or zigzag C═C bond. In this system, a zigzag bond is defined as having an angle of 60°from the tube axis, whereas an axial bond is parallel to the tube axis. Therefore, there are two isomers in the CNT oxygenated with one oxygen atom, i.e., zigzag (z_1) and axial (a_1) isomers. Geometry relaxation shows that the local geometry around the oxygen atom corresponds to ether bonds and three-membered epoxy rings in isomers z_1 and a_1, respectively, which were also observed by Dag et al.[12] Table 1 shows that these phenomena are also manifested in the C−C bond length involved in the oxygenation. Namely, the C−C bond gets broken in isomer z_1 but not in isomer a_1. Table 1 shows that isomer z_1 is more stable than isomer a_1 by 0.26 eV, which differs from Dag et al.'s report that the two isomers

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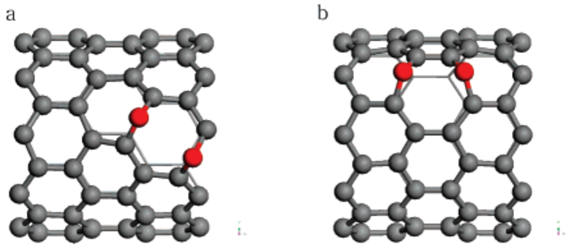

Figure 4. Two most stable isomers of (10,0) CNT oxygenized with two oxygen atoms: (a) a_2 and (b) b_2.

are within 0.02 eV of each other.[12] We believe our calculation to be more accurate because it is based on a supercell that is twice as large as theirs. Namely, their and our calculations rely on the supercells of one oxygen atom in one and two primitive cells of the pristine CNT, respectively. Table 1 shows that optimal lattice parameters are elongated by only 0.03 Å upon oxygenation in our calculation. Therefore, total energies of the systems are lowered by only 0.08 eV at most, when they are calculated at various lattice parameters around that of the pristine tube. When the energy values (−0.76 and 0.05 eV, respectively) for the species $E_1(e_1)$ for (5,5) CNT and $E_1(z_1)$ for (10,0) CNT are compared, we clearly observe that zigzag CNTs are less easily subjected to oxygenation than armchair tubes.

We have made further calculations on the binding of additional oxygen atoms on CNTs. When two oxygen atoms bind to the tube, there are many possible isomers. Table 1 shows nine of them. The two most stable isomers are shown in Figure 4. The most stable one (a_2) has ether formation at two zigzag bonds, which are parallel to each other in the same six-membered ring. Consideration of the values (0.05 and −0.43 eV, respectively) of the energy of oxygenation for z_1 and a_2 indicates that the oxygen binding is cooperative, which is analogous to the case of the armchair tube. Indeed, the formation of isomer a_2 is an exothermic reaction, which leads us to expect its production upon oxygenation of CNTs. The third most stable isomer (c_2) shown in Figure S3 of the Supporting Information also has two ether bonds in the same six-membered rings as in isomer a_2. In the figure, the fourth most stable isomer (d_2) is also shown.

However, oxygen atoms are not expected to form a contiguous helical turn at zigzag bonds in zigzag CNTs. In fact, structures a and b in Figure 5 as well as Table 1 show that the most stable isomer has the third oxygen atom on the opposite side of the circumference of the tube when three oxygen atoms are introduced. This is also demonstrated by the values (0.05, −0.43, and −0.64 eV) for $E_1(z_1)$, $E_2(a_2)$, and $E_3(a_3)$ in Table 1. From these values, we find that $E_1(z_1)$, $E_2(a_2)-E_1(z_1)$, and $E_3(a_3)-E_2(a_2)$ are 0.05, −0.48, and −0.21 eV, respectively. The values (0.05, −0.43, and −0.45 eV) of $E_1(e_1)$, $E_2(a_2)$, and $E_3(b_3)$ in Table 1 show more clearly that the third oxygenation at a contiguous parallel position is not cooperative at all. (Here, isomer b_3 is defined as three oxygen atoms attached at contiguous parallel positions at zigzag bonds, as shown in structures c and d in Figure 5). Namely, $E_3(b_3)-E_2(a_2)$ (−0.02 eV) is almost comparable to $E_1(z_1)$ (0.05 eV). Furthermore, a random positioning of the third oxygen atom in isomer c_3 results in an isomer that is less stable than either of isomers a_3 and b_3. See Figure S4 in the Supporting Information for isomer c_3. In short, oxygen atoms will tend to be distributed at two opposite sides of the circumference of (10,0) CNT tubes in pairs, not preferring the formation of a contiguous row even when the oxygen content does not exceed 5%. This is clearly different from the case of armchair CNTs, in which there is actually a strong tendency of oxygen atoms to form a contiguous row along the tube axis.

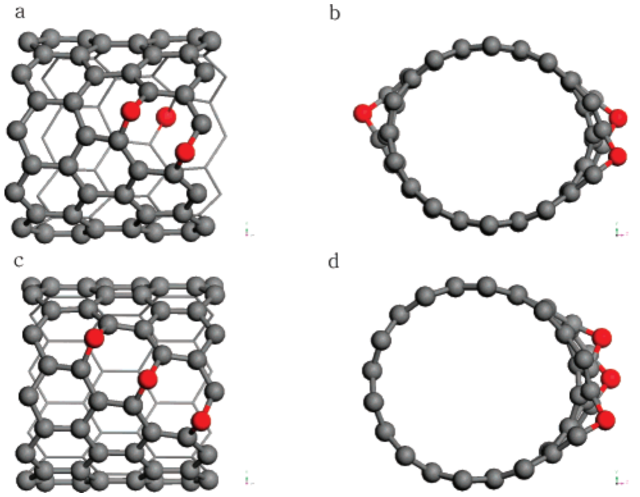

Figure 5. Two most stable isomers of (10,0) CNT oxygenized with three oxygen atoms: isomer a_3 and b_3 are shown in (a, b) and (c, d), respectively. For each isomer, two different views are shown.

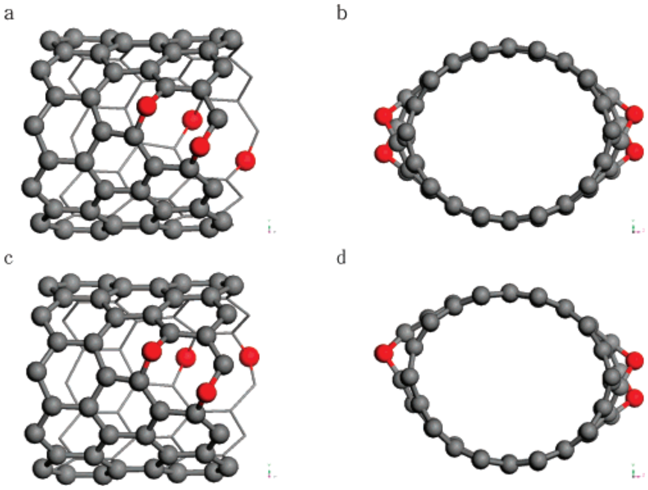

Figure 6. Two most stable isomers of (10,0) CNT oxygenized with four oxygen atoms: isomers a_3 and b_3 are shown in (a, b) and (c, d), respectively. Two different views are shown.

To investigate the effect of the tube diameter on the relative tendency of oxygenation, we have compared the energy of oxygenation (−2.40 and −1.51 eV) with four oxygen atoms for the most stable isomers of oxygenized (8,0) and (10,0) CNTs. Their oxygen content actually corresponds to 6 and 5% for (8,0) and (10,0) tubes, respectively (see structures a and b in Figure 6). This observation shows that the oxygenation tendency is sensitive to the tube diameter. A similar argument holds for armchair tubes, as can be seen from the values of E_4 for isomers a_4 shown in Table 1.

Our analysis of the electronic structure of isomer a_2 of (10,0) CNT shows that bands in [−2, 2] eV around Fermi level exclusively correspond to tube states not containing any oxygen-derived state. In fact, two lone-pair states of

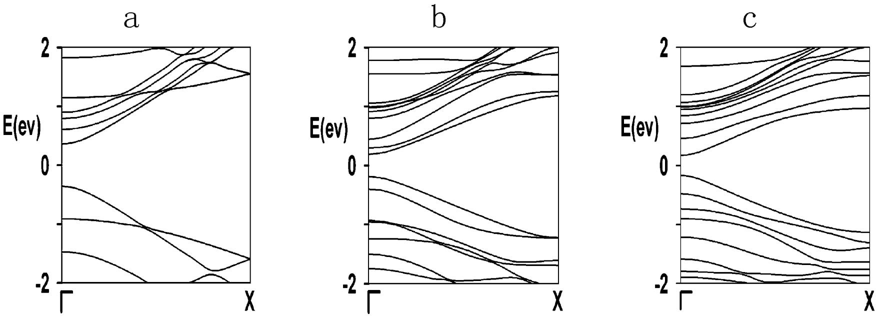

Figure 7. (b, c) Band structures of two most stable isomers ($a_4$and b_4, respectively) of (10, 0) CNT oxygenized with four oxygen atoms in comparison with (a) that of the pristine (10,0) CNT.

Table 2. Energy of Oxygenation (E_i) for Various Isomers of Oxygenized BNNTs[a]

chiral index	stoichiometry	isomer	E_i[b]	I_{B-N}[c]	I_{B-O}[d]	I_{N-O}[e]	Lx[f]
(5,5)	$B_{40}N_{40}O$ (i=1)	e_1	0.01(0.04)	2.13	1.42	1.44	10.05(10.10)
		z_1	0.93(0.94)	1.62	1.46	1.50	10.05(10.10)
	$B_{40}N_{40}O_2$ (i=2)	a_2	−0.16(−0.12)	2.20, 2.20	1.42	1.44	10.05(10.10)
		b_2	−0.05(−0.01)	2.13, 2.13	1.42	1.44	10.05(10.10)
	$B_{40}N_{40}O_3$ (i = 3)	a_3	−0.22(−0.20)	2.17, 2.25	1.42	1.44	10.07(10.10)
		b_3	−0.22(−0.19)	2.12, 2.19	1.42	1.44	10.07(10.10)
		c_3	(−0.07)	2.14, 2.19	1.42	1.44	(10.10)
	$B_{40}N_{40}O_4$ (i = 4)	a_4	(−0.41)	2.18, 2.19	1.42	1.44	(10.10)
(10,0)	$B_{40}N_{40}O$ (i = 1)	z_1	0.63(0.63)	2.13	1.41	1.44	8.68(8.68)
		a_1	0.99(0.99)	1.56	1.48	1.51	8.68(8.68)
	$B_{40}N_{40}O_2$ (i = 2)	a_2	(0.56)	2.23, 2.23	1.43	1.40	(8.68)
		b_2	(0.78)	2.25, 2.26	1.41, 1.42	1.43	(8.68)

[a] The subscript "i" indicates the number of oxygen atoms in the four and two primitive cells of (5,5) and (10,0) tubes, respectively. Also see footnote a for Table 1. [b] Energy change of oxygenation with i oxygen atoms. See the text for more details. [c] Bond length of the B═N bond involved in the oxygenation. [d] Bond length of the B−O bond involved in the oxygenation. [e] Bond length of the N−O bond involved in the oxygenation. [f] Lattice parameter of one supercell along the tube axis, which includes four and two primitive cells for (n, n) and (n,0) tubes, respectively.

oxygen are located at −2.34 and −3.34 eV below the Fermi level. Therefore, the electronic structure of the isomer is quite similar to that of the unmodified (10,0) CNT other than the splitting of degenerate bands due to the breaking of symmetry. The splitting induced by the oxygenation results in the decrease in the band gap by 0.49 eV from that (0.70 eV) of the pristine tube. A similar analysis for two most stable isomer (a_4 and b_4 shown in Figure 6) of the CNT oxidized with four oxygen atoms also results in the decrease of the band gap to 0.37 and 0.34 eV, respectively (see Figure 7. This observation indicates that optical properties can be used to monitor the chemical oxygenation of zigzag CNTs.

B. Oxygenation of BNNTs. Along with CNTs, the oxygenation of BNNTs are of also interest. To investigate this, we calculated the oxygenation energy of (5,5) BNNT, which consists of four primitive cells in a supercell. Similarly to the case of (5,5) CNT, there are two isomers e_1 and z_1 for the singly oxygenated tube. Again, Table 2 shows that isomer e_1, which is characterized by the breaking of an equatorial B−N bond and the formation of a B−O−N bond, is more stable than a_1, in which an axial B−N bond is involved in the reaction. However, comparison of the energy of oxygenation $E_1(e_1)$ (0.01 eV) with the corresponding value (−0.76 eV) for (5,5) CNT shows that the formation of a B−O−N bond is much less favorable than that of an ether bond. Therefore, an armchair BNNT is much less easily subjected to oxygenation than the corresponding CNT. However, another comparison of E_1 with the $E_1(z_1)$ for (10,0) CNT indicates that the armchair BNNT can be as easily oxygenated by one oxygen atom as (10,0) CNT. These results have been unexpected in view of the general belief that BNNTs are chemically inert. In fact, X-ray photoelectron spectroscopy (XPS) showed that there are B−O bonds in BNNTs synthesized by thermal CVD.[17]

We also sought to gain information on the cooperativity of the reaction by considering the binding of two oxygen atoms. Table 2 shows the values of E_2, the energy of oxygenation by two oxygen atoms, for the two most stable isomers. Structures of the isomers are defined similarly to the case of (5,5) CNT shown in Figure 2. For example, the structure of isomer a_2 is similar to that for isomer a_2 of (5,5) CNT shown in structures a and b in Figure 2. Comparison of $E_1(e_1)$ (0.01 eV) and $E_2(a_2)$ (−0.16 eV) shows that the oxygenation is again cooperative. An additional comparison of the latter energy with corresponding value (−0.43 eV) for (10,0) CNT again shows that the tendency for the introduction of a pair of oxygenation atoms in (5,5) BNNT is comparable to that in (10,0) CNT. Indeed, the reaction is found to be exothermic for isomer a_2, although less pronounced than the case of (10,0) CNT. Comparison of the values (−0.22 and −0.22 eV) of $E_3(a_3)$ and $E_3(b_3)$ in Table 2 shows that the addition of one more oxygen atom occurs equally at two sites on a purely energetic ground: (1) an equatorial B−N bond, which is adjacent to the two equatorial bonds already oxygenized in the case of isomer a_3, and (2) an equatorial B−N bond on the opposite side of the circumference of the tube in the case of isomer b_3. (Note that isomers a_3 and b_3 are defined similarly to those in (5,5) CNT shown in Figure 3.) However, isomer b_3 is entropically

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(17) Kim, S. Y.; Park, J.; Choi, H. C.; Ahn, J. P.; Hou, J. Q.; Kang, H. S. *J. Am. Chem. Soc.* **2007**, *129*, 1705.

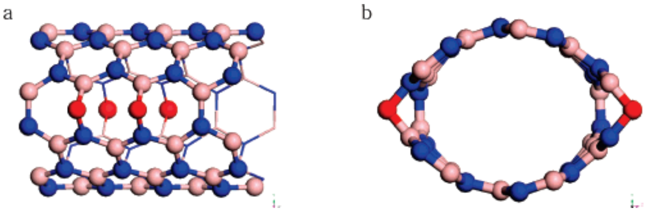

Figure 8. The most stable isomers (a_4) of (5, 5) BNNT oxygenized with four oxygen atoms. Two different views are shown.

much more favored than isomer a_3, because there are many more ways of achieving the former. In short, oxygenation of armchair BNNTs will tend to occur in pairs randomly distributed on the two opposite sides of the circumference of the tube in the form of B−O−N bonds. Figure 8 shows this in the case of four oxygen atoms, which corresponds to an oxygen content of 5%. (The tendency to form a consecutive row along the tube axis will be weaker than the case of armchair CNTs.) Although not shown, we find that the oxygenation does not introduce any appreciable change in the electronic structure around Fermi level.

Finally, we investigated the oxygenation of (10,0) BNNT. Table 2 shows that the most stable isomer is z_1, which is analogous to the stable isomer z_1 of (10,0) CNT. Table 2 shows that a B−N bond gets broken upon oxygenation in the isomer. However, the value (0.63 eV) of E_1 indicates that it is much more difficult to oxygenize the zigzag BNNT than the corresponding zigzag CNT. In fact, the reaction is endothermic for (10,0) BNNT by an appreciable amount, which is also the case of oxygenation by two oxygen atoms (see the oxygenation energies for isomers a_2 and b_2 in Table 2). In short, the oxygenation could predominantly occur in tubes of armchair chirality in the case of BNNTs.

4. Conclusion

Using the first-principles calculation method, we investigated the relative stability of various isomers of oxygenated CNTs in order to understand the molecular structure of CNTs purified by the oxygen treatment of as-grown tubes. The reaction of CNTs with oxygen molecules is largely exothermic, particularly for the (5,5) tube. When the oxygen content is ∼5% in the (5,5) tube, oxygen atoms tend to form a contiguous row of ether (not epoxide as is usually said) along the tube axis, which can be understood in terms of a zipping mechanism. When the oxygen content is between 5 and 10%, those atoms will align in two rows on the opposite sides of the circumference of the tube. In (10,0) CNT, oxygen atoms tend to be uniformly distributed in pairs of ether in two opposite sides of the tube up to 10% of oxygen content. Electronic structure analysis shows that the oxygenation of (10,0) CNT brings about the decrease in the band gap.

Similar calculations were performed on (5,5) and (10,0) BNNTs. The reaction energy of (5,5) BNNT toward oxygenation by one oxygen atom is comparable to that for (10,0) CNT, which needs attention in view of the general belief that BNNTs are chemically inert. In relation to this observation, it should be mentioned that the oxygenation tendency of BNNTs of small diameters can be significantly higher than those of BNNTs of large diameters and hexagonal boron nitride due to the strain energy.

The local chemical structure of the oxygenated BNNTs around the oxygen atom is similar to that in oxygenated CNTs, i.e., there are formations of B−O−N bonds with the breaking of the corresponding B═N bond. At higher oxygen contents, a cooperativity is predicted for (5,5) BNNT in the formation of pairs of adjacent B−O−N bonds at equatorial B−N bonds, although weaker than the case of (5,5) CNT. Indeed, the cooperativity favors the chemical insertion of two oxygen atoms in the tube over the evaporation of an oxygen molecule, which is shown by the exothermic value (−0.16 eV) of energy of oxygenation.

Upon acid treatment of BNNTs, all the data shown above indicate that the oxygenation could occur in a chirality-specific way. Namely, the reaction could predominantly occur in armchair BNNTs, particularly in the tubes of small diameters, rather than in zigzag tubes. Zigzag BNNTs will remain intact. We want to point out that the oxygenation tendency of BNNTs will also depend on the kinetic factor, i.e., the activation barrier of the reaction, whose investigation is outside the scope of this work. It is also worth mentioning that defects of the tubes, which might exist in various forms, can play an important role, which enhances the oxygenation.

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Supporting Information Available: Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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