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High coverage of hydrogen on a (10,0) single-walled boron nitride nanotube

Sang Soo Han, Sung Hoon Lee, Jeung Ku Kang, and Hyuck Mo Lee*
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology,
Kusung-dong 373-1, Yusung-gu, Daejon 305-701, Korea

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The binding energy of hydrogen atoms to a (10,0) single-walled boron nitride nanotube (SWBNNT) is calculated at 25%, 50%, 75%, and 100% coverage using the density functional theory. The average binding energy is highest at 50% coverage when the H atoms are adsorbed on the adjacent B and N atoms along the tube axis and the value is −53.93 kcal/mol, which is similar to half of the H—H binding energy. Also, the band gap (−4.29 eV) of the pristine (10,0) SWBNNT is decreased up to −2.01 eV for the H-adsorbed BNNT with 50% coverage.

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Due to low dimensionality and high surface-area-to-volume ratio, the physical properties of nanotubes can be dramatically influenced by the surface addition of selected atomic or molecular species. Such functionalization can lead to significant enhancement of properties relevant to technological applications. For instance, it has been recently demonstrated that carbon nanotubes (CNTs) functionalized with hydrogen represent a new type of a nanoscale electronic device.[1]

In contrast to CNTs, boron nitride nanotubes (BNNTs) have a uniform electronic band gap independent of the diameter and chirality of the tube and their native state is electrically insulting.[2,3] Because of large ionicity of the B—N bond in BNNTs, their properties are different from CNTs. It was reported that BNNTs prefer a nonhelical or zigzag orientation during growth,[4,5] which prefigures the advantage of BNNTs in the potential application of nanoscale electronic devices similar to CNTs. The doping behavior of BNNTs is also important since it may create acceptors or donors for the use in the electronic device such as the *p*-*n* junction. However, studies of BNNTs have been focused on growth and properties of clean BNNTs so far. The doping behavior or functionalization of BNNT is very rare compared with the studies of CNTs.

In this work, we study the chemisorption behavior of hydrogen on the sidewall of the (10,0) single-walled BNNT (SWBNNT) with 25%, 50%, 75%, and 100% coverages by the density functional theory (DFT). We will show that the binding energies of hydrogen on the BNNT wall are dependent on its coverage and the electronic structures of the tube can be modified by the chemisorption process of hydrogen.

The binding energies of hydrogen were calculated using the local-orbital DFT method implemented with the DMOL^3 package.[6] All the electron calculations were used together with the double numerical plus polarization (DNP)[7] basis set and the generalized gradient approximation (GGA) employing the Perdew-Wang scheme.[8] The DNP basis set is comparable in quality to the commonly used Gaussian analytical basis set, 6-31G**.[9] To model the interaction between hydrogen atoms and a (10,0) SWBNNT, we used a tetragonal cell of the size 25 Å×25 Å×4.38 Å with the length of *c* equal to the periodicity of the (10,0) SWBNNT, assuming a B—N bond length of 1.46 Å.[10] The supercell includes 20 B and 20 N atoms. The experimentally synthesized SWBNNTs were observed to have a range of diameters ranging from ~0.5 to 1.2 nm.[11,12] It was also reported that the synthesis of the zigzag-type BNNT is more favorable to that of the armchair type,[4,5] thus the (10,0) SWBNNT is chosen in this study since the zigzag (10,0) BNNT has a diameter of 0.81 nm. In calculating with a DMOL^3 code, all the calculations were performed only at the gamma point ($\vec{k}=0$).

Densities of states (DOSs) for both the pristine (10,0) SWBNNT and the hydrogenated one were also investigated by the CASTEP software.[13] The exchange-correlation of electrons was handled with the PW91 functional[8] of GGA level and the norm-conserving pseudopotentials generated by using the Troullier-Martins scheme were adopted to describe the electron-ion interaction.[14] We set a kinetic energy cutoff of 700 eV for the BNNTs and used the Monkhorst-Pack scheme[15] to generate the *k*-space grid. With the optimized structures of the nanotubes predicted in the above chemisorption energy studies of hydrogen with coverage, we performed single point calculations for the structures to calculate DOS because the plane-wave type DFT calculation generally requires high simulation time cost. The cell size is considered to be same as that in the chemisorption energy studies performed by the DMOL^3 package. We also found out that a *k*-point sampling of 2×2×4 is sufficient for energy convergence. Integration over a three-dimensional Brillouin zone was carried out using the total of eight *k* points.

According to Bauschlicher,[16] it was proved that hydrogen is more strongly bonded to the single-walled carbon nanotube (SWCNT) with hydrogen coverage of a high symmetry than the random structure. As a result, the SWBNNTs with hydrogen coverage of only high symmetry were considered in this study. The (10,0) SWBNNT plus H models considered here are shown in Fig. 1 in which the structures are optimized with all the atoms free. To show the adsorption structures clearly, we repeat the unit cell in the *c* direction up to double periodicity. The hydrogen binding energies are summarized in Table I. The adsorption energy ΔE_{ads} is defined as follows:

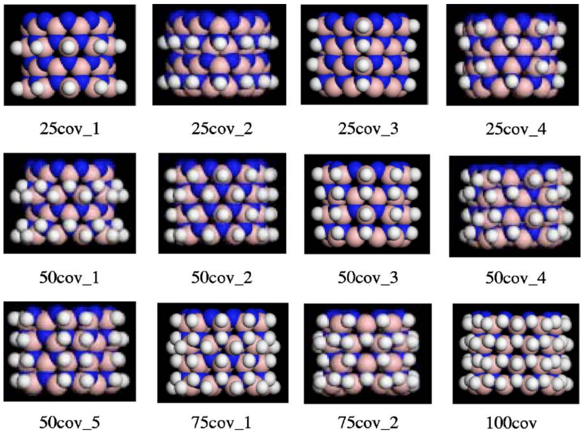

FIG. 1. (Color online) Hydrogen decorations considered in this study to investigate the binding energies of H on the exterior wall of (10,0) SWBNNT as a function of H coverage. In DFT calculations, only four layers of the BNNT (half of the present tube structures along the tube axis) were considered due to computational limitation. Here, the pink, blue, and white atoms mean boron, nitrogen, and hydrogen, respectively. In the case of 25% H coverage, the 25cov_1 indicates all boron pattern, the 25cov_2 all nitrogen pattern, the 25cov_3 the line pattern, and the 25cov_4 the zigzag pattern. In 50% coverage, the 50cov_1 means the pairs of rings pattern, the 50cov_2 all boron pattern, the 50cov_3 the line pattern, the 50cov_4 the spiral pattern, and the 50cov_5 the pairs of lines pattern. Also, the 75cov_1 is the pattern of 75% H coverage having the 20 B—H and 10 N—H in unit cell of the BNNT and the 75cov_2 is the pattern having 10 B—H and 20 N—H.

$$\Delta E_{\mathrm{ads}} = E_{\mathrm{tot}}(\mathrm{BNNT} + n\mathrm{H}) - E_{\mathrm{tot}}(\mathrm{BNNT}) - n \times E_{\mathrm{tot}}(\mathrm{H}) \qquad (1)$$

where $E_{\mathrm{tot}}(\mathrm{BNNT}+n\mathrm{H})$, $E_{\mathrm{tot}}(\mathrm{BNNT})$, and $E_{\mathrm{tot}}[\mathrm{H}]$ are the total energies of the fully optimized (10,0) SWBNNT-H structure, the nanotube alone and the hydrogen atom, respectively, and n is the number of hydrogen. The minus value of ΔE_{ads} implies that adsorption is exothermic.

In Table I, it is noticeable that the binding energies of hydrogen are higher for all the high hydrogen coverages than the binding energies of one B—H bond or one N—H bond. Especially, the N—H binding energy has a positive value when one H atom is adsorbed on the top site of one N atom in the (10,0) SWBNNT; however, it changed to a negative value if the hydrogen coverage is increased (see 25cov_2 in Table I). The result for the adsorption of a single H shows that the adsorption is site selective; in other words, a H atom prefers to be adsorbed on the top site of the B atom of the pristine SWBNNT, which agrees well with the DFT result of Wu *et al.*[17] Moreover, the B—H binding energy in the 25% (25cov_1) or 50% (50cov_2) coverage is significantly higher than that in the single B—H bond state. It is because only one B—H bond state leaves an open-shell radical state (doublet spin state) on the nanotube, while the BNNTs with high hydrogen coverage, such as 25cov_1 and 50cov_2, have a close-shell structure (singlet spin state).

TABLE I. Summary of H binding energies (kcal/mol) on the (10,0) SWBNNT exterior wall as a function of H coverage. The calculations were performed at the level of DFT/PW91 with a DNP basis set. The case that all H atoms adsorb on nitrogen atoms in coverage of 50% is not shown here because the calculation is not converged.

Coverage	ΔE_{ads}[a]	ΔE_{ave}[b]
25%		
25cov_1	−178.98	−17.90(10 B—H)
25cov_2	−274.29	−27.43(10 N—H)
25cov_3	−538.15	−53.81(5 B—H&5 N—H)
25cov_4	−518.71	−51.87(5 B—H&5 N—H)
50%		
50cov_1	−1045.76	−52.29(10 B—H&10 N—H)
50cov_2	−415.48	−20.77(20 B—H)
50cov_3	−1007.41	−50.37(10 B—H&10 N—H)
50cov_4	−1068.48	−53.42(10 B—H&10 N—H)
50cov_5	−1078.57	−53.93(10 B—H&10 N—H)
75%		
75cov_1	−1210.78	−40.36(20 B—H&10 N—H)
75cov_2	−1132.28	−37.74(10 B—H&20 N—H)
100%		
100cov	−1835.44	−45.89(20 B—H&20 N—H)
2.5%		
One B—H on BNNT		−8.10
One N—H on BNNT		+7.25

[a] $\Delta E_{\mathrm{ads}} = E_{\mathrm{tot}}[\mathrm{BNNT}+n\mathrm{H}] - E_{\mathrm{tot}}[\mathrm{BNNT}] - n \times E_{\mathrm{tot}}[\mathrm{H}]$ (n is the number of hydrogen atom)

[b] Average H binding energy calculated by the following equation: $\Delta E_{\mathrm{ave}} = \Delta E_{\mathrm{ads}}/n$

In addition, the highest stability of the BNNT structure with high hydrogen coverage is observable when hydrogen is chemisorbed on adjacent B and N atoms along the tube axis, which probably results from two reasons. Hydrogen bonding to adjacent B and N atoms would imply a loss of one B—N π bond, while that with two B atoms would have a greater disruption of the B—N π bond system. Another reason can be discovered by atomic charges of hydrogen. For example, in the case of 25% hydrogen coverage, the atomic charges have negative values as hydrogen is bonded with only B atoms (see 25cov_1 in Fig. 1), and vice versa for N—H bonds. Thus the repulsive interaction is affected between two hydrogen atoms chemisorbed on the nanotube wall and two hydrogen atoms tend to repel each other. On the other hand, if hydrogen is chemically adsorbed with adjacent B and N atoms, as in the case of 25cov_3, the charges for hydrogen atoms are negative for B—H bonds and positive for N—H bonds, indicating attractive interaction between two hydrogen atoms. The attractive force causes two H atoms to pull each other. Additionally, one can consider the attraction between nonbonded H and N atoms in the case of 25cov_3 since H atoms bonded with N atoms have positive atomic charges and other N atoms do not. In the case of 25cov_1, this attraction is not present because all H atoms bonded with B atoms have negative charges. Therefore, the most favorable hydrogen configuration at a constant coverage has H atoms upon adjacent B and N atoms.

In Table I, we can also find that the most favorable adsorption configuration is that the numbers of H-adsorbing B and N atoms are equal. However, the hydrogen binding energies at 100% coverage are lower than at 25% and 50% coverage with the equal number of B—H and N—H bonds. To form B—H and N—H bonds, the B and N atoms must occupy sp^3 hybridization, which results in the B and N bulging out the tube. For both 100% coverages, the B and N atoms still form a good tube structure since any deformation that improves one B—H or N—H bond will weaken another, which is similar to the case of CNT.[16] This means that for the 100% coverage, the B and N atoms cannot change their hybridization to enhance the B—H and N—H bond, which results in weaker adsorption than the 50% coverage where half of the B and N atoms can bulge out of the tube to maximize the B—H and N—H bonding. The reason why hydrogen binding energy at 100% coverage is higher than at 75% is that the electrostatic attraction between nonbonded B—H and N—H is maximized when numbers of the formed B—H and N—H bonds are same. If the number is different, the additional electrostatic repulsive forces between two H atoms bonded with B atoms (75cov_1) or with N atoms (75cov_2) are generated. Despite any limitation in the calculation methods used, it is clear that the formation of 75% and 100% coverage will be a very endothermic process because the H—H bond energy is 105.27 kcal/mol at the present DFT calculation level. Because the highest binding energies (−53.93 kcal/mol in the case of 50cov_5) computed for the 50% coverage are sufficiently close to one-half (−52.64 kcal/mol) of the H—H bond energy, it might be possible to achieve the coverage level in a thermodynamic process starting with H_2 and BNNT. The formation of significantly higher than 50% coverage in a thermodynamic process seems unlikely since a higher coverage would require deformation of the B and N atoms on the tube, which would weaken some of the existing B—H and N—H bonds and hence result in a smaller average H binding energy.

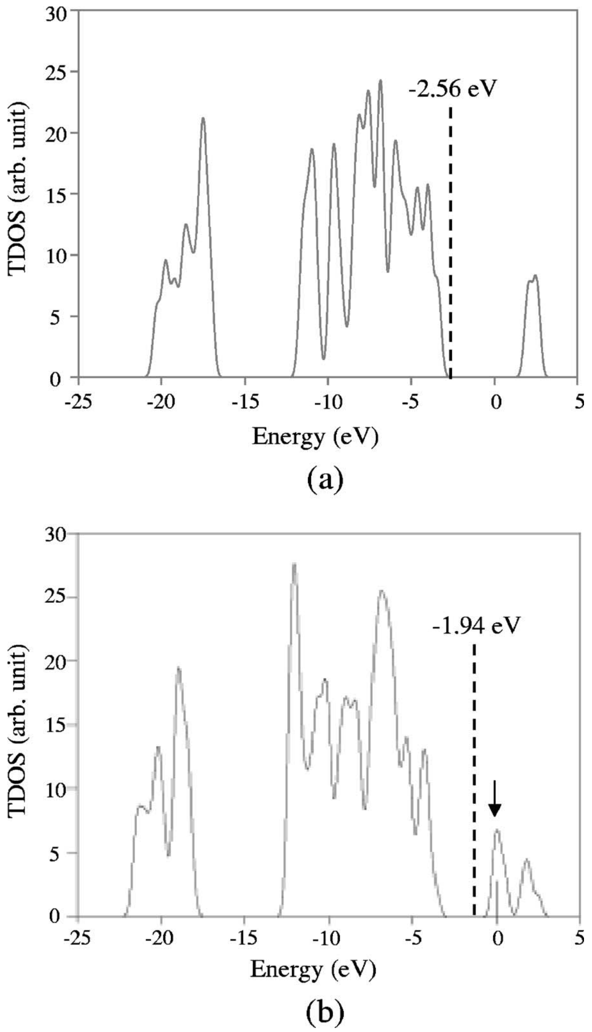

FIG. 2. TDOS for (a) pristine (10,0) SWBNNT and (b) (10,0) SWBNNT with 50% H coverage, called 50cov_5 in Fig. 1. The dotted lines in each figure refer to the Fermi energy level. The arrow in (b) indicates one band in the band gap, caused by hydrogen chemisorption.

By calculating the electronic DOS, we investigated the electronic structures of the (10,0) SWBNNT with high hydrogen coverage. Figure 2 shows the total DOS (TDOS) for electrons in pristine and hydrogen adsorbed (10,0) SWBNNT where the hydrogen coverage corresponds to 50cov_5, the most stable state in Fig. 1. We found that the pristine (10,0) SWBNNT has a band gap of 4.29 eV from the gap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in Fig. 2(a), which is similar to the published DFT result of 4.03 eV.[18] In the SWBNNT with 50% hydrogen coverage, the band gap (HOMO-LUMO gap) is decreased to 2.01 eV, indicating a semiconductor with a wide band gap. From this fact, we know that the SWBNNT can be modulated through hydrogen adsorption from an insulator (for the pristine state) to a semiconductor (for the 50% coverage state). The reason why the band structure can be changed by hydrogen adsorption is easily understood from the partial DOS (PDOS) for B and N atoms in the nanotube, although the result is not shown here. In the case of the pristine (10,0) SWBNNT, the PDOS demonstrates that the structure of the valence band is almost completely determined by nitrogen. The contribution of boron is small but its effect on the formation of states at the edges of the conduction band is greater. In the BNNT with 50% hydrogen coverage, a new peak is found near 0.0 eV in the band gap, indicated by an arrow in Fig. 2(b). The peak is mainly caused by the *s* orbital of H atoms bonded with B atoms.

As already mentioned, it is believed that the BNNT is an insulator with a 4–5 eV band gap independent of its helicity.[2,3] To modulate the band gap of the nanotube, there are two ways: carbon doping[19] and radial deformation[20] of the BNNT. According to the local density functional calculation of Blase *et al.*,[19] the calculated band gap is decreased to 2.0 and 0.5 eV for BC_2N and BC_3 nanotubes, respectively, as the carbon composition is increasesd in $B_xC_yN_z$ nanotube. Thus, the synthesis of the composite $B_xC_yN_z$ nanotube would make possible its application for electronic and photonic devices with a variety of electronic properties. Also, Kim *et al.*[20] reported that in the zigzag BNNTs the radial deformation that gives rise to transverse pressure of about 10 GPa decreases the gap from 5 to 2 eV, allowing for optical application in the visible range. We suggest a new method, hydrogen adsorption, to modulate a band gap of the BNNT. The band gap (4.29 eV) of the insulating (10,0) SWBNNT can be decreased to 2.01 eV, indicating a semiconductor with a wide band gap.

In summary, it is possible for hydrogen to be chemically adsorbed on the exterior surface of BNNT up to 50% coverage. Since the average hydrogen binding energy (per H atom) at 50% coverage is very close to half of a H_2 bond energy, it might be possible to achieve this level of coverage in a thermodynamic process starting with H_2 and pristine SWBNNT. The band structure of the SWBNNT can be modulated through hydrogen chemisorption. In detail, if hydrogen is chemisorbed on the exterior wall of BNNT up to the coverage of 50%, the pristine insulating BNNT is changed to a semiconductor with a wide band gap. It is certain that the present results for the electronic properties of BNNT activate further works on the electronic and photonic devices using BNNTs.

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*Corresponding author: Prof. Hyuck Mo Lee: Email: hmlee@kaist.ac.kr TEL: +82-42-869-3334: FAX: +82-42-869-3310

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