Selective adsorption of first-row atoms on boron nitride nanotubes: the effect of localized states

Jia Li, Gang Zhou, Haitao Liu, and Wenhui Duan*
Department of Physics, Tsinghua University, Beijing 100084, People’s Republic of China
(Dated: March 23, 2022)

First-principles calculations reveal that the adsorption of representative first-row atoms with different electronegativity, such as lithium (Li), carbon (C) and fluorine (F), on zigzag single-walled boron nitride nanotubes (BNNTs) exhibits surprising selectivity. The adsorption energy and adsorption site are dependent upon the chemical activity of adsorbate with respect to the B and N atoms in the host tube. In detail, the F atom prefers to be adsorbed on the top of the B atom, the C atom is energetically favorable to stay on the bridge site which is perpendicular to the tube-axis, and the Li atom hardly adheres to the tube (an endothermal reaction). The adsorption behavior of these three types of elements on BNNTs is elucidated based on the frontier molecular orbital theory. In addition, the mechanism of modification of electronic structures of BNNTs by adsorption is probed, and a feasible approach is proposed to tailor the electronic properties of BNNTs.

PACS numbers: 61.46.+w, 68.43.Fg, 73.22.-f

I. INTRODUCTION

Boron nitride nanotubes (BNNTs) have attracted an enormous amount of attention as a typical representative of III-V compound tubes, partially because they have the morphology of honeycomb analogous to carbon nanotubes (CNTs). However, different from CNTs, BNNTs are semiconducting with an uniform wide energy gap and their electronic properties are independent of the tube diameter, chirality and of whether a nanotube is single-walled or multiwalled. Owing to the unique geometrical structure and uniform semiconducting behavior, BNNTs are expected to have significant applications in the molecule-based logic gates and high-strength fibers.

On the other hand, for the hollow nanotube with high surface-area-to-volume ratio, the doping is recognized to be a significant and attractive approach of functionalizing the nanotube because it provides various possibilities for controlling the physical properties. In particular, previous studies showed that the doping of carbon (C) atoms into BNNTs could visibly decrease the band gap and such a gap decrease is sensitively dependent upon the content of C atoms. Subsequently, Han et al. developed a simple chemical route to successfully coat BNNTs with a conductive stannic oxide for the sensor application. Recently, Tang et al. found experimentally that the resistance and resistivity of the fluorinated BNNT are about 3 orders of magnitude less than those of the pure BNNT, and suggested that it might be important for applications in the future nanoscale electronic devices with tunable properties. Thus, uniformly doped BNNTs obtained through chemical modification could be very effective for tailoring the electronic properties, and the related mechanism and behavior are valuable to be explored in theory.

In this paper, we demonstrate a feasible way to modify the electronic properties by atomic adsorbing on perfectly fabricated BNNTs, which is different from the conventional way by doping foreign species into host systems in the nanotube growth process. Firstly, we study the adsorption of several representative first-row atoms with different electronegativity on single-walled BNNTs through first-principles calculations. And then we analyze the adsorption selectivity of BNNTs from the localized characteristics of electronic states near the Fermi level and discuss the adsorption behavior of these atoms on BNNTs based on the frontier molecular orbital theory. Finally we explore the mechanism of modification of the electronic properties of BNNTs by adsorption.

II. MODEL AND METHOD

Since many experiments have shown that BNNTs prefer a nonhelical or zigzag orientation during the growth, we emphatically address the adsorption of zigzag BNNTs. A finite-length cylindrical BN cage, consisting of 48 B and 48 N atoms, is chosen to represent the stem of a zigzag single-walled BNNT. Two mouths of the tube are terminated by the hydrogen atoms to avoid the boundary effect. In general, the interaction between two different atoms or elements could be simply evaluated in term of the Pauli electronegativity (PE) and first ionization potential (FIP). With respect to PEs and FIPs of B and N atoms, we choose three types of first-row atoms, lithium (Li), C and fluorine (F), with different PE and FIP as the representatives of adsorbate to study the adsorption properties of BNNTs.

The local-orbital density-functional method, DMol, is employed to carry out structural optimizations and total-energy calculations. The generalized gradient approximation combining the Perdew-Wang correlation...
An important and primary feature of compound tubes is that the distributions of positive and negative charges along the tube stem are much more nonuniform than those of elementary tubes (e.g., CNTs) because of the unambiguous charge transfer from one component with low electronegativity to another with high electronegativity in tubes. Typically, the calculated charge transfer from the B to N atom is $0.111$ e per B-N pair in the (8,0) BNNT. So in general the isolated BNNT could be regarded as an unique tube that consists of the equal number of “N cations” and “B anions”, and possesses the large “ionicity”. In principle, the resulting influences on the structures and properties of BNNTs could be understood in virtue of the local density of states (LDOS).

Fig. 1(a) shows the calculated LDOS of B and N atoms of the (8,0) BNNT. It can be seen that $2s$ and $2p$ states from the B and N atoms strongly mix together in the lower or higher energy region far from the Fermi level. While the occupied and unoccupied states near the Fermi level are mainly contributed by $2p$ states, rather than $2s$ states, of N and B atoms, respectively. The former (the occupied states) corresponds to the $\sigma$ bonds between the constitute atoms in virtue of the $sp^2$ hybridization, which guarantees the basic honeycomb framework, high Young’s modulus and tensile strength. In contrast, the latter (the unoccupied states) mainly determines some physical and chemical properties of BNNTs (such as conductivity and chemical activity). The further composition analysis on the corresponding frontier molecular orbitals (FMOs) demonstrates that these occupied and unoccupied states near the Fermi level exhibit quite different localized characteristics. For instance, as shown in Fig. 1(b), the highest occupied molecular orbital (HOMO) corresponds to isolated electron pairs localized at the N atoms and has the spindle-shape scheme like as $p_z$ orbitals, whereas the lowest unoccupied molecular orbital (LUMO) is present as $\pi$ states localized at the B-N pair along the tube-axis and is contributed by the B-2$p$ (major) and N-2$p$ (minor) states. The corresponding spatial orientations are well perpendicular to the cylindrical surface. In principle, the nature of localized states near the Fermi level is crucial for understanding the structures and properties of doped BNNTs. In the following text, we systematically study the adsorption behavior of single first-row atoms on BNNTs and thoroughly probe the related adsorption mechanism.

In the doping procedure, the interactions between host BNNTs and foreign species can be usually classified into the physical and chemical interactions. Indeed the chemical interaction might play more significant role than the physical interaction in practical applications of BNNTs, such as hydrogen storage and modification of the electronic property. Since the occupied and unoccupied states near the Fermi level in BNNTs have the distinctly different localized characteristics, we could deduce that the chemical interaction between BNNTs and dopants certainly will be characterized as highly selective, and the resulting adsorption behavior and effect ought to be more complicated and interesting than those in CNTs in the same doping procedure.

In general, the chemical activity of single atom could be evaluated by the PE or FIP. To more comprehensively and systematically probe the mechanism of selective adsorption of BNNTs, we choose three types of first-row atoms, Li, C and F as the representatives. The order of PE is:

III. RESULTS AND DISCUSSION

An important and primary feature of compound tubes is that the distributions of positive and negative charges along the tube stem are much more nonuniform than those of elementary tubes (e.g., CNTs) because of the unambiguous charge transfer from one component with low electronegativity to another with high electronegativity in tubes. Typically, the calculated charge transfer from the B to N atom is $0.111$ e per B-N pair in the (8,0) BNNT. So in general the isolated BNNT could be regarded as an unique tube that consists of the equal number of “N cations” and “B anions”, and possesses the large “ionicity”. In principle, the resulting influences on the structures and properties of BNNTs could be understood in virtue of the local density of states (LDOS).

Fig. 1(a) shows the calculated LDOS of B and N atoms of the (8,0) BNNT. It can be seen that $2s$ and $2p$ states from the B and N atoms strongly mix together in the lower or higher energy region far from the Fermi level. While the occupied and unoccupied states near the Fermi level are mainly contributed by $2p$ states, rather than $2s$ states, of N and B atoms, respectively. The former (the occupied states) corresponds to the $\sigma$ bonds between the constitute atoms in virtue of the $sp^2$ hybridization, which guarantees the basic honeycomb framework, high Young’s modulus and tensile strength. In contrast, the latter (the unoccupied states) mainly determines some physical and chemical properties of BNNTs (such as conductivity and chemical activity). The further composition analysis on the corresponding frontier molecular orbitals (FMOs) demonstrates that these occupied and unoccupied states near the Fermi level exhibit quite different localized characteristics. For instance, as shown in Fig. 1(b), the highest occupied molecular orbital (HOMO) corresponds to isolated electron pairs localized at the N atoms and has the spindle-shape scheme like as $p_z$ orbitals, whereas the lowest unoccupied molecular orbital (LUMO) is present as $\pi$ states localized at the B-N pair along the tube-axis and is contributed by the B-2$p$ (major) and N-2$p$ (minor) states. The corresponding spatial orientations are well perpendicular to the cylindrical surface. In principle, the nature of localized states near the Fermi level is crucial for understanding the structures and properties of doped BNNTs. In the following text, we systematically study the adsorption behavior of single first-row atoms on BNNTs and thoroughly probe the related adsorption mechanism.

In the doping procedure, the interactions between host BNNTs and foreign species can be usually classified into the physical and chemical interactions. Indeed the chemical interaction might play more significant role than the physical interaction in practical applications of BNNTs, such as hydrogen storage and modification of the electronic property. Since the occupied and unoccupied states near the Fermi level in BNNTs have the distinctly different localized characteristics, we could deduce that the chemical interaction between BNNTs and dopants certainly will be characterized as highly selective, and the resulting adsorption behavior and effect ought to be more complicated and interesting than those in CNTs in the same doping procedure.

In general, the chemical activity of single atom could be evaluated by the PE or FIP. To more comprehensively and systematically probe the mechanism of selective adsorption of BNNTs, we choose three types of first-row atoms, Li, C and F as the representatives. The order of PE is:
In the range of 0.04˚N bond is weakened, and the variations of other bonds are changed from 1.461˚ to the C atom (shown as the dashed line in Fig. 2(b)) is the bridge apart. The length of the B-N bond adhered to the C atom pushes the two bonding B and N atoms along and angles in the adsorption region (ADR) of C/BNNT deformation of the tube. The optimized bond lengths and then influences the electronic properties of BNNTs. The formation of new chemical bonds definitely changes the original electronic states, and adsorption (or interaction). The formation of new chemical bonds and angles indicate that the electronic states of the B and N atoms adjacent to the adsorbate exhibit the mixed characteristic of the \(sp^2\) and \(sp^3\) hybridizations, instead of the \(sp^2\) hybridization in the pure BNNT, and the \(sp^3\) component in the ADR of the F/BNNT is much more than that of the C/BNNT.

The more detailed analysis of the adsorption effect could be obtained from the change of electronic states. Fig. 3 shows deformation charge densities of the C/BNNT and F/BNNT. It can be seen that the B-N bond adjacent to the adsorbed C or F atom is evidently weakened with the formation of new chemical bonds between the C (or F) and B (and N) atoms. The Mulliken population analysis further verifies that the adsorption not only induces the charge transfer between the B, N and C atoms in the ADR, but also leads to the charge re-distribution of two other neighboring B (or N) atoms in the C/BNNT. Typically, the C atom accepts the electrons from the nearest neighbor B atom, and simultaneously donates the electrons to the nearest neighbor N atom. And the net charge transfer between the C atom and BNNT does not exceed 0.040 e. This reveals the C-N and C-B bonds are covalent-like. However, in the F/BNNT, the adsorption occurs only at the top of the B atom, so the charge transfer induced mainly occurs between the B and F atoms, and the N atom is less involved in. In detail, one F atom accepts 0.353 e from the B atom, which is three times larger than the charge transfer between the B and N atoms in the pure BNNT, and the B-F bond exhibits ionicity. Simultaneously, the F adsorption further leads to slight charge changes for two other neighboring N atoms and their neighboring B atoms (0.020 e/N atom and 0.035 e/B atom, respectively).

The above results can be better elucidated based on the FMO theory. Due to its strongest oxidizability, the F atom in the F/BNNT tends to directly interact with the B atom (low electronegativity) rather than the N atom (high electronegativity). The formation of chemical bond are originated from the interaction between the LUMO of the F atom and the FMOs of about 2.10 eV below

---

**TABLE I**: Optimized adsorption sites, and adsorption energies \(E_{ads}\) and adsorption heights \(H_{ads}\) of first-row atoms (Li, C and F) on the single-walled (8,0) BNNT.

| Atom | Adsorption Site | \(E_{ads}\) (eV) | \(H_{ads}\) (Å) |
|------|----------------|-----------------|----------------|
| B    |                  | 0.44            | 3.02           |
| Li   |                  | 0.32            | 2.28           |
| N    | Center\(^a\)    | 0.26            | 1.80           |
| C    | Bridge\(^b\)    | -2.00           | 1.26           |
| F    | B                | -2.51           | 1.84           |

\(^a\) Above the hexagon
\(^b\) Perpendicular to the tube-axis

Li(0.98)<B(2.04)<C(2.55)<N(3.04)<F(3.98), and that of FIP is: Li(5.392)<B(8.298)<C(11.260)<N(14.534)<F (17.422), respectively. From the spatial orientations and distributions of FMOs in BNNTs, we choose the top sites of B and N atoms, the bridge sites between B and N atoms and the center site above the hexagon as the initial adsorption sites. After full relaxations, we obtain the optimized adsorption site, adsorption energy\(^c\) and adsorption height as summarized in Table I.

It is found that the F atom prefers to stay at the top site of the B atom (see Fig. 2), and it is energetically favorable for the C atom to stay at the B-N bridge site which is perpendicular to the tube-axis (see Fig. 2). Whereas the Li atom can hardly be adsorbed on the BNNT since its adsorption energy is positive. The positive adsorption energy indicates an endothermal reaction, which is in accordance with the previous theoretical study. The reason is that the BNNT with partial ionic bonding is an electron-sufficient system, and hardly accepts the excessive electrons from the environment. Furthermore, the adsorption energy of the F atom on BNNT (F/BNNT) is larger than that of the C atom on BNNT (C/BNNT) because the electronegativity of the F atom is larger than that of the C atom. The adsorption of the F and C atoms corresponds to a classical chemical adsorption (or interaction). The formation of new chemical bonds definitely changes the original electronic states, and then influences the electronic properties of BNNTs.

Firstly, the chemical adsorption will induce a slight deformation of the tube. The optimized bond lengths and angles in the adsorption region (ADR) of C/BNNT and F/BNNT are displayed in Fig. 2. In the C/BNNT, the C atom pushes the two bonding B and N atoms along the bridge apart. The length of the B-N bond adhered to the C atom (shown as the dashed line in Fig. 2(b)) is changed from 1.461 Å to 2.214 Å, which indicates this B-N bond is weakened, and the variations of other bonds are in the range of 0.04 Å. Furthermore, the N-B-N angles are changed from 120.1°, 120.1° and 118.6° to 122.2°, 101.4° and 113.8°, respectively. And the B-N-B angles are changed from 118.8°, 118.8° and 114.4° to 110.4° and 112.7°, respectively. As shown in the inset of Fig. 2(b), the bond angles of C-N-B and C-B-N are 44.7° and 39.2°, and the lengths of C-N and C-B bonds are 1.408 and 1.566 Å, respectively. In the F/BNNT, since the F atom is only adsorbed on the top of the B atom, the induced effect on the tube’s morphology mainly occurs in the vicinity of the B atom. In detail, the N-B-N angles decrease to 110.8°, 110.8° and 105.1°, respectively. And the B-N-B angles are changed to 121.8°, 121.8° and 113.3°, respectively. Correspondingly, the first neighbor B-N bond lengths are changed from 1.458 Å and 1.461 Å to 1.542 Å and 1.571 Å, and others are slightly changed with the magnitude of 0.03 Å. Especially, the B-F bond length is 1.422 Å, which is somewhat larger than the expected value for the B-F single bond (1.37 Å)\(^d\) and the bond lengths of boron trifluoride molecule (1.31 Å)\(^e\). All F-B-N bond angles are 110.0° as shown in the inset of Fig. 2(c). These changes of bond length and bond angle indicate that the electronic states of the B and N atoms adjacent to the adsorbate exhibit the mixed characteristic of the \(sp^2\) and \(sp^3\) hybridizations, instead of the \(sp^2\) hybridization in the pure BNNT, and the \(sp^3\) component in the ADR of the F/BNNT is much more than that of the C/BNNT.
the Fermi level (which are partially contributed by B-2p states as shown in Fig. 1(a)) of the BNNT. It is interesting to note that the HOMO of the BNNT does not really contribute to the chemical bond mentioned above. And the related detail could be illustrated by the LDOS of the F/BNNT in Fig. 3(d). On the other hand, the electronegativity of the C atom is between these of the B and N atoms, and thus the HOMO (LUMO) of the C atom interacts with the LUMO (HOMO) of the BNNT when the C atom is close to the tube. As illustrated in Fig. 1(b), the LUMO and HOMO of the BNNT are mainly contributed by B-2p and N-2p states, respectively. Therefore, the C atom is adsorbed at the bridge site which is perpendicular to the tube-axis. The resulting energy levels of the C/BNNT and F/BNNT are shown in Fig. 4. The gap between the HOMO and LUMO of the C/BNNT (1.13 eV) is smaller than that of the pure BNNT (3.72 eV) due to the introduction of donor and acceptor states (as shown in Fig. 1(a)). The calculated LDOS (Fig. 3(c)) shows that the HOMO is originated from the orbitals of C, B and N atoms, but the LUMO is mainly contributed by the orbitals of the C atom. This feature indicates that if we increase the content of C atoms in C-BNNTs, the gap will decrease and a transition from semiconducting to metallic behavior might occur in some content of C atoms. This is in accordance with the previous study on B-C-N nanotubes. In the F/BNNT, the HOMO and LUMO are degenerate (as shown in Fig. 1(b)), which suggests a conducting behavior. Fig. 3(d) shows that the HOMO and LUMO are contributed by the orbitals of N atoms (major contribution) and the F atom (minor contribution). The LDOS of the F atom is only significant much below the Fermi level. This further verifies the chemical interaction between the F atom and tube is typically ionic. Since the charge does unambiguously transfer from the BNNT to the more electronegative F atom, the Fermi level is evidently shifted down into the original completely occupied states contributed by the N atoms. This means, in this way, the F doping system will exhibit metallic behavior, which is in agreement with the experiment of fluorination of BNNTs by Tang et al.\textsuperscript{5}

Similar to the case of BNNTs, the localized states at the valence and conduction band edges of other compound nanotubes, such as SiC nanotubes, are also distinctly different. They would play an important role on the physical and chemical properties (such as conductivity and adsorption property) of tubes. Modulating the localized and delocalized characteristics of electronic states by adsorption or doping could improve the potential of tubes as functional substrates for some applications to the utmost extent.

### IV. CONCLUSIONS

Using first-principles calculations, we study the adsorption of first-row atoms with different electronegativity (Li, C and F) on zigzag single-walled BNNTs. We observe that adsorption exhibits interesting selectivity. Typically, the F atom prefers to adsorb on the top of the B atom, the C atom is energetically favorable to stay on the bridge site which is perpendicular to the tube-axis, and the Li atom hardly adheres to the tube, corresponding to an endothermal reaction. This is related to the localized characteristics of occupied and unoccupied states near the Fermi level of host BNNTs and the electronegativity of adsorbate with respect to the electronegativity...
of B and N atoms in tubes. Furthermore, the adsorption of C and F atoms on BNNTs would lead to different changes on the electronic properties. The former results in the decrease of energy gap of the BNNT, and the latter leads to a transition from semiconducting to metallic behavior. It is expected that the electronic properties of BNNTs could be tailored via certain adsorption.

This work is supported by the National Natural Science Foundation of China (Grant Nos. 10325415 and 10404016), and Ministry of Education of China (Grant No. SRFDP 20050003085).

1 N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science 269, 966 (1995).
2 Y. Chen, L. Chadderton, J. Fitz Gerald, and J. S. Williams, Appl. Phys. Lett. 74, 2960 (1999); Y. Chen, J. Zou, S. J. Campbell, and G. L. Caer, ibid. 84, 2430 (2004).
3 X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. 28, 335 (1994).
4 A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B 49, 5081 (1994).
5 X. Blase, J. C. Charlier, A. De Vita, and R. Car, Appl. Phys. A 68, 293 (1999).
6 D. Golberg, P. Dorozhkin, Y. Bando, M. Hasegawa, and Z. C. Dong, Chem. Phys. Lett. 359, 220 (2002).
7 W. Q. Han and A. Zettl, J. Am. Chem. Soc. 125, 2062 (2003).
8 C. C. Tang, Y. Bando, Y. Huang, S. L. Yue, C. Z. Gu, F. F. Xu, and D. Golberg, J. Am. Chem. Soc. 127, 6552
J. J. Zhao and R. H. Xie, J. Nanosci. Nanotech. 3, 459 (2003); G. Zhou and W. H. Duan, *ibid* 5, 1421 (2005).

D. Golberg, W. Q. Han, Y. Bando, L. Bourgeois, K. Kurashima, and T. Sato, J. Appl. Phys. 86, 2364 (1999); D. Golberg, Y. Bando, K. Kurashima, and T. Sato, Chem. Phys. Lett. 323, 185 (2000).

B. Delley, J. Chem. Phys. 92, 508 (1990); B. Delley, *ibid*. 113, 7756 (2000).

J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

A. D. Becke, Phys. Rev. A 38, 3098 (1988).

N. G. Chopra and A. Zettl, Solid State Commun. 105, 297 (1998).

R. Ma, Y. Bando, H. W. Zhu, T. Sato, C. Xu, and D. Wu, J. Am. Chem. Soc. 124, 7672 (2002).

L. Pauling, *The Nature of the Chemical Bond*, 3rd Edition, (Cornell Univ. Press., Ithaca, 1960).

The adsorption energies $E_{ads}$ are calculated from the expression $E_{ads} = E_b[A/BNNT] - E_b[BNNT]$, where $E_b[BNNT]$ and $E_b[A/BNNT]$ are the binding energies of the optimized pure BNNT and A/BNNT, respectively.

Z. Zhou, J. J. Zhao, X. P. Gao, Z. F. Chen, J. Yan, P. von R. Schleyer, and M. Morinaga, Chem. Mater. 17, 992 (2005).

S. Yamamoto, R. Kuwabara, M. Takami, and K. Kuchitsu, J. Mol. Spectrosc. 115, 333 (1986).

R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).