A first principles study on organic molecules encapsulated BN nanotubes

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Abstract

The electronic structures of boron nitride nanotubes (BNNTs) doped by organic molecules are investigated with density functional theory. Electrophilic molecule introduces acceptor states in the wide gap of BNNT close to the valence band edge, which makes the doped system a $p$-type semiconductor. However, with typical nucleophilic organic molecules encapsulation, only deep occupied molecular states but no shallow donor states are observed. There is a significant electron transfer from BNNT to electrophilic molecule, while the charge transfer between nucleophilic molecule and BNNT is neglectable. When both electrophilic and nucleophilic molecules are encapsulated in the same BNNT, large charge transfer between the two kinds of molecules occurs. The resulted small energy gap can strongly modify the transport and optical properties of the system.
I. INTRODUCTION

Since its discovery in 1991, carbon nanotube (CNT) has attracted a considerable attention due to its novel properties and great potential for nanodevice applications. As a structural analogue to CNT, boron nitride nanotube (BNNT) has distinctive properties. Due to its large ionicity, BNNT is a wide-gap semiconductor. More importantly, the energy gap (~5.5 eV) does not depend on the diameter, chirality, and the number of walls of the tube. On the other hand, BNNT has excellent mechanical stiffness and thermal conductivity. BNNT also shows pronounced resistance to oxidation, and it is stable up to 700 °C in air, while CNT survives only below 400 °C. All these properties make BNNT an attractive candidate for nano-electronics.

For electronics applications, it is very desirable to modify the band structure of BNNT to obtain metallic or p-type/n-type semiconducting behavior. Many attempts at this direction have been reported. The energy gap can be adjusted by changing the chemical composition, for example, by substituting the B or N atoms with C atoms. However, it is difficult to control precisely the atom concentration of carbon within BCN nanotube at the stage of tube growth. BNNT band structure can also be tuned by organic molecules covalent functionalization or by applying transverse electric field through the Stark effect.

Another kind of methods for BNNT electronic structure engineering is encapsulation. Previously investigated compounds encapsulated in BNNT include metal atoms and fullerenes. Compared to them, there are many advantages to use organic molecule encapsulation. Organic molecules are typically air stable, simple to synthesis, and abundant. They have already been used to adjust CNT band structure. It was found that the carrier type and concentration in CNT can be easily controled by tuning the electron affinity (EA) and ionization potential (IP) of the encapsulated molecules. It is thus very interesting to study the possible electronic structure engineering by organic molecule encapsulation in BNNT.

In this paper, we investigate the electronic structures of organic molecule encapsulated BNNTs (denoted as Molecule@BN) using density functional theory (DFT). Two kinds of organic molecules are studied: electrophilic and nucleophilic molecules. The electrophilic molecules are easy to get electrons, and typically have a large EA. The two examples
of electrophilic molecules studied in this paper are Tetracyano-p-quinodimethane (TCNQ) and tetrafluorocyano-p-quinodimethane (F4TCNQ). Their adiabatic EA are 2.80 and 3.38 eV, respectively. The nucleophilic molecules are easy to lose electrons, and typically have small IP. Three typical nucleophilic molecules are selected: tetrakis(dimethylamino)ethylene (TDAE), anthracene (ANTR), and tetrathia-fulvalene (TTF). Their adiabatic IP are 5.36, 6.40, and 7.36 eV, respectively. The structure of these molecules are shown in the top row of Fig. 1.

II. COMPUTATIONAL DETAILS

Spin-polarized DFT were used to investigate the geometric and electronic structures of the molecule@BN systems. The calculations were performed with the Vienna Ab Initio Simulation Package (VASP). We adopted the Perdew, Burke, and Ernzerhof exchange-correlation functional within the generalized gradient approximation (PBE-GGA), and the projector augmented-wave (PAW) pseudopotential. 1s orbital of B, N, C, and F and 1s to 2p orbitals of S were treated as core states. The energy cutoffs used in our calculations for the plane-waves were 400 eV.

The (16,0) BNNT was chosen as an example, which has a diameter of 12.8 Å, similar to the CNT used in the previous experiment. The periodic boundary condition was employed, and each BNNT was separated by 10 Å of vacuum. A unit cell containing 64 B and 64 N atoms was used, with the minimum distance between periodically repeated organic molecule centers along the BNNT tube axis to be ~8.7 Å. This is consistent with the molecular concentration in previous experiment for CNT. The 4×1×1 Γ-centered Monkhorst-Pack k-point grid was used for the sampling of the Brillouin zone.

Geometry optimization was performed by a few steps. First, the pristine BNNT was optimized. The resulted B-N bond length was 1.451 Å, agreeing well with the experimental value (1.45 Å). The separately relaxed organic molecule was then inserted into the BNNT. Initially, the organic molecule was put with its center on the tube axis and with its long axis (C=C double bond direction except ANTR) making a 27 degree angle with respect to the tube axis. This angle was chosen to maintain the separate distance between each molecule large enough. Finally, the molecules in the BNNT were allowed to fully relax until the forces were less than 20 meV/Å, and the BNNT was fixed to its previously optimized geometry.
Our test calculation indicates that simultaneously relaxing the BNNT and molecule does not affect our results. The optimized geometry is shown in Fig. 1. The molecule geometries changed little after inserted into BNNT, which suggests the weak interaction between the BNNT and molecules due to the large distance between them.

### III. RESULTS AND DISCUSSION

We define the binding energy of the molecule and the BNNT as

\[ E_b = E_{BN} + E_M - E_{BN-M} \]

where \( E_{BN} \) and \( E_M \) are the energies of individual BNNT and molecule, respectively. \( E_{BN-M} \) is the energy of the Molecule@BN system. The calculated binding energies for the five different molecules are listed in Table I. As we can see, for all molecules, \( E_b \) is positive, which means that the molecules can be inserted into BNNT from the thermodynamical viewpoint. On the other hand, the absolute values of the binding energy are relatively small. This is consistent with the weak interaction between the BNNT and the encapsulated molecules.

The band structures of the pristine and doped BNNT are plotted in Fig. 2. The calculated band gap for the pristine BNNT is 4.5 eV, which is a little smaller than the experiment value due to the tendency of DFT to underestimate band gap. The band structure of the doped BNNT can be roughly considered as a simple combination of the band structures of the BNNT and the inside organic molecules, due to the weak interaction between them. There are small dispersions for some molecular bands, which is due to molecule-molecule interaction as suggested by our charge density analysis (see Fig. 3a). For electrophilic organic molecules, their lowest unoccupied molecular orbital (LUMO) forms the lowest unoccupied band of the Molecule@BN system, and the highest occupied band comes from BNNT.

| Molecule | TCNQ | F4TCNQ | TDEA | TTF | ANTR |
|----------|------|--------|------|-----|------|
| \( E_b \) | 92.6 | 162.6  | 71.4 | 65.8 | 73.5 |
| \( q_t \) | 0.10 | 0.24  | -0.004 | -0.008 | -0.005 |
new energy gap is 0.16 and 0.10 eV for TCNQ and F4TCNQ, respectively. Therefore, doping of electrophilic molecules turns BNNT to \( p \)-type semiconductor.

For the three nucleophilic molecules, their highest occupied molecular orbital (HOMO) corresponds to the highest occupied band of the doped BNNTs. For TDAE@BN, the lowest unoccupied band is the conduction band edge of the BNNT, and the new energy gap is 2.22 eV. For TTF@BN and ANTR@BN, the lowest unoccupied band comes from the LUMO of the doped molecule, and the energy gap is 1.95 and 2.26 eV, respectively. The energy gaps are too large to make the nucleophilic organic molecule doped BNNT to be a good \( n \)-type semiconductor.

This behavior contrasts with that of CNT, where both \( n \)-type and \( p \)-type semiconductors can be realized by organic molecule encapsulation.\(^{20,21} \) This difference is caused by the energy gap width difference between BNNTs and semiconducting CNTs. The conduction band edge of BNNT is \( \sim \)1.93 eV below the vacuum energy level, which means that a dopant with IP close to 1.93 eV may form \( n \)-type semiconducting BNNT. Such small IP values are typically not available in organic molecules. We expect that some metal atom dopings may convert BNNT to \( n \)-type semiconductor.

We note that, besides transport property engineering, organic molecule doping will strongly modify the optical property of BNNT, as suggested by previous study on CNT.\(^{29} \) The gap of pristine BNNT is too large to develop possible optical application for it. With molecule doping, the gap width can be adjusted in a large extent, which gives the possibility to develop photo-electronic device based on BNNT.

Another interesting property is the charge transfer between doped molecules and the BNNT. The charge transfer between covalently connected functional groups and BNNT has been studied previously.\(^{11} \) To calculate the charge transfer, we follow the procedure proposed by Lu et al.,\(^{27} \) in which an cylinder-integrated differential electron density curve against the radial coordinate is plotted in order to determine the boundary between the organic molecule and the nanotube. We suppose the boundary between the molecule and the BNNT is a cylinder with radius \( r_b \). This is a good approximation, as suggested by Fig. 3b. Before we plot the cylinder-integrated differential electron density curve, we would like to estimate the reasonable range of \( r_b \). For the electrophilic organic molecules, electrons transfer from the valence band of BNNT to the LUMO of molecule, so the boundary should be inside the main density distribution of the highest occupied band of BNNT \((r_b < 6 \text{ Å})\), as
shown in Fig. 3c. For the nucleophilic organic molecules, electrons transfer from the HOMO of molecule to the conduction band of BNNT, so the boundary should be inside the lowest unoccupied band of BNNT. Since the conduction band edge of the BNNT is a nearly-free-electron state, which extend to the far inner part of the tube, the boundary radius should be relatively small for nucleophilic molecules \((r_b < 3.5 \, \text{Å})\), as shown in Fig. 3d.

As suggested by Lu et al.\textsuperscript{27} the exact value of the boundary radius \(r_b\) is finally defined as the maximum/minimum position of the cylinder-integrated differential electron density curve (see Fig. 4), and the value of the charge transfer is corresponding maximum/minimum value. Differential electron density is the electron density difference between the Molecule@BN system and separated molecule and BNNT. For TCNQ@BN and F4TCNQ@BN, we have a maximum peak at 4.4 Å. Therefore, the boundary radial position \(r_b\) is 4.4 Å, which is roughly the midpoint between the molecule and the BNNT. The calculated charge transfer for BNNT to TCNQ and F4TCNQ are 0.10 and 0.24 electrons per molecule, respectively. The charge transfers between the nucleophilic molecules and BNNT are more complicated. There are several comparable maximum and minimum peaks in the cylinder-integrated differential density curve. According to the estimation of the range of \(r_b\), we set the position of the first minimum as the boundary between molecule and BNNT. The corresponding boundary radial position \(r_b\) are 2.8, 2.8, and 3.0 Å for TDAE, TTF, and ANTR, respectively. The resulted charge transfer are very small. We note that for the three nucleophilic molecules, the charge transfer is always very small no matter where the boundary is set.

Since we have high occupied band for nucleophilic molecule doping, and low unoccupied band for electrophilic molecule doping, it is thus interesting to study the possibility to dope both nucleophilic and electrophilic molecules into the same BNNT. The bulk material composed by TCNQ and TTF has been widely studied, and it is an interesting one-dimensional conductor.\textsuperscript{28} There is a large charge transfer about 0.59 electrons between TCNQ and TTF. The electronic structure of TCNQ-TTF@BN is studied, where the unit cell was doubled compared to single-type molecule doping. One TCNQ and one TTF molecules was put in the unit cell within the BNNT. Geometry optimization was performed with the BNNT fixed. The resulted binding energy \(E_b\) is 0.68 eV per unit cell. This large \(E_b\) mainly contributed by the interaction between TCNQ and TTF.

The calculated band structure of TCNQ-TTF@BN is plotted in Fig 5. Compared to band structure of TCNQ@BN and TTF@BN, the TCNQ bands are upshifted, and the TTF bands
are downshifted. This is driven by a 0.43 electrons charge-transfer between TCNQ and TTF in BNNT. However, the charge transfer between the molecules and BNNT is negligeable. The lowest unoccupied band form TCNQ and the highest occupied band from TTF from a very small band gap (67 meV) for TCNQ-TTF@BN. Such a small gap demonstrates the great potential of molecular doping to modify the optical property of BNNT. As shown in Fig 5, combing other electrophilic and nucleophilic molecules gives similar results. The gap becomes larger when IP of of the nucleophilic molecules becomes larger.

To examine the role of BNNT in the ground-state electronic structure of TCNQ-TTF@BN, we calculate the electronic structure of the TCNQ-TTF molecular chain without BNNT, where the geometry of the molecular chain is fixed to their geometry in BNNT. Such model system reproduces the bands originated from molecules in TCNQ-TTF@BN. This result indicates that the electronic structure close to the Fermi level is not affected by BNNT. With excellent thermo-stability and mechanic properties, the inner space of BNNT thus provides a good place to develop charge transfer salt based one-dimensional molecular wire.

IV. CONCLUSIONS

In summary, we calculate the electronic structure of BNNT with different molecule doping. We can obtain $p$-type semiconductor by inserting electrophilic molecules. While for typical nucleophilic organic molecules doped BNNTs, their gap are too large to be a good $n$-type semiconductor, and the corresponding charge transfers are also very small. This is because that the energy gap of BNNT is too large. We expect that some metal atom dopings may convert BNNT to $n$-type semiconductor. Based on the large extent of the band gap modification, we expect that the optical property of BNNT will be strongly modified by molecule doping. When electrophilic and nucleophilic molecules are doped into BNNT at the same time, a very small gap formed by a pair of molecular bands is obtained. The position of these two band within the BNNT gap and their spacing can be controlled by IP and EA of the molecular dopant, which leads to a powerful technique to engineer the electronic and optical properties of BNNTs.
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FIG. 1: Sketch drawing of the organic molecules and the geometries of the Molecule@BN systems.

FIG. 2: Band structures (from Γ to X) of the pristine BNNT and Molecule@BN. Dashed lines indicate the Fermi levels.

FIG. 3: (a) Isosurface of the density of the lowest unoccupied molecular band of TCNQ@BN. The density iso-value is 0.001 e/Å$^3$. (b) Isosurface of the charge density of TTF@BN. The iso-value of electron density is 0.11 e/Å$^3$. (c) the highest occupied band and (d) the lowest unoccupied band of BNNT.

FIG. 4: Curves of cylinder-integrated differential electron density against the radial coordinate in doped BNNTs. The boundary between molecules and BNNT is indicated by a blue line.

FIG. 5: Geometry (top) and band structures (bottom, from Γ to X) of the Molecule@BN system, where electrophilic and nucleophilic molecules are encapsulated in the same BNNT. The position of Fermi level is shifted to zero.
He et al., JCP, Figure 1
He et al., JCP, Figure 2
He et al., JCP, Figure 3
He et al., JCP, Figure 4
He et al., JCP, Figure 5