

Theoretical Studies of π -Conjugate Molecules Embedded in hexagonal boron nitride

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Abstract

We analyzed the electronic structures of carbon-doped hexagonal boron nitride, focusing on the comparison with the corresponding π -conjugate hydrocarbon molecules and odd-number substitution by first principle calculation. The band gaps are about the half that of the HOMO-LUMO gaps of corresponding hydrocarbons, except for the cis-butadiene structure in which aromatic hexagonal ring formation is important. Odd number doping makes metallic materials with very different work functions, depending upon the difference in B and N numbers, and has an expected application as electrodes for flexible devices.

1. Introduction

Two-dimensional carbon-based networks, such as graphene [1] and g-C₃N₄ [2], are gathering much attention due to high mobility carrier dynamics, sensitivity to molecular adsorbates, and photocatalytic activities, etc. Graphene and monolayer hexagonal boron nitride (h-BN) are two end members of carbon-based two-dimensional systems. They have similar structures with distinctly different electronic structures; graphene has zero-gap and h-BN is a wide gap semiconductor. It is, therefore, expected that the mixture of the graphene and monolayer h-BN will become semiconductors with band gap values tunable by compositions. Synthetic attempts by chemical vapor deposition using well-defined synthesized molecules have started. The missing points in the previous theoretical studies are as follows. (i) Although the C-doped structures have resemblance with π -conjugated molecules, the difference between the C-doped h-BN and molecules in the vacuum have not been analyzed. (ii) The previous studies were mainly on substituting the same numbers of B and N atoms to carbon atoms. Unevenly substituted structures have not been studied in detail[3].

In this paper, we present a detailed theoretical analysis of the C-doped h-BN from the viewpoint that has not been treated previously. We focus on the resemblance and difference of carbon doped h-BN monolayers and corresponding organic π -electron systems by first principle calculation. Additionally, electronic properties of unevenly-doped structures are studied in detail. Based on the results, we will propose that the carbon-doped h-BN can be band gap-tunable semiconductors in the case of even-number doping, and that work function-tunable metallic electrode in the case of odd-number doping.

2. Materials and Methods

All the simulations in this work were carried out on the Quantum-Espresso programs [4]. The structures simulated is shown in Fig.1.

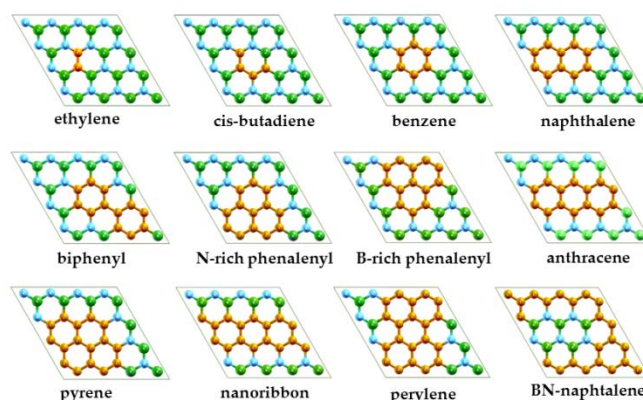


Fig. 1. Structure of the carbon-doped h-BNs analyzed in this work. They are named after corresponding organic molecules.

3. Results and Discussions

Figure 2 shows the ratio Ratio between bandgap of carbon doped h-BN and HOMO-LUMO gap of corresponding hydrocarbon molecules. Most of the ratio ranges 0.46–0.52 for the structures below C < 16, in which the carbon islands are not connected beyond the periodic cell. It is surprisingly constant despite the distance between the carbon islands not being uniform. The exception is butadiene (carbon content = 4/32), which shows the ratio of 0.68.

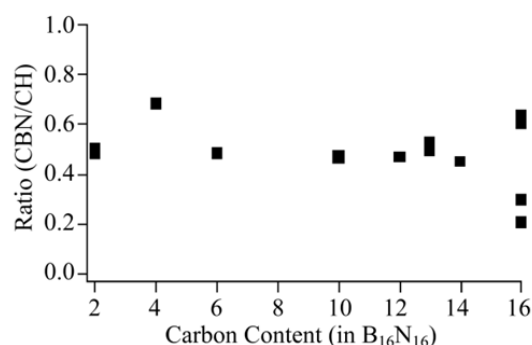


Fig. 2. Ratio between bandgap of carbon doped h-BN and HOMO-LUMO gap of corresponding hydrocarbon molecules. The reason for the discrepancy of butadiene is explained by Fig. 3. We compare the HOMO (Figure 3a–c) and LUMO (Figure 3d–f) of C₄H₆, C₄B₁₀N₁₀H₁₂ (butadiene embedded coronene-like BN) and C₄BNH₆. The carbon atoms in

$C_4B_{10}N_{10}H_{12}$ is located at the left part of the central hexagonal ring. The center hexagonal ring of (b) and (e) resembles (c) and (f), respectively, which shows the electronic structure of C-B-N can be well represented by the C_4BNH_6 molecule. By comparing the cis-butadiene and the C_4BNH_6 molecule, we notice that the HOMO and LUMO wavefunctions of C_4BNH_6 are composed of conjugate pz-orbitals (p-orbitals perpendicular to the molecular plane) of B, N, and C. The different electronegativity of B and N makes the HOMO higher and LUMO lower, and results in the HOMO-LUMO gap greater than that is expected from other geometries.

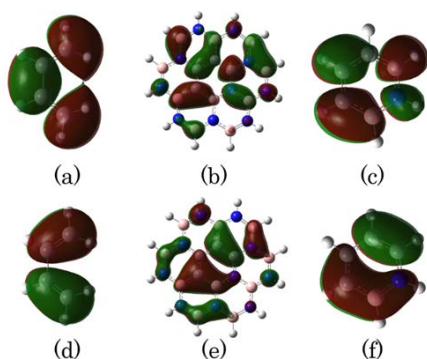


Fig. 3. LUMO (a-c) and HOMO (d-f) of butadiene, $C_4B_{10}N_{10}H_{12}$, and C_4BNH_6 .

Finally we analyze the odd number C-doping. In this case, it is inevitable to replace B and N atoms unevenly. We focus on a motif of the recently-synthesized stable radical molecule “phenalenyl”. There are two choices: C-atoms replace more B (“N-rich phenalenyl”) or C-atoms replace more N (“B-rich phenalenyl”). Their band structures are plotted in Fig. 4. It should be noted that these structures are metallic due to the odd number of π -electrons. The band dispersion of HOMO and LUMO levels are substantially large, around 1 eV for both. This means that this structure can be used as metallic electrodes for flexible electronics. In “N-rich phenalenyl”, LUMO (conduction band) crossed the Fermi level while in “B-rich phenalenyl”, HOMO (valence band) crossed the Fermi level. In other words, “N-rich phenalenyl” and “B-rich phenalenyl” are n-type and p-type, respectively. The work function of N-rich and B-rich phenalenyl were 3.01 eV and 4.88 eV, respectively.

4. Conclusions

Electronic structures of carbon-doped h-BN have been calculated. The focus points of this paper are the comparison between the corresponding π -conjugate hydrocarbon molecules and odd-number substitutions. The band gap values are about half that of the HOMO-LUMO gap of corresponding hydrocarbons, except for the butadiene structure, in which aromatic hexagonal ring formation is important. This result indicates that the analogy with organic molecules is effective to design the electronic functions of carbon-doped h-BN. Odd number doping makes metallic materials with very different band gap values. Those materials

will find applications as electrodes for flexible devices, if the B-N ratio is controlled in the synthesis.

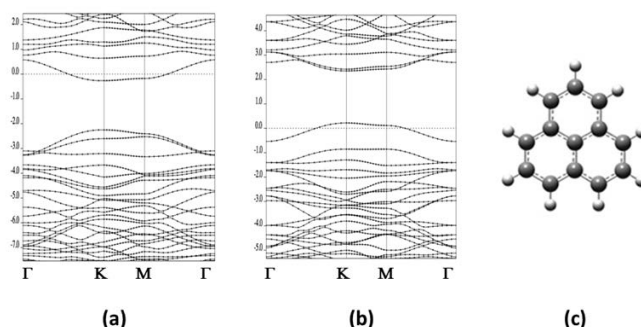


Fig. 4. The band structures of “phenalenyl” doped h-BN. (a) “N-rich phenalenyl”, seven boron atoms and six nitrogen atoms were replaced by carbon atoms. (b) “B-rich phenalenyl”, six boron atoms and seven nitrogen atoms were replaced by carbon atoms. Energy zero are Fermi energies; (c) shows the structure of “phenalenyl” ($C_{13}H_9$).

References

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