Effect of F Functional Modification on the Stability and Electronic Structure of Borene

Cuicui Sun* and Mengmeng Liu
School of Civil Engineering, Shandong Jiaotong University, Jinan 250300, China.
*Corresponding author’s e-mail: 204150@sdjtu.edu.cn

Abstract. Since the discovery of graphene, two-dimensional materials have quickly won widespread attention in the academic community. Borene is a two-dimensional isomer of boron and the lightest element Dirac material. It becomes the latest and promising two-dimensional material due to its unique structure and electronic properties. In the periodic table, B is a close neighbor of C and has a certain similarity with C. It can also form a hexagonal honeycomb structure. An additional B atom is added to the center of the ring to form a triangular lattice borene. The triangular borene has surplus electrons and belongs to a multi-electron state, which is equivalent to a metastable structure. In this paper, the first principles are used to study the F functionalized modification of the triangular borene. The aim is to transfer the surplus electrons in the system, and probe its structural stability and electronic structure characteristics. The study found that functional modification significantly improved the stability of borene. This can provide feasible ideas and practical guidance for the experimental synthesis of stable borene.

1. Introduction
With the successful preparation of single-layer graphene in 2004, scientists have become very interested in two-dimensional materials. The physical and chemical properties of two-dimensional materials have also become a hot research project by scientists at home and abroad[1]. Among a series of unique two-dimensional materials, borene has attracted widespread attention due to its unique chemical structure and impressive electronic conductivity and surface properties. In addition to the usual covalent bonds, boron can also form three-center double-electron bonds, which allows the formation of a large number of clusters of atoms with different sizes and atoms. The electronic band structure of borene is different from that of graphene. Graphene is semi-metallic, phosphorene is semiconductor, and borene is metallic. The ground state of electronic structure of boron is [He]2s22p1, the number of valence electrons is 3, but the number of atomic orbitals is 4. So the number of valence electrons of boron is one less than the number of atomic orbitals, and the valence electron layer cannot be filled when the bond is formed[2]. This ultimately leads to protruding and defective layers and complex bonds. Borene is the lightest element Dirac metal material[3], with negligible spin-orbit coupling. A recent simulation-based theory has shown that borene has partial ions of double Dirac cones near the Fermi level. Recently, scientists have proposed that the phase of borene sheet on the Ag(111) surface can be decomposed into two triangular sublattices. In a similar way, the honeycomb borene structure can be observed to be split in Dirac cones[4]. Scientists report that the electron bands of the borene monolayer sheet overlap each other at the Fermi level, resulting in a metallic structure. However, the boron sheet is easily degraded by the environment (due to defects, functionalization, hydrogen bonding, structural phase change and temperature change). And if the
boron sheet is doped or adsorbed by other atoms or groups, the energy of the boron structure will be lower, the structure is more stable. Therefore, we expect a system with lower energy with our design materials.

Based on the first principles and density functional theory, this paper studies the effect of F functional modification on the stability and electronic structure of triangular borene by calculating energy bands, density of states, and differential electron density.

2. Calculation method
This article uses the atomic-scale simulation simulator Atomistix ToolKit (ATK) to perform first-principles calculations. In the calculation process, the Brillouin K point is selected as (10×10×1). In order to eliminate the periodicity of the nanoribbons, the vacuum distance between the nanolayers between adjacent unit cells is more than 10 Å. And the exchange correlation function between electrons is Generalized gradient approximation (GGA) and PBE (Perdew-Burke-Ernzerhof) functional for processing. All atoms use SZP (single zeta polarization) to calculate the basis set, and the Brillouin zone cutoff energy used to describe the two consecutive steps of the periodic wave function is 150 Ry.

3. Results and discussion
3.1 Model and stability
By analyzing the structure of the triangular borene, we found that there are three different positions on the triangular lattice, namely, bridge, top and hollow, as shown in Figure 1.

![Figure 1. The schematic diagram of F adsorbed on triangular borene. (a) hollow site, (b) bridge site, and (c) top site. The pink represents the B atom, and the green represents the F atom.](image)

After optimization, it is found that no matter which position, when F is adsorbed on the triangular borene, the energy is significantly reduced, which shows that our previous design ideas is correct and feasible. Among them, the total energy of the bridge position structure is the lowest and the structure is the most stable. Therefore, the energy E and the adsorption energy $\Delta E$ of the three positions and the triangular borene structure are listed here, as shown in Table 1. It can be clearly seen from Table 1 that the bridge system has the lowest energy and the most stable system.

| Adsorbed atoms | Adsorbed site       | $E$/eV     | $\Delta E$/eV |
|----------------|---------------------|------------|--------------|
| F              | hollow              | -1268.44147| -0.20538     |
| F              | top                 | -1272.64347| -4.40701     |
| F              | bridge              | -1274.21450| -5.97804     |
| None           | triangular borene   | -630.38537 | /            |
| None           | F                   | -637.85109 | /            |
3.2 Electronic properties
The optimized composite structure has some changes to the structure before optimization, which is caused by the interaction between fluorine atoms and boron atoms. On this basis, the energy band and density of states are calculated for the composite structure, and the results are shown in Figure 2(b). In order to more clearly highlight the changes in the structure after F atoms are adsorbed, the energy band of the triangular borene is carried out, as shown in Figure 2(a). From the comparison of Figure 2, it is obvious that after F atoms are adsorbed, the electronic structure of the system changes significantly, and the dispersion of the conduction band minimum and valence band maximum becomes stronger, indicating that F atoms have a significant impact on the energy band structure. The Bloch states of the conduction band minimum and valence band maximum can further illustrate this problem. The triangular structure and F atoms have made great contributions to the electronic state of the system. Therefore, using the strong highly electronegative F atoms to absorb the surplus electrons in the borene is theoretically feasible.

Figure 2. (a) Energy band of triangular borene, (b) The energy band, density of states and Bloch state of borene adsorbed by F atom.

Figure 3 analyzes the electron difference density of the composite system. The electron difference density refers to the difference between the self-consistent valence charge density and the superposition of atomic valence density, which indicates the coupling between the atoms in a certain system. The red part represents obtaining electrons, while blue region indicates losing electrons. Figure 3. clearly shows that boron atoms lose electrons and F atoms gain electrons. It also proves that there is electron transfer in the system to make the system more stable. Confirm the correctness of the previous conjecture.

Figure 3. (a) Computed electron difference densities of borene adsorbed by F atom. (b) The projected density of states of borene adsorbed by F atom.
4. Conclusion
The method proposed in this paper to improve the stability of boron is to use the electronegative fluorine atoms to transfer the surplus electrons in the triangular boron structure, thereby achieving the purpose of stabilizing the triangular structure. Under this idea, three adsorption positions are proposed, hollow, bridge and top site. From calculations, it can be seen that all three are more stable than the original structure and can improve the stability of boron. The bridge position is more stable than the other two positions. A charge transfer occurs between the F atom and the triangular boron, which produces a hybrid effect. Therefore, the F changes the electronic structure of boron and improves its stability. That is to say, it is possible to conduct experimental synthesis based on the conjectures in this chapter, which can provide theoretical basis and design ideas for the experimental synthesis of more stable triangular boron.

Acknowledgments
This work was supported by the Doctoral Scientific Research Foundation of Shandong Jiaotong University (BS50004943), Scientific Research Fund Project of Shandong Jiaotong University (Z201916).

References
[1] Zhao, J., Ma, D., Wang, C., et al. (2021) Recent advances in anisotropic two-dimensional materials and device applications. Nano Research, 14(4): 897-919.
[2] Mathew, M., Radhakrishnan, S., Vaidyanathan, A., et al. (2021) Flexible and wearable electrochemical biosensors based on two-dimensional materials: Recent developments. Anal. Bioanal. Chem., 413(3): 727-762.
[3] Ranjan, P., Lee, J. M., Kumar, P., Vinu, A., (2020) Borophene: New Sensation in Flatland. Adv. Mater., 32(34): 2000531.
[4] Yao, Y., Liu, G., (2021) Density functional theory study on the electronic structure and optical properties of Li absorbed borophene. Mol. Phys., DOI:10.1080/00268976.2021.1966114.
[5] Wang, H., Zhao, Y., Xie, Y., et al. (2017) Recent progress in synthesis of two-dimensional hexagonal boron nitride. J. Semicond., 38(3): 031003.
[6] Beniwal, S., Hooper, J., Miller, D. P., et al. (2017) Graphene-like Boron–Carbon–Nitrogen monolayers. ACS Nano, 11(3): 2486-2493.
[7] Arnold, F. M., Seifert, G., Kunstmann, J., (2020) Thermodynamic stability of borophene, B2O3 and other B1−x Ox sheets. J Phys. Commun., 4(3): 031001.
[8] Chowdhury, S., Majumdar, A., Jana, D., (2019) Electronic and optical properties of the supercell of 8-Pmmn borophene modified on doping by H, Li, Be, and C: a DFT approach. Appl. Phys. A, 125(5): 360.
[9] ATK, Version 13.8, atomistix a/s, 2013, www.quantumwise.com.
[10] Perdew, J. P., Burke K., Ernzerhof, M., (1996) Generalized gradient approximation made simple. Phys. Rev. Lett., 77: 3865–3868.