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# Electronic and transport features of zigzag boron nitride nanoribbons with nonmetallic atom terminations

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ABSTRACT

Electronic properties of zigzag boron nitride nanoribbons (ZBNNRs) terminated with nonmetallic (NM) atoms H, O, S, P and F are studied systematically. Several possible cases are considered, namely, ZBNNRs with symmetrical edge terminations, asymmetrical edge terminations, and the half-bare edge case. The calculated results show that the ribbons with O, S, P, and F atom edge modifications are more stable than the H-terminated ZBNNR. For ZBNNRs terminated with O and S atoms, they are always metals regardless of the termination cases. While ZBNNR terminated with F, the electronic nature is basically similar to that for H passivated ZBNNR, either a metal or a semiconductor depends on the termination cases. More interestingly, for the ZBNNR terminated with P atom regardless of the termination cases, it exhibits a particular massless Dirac-fermion behavior, i.e., its charge carriers mimic the relativistic quasiparticles with zero rest mass and travel with an effective “speed of light”. In addition, we also investigate the electronic transport properties by constructing the nanodevices consisting of ZBNNRs terminated respectively by S and P at both edges and being fully bare edge. It is found that the I–V characteristics are significantly enhanced due to terminations. Our findings indicate that the introduction of NM atoms at edge(s) can effectively modulate the electronic and the transport properties of ZBNNRs, even a particular nature could be achieved.



## 1. Introduction

The boron nitride(BN) nano-sheet is an isostructural analog of graphene, which can be viewed as a structure when carbon atoms in graphene are replaced with alternating boron and nitrogen atoms. So far, it has been experimentally fabricated by numerous method, such as the micromechanical cleavage technique [1], chemical solution-derived method [2], the ultrasonication processing from the hexagonal BN bulks [3], chemical vapor deposition(CVD) [4], and so on. BN sheet possesses some important advantages, for example, higher chemical and thermal stability [5]. Consequently, BN sheet is probably more resistant to oxidation and more suitable for high temperature applications. In particular, unlike graphene, B and N sites in BN sheet are not equivalent. The ionic bonding due to a significant amount of charge transfer from B to N atom opens a gap and hence the BN sheet is a wide gap semiconductor with a direct gap of 4.46eV [6], so that the BN sheet holds high promise for developing nano-transistors, strikingly in contrast to zero-gap graphene.

However, intrinsic wide-gap materials are not always usable and very versatile in any cases. To enhance potential applications of the BN sheet, it is highly desirable for tuning its energy gap to obtain richer electronic features [7]. The simplest method is cutting a monolayer of BN sheet along certain crystallographic orientation to form BN nanoribbons. There are two kinds of typical nanoribbon structures, the so-called armchair BN nanoribbons (ABNNR) and zigzag BN nanoribbons (ZBNNR). A theoretical study has found that ABNNRs always display nonmagnetic semiconducting features no matter both edges are fully bare or hydrogen(H)-passivated [8]. However, situations for ZBNNRs are more complicated. The different H- passivations at both edges would lead to different electronic and magnetic properties for ZBNNRs [8–12]. When both edges are passivated with H atoms, ZBNNRs are nonmagnetic semiconductors and the indirect energy gap is observed. The fully bare ZBNNRs or ZBNNRs only with the B edge passivated by H demonstrate a half-metallic feature in the ground state, and for ZBNNRs only with the N edge passivated by H, they are magnetic

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semiconductors. Other edge modifications were also reported in the previous works [12–15], for example, through edge modifications by -Cl, -OH, and $-NO_2$ groups, the band gaps of BNNRs can be modulated to various values [14]. These interesting features make BNNRs promising for many potential applications in nanoelectronics.

In this present work, we suppose that ZBNNRs are terminated with nonmetallic atoms H, O, S, P, and F in multiple termination cases, and their electronic properties are systematically studied. But only the nonmagnetic features are considered. This is because the existence of a spontaneous magnetic orderings in one-dimensional spin lattice model is unfavorable under finite temperature for ZBNNRs [16]. In other words, it is difficult for the ZBNNR's magnetism stemmed from the fully bare or half-bare edges to be detected experimentally. Our calculations show that ZBNNRs can be a metal or semiconductor depending on termination atoms and termination cases, in particular, the ZBNNR terminated with P atom exhibits a particular massless Dirac-fermion behavior regardless of the termination cases.

## 2. Models and methods

Following the previous convention [12], the width of ZBNNRs is characterized by the number of B–N zigzag chains across width, n. Here, ZBNNRs with width n = 7 is under consideration. For bare-edge ZBNNRs, the outmost atoms at one edge are all B atoms (the B-edge), while the outmost atoms at the other edge are all N atoms (the N-edge). To consider effects of the different edge terminations, nonmetallic (NM) atoms H, O, S, P, and F are taken as representatives, as shown in Fig. 1, in which they are represented by red and yellow balls, marked as X and Y, respectively, namely X, Y= H, O, S, P, and F. Thus the NM atoms terminated ZBNNRs are referred to as YB-ZBNNR-NX. Blue and pink balls indicate B and N atoms, respectively. According to different NM atom terminations, several possible cases are considered: (1) ZBNNRs with symmetrical edge terminations, namely, both edges of ZBNNRs are terminated with the same NM atoms, denoted as XB-ZBNNR-NX, (2) asymmetrical edge terminations, that is, H atoms are fixed to passivate B (N) edge and other NM atoms terminate N (B)edge, referred to as HB-ZBNNR-NX (YB-ZBNNR-NH), (3) the half-bare edge case, only one edge is terminated with NM atoms while the other edge is bare, denoted as B-ZBNNR-NX and YB-ZBNNR-N. The rectangular box drawn with a dotted line indicates a unit cell, which presents a periodicity in the axis-line direction, and these unit cells are used for the calculation of electronic structures.

The electronic structures are calculated by the first-principles method based on the density functional theory as implemented in software package Atomistix ToolKit (ATK)11.80 [17,18], which has been widely utilized to studies of nanostructures [19–25]. To solve the Kohn-Sham equation, The Perdew-Burke-Ernzerhof(PBE) formulation of the generalized gradient approximation(GGA) is used as the exchange-correlation functional. The wave function is expanded by the double-zeta plus polarization (DZP) basis for all atoms. We employ Troullier-Martins norm-conserving pseudopotentials to represent the atom core and linear combinations of local atomic orbitals to expand the valence states of electrons. In the Brillouin zone, the k-point sampling is chosen as $1 \times 1 \times 500$, and 75 Hartree is set as the cut-off energy for the grid integration. The unit cell is used to simulate the isolated nanoribbon. For the models studied, a 1.5 nm vacuum slab is used to eliminate the interaction between the unit cell and its "images", and all calculations are performed after the geometry is optimized until all residual forces on each atom are smaller than 0.01 eV/Å. For the sake of simplicity, the Fermi level of the systems is set as zero.

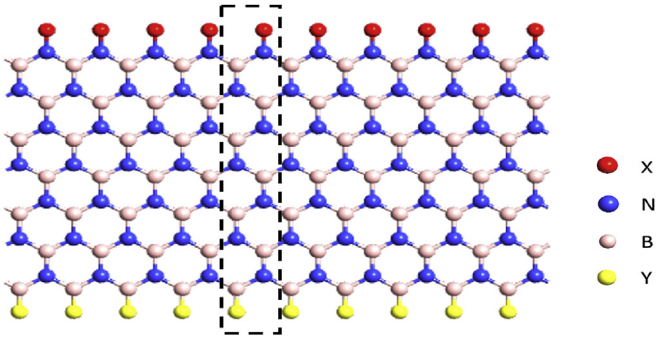


**Fig. 1.** The geometrical structures of nonmetallic atom terminated ZBNNRs, denoted as YB-ZBNNR-NX (X, Y= H, O, S, P, and F).

## 3. Results and discussion

### 3.1. ZBNNRs with symmetrical edge terminations

Fig. 1 displays the electronic properties of XB-ZBNNR-NX, including the band structure (BS) (left panel), and the total density of states (DOS, marked as Total) and atom-projected density of states (PDOS) (right two panel). The PDOS is the DOS projected on the edge N (B) atom and termination atom X which is denoted as X(N) and X (B) for X atom linked to N and B atoms, respectively, it reflects the contribution of featured atoms to the total DOS. For the purpose of comparison, we also present the electronic properties for the fully bare-edge ZBNNR in Fig. 2(a). Clearly, it shows a metallic behavior. Particularly, from the PDOS, we can see the contribution of edge N and B atoms to the electronic structure of the bare-edge ZBNNR. A large PDOS peak related to edge N and B atoms occurs at the Fermi level. This means that the metallic behavior of the bare-edge ZBNNR originates from the edge states, in good agreement with the previous theoretical result [11,13]. To intuitively demonstrate the effect of the edge states, the Bloch state is calculated, as example, the k point is selected at the intersection site of a certain subband and the Fermi level, marked by the red circle. We can see that the wave function, shown as the inset in the left panel of Fig. 2(a), is localized at the B edges of the ribbon and forms the localized edge state.

The electronic properties of the XB-ZBNNR-NX are shown in Fig. 2(b)-(f), respectively. We can see that the introduction of the NM atoms can effectively modulate the electronic structure of ribbon. The electronic structure of both HB-ZBNNR-NH and FB-ZBNNR-NF exhibits semiconducting property with an indirect band gap, as manifested in Fig. 2(b)and (f), but the situation is distinguishing. For the HB-ZBNNR-NH, the calculated PDOS shows that edge B and N atoms have a significant contribution to the lowest conduction band (LCB) and the highest valence band (HVB), respectively. The Bloch states for the conduction band minimum (CBM) and valence band maximum (VBM) present these features more prominently. While for the FB-ZBNNR-NF, the conduction bands are all from the contribution of atoms inside the ribbon and the HVB is partly from the F(N) and N atoms. The similar electronic property for both structures is because each F atom has 7 electrons in the outer shell and can form a stable structure just by one covalent bond with edge B or N atom, similar to the case of H atom, but the higher electronegativity of F atom makes such a bond mainly ionic or treated as covalent polar, distinguishingly from the case of H termination, leading to some differences of electronic structures between HB-ZBNNR-NH and FB-ZBNNR-NF.

Strikingly contrary to HB-ZBNNR-NH and FB-ZBNNR-NF, ZBNNRs terminated with O, S, and P manifest metallic behaviors,