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Half-Metallic Dirac Point in B-Edge Hydrogenated BN Nanoribbons

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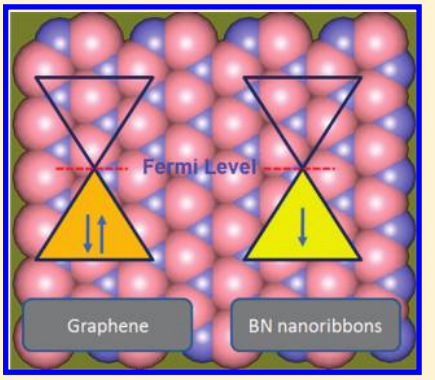
ABSTRACT: The BN zigzag nanoribbons (BNZNRs) were examined by first-principles density functional calculations, including structural relaxation. The quantum confinement and edge effects of the BNZNRs produce a magnetic ground state. When the B-edge is hydrogenated, the BNZNRs possess a new state with a spin-resloved Dirac point Fermi surface, which paves a way to realizing spin-polarized massless carriers.



INTRODUCTION

To fill the quest for the higher performance in electronic devices, it is highly desirable to find the high-speed carriers with a light effective mass. The effective mass of electrons in electronic devices is determined by their energy dispersion as a function of the wavevector k, and the dispersion is sensitive to the interaction between the valence band top and the conduction band bottom. This interaction is well described by the $k\cdot p$ theory.[1] To a first approximation, the effective mass is inversely proportional to the band gap of a semiconductor, which explains why a semiconductor with a narrower gap has a lighter effective mass.[2] Starting from this theory, Kim et al. showed that the effective mass of silicon can be significantly reduced at the interface with a metal film,[3] which provides an important way of improving the performance of semiconductors.

Although the effective mass of electrons in semiconductors can be tuned by external manipulations, to enhance the performance of electronic devices, it is still highly desirable to find materials with massless electrons. The dream now becomes possible after the discovery of graphene, which is a one-atom layer of graphite.[4−7] The band structure of graphene has been reported with a Dirac point Fermi surface, which means a linear energy dispersion and massless electrons.[8−10] As a consequence, the carriers in graphene have a speed close to light speed. Therefore, graphene has been believed to be important for the next-generation electronic devices.

Unfortunately, the reported Dirac point disappears in graphene nanoribbons and quantum dots due to the quantum confinement and edge effects,[11−16] which limit the application of graphene in electronic devices. To extend the application of graphene, it is necessary to find similar nanoribbons or quantum dot structures with high-speed carriers, which can be easily implanted into graphene-based electronic devices. The Dirac point behavior of graphene arises from the noninteraction of two adjacent p_π orbitals around the Fermi level. Therefore, a promising way of finding massless carriers is to investigate materials with different orbital symmetries in the valence and conducting bands.

A single BN layer has a honeycomb structure similar to that of graphene.[17,18] In contrast to the semimetal character of graphene, a BN single layer is a semiconductor. However, bare BN zigzag nanoribbons (BNZNRs) are normal metals, as confirmed by both theoretical and experimental studies.[19−21] The different edges of BNZNRs provide the possibility of different orbital symmetries. Therefore, it raises an interesting question of whether BNZNRs can lead to massless electrons.

In this paper, we address the aforementioned question by performing comprehensive first-principles studies on BNZNRs. Pristine BNZNRs are found to exhibit spin-resolved metallic character, as reported. However, when the edge B atoms are

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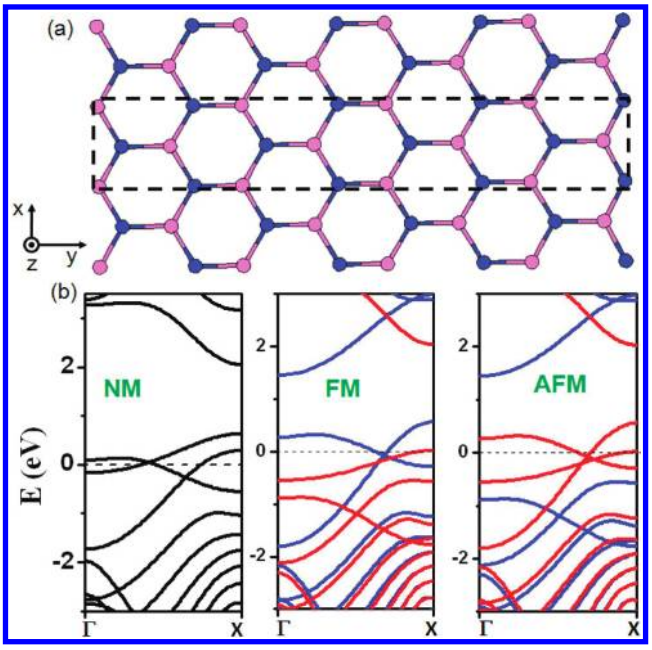

Figure 1. (a) The optimized structure of bare 8-BNZNR, where the pink and blue spheres represent the B and N atoms, respectively. (b) The calculated band structures of bare 8-BNZNR for nonmagnetic, ferromagnetic, and antiferromagnetic states. The red and blue curves refer to spin-up and spin-down bands, respectively. Γ = (0, 0, 0) and X = (1/2, 0, 0).

hydrogenated, BNZNRs show a spin-resolved Dirac point Fermi surface, which means that only the electrons of one special spin-channel have high speed. In the following, we show that the observed Dirac point Fermi surface originates from the quantum confinement and edge effects of BNZNRs.

RESULTS AND DISCUSSION

Pristine BNZNRs. Taking a BNZNR with eight zigzag chains (8-BNZNR) as our model system, we relaxed the structure without any edge modifications. The fully optimized structure retains the flat plane, and no edge reconstruction is found. The dangling bonds of terminated edge atoms are forced to form localized states, which are expected to induce the magnetic solutions. Our first-principles calculations confirmed the expectations and found that the ferromagnetic (FM) solution is more stable than the nonmagnetic state by 0.41 eV per unit cell. However, different magnetic states are found to have very small energy differences (several meV per unit cell),[21] which would prevent the system from magnetic ordering. On the other hand, the spin moments can be ordered by external magnetic fields, as reported in graphene nanoribbons.[22] Therefore, we only take FM coupling in each edge of the BNZNRs in our studies, which is easily aligned by external magnetic fields.

In Figure 1, we plotted the band dispersions of 8-BNZNR with different magnetic solutions. Both the magnetic and the nonmagnetic states are metallic, in agreement with the recent experimental report.[19] In the band structures of the magnetic states around the Fermi level, we note that the spin-down bands have a nearly linear dispersion, and both FM and antiferromagnetic (AFM) states have the same character. Because different magnetic states have a similar stability, the application of an external magnetic field can readily align the magnetic moments

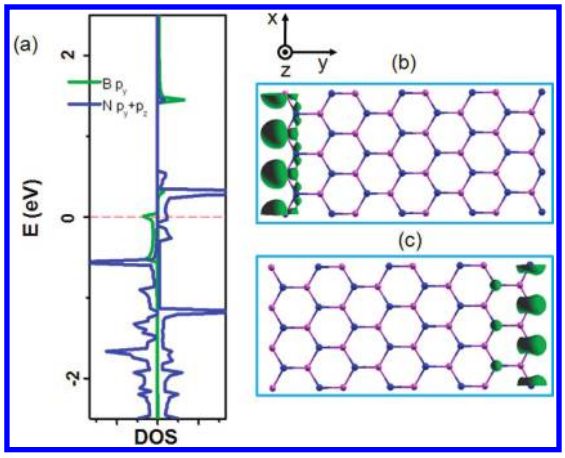

Figure 2. (a) The DOS plot of bare 8-BNZNR. (b) The partial charge density associated with the states within the energy range from E_f = −0.05 eV to E_f = +0.05 eV for the spin-up channel and (c) that for the spin-down channel.

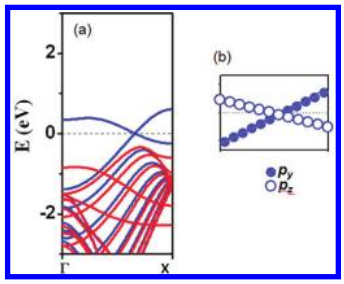

Figure 3. (a) The calculated band dispersion of 8-BNZNR with the B-edge hydrogenation. (b) The band structure around the (1/3, 0, 0) point with a large number of *k*-points. The red and blue curves refer to the spin-up and spin-down bands, respectively.

and stabilize the FM state. Therefore, in the following discussion, we focus our studies only on the FM state of BNZNRs.

To get more information about the bare 8-BNZNR, we plotted the density of states (DOS) and partial charge density in Figure 2. It is clear that the states around the Fermi level in the spin-up channel are contributed by the p_y orbitals of the B atoms, while the p_y+ p_z orbitals of the N atoms in the spin-down channel. As a consequence, the electrons in the p_y orbitals of B atoms migrate to the N atoms on the opposite edge, which is responsible for the metallic character. Thus, it is important to see if this charge migration can be prevented and realize a Dirac point in the BNZNR as a consequence.

B-Edge Hydrogenation. In removing the edge states located at the B atoms, the simplest way is to saturate the boron atoms with hydrogen atoms. After fully relaxing the structure of the B-edge hydrogenated 8-BNZNR, we calculated its band dispersion relations shown in Figure 3a. The metallic bands in the spin-up channel are fully removed, leaving behind the partially filled bands in the spin-down channel that has a Dirac point Fermi surface.

To confirm the Dirac character, we recalculated the band dispersion with a large number of *k*-points around the K-point (1/3, 0, 0). As shown in Figure 3b, the partially filled bands are linear as a function of *k*. Therefore, the B-edge hydrogenated 8-BNZNR has a spin-resolved Dirac point Fermi surface.

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The linear crossing of the two bands around the K-point is topologically determined.

As revealed by the orbital-resolved band dispersion, the bands around the Dirac point Fermi level are contributed by the p_z and p_y orbitals of the edge N atoms. The p_y orbital cannot overlap with the p_z orbital, so their noninteraction gives rise to the linear dispersion around the K-point (1/3, 0, 0).

On the other hand, by appling strain in the BNZNRs, we found that the atoms will slightly buckle, breaking the perfect planar structure. As a result, the linear dispersion around the K-point is kept, but a small energy gap apears. Therefore, to reserve the perfect Dirac point, the strain in BNZNRs should be fully released.

We also examined N-edge hydrogenated BNZNRs in a similar manner to find that the N-edge hydrogenation removes the quasi-linear energy dispersion, and the resulting BNZNRs become a normal spin-selective semiconductor. This result also indicates the importance of the edge states at the N atoms in the B-edge hydrogenated BNZNRs to the Dirac-like behavior.

Effect of Ribbon Width. Because we only take eight zigzag chains in our calculations, it is important to investigate the universality of our results with different widths. To make clear this point, we also calculated 16-BNZNR with the same method. Our results show that the Dirac point is robust against the width of ribbons.

CONCLUSION

In summary, we have performed comprehensive first-principles calculations to study the electronic behaviors of BNZNRs. Because of the quantum confinement and edge effects, the B-edge hydrogenated BNZNRs are predicted to possess a spin-resolved Dirac point Fermi surface. This might lead to promising novel applications and shows an important way to extend the applications of graphene-like materials in electronic devices.

COMPUTATIONAL METHODS

The detailed electronic structure calculations are performed by means of the density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package[23] using the projector augmented wave method for the electron−ion interaction,[24,25] the PW91 functional for the generalized gradient approximation,[26] and the plane-wave cutoff energy of 500 eV. The convergence in energy was set to 10^{-5} eV, and that of the force in geometry optimization to 0.01 eV/Å. In our computation, the one-dimensional (1D) periodic boundary condition (PBC) was applied along the growth direction of nanoribbons, and unit cell is adopted in our calculations. To ensure our results, we also performed the calculations with a double unit cell and found that the calculations give the same results. To avoid the interaction between neighboring ribbons, the supercell is large enough to ensure a distance greater than 15 Å.

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