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Half metallicity in bare BC_2N nanoribbons with zigzag edges

Hong Li [a,*], Xiang Xiao [a], Jun Tie [a], Jing Lu [b]

[a] College of Mechanical and Material Engineering, North China University of Technology, Beijing 100144, PR China
[b] State Key Laboratory of Mesoscopic Physics and Department of Physics, Peking University, Beijing 100871, PR China

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ABSTRACT

We study the electronic and magnetic properties of bare zigzag BC_2N nanoribbons (ZBC_2NNRs) by using first principles calculations. The ZBC_2NNRs which we studied are assigned to four edge types, and we carefully examine the size effect and edge magnetic coupling orders. We find that the N edge and the C edge adjacent to N atoms have a ferromagnetic coupling, while the B edge and the C edge adjacent to B atoms have an anti-ferromagnetic coupling. These novel properties arise from the unsaturated edge with specific edge determined magnetic moment distribution. All the investigated ribbons exhibit magnetic ground states with room-temperature accessible half-metallic character, irrespective of the ribbon width. Our results suggest that ZBC_2NNRs can have potential applications in spintronics.

1. Introduction

Graphite-like ternary system $B_xC_yN_z$ atomic layer materials, proposed as supplement to graphene, are prospective soft materials for nanoelectronics, optoelectronics, and energy storage applications [1]. Within the ternary phase, vast different atomic compositions are viable, and the BC_2N stoichiometry is believed to be one of the most stable $B_xC_yN_z$ materials [2–8]. As several allotropes are usually involved in BC_2N sheet, the band gaps have strikingly different experimental values of 23 meV [9], 2.0 eV [7], or indirect band gap of 1.6 eV [2]. In theory, the most stable configuration of BC_2N sheet is predicted to possess the most extensive number of C–C and B–N bonds [10–13]. As a result, the C atoms and BN pairs form respective zigzag atomic chains. This structure is predicted to be a semiconductor with a direct gap of 1.6 eV [10,12,13]. Very inspiringly, first-principles calculations show that this few-layer BC_2N possesses high carrier mobility, and its three-layer counterpart has a very high carrier mobility of 8×10^5 $cm^2 V^{-1} s^{-1}$ [14]. The high mobility usually means high device performance in nanoelectronic and optoelectronic applications.

Sustaining efforts are performed on the study of the one-dimensional (1D) ribbon counterparts of BC_2N monolayer [15–23]. Different from the graphene and BN nanoribbons, the BC_2N nanoribbons (BC_2NNRs) possess various edge arrangements due to its ternary nature even with a chosen BC_2N monolayer, which is likely to bring ample properties. For zigzag edges, magnetism is predicted with various edge configurations [17,18,21,22], distinct from their two-dimensional (2D) counterparts. This extends the applications of the BC_2NNR in spintronics. However, most of the previous obtained magnetic states are not stable at room temperature, which limits its practical application. Moreover, the possible magnetic couplings of edge atoms are not sufficiently considered in previous works.

In this work, the structure, stability, electronic, and magnetic properties of the bare ZBC_2NNRs with NN–CC, BB–CC, NN–BB, and CC–CC edge arrangement are studied using first-principles calculations. A series of ribbon width range from 0.72 to 3.12 nm are considered. After careful consideration of edge magnetic coupling orders, we find that the N edge and the C edge adjacent to N atoms show a ferromagnetic coupling, while the B edge and the C edge adjacent to B atoms show an anti-ferromagnetic coupling at ground states. Importantly, we find that all the ground states of the investigated ZBC_2NNRs present half-metallic properties accessible at room temperature.

2. Models and methods

Owing to the various arrangements of B, C, and N atoms, BC_2N sheet can have several possible geometry structures. Fig. 1a gives the theoretical predicted most stable one, which has the most extensive numbers of C–C and B–N bonds. We cut the ZBC_2NNRs from this BC_2N monolayer along a specific direction, where the respective BN and C zigzag chains retain. We denote a ZBC_2NNR with N_Z zigzag chains as N_Z–ZBC_2NNR. Here, the ribbons with even N_Z have edge arrangement NN–CC and BB–CC, while those with odd N_Z have edge arrangement NN–BB and CC–CC as shown in Fig. 2.

* Corresponding author.
E-mail address: lihong@ncut.edu.cn (H. Li).

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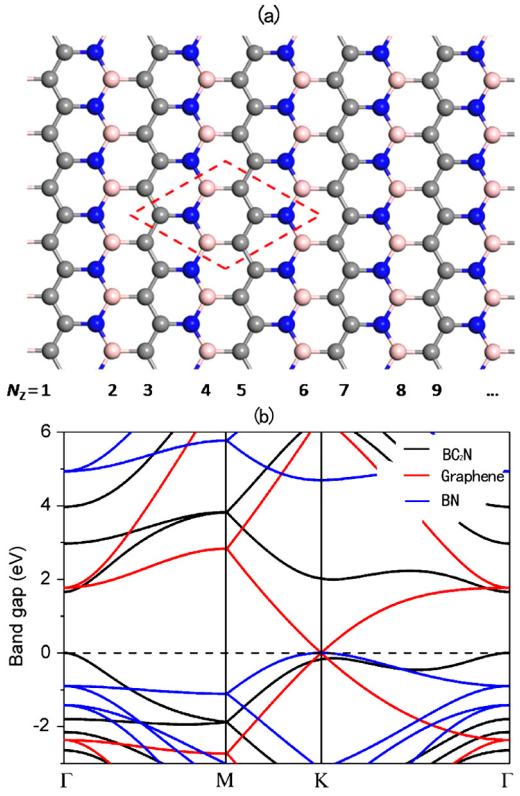

Fig. 1. (a) Atomic structures of the fully optimized BC_2N sheet. Small gray, blue and pink spheres denote carbon, nitrogen and boron atoms, respectively. The red dash line quadrilateral indicates the BC_2N unit cells. (b) Band structure of the BC_2N sheet. Those of the graphene and BN sheet are given for comparison. The Fermi level denoted by the black dash line is set to zero. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

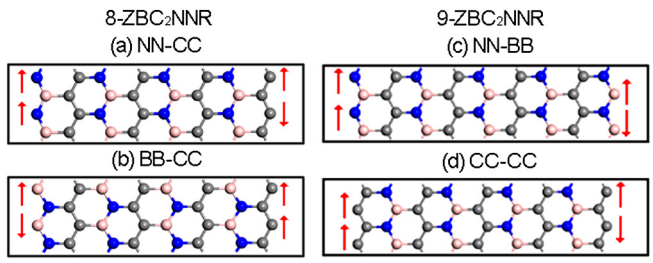

Fig. 2. Atomic structures of the fully optimized ZBC_2NNRs. The red arrows denote the spin distributions for the ground states. Small gray, blue and pink spheres denote carbon, nitrogen, and boron atoms, respectively. The black solid rectangles indicate the $2 \times 1 \times 1$ supercells of the ZBC_2NNRs. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

A supercell of $2 \times 1 \times 1$ is built, and a vacuum of 30 Å is adopted to avoid the periodic interaction between its replicas. We consider six types of edge magnetic ordering for each ribbon, *i.e.*, each edge can be ferromagnetic or anti-ferromagnetic coupling as seen in Fig. S1.

We perform spin-polarized first-principles calculations based on the density functional theory (DFT) as implemented in the DMol^3 package [24]. The exchange and correlation form of generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional are adopted [25]. We use a numerical atomic orbital basis set plus a d-type polarization function (DNP) to expand wave functions. The global orbital cutoff energy for each element is set to 5.1 Å. All the ribbons are relaxed with their initial magnetic states, *i.e.*, six spin ordering states and one nonmagnetic state. The Brillouin-zone integration is sampled by $5 \times 1 \times 1$ Monkhorst–Pack grids [26], and a convergence threshold of 1.0×10^{-6} Ha on the energy and 0.001 Ha/Å on the maximum force are adopted. Electronic structures are then calculated on the corresponding optimized geometries with $25 \times 1 \times 1$ k-points.

3. Results and discussions

The fully relaxed geometry structure of the BC_2N sheet is given in Fig. 1a. Analogous to their all carbon analog graphene, the BC_2N monolayer forms strong planar hexagonal honeycomb structure. We denote the BC_2N unit cell by a red quadrilateral marked in Fig. 1a, and the optimized lattice constants are $a = 4.98$ Å and $b = 5.00$ Å. The optimized bond lengths of the B–N, B–C, N–C, and C–C bonds are $d_{B-N} = 1.45$ Å, $d_{B-C} = 1.51$ Å, $d_{N-C} = 1.39$ Å, and $d_{C-C} = 1.42$ Å, respectively. The calculated binding energy of the BC_2N sheet is -7.24 eV/atom, while those of graphene and BN sheet are calculated to be -7.91 eV/atom and -7.03 eV/atom, respectively. It indicates that the BC_2N sheet is less stable than graphene, but should be more stable than BN sheet. Though this specific BC_2N sheet hasn't been laboratorial synthesis yet, the high thermostability indicates a high possibility to be synthesis with improved experimental technique. The band structure of BC_2N sheet is given in Fig. 1b with those of graphene and BN sheet given for comparison. The BC_2N sheet is a nonmagnetic semiconductor with a direct band gap of 1.66 eV at Γ point, different from the semi-metallic graphene with zero gap at K point [27] and the insulator BN sheet with a direct band gap of 4.70 eV at K point [28,29]. Our results of the geometry structure, binding energy, and band information are consistent with previous theoretical calculations as compared in Table S1 [18,21]. The analogous structure, relative stability, and moderate band gap illustrate that the BC_2N sheet could be an excellent complement to graphene and BN sheet for nanoelectronic applications.

We then investigate the geometry structure for zigzag BC_2N nanoribbons. Fig. 2 shows the optimized atomic configurations of the bare 8-ZBC_2NNRs with NN–CC and BB–CC edge arrangement and those of the bare 9-ZBC_2NNRs with NN–BB and CC–CC edge arrangement. All the edge N and C atoms move inward a little bit, while the edge B atoms move outward slightly. For all the atoms that bond to the edge atoms move outward a bit. As a result, the edge bond length would shorten by 1.5%∼4.6% or prolong by 0.3%∼4.7%. These are also adaptable to wider ribbons. For details, we give all the edge bond lengths and inner bond lengths for the NN–CC 8-ZBC_2NNR, BB–CC 8-ZBC_2NNR, NN–BB 9-ZBC_2NNR, and CC–CC 9-ZBC_2NNR in Table S2.

To ascertain the ground state, we examine six spin coupling configurations *vs.* nonmagnetic configuration for each ZBC_2NNR. That means the edge spin coupling cases are sufficiently considered, where each edge can be ferromagnetic or anti-ferromagnetic ordering as shown in Fig. S1. Each ribbon has a magnetic ground state, and we mark the magnetic ordering with red arrows in Fig. 2. We can see that all the N edge and the C edge adjacent to N atoms show a ferromagnetic coupling, while all the B edge and the C edge adjacent to B atoms show an anti-ferromagnetic coupling at ground states. Guo et al. [18] have examined the same ZBC_2NNRs with H-passivation and Kaneko et al. [30] have examined the same bare 8-ZBC_2NNRs with BB–CC edge arrangement using Tight-binding method, but the magnetic states are not examined in their works. Our former work shows that the bare ZBC_2NNRs with another CN–CB edge arrangement would reconstruct at the edge and no magnetic exhibited [21]. Lu et al. [17] have carefully examined the bare ZBC_2NNRs with even N_z truncated from a strip-like BC_2N sheet, and our ground-state edge coupling orders of ribbons with even N_z consist with their results when the edge arrangement share the same rules.

We next investigate the stability of these ZBC_2NNRs with different edge arrangement and ribbon width using binding energy (E_b). We define the E_b as,