Dangling Bond States, Edge Magnetism, and Edge Reconstruction in Pristine and B/N-Terminated Zigzag Graphene Nanoribbons

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Recently it was reported that the edges of the pristine zigzag graphene nanoribbons (ZGNRs) tend to be reconstructed as a result of the instability induced by the dangling bonds of edge carbon atoms [see, e.g., PRL 101, 115502(2008), PRL 101, 096402(2008), PRB 80, 073401(2009)]. The edge reconstruction brings significant changes to the ZGNRs, such as insulator—metal transition and suppression of the edge magnetism. In this work, the dangling bond states, edge magnetism, and edge reconstruction in pristine and B/N-terminated zigzag graphene nanoribbons are investigated by density functional theory calculations. It is found that a big difference is observed in the edge magnetism of the pristine and B/N-terminated ZGNRs and it arises from the different features of the dangling bond states in these systems. Interestingly, electron (N) doping can stabilize the edges, while hole (B) doping cannot, which also originates from the different features of the dangling bond states. Finally, when the effects of the dangling bond states are removed by H passivation, either in pristine ZGNRs or in B/N-terminated ZGNRs, no edge reconstruction occurs. The mechanism of electron doping or H passivation can be helpful in situations where the properties intrinsic of the zigzag edge shape are to be utilized and thus the spontaneous reconstruction process is to be avoided.

I. Introduction

Graphene nanoribbons (GNRs) have captured intensive attention in recent years due to their novel electronic and transport properties and their promising potential for applications in future nanoelectronic circuits.1–15 Among such nanoribbons, GNRs with zigzag edges (ZGNRs) have received special interest since they are magnetic and are believed to be very important building blocks in spintronic devices.15–22 One exciting point is that half-metallicity can be achieved in ZGNRs by various ways, such as external transverse electrical field, edge decoration, and hole (B)—electron (N) doping schemes.15,19–23 This has initiated even more interest in the application of ZGNRs since completely spin-polarized transport, which has long been the search object in spintronics with great efforts, can be realized. However, all these attractive prospects of ZGNRs are based on their special zigzag edge shape and the subsequent peculiar electronic structure, such as localized edge states and edge magnetism. Recent study shows that pristine ZGNRs with dangling bonds at the edges are not stable and the edges tend to be reconstructed with two consecutive hexagons transformed into one heptagon and one pentagon and the ultimate edges become armchair-like.24–27 In fact, this process has already been observed experimentally.28,29 Thus, the structure of such edge-reconstructed ZGNRs bears the features from both the ZGNRs and the armchair graphene nanoribbons (AGNRs). This results in many interesting properties in this type of ZGNRs, such as insulator-to-metal transition and suppression of edge magnetism. However, such edge reconstruction processes and the subsequent changes in the properties are reported only in the pristine ZGNRs. It is well-known that the structural and electronic properties of graphene nanoribbons can be tuned by various chemical ways. Naturally, it will be very interesting to investigate whether this process will occur or not in these chemically decorated and frequently studied ZGNRs. Moreover, it is also important to figure out ways for controlling the occurrence of edge reconstruction.

In this work, we focus on the study of the relative stability and electronic structure of the pristine and B/N-terminated ZGNRs with or without edge reconstruction by performing density functional theory (DFT) calculations. The properties of the pristine ZGNRs are first revisited mainly for the sake of comparison with those of the B/N-terminated ones. It is found that the edge magnetism is determined by both the dangling bond states and the edge states. Because of the different contributions of these two terms, the edge magnetism is quite different in the unreconstructed pristine and B/N-terminated ZGNRs. Meanwhile, it is very interesting to see that N doping can prevent the edges of ZGNRs from being reconstructed while B doping cannot, which also has the origin from the dangling bond states. Additionally, it is found that H passivation is always a very strong way for stabilizing the zigzag edge in either the pristine ZGNRs or B/N-terminated ZGNRs.

The rest of this paper is organized as follows: in Section II we give a brief description of the structures studied in this work and the computational method, while in Section III the main results are presented and discussed. Finally in Section IV we draw out conclusions.

II. Computational Details

The calculations are performed by using the SIESTA code, which employs norm-conserving pseudopotentials and linear combinations of atomic orbitals as basis sets.30 The wave

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The function is expanded with a double-$\zeta$ polarized (DZP) basis set and the exchange-correlation potential is treated at the level of generalized gradient approximation (GGA), with the form of Perdew–Burke–Ernzerhof (PBE). The fineness of real space grid is determined by an equivalent plane wave cutoff 200 Ryd. In this work, we take 10-ZGNR (10 zigzag carbon chains along the $z$-axis, the periodic direction) as an example and the supercell of the pristine ZGNR consists of two unit cells with the length of 4.92 Å (see Figure 1). The lattice vectors along the $x$- and $y$-axis are set to be 35.0 and 15.0 Å, respectively, which include a vacuum big enough to avoid interactions from the adjacent neighbors. The Brillouin zone is sampled by a $1 \times 1 \times 40$ $k$-point grid. All the structures are fully relaxed until the force tolerance of 0.04 eV/Å is reached. As a matter of fact, to investigate the size dependence we have also done calculations for other smaller and larger ZGNRs (for example, 6-ZGNR and 14-ZGNR). Since the same findings are always observed and size independent, we only present our results for the 10-ZGNR in the following.

### III. Results and Discussions

For comparison, we first study the pristine ZGNRs with and without edge reconstruction. The unreconstructed system is a semiconductor with an energy gap of $\sim 0.6$ eV (see Figure 2a). The magnetic moment on each edge carbon atom is $1.2 \mu_B$, which is much larger than that ($0.2$–$0.3 \mu_B$) reported in the H-passivated system. It is found that the big difference arises from the contribution of the dangling bond states. It is well-known that in zigzag graphene nanoribbons, localized edge states are formed, with different spins localized at different edges. In detail, the valence edge states with $\alpha$-spin and the conduction edge states with $\beta$-spin are on the same side, while the valence edge states with $\beta$-spin and the conduction edge states with $\alpha$-spin are on the other side (see Figure 3a–d). Interestingly, the dangling bond states are very similar to the edge states in that they are formed both in the valence bands and in the conduction bands. Moreover, these states are spin degenerate and also localized at the edges with different spins localized at different sides (see Figure 3e–h). Since the dangling bond states and the edge states with the same spin are localized at the same side, we have $1.20 \mu_B$ magnetic moment on each edge carbon atom, which is larger than that in the H-passivated system ($0.28 \mu_B$ in our calculations). H passivation removes the dangling bond states shown in Figure 2a and thus greatly reduces the magnetic moment. It should be noted that the degeneracy of the dangling bond bands in both the valence band and the conduction band in Figure 2a is 1 with the bands lying above or below the Fermi level, while it is 2 in the work of Koskinen et al. where non-spin polarized calculations were performed with the bands crossing the Fermi level. Our tests without spin polarization give the same results as in the results of Koskinen et al. Obviously, for

![Figure 1](image1.png)

**Figure 1.** The fully relaxed geometry structure for (a) a pristine 10-ZGNR; (b) a 10-ZGNR with single edge reconstruction; (c) a 10-ZGNR with double edge reconstruction. The shadowed parts indicate the supercells adopted in the calculations. The edge atoms are labeled by numbers $A(A'), B(B'), C(C'),$ and $D(D')$.

![Figure 2](image2.png)

**Figure 2.** The band structure for (a) the undoped ZGNR; (b) the B-terminated ZGNR; (c) the N-terminated ZGNR without edge reconstruction and (d) the undoped ZGNR; (e) the B-terminated ZGNR; and (f) the N-terminated ZGNR with edge reconstruction. The dangling bond bands are indicated by filled squares, filled circles, filled diamonds, and empty triangles. Since all the bands are spin degenerate, only one spin is shown.
such magnetic systems, the results from spin-polarized calculations will be more reasonable.

In the edge-reconstructed ZGNRs, the original zigzag edges evolve into armchairlike edges (see Figure 1c). This is due to the instability induced by the unoccupied dangling bond states that lie very close to the Fermi level in the bare zigzag edges. It results in the transformation of sp²-hybridization to sp³-hybridization and thus a more stable triple bond is formed at the edges. The fully relaxed triple bond length (see the bond, for example, between atom A and atom B in Figure 1c) obtained in our calculations is 1.256 Å, which is very close to the C≡C bond length 1.20 Å in acetylene. It is found that the energy of the ZGNR with double edge reconstruction is 1.46 eV/cell lower than that of the pristine ZGNR [see Table 1]. This means that the edges of the ZGNRs tend to be reconstructed, which agrees well with previous studies. Accompanying with this, the magnetic moment of 1.20 \( \mu_B \) on each edge carbon atom in the

<table>
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<th>edge detail</th>
<th>C</th>
<th>N</th>
<th>B</th>
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<th>B–H</th>
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<tr>
<td>( \Delta E ) (eV)</td>
<td>-1.46</td>
<td>5.38</td>
<td>-0.50</td>
<td>2.55</td>
<td>3.72</td>
<td>2.20</td>
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\( \Delta E \) is the energy increase after double edge reconstruction.

![Figure 3](image_url)
pristine edges is completely suppressed to 0 in each reconstructed edge.

By inspection into the changes of the edge states and the dangling bond states after edge reconstruction, we find that (1) the dangling bond states of each spin in the valence bands are symmetrically localized at the two edges (see Figure 4a,b); (2) although the edge states are still formed, these states with the same spin are also symmetrically localized at the two edges (not shown, but similar to Figure 4a,b); (3) the edge states both in the valence bands and the conduction bands become degenerate and all lie below the Fermi level (see Figure 2d). Thus the edge states and the dangling bond states with different spins are equally occupied, which results in a nonmagnetic system. One interesting thing to note is that both in the valence bands and in the conduction bands the dangling bond bands of each spin are double degenerate. However, in contrast to the dangling bond states in the valence bands, the states in the two degenerate dangling bond bands in the conduction bands are localized on different sides; specifically, the states from one of the bands for both spins are localized on one side (see Figure 4c,d) and those from the other band for both spins are localized on the other side (not shown).

In the numerous studies of GNRs, up to now it has been widely investigated about how to tune their properties by various ways, such as doping, defects, edge modification, molecule adsorption, and external electrical field.15,19–22,25–28 Such tuning greatly enlarges the application possibilities of GNRs. Especially, due to the similar atomic radius and mass but with one electron less or more than carbon (C), boron (B), or nitrogen (N) atoms are frequently used as the dopant for tuning the properties of GNRs. Naturally, the stability of such B- or N-doped ZGNRs is a problem worthy of careful study. Because of the lower potential at the edges, generally B or N dopants tend to segregate to the edges when they are doped into the GNRs. In fact, our study of total energy as a function of the dopant position shows that the system is in the most stable state when the dopant lies at the edges. Since edge reconstruction may significantly affect the expected tuning effects of B or N doping, then one question arises; will edge reconstruction occur in these B- or N-doped ZGNRs? To investigate this problem, we replace the C atoms at each edge indicated by A(A'), B(B'), C(C'), and D(D') in Figure 1a,c by N or B atoms. Note that by increasing or decreasing the doping concentration, internal C atoms or only part of the edge atoms may be substituted by B/N atoms. Here, we consider one specific case with only the edge C atoms all replaced by B/N atoms and we call these systems as B/N-terminated ZGNRs.

After full relaxation of the structure, for N doping it is found that the total energy of the edge-reconstructed system is increased by 5.38 eV/cell compared with that of the unreconstructed system. However, for B doping the total energy is decreased by 0.50 eV/cell by edge reconstruction (see Table 1). This means that N doping can stabilize the zigzag edges of ZGNRs and edge reconstruction does not occur in N-doped ZGNR, but for B doping, reconstructed edges are more stable. Meanwhile, in the cases without edge reconstruction, the magnetic moment on the B atom (0.77 $\mu_B$) is smaller than that of the pristine ZGNRs (1.20 $\mu_B$) but much larger than that on the N atom (0.10 $\mu_B$). Since the structural stability and the edge magnetism of ZGNRs are directly related to the dangling bond states, we have investigated the changes of electronic structures, especially the changes of the dangling bond states introduced by the B or N doping.

In the B doping, the edge states in the valence bands are pushed far above the Fermi level and very close to the edge states in the conduction band. Thus the edge states are all empty and give no contributions to the magnetic moment (see Figure 2b). In the meantime, one valence dangling bond band is also raised into the conduction bands and even higher than the original conduction dangling bond bands (see Figure 2b). The other valence dangling bond band is raised right below the Fermi level, thus the magnetic moment in this system is decided by this band and we have 0.77 $\mu_B$ on each edge B atom. Since there are unoccupied dangling bond bands, like in the pristine ZGNRs, and the occupied dangling bond band is very flat and close to the Fermi level, the system is not stable and tends to be edge-reconstructed. In the meantime, the magnetic moment on each B atom is reduced to 0.43 $\mu_B$ due to the changes of the dangling bond states and edge states arising from the edge reconstruction.

Figure 4. The dangling bond states at the $\Gamma$-point for the undoped ZGNR after edge reconstruction: (a) one state with $\alpha$-spin in the valence band; (b) one state with $\beta$-spin in the valence band; (c) one state with $\alpha$-spin in the conduction band; (d) one state with $\beta$-spin in the conduction band. (a,b) [15,19] are from the same band.
However, we also notice that the energy decrease induced by edge reconstruction is as small as 0.5 eV per supercell and there is still one dangling bond band right below the Fermi level (see Figure 2e), thus both the unreconstructed and reconstructed systems are not very stable ones.

In contrast, in the N doping edge states are still formed but the edge states in the conduction bands are pushed below the Fermi level and very close to the edge states in the valence band (see Figure 5a–d). Thus edge states from both the conduction bands and the valence bands are almost equally occupied. Meanwhile, N introduces one more electron than C, which goes to the unoccupied dangling band, thus there is a lone pair of electrons in the dangling bond states. That is why all the dangling bond bands are below the Fermi level (see Figure 2c). Now all the localized dangling bond states (see Figure 5e–h) and edge states with different spins are almost fully occupied, and as a result, a negligible magnetic moment is observed at the edge N atoms. Since there are no unoccupied dangling bond states in the N-doping case, the system is very stable and edge reconstruction does not occur. In fact, edge reconstruction in the N-terminated case will bring two unoccupied dangling bond bands and the other dangling bond bands are very close to the Fermi level (see Figure 2f), which will lead to the structural instability.

**Figure 5.** The edge states for (a) $\alpha$-spin in the valence band; (b) $\beta$-spin in the valence band; (c) $\alpha$-spin in the conduction band; (d) $\beta$-spin in the conduction band and the dangling bond states for (e) $\alpha$-spin in the valence band; (f) $\beta$-spin in the valence band; (g) $\alpha$-spin in the conduction band; (h) $\beta$-spin in the conduction band at the $\Gamma$-point in the N-doped ZGNRs. For dangling bond states in both the valence bands and the conduction bands, only one state of each spin is shown.
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References and Notes