

Electronic Structure Calculations on Edge-functionalized Armchair Boron Nitride Nanoribbons

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Abstract. Boron nitride nanoribbons (BNNRs) are quasi 1-D stripes of 2-D hexagon boron nitride. Here we study the electronic properties of armchair BNNRs edge-functionalized by O atoms with the state-of-the-art density functional theory, using a hydrogenated analogue as a reference. The edge functionalization by O atoms on armchair BNNRs was found to give peroxide-like structure. Unlike the zigzag BNNRs in our previous study, which become metallic, the O-functionalized armchair BNNR remains semiconducting with a bandgap of 2.65 eV, albeit it is already reduced from the bandgap of 4.48 eV for the hydrogenated analogue. We further reduced the peroxide with H atoms to OH groups, which leads to a bandgap of 4.08 eV and alternating 5- and 7-member rings along the two edges due to the presence of two chains of hydrogen bonds. The ribbon becomes nonplanar with rippled edges. Energy bands and total and projected density of states are discussed. The work of this study could potentially help improve the materials landscape for efficient nanoelectronic and optoelectronic devices

1. Introduction

Hexagonal boron nitride (h-BN) is a one-atom-thick layered material with a flat 2-D structure isoelectronic and isomorphic to the graphene honeycomb lattice. An h-BN consists of an equal number of boron and nitrogen atoms in sp^2 hybridization that are bonded together by strong covalent bonds but with a remarkable ionic character. The h-BN is a large bandgap insulator and recently has been experimentally prepared [1]. In addition to the 2-D h-BN, the quasi 1-D stripes of h-BN, namely boron nitride nanoribbons (BNNRs), have received a great deal of attention both theoretically and experimentally [2, 3].

As a complementary work to our previous studies on zigzag BNNRs [4], here we report an ab initio study of the effects of edge functionalization by O atoms on the electronic properties of an armchair BNNR. Unlike in the zigzag counterpart where the edges are characterized by atom wires consisting of equidistant O atoms and are responsible for the ribbon's metallic behavior, we found that in the armchair ribbon, the O atoms form peroxide-

like structure on the armchair edges, giving semiconducting features. The peroxide structure is further reduced with H atoms, giving an armchair BNNR that is edge-terminated by OH groups, which form rippled chains of hydrogen bonds. Interpretation of results is assisted by energy bands, total density of states (TDoS), and projected density of states (PDoS) presented for all of the functionalized ribbons.

2. Computational Methodology

The electronic structures and optimized geometries are computed by using the SIESTA DFT-based code [5]. We use a double- ξ basis set with additional polarization orbitals. The spin-dependent local density approximation is adopted for the exchange correlation functional, and the Troullier-Martins scheme is used for the norm-conserving pseudopotentials. All armchair BNNRs are modeled within a supercell with at least 10 Å of vacuum between noninteracting neighboring cells. All atoms are relaxed with a force tolerance of 0.02 eV/Å, and the unit cell vectors are relaxed with the maximum stress component being smaller than 0.02 GPa. The numerical integrals are performed on a real space grid with an equivalent cutoff of 300 Ry, and 128 k-points are used to sample the irreducible Brillouin zone. These calculations were performed on the Oak Ridge National Laboratory Institutional Cluster (OIC), which provides high-performance computing service for parallel computing applications.

3. Results and Discussions

All edge-functionalized BNNRs are defined by the notation n-aBNNR-X, where “n” refers to the number of BN dimers per unit cell across the ribbon width, “a” denotes that the BNNRs have an armchair orientation, and “X” is the functionalizing atoms attached to the edges. We will show that different electronic behaviors can be obtained as the two edges are passivated with different atoms or chemical groups. Wide ribbons are considered since they prevent the interaction between the functional groups on the edges, which are shown to introduce a slight deformation. We study the electronic properties of hydrogenated, oxidized, and OH edge-functionalized structures of BNNRs in the armchair edge orientation, namely, 37-aBNNR-H, 37-aBNNR-O, and 37-aBNNR-OH. The fully relaxed geometries of the ribbons are shown in Figures 1 and 2.

First we examine the 4.65-nm-wide hydrogenated ribbon 37-aBNNR-H (Figure 1-f). Although similar ribbons of different width are well studied, we revisit it here in order to deliver a self-contained story by using its electronic structure as a reference for armchair BNNRs functionalized with O or OH. On the basis of first-principles calculations, Figure 1-a shows the energy band diagram, which exhibits a direct energy bandgap of 4.48 eV at the Γ point of the BZ. Both the conduction and the valence bands present dispersive electronic states. The 37×4 bands are distributed below the Fermi energy level and describe the sigma-bonds corresponding to the atomic valence orbitals in sp^2 hybridization of the BN-network and the p_y -derived pi-bonding states. Also, two more dispersionless bands are associated with the atomic orbitals of the terminating H atoms.

The substitution of the H atoms on the edges by six-valence-electron O atoms produces the 37-aBNNR-O ribbon (Figure 1-g). Unlike the zigzag BNNRs studied previously where the edges are characterized by atom wires consisting of equidistant O atoms leading to metallic behavior [4], the O atoms of 37-aBNNR-O form a peroxide-like structure on the armchair edges. The optimized lattice does not change the planar structure across the ribbon

width except for the O atoms, which are tilted above and below the ribbon plane as a result of a O-O bond length of 1.52 Å that is longer than the B-N bond length of 1.43 Å. Each of these atoms is linked to the sp^2 hybridized B or N atoms in the ribbon through a hybrid sp^3 orbital and accommodates two lone pairs, whose states are localized at very low energies. The O-N bond length is 1.384 Å, and the O-B bond length is 1.376 Å. The O-O bond length of 1.52 Å is nearly identical to the value of 1.49 Å of typical inorganic peroxides. An energy bandgap reduction down to 2.65 eV with respect to the hydrogenated ribbon is observed, due to the appearance of two groups of new bands (Figure 1-b), each with nearly double degeneracy, whose origin is the p-states of the O atoms. This can be confirmed by analyzing the contribution of each O atomic orbital to the TDoS shown in Figure 1-e. The PDoS shown in Figure 1-c and d reveal that the dispersionless states within the ribbon gap are localized on the functionalizing O atoms. Spin-resolved calculations show that the ground state is spin degenerate.

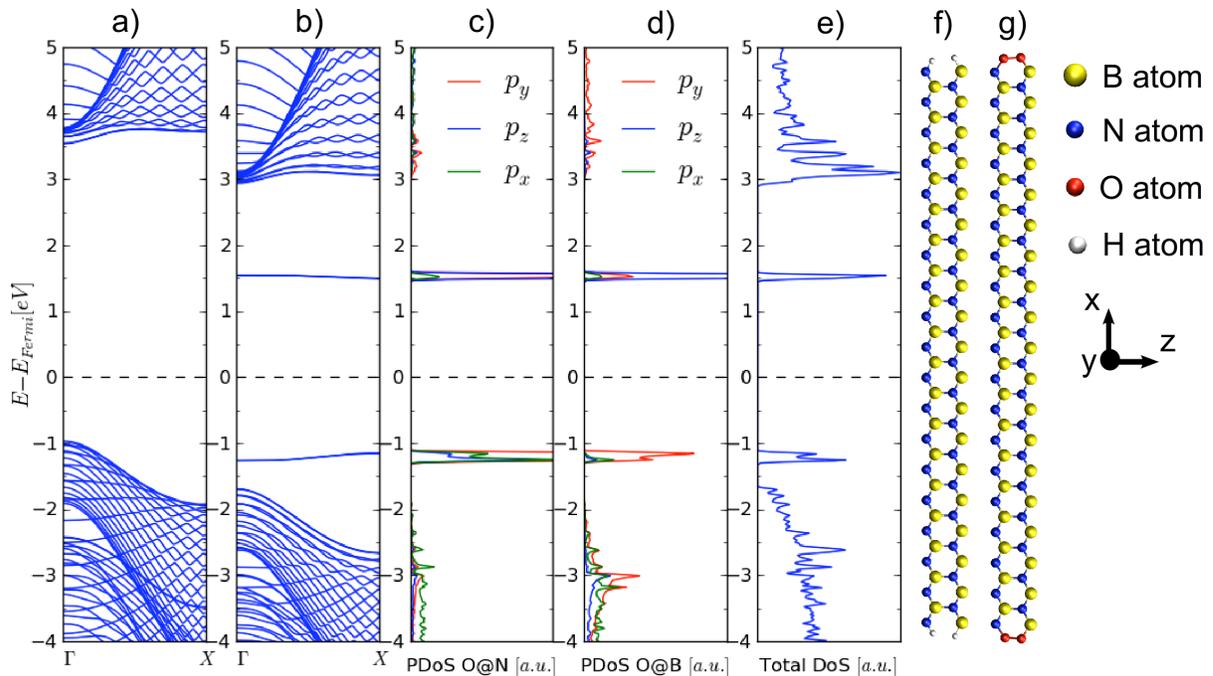


Figure 1. (a) Energy band diagram for the nonmagnetic 37-aBNNR-H for which all states are spin degenerate. (b) Energy band diagram of the nonmagnetic ground state of the 37-aBNNR-O where two dispersionless states in the ribbon gap can be observed. (c) and (d) Projected DoS of the O atoms linked to the B and N atoms at one of the armchair edges; these reveal that the major contribution to those localized states comes from the p-orbitals of the O atoms. The gap of the O edge-functionalized ribbon is thus reduced down to 2.65 eV from the 4.48 eV of the hydrogenated ribbon. (e) Total DoS of the system. (f) and (g) Fully relaxed geometries of 37-aBNNR-H and 37-aBNNR-O, respectively. Horizontal dashed lines indicate the Fermi energy level.

Before we evaluate the total energy of the O edge-functionalized armchair BNNRs featuring peroxide-like geometry, we can expect from the peroxide chemistry that the stability of 37-aBNNR-O may be compromised by the reactivity of the oxygen atoms in a peroxide-like geometry. In order to lower the reactivity of the O edge-functionalized ribbon, we reduce the peroxide with H to study an OH edge-functionalized ribbon 37-aBNNR-OH

(Figure 2-e). By comparison of the total energies between 37-aBNNR-OH and 37-aBNNR-O and a H_2 molecule, the OH edge-functionalized ribbon lowers its total energy by ~ 18 eV with respect to the oxidized ribbon, clearly indicating that the reduction of the oxygen atoms on the edges is a favorable chemical reaction. Figure 2-a shows the energy band diagram where a doubly degenerate bonding state allows for a bandgap reduction down to 4.08 eV with respect to the hydrogenated case. We note that the different contributions of O atomic orbital to the TDoS of those two states depend on the atom to which the OH is attached. The PDoS shown in Figure 2-b reveals that the contribution to the TDoS close to the Fermi energy primarily comes from the p_y orbital (perpendicular to the ribbon plane) in the case of the O attached to the N atom. In comparison, as can be seen from the PDoS shown in Figure 2-c, more significant and nearly equal contributions to the TDoS come from the p_x and p_z orbitals for the O attached to the B atom.

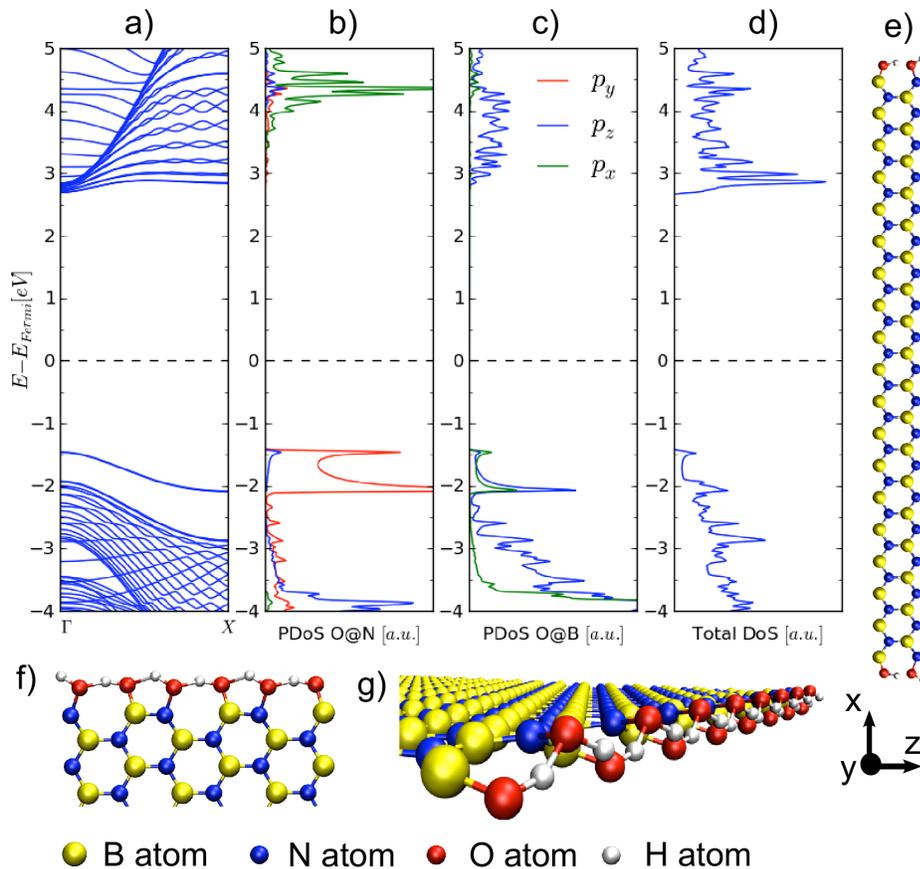


Figure 2. (a) Energy band diagram of the nonmagnetic ground state of the 37-aBNNR-OH, represented in (e). The attachment of hydroxyl groups to the ribbon edges reduces the bandgap with respect to the hydrogenated case down to 4.08 eV due to the appearance of two bonding states related to the O atoms. The projected DoS of the O atoms of the hydroxyl groups linked to the edge N and B atoms shown in (b) and (c) reveals that the major contribution to new states comes from the p-orbitals of the O atoms. The total DoS is shown in (d). OH groups form hydrogen bonds along the edges, which lead to alternating 5- and 7-membered rings shown in (f), and nonplanar ribbon with rippled edges shown in (g).

We point out that a similar 13-BNNR-OH ribbon has been studied by Wu et al. [6], where

they showed a band diagram and a TDoS that are similar to our results. Wu et al. also found that the OH termination induced a local distortion at the edges mainly due to the short distance between two neighboring groups. Here we present further interpretations that the local distortion is in fact associated with hydrogen bonds. We observe that the relaxation ends up with the H atom of each OH group pointing toward the O atom on the neighboring OH group. The final orientations of the OH groups are in such a way that one of the two lone pairs on an O atom would orient toward the H atom on the neighboring OH group forming a hydrogen bond. For extended nanoribbons, the hydrogen bonds repeat along the two edges, forming two chains of alternating 5- and 7-member rings (Figure 2-f). Note that changing the hydrogen bond donors/acceptors would give an opposite direction for the hydrogen-bonded chain but it would not change the electronic structure significantly. Because of the hydrogen-bonded chains, the ribbon becomes nonplanar with rippled edges, including the B/N atoms connected immediately to the O atoms (Figure 2-g). We are further checking the effects of doubling the unit cell on the period of the hydrogen-bonded chains and the rippled ribbon structure.

4. Summary

Using DFT-based calculations, we have studied the geometry and electronic structure properties of O and OH edge-functionalized armchair BNNRs. From the comparison of the total energy of OH group terminations with that of mere edge oxidations, it is expected that the edge-oxidized ribbons are less stable. We have unveiled the contribution of the oxygen p-orbitals to the new states introduced in the ribbon gap upon functionalization. The large bandgap insulating behavior of hydrogenated armchair BNNRs is conserved upon edge oxidation or functionalization with hydroxyl groups but a reduction of bandgap by 0.4-1.8 eV is observed. These functionalizations may find applications in nanoelectronic applications.

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