

Intrinsic Half-Metallicity in Modified Graphene Nanoribbons

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We perform first-principles calculations based on density functional theory to study quasi-one-dimensional edge-passivated (with hydrogen) zigzag graphene nanoribbons of various widths with chemical dopants, boron and nitrogen, keeping the whole system isoelectronic. The gradual increase in doping concentration takes the system finally to zigzag boron nitride nanoribbons (ZBNRs). Our study reveals that for all doping concentrations the systems stabilize in antiferromagnetic ground states. Doping concentrations and dopant positions regulate the electronic structure of the nanoribbons, exhibiting both semiconducting and half-metallic behaviors as a response to the external electric field. Interestingly, our results show that ZBNRs with a terminating polyacene unit exhibit half-metallicity irrespective of the ribbon width as well as applied electric field, opening a huge possibility in spintronics device applications.

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Nanomaterials of carbon, like nanotubes, fullerenes, etc., have been of great interest in condensed-matter and material science because of their novel low-dimensional properties [1,2]. Over the past few decades, cutting edge research has been carried out for advanced device integration, exploring the electronic and mechanical properties of these systems. A recent addition in this journey is graphene: a strictly two-dimensional flat monolayer of carbon atoms tightly packed into a honeycomb lattice [3,4]. Since its innovation [5–7], it has made possible the understanding of various properties of two dimensions through simple experiments and has opened up huge possibilities for electronic device fabrications [8–10]. A large number of theoretical and experimental groups all over the world have gathered on this two-dimensional platform to search for the “plenty of room” at this reduced dimension [11].

Electronic properties of low-dimensional materials are mainly governed by their size and geometry. Recent experimental sophistications permit the preparation of finite size quasi-one-dimensional graphene, named as graphene nanoribbons (GNRs) of varying widths, either by cutting mechanically exfoliated graphenes and patterning by lithographic techniques [12,13] or by tuning the epitaxial growth of graphenes [14,15]. Different geometrical terminations of the graphene monolayer give rise to two different edge geometries of largely varying electronic properties, namely, zigzag and armchair graphene. Several theoretical models, e.g., the tight-binding model within Schrödinger [16–18], Dirac formalism for mass less fermions [19–21], density functional theory (DFT), etc., have been applied to explore the electronic and band structure properties of GNRs. There exists a few many-body studies exploring the electronic and magnetic properties of these systems [22,23].

DFT studies suggest that the antiferromagnetic quasi-one-dimensional (1D) zigzag edge graphene nanoribbons

(ZGNRs) show half-metallicity at a finite external electric field across the ribbon width within both local density approximation (LDA) [24] and generalized gradient approximation (GGA) [25]. Half-metallic materials show a zero band gap for electrons with one spin orientation and an insulating or semiconducting band gap for the other, resulting in a completely spin polarized current. This interesting property has been observed in some materials like Heusler compounds [26], manganese perovskites [27], metal-DNA complexes [28], etc. Modification of edges and systematic doping indeed change the electronic properties of GNRs and thus give new inroads in the fine tuning of its band gap, controlling the nature of the spin polarization [29–32]. Experimental progresses have enabled realization of such materials to a great extent [12,13,33–36]. In this Letter, we focus on the effect of chemical doping on edge-passivated ZGNRs. By chemical doping, we mean the replacement of carbon atoms by some other elements, keeping the system isoelectronic.

This can only be achieved if two carbon ($1s^2 2s^2 2p^2$) atoms in ZGNRs are replaced by one nitrogen ($1s^2 2s^2 2p^3$) and one boron ($1s^2 2s^2 2p^1$) atom. The effect of these chemical dopants has already been studied both experimentally and theoretically in the case of nanotubes [37]. It has been observed that, the ratio of carbon atoms to these dopants has significant impact on the magnetic behavior of the nanotubes and an increase in boron and nitrogen concentration gradually opens up the gap between the valence and conduction band. Here we start with an undoped hydrogen passivated 8-ZGNR (8 zigzag chains) and incorporate the dopants by replacing the two middle zigzag carbon chains by two zigzag boron-nitrogen (B-N) chains in such a way that, each C-C unit is replaced by one B-N unit, resulting in a situation where the middle of the ZGNR looks like a polyborazine (Fig. 1). We then systematically increase the doping concentration by replacing the two

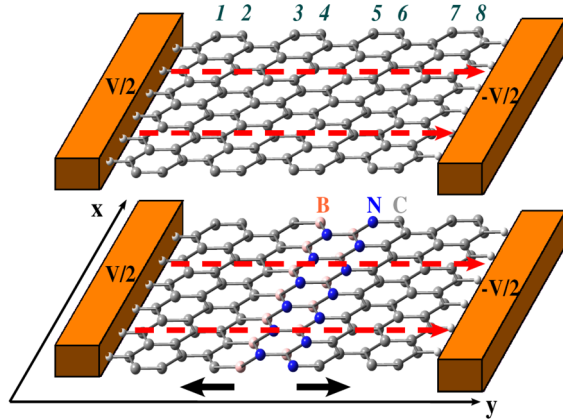


FIG. 1 (color online). Schematic representation of the systems considered. The upper device is fabricated with a hydrogen passivated 8-ZGNR (8 zigzag chains) without any doping. The lower device depicts the doping positions in an 8-ZGNR, replacing two middle zigzag carbon chains by isoelectronic boron-nitrogen chains. Doping concentration increases gradually along the directions of solid arrows. Electric field (dashed arrows) has been applied along the cross-ribbon width, which is the y -axis direction.

adjacent zigzag carbon chains, just next to the polyborazine at the middle and keep doing so up to the edges. Ultimately we end up at the zigzag boron nitride nanoribbon (ZBNR), where all the C-C units are replaced by B-N pairs. Although the ZGNRs and ZBNRs are isoelectronic, they exhibit completely different electronic properties. Like bulk hexagonal boron nitride, quasi-one-dimensional ZBNRs show wide gap insulating behavior [38–40]. In this Letter, we consider chemically doped ZGNRs with varying widths and study their electronic properties with and without external electric field.

We perform first principle periodic calculations based on density functional theory adopting the SIESTA package [41]. Within generalized gradient approximation (GGA), considering Perdew-Burke-Ernzerhof (PBE) exchange and correlation functionals [42] with a double zeta polarized (DZP) basis set, we have performed spin polarized calculations. The pseudopotentials are constructed from 3, 4, and 5 valence electrons for the B, C, and N atoms, respectively. GGA takes into account the semilocal exchange correlations which have significant impact on low-dimensional spin systems like GNRs and boron nitride nanoribbons (BNRs). We have considered the nanoribbons translated infinitely along the x axis, as shown in Fig. 1. We consider the lattice vectors along the y and z axis as 50.0 Å and 16.0 Å, respectively, creating sufficient vacuum to avoid the interactions between the adjacent unit cells. We have considered a 400 Ry energy cutoff for a real space mesh size and a k -point sampling of 36 k points, uniformly distributed along the 1D Brillouin zone. We have considered nanoribbon widths of 8, 12 and 24 zigzag chains with varying concentration of doping and relax all

of the structures with both ferromagnetic and antiferromagnetic spin orientations. A transverse electric field has been applied along the cross-ribbon direction, i.e., along the y axis (see Fig. 1) on the ground state structures to mimic the band gap engineering for both the spins.

All the systems show a zero ground state magnetic moment. The band structure analysis shows that, the undoped ZGNRs are narrow gap semiconductors with similar gaps for up and down spins. On application of an external electric field, one of the spin gaps closes at a certain critical field strength, making the system half-metallic. The direction of applied field governs the nature of the conducting spin channel [24,25]. On the other hand, the ZBNRs are known as wide gap insulators and the gap closes on application of an electric field without any spin polarization of the current [39]. These are two extreme cases. Gradual replacement of zigzag carbon chains at the middle of the ZGNRs with zigzag B-N chains takes the ZGNRs to ZBNRs and the electronic and band structures change accordingly. In Fig. 2, we have shown the density of states (DOS) of the 8-ZGNR with the replacement of 2(a1) 2, 2(b1) 4, and 2(c1) 6 middle zigzag carbon chains. The undoped 8-ZGNR shows a band gap of 0.5 eV for both of the spins [25]. Replacement of 2 middle zigzag carbon chains gives a nonzero DOS near the Fermi energy for one of the spins, reducing the gap significantly but keeping the other spin channel semiconducting. The system with 4 zigzag B-N chains at the middle makes one of the spin channels conducting. But there is an increase in the gap for the other spin channel. Interestingly, the system with 6 zigzag B-N chains at the middle and two zigzag carbon chains at the edges shows a decrease in both the spin gaps, a distinct behavior different from the other two cases. The DOS analysis in the first two cases suggests that the increase in doping concentration closes one of the spin

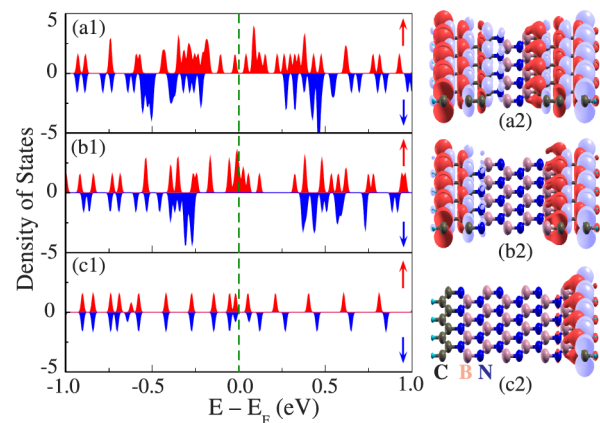


FIG. 2 (color online). The density of states as a function of energy, scaled with respect to the Fermi energy for the 8-ZGNR with (a1) 2, (b1) 4, and (c1) 6 zigzag carbon chains replaced by the zigzag boron-nitrogen chains at the middle of the nanoribbon. The spin density profile of these systems are shown in (a2), (b2) and (c2), respectively.

gaps and opens up for the other spin channel. These observations clearly indicate a deviation from the symmetric spin distribution in bipartite ZGNRs.

The ground state of ZGNRs with zero magnetic moment, show antiparallel spin alignment between nearest neighbors, a typical nature of a bipartite lattice which has been noted earlier [24,25]. Although all the atoms in one edge are aligned ferromagnetically, they show antiferromagnetic coupling within two edges. However, in the ZBNNRs, both the spins prefer to mix homogeneously throughout the whole lattice without any dominance of a particular spin on any site. Figure 2 shows the spin distributions of the intermediate systems, i.e., zigzag boron-nitrogen chain doped ZGNRs. The figure suggests that, whenever carbon atoms find nitrogen or boron as a nearest neighbor, the bipartite symmetry breaks. Moreover, due to the Lewis acid character, the boron atoms pull the electrons from adjacent carbon atoms, resulting in a charge transfer from carbon to boron and creating a potential gradient across the ribbon width (see Fig. 2). Boron and nitrogen face different spins on the adjacent carbon atoms in either side of the doped zigzag lines. Thus unsymmetrical spin diffusion on either side destroys the spin symmetry, which is reflected in the DOS calculations. The spin distribution of the system with 6 zigzag B-N chains at the middle and terminating polyacetylene chains [Fig. 2(c2)] shows localization of spins on one of the edges only, resulting in a completely inhomogeneous electronic structure resembling neither ZGNRs nor ZBNNRs. Note that, all the other doped systems are mixtures of polyborazine and polyacene units which are the constituents of ZGNRs and ZBNNRs, respectively, and thus exhibit mixed properties. In fact, carbon dopants in this system (ZBNNR with terminating polyacetylene chains) insert finite density of states for both the spins within the large insulating gap of ZBNNR. To estimate the contribution of the terminating carbon atoms, we perform calculations for the projected density of states (PDOS), which indeed show that, the DOS near the Fermi energy come solely from the edge carbon atoms.

PDOS analysis for all the systems shows that the maximum contribution comes from the carbon atoms and the extent of their contributions reduces from the edges towards the middle. However, the carbons, attached to the boron atoms and subsequent carbon atoms on the same side of doped ZGNRs shows higher contributions than that of the other side, which is attached to the nitrogen atoms. This observation unambiguously proves that, the half-metallicity in boron-nitrogen doped ZGNRs originates from the charge transfer from the carbon to boron atoms. This can be further explained from the bare on site Coulomb repulsion values of carbon (~ 9.66 eV), boron (~ 8.02 eV) and nitrogen (~ 14.46 eV), which have been estimated as the difference between the ionization potential and electron affinity of the bare atoms. Because of reduced on site Coulombic repulsion, the electrons prefer to flow

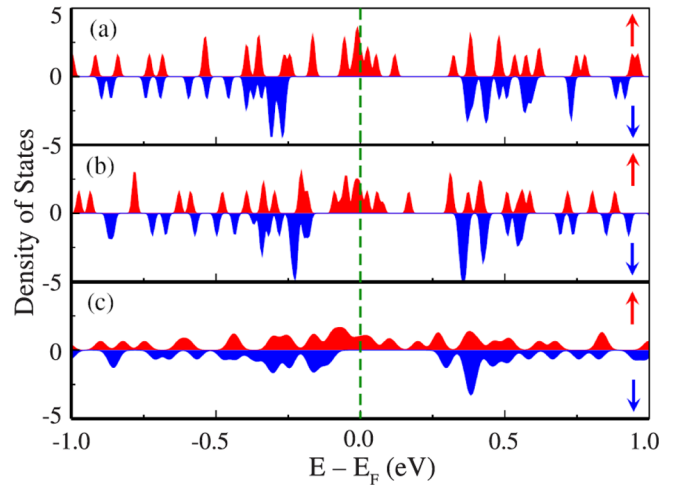


FIG. 3 (color online). The density of states as a function of energy, scaled with respect to the Fermi energy for (a) 8, (b) 12, and (c) 24 ZBNNRs with terminating polyacene unit.

from carbon to boron, whereas the charge transfer from carbon to nitrogen is hindered by the large Coulombic repulsion on nitrogen sites. Although these atomic values re-normalize in the case of complex systems like nanoribbons, their relative differences remain almost unaffected.

Calculations with varying ZGNR width with all possible doping concentrations result in similar observations. Our study reveals that the systems with two zigzag carbon chains on either edges and all zigzag B-N chains at the middle shows half-metallicity irrespective of the ribbon width, which has been shown in Fig. 3. PDOS analysis for all the widths confirms the Lewis acid character of boron for the observed half-metallicity. The insulating gap for the other spin channel decreases with an increase in ribbon width, manifesting the characteristics of both ZGNRs and ZBNNRs in absence of doping [24,25,39]. In Fig. 4, we have shown the variation of the band gap for both the spin

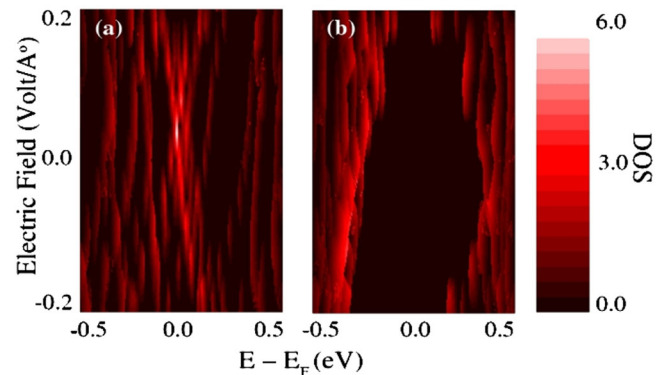


FIG. 4 (color online). Contour plot of the density of states as a function of energy, scaled with respect to the Fermi energy for (a) conducting and (b) insulating spin channels of the 8-ZBNNR with a terminating polyacene unit with varying electric field.

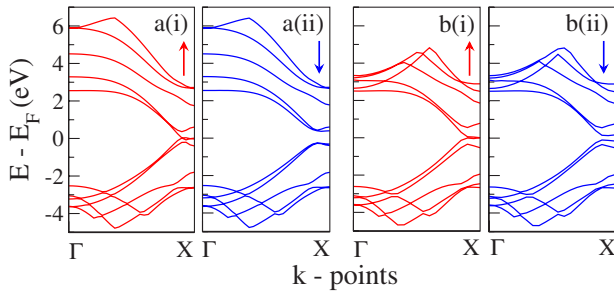


FIG. 5 (color online). The spin polarized band structure (5 valence +5 conduction) of the 8-ZBNNR with a terminating polyacene unit, as obtained from (a) SIESTA and (b) VASP calculations for (i) up and (ii) down spins separately. The Fermi energy (E_F) is set to zero.

channels for an 8-ZBNNR system with terminal polyacene units. Application of electric field on ZBNNRs with polyacene edges for all widths shows that, the half-metallic behavior sustains over even a sufficiently large e -field strength. The magnitude of the semiconducting spin gap (>0.3 eV) suggests the possibilities of the experimental realization of such half-metallic antiferromagnets even at room temperature (0.025 eV).

We have also verified that, the intrinsic half-metallicity as obtained for ZBNNRs with a terminating polyacene unit from SIESTA with localized basis remains qualitatively the same with an extended plane augmented wave [43] basis within the DFT package VASP [44]. In Fig. 5, the spin polarized band structure results for 8-ZBNNR from both SIESTA and VASP at the same level of calculations are shown. As can be seen, although the gap for the insulating spin channel decreases for extended basis states, it remains far above the room temperature, highlighting our claim for intrinsic half-metallicity in ZBNNRs.

In conclusion, we have studied the ZGNRs with systematic chemical doping, replacing the zigzag carbon chains with zigzag boron-nitrogen chains in the middle of the nanoribbons, keeping the systems isoelectronic with the undoped ZGNRs to search for better half-metallic materials. Our study suggests that, the nanoribbons with a terminating polyacene unit and all zigzag boron-nitrogen chains at the middle have the potential to act as a half-metallic antiferromagnet for all widths. We have identified the Lewis acid character of boron that results in charge transfer from carbon to boron to invoke half-metallicity in graphene based materials. This property sustains over a large external electric field strength even at room temperature, opening huge possibilities for the realization of graphene based spintronic devices with complete control over the spins.

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