Spin channels in functionalized graphene nanoribbons

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Abstract

We characterize the transport properties of functionalized graphene nanoribbons using extensive first-principles calculations based on density functional theory (DFT) that encompass both monovalent and divalent ligands, hydrogenated defects and vacancies. We find that the edge metallic states are preserved under a variety of chemical environments, while bulk conducting channels can be easily destroyed by either hydrogenation or ion or electron beams, resulting in devices that can exhibit spin conductance polarization close to unity.

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Graphene is currently the subject of intense experimental and theoretical investigations, thanks to remarkable and novel physical features. Linear dispersion around the Fermi energy ($E_F$), high crystallinity and mobility, ballistic transport on the sub-micrometre scale (even at room temperature), and a two-dimensional structure that is amenable to lithographic techniques offer great promise for nanoelectronics applications, from field effect transistors to interconnects to spintronics and related applications.

Electronic-structure calculations have shown that (real-space) edge states emerge in zigzag graphene nanoribbons (ZGNR); the resulting peak in the density of states (DOS) at $E_F$ induces a magnetic instability that leads to a ground state with antiferromagnetic (AFM) ordering, where the spins on the two ribbon edges have opposite orientations. Under an applied electric field either half-metallic or half-semiconducting behavior can be observed, of extreme interest for spintronics applications. However, the magnitude of the field perpendicular to the ribbon required to close the band gap for one of the spins can be as large as 0.1 V Å$^{-1}$, although it is a decreasing function of the ribbon width. In contrast with electronic-structure predictions, recent measurements show a weak dependence of the energy gap on the crystallographic direction, highlighting the critical role that edge structures, passivations and scattering taking place at rough boundaries can play.

Since edge terminations, passivations and defects play a key role in the performance of graphene devices, we characterize in this Letter the avenues available to control electronic and spin transport with chemical functionalizations or ion- or electron-beam treatments. We study single- and double-bonded moieties (H, OH, F, Cl, Br, S, O, NO$_2$, and NH$_2$) and hydrogenated defects and vacancies with extensive DFT first-principles calculations. We use an original approach suitable to describe the electronic structure and ballistic transport in large-scale nanostructures, based on the chemically accurate and minimal basis of maximally-localized Wannier functions (ML-WFs).

First, we consider in the band structure and DOS of the ground state for the representative single- and double-bonded ribbons H:ZGNR-8, S:ZGNR-8 and O:ZGNR-8 (we use here the
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Figure 1: Band structure and DOS for the AFM ground state of (a) H:ZGNR-8, (b) S:ZGNR-8 and (c) O:ZGNR-8. Dashed and dotted lines and labels identify some relevant band edges (see text). The energy scale is such that $E_F=0$ eV.

The convention of indicating the species functionalizing the edge of the GNR first, and the width of the ribbon in graphene units last). As widely reported, the ground state for H:ZGNR-$N$ is AFM and insulating, with the two bands close to $E_F$ originating from bonding and antibonding Bloch sums of the $p_z$ carbon orbitals. A similar description applies to other monovalent passivating species, such as OH or F, or even to more complex electropositive or electronegative ligands, such as NH$_2$ and NO$_2$, since in these latter cases the bands originating from the lone pairs remain below the top of the valence. We label the band edges generated by the $p_z$ orbitals $A_1$, $A_2a$, $b$ and $A_3$ (see Figure 1).

As $k$ goes from the Brillouin-zone (BZ) center to the edge, the states in these two bands evolve from being delocalized in real space inside the ribbon (i.e. in the “bulk”) to becoming localized at the two ribbon edges. As it will be shown later, such observation is critical to engineer the balance between unpolarized bulk ribbon conductance and the conductance channels at the ribbon edges.

Double-bonded ligands, such as O and S (Figure 1(b) and (c)), give rise to a different picture: the orbitals of the passivating species undergo $sp^2$ hybridization, with one $sp^2$ orbital contributing to a $\sigma$ carbon-ligand bond and the other two accommodating two lone pairs; the remaining $p_z$ orbital participates in the $\pi$ carbon-ligand bond. Remarkably, the semiconducting character of the hydrogenated ZGNR is reverted to metallic in presence of these edge passivations. Indeed, for these double-bonded functionalizations the $A_1 - A_2$ and $A_3 - A_2$ bands merge even in
Figure 2: Band structure (red dots) and its MLWFs interpolation (solid black lines) for O:ZGNR-8, obtained by including, respectively: (a) all MLWFs (see text), (b) all MLWFs but the $p_z$ MLWFs on the oxygens, (c) all $p_z$ MLWFs, (d) all $\sigma$ MLWFs, and (e) all $\sigma$ MLWFs and the lone-pair $sp^2$ MLFWs. NM state is chosen for clarity.

the AFM ground state, but at energies higher than $E_F$; this can be contrasted with non-magnetic (NM) H-ZGNRs, where the bands merge exactly at $E_F$. The fully occupied $A_1 - A_2$ band of AFM H:ZGNR-8 becomes a mostly occupied band for S passivations (Figure 1(b)) and a mostly empty band for O passivations (Figure 1(c)) - the more electronegative oxygen is extracting charge from the ribbon. The double-bonded moieties show two new bands (whose extrema at $k = 0$ are denoted by $LP_1'$ and $LP_1''$) that remain very close in energy across most of the BZ. Direct inspection of their charge density shows a marked lone-pair character, and so they are the analogue of the lone-pair bands alluded to before for other monovalent functionalizations (e.g. NH$_2$), with the key difference that these now cross the Fermi level. Differences between the AFM ground state and the NM solution are much less pronounced for these double-bonded moieties than for H:ZGNR-N (see also later, Table 1), the only effect being a small splitting arising for these two lone-pair bands. Indeed, the origin of the magnetic instability, arising in H:ZGNR-N from the large DOS of the NM state at $E_F$, disappears in the presence of double-bonded species (Figure 1(b), (c)). Charge density plots for the $A_1-A_2-A_3$ bands reveal, for O:ZGNRs, an opposite behavior with respect to hydrogenated ribbons: eigenstates near $k = 0$ are mostly localized onto edge O atoms, whereas localization in the bulk of the ribbons is found towards the zone boundary.

Clear chemical insight on the nature of all the energy bands is obtained after we extract ML-
WFs \(^{27,28,29,31}\) from the occupied and the \(\pi\) unoccupied manifolds of these ribbons; we choose here as an example the NM state of O:ZGNR-8. The resulting MLWFs map the Bloch bands onto an explicit “tight-binding” basis of localized orbitals, composed of one \(p_z\) MLWF for every C and for every O, one \(\sigma\) bonding MLWF for every C-C and for every C=O bond, and two lone-pair \(sp^2\) MLWFs for every O. The band structure of the ribbon in the full BZ can then be straightforwardly interpolated across the BZ by diagonalizing the Hamiltonian in this minimal basis set,\(^{27,32}\) or in different subsets. We show in Figure 2 our results: the first panel compares the band structure obtained by diagonalization in the minimal MLWFs basis and the full calculation in a complete plane-wave basis set, showing that the manifolds of interest are all reproduced with extreme accuracy. The central role played by the oxygen \(p_z\) MLWFs is highlighted in panel (b): removing these from the minimal basis is sufficient to destroy the agreement around \(E_F\), resulting instead in energy bands similar to those of NM H:ZGNR-8, where the \(A_1 - A_2\) and \(A_3 - A_2\) bands merge, in proximity of the BZ boundary, at \(E_F\). The manifold obtained by all the \(p_z\) (including those on the oxygens) is shown in panel (c), while the \(\sigma\) manifold is in panel (d); in this latter case, quantitative agreement is obtained only after the lone-pair \(sp^2\) MLWFs on the oxygens are added to the \(\sigma\) basis set (panel (e)), since these lone pairs not only give rise to the two lone-pair bands \(LP_1\) and \(LP_2\), but are needed to bring the \(\sigma\) manifold in full agreement with the exact reference result. The two manifolds in (c) and (e) represent a virtually exact decomposition of the original band structure, highlighting once again the role of MLWFs in capturing a faithful physical picture in the smallest possible representation.

The two lone-pair bands, originating from the \(sp^2\) MLWFs, are very dispersive, with a bandwidth of 3 eV for O:ZGNR-8 and 9 eV for S:ZGNR-8; the larger size of the sulphur is responsible for the broader dispersion, with the largest hopping element in the Hamiltonian being -0.9 eV for O:ZGNR-4, and -2.94 eV for S:ZGNR-4. Nevertheless, there is no instability toward dimerization at the edges, even if the bond lengths for O-O and S-S of 1.48 and 2.05 Å are comparable to the 2.46 Å spacing along the ribbon edge. Only halogenation with larger species (Cl and Br) gives rise to unit-cell doubling, with neighboring halogens assuming opposite tilts with respect to the ribbon.
Table 1: Unit-cell ground-state formation energy \( (E_{AFM}^f) \), magnetic instability \( (E_{NM} - E_{AFM}) \), magnetic interaction strength \( (E_{FM} - E_{AFM}) \) and magnetic moments in the FM state \( (\mu_{FM}) \) for ribbons of different widths and passivations. Energies are in eV, magnetic moments in Bohr magnetons.

| ribbon     | \( E_{AFM}^f \) | \( E_{NM} - E_{AFM} \) | \( E_{FM} - E_{AFM} \) | \( \mu_{FM} \) |
|------------|-----------------|-------------------------|-------------------------|--------------|
| OH:ZGNR-4  | -3.38           | 0.036                   | 0.011                   | 0.37         |
| F:ZGNR-4   | -2.70           | 0.047                   | 0.014                   | 0.35         |
| H:ZGNR-4   | 0.38            | 0.059                   | 0.014                   | 0.39         |
| H:ZGNR-6   | 0.42            | 0.081                   | 0.015                   | 0.45         |
| H:ZGNR-8   | 0.42            | 0.083                   | 0.007                   | 0.62         |
| O:ZGNR-8   | -0.103          | 0.008                   | 0.000                   | 0.19         |
| S:ZGNR-8   | 0.99            | 0.002                   | 0.000                   | 0.17         |

The thermodynamic stability of the different ribbons is summarized in Table 1: negative formation energies are found for OH, F and O passivations. The AFM state is the ground state for all the systems considered, but the energy difference between the FM and AFM states decreases with the ribbon width (see Table 1 and Ref. 12). Room-temperature FM coupling between the edges could be stabilized by an applied magnetic field or induced by defects or adsorbates. Adsorbates can also break the spin-up/spin-down symmetry in the AFM state, induc-

Figure 3: (left) DOS of a H:ZGNR-4 (both FM and AFM states) in the presence of several periodic defects (one defect for 8 ZGNR unit cells): on-top H (top panels), C vacancy (central panels), and hydrogenated C vacancy (bottom panels). The local structure of the defects is shown in the middle inset. Dashed lines correspond to the pristine ribbon, “negative” DOS is for the minority spin. (right) Band structures for both FM and AFM states, black solid lines (red diamonds) correspond to the majority (minority) spin.
Figure 4: Top panel: structural model of the long ZGNR, used for conductance calculations. Left bottom panel: spin-up ($G^\uparrow$) and spin-down ($G^\downarrow$) conductance and conductance polarization ($P_G$) of an infinite H:ZGNR-24 in the FM state, whose central section (~197 Å) has been randomly hydrogenated. Averages (solid thick lines) are taken over 30 random configurations (solid thin lines). Shaded (grey) regions represent, at each energy, the standard deviation. Dashed (red) curves represent the same quantities for the pristine ribbon. Right bottom panel: same as in (a) for the AFM state.

Spin stiffness along the edges, as reported recently, is remarkably high, raising hopes of room-temperature coherence for these one-dimensional systems at length-scales comparable to those of microelectronics devices.

A breakthrough application for graphene ribbons would be in the role of spin valves; indeed, energy windows where electronic states with only one spin are available occur under different circumstances. We first explore this point in Figure 3, where we compare the DOS and band structures of three defected H:ZGNR-4 in the presence of bulk ribbon hydrogenations, carbon vacancies (as e.g. induced by ion irradiation) or both; in all cases the breaking (enhancement) of the spin-up/spin-down symmetry (asymmetry) of the AFM (FM) state is observed. On the other hand, in any real device no degree of order along the ribbon can be expected, and spin-polarized currents along the edges would be overshadowed by the spin-unpolarized transport channels available inside the bulk of the ribbon; around $E_F$, these are dominated by the MLWFs $p_z$ contributions.
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Figure 5: Top panel: spin-up \((G_{\uparrow})\) and spin-down \((G_{\downarrow})\) conductance and conductance polarization \((P_G)\) of an infinite H:ZGNR-12 in the FM state, whose central section \(\sim 197 \, \text{Å}\) has been randomly hydrogenated. Averages (solid thick lines) are taken over 30 random configurations (solid thin lines). Shaded (grey) regions represent, at each energy, the standard deviation. Dashed (red) curves represent the same quantities for the pristine ribbon. Bottom panel: same as in (a) for the AFM state.

detailed before. Thus, engineering a ZGNR device for spintronics applications will require removing the unpolarized bulk conduction channels while preserving edge conductance. This could be achieved with hydrogenations, or ion or electron beams; these are all now recognized as effective tools to tailor electronic and transport properties, and proton irradiation even induces ferromagnetism in NM graphitic samples.

We investigate here this possibility, and show that the availability of spin-polarized edge states allows for the design of simple and robust spin-valves. Our strategy is based on the observation that most or all functionalizations to the bulk of the ribbon induce \(sp^2\) to \(sp^3\) re-hybridization, and remove the “half-filled” \(p_z\) MLWFs from the energy window around \(E_F\). This mechanism is central to the realization of a spin valve where unpolarized conduction channels are removed from the bulk of the ribbon, while preserving at the same time the edge states. Chemical reactions with atomic hydrogen represent the simplest route, and we show in Figure 4 the quantum conductance calculated for a realistic device: an infinite H:ZGNR-24 (\(\sim 50 \, \text{Å}\) width) whose central section (3840 atoms, \(\sim 197 \, \text{Å}\)) has been randomly hydrogenated with a 0.5% defect concentration. The conductances \(G_{\uparrow}\) and \(G_{\downarrow}\) for both spin channels as well as the conductance polarization \(P_G\) (defined
as \( P_G = (G_\uparrow - G_\downarrow) / (G_\uparrow + G_\downarrow) \) are averaged over 30 configurations, each with random hydrogenations. For comparison, we show in Figure 5 the same quantities for the H:ZGNR-12 ribbon (the central section now contains 1920 atoms). In the FM state, the spin valve character of such system is immediately apparent, with a pronounced spin up or spin down conductance peak just below or above \( E_F \), where no significant contribution from the other spin is found. Therefore, tuning the applied bias voltage will turn on and off the injection of electrons with a given spin with an efficiency that may reach 100% for single devices. In the AFM state, while a random distribution of defects would induce a spin polarization due to the breaking of the symmetry between spin up and spin down channels, the average effect is zero. Yet, mesoscopic fluctuations mean that for each and every device spin valve effects would be very relevant even in this case, as already inferred for graphene ribbons with rough edges.\(^{22}\) Such effects appear to be more relevant for the smaller ribbon (Figure 5). Irradiation with ion or electron beams, that nowadays can be focused onto areas as small as a few nm or a few Å in diameter respectively, would lead to similar effects, since the creation of vacancies (hydrogenated or not) in the bulk of the ribbon also destroys the unpolarized conduction channels (see Figure 3). Provided one edge of the ribbon can be physically protected, a wide variety of chemical functionalizations - starting from double hydrogenations at the opposite edge - would achieve the same objective.

In conclusion, we have calculated the electronic-structure and quantum conductance in realistic, functionalized graphene nanoribbons with full chemical accuracy, thanks to the use of an accurate but minimal MLWFs basis. Defects in spin-polarized ZGNRs - following hydrogenation or treatment with ion or electron beams - can be effectively used to remove the unpolarized conduction channels in the bulk of the ribbon, while preserving edge states. Similar results can be devised using chemical routes for graphene functionalization/hydrogenation.\(^{40}\) For instance, very recently the reversible hydrogenation of a graphene sheet has been experimentally proven, leading to the \( sp^2 \) (graphene) to \( sp^3 \) (graphane) transformation of the carbon network.\(^{41}\) The resulting asymmetry between the spin-up and spin-down channels makes these systems ideal candidates for spin-polarized transport with a very high degree of spin polarization.
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We use density functional theory (DFT) within the Perdew-Burke-Ernzerhof approximation and the plane-wave QUANTUM-ESPRESSO package with a 40 Ry cutoff for the wave functions, 480 Ry for the charge density, $16 \times 1 \times 1$ Monkhorst-Pack sampling of the BZ, electronic occupations of metallic systems using Marzari-Vanderbilt cold smearing of 0.007 Ry, and ultrasoft pseudopotentials to represent ionic cores. 13 Å and 7 Å separate the ribbon periodic replica in the directions perpendicular and parallel to the ribbon plane. Defected ribbons and edges are built by replicating 8 times the bare ribbon unit cell along the ribbon axis direction and the corresponding BZ sampled with a $2 \times 1 \times 1$ MP grid. The geometries of all the considered ribbons are optimized by relaxing the atomic positions until all components of all forces are smaller than $10^{-3}$ Ry/au. Tests on sample systems revealed
almost full convergence of the calculated properties with respect to the parameters used in the calculation. Formation energies are calculated as \( \Delta E = E_{\text{tot}} - \sum n_i \mu_i \), where \( E_{\text{tot}} \) is the total energy of the given system and \( n_i \) the number of atoms of species \( i \) (with chemical potential \( \mu_i \)) in the unit cell. We used as reference the total energy per atom of bulk graphene, \( \text{H}_2 \), spin polarized \( \text{O}_2 \), \( \text{F}_2 \), and the \( \text{S}_8 \) molecule.

It should be pointed out that DFT has been proven to correctly describe the properties of graphene and carbon-based nanostructures in the presence of different chemical environments,\(^{21,48,49,50}\) with LDA and GGA results usually bracketing more accurate estimates obtained with hybrid functionals. While a proper description of optical properties often requires the introduction of many-body corrections,\(^{51,52}\) quantitative agreement with conductance measurements has been obtained even within a tight-binding framework.\(^8\)

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