



Transport properties of chemically functionalized graphene nanoribbon



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ABSTRACT

We perform a theoretical calculation in chemically functionalized zigzag graphene nanoribbons, which are terminated with different single atoms or groups, using density functional theory and nonequilibrium Green's function techniques. The calculation results reveal that these different species of atoms and groups have a significant impact on the edge states near Fermi level as well as the spin-dependent electronic transport properties. The calculated I - V curves exhibit negative differential resistance, which can be used for application in molecular spin electronic device.

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1. Introduction

Following the successful isolation of graphene by Geim and Novoselov [1], there has been growing interest in graphene nanoribbons (GNRs) patterned from graphene. In particular, zigzag GNR (ZGNR) is one of the systems most intensely studied due to the presence of edge states in the electronic structure, which is crucial in the spintronics application. Generally, in most studies, the edge dangling σ bonds are completely terminated by H atoms. Some feasible approaches to change the properties of ZGNR have been proposed, such as gate voltage [2,3], various edges [4,5], adsorption [6], doping [7–11] and chemical functionalization [12,13]. However, few recent researches show that the edge atomic substitutions, edge functional groups and chemisorptions can modify the electronic properties of GNRs effectively [14]. Owing to their relatively high electron density at the zigzag edges, the edge localized states could be highly sensitive to variations in the edge chemistry. As the edge states are located near the Fermi level, each different termination could affect the transport properties uniquely. These groups at the sides cause semiconductor–metal transitions, lifting the spin degeneracy and widening the bandgap. The carbon π orbitals at the edges are found to shift induced by functional groups. Moreover, the experimental investigation on the magnetism of graphene oxide (GO) has been reported very recently [15]. Khlobystov and co-workers have reported the sulfur-terminated GNRs both theoretically and experimentally [16,17].

Recently, molecular electronics and spintronics have attracted scientists' attention since conventional silicon-based microelectronics is likely to reach its limit of miniaturization by the laws

of physics [18]. Spin-polarized transport in ZGNRs might also be possible due to the predicted existence of a half-metallic state in the presence of a transverse electric field. This finding provides us insights to understand carrier transport in GNRs. Many interesting physical properties such as single-electron characteristic [19], negative differential resistance (NDR) [20,21], molecular rectification [22,23], and field-effect characteristics [24,25] have been found in such devices. The discovery of NDR in semiconductor diodes opens a new chapter in semiconductor device physics [26]. However, in GNR devices tunneling through the barrier can actually dominate the transport. Such tunneling currents can lead to NDR, with a wide range of potential device applications. The origin of the mechanism leading to NDR is still under intense debate. Much theoretical work has been devoted to the analysis of the impact of lattice symmetry and potential impurity or defect scattering in the I/V characteristics. In order to design such devices, any theoretical scheme to manipulate the carrier spin in graphene nanostructures is still in need, albeit the existent proposals mentioned above.

Thus far, in most studies of transport properties of GNRs, ZGNRs are treated as the same type, because they have very similar metallic electronic properties and transmission spectra under zero bias voltage [27,28]. In order to systematically understand the electronic transport properties in ZGNRs, however, in this work, we investigate the spin-dependent electronic transport properties of the molecular devices based on ZGNRs. The effects of the spin-polarized edge states, chemical modification, and symmetry on transport behavior are considered. The results show that the band structure, transmission spectra and I - V curve are strongly dependent on the choice of saturating atoms or molecular groups on the zigzag edges. We find that each different termination is suggested to tune the electronic structure uniquely.

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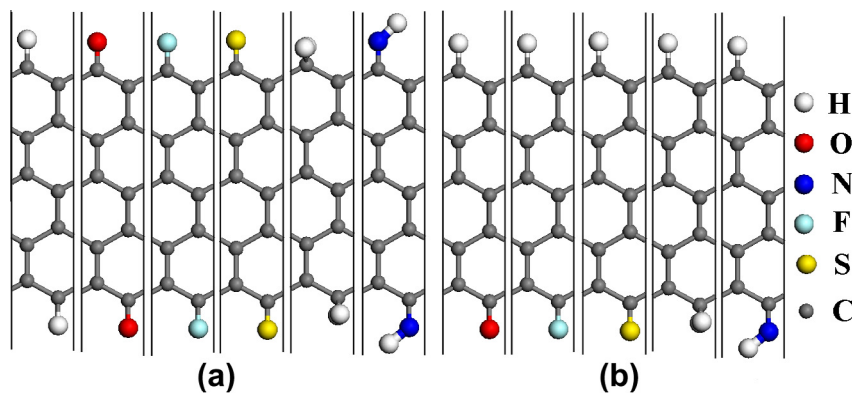


Figure 1. Unit cells of ZGNRs terminated with atoms/functional groups. (a) The two edges are terminated with the same atoms and functional groups (O, F, S, H₂, NH), and (b) one edge is terminated with H atom, the other edge is terminated with different atoms or functional groups (O, F, S, H₂ and NH).

2. Theoretical details

In what follows, the terminations studied include hydrogen, fluorine, sulfur and oxygen atoms as well as two hydrogen and imine functional groups as illustrated in Figure 1. At first, in order to simulate infinite long GNRs, we use supercell where each plane is separated from its replica by 10 Å. The $N = 5$ ZGNR assumed in the simulations and depicted in Figure 1 has a width given by $a_0(3N - 2)/2\sqrt{3} \approx 9.23$ Å, where N denotes the number of parallel longitudinal zigzag C chains making up the zigzag ribbon and $a_0 = \sqrt{3}d$ with $d = 1.42$ Å (which is the bond length of two-dimensional graphene). It is always observed that the length of the C–C bond near the edges is slightly different from those in the central region of the ribbon with various atoms/groups.

Our calculations have been performed by applying the nonequilibrium Green's functions (NEGF) combined with the density functional theory (DFT). In each case, the whole structure has been relaxed until residual forces are smaller than 0.05 eV/Å. Structure optimizations and local density of states (LDOS) calculations are performed using DMol³ [29–31]. The local density approximation (LDA) is employed to optimize the geometrical structures during self-consistent iterations, with the Perdew–Wang (PWC) [32] parameterization of the local exchange–correlation energy. The generalized gradient approximation (GGA) is used to calculate the total energy and various electronic properties of different structures, with the Perdew–Burke–Ernzerhof (PBE) parameterization of the gradient-corrected functional. The Brillouin-zone integration is performed with $1 \times 1 \times 40$ Monkhorst Pack k points. A developed ab initio software package Atomistix Toolkit (ATK) [33] has been utilized to calculate completely self-consistently the electrical properties of two-probe nanodevices including three parts: left electrode, central scattering region, and right electrode. A single- ζ plus polarization basis set and an energy cutoff of 300 Ry for real-space mesh size are chosen. All parameters for calculation are chosen after testing and ensure a good enough convergence of total energies. Once the self-consistent calculations of two electrodes are completed, the electrochemical potentials are given by $\mu_l(0)$ and $\mu_r(0)$ for left and right electrodes, respectively. Under external bias V_b , they will be shifted rigidly relative to each other. Thus, the spin-dependent current I_σ through the central scattering region can be calculated by Landauer–Büttiker formula

$$I_\sigma(V_b) = \frac{2e}{h} \int_{\mu_l(V_b)}^{\mu_r(V_b)} T_\sigma(E, V_b) dE$$

For every spin state σ the electron transmission coefficient under external bias V_b is $T_\sigma(E, V_b) = T_r[\Gamma_l G^R \Gamma_r G^A]_\sigma$ where $G^{R(A)}$ is the advanced Green's function of the scattering region, $\Gamma_{l(r)}$ is the con-

tact broadening functions associated with the left (right) electrodes. More details of the method and relevant references can be found in some previous reports [34–36].

3. Results and discussion

This Letter discusses the parallel spin state, which plays a greater role in the transport properties [9]. At the same time, it is reported that when the layer is odd, it has a linear I – V . To understand this conductance modulation, we have plotted the spin-dependent band structure of ZGNR terminated with the same atoms/groups in Figure 2, and a metallic property is observed in both spin direction. It is interesting to notice that, despite the saturated atoms or groups, such as H, F, S and H₂, the effect on the band structure is very similar, the only difference being a slight shift in the position nearby the Fermi level. The results show that ZGNRs with both sides terminated with H and F have a similar band structure, and there exist two nearly flat bands nearby the Fermi level (± 0.3 eV), which correspond to the local spin state and have an important impact on the electronic properties of the ZGNRs. Since the other configuration is also spin-polarized, H and F all saturate the sp^2 σ orbital, make σ and σ^* band to move away from the Fermi level. And the π orbital of C atom is affected by the effective potential of edge atoms/groups. For the H-terminated ZGNR, the negative potential is changed a little. The edge states of two spin directions close to the X point show a separation.

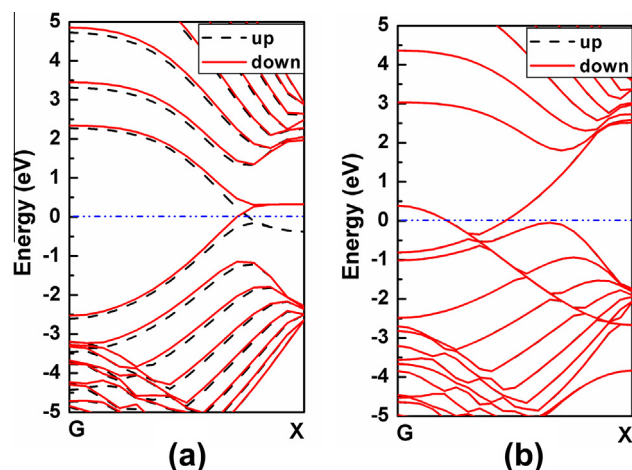


Figure 2. The band structures for ZGNRs with both edges terminated with (a) H atoms and (b) O atoms.

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