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Conductance gap induced by orbital symmetry mismatch in inhomogeneous hydrogen-terminated zigzag graphene nanoribbons

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ABSTRACT

Using the non-equilibrium Greens function method in combination with the density functional theory, we investigate the electronic transport properties of zigzag graphene nanoribbons (zGNRs) passivated with Hydrogen atoms. The coexistence of sp^2-edges and sp^3-edges in zGNRs can induce quite stable conductance gaps in a large range from 0 to 3.5 eV, which can even occur in a wide zGNR with a width up to 10 nm. We found that the orbital symmetry mismatch between the sections with sp^2 and sp^3 edges is responsible for the totally suppressed conductivity of the edge states, and the gap size is determined by the minimal energy difference between the second highest valence band and the second lowest conduction band of the corresponding sp^2-edged ribbons. These findings provide a very attractive design and fabrication strategy for controlling the energy gap of graphene nanoribbons.

1. Introduction

Nowadays, high-quality graphene nanoribbons (GNRs) [1–8] with controlled widths and smooth edges can be well fabricated experimentally. Transport measurements have shown that all the GNRs fabricated either by lithography [3,6,9], chemical cutting of graphene sheets [10], chemical vapor deposition [4,5,11,12], or unzipping of carbon nanotubes [7,8] are semiconductors with a width-dependent energy gap. All these results have made GNRs very attractive for a variety of applications. However, there also raise a serious question about the origin of such unified semiconductor feature, since in theory, the electronic properties of GNRs are heavily dependent on the edge structures [13–15]. The armchair GNRs (aGNRs) are known to be semiconductors and their energy gaps decrease exponentially with the increase of the widths. However, the zGNRs are always metallic with width-independent spin-polarized edge states.

It should be mentioned that the measured energy gap is argued to be transport gap or called conductance gap (C_{gap}), which can be induced by various factors [16–20]. For examples, the edge-roughnesses, the structural defects, and the chemical impurities have been used to explain the measured gap of zGNRs in experiments [4,6,16]. However, such effects could also drastically reduce the electronic mobility of the ribbons [4,6] and influence their practical applications on electronic devices. Actually, the high-quality zGNRs which produced by unzipping of carbon nanotubes (CNTs) [7] or by the chemically derived methods [1,4] are expected to have very smooth edges and well-controlled graphene structures. The measured electronic mobility of these ribbons is also very high. Therefore, it's important to find a way that can induce the measured gap in zGNRs but not reduce the electronic mobility.

In principle, both sp^2 and sp^3 terminations can be formed at the edges of zGNRs during the process of edge-saturations with hydrogen atoms in experiments [21–23]. Careful computational studies of hydrogen terminated ribbons [20,24] have demonstrated that the H2-terminated zGNRs (H2-zGNRs), with sp^3 edges, are more stable than the H-terminated zGNRs (H-zGNRs), with sp^2 edges. The sp^2 edge geometry is favored only at extremely low hydrogen partial pressures and it can not generate a band gap at all [25]. While H2-terminations can only induce a band gap in ultrathin H2-zGNRs. Such a gap rapidly decreases to zero when the width increases to only 7-zigzag rows (about 1.5 nm) [24]. At the same time, the zGNRs with mixed H- and H2-terminations have also been studied [26–28]. Such as H2-zGNRs-H, in which the sp^3 and sp^2 terminations are placed respectively on each side of the ribbon, and H/H2-zGNRs, in which both H- and H2-terminations are periodically located on both sides. However, only a gap of about 0.61 eV was observed [29] in the narrow H/H2-zGNRs with a special H/H2-configuration called as z211 [20].

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Here, we demonstrate that the coexistence of sp^3-edges and sp^2-edges in zGNRs can open a steady conductance gap using the first principles methods. Our results show that with a short section of sp^3-edges embedding in sp^2-edges, or a short section of sp^2-edges embedding in sp^3-edges, a big conductance gap in a large range from 0 to 3.5 eV can be formed in zGNRs. Such a gap becomes quite stable when the size of embedded section goes over 6 units and it can even persist in wider ribbons with the width up to 10 nm. In these systems, the conductivity of the edge states is completely suppressed due to the orbital symmetry/parity mismatch between the sections of different edge-terminations. Thus the size of the gap can be simply determined by the minimal energy difference between the second highest valence band and the second lowest conduction band of the sp^2-terminated zGNRs.

2. Models and methods

A section of 20 unit-cell-long zGNRs with different widths has been chosen, in which the sp^2 and sp^3 edges are introduced by H- and H2-terminations, respectively. Two types of mixtures have been considered. One consists of a short section of sp^3-edges embedding in the zGNRs of sp^2-edges. It can be denoted as N-zGNRs + N_{H2}H2, where, N is the width of the zGNRs (in terms of the number of zigzag rows), and N_{H2} is the length of the H2-terminated section (in terms of the number of the cells H2-terminated). Analogously, the section of sp^2-edges embedding in the zGNRs of sp^3-edges can be denoted as N-H2-zGNRs + N_HH, where, N is the width of the H2-zGNRs, and N_H is the length of the sp^2-edges. Our calculations have shown that both models can lead to very similar conclusions. For the sake of the simplicity, we mainly presented here the results from the former type of the devices, one can see the structure of 6-zGNR + 6H2 in Fig. 1. In order to examine the length-dependence, the N_{H2} varied from 1 to 10 with the width N being fixed at 6. Simultaneously, to understand the width-dependence, the N changed from 4 to 14 with the N_{H2} being fixed at 6. The number of atoms which included in the center scattering region (CSR) of the narrowest device 4-zGNR + 6H2 and the widest device 14-zGNR + 6H2 are 212 and 606, respectively.

Quantum transport calculations were carried out by using an ab initio code, TRANSIESTA-C [30], which is based on real-space, nonequilibrium Greens function formalism in combination with the density-functional theory, as implemented in the SIESTA 3.1 package [31]. Norm-conserving pseudopotentials and pseudoatomic orbitals in the optimized double-ζ polarized basis set (DZP) were used to represent the core electrons and the valence electrons, respectively. A vacuum layer of 16 Å was introduced in the direction perpendicular to the ribbons, and two cells of the surface atoms of the left and the right semi-infinite electrodes were included in the CSR. Self-consistent calculations were performed with revised Perdew-Burke-Ernzerhof (RPBE) formulation of the generalized gradient approximation (GGA) exchange correlation functional [32], with a mixing rate of 0.05 and a mesh cutoff of 150 Ry.

The relaxed structures have been obtained by using $1 \times 1 \times 7k$ grids to guarantee the convergence of the properties. All atoms were fully relaxed until the atomic forces were smaller than 0.002 eV/Å. $1 \times 1 \times 25k$ grids were used to analyze the electronic structure. The obtained structure of the 6-zGNR + 6H2 is displayed in Fig. 1. We found that the C–C bond lengths near the H2-terminated edges were changed significantly from the initial C–C bond length of 1.42 Å (a typical value for graphene). When the lattice length of the H2-zGNR unit was fixed at 2.46 Å during the optimization, the obtained lengths of d1 and d2 as labeled in the figure were 1.47 Å and 1.39 Å, respectively. When the whole supercell as shown in Fig. 1 was optimized with the lattice length fixed at 4.92 nm (20 units of zGNR), the d1 and d2 changed to 1.49 Å and 1.36 Å, respectively. This implied that the bond order between sites A and B, as well as that between sites B and A′ was completely changed. The edge C atoms with H2-terminations were sp^3-hybridized and (C═C)-like bonds were formed between B and A′ sites.

3. Results and discussion

We first examined the length effect of sp^3-edges. The obtained zero-bias conductance spectra of 6-zGNRs + N_{H2}H2 with the $N_{H2} = 1 \sim 10$ were plotted in Fig. 2. For comparison, the conductance spectra of the 6-zGNRs with pure sp^2-edges (labeled as H-zGNR)) or pure sp^3-edges (labeled as H2-zGNR) were also included. One can see that a sharp conductance peak presents right at the Fermi level of the H-zGNR as the result of the highly conductive edge states [3]. A gap about 0.48 eV presents around the Fermi level of the H2-zGNR as expected [24]. By introducing sp^3-edges (N_{H2}) in a pure sp^2-edges, the conductance spectra show two drastic changes, namely the significant decrease of the conductance around the Fermi level and the presence of some conductance dips. A wide conductance gap with a value about 2.86 eV appears when $N_{H2} = 5$. And it is interesting to see that the size of the gap does not change with further increasing the number of N_{H2}. Obviously, the widely opened gap is originated from the totally suppressed conductivity of the edge-states in H-zGNR due to the introduction of sp^3-terminations. Meanwhile, one can see that the first nonzero-conductance plateau is of one G_0, indicating that the ballistic transport characteristic of the zGNR keeps very well. Or to say, the high electronic mobility still remains in systems. It is

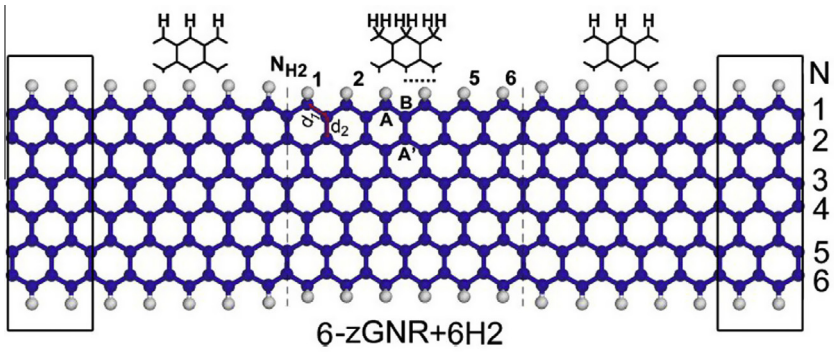

Fig. 1. Optimized structure of 6-zGNRs + 6H2, the atoms included in the left and right rectangles are the surface atoms of the left and right electrodes, and the two dashed lines indicate the interfaces between the H-terminated and H2-terminated sections.