



Structural stability, magneto-electronics and spin transport properties of triangular graphene nanoflake chains with edge oxidation



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ABSTRACT

Tuning the magneto-electronic properties of graphene-based structures into distinguished performance is an interesting but challenging work. To address this issue, we here construct several chain-like 1D nanostructures by stitching zigzag-edged triangular graphene nanoflakes with different manners and subsequently oxidized at edges. The high stability of these structures is identified by the calculated edge adsorption energy, phonon spectrum, and molecular dynamics simulations. Unlike edge-hydrogenation case, termination oxygen atoms here are highly magnetized and can control such 1D chain magneto-electronic features substantially. The calculations predict that such 1D chains are very versatile, and behaviors are sensitive to geometry, likely acting as a ferromagnetic metal and half-metal and bipolar magnetic semiconductor, or an antiferromagnetic metal and semiconductor. In particular, such a ferromagnetic half-metallic feature can occur in the ground state and possesses a wide bandgap, suggesting that they are excellent magnetic materials. The calculated spin transport characteristics reveal that such a chain-based device promises not only a perfect double spin-filtering effect, but also an excellent dual spin diode feature and a giant magnetoresistance (GMR) effect. The advantages over graphene nanoribbons are thus expected.

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1. Introduction

A bloom of research activities in nanoscience and a rapid development in carrying the diverse potential applications into nanotechnology have been seen in the past two decades. In particular, graphene, one well-known monolayered two-dimensional (2D) atomic crystal formed by arranging C atoms closely into a benzene ring structure, has attracted great attention due to its fascinating electronic, magnetic, mechanical and thermal properties [1–8]. Nevertheless, the properties of materials are intimately related to the dimensionality. For example, graphene nanoribbons (GNRs), typically armchair-edged GNRs (AGNRs) and zigzag-edged GNRs (ZGNRs), obtained by cutting or lithographic patterning of mechanically exfoliated graphene mono-layers, demonstrate more unique physics and chemistry nature because of the quantum confinement effect and the presence of edge states [9]. H-passivated ZGNRs in the ground state are semiconductors with an antiferromagnetic (AFM) coupling at two edges. But in the

nonmagnetic (NM) and ferromagnetic (FM) states, they are metals [10,11]. While for the H-passivated AGNRs, they are nonmagnetic semiconductors and the bandgap possesses a 3p oscillatory property [10]. ZGNRs were synthesized in 2008 [12] and their room-temperature ferromagnetism was also observed experimentally in 2014 [13]. ZGNRs thus have been studied widely for developing future spin devices [14,15]. Besides, another important derivative for graphene is the graphene nanoflakes (GNFs) [16–27], such as triangular GNFs. They can be obtained by standard nanolithography technology [28], but the best way at present is by tailoring graphene along special crystallographic directions [29]. Because GNFs hold the advantage of simple structure, more magnetic edges [17,26], and designable magnetism [20,27], they have become very important nanostructures in nanoelectronics [21–27].

Tuning the electronic structure and magnetism of GNRs or GNFs into distinguished performance is of important but challenging task. The common routines used for such functionalizations mainly include edge modifications [30,31], chemical doping [31,32], introducing mechanical deformations [33], constituting heterostructure [34], applying external electric field [35], and so on. In particular, with the development of experiment technology, the edge modification is turning to be diverse and ordered. Numerous

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elements or groups can be utilized as terminations for edge modifications since the dangling bonds based on the unpaired electrons at the edges of the pristine GNRs or GNFs are very reactive and can be linked easily. Especially the edge modification with O-containing functional groups has attracted a lot of research. This is because we often obtain large volumes of graphene by firstly synthesis of graphite oxide, then exfoliation into monolayers, and finally chemical reduction [36,37]. Especially, the graphene fabrication by oxygen plasma etching [38] or intercalation of oxidizing acids [12], thereby oxidation might be the most likely reaction emerging at the edges. Furthermore, the pristine GNR or GNF edges might be oxidized easily when exposed in the air. Therefore, the edge passivation only by H is not fully enough to cover the realistic edge chemistry. The theoretical study showed that ZGNRs with edge oxidation are more stable than hydrogenation due to the larger electronegativity of O atom relative to C atom [39,40], and the edge oxidation with hydroxyl, lactone groups can lower the onset electric field required to induce half-metallic behavior and extend the overall field range at which the systems remain half-metallic in the AFM ground state [40], in contrast with the case of H-terminated nanoribbons [35]. The electronic and magnetic properties of O-functionalized AGNRs were also investigated theoretically [41]. It showed that there exist three geometries for such AGNRs, and the planar passivation structure exhibits magnetic metallic properties while two non-planar passivation structures behave as non-magnetic semiconductors [41].

In this paper, we propose several new chain-like 1D nanostructures, formed by stitching edged zigzag triangular GNFs with different manners and subsequently oxygenated at edges. Their structural stability, magneto-electronics, and spin transport properties are studied in depth using first-principles method based on the density functional theory combined with the non-equilibrium Green's function (NEGF) technique. Their higher geometrical stability are verified by the calculated edge adsorption energy, phonon spectrum, and molecular dynamics simulations. They can be a metal, semiconductor, half-metal, or bipolar magnetic semiconductor in different magnetic states. In particular, such a half-metallic nature can occur in the FM ground state and possesses a wide bandgap, suggesting that they are excellent magnetic materials. The calculated spin transport characteristics reveal that such a chain-based device possesses not only a perfect (100%) double spin-filtering effect, but also holds an excellent dual spin diode feature and a giant magnetoresistance (GMR) effect. Our studies imply that constructing such special structures might be an effective strategy for improving graphene performance.

2. Structure model and theoretical method

The bare-edged zigzag triangular graphene nanoflake (ZTGNF) is shown in Fig. 1(a). Generally, the size of ZTGNFs is characterized by the number of hexagonal rings, R , on each side. In one ZTGNF, the total number of C atoms can be counted by $n = R^2 + 4R + 1$. All the C atoms distribute in two sets of sublattices, A and B, and the number difference of C atoms in two sublattices is $R-1$. We here chose ZTGNF with $R = 5$ as an prototype example because it is enough to represent the basic electronic properties of ZTGNFs, and their ordered arrangement is considered by stitching ZTGNFs to construct special one-dimensional structures, i.e., various ZTGNF chains (ZTGNFCs). Four types of possible stitching strategies are taken into account, as schematically shown in Fig. 1(b)–(e). That is: (1) All upward ZTGNFs are stitched by a “bottom-side alignment, vertex to vertex” way, and two adjacent ZTGNFs are linked by one four-membered ring after geometrical optimization, as shown in Fig. 1(b), this 1D ZTGNFC is hereafter referred to as M1. (2) All

rightward ZTGNFs are positioned with same orientation and connected by a “vertex to bottom-side” method to form a 1D ZTGNFC, and two adjacent ZTGNFs are bonded by two five-membered rings after optimization, which is denoted as M2, as displayed in Fig. 1(c). (3) All leftward and rightward ZTGNFs are stitched with a “bottom-side by bottom-side” and “vertex to vertex” manner to construct a 1D diamond-shaped ZTGNFC, and two adjacent ZTGNFs produce a link with four hexagonal rings after optimization, naming such a structure as M3, as displayed in Fig. 1(d). And (4) all upward and downward ZTGNFs alternatively emerge and are stitched by a “bottom-side alignment, vertex to vertex” way to yield a 1D ZTGNFC, and two adjacent triangular nanoflakes are associated by one bond after optimization, as manifested in Fig. 1(e), denoted as M4. These resulting structures can be viewed as forming well-defined morphologies by the self-assembly of nano-scale objects, which is recently studied in depth [42]. Obviously, the diversity of 1D chains have entirely different stitched interfaces between two adjacent ZTGNFs, which will be expected to affect the electronic and magnetic behaviors greatly. To explore the edge chemistry effects for such structures, we suppose that side C atoms of all the 1D chains are terminated by single O atoms (O-ZTGNFCs). After final optimization, small geometrical distortions can be observed at the sides of ZTGNFs. However, all the atoms, including O atoms, still stay in the same plane. In order to be convenient for comparison, two ZTGNFs in all the 1D chains are selected as a unit cell for calculations, which are denoted by the dashed rectangles, as plotted in Fig. 1(b)–(e).

The geometric optimization as well as the calculations of magneto-electronics and spin transport properties for systems are carried out by using the first-principles methods based on the density functional theory (DFT), as implemented in the Atomistix ToolKit (ATK) code [43–49]. The exchange correlation energy is described by the spin-dependent generalized gradient approximation (SGGA) in the scheme proposed by Perdew–Burke–Ernzerhof (PBE). The Troullier–Martins norm-conserving pseudo-potentials are employed to represent the atom core and linear combinations of atomic orbitals to expand the valence states of electrons. Considering the electrical polarized effects of atoms, the double-zeta plus polarization (DZP) basis set is used for all atoms. The k-point sampling is $1 \times 1 \times 100$ in the x, y, and z directions, respectively, where the z is the period direction of 1D chains, and the cut off energy is set to 150 Ry. For the models studied, a 15 Å vacuum slab is used in x and y directions to eliminate interaction between the model and its “images”, and all calculations are performed after the geometry is optimized until all residual forces on each atom are smaller than 0.01 eV/Å. For simplicity, the Fermi level (E_F) is set as zero in all calculations of electronic structures.

3. Results and discussions

3.1. Structural stability

To assess the energetic stability of optimized O-ZTGNFCs, we calculate the edge adsorption energy $E_{\text{ads(O)}}$, which is defined as $E_{\text{ads(O)}} = [E_{\text{O-Z}} - (E_{\text{Z}} + n_{\text{O}}E_{\text{O}})]/n_{\text{O}}$, where $E_{\text{O-Z}}$ and E_{Z} are, respectively, the total energies of O-terminated and bare-edge ZTGNFCs in a unit cell, E_{O} is the energy of one isolated O atom, and n_{O} is the number of termination O atoms in a unit cell. The calculated results for various O-ZTGNFCs are summarized in Table 1. One can see that edge adsorption energies for four models all fall into a range of -7.518 to -7.598 eV per atom. According to the definition, the edge adsorption energy with negative value means that the corresponding structure is energetically favorable and might exist stably in experiment. The lower the edge adsorption energy is, the

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