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Enhanced half-metallicity in carbon-chain–linked trigonal graphene

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ABSTRACT

The spin polarization property of a zigzag-edge trigonal graphene (ZTG) linked with different-length carbon chains C_n is investigated theoretically. It has been found that the enhancement of such a property completely depends on that the number of carbon atoms in a chain being odd or even. If it is an even number, the spin polarization is only changed slightly due to the nearly nonmagnetic property of these carbon chains. In contrast, while it is an odd number, the spin polarization is enhanced significantly to a larger energy range, i.e., showing a prominent half-metallicity and perfect spin-filter effects, owing to interactions of the ZTG and carbon chains with the strong ferromagnetism property. Deepgoing analyses show that these results are intimately related to a polyyne-like configuration for carbon chains in nanojunctions and the transition from the bipolar magnetic semiconductor to half-metallicity. Our findings suggest that this simple structure might promise importantly potential applications for developing nano-scale spintronics devices.

1. Introduction

Magnetism in solids is generally associated with transition metal elements with *d* electrons. However, recent studies have shown that spin magnetism related to sp electrons with a remarkable longer spin-coherence time and distance can be found in graphene-based materials. Therefore, they are considered to be a promising candidate for future nanospintronic applications [1–5]. Especially for the reduced-dimensionality derivative of graphene, zigzag graphene nanoribbons (ZGNRs), due to distinct magnetic (or spin) states at their edges, namely, ferromagnetically ordered edge states at each zigzag edge and an antiferromagnetic arrangement of spins between two zigzag edges [2,5–8], they have been suggested to play an important role in 'spintronic' devices [4–13]. Currently, several possible methods [9–13] have been proposed to modulate the magnetic coupling of ZGNRs from antiferromagnetism (AFM) to ferromagnetism (FM). For example, injecting carriers (electrons or holes) [9], applying electrical field [10] or magnetic field [6,11], modifying sided states [11], introducing defects [12], doping heteratom [13], and so on, to break the spin degeneracy.

Another class of important derivatives of graphene is finite-size 0D graphene nanoflakes (GNFs). They are nanometer-scale materials usually with a well-define shape, such as triangular, rectangular and hexagonal shapes [14–18], which have already been manufactured by the standard nanolithography [19] and soft-landing mass spectrometry methods [20]. At present, the most excellent experimental method to obtain various GNFs is by cutting a graphene along specific single crystallographic directions [21]. Among GNFs, zigzag-edge trigonal graphenes (ZTGs) are the most prominent due to featuring a simple structure and showing unique electromagnetic properties, which have recently been investigated widely [14,16,18,22–24]. The ZTGs with the ferromagnetic ground state upon the intrinsic spin polarization can be viewed as an interesting new class of nanomagnets. Their net magnetic moments originate from the difference in the number of carbon

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atoms in two sets of sublattices, A and B, and can be calculated by Lieb's theorem [25]: $M = \frac{1}{2}|N_A - N_B|g\mu_B$, where $g = 2$ for the electron, μ_B is the Bohr magneton, and N_A and N_B denote the number of carbon atoms in A and B sublattices, respectively. For a monohydrogenation-edged n-ZTG, $C_{n^2+4n+1}H_{3n+3}$, where n denotes the number of edge hexagonal cells in one side of the triangle, its total net spin magnetization is $(n-1)\mu_B$ obtained by the above-stated theorem. However, a pristine ZTG is a magnetic semiconductor and its spin filtering effects are extremely imperfect [18]. Therefore, how to achieve the half-metallicity is of fundamental importance and practical significance for applications in spintronics.

The linear atomic carbon chains can also be regarded as a family of graphene derivatives or extremely narrow GNRs, which can be used as a transport channel for on-chip interconnects of molecular electronic nanodevices. Recently, using a high energy electron beam, linear carbon atomic chains have been carved out of graphene [26,27]. Acting as possible spintronics devices, linear carbon atomic chains have attracted much investigation interests. For example, Li et al. [28] reported that the modified carbon chains between nonmagnetic Au electrodes could produce a perfect spin filter effect. Wei et al. [29] found that a carbon chain switched off electric current when magnetic fields of left and right leads were anti-parallel, and Senapati et al. [30] proposed that large magnetoresistance in Co-terminal carbon chains contacted between Au electrodes might be achieved. Particularly, Ravagnan et al. [31] predicted that if the graphene leads are rotated by different degree, the electronic states and spin magnetization of carbon chains could be changed significantly.

In this paper, we consider a strategy to improve the spin polarization of the ZTG by a linking with carbon chains. It has been found that its spin polarization is only changed slightly if even-numbered atom chains are linked, but it can be significantly enhanced to a larger value and wider energy range when odd-numbered atom chains are linked. These results are intimately related to a polyyne-like configuration for carbon chains in nanojunctions and the transition from the bipolar magnetic semiconductor to half-metallicity.

2. Structure model and theoretical method

Fig. 1 shows the geometrical structures investigated. In order to avoid an overmuch calculating cost, we only select one smaller ZTG, 3-ZTG, as a representative, and its zigzag edges are terminated by H atoms to eliminate the dangling bonds on edge carbon atoms. The 3-ZTG is linked with two symmetric equi-length carbon chains at its two sides, respectively, to form the hybrid structures of carbon chain/ZTG/carbon chain. The length of a carbon chain is referred to as C_n, where n denotes the number of carbon atoms in a chain. We choose $n = 1, 2, 3, 4$, and 5 to evaluate the length effects of carbon chains. By such modifications, we expect that new electronic states and magnetic properties will be introduced. To investigate these, each optimized structure by a separate calculation based on the density function theory (DFT) is positioned between two Au (100) electrodes with a typical Au–C distance of 2.0 Å, making it consistent with the experiment result [32], to construct a nanojunction, that is, taking electrode effects into account. Subsequently, the geometries of the scattering region are optimized further until all residual forces on each atom are smaller than 0.05 eV/Å.

Geometric optimizations as mentioned above and calculations of electronic structure are performed by using the spin-polarized DFT [33] combined with the non-equilibrium Green's function (NEGF) method as implemented in Atomistix ToolKit (ATK). We employ Troullier–Martins norm-conserving pseudopotentials to represent the atom core and linear combinations of local atomic orbitals to expand the valence states of electrons. The local spin density approximation (LSDA) is used as the exchange–correlation functional. Single-zeta plus polarization (SZP) basis set are adopted. The k-point sampling is 1, 1, and 300 in the x, y, and z directions, respectively, where the z is the electronic transport one, and the cutoff energy is set to 200 Ry. Open boundary conditions are used to describe the electronic properties of nanojunctions. In all these nanojunctions, a 15 Å vacuum space was used to eliminate interactions between the molecule and its neighboring "images". Eight Au atoms in two Au (100) layers represent an electrode cell, and thirteen Au atoms are included into the scattering region for calculations.

3. Results and discussion

To find the structural stability of optimized 3-ZTG linked with carbon chains, we firstly calculate the binding energy by a definition $E_b = (E_s - n_c E_c - n_H E_H)/(n_c + n_H)$, where E_s, E_c, and E_H are the total energy of the ZTG, one C atom, and one H atom, respectively, and n_c and n_H are the

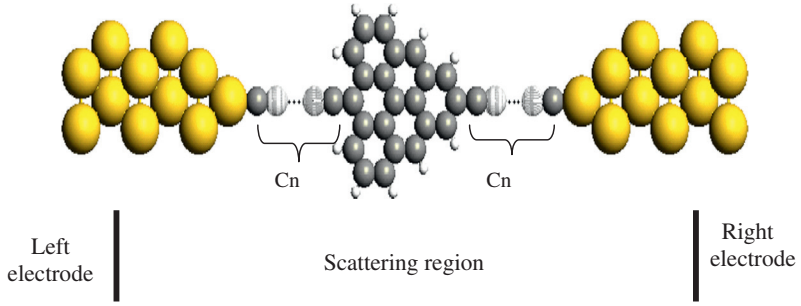

Fig. 1. Nanojunctions comprise of ZTG linked with carbon chains C_n ($n = 1-5$) contacted with Au electrodes.