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Modulating magnetic ordering of the zigzag-edge trigonal graphene by functionalizations

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ABSTRACT

A pristine zigzag-edge trigonal graphene (ZTG) is a magnetic semiconductor, thus its spin polarization is extremely low. Here, we report the calculated results on enhancing the spin magnetism of a zigzag-edge trigonal graphene (ZTG) by functionalizations, including the heteroatom doping, edge modifications, and introducing topologic defects. It is found that the ZTG features a good tuning ability for functionalizations to improve its spin polarization. When one boron (B) atom is doped to replace one carbon atom in the B sublattice of graphene, a higher spin polarization can be achieved, and the edge modification by Cu, Co, O or B atom can modulate the magnetic ordering significantly due to the spin-polarized charge transfer between the ZTG and terminations, especially for O and Co terminations. And also, the introduced defect (a vacancy and a Stone–Wales defect) can obviously tune local magnetic structures owing to geometrically structural deformations (variations of bond length and bond angle). For these behaviors, in-depth analyses are performed. Our findings suggest that the desirable functionalized ZTG structures might promise importantly potential applications for developing nano-scale spintronics devices.

1. Introduction

In current technological applications, magnetic materials are based on *d* and *f* elements. Recent found graphene-based nano-scale magnetic materials would greatly extend the limits of technologies relying on magnetism. Therefore, the spin magnetism of graphene has attracted a considerable research interest [1–3]. For graphene nanoribbons, one predicts that they will play an unprecedented role in spintronic applications because of its unique edge magnetism. However, studies have shown that the ground state of zigzag graphene nanoribbons (ZGNRs) is antiferromagnetic (AFM) with zero net spin [4], thus, its application for spin-polarized transport is limited. Heretofore, many effective approaches have been proposed to stabilize ferromagnetic (FM) state or to break the spin degeneracy in ZGNRs, such as applying electrical field [5] or magnetic field [6], edge modification [7], doping [8], and introducing topologic line defects [9]. Based on these ways, some important phenomena are found, and promising spintronic devices are designed, such as giant magnetoresistance devices and conductance switchers [10], spin-filtering devices [11], bipolar spin diodes [11,12], spin-polarized current amplifiers [12], bipolar field-effect spin-filtering devices [13], and ambipolar memory devices [14].

The zigzag-edge trigonal graphenes (ZTGs), one kind of finite-size 0D graphene nanoflakes (GNFs), are some important derivatives of graphene, which can be obtained experimentally by cutting a graphene along specific single crystallographic directions [15]. The unique electronic properties and potential applications of these simple structures have been investigated widely, for example, several recent works have touch on the rectifying behaviors of functionalized ZTGs [16,17]. More particularly, the ZTGs

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with the ferromagnetic ground state due to the intrinsic spin polarization can be viewed as an interesting new class of nanomagnets. Their net magnetic moments, originating from the difference in the number of carbon atoms in two sets of sublattices, A and B, can be calculated by Lieb's theorem [18]: $M = |N_A - N_B|\mu_B$, where μ_B is the Bohr magneton, and N_A and N_B denote the number of carbon atoms in A and B sublattices, respectively. Thereby, the total net spin magnetization for a monohydrogen terminated n-ZTG is $(n-1)\mu_B$, where n denotes the number of edge hexagonal cells in one side of the trigon. Recently, the gold 10-mer has been studied [19], and it shows that $Au_{10}\_D_{3h}$ and $Au_{10}\_C_{2v}{}^{JT}$, similar shapes to trigonal graphenes, possess s-electron ferromagnetism and remarkable spatial charge–spin separations, which could be useful in spintronics. The spin magnetism of a pristine ZTG originates from p-electron of carbon atoms, and magnetic semiconducting features make it having a very low spin filtering effect [20]. Therefore, how to enhance its spin polarization is of fundamental importance and practical significance for applications in spintronics.

In this paper, we consider the improvement of the spin polarization of the ZTGs by various functionalization ways, including the heteroatom doping, the edge modifications, and introducing defects. It is found that a ZTG features a good tuning ability for functionalizations to enhance its spin polarization, and the changing details of local magnetic ordering and electronic structures are intimately related to the doping sites, types of termination atoms, and defective configurations.

2. Structure model and theoretical method

Fig. 1(a) shows the geometrical structure we investigate, which is composed of the n-ZTG connected onto two Au (100) electrodes to construct a nanojunction, namely, taking electrode effects into account. 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. Three different modified ways are considered to modulate the spin polarization of 3-ZTG. In Fig. 1(b), it displays different atomic sites, ①–④, for doping to form the dopant-substituted ZTG structures, and in turn to investigate in detail the doping site effects on modulating the spin polarization. Here, we only take the Boron (B)-doping as an example because B is the most commonly used graphene dopants in experiments [21] and its similar size to the C atom allows it to substitute into the ZTG with a minimal strain, which is favorable to keep the structural stability of a small ZTG. Additionally, there almost exists the same possibility in an experimental doping for different sites ①–④, therefore, these sites are taken into account in our simulations, respectively. The calculated total energy shows that it is more energetically favorable for atomic sites, ①–④, doped to form the dopant-substituted ZTG structures than other sites doped. In the structure shown in Fig. 1(c), we consider differently edge-modified effects. Several kinds of important terminations are studied: (1) noble metals (NM) Cu, (2) 3d-transition metal (TM) Co, and (3) nonmetal B and O. B atom has one less valence electron than C atom, but O atom possesses two more valence electron than C atom. Fig. 1(d) shows that one single-atom vacancy defect is introduced. In calculations, two cases of the vacancy edge with and without mono-hydrogen terminations are taken into account, respectively. And also, a Stone–Wales defect is considered. By these functionalizations, we expect that novel electronic states and magnetic properties will be introduced. For all modeling, each optimized ZTG structure by a separate calculation based on the density function theory (DFT) is sandwiched between two Au (100) electrodes with a typical Au–C distance of 2.0 Å, which makes it consistent with the experiment result [22], as shown in Fig. 1(b–d). Subsequently, these junction geometries are optimized further until all residual forces on each atom are smaller than 0.05 eV/Å.

The calculations of electronic structure are performed by using the spin-polarized DFT combined with the non-equilibrium Green's function (NEGF) method as implemented in Atomistix ToolKit (ATK) [23,24]. It has been confirmed

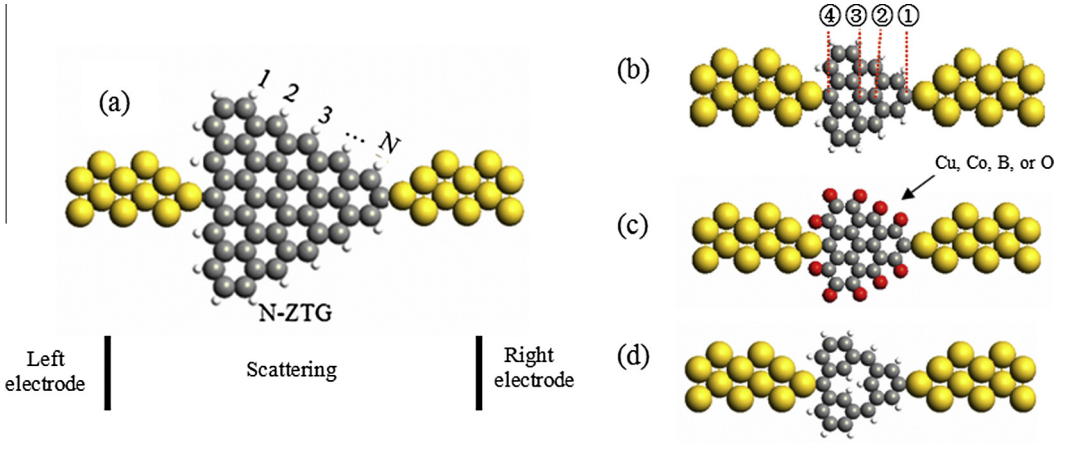

Fig. 1. (a) A nanojunction comprises of the ZTG contacted with Au electrodes, (b) different atomic sites, ①–④, for doping to form the dopant-substituted ZTG structures, (c) different edge-modifications for the ZTG, and (d) introducing a defect for the ZTG.