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Band gap opening in zigzag graphene nanoribbon modulated with magnetic atoms

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ABSTRACT

The effects of magnetic atom on the band structure of zigzag-edged graphene nanoribbons are investigated by the density functional theory. The results show that for narrow zigzag-edged graphene nanoribbons, the band gap can be opened duo to the spin-up/spin-down charges being re-enriched on the edge sites. However, for the wide zigzag-edged graphene nanoribbons, a spin-up/spin-down half-metallic property can be observed. Moreover, it is found that the Seebeck coefficients in the narrow zigzag-edged graphene nanoribbons are reversed and enlarged, which provides a way to design novel thermoelectric device.

1. Introduction

Recently, the material obtained by cutting the graphene sheet [1–3] or unzipping the single-walled carbon nanotubes [4], named graphene nanoribbon (GNR), has attracted more and more attention duo to its exceptional electronic/phononic transport properties [5–13]. According to the regular edge shape along the extend direction, the GNR can be organized as armchair GNR (AGNR) and zigzag GNR (ZGNR). Among them, The ZGNR has received a great attention due to its surprising electronic and magnetic properties [14,15]. In the ground state of ZGNR, a band gap at Fermi energy (E_F) is opened duo to the antiferromagnetic ordered spin states at the edges [16]. And ZGNR can be half-metallic under the condition of edge decoration and electrical field [17–19]. However, recent theoretical studies based on density functional theory (DFT) indicated that the intrinsic antiferromagnetic (AFM) state of ZGNR is unstable unless at extremely low ultravacuum pressures [20] and low temperature $T \leq 10$ K [21]. Until now, the edge magnetism in ZGNR has never been directly observed in experimental study except an indirect observation [22]. ZGNRs will simply exhibit paramagnetic behavior when the temperature is higher than 10 K [21]. In other words, the band gap of ZGNRs will be closed. The metallic property makes ZGNRs unsuitable for direct application as a channel in rectifying devices and other semiconducting devices. It is needed to ensure that ZGNRs can be semiconductor at higher temperature, such as room temperature, for practical application. On the other hand, the spin-up/spin-down electrons near the E_F in the carbon atom can be spit by an external magnetic field **B**, $\varepsilon_\downarrow - \varepsilon_\uparrow = g\mu_B\mathbf{B}$, where g is the effective electron gyromagnetic factor and μ_B is the Bohr magneton. It may be useful to open the band gap of ZGNR by applying a microscopic magnetic field on the edge carbon atoms at finite temperature.

In the present work, we focus on the effect of magnetic atom on the band structure of ZGNRs by DFT calculations. The results show that, the narrow ZGNRs whose width lesser than 1.4 nm can be switched between metal and semiconductor by applying or removing the magnetic atom at one of the edge atoms, while the wide ZGNRs can present a spin-up/spin-down half-metallic behavior as long as the width of ZGNR lesser than 6 nm (30ZGNR). These results arise from the lowered/raised occupied/unoccupied edge states by the magnetic atom. In addition, the Seebeck coefficient of narrow ZGNR will be reversed and enlarged about 700%, which can be considered in the future design of ZGNR-based high-performance electronic/thermoelectric devices.

2. Model and computational method

The model structure is shown in Fig. 1(a). A microscopic magnetic field (MMF), $\boldsymbol{B} = -B\hat{z}$, is applied on one of the outermost carbon atoms duo to the symmetry of the ZGNR along the $\hat{y}$ direction. This process can be realized by many techniques, such as magnetic scanning tunneling microscopy tip [23], or magnetic

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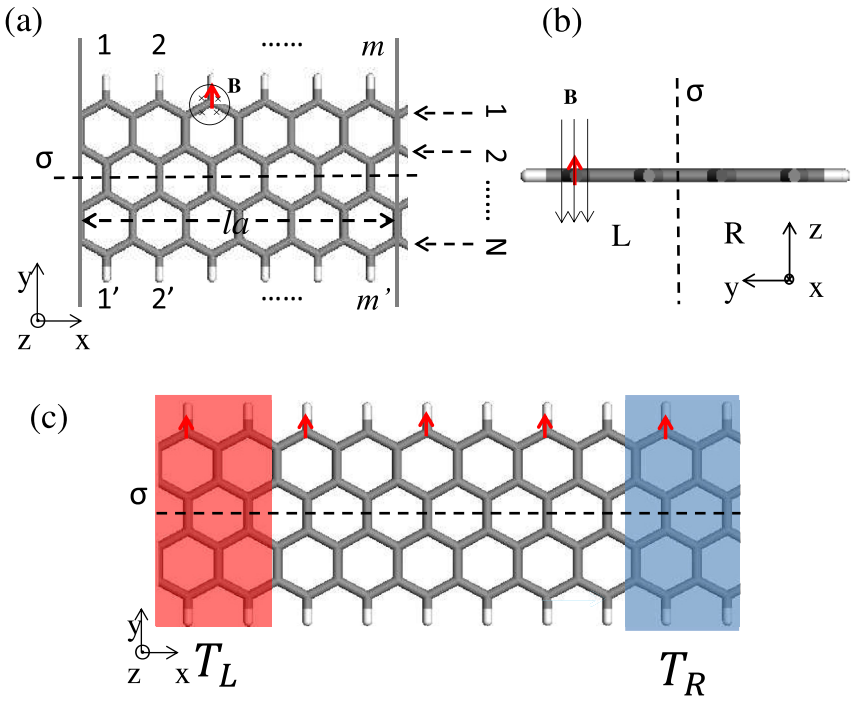

Fig. 1. (a) Diagram of zigzag graphene nanoribbon (NZGNR) with magnetic atom. Due to the symmetry of the ZGNR along the $\hat{y}$ direction, the magnetic atom is just at the upside (L). l stands for the number of unit cell a in the supercell. N indicates the width of the nanoribbon. m/m' is the index of the edge carbon atoms in the supercell. (b) The side view of the ZGNR. σ is the symmetry axis of the ZGNR. (c) The thermoelectric device based on 4ZGNR. Here the T_L/T_R is the temperature of the two heat source and the T_L is slightly higher than T_R. The circle with cross-lines is the area of microscopic magnetic field **B**. The spin states of magnetic atoms in the microscopic magnetic field are shown by the thick (red) arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

atoms [24]. Because of the action of MMF and the paramagnetic property of ZGNR, the edge carbon atom in the MMF will be magnetized and become a magnetic atom (MA), the electron state of the magnetic atom will be spin-up state. In our calculation, the initial spin state of the magnetic atom is set to 1 and others are 0. We classify ZGNRs by the number of the carbon chains in width as NZGNR. Gray horizontal lines are added to the structure in order to indicate the boundaries of the corresponding supercell along the periodic direction $\hat{x}$, and l stands for the number of unit cell a ($a = 0.2443$ nm from first-principles calculation) in the supercell, m/m' is the index of the edge carbon atoms in the supercell. The thermoelectric device based on 4ZGNR is shown in Fig. 1(c). Here the T_L/T_R is the temperature of the two heat source and the T_L is slightly higher than T_R. Each type of heat source is composed by two GNR unit cells to limit the interaction in neighbor. The spin states of the magnetic atoms are shown by the arrows.

Our calculations are performed by using the first-principles method which based on the fully self-consistent DFT [25,26]. The signal-ζ plus polarization basis set is employed to balance the calculation accuracy against the efficiency. The plane wave cut-off in Hamiltonian and overlaps calculation is set to 150 Ry. The interaction potential between the core electrons and the outer electrons are described by norm-conserving pseudopotentials, and the exchange-correlation potentials between the outer electrons are described by the local density approximation (LDA). Duo to the large vacuum layer in x and y direction (>8 Å), the k-point sampling is set to $1 \times 1 \times 100$. These choices are appropriate for the electronic calculations of carbon system [27,28]. All the structures are fully relaxed until the max residual force on atoms is less than 0.01 eV/Å before the electronic property calculation. Duo to the weak electron–phonon coupling [29], the electron–phonon interaction is neglected in our calculation. Considering that the unstable AFM state and the paramagnetic behavior of ZGNR when T larger than 10 K, the non-magnetic state is adopted as the initial state of ZGNR to simulate the ZGNR at finite temperature.

The Seebeck coefficient S, a material thermoelectric response to an applied temperature differential ΔT ($0 < \Delta T = T_L - T_R \Delta (T_L + T_R)/2$, as the structure shown in Fig. 1(c)), can be expressed by the Landauer formula as [30,31],

$$S = \frac{1}{eT}\frac{L_1(\mu)}{L_0(\mu)}, \tag{1}$$

where $L_m(\mu)$ is given by,

$$L_m(\mu) = \frac{2}{h}\int_{-\infty}^{\infty} dE T(E)(E-\mu)^m \left(-\frac{\partial f(E,\mu)}{\partial E}\right), \tag{2}$$

here the $f(E,\mu)$ is the electron Fermi–Dirac distribution function with electrochemical potential μ, the transmission $T(E)$ from the hot side to the cold side can be obtained by Green's function: $T(E) = Tr(G^r \Gamma_H G^a \Gamma_C)$. Here the $G^{r(a)}$ is the retarded (advanced) Greens function of the center region, and $\Gamma_{L(R)}$ is the contact broadening function which describe the coupling between the center region and the hot (cold) side.

3. Results and discussion

The band structures of different width ZGNRs with and without magnetic atoms are shown in Fig. 2. Here the supercell is composed by two unit cell ($l = 2$). It can be seen from the upper plane that the occupied orbital π and unoccupied orbital π^* overlapped at the E_F, forming the well-known edge state [32–34], namely, the wave function in the edge state is mostly localized on the edge sites. This indicates that all the ZGNRs are metallic. However, when a