Spin filtering and large magnetoresistance behaviors in carbon chain-zigzag graphene nanoribbon nanojunctions

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ABSTRACT

Using the non-equilibrium Green's function method combined with the density functional theory, we investigate the electron and spin transport properties of carbon chains covalently connected with zigzag-edged graphene electrodes at finite bias with the parallel (P) and antiparallel (AP) magnetism configurations. When two zigzag-edged graphene electrodes are H2–ZGNR–H structures, spin filtering effect can be realized only with AP magnetism configuration. While one electrode is replaced with the H–ZGNR–H structure, we observe a dual spin filtering effect with above two magnetism configurations. But the spin transport properties of carbon chains can also be affected by the linking way of the carbon chain ends. Deeper analyses show that the spin-related properties are related to the electrodes, magnetism configurations, and the connection structure between electrodes and carbon chains.

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1. Introduction

Spintronics is a popular topic in condensed matter physics, materials chemistry, and electronics industry, searching for suitable spintronic materials is a basic but crucial task [1–3]. Zigzag-edge graphene nanoribbons (ZGNRs) are known to display very peculiar electronic properties, with wavefunctions sharply localized along the GNRs edges at low energies, which significantly affect their transport properties. It is known that spontaneous magnetic orderings in one- and two-dimensional spin lattice model are difficult to achieve at finite temperature [4]. Kunstmann et al. consider the intrinsic magnetism would not be stable at room temperature in graphene nanoribbons [5]. Moreover, it has been estimated that the spin correlation length ξ limits the long-range magnetic order to 1 nm at 300 K while temperatures less than 10 K [6]. While the creation of localized domain walls at different types of topological imperfections at zigzag graphene edge is the possible ways of increasing the range of magnetic order [6]. A feasible approach to realize graphene-based electronics is to construct the device junctions by connecting GNRs with different widths and orientations [7]. For example, the application of an external magnetic field was shown to trigger a transition from parallel to antiparallel magnetic edges, resulting in giant magnetoresistance phenomena and efficient spintronics devices [8]. At present, four methods are of great importance in designing desirable devices, which are the manipu-

lating localized edge states of ZGNRs [9,10], matching the electrode band symmetry [11–13], tuning the electronic structure of the central molecule [14–18] and tuning the magnetic configuration of the two leads [19,20]. The ZGNRs with mono-hydrogen terminations are spin-polarized, which can be transformed to half-metals by edge modification [21], applying external electric field [8], doping other atoms [22] and drawing topologic line defects [23]. In order to stabilize the edges of the GNRs, the dangling bonds of the edge carbon atoms have to be passivated by various ways, including symmetric hydrogenation (with one hydrogen atom saturating each dangling bond, referred to as H–ZGNR–H, and asymmetric hydrogenation (referred to as H2–ZGNR–H), which are C–H2 bonded at one edge while C–H bonded at the other. More importantly, the H2–ZGNRs–H scheme is stable under room temperature with molecular dynamics simulations [24]. Recently, researchers demonstrated that the composition of sp^2 and sp^3 types at the edges of the GNRs can be easily controlled through studying on the chemical potential of hydrogen, which indicates that the monohydrogen-terminated and dihydrogen-terminated grapheme nanoribbon heterojunction can be fabricated with experiment via temperature and pressure of H_2 gas, and this graphene nanoribbon heterojunction can be observed by scanning tunneling microscopy (STM) images [25–27]. In addition, carbon atomic chains as spin-transmitters, which can be recently achieved via chemical methods [28], have been studied widely [29–31]. The magnetic and electronic properties of the complex Cn–GNR system can be tuned by tailoring the shape of graphene edges (armchair or zigzag) [29]. The possibility for controlling carbon chain conductance, optical properties, and spin magnetization, purely by twisting its sp^2 termination, has

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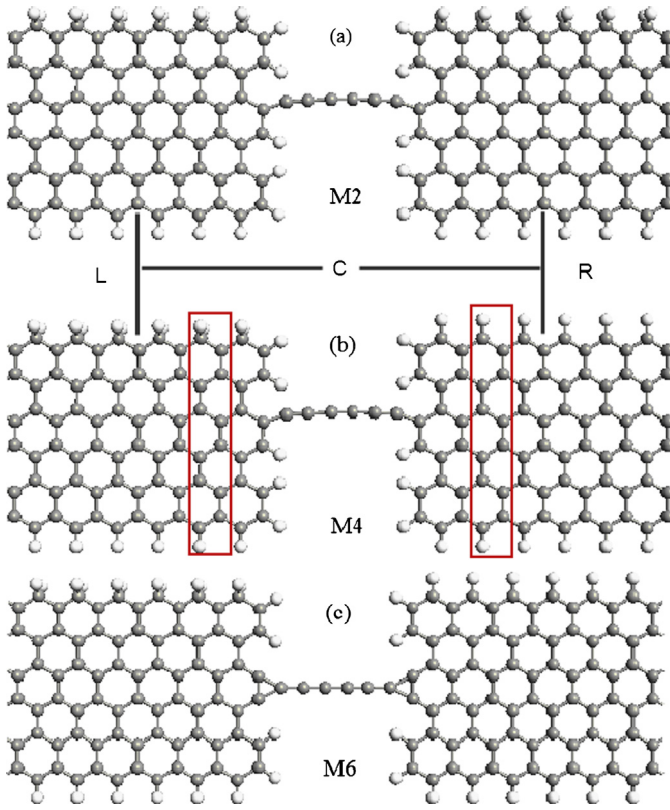
Fig. 1. The geometric structure, the carbon atom chain connected between grapheme electrodes, and the solid rectangle denotes the unit cell of graphene. L, R, and C mean the left and right electrodes, and the central scattering region.

been demonstrated [30]. Zeng et al. proposed that carbon chain-bridging GNR electrodes can be as a good spin-filter or spin-valve, but the bias region for perfect spin-filtering is less than 0.2 V [31]. In fact, the connection between chain and electrode such as para-linkage and meta-linkage in benzene also can lead to different conductance and spin effect [32].

In this article, using the non-equilibrium Green's function method combined with the density functional theory, we investigate the electronic transport properties of a carbon chain covalently connected to two zigzag-edged graphene electrodes at finite bias with the parallel (P) and AP magnetism configuration. When two electrodes are H2–ZGNR–H, the spin filtering effect can be realized only with AP magnetism configuration. While one electrode is replaced with H–ZGNR–H, we observe a dual spin filtering effect with above two magnetism configurations. Then, the carbon chains are connected to two adjacent carbon of electrode, the ability of electron transmission shows weak with P magnetism configuration, but the spin filtering effect can be realized only with AP magnetism configuration. Moreover, magnetoresistance effect as large as $10^6\%$ can be achieved.

2. Models and method

The ribbon width of ZGNRs is generally characterized by the number of zigzag C chains, N, along the direction perpendicular to the nanoribbon axis. Here, we take the ZGNR with $N = 6$ as electrode. The left electrode is the H2–6ZGNR–H structure, while the right electrode is the H2–6ZGNR–H or H–6ZGNR–H structure, and carbon chain is consist of 5 (6) carbon atoms. Considering the electrode and the length of carbon chains, we design six models. Figs. 1(a)–(c) show the structures of M2, M4 and M6, each device composes of the left electrode, scattering region (the device re-

gion), and right electrode, marked by L, C, and R, respectively. The scattering region contains the six carbon atom chains and three units of graphene on each side. When the atom number of carbon chain is five, we get M1, M3 and M5 on the basis of M2, M4 and M6. The structural relaxations and transport calculations for all of the above systems are performed by using the density functional theory (DFT) combined with the non-equilibrium Green's function (NEGF) method [33] as implemented in the Atomistix ToolKit11.2.3 (ATK11.2.3). We employ Troullier–Martins norm-conserving pseudo-potential to present the atom core and linear combinations of atom orbitals to expand the valence state of electrons. The local spin density approximation (LSDA) is used as the exchange-correlation functional. The real space grid techniques are used with the energy cutoff of 150 Ry as a required cutoff energy in numerical integrations and the solution of Poisson equation using fast Fourier transform (FFT). The geometrical structures are optimized until all residual forces on each atom are smaller than 0.05 eV/Å under the periodic boundary condition. The wave functions of all atoms are expanded by single-zeta polarized (SZP) basis set. The current I_σ through systems as a function of the applied external bias V_b, can be calculated from the Landauer-like formula [34]:

$$I_\sigma(V_b) = (e/h) \int_{\mu_r(V_b)}^{\mu_l(V_b)} T_\sigma(E, V_b)\big[f_l(E, V_b) - f_r(E, V_b)\big] dE, \quad (1)$$

where $\sigma = \uparrow$ (spin up) and $\downarrow$ (spin down), $T_\sigma(E, V_b)$ is the bias-dependent transmission coefficient, $f_{l/r}(E, V_b)$ is the Fermi–Dirac distribution function of the left (right) electrode. As a result, the electrochemical potentials correspond to $\mu_l(V_b) = \mu_l(0) - eV_b/2$ and $\mu_r(V_b) = \mu_r(0) - eV_b/2$. Considering the fact that the Fermi level is set to be zero, the region of the energy integral window $[\mu_l(V_b), \mu_r(V_b)]$ can be written as $[-V_b/2, V_b/2]$.

3. Results and discussion

We examine the magnetic properties of H2–ZGNR–H, and find that the ferromagnetic (FM) state is ground state because its total energy is much lower than that of the nonmagnetic and AFM states at room temperature. After above-stated structures are constructed and subsequently optimized, an obvious bond-length alternation (BLA) on the chain can be observed, which is in a range of 1.25–1.38 Å, namely, displaying a polyyne-like bonding configuration, which is produced to lower the energy [35], similarly to a Peierls-type distortion. The structure with the single and triple bond alternation formed in carbon chains is called as the "singlet–triplet rule" [36]. Additionally, we find that the C–C bonds length between end carbon atom of chain and graphene is longer, around 1.46 Å (M1–M4) and 1.6 (M5 and M6), and the C–H bond length is 1.16–1.17 Å.

Isosurface plots of the spin charge density difference of α- and β-spin states ($\nabla\rho = \rho_\alpha - \rho_\beta$) at FM state for M1–M6 with the P and AP spin configurations are shown in Table 1, and the isosurface level is taken as $\pm 0.005|e|/\text{Å}^3$. To our surprising, the H2–6ZGNR–H component shows an obvious stronger magnetism than the H–ZGNR–H. The weak magnetism can be observed on the carbon atoms with C–H2 edges, while the carbon atoms next to them exhibit stronger magnetism. The magnetism mainly distributes at the edged carbon atoms for the right H–6ZGNR–H due to the unsaturated π bonds of those atoms. The carbon spin polarization of A sublattice is much stronger than that of B sublattice, and the spin of A and B sublattices is antiparallel. The carbon atoms on the chain are also spin-polarized due to the strong interactions between these atoms. Our calculations show that there always exists the net spin magnetism 1.17–1.29 μ_B for the 5C