Spin thermoelectric effects in organic single-molecule devices

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ABSTRACT

The spin thermoelectric performance of a polyacetylene chain bridging two zigzag graphene nanoribbons (ZGNRs) is investigated based on first principles method. Two different edge spin arrangements in ZGNRs are considered. For ferromagnetic (FM) ordering, transmission eigenstates with different spin indices distributed below and above Fermi level are observed, leading directly to a strong spin thermoelectric effect in a wide temperature range. With the edge spins arranged in the antiferromagnetic (AFM) ordering, an obvious transport gap appears in the system, which greatly enhances the thermoelectric effects. The presence of a small spin splitting also induces a spin thermoelectric effect greater than the charge thermoelectric effect in certain temperature range. In general, the single-molecule junction exhibits the potential to be used for the design of perfect thermospin devices.

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1. Introduction

A molecule may be trapped between two gold electrodes to form a molecular junction. When a temperature difference exists between the two gold electrodes, the junction Seebeck coefficient can be measured at room temperature with a modified scanning tunneling microscope (STM) setup [1]. The pioneering experiment has inspired a considerable amount of theoretical research on the thermoelectric properties of molecular junctions [2–6]. Very recently, rapid development of spin detection technique has made it possible to measure the spin Seebeck coefficient in the metallic magnet [7]. This so-called spin Seebeck effect, which is also detected in ferromagnetic semiconductor [8] and magnetic insulator [9], provides an effective avenue to generate pure spin current without the charge current. Many theoretical studies on the spin thermoelectric effects in various systems have also been reported [10–17].

Graphene, the sp^2-hybridized phase of carbon, was first obtained by mechanical exfoliation in 2004 [18]. Soon after, it has been one of most promising materials for future high-performance devices due to its unique properties such as ultrahigh electron mobilities, superior thermal conductivity, and excellent optical properties [19–25]. Its application in real devices, however, is limited by the zero band gap. As a possible avenue to open the gap is to reduce its dimensionality, graphene nanoribbons (GNRs), with their localized electronic states along the edge directions, have become a focus of study in spintronics. The band theory of ferromagnetism shows that the spin configuration of ground state GRNs has a pair of opposite spins orientated along each of the ribbon edges [26, 27], which cancel out each other for a zero total spin to open up a band gap with spin degenerate. According to boundary geometry characteristics, GNRs can be divided into two groups: armchair GNRs (AGNRs) and zigzag GNRs (ZGNRs). Experimentally, the one-dimensionally periodic structure can be fabricated with either E-beam lithography [28], chemical method [29], mechanical method [30] or by unzipping multi-walled carbon nanotubes [31]. Recently, clean and perfect armchair/zigzag edges have also been fabricated with electron beam-initiated mechanical rupture or tearing in high vacuum [32]. In addition, when an in-plane homogeneous electric field is applied across ZGNRs, the half-metallic property—with the metallic nature for electrons with one spin orientation and the insulating property for electrons with the other spin orientation—is achieved [33]. The spins on the edges of ZGNRs can be arranged in the uniform orientation with a suitable magnetic field [34]. The band structure analysis shows that the ferromagnetic (FM) ZGNR behaves in a metallic way with magnetic property, which makes it possible for it to serve as the electrode material in spintronics [35,36]. Molecular dynamics simulation has also shown that ZGNRs and AGNRs are rather stable at room temperature when the edge carbons are passivated with hydrogen [37]. Very recently, Hossain et al. have successfully measured and characterized thermoelectric properties of GNRs, and the GNRs-based devices are found to well survive a temperature up to 450 K [38]. These facts endorse GNRs as legitimate candidates for perfect thermoelectric devices. By applying a temperature difference, one can drive electrons with different spin indices in opposite directions, which is attributed to

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an asymmetric electron–hole transmission spectrum for electrons with different spin indices [39].

Due to the similar chemical structures in the zigzag edges of GNRs and polyacetylene chain, the polyacetylene chain is easily linked to ZGNRs via covalent bonds [40]. In this paper, we explore the spin thermoelectric performance of a polyacetylene chain sandwiched between two ZGNR electrodes by using first principles calculations. For the FM ordering, the spin thermoelectric effect is obviously stronger than the charge thermoelectric effect, due to the presence of transmission eigenstates with up/down spin indices below/above the Fermi level, respectively. When the spin orientation on one side of the ZGNR is inverted (antiferromagnetic (AFM) ordering), the transmission probabilities near the Fermi level are greatly suppressed, and a transport gap appears. This would greatly enhance the thermoelectric effects. Meanwhile, a small spin splitting for transmission spectrum near the Fermi level is also observed, which results in a spin thermoelectric effect stronger than the charge thermoelectric effect in a wide temperature range. Our results also indicate that longer molecule is more promising for the design of perfect thermo-spin devices.

2. Computational methods

The molecule length is labeled with the number of the carbon atoms in the polyacetylene chain. At first, the polyacetylene chain consisting two ZGNR unit cells is fully relaxed with VASP software. One can then design the two-probe single molecule device with the help of the device studio software [42]. The spin-resolved electron transmission probability τ_σ, which represents the chance of the electron with energy ε and spin index $\sigma(=\uparrow, \downarrow)$ to make a transition from the left electrode to the right electrode via the molecule in between, can be calculated with the Landauer–Büttiker formula [43]

$$\tau_\sigma(\varepsilon) = Tr\left[\Gamma_\sigma^L G_\sigma^r \Gamma_\sigma^R G_\sigma^r\right](\varepsilon). \tag{1}$$

It can be worked out with a first principles package Nanodcal [44,45], which is based on the standard non-equilibrium Green's function combined with the density functional theory (NEGF-DFT) methods [46,47]. $\Gamma_\sigma^{L(R)}$ in Eq. (1) is the line-width function of the L(R) electrode, which can be calculated as $\Gamma_\sigma^{L(R)} = i\{\Sigma_\sigma^{L(R)} + [\Sigma_\sigma^{L(R)}]^+\}$, where $\Sigma_\sigma^{L(R)}$ denotes the spin-dependent retarded self-energy function from the contributions of the L (R) electrode. The parameter G_σ^r represents the retarded Green's function of the two-probe system, which could be obtained with $G_\sigma^r(\varepsilon) = [\varepsilon S_\sigma - H_\sigma - \Sigma_\sigma^L - \Sigma_\sigma^R]^{-1}$. S_σ is the overlap matrix from the central scattering and H_σ the Hamiltonian of the center molecule. The advanced Green's function G_σ^a is calculated by taking complex conjugate of the retarded Green's function G_σ^r. In the process of numerical calculations, the valence electronic orbitals are described by the double-ς basis sets. The local spin density approximation (LSDA) adopted is enough to describe the carbon-based materials. The mesh cut-off energy is 100 Ryberg, and the self-consistent calculations are completed when the energy tolerance becomes less than 10^{-4}. When a temperature difference ΔT is applied between left and right electrodes, a spin-dependent thermoelectric voltage ΔV_σ is induced on the condition that the electric current in the channel σ is zero. Once the spin-dependent transmission function τ_σ is worked out with Nanodcal package, the spin-dependent Seebeck coefficient can be calculated as [48],

$$S_\sigma = \frac{\Delta V_\sigma}{\Delta T} = -\frac{1}{|e|T}\frac{L_{1,\sigma}(\varepsilon, T)}{L_{0,\sigma}(\varepsilon, T)}, \tag{2}$$

and the spin-dependent electronic thermal conductance is

$$\kappa_{el,\sigma}(\varepsilon, T) = \frac{1}{h}\left[L_{1,\sigma}eS_\sigma + \frac{L_{2,\sigma}}{T}\right]. \tag{3}$$

Here the parameter $L_{\nu,\sigma}$ ($\nu = 0, 1, 2$) is calculated as

$$L_{\nu,\sigma} = \int d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon - \mu)^\nu \tau_\sigma(\varepsilon). \tag{4}$$

The charge voltage induced by the temperature difference can be written as $\Delta V_C = (\Delta_\uparrow + \Delta_\downarrow)/2$ and $\Delta V_S = (\Delta_\uparrow - \Delta_\downarrow)/2$ is the corresponding spin voltage. The charge and spin Seebeck coefficients are then defined as [48],

$$S_C = \frac{\Delta V_C}{\Delta T} = \frac{1}{2}(S_\uparrow + S_\downarrow) \tag{5}$$

and

$$S_S = \frac{\Delta V_S}{\Delta T} = \frac{1}{2}(S_\uparrow - S_\downarrow), \tag{6}$$

respectively. In addition, the charge and spin thermoelectric figure of merits (FOMs) are given as [48–50],

$$Z_C T = \frac{S_C^2(G_\uparrow + G_\downarrow)T}{\kappa_{el,\uparrow} + \kappa_{el,\downarrow} + \kappa_{ph}} \tag{7}$$

and

$$Z_S T = \frac{S_C^2(G_\uparrow - G_\downarrow)T}{\kappa_{el,\uparrow} + \kappa_{el,\downarrow} + \kappa_{ph}}, \tag{8}$$

respectively. Here G_σ is the linear conductance in the channel σ, which can be calculated with $G_\sigma = \frac{e^2}{h}L_{0,\sigma}$. κ_{ph} in Eqs. (7) and (8) is the phonon thermal conductance of the organic single-molecule device, which can be calculated with [51,52],

$$\kappa_{ph} = \frac{\hbar}{2\pi}\int_0^\infty d\omega \tau_{ph}(\omega)\frac{\partial f_{ph}(\omega)}{\partial \omega}, \tag{9}$$

where $\tau_{ph}(\omega)$ denotes the transmission probabilities of the phonons with the frequency ω, which can be obtained with a Landauer type equation [53]. $f_{ph}(\omega)$ in Eq. (9) is the Bose–Einstein distribution of heat carriers at the ZGNR electrodes.

3. Results and discussions

The two-probe spin thermoelectric device consists of two ZGNR electrodes bridged by a polyacetylene chain, forming a single-molecule device. The schematic diagrams of two different edge spin arrangements in ZGNRs are considered in this work. One has the uniform spin orientation in two zigzag edges [the FM spin configuration], as depicted in Fig. 1(a), and the other has the opposite spin orientations in two zigzag edges [AFM spin configuration], as depicted in Fig. 1(b). We also plot the spatial distribution of the charge difference between up-spin and down-spin electrons (spin density) for two different spin arrangements in Figs. 1(c) and (d), respectively. As the zigzag geometrical features at the molecule–electrode contact are well kept, so are the edge localized states. The π-conjugated organic molecule exhibits the same magnetic order as the edge carbon atoms of ZGNRs do. Fig. 1(e) displays the relaxed carbon–carbon bond lengths of the conjugated organic molecule, where the result shows a typically alternating oscillatory pattern from the molecule–electrode contact to the center region of the molecule. Meanwhile, the bond length distribution is found to show an axisymmetric pattern about the center of the organic molecule.

The spin-resolved transmission probabilities of the molecule devices for two different spin arrangements are shown in Figs. 2(d1) and (d2), respectively. When the spins on the edge carbon atoms of ZGNRs are arranged in uniform orientation [FM spin configuration in Fig. 1(a)], the transmission spectrum shows a