Spin-dependent thermoelectric properties of a magnetized zigzag graphene nanoribbon

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ABSTRACT

Spin caloritronics refers to generating spin current by thermal gradient. Spin caloritronics is an emerging new subfield of condensed matter physics concerned with coupled spin, charge, and energy transport in small structures and devices. In this paper, thermally induced spin transport in a magnetized zigzag graphene nanoribbon is explored. Using non-equilibrium Green's function (NEGF) method in a tight-binding model, a temperature gradient applied between the left and right nonmagnetic electrodes, as thermal reservoirs in a magnetized zigzag graphene nanoribbon model junction so that the flowing of the up-spin and down-spin currents in the opposite directions can be induced which may be modulated by tuning of the back gate voltage. Furthermore, some thermoelectric properties of the junction, such as the spin-dependent Seebeck effect, electrical conductance, electron thermal conductance, and thermoelectric efficiency (ZT) of the model evaluated. Our calculations for the thermoelectric properties of the magnetized zigzag graphene nanoribbon indicate that for the zigzag edge graphene nanoribbon, the spin-dependent ZT is greater than the ZT of the electric charge. This means that for applications of spin thermal transport, the use of the zigzag edge graphene nanoribbons is appropriate.

1. Introduction

Experimental data have clearly shown that organic molecules can serve as spacer for purposes of electronic transport [1-7]. In these experiments, spin polarized transport through magnetic molecular layers sandwiched between non-magnetic layers has been demonstrated for systems involving carbon nanotubes [1], other organic π-conjugated systems [2-5], molecular bridges [6] and self-assembled organic monolayers [7]. However, Graphene as an organic material has relatively weak spin-orbit interaction and weak hyperfine interaction, so that spin memory can be as long as a few seconds [8]. Such features make Graphene as an ideal material for spin-polarized electron injection and transport applications in molecular junctions. Furthermore, spin-polarized transport through organic molecules sandwiched between two contacts has also been investigated theoretically [9-11]. In addition to the charge transport, the thermal transport through the junctions has been investigated [12-14]. Thermoelectric effects result from the coupling between charge and heat currents in electric conductors. The Seebeck effect, for example, is the direct conversion of temperature differences into electricity [15]. However, despite decades of research on thermoelectric materials and appliances, the

efficiency of thermoelectric devices such as Peltier coolers and Seebeck thermopower generators has remained low. Spin caloritonics is a promising approach for increasing the efficiency and versatility of thermoelectric devices involves exploiting the spin of the electron, in addition to its charge and heat transport properties. It is hoped that spin caloritronics will lead to the design of new thermoelectric devices. Additionally, spin caloritronics provides a way to achieve the lower-energy consumption as well as improved performance in thermal energy conversion devices [16-19]. A recent important discovery of spin caloritronics is the observation of spin Seebeck effect by Uchida et al [20]. They found that the spin-polarized currents of up-spin and down-spin, which flow in the opposite directions, can be generated only from a temperature gradient, requiring no electrical bias [20,21]. It has been shown that Graphene has potential for thermoelectric devices, both theoretically and experimentally [22]. Cutting Graphene into a nanoribbon reduces its thermal conductivity and hence enhances its thermoelectric performance [23]. Therefore, it seems Graphene is a good candidate for designing the thermoelectric devices based on spin caloritronics. Considering the physical insights and promising prospects of Graphene nanoribbons for spin caloritronics

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applications, we investigated the thermoelectric properties of magnetized zigzag edge Graphene nanoribbons (MZGNRs). We demonstrate that the opposite spin currents can be generated in MZGNRs with a temperature gradient, rather than with a bias voltage. Additionally, a back gate voltage can be implemented to modulate the spin currents, which induces an operation similar to a thermal spin transistor with complete spin polarization [16,24]. Due to the long spin diffusion length and weak electron-phonon coupling in Graphene, the coherent transport of spin polarized electrons is assumed. In other words, two-channel (up-spin and down-spin) circuit theory in spintronics can be applied to study the magneto thermoelectric properties of the MZGNRs. However, the direct theoretical calculations of the spin-dependent thermoelectric transport in magnetic junctions based on two dimensional carbon sheets, to our knowledge, are still sparse, though the experimental studies on spin transport in magnetic junctions have yielded a plenty of results and applications [25,26]. It is therefore quite necessary to investigate the spin-dependent thermoelectric properties from theoretical different aspects. In this work, we considered a model junction as ZGNR/MZGNR/ZGNR in which MZGNR is a magnetized zigzag edge Graphene nanoribbon with finite size is sandwiched between two non-magnetic semi-infinite zigzag edge Graphene nanoribbons (ZGNRs) served as thermal reservoirs. We calculate the spin-dependent currents in the model junction based on Landauer formalism in the framework of non-equilibrium Green's function (NEGF) method [27,28]. Furthermore, we investigate the spin-dependent Seebeck effect which demonstrates that spin currents can be induced by a temperature bias. To proceed, the spin-dependent figure of merit evaluated which is a measure of the thermoelectric efficiency of the junction [29]. The model and computational method are described in Sec. 2, results and discussion are presented in Sec. 3 followed by conclusions in Sec. 4.

2. Model and the computational scheme

Figure 1 presents a simplified scheme of the studied nanostructure model. As mentioned before, a MZGNR with finite size is sandwiched between two non-magnetic ZGNR, which are the semi-infinite thermal reservoirs described by an effective self-energy function. The z axis is taken to be perpendicular to the surface of ZGNRs as the thermal electrodes and the x and y axes are parallel to the surface, as depicted in Fig. 1. The magnetic state of MZGNR can be controlled by an external magnetic field [28] or by the arrays of radicals where linked chemically to carbon atoms in the layer, so that the whole molecule in central region will have more up-spin (down-spin) than down-spin (up-spin) and hence possesses a magnetic moment proportional to the molecule length. Thus, stable all-carbon structure with the ferromagnetic interaction can be created [30]. Then, with the dominance of a type of spin and in the presence of a temperature gradient, it will be possible to flow a spin-polarized current through the junction by tuning of the back gate voltage. According to the model junction schematically shown in Fig. 1, the spin-

dependent thermal (electronic) conductance is mainly determined by the central part of the junction. Thus, the energy (electronic) structure of this part should be resolved in detail.

The Hamiltonian matrix for a typical junction such as ZGNR/MZGNR/ZGNR model in terms of sub-matrix Hamiltonians may be written as:

$$H = \begin{pmatrix} H_L & H_{LC} & 0 \\ H_{CL} & H_C & H_{CR} \\ 0 & H_{RC} & H_R \end{pmatrix} \tag{1}$$

where $H_{L(R)}$ is a one-band tight-binding approximation description of the left (L) and right (R) thermal reservoirs. H_c the Hamiltonian of the MZGNR, H_β with $\beta = L, R$ the Hamiltonian of left (right) reservoir and $H_{c\beta}$ the Hamiltonian of the coupling between the central layer and reservoirs within the tight-binding model have the following forms:

$$H_c = (\varepsilon_0 - \vec{\sigma} \cdot \vec{h}) \sum_i c_i^\dagger c_i + t \sum_{i,j} (c_i^\dagger c_j + c_j^\dagger c_i) \tag{2}$$

$$H_\beta = \varepsilon_0 \sum_i c_i^\dagger c_i + t \sum_{i,j} (c_i^\dagger c_j + c_j^\dagger c_i) \tag{3}$$

$$H_{c\beta} = t \sum_{i,j} (c_i^\dagger c_j + c_j^\dagger c_i) \tag{4}$$
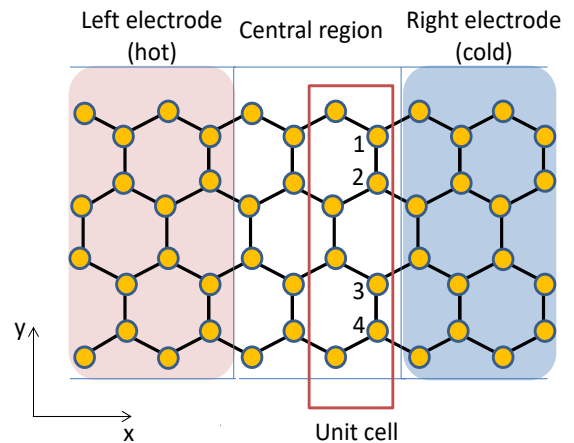
Fig. 1. Plot shows the schematic illustration of ZGNR/MZGNR/ZGNR model junction. The two electrodes are kept at different temperatures. The central region is under the effect of gate voltage.

where $c_i^\dagger (c_i)$ creates (destroys) an electron at site i. The hopping integral t is equal to $t = -2.5eV$ for the nearest-neighbors and zero otherwise. In addition, the term $-\vec{\sigma} \cdot \vec{h}$ is the internal exchange energy where $|\vec{h}| = 1eV$ and $\sigma = \uparrow, \downarrow$ denoting the molecular field at site i and the conventional Pauli spin operator, respectively. The retarded Green's function $G^r(E)$ is given by:

$$G_\sigma^r(E) = [(E + i\eta)I - H_c - \Sigma_\sigma^r(E)]^{-1} \quad (5)$$

where $\Sigma_\sigma^r(E) = \Sigma_L^r(E) + \Sigma_R^r(E)$ is the total self-energy which describes the effect of the left and right electrodes. Then, the electron transmission can be computed by the following equation for the non interaction system:

$$T_\sigma(E) = Tr[\Gamma_{\sigma,L} G^r \Gamma_{\sigma,R} (G^r)^\dagger] \quad (6)$$

$$\Gamma_{\sigma,\beta}(E) = i[\Sigma_\beta^r(E) - (\Sigma_\beta^r(E))^\dagger] \quad (7)$$

The function $\Gamma_{\sigma,\beta}(E)$ describes the line-width broadening resulting from the coupling of the central region to the electrodes. Therefore, the spin-dependent electronic transmission spectra of MZGNR are independent of the temperature, and the effect of temperature only appears in the Fermi distribution function for calculating the thermally-induced currents based on the Landauer formula:

$$I_\sigma = \frac{e}{h} \int T_\sigma(E)[f_L(E) - f_R(E)]dE \quad (8)$$

where $f_{L(R)}$ is the Fermi distribution function for the left (right) electrode and $f_L(E) - f_R(E) = \left[1 + \exp\left(\frac{E-\mu}{K_B T_L}\right)\right]^{-1} - \left[1 + \exp\left(\frac{E-\mu}{K_B T_R}\right)\right]^{-1}$ which is intimately related to the temperature of the electrodes. T_L and T_R are left electrode and right electrode temperatures respectively. Due to difference in the Fermi distributions, the carriers with energy higher than the Fermi energy flow from the left electrode (higher temperature) to the right one (lower temperature), resulting in electron current. Non equilibrium Green's function method is applied to get phonon transmission $T_{ph}(\omega)$, where ω is the phonon frequency. Afterwards, we use Landauer-Büttiker formalism to get quasi ballistic thermal conductance [31]:

$$k_{ph} = \frac{k_b^2 T_0}{h} \int_0^\infty dx \frac{x^2 e^x}{(e^x - 1)^2} T_{ph}\left(\frac{k_b T_0}{\hbar} x\right) \quad (9)$$

where k_B, h, and T_0 are Boltzmann constant, Planck constant, and absolute temperature, respectively.

Thus, with electronic transmission and thermal conductance at hand, we may calculate the spin caloritronic effects which can be characterized by spin-dependent thermoelectric properties of the junction via the following quantities [32-34]:

$$G_\sigma = e^2 L_{0\sigma} \quad (10)$$

$$k_{e,\sigma} = \frac{1}{T_0}\left(L_{2\sigma} - \frac{L_{1\sigma}^2}{L_{0\sigma}}\right) \quad (11)$$

$$S_\sigma = -\frac{1}{eT_0}\frac{L_{1\sigma}}{L_{0\sigma}} \quad (12)$$

where the transport coefficient $L_{n\sigma}$ given as [35]:

$$L_{n\sigma} = \frac{1}{h} \int T_\sigma(E)(E-\mu)^n \left[-\frac{\partial f(E)}{\partial E}\right]_{\mu,T} dE \quad (13)$$

The reference electrochemical potential μ and temperature T_0 are set as $\mu = \frac{1}{2}(\mu_L + \mu_R)$ and $T_0 = \frac{1}{2}(T_L + T_R)$, respectively. the ability of a material to efficiently produce thermoelectric power is usually described by power factor (pf) and the thermoelectric efficiency denoted by ZT. In spin caloritronics we can generalize this concept for the resulting charge and spin currents due to the temperature gradients separately. So the charge and spin power factor and thermoelectric efficiency for a magnetic system can be defined versus Seebeck coefficients as:

$$pf_{ch(sp)} = S_{ch(sp)}^2 G_{ch(sp)} \quad (14)$$

$$(ZT)_{ch(sp)} = \frac{\left|G_{ch(sp)}\right| S_{ch(sp)}^2 T_0}{k_{e,ch(sp)} + k_{ph}} \quad (15)$$

Where κ_{ph} is the lattice thermal conductance and:

$$S_{ch(sp)} = S_\uparrow + (-)S_\downarrow \quad (16)$$

$$G_{ch(sp)} = G_\uparrow + (-)G_\downarrow \quad (17)$$

$$k_{e,ch(sp)} = K_{e,\uparrow} + (-)k_{e,\downarrow} \quad (18)$$

3. Results and discussion

To investigate if the behaviors discussed above are robust under temperature changes, we calculated the spin-dependent currents at left electrode temperature (T_L) for particular values of the gate voltage within $V = \pm 0.1V$. Fig. 2 shows I_σ as a function of T_L for $T_R = 0K$. When T_L raises, $f_L - f_R$ broadens and some charge carriers are excited to the higher energies. The up-spin and down-spin currents increase with increasing T_L.
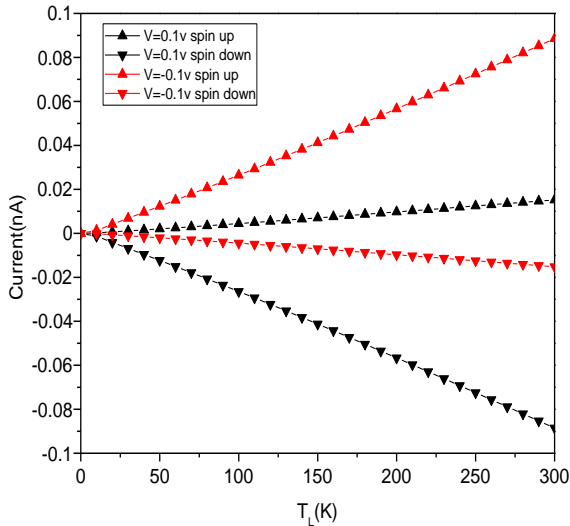
Fig. 2. (Colour online) Plot shows the spin-dependent currents versus the left electrode temperature (0-300 K) for different gate voltages ($V = \pm 0.1\,V$). The up-spin and the down-spin currents flow in the opposite directions and increase with increasing T_L.

In the absence of gate voltage, the spin currents with the same amounts flow in the opposite direction by increasing the electrode temperature. However, when a gate voltage is applied to the junction, the up-spin and down-spin currents do not have the same values, so that for the negative voltage $V = -0.1\,V$ the up-spin current and for the positive voltage $V = +0.1\,V$ the down-spin current is dominant. By increasing the gate voltage in the positive (negative) direction, the up-spin (down-spin) current reaches to the value of zero.

As shown in Fig. 3, for the negative gate voltages, the spin polarization is (+100%) and for the positive gate voltages, the spin polarization is (-100%). This means that for the negative gate voltages, the up-spin polarized current and for the positive gate voltages, the down-spin polarized current is flowed.
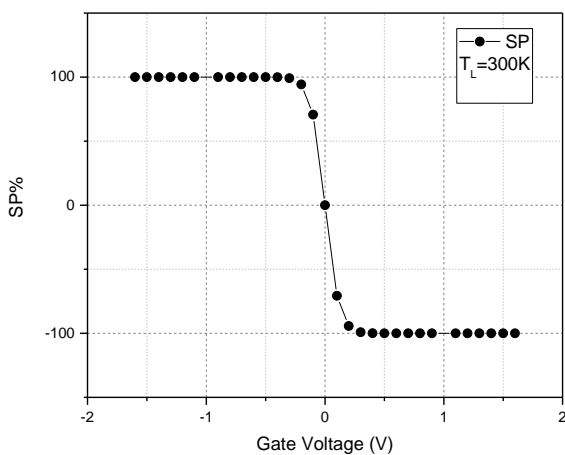
Fig. 3. Plot shows the polarization of spin currents as a function of gate voltage in the model junction.

To proceed, we investigate the spin-dependent Seebeck effect in the MZGNR model junction. When an electric current flows due to a temperature gradient,

because of the energy transport by electron, then a thermal current may be generated simultaneously. The thermal current can be converted to a thermopower voltage under open circuit conditions. Therefore, the thermopower or Seebeck coefficient (S) is used to characterize the relationship between an induced thermoelectric voltage and a temperature gradient. With $\mu_L = \mu_R = 0$, $T_R = 0\,K$ and $T_L = 300\,K$, Fig. 4 shows S_σ, the spin-dependent Seebeck coefficient as a function of gate voltage. In the given gate voltage range, both $S_\uparrow$ and $S_\downarrow$ have a maximum absolute value of around 1.8 mV/K. As shown in Fig. 4(a), S_{sp} is rather flat inside the spin gap and across the localized bands. This can be inferred from Fig. 4(b), where $S_\uparrow$ and $S_\uparrow$ have an almost constant difference due to the inversely symmetric Seebeck coefficients between two spin channels and their linear dependence on gate voltage in between two transmission peaks. Next, we explore the thermoelectric properties of the MZGNR. Fig. 5 indicates the thermal conductance and electronic conductance of the model junction, respectively. As shown in Fig. 5(a), the electron thermal conductance has a peak in $k_e = 0.19\,pW/K$ at gate voltage $V = \pm 1.17\,V$. In addition, the electronic conductance has a peak in $G = 530\,nS$ at gate voltage $V = \pm 0.7\,V$, as shown in Fig. 5(b). To proceed, we estimate the thermoelectric efficiency (ZT) of the MZGNR junction model. According to Ref. 31, we assume that the phonon thermal conductance is 1.6 nW/K for 4-MZGNR. $Z_{sp}T$ and $Z_{ch}T$ is as high as Gate Voltage= ± 0.74 V, as shown in Fig. 6, which can be attributed to the flatness of S_{sp} and a little variation of the thermal conduction. Hence, the coincidence of outlines of $Z_{sp}T$ and $(G_{sp})Z_{sp}T$ has a high peak compared to $Z_{ch}T$.
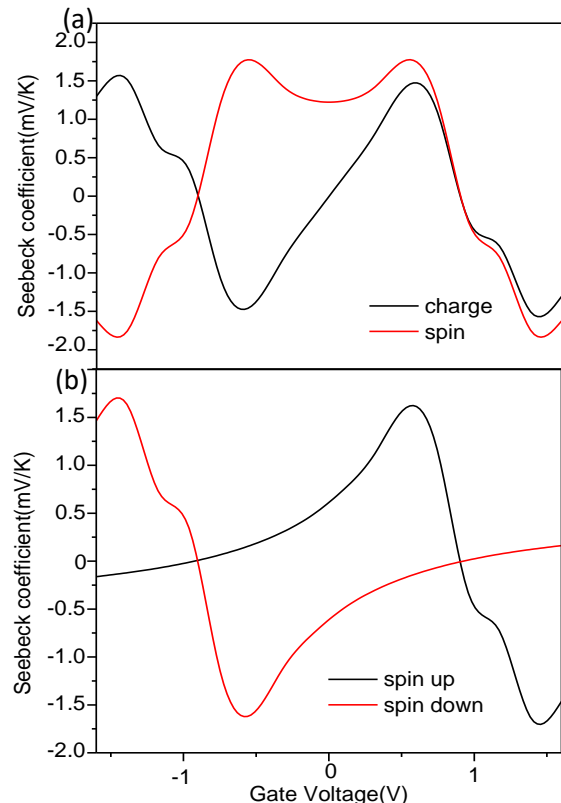

Fig. 4. (Colour online) Panel (a) shows the charge Seebeck coefficient (black solid line) and spin-dependent Seebeck coefficient (red solid line)

as a function of gate voltage. Panel (b) shows the Seebeck coefficient of up-spin (black solid line) and down-spin (red solid line) as a function of gate voltage in the model junction. In the given gate voltage range, both $S_\uparrow$ and $S_\downarrow$ have a maximum absolute value of around 1.8 mV/K.
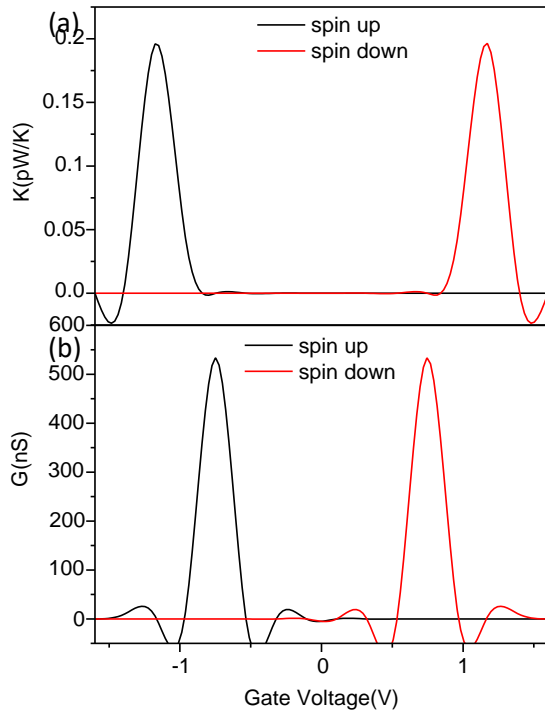
Fig. 5. (Colour online) (a) Electron thermal conductance for up-spin (black solid line) and down-spin (red solid line) currents as a function of gate voltage. The electron thermal conductance has a peak in $k_e = 0.19 pW/K$ at gate voltage $V = \pm1.17\,V$ (b) Electronic conductance for up-spin (black solid line) and down-spin (red solid line) as a function of gate voltage in the model junction. The electronic conductance has a peak in $G = 530\,nS$ at gate voltage $V = \pm0.7\,V$.
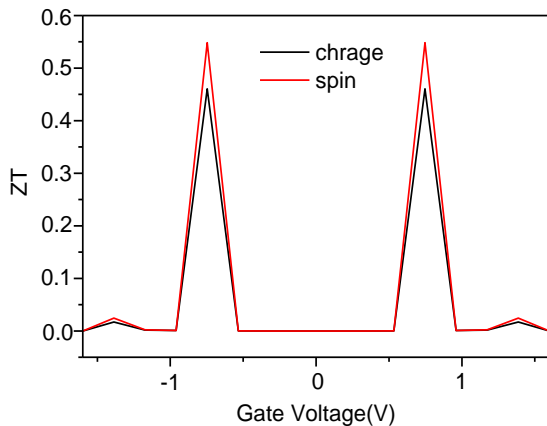
Fig. 6. (Colour online) Plot shows charge thermoelectric efficiency (ZT) (black solid line) and spin-dependent thermoelectric efficiency (ZT) (red solid line) as a function of gate voltage in the model junction. $Z_{sp}T$ and $Z_{ch}T$ are as high as Gate Voltage= ±0.74 V

4. Conclusion

In summary, we have investigated the spin caloritronic properties of a MZGNR using tight-binding model combined with the NEGF approach. We find that electronic transmissions through the MZGNR can be controlled by a temperature gradient between the left and right electrodes in a given gate voltage. A strongly spin polarized current can be generated in MZGNRs using temperature gradient instead of the external electric bias. The establishing and controlling the thermally induced spin polarized current in MZGNRs by the gate voltage has a significant impact on the performance of the thermally nanodevices. In addition, we investigated the spin-dependent Seebeck coefficient in the presence of the gate voltage in MZGNR junction model, leading to a suitable structure for usage in spin caloritronics. Furthermore, our calculations for the thermoelectric properties of the MZGNR indicate that for the zigzag edge Graphene nanoribbon, the spin-dependent thermoelectric efficiency (ZT) is greater than the thermoelectric efficiency of the electric charge. This means that for applications of spin thermal transport, the use of the zigzag edge Graphene nanoribbons is appropriate.

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