Edge Hydrogenation-Induced Spin-Filtering and Rectifying Behaviors in the Graphene Nanoribbon Heterojunctions

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ABSTRACT: By using nonequilibrium Green’s functions in combination with the density functional theory, we investigate the electronic transport properties of edge hydrogenated zigzag-edged graphene nanoribbon heterojunctions. Results show that a perfect spin-filtering effect with 100% spin polarization and a rectifying behavior with a ratio larger than 105 can be realized by dihydrogenation, which can also be modulated by changing the widths of the two component ribbons.

1. INTRODUCTION

Graphene, a 2D lattice of carbon atoms, has attracted extensive attention recently.1−10 In particular, many investigations have focused on the zigzag-edged graphene nanoribbons (ZGNRs) owing to its potential applications in spintronics. Many interesting physical properties, such as current rectification,11−13 negative differential resistance,14,15 spin filtering,11−13,16−18 large values of magnetoresistance,13,18−23 etc., have been found in ZGNR-based devices. Recently, Zeng et al.11 proposed that a ZGNR-based device could be designed as the [1,0] magnetic configuration, namely, one electrode is magnetized while the other is nonmagnetic. Their results showed that such a configuration possesses more advantages in applications than the conventional parallel [1,1] or antiparallel [1,−1] magnetic configurations. Therefore, on the basis of [±1,0] magnetic configurations, they studied the monohydrogen-terminated ZGNR device11 and the monohydrogen-terminated and oxygen-terminated ZGNR heterojunction.13 However, the performances of these devices (i.e., rectifying performance) still need improvement.

For most of ZGNR-based devices studied previously, the carbon atoms at the edges of ZGNRs were of sp2 type, namely, they were terminated by one hydrogen atom. Besides sp2 type, the carbon atoms at the edges of ZGNRs can also be converted into the sp3 type by adsorbing two hydrogen atoms.24−26 Recently, researchers demonstrated that the composition of sp2 and sp3 types at the edges of the GNRs can be easily controlled through the chemical potential of hydrogen,27,28 which means that the monohydrogen-terminated and dihydrogen-terminated graphene nanoribbon heterojunction can be fabricated in the experiment. However, no attempt has been made so far to study the transport properties of this heterojunction at finite bias voltages. Therefore, in the present work, we report a design of the monohydrogen-terminated and dihydrogen-terminated ZGNR heterojunctions and their performances. Our results show that this heterojunction can be designed as the [±1,0] magnetic configurations. Meanwhile, perfect spin-filtering transport and large rectification can also be observed. More importantly, its rectifying ratio (larger than 105) is several orders of magnitude higher than that of monohydrogen-terminated ZGNR device designed as a conventional [1,−1] magnetic configuration,12 indicating a better prospect for device application.

2. MODEL AND COMPUTATIONAL DETAILS

As shown in Figure 1, the monohydrogen-terminated and dihydrogen-terminated ZGNR heterojunctions can be formed using two component ribbons with different widths, called M-ZGNR-H/N-ZGNR-H2. The ZGNR-H (ZGNR-H2) indicates that the carbon atoms at both edges are terminated by one hydrogen atom (two hydrogen atoms), and M (N) is the number of carbon dimer lines across the ribbon width. We can thus investigate three different heterojunctions, namely, 6-ZGNR-H/6-ZGNR-H2, 8-ZGNR-H/8-ZGNR-H2, and 6-ZGNR-H/7-ZGNR-H2. For convenience, these three heterojunctions are denoted as M1, M2, and M3, respectively. Initially, we calculated the total energy and the magnetic moment of the spin configurations (nonmagnetic, antiferromagnetic, and ferromagnetic) of ZGNR-H2 with various widths. Results show that, when the N is less than 9, the total energies for the three spin configurations are almost the same, and their spin magnetic moments are zero.24 Therefore, the nonmagnetic state is the ground state of N-ZGNR-H2 (N = 6, 7, 8), and M1−M3 can be designed as the [±1,0] magnetic configurations. We choose the [1,0] magnetic configuration as a typical magnetic configuration to study the spin transport.

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properties of M1–M3. The [1,0] magnetic configuration, namely, ferromagnetic coupling (spins at both edges with the same spin directions) for left electrode and nonmagnetic state for right electrode, can be configuration of ground state for M1–M3 under the application of a magnetic field. Electronic transport properties of these systems are investigated by using the ATOMISTIX TOOLKIT (ATK) package, which adopts a nonequilibrium Green's function method in combination with density functional theory. In our transport calculations, a single-ζ plus polarization basis set is used for all systems to achieve a balance between the calculation efficiency and the accuracy. The core electrons are described by norm-conserving pseudopotentials, and the local-density approximation (LDA) is used for the exchange-correlation potential. The k-point sampling is 1, 1, and 100 in the x, y, z direction, respectively, and the cutoff energy is set to 150 Ry. The nonlinear current through the central scattering region is calculated using the Landauer formula:

\[
I_0(V_b) = \frac{e}{h} \int T_\sigma(E, V_b) \left[ f_l(E - \mu_l) - f_r(E - \mu_r) \right] dE
\]

where the \( \sigma = \uparrow \) (spin up) and \( \downarrow \) (spin down); \( \mu_l, \mu_r \) are electrochemical potentials of the left and right electrodes, and the difference of them is \( \mu_l - \mu_r = eV_b \). The energy region of the transmission spectrum that contributes to the current is referred to as the bias window.

\[
T_\sigma(E, V_b) = \text{Tr} \left[ \Gamma_l G^R \Gamma_r G^A \right]_\sigma
\]

where \( G^{R(A)} \) is the retarded (advanced) Green’s functions of the central region and \( \Gamma_l(r) \) is the contact broadening functions.

3. RESULTS AND DISCUSSION

Figures 2a–c display the current as a function of applied bias for all systems. The distinct features are as follows: (1) For M1, the spin-up electron easily flows through the system at positive bias, while it is almost forbidden at negative bias. However, the flow of the spin-down electron is opposite to that of spin-up electron. This finding means that the M1 can act as a dual spin filter or a dual spin diode. These properties are similar to that in the ZGNR-H device, but the performances in the M1 have been greatly improved. From the insets of Figure 2a, we can see that the corresponding spin polarization, \( \frac{I_+}{I_-} \), reaches 100%, and the maximum rectifying ratio for spin-up current can reach \( 1.8 \times 10^5 \). This rectifying ratio is quite comparable to that of the typical solid-state rectifier. (2) Similar transport characteristics are also observed in M2. It is found that the maximum spin polarization for M2 also reaches 100% at positive bias. However, the rectifying ratio for spin-up current is several orders of magnitude lower than that of the M1. (3) The \( I-V \) characteristics of M3 is different from that of the M1 and M2. Figure 2c shows that the obvious rectification happens only for the spin-up current, and its maximum ratio is about 160. Moreover, its maximum spin polarization is only about 80% at positive bias, showing an obvious decrease in magnitude compared with that of M1 and M2.

These interesting phenomena can be understood with the help of the transmission spectra and band structures of both left and right electrodes for M1–M3 at zero bias (Figure 3). From Figures 3a–c, we can see that the N-ZGNR-H \( (N = 6, 7, 8) \) are...
mirror operation, which is in good agreement with the reported functions of $\pi/C_0$ and $\pi/C_0$ for 6-ZGNR-H to 6-ZGNR-H$_2$, respectively. From Figure 3d, we find that the $\pi$ ($\pi^*$) subband has odd (even) parity under the $yz$ midplane mirror operation, which is in good agreement with the reported results. However, it is interesting to note that, when the edge carbon atoms are terminated by two hydrogen atoms, the case is opposite, namely, the $\pi$ ($\pi^*$) subband in 6-ZGNR-H$_2$ has even (odd) parity under the $yz$ midplane mirror operation. This implies that the electron transmission from $\pi$ ($\pi^*$) state of 6-ZGNR-H to $\pi$ ($\pi^*$) state of 6-ZGNR-H$_2$ is forbidden. This finding explains why we see a large transmission gap in M1. Moreover, the sharp spin-up transmission peak below the Fermi level in M1 should mainly originate from the coupling between the lower edge of the $\pi^*$ subband in 6-ZGNR-H and the upper edge of the $\pi$ subband in 6-ZGNR-H$_2$.

In order to explain the transport properties of the M1 and M2 at finite bias, in Figure 4, we give the spin-up transmission spectrum and the band structure of both the left (spin-up) and the right electrodes for M1 at $\pm 0.4$ V, respectively. When the positive bias is applied, the energy bands are shifted downward and upward for the left and right electrodes, respectively. We can see that, when the bias is 0.4 V, the transmission peak below the Fermi level at zero bias is shifted downward. Meanwhile, a new transmission peak appears near the left chemical potential due to the wider matching region between the $\pi^*$ subband of the left electrode and the $\pi$ subband of the right electrode. When the negative bias is applied, the shift of the energy bands for both electrodes is opposite to the positive case. If the bias is $-0.4$ V, the $\pi$ ($\pi^*$) subbands for both electrodes cannot couple with each other to contribute to the transmission due to parity mismatching of the orbitals with respect to $yz$ mirror, and thus the transmission coefficient is essentially zero in the energy region $[-1.0, 1.0 \text{ eV}]$. The obvious transmission coefficient cannot be observed in the energy region $[-1.0, 1.0 \text{ eV}]$ until the $\pi$ subband maximum in the left electrode touches the $\pi^*$ subband minimum in the right electrode. As the total magnitude of the transmission coefficients within the bias window at 0.4 V is significantly larger than that at $-0.4$ V, the rectification effect is obvious. According to the above analysis, it is expected that the transport characteristics of spin-down electron will be opposite to that of spin-up electron at positive and negative bias. Moreover, it is also easy to understand that the decrease of rectifying ratio of spin-up current in M2 should mainly result from the smaller band gap in 8-ZGNR-H$_2$ compared with that in 6-ZGNR-H$_2$, as shown in Figures 3a,b.

For M3, the outstanding characteristics is its rectifying performance. However, similar to 7-ZGNR-H$_2$, the $\pi$ and $\pi^*$ subbands of 7-ZGNR-H$_2$ have no definite parity. It is no doubt that the mechanism of rectification in M3 is different from that of M1 and M2. We can see from Figure 3c that though the energy bands of both left and right electrodes are available to match with each other in the energy region $[0.12, 0.26 \text{ eV}]$, the transmission coefficient (less than 0.02) is apparently depressed in this region. To understand the origin of transmission coefficient being depressed, in the insets of Figure 3c, we plot the spin-up local density of states (LDOS) at 0.22 and $-0.16 \text{ eV}$, respectively. Clearly, the spin-up states at both 0.22 and $-0.16 \text{ eV}$ are almost absent in the 6-ZGNR-H and 7-ZGNR-H$_2$ interface. This indicates that there exists a barrier and thus the transmission is due to electron tunneling between the 6-ZGNR-H and the 7-ZGNR-H$_2$, which is
The Fermi level is set to zero. This means that the localization of the LDOS of the 6-ZGNR-H and the 7-ZGNR-H₂ leads to the depression of transmission in the energy region \([0.12, 0.26 \text{ eV}]\). As a result, the distribution of the transmission coefficient is asymmetric with respect to the Fermi level.

In order to understand the rectifying performance in M3, we show a series of spin-up transmission spectra in Figure 5 at 0, ±0.20, and ±0.28 V, respectively. When the positive bias is applied, the transmission peaks below the Fermi level are shifted downward. Meanwhile, a new transmission peak appears near the bias window. However, when the negative bias is applied, as the band gap of the right electrode is shifted toward the negative energy direction following the shift of right chemical potential, the bias window is too narrow to include the transmission peak below the Fermi level. Furthermore, the transmission peak located above the Fermi level is only slightly shifted when the bias is increased from 0 to ±0.28 V. As a result, the current value at negative bias is determined by the depressed transmission region, and thus a strong rectification appears correspondingly. From these results, we can infer that the large rectification in M3 should mainly originate from asymmetric distribution of transmission spectrum with respect to the Fermi level, which results from the localization of the LDOS of 6-ZGNR-H and 7-GNR-H₂ in the corresponding energy region.²⁶

The length effect is always important in nanodevices. So we investigate the length dependence of electronic transport properties in M1 and M3 by increasing the number of carbon unit cells in the scattering region. Here we present the transport results when the number of carbon unit cells in the central scattering region are 8 and 10. Figure 6a shows that the perfect spin splitting effect with 100% spin polarization and a rectifying behavior with a ratio larger than 10⁵ can be observed. The spin-filtering and rectifying behaviors in M1 and M2 should result from the fact that, when the edge carbon atoms of ZGNR are terminated by two hydrogen atoms, the \(\pi^*\) subband has opposite parity with respect to the zy midplane mirror operation compared with that of ZGNR-H. However, the obvious rectifying behavior in M3 is due to asymmetric distribution of transmission spectrum with respect to the Fermi level, which roots in localization of the LDOS of 6-ZGNR-H and 7-GNR-H₂ in the corresponding energy region. The results also show that the lengths of heterojunctions do not affect the qualitative transport properties in M1 and M3.

4. CONCLUSIONS

In conclusion, we have investigated the electronic transport properties of ZGNR-H and ZGNR-H₂ heterojunction and found that perfect spin filtering effect with 100% spin polarization and a rectifying behavior with a ratio larger than 10⁵ can be observed. The spin-filtering and rectifying behaviors in M1 and M2 should result from the fact that, when the edge carbon atoms of ZGNR are terminated by two hydrogen atoms, the \(\pi^*\) subband has opposite parity with respect to the zy midplane mirror operation compared with that of ZGNR-H. However, the obvious rectifying behavior in M3 is due to asymmetric distribution of transmission spectrum with respect to the Fermi level, which roots in localization of the LDOS of 6-ZGNR-H and 7-GNR-H₂ in the corresponding energy region. The results also show that the lengths of heterojunctions do not affect the qualitative transport properties in these devices. These results may be useful in the design of high performance spin filter and spin rectifier.

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