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ARTICLE TYPE

Effect of edge-modification on transport properties of finite-sized Graphene nanoribbon based molecular devices

Zongling Ding,*[a] Zhaoqi Sun[a], Guang Li[a], Fanming Meng[a], Mingzai Wu[a], Yongqing Ma[a] and Xiaoshuang Chen[b]

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The transport mechanisms of several finite-sized graphene nanoribbon based junctions have been computationally investigated using density functional theory and Green's functional method. The acceptor type and donor type functional groups are introduced serving as the electrode connection and edge modification, respectively. There is orders of magnitude improvement for the electron transmission probabilities by introducing acceptor and donor groups. The electronic coupling mode, carrier concentration and distribution, molecular orbital can be manipulated by modification groups.

Introduction

In recent years, carbon based materials, such as graphene and carbon nanotubes have been widely concerned both on theoretically and experimentally due to their remarkable structural, electrical and chemical properties[1-6]. Graphene has been a hot topic and an important candidate in area of electronic applications because of the unique electronic transport properties[7-10]. Numerous research work about two dimension graphene, quasi-one dimensional graphene nanoribbons (GNR) and zero dimensional GNR slices have been reported[11-17]. With the development of experimental methods, people can carry through cutting graphene to different configurations to achieve different functional requirements[18,19]. Thus, dangling bonds appear at the edge carbon atoms of finite-sized GNRs. The passivation of the opening edge provides an effective way for the functional modification of GNR slice based materials[20]. There are many methods to saturate the dangling bonds[21-25]. When used as edge functional modification type, the modification atoms or groups can tune the electronic distribution and concentration, the hybridization and the symmetry of the systems[26], thus manipulate the molecular orbital. When used as connection types with electrodes, the edge modification groups can tune the coupling method and the contact conductance of the junctions[27]. Therefore, the edge modification is important to the transport properties of the finite-sized GNR based molecular devices.

In this article, several special edge modification group pairs have been considered in order to study the transport mechanisms of the finite-sized GNR based junctions. There are much valuable research work of modified GNRs based molecular devices have been reported. However, by introducing donor or acceptor groups to achieve edge passivation and electrode connection of the system at the same time is an effective and novel method of material modification. The carrier concentration and distribution have also been tuned. Furthermore, with the size became smaller, quantum effect become the main mechanism in electronic transport process. Therefore, further investigations are required for the effect of edge modification on the conducting ability of finite-sized GNR based molecular devices.

Theory and Calculation methods

The theoretical study of GNR-based nano-scale quantum devices has been researched at the first principle level. The geometry optimization and the electronic properties are performed by using the density-functional theory in B3LYP level[28, 29] with mixed basis set (the LanL2DZ basis set for electrode Au atoms, and 6-31G basis set for other atoms). Electron transport in the junctions can be described by electron scattering theory. Considering a simplest system of two electron reservoirs connected by one of the edge modified GNR slices, under the external bias, electrons in the source electrode will be driven to the drain electrodes. The whole process is dominated by electrons scattering through different scattering channels, which is the molecular orbital in the central molecule core systems. A generalized all-electrons first principle approach based on scattering theory and Green's functional theory has been used to study the electron transport properties in GNR based molecular electronic devices.

The electronic transport properties are calculated by using the quantum chemistry for molecular electronics (QCME) code[30-32]. The tunnelling current density from the source to drain can be obtained with the following formula,

$$i_{1\mathrm{D}} = \frac{2\pi \mathrm{e}}{\hbar}\int_0^{\infty}[f(E-\mathrm{e}V)-f(E)]T_{l'l}\,n^{\mathrm{S}}(E)\,n^{\mathrm{D}}(E)\,\mathrm{d}E \qquad (1)$$

where $n^S(E)$ and $n^D(E)$ is density of states of the source and drain at the energy level E, respectively. $f(E)$ is the Fermi distribution function $f(E)=\frac{1}{e^{[(E-E_f)/k_BT]}+1}$. $T_{l'l}$ is the transmission probability describing the scattering process from the initial state $|l\rangle$ to the final state $|l'\rangle$, which can be expressed as

$$T=\left|\sum_{\eta}\sum_{i,m}\sum_{K,K'}V_{\xi'_m K'}g^{\eta}_{K'K}V_{K\xi_i}\right|^2 \qquad (2)$$

where V_{AB} is the coupling energy between the layer sites A and B and $g^{\eta}_{K'K}$ represents the carrier-conduction contribution from the scattering channel ε_η.

Results and Discussions

Models

As we all know there are two types of edge termination for finite-sized GNRs, named zigzag (ZZ) and armchair (AC), respectively. In this article, we choose a 4×4 (4 carbon atoms on the zigzag edges and 4 carbon atoms on the armchair edges) prototype graphene nanoribbon slice with both zigzag and armchair edges as the basic molecular core. Here, all of the carbon atoms on the both sides of AC edges have been passivated by hydrogen atoms, and the carbon atoms on both sides of ZZ edges have been modified by functional group pairs. As mentioned in Ref.25, by introducing donor-acceptor group pairs on the ZZ edges of GNRs can achieve particular electronic properties. Furthermore, NO_2-NO_2 or NH_2-NH_2 functional group pairs which can change the concentration of carriers while keep the symmetry of the system is also interesting models. The donor/acceptor groups can achieve edge passivation and electrode connection of the system at the same time. Thus, four modification types of edge functional group pairs: Hydrogen-Hydrogen (H-H), donor type modified pair NH_2-NH_2 (D-D), acceptor type modified pair NO_2-NO_2 (A-A) and donor-acceptor groups modified pair NH_2-NO_2 (A-D) for the dangling bonds of the ZZ edge carbon atoms have been considered. The molecular device models are composed of edge modified GNRs sandwiched between Au(111) metallic electrodes. In this work, we use a triangle gold cluster connect with the edge-terminated groups of the molecular core (H, NH_2, NO_2) as the contact geometry in all model systems for simplicity. The schematic diagrams of the edge modified GNR-based molecular devices with different edge passivation are shown in figure 1. For simplicity, we define the junction system as follows, when Au electrodes connect to the AC edges, that is, we consider the transport properties along the crystallographic orientations of ZZ edges. The systems are defined as the H-H ZZ, A-A ZZ, D-D ZZ or A-D ZZ. The H-H AC, A-A AC, D-D AC or A-D AC for the junctions with Au electrodes connect to the ZZ edges. For example, the notation A-A ZZ indicates a junction constructed by connecting the AC edges of GNR slice (in which the ZZ edge carbon atoms are modified by NO_2-NO_2 functional pairs) with Au electrodes. There are two main effects of the modified group pairs: one is that it serves as edge functional modification groups, and another is as the connection between molecular core and Au electrodes. The electron transport properties along the two directions of ZZ and AC edges of the junctions are performed, respectively.

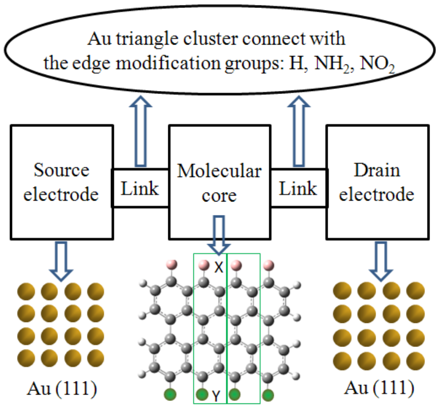

Figure 1. The schematic diagrams of the edge modified GNR-based molecular devices with different edge passivation. X and Y stands for the edge passivation type.

The effect of edge-modification on the transport properties of 4x4GNRs-based junctions

It is known that the conductance of molecular devices can be divided into two parts. One depends on the molecule-electrode interface and another depends largely on the molecular core. For the X-X ZZ model systems (X stands for the decoration type of the ZZ edge carbon atoms, X= H, A, D), the carbon atoms on AC edges have been passivated by hydrogen atoms in all the junctions, the functional pairs (H-H, A-A, D-D or A-D) on the ZZ edge carbon atoms serve as the edge-modification pairs. That is, four junctions have been considered with the same connection type and different edge modification type. Edge modification pairs can change the carrier concentration of the system. The carrier distribution in the frontier molecular orbitals (MOs) of the GNR slices can be changed, and thus the electronic and transport properties of the GNR slices-based devices can be tuned. So in this part, we focus on the effect of edge-modification on the transport properties. The calculated density of states (DOS), quantum conductance (G/G_0, where $G_0=2e^2/h$ is the conductance quantum unit and bias voltage=2V) and electron transmission probabilities (T) are shown in figure 2, respectively.

From fig.2 (a)-(d), we can observe that with introducing the donor/acceptor groups, the DOS near the Fermi energy increase about two or three times than that of the H-H ZZ system. While the DOS for A-D ZZ system near the Fermi energy decrease because donor-acceptor pair groups inject electron and hole simultaneously, providing the equilibrium distribution of carriers. The electrons of the four systems are delocalized, thus can contribute to improve the electron transport probabilities. From fig.2 (e)-(h), one can see that the transmission probability of A-A ZZ, D-D ZZ and A-D ZZ systems is much higher than that of the H-H ZZ system. There are several obvious peaks of the transmission probabilities in some energy region. New peak indicate the MOs at this energy region can be used as the conducting channel. Comparing with the pure hydrogen passivated system, the first strong peak of transmission probabilities is shift to lower energy region, which indicate that the junction can achieve resonant tunnelling (showing large conductance or current) at lower bias voltage. The A/D pair causes new peaks of transmission probability at some energy regions, providing more conducting channels. Therefore, the transmission of the A/D group modified systems is much stronger than that of the H-H system. The transport properties of the nanomolecular devices depend on the transmission probability and the DOS. Due to finite size effect, the curves in fig.2 (i)-(l) show that obvious quantum conductance are obtained in the four systems. The conductance stairs occurs at the positions, corresponding to a peak of the DOS and T. The coincidence between the peak position of the DOS, T and the conductance stairs indicates a resonant tunnelling process in the junctions. Comparing the four modified mechanisms, resonant tunnelling process is found in all the junctions, while the resonance level of each system are obvious differences. By introducing donor/acceptor groups, the conductance of D-D ZZ and A-D ZZ systems has order of magnitude increase under lower bias voltage. As shown in fig.2 (k), the conductance of A-A ZZ system is smaller under low bias voltage. There are large increases until the bias voltage increase to about 2.4V, that coincidence with the results in fig.2 (g) and fig.4 (a). The Fermi energy of the electrode can be tuned by source and drain voltage. With increasing the bias voltage, more molecular orbital can be opened to serve as electron transport channels. Thus, the conductance can be increased under higher bias voltage.

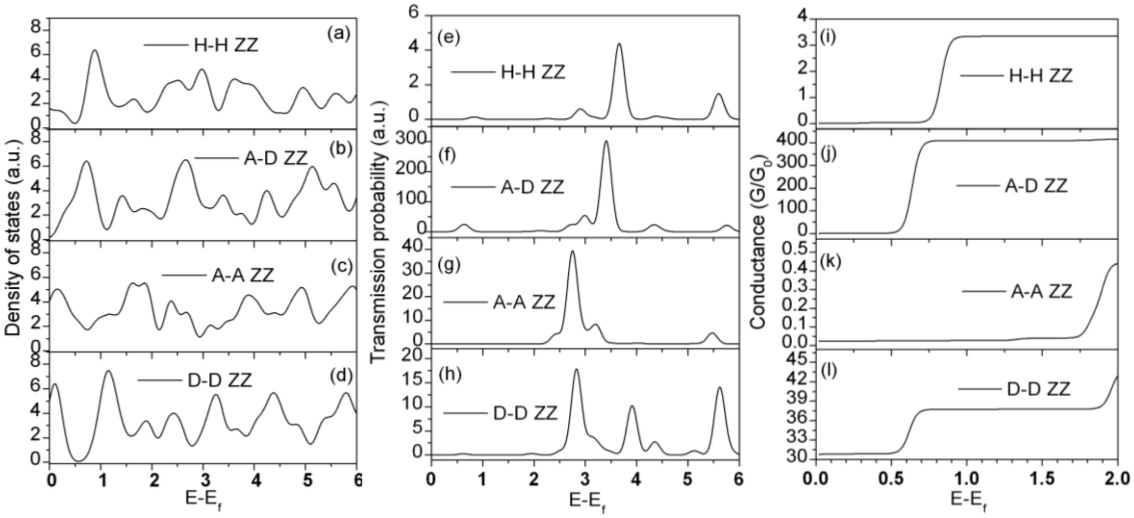

Figure 2. The density of states (DOS), transmission probability and quantum conductance (plot as G/G0 with G0=2e2/h being the conductance quantum, bias voltage=2V) curves of H-H ZZ, A-D ZZ, A-A ZZ and D-D ZZ 4×4 edge modified GNR-based junctions.

The results of the isodensity of molecular orbits show that when the edge carbon atom is passivated by hydrogen atoms, sp2-like types of edge bonds are found. Hydrogen atoms do not change the sp2 hybridization of the systems. But, when the edge carbon atoms are modified with NH_2 or NO_2 groups, the degree of freedom in the vertical plane may cause sp2-sp3 re-hybridization at the edge bonds. On the one hand, the donor/acceptor functional groups can introduce sp2-sp3 re-hybridization; on the other hand, they change the carrier concentration and distribution of the GNR slices. In particular, for the A-D pair system the NO_2-NH_2 pair groups break the inversion symmetry of the slices and also keep the equilibrium distribution of carriers. Furthermore, in the finite-sized GNR slices, the electronic properties such as the molecular orbital and the electron distributions can be tuned by the finite size effect. These mechanisms combined to tune the MOs of the GNR slices, and thus the transport properties of the junctions are changed. It is worth mentioning that for the junction models considered in this part, Au electrodes are connected with the molecular core through hydrogen atoms. This actually has a large contact resistance. Therefore, if one choose other atoms with small contact resistance (such as sulphur atom), the conductance should increase significantly.

The effect of connection type on the transport properties of 4x4GNRs-based junctions

In this part, based on the X-X AC model systems, we focus on the effect of electrode connection type on the transport properties. For the X-X AC systems, the functional pairs (H-H, A-A, D-D or A-D) on the ZZ edge serve as electrode connection groups, the hydrogen atoms on AC edges serve as edge passivation. That is, four junctions have been considered with the same edge modification type and different connection type. The acceptor/donor functional pairs can tune the coupling mode between the molecular core and Au electrodes, and thus control the connection conductance of the GNR slices-based molecular devices. The calculated density of states (DOS), quantum conductance (plot as G/G_0 and bias voltage=2V) and electron transmission probabilities (T) are shown in figure 3, respectively.

Comparing with H-H pair, new DOS peaks appear near the Fermi level because of the introduction of acceptor/donor functional groups. It is clearly shown in fig.3 (a)-(d). These new peaks indicate that the electronic coupling between Au electrodes and molecular core are much stronger by using the functional group NH_2 or NO_2 as connection. Thus, the contact conductance will be greatly enhanced. From the transmission probability curves shown in fig.3 (e)-(h), one can see that the T of A-A AC, D-D AC and A-D AC systems is about one order of magnitude higher than that of the H-H AC system. From the G-V curves in fig.3 (i)-(l), one can see that all of the four junctions exhibit significant quantum conductance and resonant tunnelling effect. The conductance stairs also occurs at the peak positions of the DOS and T curves. The first obvious stair of quantum conductance of the A-A AC, D-D AC and A-D AC systems is shift to lower energy region, which indicate that the electrons can be exited and achieve resonant tunnelling at lower bias voltage.

The overall conductance has been improved especially at lower energy regions. Comparing with the ZZ systems (NH_2 and NO_2 serve as edge functional modification groups), the effect of NH_2 and NO_2 groups on the T are mainly at low energy regions near the Fermi level when they are used as electrode connection types.

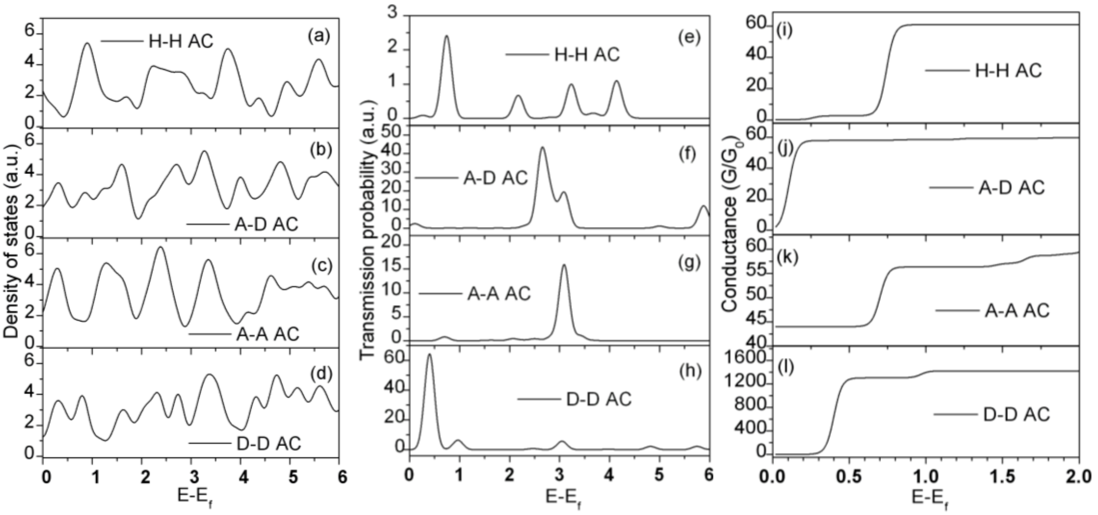

Figure 3. The density of states (DOS), transmission probability and quantum conductance (plot as G/G0 and bias voltage=2V) curves of H-H AC, A-D AC, A-A AC and D-D AC 4×4 edge modified GNR-based molecular devices.

The comparison of transport properties for ZZ and AC systems

In order to compare the transport properties of the AC and ZZ systems, we choose two junctions as example: A-A ZZ and A-A AC. In these two junctions, acceptor type functional groups NO2 have been considered as the edge modification and connection types, respectively. It is known that the transport properties can also be tuned by the source-drain bias voltage, so we further studied the conductance and current under 6V bias. The current-voltage, quantum conductance (plot as G/G0 and bias voltage=6V), DOS and transmission probability curves of A-A ZZ and A-A AC 4×4 edge modified GNR based junctions (the solid and dashed lines correspond to the left and right axes, respectively) are shown in figure 4.

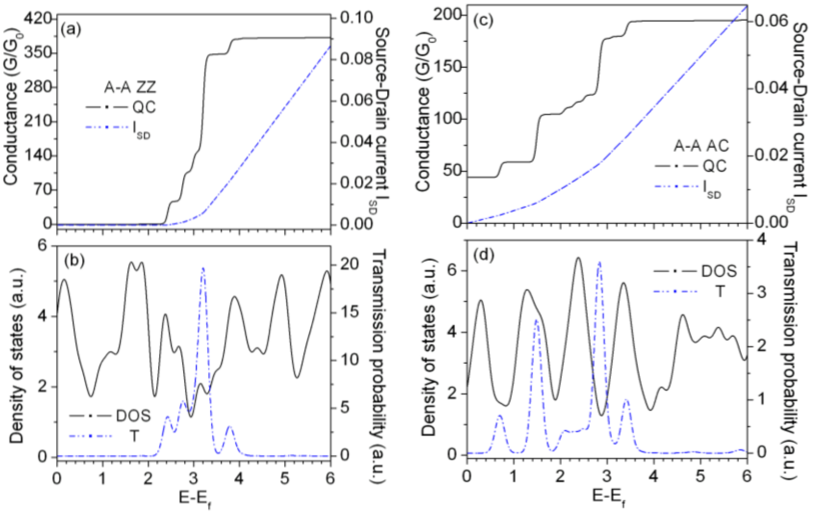

Figure 4. The current-voltage, quantum conductance (plot as G/G0 and bias voltage=6V), DOS and transmission probability curves of (a) and (b) for A-A ZZ and (c) and (d) for A-A AC 4×4 edge modified GNR -based junctions (the solid and dashed lines correspond to the left and right axes, respectively).

Compared with that of 2V bias, in 6V case new peaks of the transmission probabilities appear at larger energy region and the quantum conductance is increase obviously. The Fermi energy of the electrode can also be tuned by source and drain voltage. More electrons can be excited and more molecular orbital can be opened with the increase of bias voltage. Thus, there are more channels for the electron transport, and then the conductance is increased. From fig.4 (a) to (d), quantum conductance and nonlinear current characteristic are shown obviously. The coincidence of the conductance stairs, inflection point of current and the peak position of DOS and T confirm the resonant tunnelling mechanism discussed above. The conductances of the two systems have significant differences at low-energy region near the Fermi level: A-A ZZ system show a large gap while A-A AC system has a certain conductance. For the ZZ system, the connection type between Au electrodes and hydrogen atoms cause a large energy barrier. For the AC system, there are large electron coupling between Au electrodes and NO_2 groups. Furthermore, the edge carbon atoms arrangement of the GNR slices may partial influence the electron coupling and potential barrier. The overlap of electron cloud between carbon atoms on the zigzag edge is larger than that of the armchair edge. Therefore, ZZ systems which have larger contact resistance need larger energy to run over the potential barrier. As further evidence, the isodensity of molecular orbits also have been studied. The results further indicate that the overlap of electron cloud between Au electrodes and NO_2 groups are larger than that of H-H systems. The overall electron isodensity of the donor/accepter modified systems are more delocalized. In short, the transport properties of the junction are sensitive to the functional groups both serve as edge-modification and electrode connections. By effectively combining the two methods, the quantum conductance can be improved significantly.

Conclusions

In this paper, the 4×4 finite-sized graphene nanoribbon slices are chosen as the prototype structure. In order to understand how the acceptor/donor (NO_2/NH_2) functional groups have effect on the electronic structure and transport properties of finite-sized GNR slices, several edge functional modification types have been considered. We focus on two series of GNR-based molecular devices: one for the functional groups serve as edge modification, the other is the functional groups serve as electrode connection types. The contact conductance and overall conductance are sensitive to the connection and modification types. Comparing with the pure hydrogen systems, the quantum conductance and electron transmission probabilities have orders of magnitude improvement by introducing acceptor/donor groups. In practical applications, if one effectively combining the two methods by choosing atoms or groups with small contact resistance and better functional edge modification, the quantum conductance should increase significantly.

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[a] *School of Physics and Material Science, Anhui University, Jiu Long Road 111, Hefei, China, 230601. Fax: +86-551- 6386 1257; Tel: +86-551-6386 1257; E-mail: zlding@ahu.edu.cn*

[b] *National Lab. of Infrared Physics, Shanghai Institute for Technical Physics, Chinese Academy of Sciences, Yu Tian Road 500, Shanghai, China, 230083. Fax: +86-21-6583 0734; Tel: +86-21-3505 2062; E-mail: xschen@mail.sitp.ac.cn*

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