Manipulation the Transportation Properties of Benzene Molecules via the Connected Transition Metal Atoms

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ABSTRACT: The first principles based on density functional theory and non-equilibrium Green method, we try to manipulate the transport properties in molecule consisting of two phenyl-rings via the connected transition metal atoms. The molecule is put between two ZGNR electrodes and the connected transition metal atoms Co, Fe, Mn and Cr are considered. We find that the current across connected transition metal atom Cr system is quite smaller than those across other connected transition metal atoms, and then less attention is paid to the transport properties of Cr connected benzene molecules system. In the parallel and anti-parallel configurations of Co and Fe connected transition metal atom systems, negative differential resistance is found, while in the anti-parallel configuration of Mn connected transition metal atom system, no negative differential resistance is found. At low biases, magnetic resistance happens in Co, Fe and Mn connected atom systems. Spin filtering effects are obtained. Proper analyses are given to explain the above results. In addition, in the above four types of transition metal atom connected systems, the current is too small in Cr connected case, the stability is not good in Fe connected case, and no fine rectification in the anti-parallel configuration. So Co connected case is the best choice.

1 INTRODUCTION

Recently, great attention has been paid to the one dimensional sandwich like constructed with transition metals (TM) and organic molecules, e. g., the simplest organic molecules benzene (Bz=C6H6) due to their one-dimensional structures, peculiar properties, and potential applications. Studies have presented that transport properties of such one dimensional wires strongly depend on both TM atoms and species of organic molecules. For example, [V(Bz)]\textsubscript{∞} and [Mn(Bz)]\textsubscript{∞} are ferromagnetic half-metals, whereas [Cr(Bz)]\textsubscript{∞} is a nonmagnetic insulator. Furthermore, no magnetic moment appears in [Mn(Cp)]\textsubscript{∞} (Cp = cyclopentadienyl, C5H5), while [Cr(Cp)]\textsubscript{∞} and [Fe(Cp)V(Cp)]\textsubscript{∞} have ferromagnetic ground states. But no systematical study has
been done. So it is of great interest in studying the electron transport through one dimensional sandwich like constructed with transition metals (TM) and organic molecules for the purpose of using this type of molecules as components in molecular-scale circuit, which can greatly decrease the size of present electron devices, while simultaneously increase the working velocity of electron device. In recent years, lots of works related to organic molecular devices have been done and many interesting phenomena based on organic molecular devices have been attained. For example, molecular rectifiers, switchers and transistors, spin filtering effects, magnetic resistance, which is the properties of classical electron device, have been designed and investigated widely in sandwich like constructed with transition metals (TM) and organic molecules. Previous studies showed that the conductance of the phenyl rings is influenced significantly by the conformation, and therefore, the phenyl rings can show the switching effect by changing the conformation such as rotating the ring from coplanar case to perpendicular case. For example, in the year 2007, the spin-polarized transport properties of the 1,12-tri-benzene-dithiolate molecule coupled to two magnetic nickel contacts have been studied, and the magneto-transport properties were found to be very sensitive to deformations of one of the three benzene rings is rotated from the equilibrium position. In our present work, we found magneto-resistance and fine spin filtering effects in a device of Co-phthalocyanine connected to two zigzag graphene nanoribbon electrodes (ZGNR). Since the graphene sheet was fabricated experimentally in 2004, lots of studies reveal that the ZGNR is a good candidate for electrodes in spintronic devices. The zigzag-edged GNRs can be non-magnetic, antiferromagnetic or ferromagnetic states depending upon the external means. Under an external magnetic fields, two electrodes can point in the same or opposite direction, the ZGNR electrodes can show the (P) [1,1] or antiparallel (AP) [1,-1] spin configuration. Besides, dual spin filtering effect was shown in 8-ZGNR (the number 8 indicates the width of the ZGNR) but not in a 7-ZGNR, which can be used for devising some molecular devices like molecular bipolar spin diodes. Further, the spintronic molecular device based on two phenyl rings connected by different TM has not been reported yet.

So in present work, we study the transport properties in the molecule of two phenyl-rings connected by different TM atoms by first principles. Interesting transport properties like NDR, rectification, magnetic resistance and spin filtering effects are obtained in the designed molecule. The current across connected transition metal atom Cr system is quite smaller than those across other connected transition metal atoms. In the parallel and anti-parallel configurations of Co and Fe connected transition metal atom systems, negative differential resistance is found, while in the anti-parallel configuration of Mn connected transition metal atom system, no negative differential resistance is found. At low biases, magnetic resistance happens in Co, Fe and Mn connected atom systems. Spin filtering effects are obtained. However, in the above four types of transition metal atom connected systems, the current is too small in Cr connected case, the
stability is not good in Fe connected case, and no fine rectification in the anti-parallel configuration. So we think the Co connected case is the best choice.

Figure 1. (Color online) The schematic diagram of the hetero-junction of TM atom connected two phenyl rings molecule sandwiched between 4-ZGNR electrodes. The TM atom can be Co, Fe, Mn, or Cr, respectively. The direction Z is the transport direction and X is the direction of GNR width. The letters L, C and R represent the left electrode, the scattering central region and right electrode, respectively.

2 SIMULATION MODEL AND CALCULATION METHOD

In the Fig. 1, we show the proposed molecular a two-probe system: transition metal atoms connected two phenyl-rings sandwiched between two 4-ZGNR electrodes and the connected TM atoms can be Co, Fe, Mn or Cr, respectively. The number 4 indicates the width of the ZGNR. The N atoms help to anchor the phenyl ring to the metal contact. Certainly, our conformation has been tested in both 8-ZGNR and 4-ZGNR, and results reveal that the transport properties are almost the same. And here we consider the 4-ZGNR as our electrodes. In order to eliminate the interaction between ZGNRs in neighboring cells, we modeled a supercell with a large enough vacuum layer in x and y directions. The molecular junction is divided into three parts: left electrode, scattering central region and right electrode. The central region is indicated by two red lines and both the left and right electrodes are described by a supercell with two repeated ZGNR unit cells along transport direction. The magnetic fields can be set in the same or opposite direction at two electrodes which can show the parallel (P) or antiparallel (AP) spin configuration.

The geometric optimization and spin-resolved electron transport properties are calculated by a developed first-principles software package Atomistix ToolKit, which is based on the spin-polarized density-functional theory combined with non-equilibrium Greens functions. In our calculations, the core electrons are described by norm-conserving pseudopotentials, and the local spin density approximation (LSDA) with the Perdew-Zunger exchange-correlation
potential is employed. Moreover, a cutoff energy of 150 Ry and a Monkhorst-Pack k-mesh of (1, 1, 100) are chosen to achieve the balance between calculation efficiency and accuracy. A single-$\zeta$ polarized (SZP) basis set is adopted for electron wave function and the convergence criterion for Hamiltonian and the electron density are $10^{-5}\text{eV}$. The structures of every single phthalocyanine molecules are optimized firstly, and then are optimized in the environment of two-probes, respectively. All the structures are fully relaxed using quasi-Newton method until the force tolerance of 0.02 $eV/\text{A}$ is reached. Details of the calculation method can be seen elsewhere.

3 RESULTS AND DISCUSSIONS

Fig. 2 shows the total current $I$ versus bias voltage $V$ for the four types of TM atom connected systems under two external magnets, P and AP. The total current for the P case is much bigger than that for the AP case for the four different TM atom connected systems at low biases as can be seen from Fig. 2. So magnetoresistance happens. However, the current across connected transition metal atom Cr system is quite smaller than those across other connected transition metal atoms. So it is not proper for the design of real molecular devices. In addition, for the Co, Fe and Mn connected atom systems, the current increases quickly with the increase of the applied bias at the beginning, while with the continuing increasing of bias, the current starts to decrease quickly. And then fine NDR are obtained. Although the I-V curve of Fe and Mn connected systems have the same tendency as that of Co connected system, the stability of Fe is not good.
and the rectification and NDR effect is not better than that of Co connected system. And when the width of the ZGNR increases, the transport properties keep well. So the transport properties will not be influenced by the width of the ZGNR electrodes.

We also study the spin-resolved transport properties for the four types of TM atom connected systems as shown in Fig. 3. Dual spin filtering effect happen in the P and AP configurations of Co and Fe connected system, and in the P configuration Mn and Cr TM atom connected systems. And spin filtering effects also happen at the negative biases in AP configurations of Mn and Cr TM atom connected systems. So the TM atom connected systems can be used as spin filters.

Figure 3. (Color online) The spin-resolved I-V curves for the four types of TM atom connected molecular systems. (a, e) for TM Co atom connected two benzene rings system for (b, f) TM Fe atom connected two benzene rings system, (c, g) TM Mn atom connected two benzene rings system, (d, h) TM Cr atom connected two benzene rings system. The left are that for the P configuration and the right are that for the configuration. The black line indicate the spin up current and the red line indicate the spin down current.

In the following, we give explanation via transmission spectra to the above useful phenomenon. The current through the system is obtained by integrating the transmission function in the bias window using the Landauer-Büttiker formula: where \( h \) is the Planck’s constant, \( e \) is the electron charge, \( f(E, \mu_L) \) is the Fermi-Dirac distribution. And \( \mu_L \) and \( \mu_R \) are electrochemical potentials of the left and right electrodes: \( \mu_L = E_f - eV_b \) and \( \mu_R = E_f + eV_b \) under the applied bias \( V_b \). So
the value of the current depends on the transmission coefficients in the bias window, which further depends on the coupling between the central region and the electrodes.

So we show the transmission spectra for the P configuration of TM Co atom connected system and for the AP configuration of TM Mn atom connected system at the bias of 0.3, 0.4, 0.5 V in Fig. 4 and Fig. 5, respectively. The above three selected biases are good representative bias that can
demonstrate the origin of rectification and spin filtering effects. As can be seen from Fig. 4 that the spin down transmission for TM Co atom connected two benzene rings system is nearly zero at the effective bias window, while the spin up transmission in the bias window shows transmission peak (see Fig. 4). So fine spin filtering effect happens in the TM Co atom connected two benzene rings system. The same transmission trends happen for the AP configuration of TM Mn atom connected two benzene rings system as shown in Fig. 5. And for P case of the TM Co atom connected two benzene rings system, the transmission peak decreases quickly in the bias window with the bias increasing from 0.4 V to 0.5 V, which lead to NDR. However, the transmission peak for the AP configuration of TM Mn atom connected two benzene rings system decrease little, so there is no obvious NDR.

4 SUMMARY

In the manuscript, we studied the transport properties in molecule consisting of two phenyl-rings via the connected transition metal atoms by the first principles based on density functional theory and non-equilibrium Green method. We demonstrated that the current across connected transition metal atom Cr system is quite smaller than those across other connected transition metal atoms, and then less attention was paid to the transport properties of Cr connected benzene molecules system. NDR is found in the parallel and anti-parallel configurations of Co and Fe connected transition metal atom systems, while in the anti-parallel configuration of Mn connected transition metal atom system, no negative differential resistance is found. At low biases, magnetic resistance happens in Co, Fe and Mn connected atom systems. Spin filtering effects are obtained in the four types of TM atom connected system. Analyses via transmission spectra were give to explain the above results. In addition, the current is too small in Cr connected case, the stability is not good in Fe connected case, and no fine rectification in the anti-parallel configuration. So Co connected case is the best choice.

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