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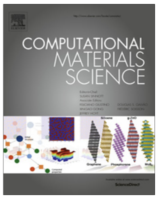

Radical based molecular transport system as good molecular spintronics device predicted by first-principles study

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ABSTRACT

Using a first-principles approach based on non-equilibrium Green's functions combing density functional theory, the transport properties of "radical-σ-radical" molecule sandwiched between two gold leads are investigated. The strong negative differential resistance (DNR) effect and spin filtration are obtained. We also find that the bias can manipulate the spin current sign and the magnetization configuration, which indicates that such molecular transport system (TS) has strong magnetoelectric effect and promises potential applications in the field of molecular spintronics in the future.

1. Introduction

Recently, one of important topic in chemistry [1–5] is molecular spintronics because it combines the merits of molecular electronics [6] and spintronics [7]. As a new and promising field that studies the spin transport properties in molecular systems, molecular spintronics has potential applications such as magnetic recording and memory devices [8–19]. To find appropriate materials for molecular spintronics is one of significant mission for researchers. As open-shell molecules composed of light elements, high spin organic radicals are good materials for molecular spintronics due to weak spin-orbit couple and hyperfine interactions. Many investigations demonstrate that the organic radicals are used in spin filters [20,21], batteries [22–25], assisted materials for production of high-quality graphene [26], building blocks for functional molecular materials [27], organic light-emitting diodes [28], half-metals [29], *etc.*

Motivated by the researches mentioned above, here, we perform a first-principles calculation on a stable organic radical of phenoxyl [30,31] for predicting the property of low bias spin-polarized NDR effect. The NDR effect is that the current decreases as bias increases in a certain bias region and has many applications such as frequency multipliers, high-frequency oscillators, fast switches and memories. The calculated results clearly demonstrate that the molecular TS shows intensively spin-polarized current NDR effect and spin filtration effect under very low bias and that the bias can reverse the spin current sign and manipulate the magnetization configuration of two phenoxyls, which promise the potential applications in molecular spintronics devices with low-power dissipation in the future. In addition, the molecular NDR effect is practical in the future only if it present below low bias region [32]. For these reasons, the present work is valuable.

2. Computational model and method

The molecular junction we proposed is a two probe system, in which σ barrier separating two benzene-based radicals are sandwiched between two Au leads. Fig. 1 shows the schematics of TS where two radicals are all phenoxyls. The molecule covalently contact Au Lead by thiolate (the H—S bond of thiol is cleaved). The whole TS is divided to three parts: left lead, scattering region and right lead. For avoiding the interaction between TS and its mirror images, one-dimensional Au lead is put in large vacuum layer in x- and y-directions. Except gold atoms, all atomic positions of scattering region are fully relaxed until the force tolerance to 0.05 eV/Å.

The spin transport characteristics of TS are investigated by a first-principles approach which combines density functional theory (DFT) calculations with nonequilibrium Green's function technique performed in the ATK code [33–35]. The exchange and correlation energy are described by the generalized gradient

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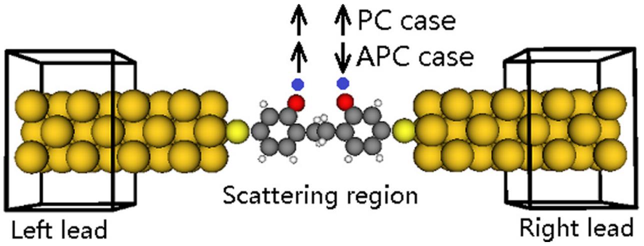

Fig. 1. Schematic of transport system constructed by two gold leads sandwiching benzene based radicals. Color code: Au (deep yellow), S (shallow yellow), O (red), C (black) and H (grey). The blue dots near radical are unpaired electrons. The arrow is the spin direction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approximation in the Perdew-Burke-Ernzerhof form [36]. The Troullier-Martins nonlocal pseudopotential is used to model core electrons and the double-zeta polarized basis are used for all elements including gold, sulfur, oxygen, hydrogen, carbon, and nitrogen atoms. The cutoff energy and the k-points sampling is 150 Ry and 1 × 1 × 50, respectively. The electrons temperature we used is 300 K. The spin-polarized currents are calculated as

$$I_{maj(\min)} = \frac{e}{h}\int_{-\infty}^{+\infty} T_{maj(\min)}(V_b, E)\left[f_L(E-\mu_L) - f_R(E-\mu_R)\right]dE \qquad (1)$$

where $f_{L,R} = 1/(1 + e^{(E-\mu_{L,R})/k_BT})$ is the Fermi-Dirac distribution; $\mu_{L,R}$ are the chemical potentials of the left lead (L) and the right lead (R). The h, V_b and $T_{maj(\min)}(V_b, E)$ is Planck constant, bias and transmission coefficients, respectively. The $T(V_b, E)$ is calculated by the standard equation

$$T_{maj(\min)}(V_b, E) = Tr\left[\Gamma_L(V_b, E)G_{maj(\min)}(V_b, E)\Gamma_R(V_b, E)G^{\dagger}_{maj(\min)}(V_b, E)\right]. \qquad (2)$$

The $G_{maj(\min)}(V_b, E)$ and $G^{\dagger}_{maj(\min)}(V_b, E)$ are the spin-dependent retarded and advanced Green's function of the extended molecule, respectively. The $\Gamma_{L/R}$ is the coupling matrix between the scattering region and the left/right lead. It is worth mentioning that the steady-state DFT [37,38] also accurately describe the low bias NDR effect and spin filtration for the molecular transport systems.

3. Results and discussion

Fig. 2(a) plots the current-voltage (I-V) curves for the parallel magnetization configuration (PC) and the antiparallel magnetization configuration (APC) of two phenoxyls. The PC (APC) case is that the spin direction of two phenoxyls is parallel (antiparallel). For the PC case, the minority spin current (I_{PC_min}) linearly increases to the current peak around 0.20 V with the bias and then suddenly decreases around 0.24 V. After 0.24 V, the I_{PC_min} slowly decreases to the current valley around 0.44 V. The NDR effect with the peak-to-valley (PVR, the ratio between current peaks and current valley) of 434% presents. The majority spin current (I_{PC_maj}) is inhibited and always much less than the I_{PC_min}. For the APC case, the I_{APC_min} also linearly increases to the current peak around 0.18 V and then slowly decreases to the current valley around 0.40 V. The strong NDR effect with the PVR of 1304% presents. The I_{APC_maj} slowly increases with the bias and is smaller than the I_{APC_min} under 0.24 V. After 0.24 V, the I_{APC_maj} is abnormally larger than the I_{APC_min} due to the strong NDR effect of I_{APC_min} mentioned above. That is to say, the NDR effect can change the sign of spin current, which promise the potential applications in the field of molecular spintronics in the future. The total current ($I_{min} + I_{maj}$) for PC and APC cases also show the NDR effect [shown in the insert of Fig. 2(a)].

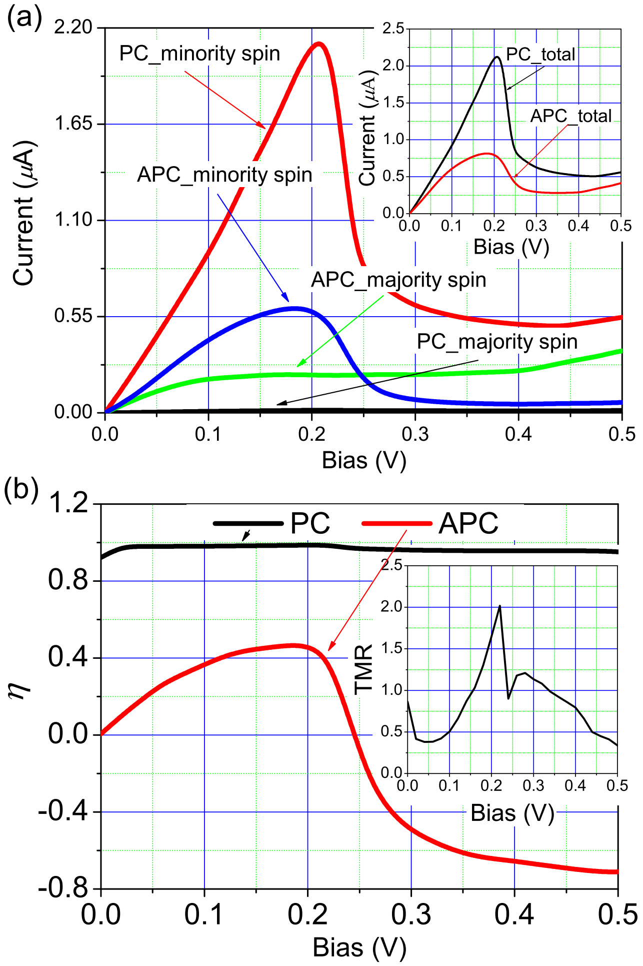

Fig. 2. (a) I-V curves for transport system. The inset is the total current for PC and APC cases. (b) Spin injection factor for transport system. The inset is the tunneling magnetoresistance ratio.

The spin injection factor η [defined by spin currents: $\eta = (I_{min} - I_{maj})/(I_{min} + I_{maj})$, the conductance is used at zero bias] is an important quantity for spintronics devices. Fig. 2(b) shows bias dependent η for both PC and APC cases. Due to the bias dependent spin-polarized currents, the η for the PC case is above 95% while for the APC case is positive and then negative as bias increases, which indicate that such molecular TS can be used as perfect spin filter and spin injector with bias modulating spin sign. Using the common optimistic definition, the tunneling magnetoresistance (TMR) is inferred as $(I_{PC} - I_{APC})/I_{APC}$ where I_{PC} and I_{APC} are the total current for the PC and APC cases, respectively. The insert of Fig. 2(b) shows the TMR versus bias. From it, one can see that the TMR is oscillating and below 200% due to the NDR effect of I_{PC} and I_{APC}. Although the TMR is not large enough, such molecular TS can somewhat be used as a spin valve.

The bias dependent spin-polarized current and total current can be understood from the behavior of $T(V_b, E)$, frontier molecular orbitals (MOs) and the local density of states (LDOS). Fig. 3 shows several MOs and their energy around Fermi level at zero bias. For the majority spin channel of PC case, one can see that the highest occupied molecular orbital (HOMO) and HOMO-3 are delocalized π orbital and entirely distribute on the two phenoxyls while the HOMO-1 and HOMO-2 are delocalized p_x orbital and only distribute on the two O atoms. For the minority spin channel of PC