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Bias changing molecule–lead couple and inducing low bias negative differential resistance for electrons acceptor predicted by first-principles study

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ABSTRACT

A first-principles study of the transport properties of 3,13-dimercaptononacene–6,21-dione molecule sandwiched between two gold leads is reported. The strong effect of negative differential resistance with large peak-to-valley ratio of 710% is present under low bias. We found that bias can change molecule–lead couple and induce low bias negative differential resistance for electrons acceptor, which may promise the potential applications in molecular devices with low-power dissipation in the future.

1. Introduction

Negative differential resistance (NDR) is a nonlinear transport property that the current increases at first and then decreases as bias increases. It has significant applications in many electronic devices such as analog-digital converters [1], high-frequency oscillators [2], and logic circuits [3]. Molecular NDR effect [4–43] has attracted much investigational interest because the molecule has been considered as one of the most potential substitutes of the traditional Si-based semiconductor transistor in the future. It is a pity that most molecular NDR effects mentioned above show the current peak (I_{peak}) and current valley (I_{valley}) at high bias region (>1.00 V). Only several molecular devices show NDR effect under low bias [8,14,24,53,57]. Scientists and engineers [44] point out that if the molecular NDR effect is practical in the future, it should be present below low bias region. In addition, low bias NDR effect means low power dissipation. So, the low bias molecular NDR effect may promise the potential applications in the future.

There have been several mechanisms to explain the molecular NDR effect including: metal filaments or impurities packaged in the molecular layer, bias-induced charging or geometrical deformation in the molecules, bond fluctuation, polaron formation, vibronic mediation, etc. Here, we proposed a mechanism that low bias molecular NDR effect can be induced by the change of lead–molecule couple driven by bias. We perform the first-principles calculations of the transport properties of 3,13-dimercaptononacene–6,21-dione molecule sandwiched between two gold leads. We find that the couple of thiolate–gold is changed by the bias and thus the low bias molecular NDR effect is present, which indicates that the low bias molecular NDR effect can be induced by changing the lead–molecule couple for strong electrons acceptors such as acenequinone molecule.

2. Computational method

Our calculations are based on a self-consistent first-principles method which combines the nonequilibrium Green's function formalism with density functional theory. The package of Atomistix Toolkit [45–52] is used in the calculations. The k-points sampling is 1, 1, and 50 in the x, y, and z directions. The cutoff energy is 150 Ry while the basis set is DoubleZetaPolarized. The exchange–correlation interaction is treated within generalized gradient approximation using the Perdew–Burke–Ernzerhof functional [53]. The convergence criterion for the total energy is 10^{-5} via the mixture of the Hamiltonians. The electrons temperature we used is 300 K. The currents are calculated as

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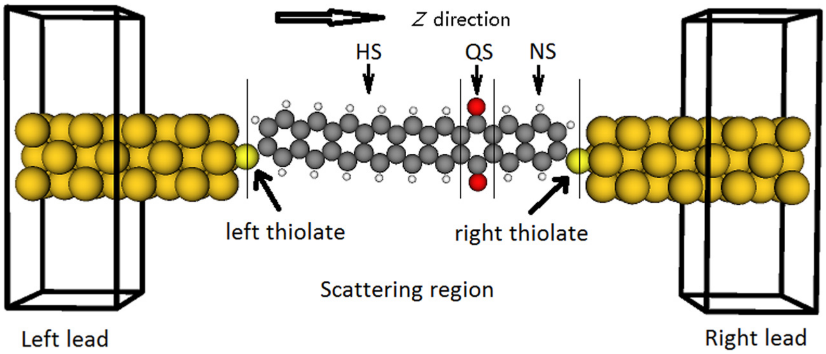

Fig. 1. Schematics of transport system constructed by two gold leads sandwiching 3,13-dimercaptononacene–6,21-dione molecule. Color code: Au (deep yellow), S (shallow yellow), O (red), C (black), and H (grey). HS, NS and QS are hexacene-2-thiolate section, naphthalene-2-thiolate section and quinone section, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

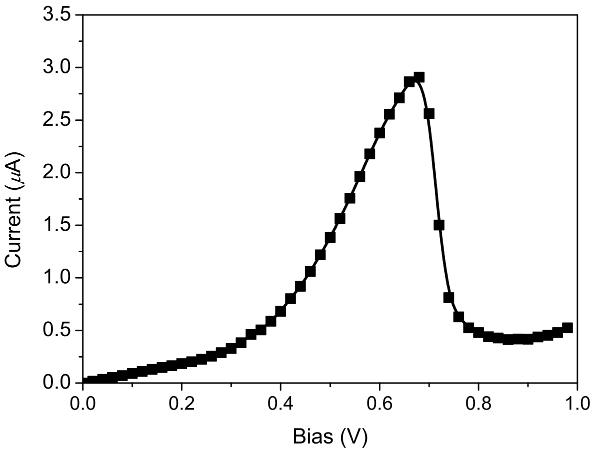

Fig. 2. The I–V curve for the molecular transport system.

$$I = \frac{2e}{h} \int_{-\infty}^{+\infty} T(V_b, E)\left[f_L(E-\mu_L) - f_R(E-\mu_R)\right] dE \tag{1}$$

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 $T(V_b, E)$ are Planck constant, bias and transmission coefficients, respectively. The $T(V_b, E)$ is calculated by the standard equation

$$T(V_b, E) = Tr\left[\Gamma_L(V_b, E)G(V_b, E)\Gamma_R(V_b, E)G^{\dagger}(V_b, E)\right] \tag{2}$$

Fig. 1 shows the schematics of transport system constructed by two gold leads sandwiching 3,13-dimercaptononacene–6,21-dione molecule. The molecule contacts one-dimensional gold lead by thiolate (the S–H bond of thiol is cleaved) due to that the coupling between gold atoms and thiolate is strong. The whole transport system is divided into three parts: the left lead, scattering region and right lead. One-dimensional gold lead with large vacuum layer in x- and y-directions is constructed in order to avoid the interaction between transport system and its mirror images. Except for gold atoms, the scattering region is relaxed until the force tolerance of 0.05 eV/Å is achieved.

3. Results and discussion

Fig. 2 shows the current–voltage (I–V) curve of the molecular transport system. From Fig. 2, one can see that the current increases until the I_{peak} presents at $V_b = 0.68$ V. After 0.68 V, the current suddenly decreases until the bias is 0.86 V. The NDR behavior is present and the peak-to-valley ratio [PVR, here, it is the ratio of $I_{\text{peak}}/I_{\text{valley}}$] is as large as 710%. Studying the bias-dependent $T(V_b, E)$, Local density of states (DOS) can help us to penetrate the mechanisms which result in the I–V characteristics. Fig. 3 shows the $T(V_b, E)$ spectrum at several biases. From Fig. 3, for zero bias, one can see that there is a $T(V_b, E)$ peak at 0.34 eV. Fig. 4(a) shows the local DOS at 0.34 eV where the $T(V_b, E)$ peak locates at zero bias. Combining the analysis of molecular projected self-consistent Hamiltonian (MPSH), the zero bias Local DOS in the scattering region at the energy of 0.34 eV is contributed by the MPSH-LUMO (LUMO is the lowest unoccupied molecular orbital) level. That is to say, $T(V_b, E)$ peak around Fermi level for zero bias is contributed by the MPSH-LUMO level. From Fig. 4(a), one can also see that the couple between molecule and left lead is stronger than that between molecule and right lead because the energy states located on the left thiolate are slightly more than that located on the right thiolate.

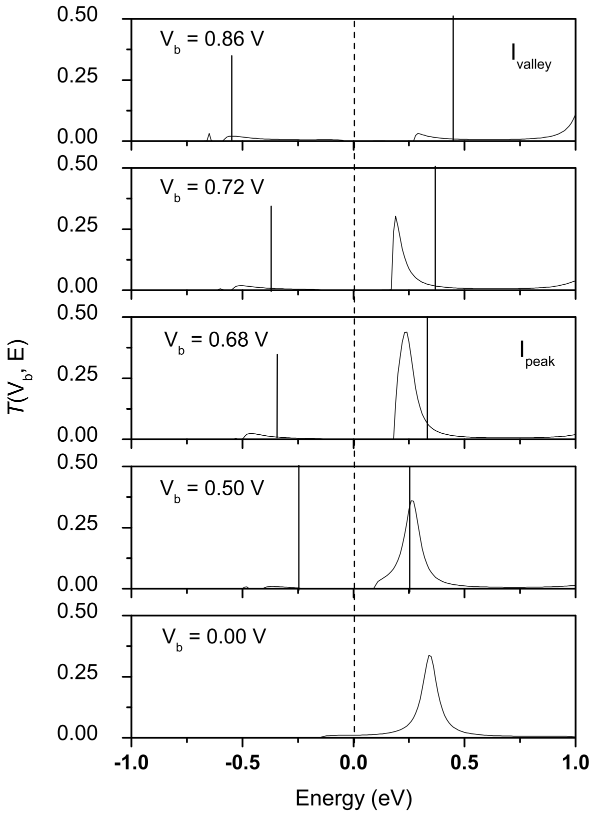

Fig. 3. The $T(V_b, E)$ spectra at several biases. The energy region between two solid lines is transport window. Dash line is Fermi level.