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The weak π–π interaction originated resonant tunneling and fast switching in the carbon based electronic devices

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The weak $\pi - \pi$ interaction originated resonant tunneling and fast switching in the carbon based electronic devices

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By means of the nonequilibrium Green’s functions and the density functional theory, we have investigated the electronic transport properties of $C_{60}$ based electronic device with different intermolecular interactions. It is found that the electronic transport properties vary with the types of the interaction between two $C_{60}$ molecules. A fast electrical switching behavior based on negative differential resistance has been found when two molecules are coupled by the weak $\pi - \pi$ interaction. Compared to the solid bonding, the weak interaction is found to induce resonant tunneling, which is responsible for the fast response to the applied electric field and hence the velocity of switching. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [doi:10.1063/1.3685777]

I. INTRODUCTION

In recent years, molecule-based electronic devices have a growing interest in the science and technology of nanometer-scale systems. Interesting physical phenomena including molecular switching,1,2 molecular rectification,3,4 molecular spintronics,5,6 Kondo effect,7 field-effect characteristics,8–10 and negative differential resistance (NDR),11–16 etc. have been observed in such devices. NDR is widely utilized in electronic devices such as oscillators, amplifiers, memories, and electrical switching.17 Recently, possible mechanisms have been proposed to explain the NDR behavior, such as two-step reduction process,11 charge transfer,3 intermolecular interaction,12 local orbital symmetry matching between the electrodes and the molecule,13 the channel conduction being suppressed,14 structural change15 and so on. However, most of the observed ON/OFF ratio and response speed are insufficient for practical application. It is highly desirable to design high performance switching device with high ON/OFF ratio and fast response to the applied electric-field. In 1989, Lyo et al. observed the NDR behavior by using scanning tunneling microscopy (STM) and suggested that the NDR can be applied to fast switching in certain types of electronic devices.20 The NDR behavior induced by intermolecular interactions has also been reported in previous works.12,14 However, little attention has been paid to the influence of different intermolecular interactions on the electronic transport properties. In fact, strong intermolecular interaction broadens the molecular energy levels and causes the electronic transport properties change gradually under the applied bias. However, the electronic transport in weak interaction system is determined by resonant tunneling and may induce fast switching.21

In the present work, we investigate the effect of different intermolecular interactions on electronic transport properties of $C_{60}$ based electronic device. Although it is well known22–27 that $C_{60}$ molecule has poor conductance due to its large gap between the highest occupied molecular orbital (HOMO)
and the lowest unoccupied molecular orbital (LUMO), a single C_{60} molecular device exhibits metallic properties.\textsuperscript{22, 23, 26} Taylor \textit{et al.} found that the metallic properties arises from the charge transfer from the electrodes to the molecular region.\textsuperscript{23} Zeng \textit{et al.} and Fan \textit{et al.} sandwiched C_{60} molecule in meta electrodes and observed NDR behavior.\textsuperscript{22, 26} However, the extent of coupling degree between the C_{60} molecule and the metal electrodes obviously affects the electronic transport properties. Our present study is focused on the effect of weak intermolecular interaction. As a select, cutting single-walled carbon nanotubes (SWCNTs) and rejoining the ends with organic molecules provides a novel method to construct stable molecular devices. SWCNTs are ideal contacts for flexible and modular devices.\textsuperscript{28–30}

This paper is organized as follows: the simulation model and computational details are illustrated in Sec. II; the results and discussions are presented in Sec. III, and finally a short conclusion is given in Sec. IV.

II. SIMULATION MODEL AND COMPUTATIONAL DETAILS

Fig. 1 shows the typical molecular devices we will use. Two different kinds of intermolecular interactions were considered. M1 represents the strong chemical bonding, and M2 the weak $\pi - \pi$ stacking interaction is. For M2, two different distances (namely 3.0Å and 4.0Å) have been considered in our calculations. The system is divided into three regions: the left and the right electrodes, and the scattering region between the electrodes. All the geometrical optimizations and the electronic transport properties were calculated using the first-principles method based on the fully self-consistent non-equilibrium Green’s functions formalism and density functional theory.\textsuperscript{31, 32} The configurations were relaxed until their force tolerance being less than 0.05eV/Å. During the calculation, the core electrons are modeled by normconserving pseudopotentials, while the valance electrons wave function were expanded by a SIESTA basis set. The single $\xi +$ polarization basis set was used for the geometrical optimization and the electronic transport properties calculation. The exchange and correlation terms are represented by the generalized gradient approximation (GGA) in the Perdew, Burke, and Ernzerhof form.\textsuperscript{33} The cutoff energy is set at 150Ry and the Brillouin zone is sampled by a $1 \times 1 \times 100 \mathbf{k}$-point grid. The nonlinear current through the scattering region...
Fig. 2. (a) describes the transmission spectrum at zero bias for the molecular device which is illustrated in M1, while both (b) and (c) describe the transmission spectra at zero bias for M2 with d being 3.0 Å and 4.0 Å, respectively. The vertical dash lines stand for the Fermi levels and it is set to be the origin of energy.

is calculated by the Laudauer formula\(^{34}\)

\[
I(V_b) = \frac{2e}{\hbar} \int_{\mu_l(V_b)}^{\mu_r(V_b)} T(E, V_b) [f(E - \mu_l) - f(E - \mu_r)]dE,
\]

where \(\mu_l(V_b)\) and \(\mu_r(V_b)\) are electrochemical potentials of the left and right electrodes and the \(f\) is the Fermi distribution function. With the applied bias potential \(V_b\), the electrochemical potentials will shift up and down, respectively. As a result, the electrochemical potentials correspond to \(\mu_l(V_b) = \mu_l(0) - ev_b/2\) and \(\mu_r(V_b) = \mu_r(0) + ev_b/2\) when the external bias is \(V_b\). Consider the fact that the Fermi level is set to be zero, the region of the energy integral window \([\mu_l(V_b), \mu_r(V_b)]\) can be written as \([-V_b/2, V_b/2]\). The electron transmission coefficient \(T(E, V_b)\) can be written as

\[
T(E, V_b) = Tr[\Gamma_r G^R \Gamma_l G^A],
\]

where \(G^{R(A)}\) is the retarded (advanced) Green’s function of the scattering region, and \(\Gamma_{l(r)} = i(\Sigma_{l(r)}^R - \Sigma_{l(r)}^A)\) is the coupling functions of the scattering region to the left and right electrodes. where \(\Sigma_{l(r)}^R\) and \(\Sigma_{l(r)}^A\) are the self-energy matrices used to include the effect of the electrode.

### III. RESULTS AND DISCUSSION

Fig. 2 shows the transmission spectra at zero bias for the molecular devices illustrated in Fig. 1. From Fig. 2(a), it can be seen that the LUMO lies above the Fermi level. The gap between the HOMO and the LUMO is about 1.5 eV. These results mean that the \(C_{60}\) dimer have a large HOMO and LUMO gap (HLG), and the electronic transport properties are dominated by the LUMO at lower bias. Besides, we found from the calculations that the equilibrium conductance of 0.032 \(G_0\) is smaller than that of the single \(C_{60}\) molecular device. These results are in good agreement with those reported in\(^{27}\) where a \(C_{60}\) dimer is sandwiched between the \(Au(100)\) electrodes.\(^{27}\) Comparing Fig. 2(b) with Fig. 2(a), we can observe that as the chemical bonding between the two \(C_{60}\) molecules is broken (namely the \(C_{60}\) dimer becomes two dissociative \(C_{60}\) molecules), the HOMO moves up further with
FIG. 3. Calculated current as a function of the applied voltage for the molecular device. M1 stands for the current-voltage curve of model M1, while M2 and M3 correspond to d is 3.0 Å and 4.0 Å in M2 system, respectively. The inset (a) is the magnified current-voltage curve for M3.

respect to the Fermi level and all the transmission peaks become sharp. The above results indicate that the different intermolecular interactions have different effects on molecular energy levels and electronic transport. To understand this phenomenon, we calculated the Mulliken population for all the systems. It turned out that the charge transfer from the CNT leads to the C_{60} dimer is 0.2354 e, while to the dissociated C_{60} molecules (d is 3.0 Å) it is 0.3604 e. It is well known that the more stable the molecule, the harder to rearrange its electron density. One can understand that the C_{60} dimer is more stable than two dissociative C_{60} molecules coupled by weak π−π interaction. As a result, the dissociative C_{60} molecules accept more external electrons. It is well known that if the transferred charge is less than e, it only makes the HOMO moving up. Thus, the HOMO closes to Fermi level as the two C_{60} molecules coupled by strong chemical bonding. However, when the two C_{60} molecules coupled by π−π stacking and the d is 3.0 Å, the current decreases obviously as the voltage increases from 1.2 V to 1.3 V and the PVR reaches to 7.73. This NDR fast response behavior could be used for swifty electrical switching. Furthermore, as the distance d is increased from 3.0 Å to 4.0 Å, the intermolecular interaction becomes weaker, and the current is very small as shown in M3.

To further explore the I-V characteristic of M3, we obtained the magnified current-voltage curve as shown in the inset in Fig. 3(a). It is seen that the I-V characteristic also presents fast response NDR...
behavior. In addition, the multiple NDR behavior can also be observed in M3, and the biggest PVR reaches 32.4. From these results, we can infer that the weak π−π interaction may induce NDR with fast response to the applied electric-field.

To understand the different NDR behaviors observed in the strong and the weak intermolecular interaction systems, in Fig. 4, we plot the transmission spectra under the biases \( V_b = 0.6 \text{V}, 0.8 \text{V}, \) and \( 1.3 \text{V} \) for M1 system, and the biases \( V_b = 1.2 \text{V} \) and \( 1.3 \text{V} \) for M2 system \((d = 3.0 \text{Å})\), respectively. In the weak interaction systems, the NDR fast response behaviors share the same mechanisms, and the current values of M2 is very closed to that of M1. In order to give a better comparison, we chose M2 as the representative of the weak interaction systems. As described above, the nonlinear current through the molecular device is calculated by formula (1). Thus, we can know that the current is determined by the shaded area. From Fig. 4(a), it is found that when the bias is 0.6V, the three frontier molecular orbitals: LUMO, UMO+1, and LUMO+2 lie inside the bias window and all of them contribute the transport channels. When the bias increases to 0.8V, the transmission coefficients of the LUMO decrease obviously and the transmission coefficients of the bias window and all of them contribute the transport channels. When the bias increases to 0.8V, the transmission coefficients of the LUMO+1 and the LUMO+2 have a small decrease. As the bias reaches to 1.3V, the transmission coefficients of the LUMO+1 and the LUMO+2 further decrease. From these results, we can conclude that the slow response NDR in strong interaction system originates from the dominating transmission peaks decreasing continuously. However, the case is different in the weak interaction system. From Fig. 4(d), we can find that there are three high and sharp transmission peaks corresponding to LUMO+2, LUMO+3 and LUMO+4 inside the bias window at the bias 1.2V. As we put eyes on Fig. 4(e), it is found that when the bias is increased to 1.3V (only change 0.1V), all the three transmission peaks disappear and only a low transmission peak corresponding to LUMO+5 enters into the bias window. This means that when the voltage is 1.2V, there are three resonant tunneling channels inside the bias window, but as the voltage increases to 1.3V the energy levels rearrange and the resonant tunneling channels mismatched, which leads to the transmission peaks disappearing rapidly. Thus, the NDR fast response behavior in the weak intermolecular interaction systems origins from the electronic resonant tunneling.
FIG. 5. The MPSH of the dominating molecular orbitals in the bias window. (a) and (b) correspond to system M1 and M2, respectively.

To understand the electronic transport channels response to applied electric-field. We plotted in Fig. 5 the molecular projected self-consistent Hamiltonian (MPSH) of the dominating molecular orbits at different biases. The MPSH is the molecular part extracted from whole self-consistent Hamiltonian for the scattering region. MPSH analysis helps us to qualitatively understand the origin of the transmission peaks. It is well known that when an orbital is delocalized across the molecule, an electron entering the molecule at the energy of the orbital has a high probability of reaching the other end, and a peak will appear in the corresponding energy position in the transmission spectra. Comparing Fig. 5(a) with Fig. 5(b), we can conclude that the localization of the dominating molecular orbits changes gradually as the bias increases from 0.6 V to 1.3 V in the strong interaction system. However, in the weak interaction system, the MPSH of the dominating molecular orbits changes enormously as the bias increases from 1.2 V to 1.3 V. When the two C60 molecules are coupled by strong chemical bonding, the electrons will coherently transport from the left C60 molecule to right, and the molecular orbits are broadened. In this case, despite the energy levels mismatching, the molecular orbitals will still overlap. As a result, the MPSH of the dominating molecular orbitals gradually change with the bias increases. However, when two C60 molecules coupled by the weak π – π stacking, the electrons transport from one C60 molecule to another by resonant tunneling as the energy level matched well. So, it can be understood that the dominating molecular orbits localized wholly as the bias increases from 1.2 V to 1.3 V in the weak interaction system.
interaction system. Therefore, it is suggested that the NDR fast response behavior originates from the resonant tunneling induced by weak $\pi - \pi$ interaction.

IV. CONCLUSION

In summary, the combination of the nonequilibrium Green’s functions and the first-principles quantum transport calculations allows us to explore the electronic transport behavior of the carbon based molecular device with the involvement of the strong bonding and the weak $\pi - \pi$ nonbonding intermolecular interactions. It is exciting to find that the letter improves the response substantially through the NDR effect via a mechanism of resonant tunneling.

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