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Electronic transport properties in doped C_{60} molecular devices

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By applying nonequilibrium Green's functions in combination with the density-functional theory, we investigate the electronic transport properties of molecular junctions constructed by C_{60}, $C_{59}N$, and $C_{59}B$. The results show that the electronic transport properties of molecular junctions can be modulated by doped atoms. Negative differential resistance behavior can be observed in a certain bias range for C_{60} molecular junction but cannot be observed in $C_{59}N$ and $C_{59}B$ molecular junctions. A mechanism is proposed for the doping effect and negative differential resistance behavior. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3082085]

In recent years, the electron transport properties of molecular devices have been paid much attention because of many interesting physical properties found in these devices, such as negative differential resistance (NDR),[1–6] single-electron characteristics,[7] highly nonlinear current-voltage relationship,[8] current rectification,[9,10] and so on. More recently, spintronic transport phenomena in molecular devices have also been reported.[11,12] It is known that transport properties of molecular devices depend on not only molecule itself but temperature,[13] the nature of bonding between the molecule and the electrode,[14,15] the geometry of the contacts,[2] molecule-electrode distance,[16,17] molecular orientation,[18] the effect of donor/acceptor side groups,[1,6,19,20] etc.

In the present work, we investigate the electronic transport properties of molecular junctions constructed by C_{60}, $C_{59}N$, and $C_{59}B$ coupled to Au electrodes by applying nonequilibrium Green's functions in combination with the density-functional theory. The study of transport properties of C_{60} has received much attention because it is one of the most prospective candidates in the practical molecular devices. Joachim *et al.*[21,22] found that the current-voltage characteristics present a linear behavior at low bias, and squeezing a C_{60} molecule by applying a small force can result in a shift in the molecular orbital levels. Zeng *et al.*[23] found NDR behavior in C_{60} molecular junction. Taylor *et al.*[19] found that the charge transfer from the electrodes to the molecular region plays a crucial role in aligning the lowest unoccupied molecular orbital (LUMO) of the C_{60} to the Fermi level of the electrodes. Seideman and co-workers[24,25] studied the current-induced oscillation behavior in Au–C_{60}–Au heterojunctions using their theoretical methods. Recently, Fan *et al.*[26] observed the NDR behavior in squashed C_{60} molecular devices, and found that the NDR can be tuned by the deformation degree of the C_{60} molecule. The present work focuses on the effects of doped atoms on electron transport properties for the molecular junctions constructed by C_{60}, $C_{59}N$, and $C_{59}B$.

The molecular junctions we study are illustrated in Fig. 1. The structures were optimized and the quantum transport calculations were carried out by an *ab initio* code package, TRANSIESTA-C.[27]

Figure 2(a) shows that the current through the three molecule junctions as a function of the bias applied to the devices. From the figure, we find that all the three molecular junctions display metallic transport behavior. It is known that an isolated pristine C_{60} molecule is a semiconductor. When it is embedded between two metal electrodes, the system displaying metal transport behavior should result from the fact that the interaction between the C_{60} molecule and the metal electrodes may lead to the electrons doped into the C_{60} molecule. From the figure, we can see clearly that when the bias is lower than $|V|=0.6$ V, the currents are $M1>M2>M3$. In particular, the current of $M3$ is remarkably smaller than that of $M1$ and $M2$. This means that at low bias, the introduction of the donor atom (nitrogen) and acceptor atom (boron) can weaken the electron transport, especially the acceptor doping significantly suppresses the electron transport. From the figure, it can be found that when the bias takes a value between $|V|=0.6$ and $|V|=1.0$ V, the current of $M1$ decreases obviously with the increase in the bias, which shows NDR behavior in the bias range. However, we do not find the NDR behavior for other two cases. It can be seen that the current

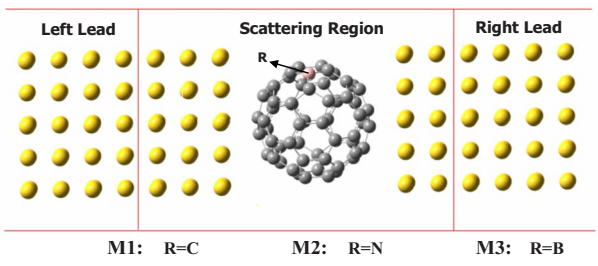

FIG. 1. (Color online) Schematic plot of the molecular junctions: the molecule is coupled to two semi-infinite Au electrodes, and the extended molecule consists of molecule $5\times5(100)$ three layers of Au slab in the left lead, and two layers of Au slab in the right lead. $M1$, $M2$, and $M3$ correspond to C_{60}, $C_{59}N$, and $C_{59}B$ junctions, respectively. The distance between electrode surface and molecule is 2.1 Å, which corresponds to the lowest energy of the expanded molecules.

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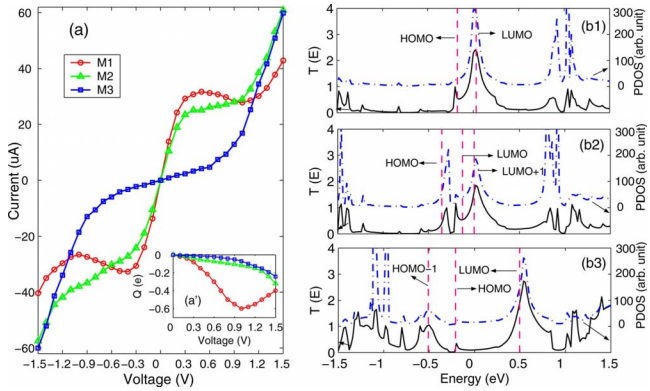

FIG. 2. (Color online) (a) Currents as function of bias for $M1$, $M2$, and $M3$. The insert (a′) is the change in transferred charges from the electrode to the molecule at different biases.](b1)—(b3)] Refer to the transmission coefficient (solid lines) and the corresponding PDOS (dash-dot lines)on the electron energy at zero bias, correspond to $M1$, $M2$, and $M3$, respectively. The vertical dashed stand for the molecular orbitals and the Fermi level is set to be the origin of energy.

of $M2$ is increased smoothly, while the current of $M3$ increases rapidly in this bias range. In order to understand this phenomenon, in Fig. 2 (a′), we plot the change in the charge transferred from the electrodes to the molecule as a function of bias. With the increase in the bias, it is clearly seen that the transferred charge is increased at low biases. However, when the bias is larger than 1.0 V, we observe the transferred charge being reduced for the C_{60} systems, but not for $C_{59}N$ and $C_{59}B$ systems. As we know, transferred charge is closely related to the coupling between the electrodes and molecule, and then affects the molecular conductance.[3,6,19] The charge transfer of C_{60} system does not present a monotonic behavior with the change in bias, which matches with *I-V* curve very well for the explored bias region. This means the NDR behavior results from the change in the transferred charge.

In order to explain the origin of the transport characteristics of the molecular junctions, in Figs. 2(b1)-(b3) we show the transmission coefficient $T(E,\ V_b)$ and the corresponding projection of the density of states (PDOS) at zero bias ($V_b=0$) for the system $M1$, $M2$, and $M3$. From Figs. 2(b1)-(b3), we can find that the highest occupied molecular orbital (HOMO)/LUMO gap (HLG) are 0.207 69, 0.479 37, and 0.605 41 eV for $M1$, $M2$, and $M3$, respectively. It is known that the larger the HLG, the more stable the molecule, and therefore the harder it is to rearrange its electron density under the presence of an external electron. Both the acceptor and donor doping lead to an increase in the HLG, and thus reduce the molecular conduction. From Fig. 2(b1), we find that near Fermi level there are two big transmission peaks, which originates from the HOMO and the LUMO, respectively. Especially, the latter is a stronger and broader transmission peak, which corresponds to a strong electronic transport channel being opened in the system. Thus we can infer that there is a strong coupling between the gold electrode and molecule, which dominates the electron transport in C_{60} systems. From Fig. 2(b2), we can see that there are three transmission peaks near Fermi level, which originates from HOMO, LUMO, and LUMO+1. As we know, $C_{59}N$ molecule is constructed by using nitrogen atom substituting carbon atom of C_{60} molecule. The introduction of the nitrogen atom leads to the shift in the molecular orbital. There are three frontier molecular orbitals, namely, HOMO, LUMO, and LUMO+1 lying in the vicinity of Fermi level, and the transmission peaks corresponding to HOMO and LUMO are also different from those of C_{60} molecular junction, which means the coupling between the molecule and electrodes being also different from that of C_{60} molecular junction. As a result, the *I-V* characteristics of $C_{59}N$ system are different from those of C_{60} system. At low bias, the current of $M2$ increases quickly, which result from the fact that the frontier molecular orbitals HOMO, LUMO, and LUMO+1 have large contributions to the conduction current. This shows the stronger coupling between the molecular orbitals and electrodes. However, when a carbon atom is substituted by an acceptor atom boron, we find from Fig. 2(b3) that there are three molecular orbitals, namely, HOMO−1, HOMO, and LUMO entering into the energy range explored here, but only HOMO lying near Fermi lever. A large transmission

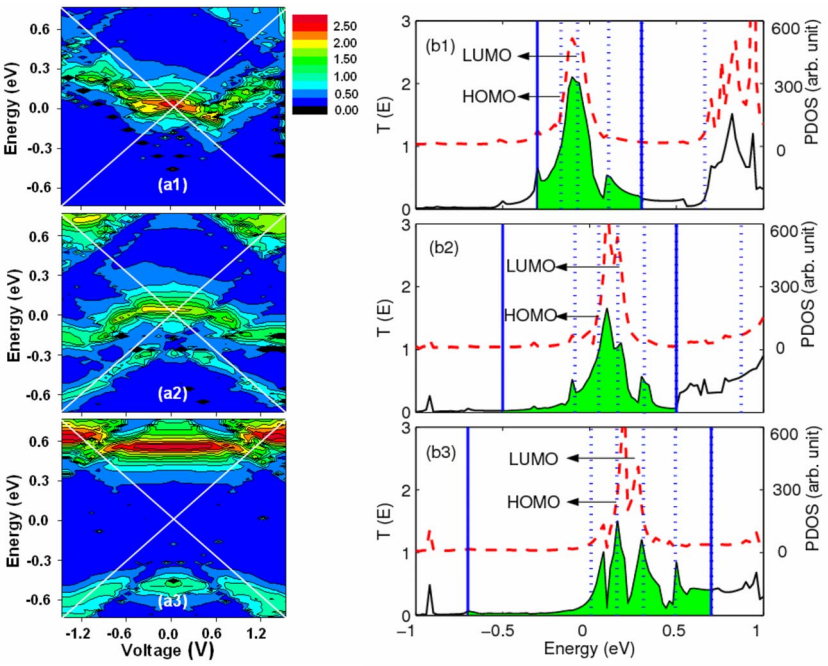

FIG. 3. (Color online) [(a1)—(a3)] Show the total transmission as a function of the bias voltage and electron energy for $M1$, $M2$, and $M3$, and the white lines stand for bias windows. [(b1)—(b3)] Describe the transmission coefficient and the corresponding PDOS for the system $M1$ under biases V_b=0.6, 1.0, and 1.4 V, respectively. The region between the solid lines is the bias window, the dotted lines correspond to frontier molecular orbitals, and the shaded area denotes the integral area in the bias window.

valley with very small transmission coefficient lies about the Fermi level, which means weak coupling between the HOMO orbital and electrodes. This leads to the current being very small at low bias, as seen in Fig. 2(a). From the above results, it is known that a carbon atom of C_{60} molecule being substituted by a donor atom (nitrogen) or an acceptor atom (boron) leads to not only an increase in HLG and shift in the molecular orbitals obviously, but also the change in the coupling degree between the molecular orbitals and electrodes. As a result, the currents display different behaviors for the three molecular junctions $M1$, $M2$, and $M3$.

To further understand the transport characteristics of the molecular junctions, in Figs. 3(a1)-(a3), we give the total transmission coefficient as a function of the bias and electron energy. From Figs. 3(a1) and (a2), we find that there are bigger transmission coefficients in bias windows for both $M1$ and $M2$ systems, which leads to a rapid increase in the current with bias at lower bias region for $M1$ and $M2$. However, there is small transmission coefficient entering into the bias window for $M3$ at lower bias, so the I-V curve of $M3$ shows likely flat at lower bias. As the bias is increased, in the bias range from $|V|=0.6$ to $|V|=1.0$ V, we can see from Fig. 3(a3) that there are more transmission coefficients entering into the bias window and contribute to the electronic currents, but in Figs. 3(a1) and (a2), the transmission coefficients entering into the bias window are smaller. Especially in Fig. 3(a1), the total magnitude of transmission coefficient in the bias window becomes smaller with the increase in the bias, so the NDR behavior appears in $M1$ system, as seen in Fig. 2(a). On the contrary, in Fig. 3(a3) we can find more transmission coefficient entering into the bias window in the higher bias, so we can find the current of $M3$ increases rapidly with the increase in the bias. When the bias is larger than 1.0 V, we can find that from Figs. 3(a1)-(a3), there are lots of new transmission coefficients entering into bias windows, so we can see the currents rapidly increase with bias for all the three molecular junctions.

In order to understand the NDR behavior more clearly, in Figs. 3(b1)-(b3), we give the transmission coefficient and the corresponding PDOS of $M1$ under biases $V_b=0.6$, 1.0, and 1.4 V, respectively. As we known, the current is determined by $T(E, V_b)$ in the bias window and is further only determined by the integral area (namely, the shaded area in the bias window). When the bias is 0.6 V, we can find from Fig. 3(b1) that there is a strong and broad transmission peak originating from LUMO that lies in bias window, which leads to a large current. When the bias takes the value between $V_b=0.6$ V and $V_b=1.0$ V, the bias window is increased with the bias voltage, but the total integral area gets smaller. As a result, the current decreases and NDR appears. From Fig. 3(b3), we find that when the bias is further increased, other integral area enters into the bias window and the current increases again and the NDR disappears. From the above results, we can infer that the NDR behavior originates from the change in the coupling degree between the frontier molecular orbitals and electrodes.

In summary, the results show that all the three molecular junctions display metallic transport behavior. At low bias, the introduction of the donor atom nitrogen and acceptor atom boron can weaken the electron transport, especially the acceptor doping significantly suppresses the electron transport. When the bias is in the range from $|V|=0.6$ to $|V|=1.0$ V, the currents of C_{60} and $C_{59}N$ molecule junctions are remarkably suppressed, especially, in the former, NDR behavior appears in this bias range. However, the current of $C_{59}B$ molecule junction increases rapidly with the increase in the bias. These results show that the electronic transport properties of molecular junction can be modulated by doped atoms, which results from the fact that the introduction of the doping atoms leads to an increase in HLG and shift in the molecular orbitals obviously, as well as the change in the coupling degree between the molecular orbitals and electrodes.

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