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The site effects of B or N doping on I-V characteristics of a single pyrene molecular device

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Using the non-equilibrium Green's function method combined with the density functional theory, the electronic transport properties of boron (B) or nitrogen (N) doped pyrene molecular devices are investigated. The results show that effects of B or N doping on I-V characteristics of a single pyrene molecular device are not constant and can be changed by varying doped sites. More importantly, significant negative differential resistance (NDR) behaviors are found in B-doped pyrene molecular devices. The peak-to-valley ratio which is a typical character of NDR behavior is also sensitive to the B doped site. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4745842>]

The research on the molecular devices and their transport properties has attracted increasing attentions in recent years, in an attempt to find a possible solution to the miniaturization impasse of the semiconductor industry once its atomic limit approaches. Various molecular devices have been made to realize the functions existing in microelectronic devices such as switching,^{1–3} rectification,^{4–6} negative differential resistance (NDR),^{7–10} and spin filter.^{11,12} In addition, researchers also do their utmost to explore modulating ways extending the properties of these molecular devices. Until now, usual ways including deforming,^{13,14} tailoring,^{15,16} replacing,^{17,18} doping,^{19,20} and so on have been demonstrated theoretically or experimentally.

Chemical doping with foreign atoms is generally chosen to modify the electronic transport properties of carbon materials.^{21,22} Among them, boron or nitrogen atoms are regarded as typical substitutional dopants and adopted frequently in carbon materials due to their similar atomic sizes and electronic structures. Moreover, the binding between B, N, and C is covalent and very strong, compared to that of the host C–C bond. As a result, the incorporation of N or B atoms with carbon will influence the electronic and transport properties of the host carbon materials by introducing extra carriers. Especially, the doped carbon nanotube and graphene has been synthesized successfully in experiment, which make the chemical doping with boron or nitrogen atoms on carbon material become a research hotspot.^{23,24} For instance, Tagami's group and Heimel's group found the transport characters of inorganic molecules can be tuned from the semiconductive to the metallic by substituting with the boron or nitrogen atom.^{25,26} By adding up the effects of the nitrogen and the boron impurity, the resistance of a metallic carbon nanotube can vary greatly to perform a switching behavior as a function of the applied electric field.²⁷ For single C₆₀ molecular junction, B- or N-doping can modulate its electronic transport properties remarkably and make the intrinsic NDR behavior disappear.²⁸ But a rectifying behav-

ior can be found in the C₆₀ dimer bridge when one is doped with N atom and the other is doped with B atom.²⁹

Recent studies show the doping with the boron or nitrogen atoms can change the electronic characteristics of graphene to achieve some interest transport properties such as field effect transistor,³⁰ NDR,³¹ spin-polarized tunneling,³² half-Metallicity,³³ spin filtering,^{34,35} rectifying,³⁶ etc. Although several groups had already noticed the doping site of boron or nitrogen atoms also plays an important role on their modulated effect, the relative investigations are little and incomplete until now.^{30,32,33} With an aim to further understand the site effects of B, N doping, we theoretically study the transport properties of single pyrene molecular device because it is a typical π -conjugated molecule and can also be viewed as simply as an intrinsic semiconductor or a small piece of graphene. The calculated results indicate that effects of B or N doping on I-V characteristics of a single pyrene molecular device are not constant and can be changed through varying doped sites. More importantly, significant NDR behaviors are found in B-doped pyrene molecular devices. The peak-to-valley ratio which is a typical character of NDR behavior is also sensitive to the B doped site.

The molecular devices we study are illustrated in Fig. 1. The pyrene molecule is bonded to two Au (111)-(3 × 3) surfaces through terminal thiol groups. The sulfur atom is chosen to be located at the hollow site of the gold triangle and the Au–S distance is 2.5 Å.³⁷ Five models M1–M5 corresponding to undoping, N doping on the x-site, N doping on the y-site, B doping on the x-site, and B doping on the y-site are considered in this paper. The calculated method we adopted is an *ab initio* code package (ATOMISTIX TOOLKIT) based on the non-equilibrium Green's function formalism and the density functional theory.^{38,39} The exchange-correlation potential is described by the local density approximation (LDA), which works rather well for light elements and systems where electrons are delocalized. Core electrons are modeled with Troullier-Martins nonlocal pseudopotential, and valence electrons are expanded in a SIESTA localized basis set. Single-zeta plus polarization (SZP) basis set for Au atoms and double-zeta plus polarization (DZP) basis

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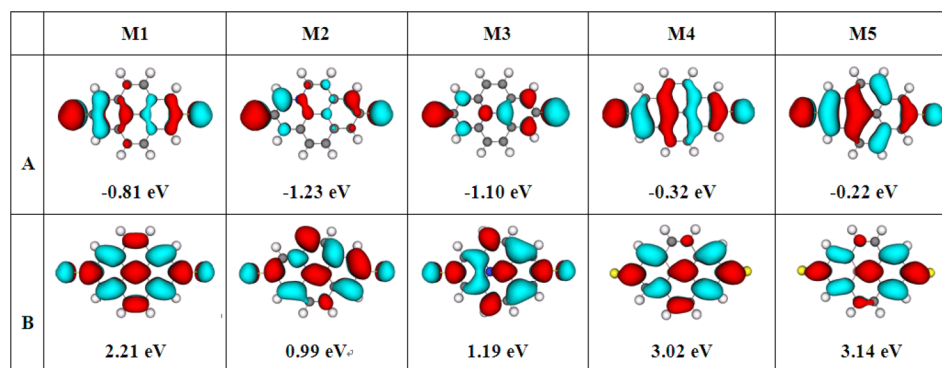


FIG. 3. Spatial distributions of the HOMO (A) and LUMO (B) states for three devices at zero bias.

through the whole molecule including two sulfur atoms, and energy levels of the HOMO and LUMO are -0.81 eV and 2.21 eV, respectively. The HOMO-LUMO gap (HLG) is very wide, and no direct interaction exists between them. Although the transmission peak of the HOMO is high and broad, it is far away from the Fermi energy level and a tail of the transmission peak just extends to the Fermi energy level (see Fig. 2(b)). As a result, the transmission coefficient on the Fermi energy level is very low leading to the weak electronic transport ability of single pyrene molecular devices.

When a nitrogen atom dopes the pyrene molecule on the x-site, in Fig. 2(c), the transmission spectrum entirely moves to a lower energy and energy levels of both the HOMO and LUMO shift to -1.23 eV and 0.99 eV, respectively. The shifting range of the LUMO resonance exceeds the shifting range of the HOMO resonance, which decreases the HLG obviously. As a result, a new transmission peak appears at the intersection of the tails of HOMO and LUMO transmission spectra (about at 0.1 eV) due to the interaction of them. However, N-doping localizes the spatial distributions of the MPSH on the HOMO and decreases its transmission coefficient. Accordingly, the transmission coefficient of the new transmission peak is very small. So, the average transmission coefficient around the Fermi energy level is nearly same to that of M1. Therefore, the current curve of M2 nearly overlaps with the current curve before 2.0 V, as shown in Fig. 2(a).

While a nitrogen atom dopes the pyrene molecule from x-site to y-site, in Fig. 2(d), the transmission spectrum and the frontier orbitals also perform similar evolutions as M2, but some differences appear. First, the transmission spectrum of M3 also entirely moves to a lower energy, but energy levels of the HOMO and LUMO just shift to -1.10 eV and 1.19 eV, which is smaller than the shifting amplitude of M2. Second, the transmission coefficient of HOMO of M3 also decreases but is higher than that of M2. This is because the localization of the spatial distribution of MPSH for M3 is less than that for M2, which can be seen clearly in Fig. 3. Consequently, the transmission coefficient of the new transmission peak on the intersection of the tails of the HOMO and LUMO (about 0.29 eV) is larger than that of M2, which enlarges the average transmission coefficient around the Fermi energy level. Therefore, when the doped site is changed to y-site, an N-doping can enhance the device's electronic transport ability obviously.

In Fig. 2(e), the transmission spectrum entirely moves to higher energy and energy levels of the HOMO and LUMO

shift to -0.32 eV and 3.02 eV, respectively, when a boron atom dopes the pyrene molecule on the x-site. As can be seen, the HOMO which is very close to the Fermi energy level becomes the main electronic transport resonant level. In addition, B-doping delocalizes the spatial distributions of the MPSH on the HOMO and enhances its transmission coefficient. As a result, the average transmission coefficient around the Fermi energy level increases greatly. While a boron atom dopes the pyrene molecule changing from x-site to y-site, the HOMO, the LUMO and the transmission spectrum further moves to a higher energy. The energy level of HOMO shifts to 0.22 eV and is closest to the Fermi energy level in the five models. In addition, the B-doping on the y-site further delocalizes the spatial distribution of the MPSH on the HOMO and enhances its transmission coefficient. The average transmission coefficient around the Fermi energy level of M5 is biggest in the five models. Therefore, the equilibrium conductance of the five models is $G_{M5} > G_{M4} > G_{M3} > G_{M2} > G_{M1}$, as displayed in Fig. 2(a).

To find origins of a shift of the HOMO and LUMO under doping, we calculate the self-consistent Mulliken charge distributions of M1-M5 at zero bias. The previously related works have confirmed that a shift of resonance levels can be induced by the electron transfer.^{42,43} The shift of resonance levels to a higher energy is produced by a charge transfer from electrodes to a molecule, vice versa. The self-consistent Mulliken charge distributions of M1 are exhibited in Fig. 1. The net charges of hydrogen atoms are negative which denote they lose charges. The net charges of carbon atoms and sulfur atoms are positive which mean they obtain charges. The sum of net charge of all atoms is 0.312 e. After carefully observing, we can see that net charges of carbon atoms depend on their position obviously. The outside carbons accept more charges than the center carbon atoms, leading to the difference of net charges between the x-site carbon atom and y-site carbon atom.

When a nitrogen atom dopes the pyrene molecule, the calculated net charges of the N atoms in M2 and M3 are -0.438 e and -0.441 e, respectively. Furthermore, we also find that N-doping seldom changes net charges of other atoms no matter they are on x-site or y-site. Consequently, the total net charges of M2 and M3 are -0.187 e and -0.131 e, which means the molecules transfer the charges to the electrodes. For this reason, resonance levels of M2 and M3 all shift to lower energies and the shift degree of M3 is less than that of M2 due to the difference of their total net charges. When the pyrene molecule is adopted by a boron

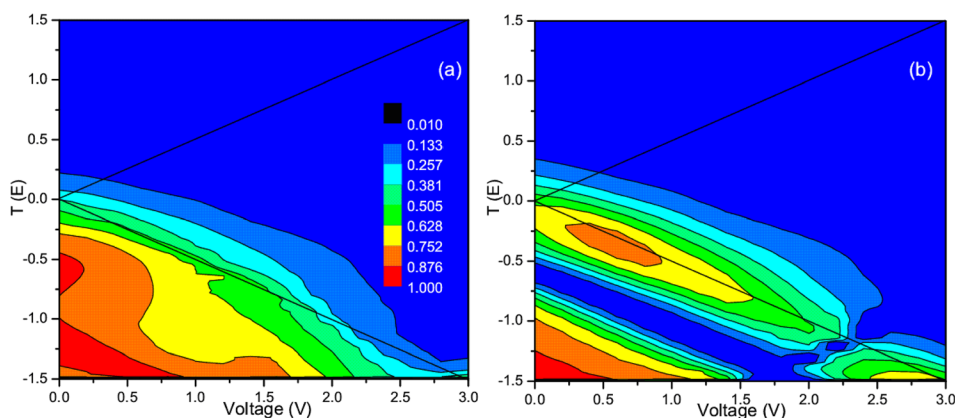


FIG. 4. (a) and (b) The transmission coefficients of M4 and M5 as a function of the bias in the range [0.0 V, 3.0 V]. The black dashed lines indicate the bias window.

atom, the calculated net charges of the B atoms in M4 and M5 are 1.037e and 1.091e. Consequently, the total net charges of M4 and M5 are 1.287e and 1.402e. Because the charges transfer from electrodes to the molecule, the resonance levels of M4 and M5 all shift to higher energies and the shift degree of M4 is less than that of M5 also due to the difference of their total net charges.

When a bias is applied, the system is driven out of equilibrium. In Fig. 2(a), the currents of the five models are not all increasing linearly with the bias and two obvious NDR behaviors can be found in I-V curves of M4 and M5. To explain these, we plot the total transmission coefficients as a function of the bias in Fig. 4. As we have described, the transmission spectra are the most intuitive representation of quantum transport behaviors according to the Landauer formula. The nonequilibrium current is the integration of the transmission coefficient in the bias window $[-V_b/2, +V_b/2]$. When a boron atom dopes the molecule on the x-site, the resonance levels and transmission spectra shift to a higher energy due to the charge transfer from electrodes to the molecule. So, the LUMO is far away from the Fermi energy level and is always outside of the bias window which can be seen clearly in Fig. 4(a). When the bias increases, the tail of the main electronic transport resonance level (HOMO) comes into the bias window gradually and the total transmission coefficient reaches a maximum at $V_b = 1.2$ V. However, the HOMO always moves to a lower energy with the increasing of bias. After 1.2 V, the total transmission coefficient in the bias window decreases bit by bit. As a result, the current decreases and the NDR behavior appears. In Fig. 4(b), we can find the HOMO of M5 is closer to Fermi energy level than that of M4 due to the more charge transfer from electrodes to the molecule. In addition, it is also the only main electronic transport resonance level and still moves to a lower energy with the increasing of bias. Therefore, the total transmission coefficient in the bias window also increases first and then decreases, which means the NDR behavior can also be found in the I-V curve of M5.

In summary, applying the density-functional theory and the non-equilibrium Green's function method, we have investigated the electronic transport properties of B- or N-doped pyrene molecule sandwiched between Au electrodes. The results show that B- or N-doped effects on electronic transport properties are not constant and can be changed by shifting doped sites. It is because the change of the MPSH

states and the shift of energy levels for the HOMO and LUMO induced by the electron transfer are different when B or N atom dopes the molecule on the different doped sites. In addition, significant NDR behaviors are found in B-doped pyrene molecular devices, which attribute to that the main electronic transport resonance level (HOMO) moves to a lower energy with increasing of bias. Moreover, the peak-to-valley ratio of this behavior can be controlled by a change of the B-doped sites. These are very useful for the future molecular engineering to design ultra-small functional nanodevices.

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