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Insight into negative differential resistance in polyphenylene molecular device with graphene electrodes

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ABSTRACT

The organic molecule deposited between gaphene electrodes to form a molecular device has been demonstrated experimentally. Motivated by this case, devices consisting of the polyphenylene molecule bonded covalently with armchair-edged graphene nanoribbon (AGNR) electrodes are constructed and the selective doping with N atom is considered theoretically. Our modeling calculations show that such devices hold the nonlinear and doping-site-dependent transport properties, prominently with multi-peak NDR (negative differential resistance) effect. And, for a peculiar doping site, a very large NDR can be observed, which could be attributed to interactions of the molecular core and doped AGNR electrodes, namely, these hybridized wave functions hold distinctly different delocalization in different benzene rings of the polyphenylene molecule when the applied bias is altered. Also shown is that this large NDR is robust regarding the length increasing and rotation of molecule.

1. Introduction

It is predicted that the molecular materials are very promising candidates for developing ultra-small electronic devices [1–3], thus their exceptional electronics features have been investigated actively in past decades both theoretically and experimentally. Researchers have not only successfully synthesized or theoretically designed many new suitable molecular nanomaterials for molecular devices, but also found their many attractive device properties, such as the current switching effect with large negative differential resistance(NDR) [4,5], diode-like [4,6] and transistor-like behaviors [7],spin-filtering and giant magnetoresistance effects [8],etc., which, in turn, intensifies the research activities for molecular devices. Among device properties, NDR effect has been regarded as one of research focuses. This is because NDR effect is a very important physical phenomenon typically observed in semiconductor devices in the resonant tunneling regime and plays a crucial role in numerous applications [9–12], such as fast switches, high-frequency oscillators, memory elements, amplification, logic circuits, and so on. Currently, studies on NDR of molecular devices have achieved some important advances [13–16], but high-performance and high-stability NDR effects need to be explored further.

In the experiment, when the molecular core is adsorbed on the electrodes to construct a molecular device, its stability is not only a primary requirement but also a great challenge. Due to the special nature of the gold, it has become the first choice as electrode material in previous investigations. However, owing to high atomic mobility, the gold electrode is destabilized at room temperature [17], especially unstable at the interface between the molecular core and gold electrodes. Accordingly, to find stable electrode materials is a key issue for developing applicable molecular devices. The controlled formation of graphene nanoribbon (GNRs) [18] or cutting a graphene along specific single crystallographic directions to form well-define edge-shaped GNRs [19] provides a new possibility to overcome the drawback of gold electrodes. This is because if organic molecular devices with GNRs acting as electrodes are fabricated, the strong C–C covalent bond structure between the molecule and graphene has enough stability to fix a molecule far above room temperature, and contact barriers on interfaces are also suppressed greatly. More attractively, it is easily for GNR electrodes to be functionalized by various nanotechnologies, which can tune the transport properties by altering electronic structure of electrodes and by interactions of π–π conjugated bonds of the molecular core and graphene electrodes. Therefore, this type of

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molecular devices with GNRs acting as electrodes, up to now, has been widely investigated [20–22]. Especially, Prins.et al. [20] recently reported that the molecular devices were made by depositing organic molecules, anthracene-functionalized curcuminoid wires (1,7-(di-9 -anthracene)-1,6-heptadiene-3,5-dione, abbreviated as 9Accm) inside GNR nanogap and this molecular junctions displayed gateable I-V characteristics at room temperature, which demonstrates that GNR electrodes are feasible and advantageous for constructing molecular devices. Furthermore, it is highly possible for heteroatom to be unintentionally or intentionally introduced into GNRs in the fabrication process, therefore, studies on effects of the doping for GNR electrodes are highly desirable. However, as far as we know, no experimental and theoretical studies so far have demonstrated how the doping at electrodes influences the transport properties of an organic molecular device. Therefore, in this paper, we take a polyphenylene molecule as a representative and sandwich it between two AGNR (armchair-edged GNR) electrodes, focusing on simulating the selective N-doping effects of electrodes. Our calculations show that the nonlinear and doping-site-dependent transport properties for such devices are prominently, as well as multi-peak NDR effect can be found. Especially for a certain doping site, a very large NDR happens, which could be attributed to hybridization and overlapping of the wave functions of the molecule core and N-doped AGNR electrodes. Also shown is that this large NDR is robust regarding the length increasing and rotation of molecule.

2. Model and method

Molecular device models studied are shown in Fig. 1, where the numbers, 1–6, represent six selective positions for N-doping and a polyphenylene molecule with four benzene rings B1–B4 is connected to two N-doped 11-AGNR electrodes. The prefix “11” before AGNR represents this ribbon width, that is, the number of dimer lines across the ribbon width. We choose N atom acting as dopant for AGNR electrodes, this is considering that the N atom is typical substitutional dopant for graphene, its binding with the C atom is covalent and quite strong, comparably to that of host C–C bond [23], and the incorporation of N atom into the graphene will influence its electronic and transport properties by introducing extra carriers and altering energy band structures [24]. To keep structural stability, the model is saturated with hydrogen atoms. The molecular device is divided into three parts: the left electrode(LE), the scattering region (SR), and the right electrode(RE). Each electrode is described by a supercell with two repeated AGNR unit cells, where one carbon atom is substitutionally doped by one N atom at selective positions, 1–6, respectively, which constructs six different device models, referred as M1–M6 for simplicity. The scattering region includes the polyphenylene molecule and two repeated AGNR unit cells. The isolated polyphenylene molecule is optimized initially by setting two different geometrical configurations: all benzene rings in plane and out of plane alternately, we find that the latter is energetically more favorable. This optimized structure is introduced into the nanogap between two N-doped AGNR electrodes and linked onto such electrodes by setting C–C bonding length 0.14 nm.Then, the entire scattering region is optimized further until all residual forces on each atom are smaller than 0.2 eV/nm, and it is found that B1 and B3 just lie in the same plane while B2 and B4 locate in another plane, and two planes hold an angle, ~20°. The scattering region is involved in the self-consistent cycle to take into account the molecule-electrode coupling and screening layer effects.

The geometry optimization and calculations of electronic properties are performed by using first-principles method based on the density functional theory (DFT) combined with the non-equilibrium Green's function (NEGF) technique as implemented in Atomistix ToolKit (ATK) [25,26]. In order to solve the Kohn-Sham equation, The Perdew-Burke-Ernzerhof(PBE) formulation of the generalized gradient approximation(GGA) is used as the exchange-correlation functional. Considering the polarized effects of atoms, the single-zeta plus polarization (SZP) basis set is used for H atoms, and the double-zeta plus polarization (DZP) basis set is used for other atoms. The k-point sampling is 1, 1 and 500 in the x, y, and z directions, respectively, where z is the transport direction. For all models studied, a 1.5 nm vacuum slab is used to eliminate interaction between the model and its neighboring “images”. Once the convergence in self-consistency calculations is achieved, the current through a device is computed by the Landauer-like formula [27–29]: $I=(2e/h)\int_{\mu_R}^{\mu_L}T(E,V)dE$, where V is the electric potential difference between left and right electrodes, $\mu_L(\mu_R)$ is the chemical potential of the left (right) electrode and $[\mu_R,\mu_L]$ is an energy region contributing to the current integral, called the bias window. $T(E,V)$ is the transmission coefficient at the energy E and bias V. In all calculations, the average Fermi level is set as zero.

3. Results and discussion

3.1. Electronic structures of AGNR electrodes

For the sake of comparison, we firstly calculate the band

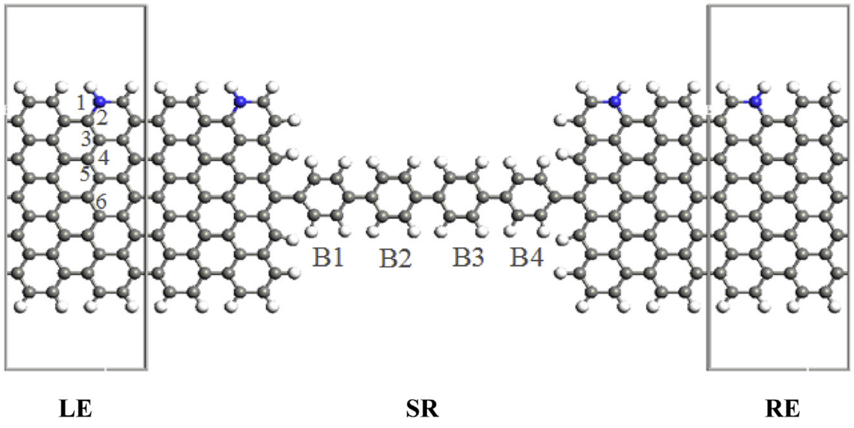

Fig. 1. Geometrical structure. Two semi-infinite AGNRs are doped periodically with N atoms at six selective positions 1–6, respectively, serving as two electrodes, and a polyphenylene molecule with four benzene rings B1–B4 is sandwiched in the nanogap to construct a molecular device.