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Molecular rectification modulated by alternating boron and nitrogen co-doping in a combined heterostructure of two zigzag-edged trigonal graphenes

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A B S T R A C T

The rectifying properties of a heterostructure combined with two trigonal graphenes are investigated by first-principles approach. The graphenes have left (left and right) vertical benzenes substituted with alternating nitrogen and boron atoms. The results indicate that co-doping atoms have distinct influences on the rectifying performance of such devices. When the left trigonal graphene is doped and two trigonal graphenes are bound through a BH pair, a reverse rectifying behavior can be observed. However, a forward rectifying behavior is observed when they are bound through an NH (NB) pair. The rectifying effect is more prominent for the NB pair.

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1. Introduction

With the continuous miniaturization of silicon-based electronic devices and the rapid development of microelectronics, molecular devices are considered as to be some of the most promising candidates for future electronic devices. In recent years, molecular devices have elicited significant interdisciplinary interest. Many experimental and theoretical investigations indicate that the use of a single molecule to construct an electronic device is capable of realizing basic electronic functions such as negative differential resistance (NDR) [1], current rectification [2,3], and current switching [4,5]. The molecular rectifier, which was first proposed by Aviram and Ratner in 1974 [6], will have a crucial role in the development of future molecular electronics because it is the simplest functional element that can be used to build an electronic circuit [7]. At present, many studies have been performed on molecular rectifiers [8–16].

Graphene has offered a new opportunity for nanoelectronics investigations since its first preparation in 2004 [17]. However, 2D graphene is a semimetal material, which significantly limits its applications in microelectronics. Chemical doping with foreign atoms is generally chosen to adjust the band gaps from the perspective of semiconductor technology. Among foreign atoms, boron and nitrogen atoms are regarded as representative substitutes and are adopted frequently in graphene because the binding between B, N, and C is covalent and strong compared with the bond of the host CC [18]. Remarkably, doped graphene has been synthesized successfully in an experiment [19], which makes the chemical doping with boron and nitrogen atoms on graphene a hot research topic, and doped graphene can achieve some interesting transport properties, such as rectifying [20], spin-polarized tunneling [21], half-metallicity [22], NDR [23], field effect transistor [24], and spin filtering [25]. Zigzag-edged trigonal graphene nanoflakes (ZTGNFs) are nanosized graphene flakes that are produced by the geometric cutting of graphene. At the same time, few studies have addressed the rectifications of functionalized trigonal graphene nanoflakes, such as a combined heterostructure of two NB-doped trigonal graphene nanoflakes [8], in triangular-shaped graphene nanoflakes connected to gold (Au) electrodes via different numbers of thiol groups at each side and by edge modification-controlled ZTGNF junctions [9]. Nevertheless, these studies are still incomplete: various formations and mechanisms that generate opposite directional rectifying effects for ZTGNFs must be explored intensively and extensively. In this Letter, we report the results of theoretical studies on inverse rectification that can be achieved by alternating boron and nitrogen doping in a combined heterostructure of two ZTGNFs.

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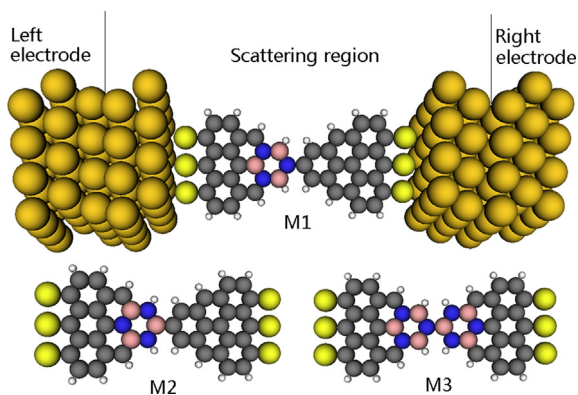 *E-mail address:* ybsy_guo@163.com (Y. Guo).

Fig. 1. Schematic of molecular devices M1–M3 in our simulations: a combined heterostructure of two ZTGNFs coupled with Au electrodes through thiol groups, where left (left and right) vertical benzenes are substituted by alternating nitrogen (N) and boron (B) atoms.

2. Simulation model and computational details

Fig. 1 shows our constructed models of two ZTGNFs, which bridge both flat Au(111)-(4 × 4) electrodes via thiol groups. The ZTGNFs are saturated with hydrogen atoms. The investigated system can be divided into three parts: the left electrode, the central scattering region, and the right electrode. The scattering region contains parts of Au electrodes to include the screening effects in the calculations. Models M1, M2, and M3 correspond to the NH, BH, and NB pairs that are bounding two ZTGNFs, respectively. The distance between the Au electrodes surface and the terminal S atom, which is chosen to be located at the hollow site of the Au triangle, is 2.45 Å.

As stated in our previous study [26], the geometric optimization and electron transport calculations are all performed by using density functional theory (DFT) in combination with the nonequilibrium Green's function (NEGF) technique as implemented in the software package Atomistix ToolKit [27–30]. The reliability of the method has been demonstrated in some studies, whose calculated results could be compared with experimental data [31–34]. The ZTGNFs that is placed between two Au electrodes is relaxed when a force tolerance of 0.05 eV/Å is achieved. The generalized gradient approximation scheme of Perdew–Burke–Ernzerhof (GGA.PBE) is used to describe the exchange-correlation potential in the self-consistent DFT electronic structure description. The core electrons are modeled with Troullier–Martins [35,36] norm-conserving pseudopotentials, while valence electrons are expanded in a SIESTA localized basis set. We used the double-ζ polarized basis set for all of the atoms of the scattering region and the single-ζ polarized basis set for the Au atoms, to save the computational effort and improved the calculation precision and reliability. The Brillouin zone has been sampled with $1 \times 1 \times 200$ points, and a mesh cutoff energy of 150 Ry is selected to achieve a balance between the calculation efficiency and accuracy. The convergence criterion for the Hamiltonian and electron density is set to 10^{-5} in total energy. The nonlinear current through the electrode–molecule–electrode sandwich system as a function of the external applied bias can be calculated by using the Landauer–Büttiker formula [37]. Hence, the current is determined by the integral area of the transmission curve inside the bias window.

3. Results and discussions

The current is of direct interest because it corresponds to an experimentally observable quantity. Our self-consistent calculated currents as a function of the applied bias voltages for all of the three models in the bias region of interest are shown in Fig. 2(a).
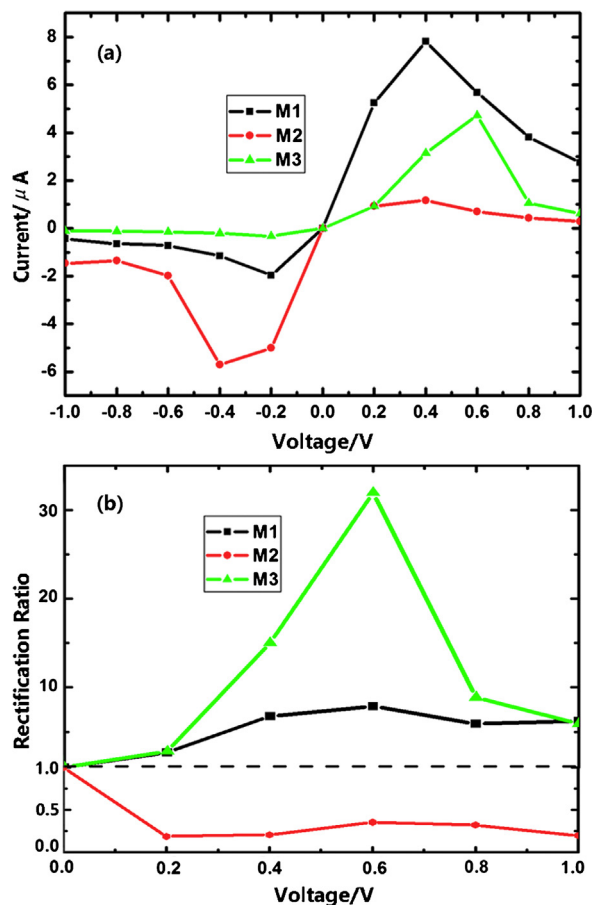

Fig. 2. (a) $I-V$ curves and (b) rectifying ratio change with the applied bias for models M1–M3.
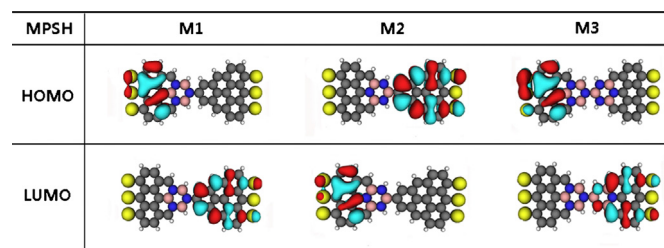

Fig. 3. Spatial distribution of the HOMO and LUMO states for three models at zero bias. Red and blue indicate the positive and negative signs of the wave functions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

The current–voltage ($I-V$) curves of these models show clearly asymmetric behavior, which has gained widespread interest because this type of behavior is necessary for electronic rectifiers. More specifically, several important features in the evolution of the currents are clearly visible. (1) For models M1 and M3, the currents at the positive bias are larger than those at the same negative bias. However, model M2 displays the opposite behaviors. (2) The asymmetry of the $I-V$ characteristic relation in model M3 is much more obvious than that in the other two models. This asymmetry is exhibited in Fig. 2(b) and is evaluated by a rectification ratio which is defined as the ratio of the currents under positive and negative biases for the same voltage magnitude and is calculated by $R(V) = I(V)/|I(-V)|$. Thus, $R > 1$ ($R < 1$) corresponds to forward (reverse) rectification, respectively. The largest rectification ratio in M3 increases up to 32 at 0.6 V.