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Covalent coupling of porphines to graphene edges: Quantum transport properties and their applications in electronics

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ABSTRACT

Recently, He et al. succeeded in covalently linking porphines to graphene edges on a Ag(111) substrate by dehydrogenative coupling [Nat. Chem. 9 (1) (2017) 33–38], thus created a new hybrid material with tunable functionalities. Motivated by this work, we further investigate the electron transport properties of three porphine/graphene coupling motifs observed by scanning-probe technology with submolecular resolution in the experiment. By using density-functional theory combined with the Keldysh nonequilibrium Green's technique, we find many interesting electron transport phenomena in these new hybrid structures. Conductivity enhancement can be observed when porphines are covalently bound to the edges of specific armchair graphene nanoribbon (AGNR) and symmetric zigzag GNR (ZGNR). However, the origin of conductivity enhancement in the AGNR related hybrid system is completely different from that in the ZGNR related system. Moreover, negative differential resistance (NDR) behaviors can be found in ZGNR related coupling configurations. In particular, two different NDR mechanisms are found in these hybrid systems.

1. Introduction

Porphyrins, a star of materials chemistry, have many potential applications in single-molecule devices [1], gas sensors [2–4], solar batteries [5–7]. In particular, porphyrins that chemisorb strongly to metal electrodes show a number of fascinating charge transport properties including field effect [8], long-range electron tunneling [9], rectifying effect [10,11], etc. If protons of two nitrogen atoms in porphyrins are replaced by transition metal ions, porphyrin derivatives known as metalloporphyrins can be synthesized. As metalloporphyrins contain different kinds of transition metal ions, the difference in the number of electrons gives rise to an abundance of spin states. This makes metalloporphyrins suitable candidates for designing spintronic devices, such as spin filters [12] and spin valves [13]. At present, porphyrins and their derivatives have been considered as a starting point for developing single-molecule based electronic devices. Moreover, graphene, composed of one layer of carbon atoms, will trigger a new industrial revolution in the field of electronics [14,15]. So far, graphene has showed a broad application prospect in future electronic devices due to its outstanding electronic properties such as high carrier mobility [16,17], long spin-coherence distance [18], and anomalous quantum hall effect [19]. Meanwhile, graphene can also be considered as electrical interconnects in nanoscale electronic devices [16,17]. Thus, synthesizing a multifunctional hybrid material by utilizing both the exceptional properties of porphyrins and graphene is the goal that chemists and materials scientists are pursuing.

In fact, as early as 2009, Xu et al. [20] have reported the first organic-solution-processable functionalized-graphene hybrid structure with porphyrins. However, it is difficult to achieve complex multicomponent architectures in their experiments due to poor control over porphyrin's contact positions. To meet the precision necessary for molecular electronics, He et al. [21] developed a precise and controlled method to attach single porphines (the simplest porphyrins) to the edges of graphene. Meanwhile, they observed several well-defined bonding structures which feature different numbers of C–C bonds to graphene with armchair and zigzag edges.

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The benefit of the resulting hybrid material is that it realizes the complementary electronic properties in the graphene and the porphyrins. This can be summed up in several important aspects as follows: (1) Graphene that possesses a lot of electronic applications could be more useful in solar energy conversion cells after covalent coupling with the porphyrins. (2) He et al. [21] found that intrinsic features of porphyrins for metallation are preserved in the resulting hybrid material, thus it can develop new sensors. This also makes this hybrid material useful in spintronics. At present, many theoretical studies showed that some inorganic/organometallic materials can be designed as spintronic devices [22,23]. However, experimental realization of these materials is a big problem because practical synthesis methods are lacking. This problem may be solved by this resulting hybrid material because the porphyrins can coordinate different transition metals in the center of the tetrapyrrole ring. (3) The engineering of the electronic gap in the hybrid structures could be realized when the porphyrin units are orderly connected in the edges of graphene nanoribbons.

Covalent linking of porphyrins to graphene could open the opportunity to create a hybrid material with tunable properties. It is very important and timely to investigate corresponding transport properties, which is closely relevant to their practical applications in molecular electronics. In this work, we investigate the electron transport properties of three porphine/graphene coupling motifs observed by scanning-probe technology with submolecular resolution [21]. On the basis of density-functional theory calculations combined with the Keldysh nonequilibrium Green's technique, we found very interesting quantum transport properties in these porphine/graphene coupling configurations, and confirmed that these hybrid structures can realize a variety of molecular functionalities.

2. Method and model

In the present work, we characterize the geometrical structures of the porphine/armchair graphene nanoribbon (AGNR) and the porphine/Zigzag GNR (ZGNR) interfaces as model systems [21]. Fig. 1 shows the geometrical models that demonstrate porphine/GNR coupling configurations. Fig. 1(a) displays the first coupling configuration, where the porphine forms two C–C bonds at β-positions. It is noted that here the porphine is linked to the edge of W-AGNR (W = 5, W is the number of carbon dimer lines across the ribbon width), thus this configuration is names as 5-AGNR@Porphine. Similarly, when the porphine is coupled to 6-AGNR and 7-AGNR, the corresponding configurations is named as 6-AGNR@Porphine and 7-AGNR@Porphine, respectively. The other two coupling configurations are shown in Fig. 1(b) and (c). Clearly, porphines form three C–C bonds (at β-, meso-, β-positions) and four C–C bonds (at β-, β-, meso-, β-positions) at the edges of ZGNR. In order to facilitate discussion, these two coupling motifs are called as configurations A and B, respectively. For the ZGNR, we investigate the effects of configurations A and B on the transport properties of asymmetric ZGNR and symmetric ZGNR. For convenience, configurations A and B in ZGNR are named as ZGNR@Porphine(A) and ZGNR@Porphine(B), respectively. For example, the coupling configurations in Fig. 1(b) and (c) are called as 3-ZGNR@Porphine(A) and 3-ZGNR@Porphine(B), respectively. Based on the coupling configurations mentioned above, the corresponding two-probe systems are constructed to investigate their quantum transport properties and potential applications in electronic devices. These specific two-probe configurations can be found in the top of Figs. 2(a)–(c) and 3(a)–(d). Clearly, these two-probe systems include three regions, namely, left electrode, central scattering region, and right electrode. For all two-probe systems, each electrode is constructed by a supercell which contains two repeated carbon unit cells. For the central scattering regions, AGNR related two-probe system is AGNRs of 10 unit cell length [see the top of Fig. 2(a)–(c)], and other ZGNR related two-probe systems are ZGNRs of 13 unit cell length [see the top of Fig. 3(a)–(d)].

The electron transport properties of the porphine/GNR hybrid systems were performed using density-functional theory combined with the Keldysh nonequilibrium Green's technique, as implemented in the ATOMISTIX TOOLKIT package [24,25].

For 6-AGNR and 7-AGNR related systems, the double-ξ polarized basis set is used for nitrogen atoms, and the single-ξ polarized basis set is used for carbon and hydrogen atoms. For other two-probe systems, the double-ξ polarized basis set for all atoms is adopted. The local density approximation, a $1 \times 1 \times 100$ K-point mesh, and a cutoff energy of 150 Ry are employed. The geometries are fully relaxed until the force on each atom is less than 0.05 eV/Å. The spin polarization in the ZGNR related systems is ignored in our work because it is unstable at room temperature [26–28].

The transmission coefficients at zero bias are calculated by the standard expression:

$$T(E, V_b) = Tr\left[\Gamma_l G^R \Gamma_r G^A\right], \tag{1}$$

where G^R and G^A are the retarded and advanced Green functions of the central scattering region, respectively.

At finite bias, the current through the hybrid systems are calculated using Landauer-Büttiker formula [29].

$$I(V_b) = \frac{2e}{h}\int T(E,\ V_b)[f_l(E-\mu_l) - f_r(E-\mu_r)]dE, \tag{2}$$

where $\mu_{l(r)}$ is the electrochemical potential of left and right

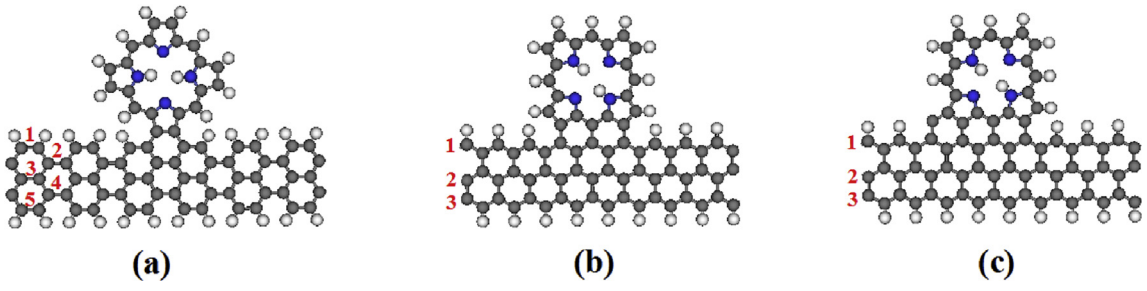

Fig. 1. Geometrical models that demonstrate porphine/GNR coupling configurations. (a) Two C–C bonds at β-positions. (b) Three C–C bonds at β-, meso-, β-positions. (c) Four C-C bonds at β-, β-, meso-, β-positions. According to the previous convention, AGNRs are classified by the number of dimer lines across the ribbon width, and ZGNRs are classified by the number of the zigzag chains across the ribbon width. The scanning tunneling microscopy images of these bonding motifs can be found in Ref. [21]. (A colour version of this figure can be viewed online.)