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Strong Current-Polarization and Negative Differential Resistance in FeN₃-Embedded Armchair Graphene Nanoribbons

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Motivated by the recent advances of transition-metal-nitrogen-carbon (TM-N-C) materials in catalysis, we investigate the electronic structure and transport properties of FeN₃-embedded armchair and zigzag graphene nanoribbons (FeN₃@AGNRs, FeN₃@ZGNRs) with different widths. The first-principles results indicate that the FeN₃ induces significant changes on the band structures of both ZGNRs and AGNRs, making the resultant systems quite different from the pristine ones and own room-temperature stable ferromagnetic (FM) ground states. While only FeN₃@AGNRs possess a significant spin-dependent negative differential resistance (NDR) and a striking current polarization (nearly 100%) behaviors, due to that FeN₃ introduces two isolated spin-down states, which contribute current with different performances when they couple with different frontier orbits. It is suggested that by embedding FeN₃ complexes, AGNRs can be used to build spin devices in spintronics.

Key words: Transition-metal-nitrogen-carbon, Current polarization, Electronic transport, Non-equilibrium Green’s function

I. INTRODUCTION

Transition-metal-nitrogen-carbon (TM-N-C) materials have received much attention recently, due to promising applications in catalysis [1–5]. Graphene possesses novel properties and wide applications [6]. TM atoms can be loaded on graphene via adsorbing on defects or isolating at edges [7–11]. The resultant TM-graphene can be either magnetic or nonmagnetic [12, 13], depending on the type of TM atoms and the post-formed substructures. Nitrogen-doped graphene (N-graphene) can adequately confine a large number of TM atoms via various chemical activities, due to the existence of many N-doping induced activities [14–19]. And experimental measurements show that the obtained TM-N-graphene could possess enhanced stability and comparable high catalytic activity to TM-graphene and to other TM-N-C materials [20].

Recently, we have proven that conversion of dinitrogen to ammonia is achievable in FeN₃-embedded graphene (FeN₃@graphene), due to the existence of a strong spin-polarization near Fe center [5, 21]. Previous studies suggest that the number of 3d electrons retained in TM center plays a critical role in determining the catalytic ability of TM-N-C systems [22], since they concern the strength of spin-polarization significantly [15, 23, 24]. A strong spin-polarization is also a highly desired property in spintronics. For instance, graphene nanoribbons (GNRs) have rich and extraordinary electronic properties, but only zigzag-edged GNRs (ZGNRs) are widely proposed for building spin devices, due to anti-ferromagnetic (AFM) edge states [25–27]. On the contrary, armchair-edged GNRs (AGNRs) are intrinsically nonmagnetic and are hard to magnetize, and thus have rarely been proposed for spintronics [28–32]. Hence, we are keen to know when FeN₃ complexes are embedded, whether the resultant FeN₃@AGNRs and FeN₃@ZGNRs are magnetized and whether both of them can be used for building spin devices.

In this work, the electronic structure and transport property of both FeN₃@AGNRs and FeN₃@ZGNRs with different widths are evaluated from first principles calculations. Our results show that a significant spin-dependent differential negative resistance (NDR) and a striking current-polarization (near 100%) present only in FeN₃@AGNRs, demonstrating the possible device applications of such systems in spintronics.

II. MODEL AND COMPUTATIONAL METHOD

Considering that AGNRs are classified into three families by their width-dependent energy gaps (W=3m, 3m+1, 3m+2) [25, 26], three FeN₃@AGNRs with width W=12, 13, and 14 were investigated, whereas only an FeN₃@ZGNR with W=8 was considered. To eliminate the periodic interaction, 4 cells of AGNR and 6

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FIG. 1 Top and side views of iso-surface plots of the spin-resolved charge density of FeN$_3$@13-AGNR (a), and those of FeN$_3$@8-ZGNR (b) (the red for spin-down and green for spin-up charge densities), with the iso-value set 0.02 eÅ$^{-2}$, and the optimized structures of the FeN$_3$@13-AGNR and the FeN$_3$@8-ZGNR were given in the insets of FIG.1 (a) and (b) in the upper left corner (the red, blue, gray, and white colors represent the iron, nitrogen, carbon, and hydrogen atoms), as well as the band structures of pristine 13-AGNR (c), FeN$_3$@13-AGNR (d), pristine 8-ZGNR (e), and FeN$_3$@8-ZGNR (f) (the red dotted lines for spin-down and the black solid lines for spin-up electrons), respectively.

III. RESULTS AND DISCUSSION

Total energy calculations show that the energy difference ($\Delta E$) for the FeN$_3$@ZGNR between the ferromagnetic (FM) state and anti-ferromagnetic (AFM) state is about 0.94 eV, and that between the FM and nonmagnetic (NM) states is about 1.04 eV. Obviously, FeN$_3$@8-ZGNR is still spin-polarized. Different from the pristine ZGNRs, FM becomes the ground state which is quite stable at room temperature. Yet for FeN$_3$@13-ANGR, the $\Delta E$ between FM and NM states is about −0.82 eV and the AFM state is even not reached. Contrary to the pristine AGNRs, FeN$_3$@AGNR is magnetic and has a room-temperature-stable FM ground state. Obviously, the embedding of FeN$_3$ brings a significant change on the electronic characteristics of GNRs, especially for AGNRs.

All the calculations were carried out in SIESTA code (Version 4.0), by applying nonequilibrium Green’s functions (NEGFs) in combination with the spin-resolved density functional theory (DFT) [33]. The revised Perdew-Burke-Ernzerhof (rPBE) generalized gradient approximation (GGA) was chosen for exchanging correlation potential. A 150 Ry cut-off energy was set for real space grids. An energy shift parameter of 0.01 Ry was used to determine the cutoff radii of atomic orbitals. A tolerance of 0.02 eV/Å on each atom was used to control the residual force for structural relaxations. The grids of 1×1×11 and 1×1×23 were adopted to sample the Brillouin zone (BZ) for structural relaxations and band-structure analysis, and the grid of 1×1×100 for transport calculations, respectively.

cells of ZGNR were included in the supercells of the FeN$_3$@AGNR and FeN$_3$@ZGNR, which are of a length about 1.7 nm and 1.5 nm, respectively. The vacuum layer of a distance about 15 Å was used along x and y directions. As examples, the optimized structures of the FeN$_3$@13-AGNR and the FeN$_3$@8-ZGNR were given in the insets of FIG. 1 (a) and (b) in the upper left corner, respectively.

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FIG. 2 The band structures of FeN$_3$@12-AGNR (a), FeN$_3$@13-AGNR (b), and FeN$_3$@14-AGNR (d), (red dotted lines for spin-down, and black solid lines for spin-up), as well as the normalized PDOS of FeN$_3$@13-AGNR (c) (negative for spin-down and positive for spin-up) at their FM ground states.

netic moment comes from Fe atom and only a very small part from the neighboring N atoms. While for the FeN$_3$@ZGNR, the net electrons distribute both along the zigzag edges and near the FeN$_3$ center. Obviously, the net electrons on the two edges and the center have the same spin orientation, indicating that the embedding FeN$_3$ changes the interaction between the edge states of ZGNR from anti-ferromagnetic to ferromagnetic. The spin-resolved band structure of pristine 13-AGNR and FeN$_3$@13-AGNR at the ground state is given in FIG. 1 (c) and (d), and that of the 8-ZGNR and FeN$_3$@8-ZGNR in FIG. 1(e) and (f), respectively. One can see that the embedding induces obvious spin-splits near the Fermi level for both FeN$_3$@AGNR and FeN$_3$@ZGNR. Their electronic structures are indeed modified drastically by the embedding. Especially for the FeN$_3$@AGNR, there exist two isolated spin-down states near the Fermi level, suggesting a strongly spin-dependent transport behavior. Since the valence band maximum (VBM) and conduction band minimum (CBM) play a decisive role in determining the transport properties. To provide a general view of the effect of embedding on the band structures of the three families AGNRs. The band structures of FeN$_3$@12-AGNR, FeN$_3$@13-AGNR, and FeN$_3$@14-AGNR are plotted in FIG. 2 (a), (b), and (d), respectively. One can see that although there exist some differences in the band gap of the three ribbons, they have a similar overall picture on the band structures. Especially, two isolated spin-down states below the Fermi level can be found in each ribbon, suggesting the similar spin-dependent transport properties of the three families of the embedded AGNRs.

For the sake of analysis, the projected density of state (PDOS) of the FeN$_3$@13-AGNR is calculated and given in FIG. 2(c). It shows clearly that the two isolated spin-down states are mainly derived from the 3d electrons of Fe atom and the 2p electrons of C atoms, unambiguously proving the origins of the observed FM ground state. This also means that some 3d electrons have transferred into graphene network via the three N atoms and thus contributed to electronic transport. More importantly, one can see that only the 3d electrons of spin-down orientation have a wide distribution in energy. Hence, the 3d electrons have a significant contribution only to spin-down transport. This feature is quite useful for spin-dependent transport.

We calculated electronic transport properties and the obtained current-voltage ($I$-$V$) characteristics of FeN$_3$@13-AGNR and the pristine one are plotted in FIG. 3(a). It shows clearly that the current of spin-down system reduces rapidly as the bias increases from 0.9 V to 1.1 V, suggesting that the system possesses an obvious spin-dependent negative differential resistance (NDR) behavior, which is quite useful for building spin-dependent electronic switches. Moreover, one can see that the embedding induces only a significant reduction on the threshold voltage of the spin-down system from 1.0 V to 0.4 V, and thus the spin-down currents are much higher than the spin-up current for the biases below 1.1 V. This means that the system possesses a strong current-polarization ($\xi$), which can be defined as $\xi=|I_{\text{UP}}-I_{\text{DN}}|/(I_{\text{UP}}+I_{\text{DN}})$. We calculated the bias-dependent $\xi$ and the obtained result is plotted in FIG. 3(b). For the bias from 0.2 V to 1.0 V, one can see perfect current-polarization with a ratio almost 100%, very advantageous for high-performance spin device applications. Considering the similar structures of the three families of FeN$_3$@AGNRs, one can draw a conclusion that FeN$_3$@AGNRs possess a striking current-polarization and a large spin-dependent NDR behavior, which are quite useful in spintronics.

Curious about the underlying mechanism, we illustrated the contour of bias-dependent transmission $T(E, V_b)$ of the spin-up and spin-down systems of the FeN$_3$@13-AGNR in FIG. 3 (c) and (d), where the bias window for current calculations was marked by two white lines. For spin-up systems, one can see that meaningful transmission appears in the bias window only as the bias increases to 1.0 V, while for spin-down system, meaningful transmission starts to appear in the bias window as $V_b=0.4$ V, and it is retained to form a belt with bias increasing. Thus spin-down current in the bias ranging from 0.4 V to 1.0 V is always much larger than the spin-up current, which is almost zero, resulting in the striking current-polarization. Noting that a valley exists in the formed transmission belt around $V_b=1.0$ V (denoted by a red arrow in the FIG. 3(d)), indicating the smaller current at this region that well explains the NDR behavior of spin-down system. Hence, the formed transmission belt is significant for understanding both the observed NDR and current-polarization of the system.

To reveal the source of the formed transmission belt,
FIG. 3 The current-voltage ($I$-$V$) characteristics of pristine 13-AGNR, and FeN$_3$@13-AGNR (a), as well as the current polarization ($\xi$) of FeN$_3$@13-AGNR (b). And the contour of the bias-dependent transmission $T(E, V_b)$ of (c) the spin-up and (d) the spin-down systems of FeN$_3$@13-AGNR.

FIG. 4 The bias-dependent spin-down band structure of the left electrode (left panels), the spin-down transmission curve (middle panels), and spin-down band structure of the right electrode (right panels) of the spin-down system in FeN$_3$@13-AGNR under bias 0.6, 1.1, and 1.4 V, respectively.

we plotted the band structures of the left and right electrodes, as well as the transmission of spin-down system of FeN$_3$@13-AGNR with $V_b$=0.6, 1.1, and 1.4 V in FIG. 4 (a), (b), and (c), respectively. One can see a sharp transmission peak appears in the bias window as $V_b$=0.6 V, due to that there exist overlaps between the VBM of left electrode and the CBM of right electrode. Obviously, the VBM and CBM will still be overlapped as the bias further increases, while the VBM will be overlapped with another CB with a higher energy as $V_b$=1.1 V, resulting the formation of the transmission belt. As has been noted in FIG. 2(c), the VBM of the spin-down system in FeN$_3$@AGNRs is composed of 3d electrons of Fe atom and the 2p electrons of C atoms, while it is not for spin-up system. Hence, it is the FeN$_3$ complexes, which have quite different effects on the spin-up and spin-down systems, giving rise to the striking current-polarization and spin-dependent large NDR behaviors in FeN$_3$@AGNRs. We have also calculated the $I$-$V$ characteristics of FeN$_3$@ZGNR and plotted the results in FIG. S1 (supplementary materials). It shows that both the striking current-polarization and large NDR behaviors observed in FeN$_3$@AGNRs, have not been found in such systems.
IV. CONCLUSION

By applying DFT+NEGF calculations, we have investigated the electronic structure and transport properties of FeN₃-embedded GNRs. Strong current-polarization (nearly 100%) and NDR behaviors have been observed in the FeN₃-embedded AGNRs. It is revealed that the FeN₃ complexes induce quite different effects on the band structures of the spin-up and spin-down systems, resulting in the largely spin-dependent transport behavior and striking current-polarization. Our findings suggest that AGNRs can also be magnetized by embedding of TM atoms and thus have promising applications in spintronics.

Supplementary materials: The calculated spin-up and spin-down currents of the FeN₃@8-ZGNR are shown in FIG. S1.

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