Self-doping and magnetic ordering induced by extended line defects in graphene

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Self-doping and magnetic ordering induced by extended line defects in graphene

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Based on first-principles calculations, we reveal that the interactions between extended line defects (ELDs) of type “585” (formed by five and eight membered rings) ELDs embedded in graphene can induce ordered magnetism and self-doping of graphene. By reducing the distance between 585 ELDs, a distinct charge transfer is predicted from the center of 585 ELDs to their edges, which induces a Dirac point shift below the Fermi level, resulting in distance- or density-dependent n-type doping in the graphene. Relevant to the above finding, we found a distance-dependent spin polarization at the edges of 585 ELDs, attributable to the rigidity of the π electronic structure. Our finding suggests a promising approach for achieving n-type graphene for spintronic devices by creating 585 ELDs.

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I. INTRODUCTION

Due to its nonprimitive bipartite hexagonal structure, graphene exhibits fascinating electronic properties [1–4]. The magnetism that has been observed experimentally in graphene [5–7] has attracted extensive attention for its applications in spintronics. Normally, a π vacancy in graphene can induce spin polarization, while due to its nonprimitive lattice and the random creation of π vacancies by impurities, practically ordered magnetism can hardly be realized [8]. Furthermore, the intrinsic magnetism of graphene has been a controversial issue not only experimentally [7,9] but also theoretically [8,10,11]. It is partially attributed to the difficulty in controlling experimental conditions, as well as the complex distribution of point defects in samples.

In contrast to the disordered point defects, grain boundaries [12–14] in graphene exhibit one-dimensional (1D) ordered structures, which can significantly alter the electronic characteristics of the material [15–17]. Grain boundaries in graphene are mainly formed by the mismatch between graphene flakes during growth. These 1D line defects are often ordered and can induce local density of states close to the Fermi level [18], which may cause a magnetic stability of the system. By the chemical vapor deposition (CVD) method [19,20], graphene can be synthesized with its lattice orientation being guided by the well-controlled surface morphology of the substrate during its growth. Experimentally, only extended line defects (ELDs) containing five and eight membered rings (585) were successfully synthesized in graphene [21]. As illustrated in Fig. 1(a), this line defect resembles a zigzag ribbon with its edges passivated by carbon dimers. Due to its unique structure, various electronic characteristics have been investigated theoretically [22–25]. Tunable magnetism may appear when an external strain is applied along the zigzag direction [26]. Charge states can also induce 1D magnetism ordering along the edges of 585 ELDs [27]. A zigzag ribbon embedded with 585 ELDs presents a half metallic character, with its two edges possessing ferromagnetic coupling [28]. Due to the localized density of states close to the Fermi level, a magnetic instability exists at the 585 ELD, which can be stabilized by an external effect (e.g., strain and electron doping). However, the question arises whether the ELD possesses an intrinsic ferromagnetic stable state when it is not isolated. When the distance between 585 ELDs decreases, the concepts of edge, as well as defect, will disappear. Compared with graphene embedded with an isolated 585 ELD, the system with tightly linked 585 ELDs possesses significantly different electronic characteristics. The allotrope formed only by 585 ELDs shows significant electronic anisotropy [29]. A negative differential resistance has been reported [30] when 585 ELDs are separated by one hexagonal ring. However, the situation between these two extremes (isolated and tightly linked 585 ELDs) has not been studied so far. Therefore, it is important to study the evolution of the electronic characteristics between these extremes.

In this paper, a systematic study of graphene embedded with 585 ELDs was performed by gradually decreasing the distance between the defects. In this process, spontaneous spin polarization was found to occur for the systems with small distances. The ordered magnetic moment is mainly located at the edges of the 585 ELD and decays rapidly to the interior of hexagonal rings. Due to the charge transfer from the center to the edges of the 585 ELD, the Dirac point shifts below the Fermi level, acting as n-doping of graphene. The concentration of the carriers obviously increases with decreasing distance. Due to the rigid π conjugation in the bulk of hexagonal rings and in the center of the ELD, the additional electrons arising from self-doping result in the appearance of spin polarization at the edges of the ELD.

Because of the high carrier mobility of graphene, the realization of p-type and n-type doping in graphene is desirable in the applications of electronic devices. Various effects, including adatoms [31], doping foreign atoms [32], and gate voltage [33], can induce an energy shift of the Dirac point. However, more stable p- or n-type-doped graphene is required for practical applications. Experimentally, p doping has been observed at the grain boundaries in graphene [34]. In our study,
FIG. 1. (Color online) (a) Geometric structure of graphene with embedded 585 ELDs. The carbon dimer in the center of each 585 ELD is highlighted by a rectangle and denoted as C₂. Two distinguishable sites forming an edge zigzag chain are denoted as edge A and edge B, respectively. The zigzag chains are denoted as 1, 2, 3, …, n. A unit cell is indicated by a dashed rectangle. (b) Bond lengths in a 585 ELD as a function of the width (N) of ZGRs. In the figure, the bond lengths of three kinds of bond are shown: the bond length of C₂ and the bond lengths forming a zigzag edge chain. For the latter, two different bonds are defined as eight (forming eight membered rings) and five (forming five membered rings), respectively. (c) Formation energies of the systems with different widths (N) of ZGRs. (d) Energy variation of the zigzag chains.

we propose that n-type doping can be realized by decreasing the distance between 585 ELDs in graphene. We found that the effective Coulomb onsite repulsion between the electrons at the edges of 585 ELDs monotonously decreases with reducing the distance between 585 ELDs, which induces self-doping of the systems. Our findings show that the magnetism and doping level can be tuned by changing the distance between 585 ELDs in graphene.

II. COMPUTATIONAL DETAILS

To optimize the geometric structures, first-principles calculations were carried out within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) type [35]. A double-$\zeta$ polarized (DZP) basis set and norm-conserving pseudopotential were applied as implemented in the SIESTA package [36–38]. The force tolerance between atoms was set to be 0.005 eV/Å to fully relax the geometric structures. The real space grid was described with a 250 Ry plane wave cutoff. The vacuum between slabs in neighboring periodic cells was set to 20 Å to avoid unphysical interactions. For the electronic structure calculations, $10 \times 30 \times 1$ Monkhorst-Pack k-points were applied. To describe accurately the energy difference between different magnetic configurations, the tolerance of self-consistent field (SCF) was set to be less than $10^{-4}$. Further, we applied the GGA + $U$ method [39] to calculate the magnetic moment and stability of the magnetism of the systems, where the value of the effective onsite repulsion $U_{\text{eff}}$ was determined with the linear response $U$ approach [40], as implemented in the Quantum ESPRESSO package [41].

To evaluate the relative stabilities of 585 ELDs, we defined the formation energy as $E_{\text{formation}} = E_{\text{Total}}/N_{\text{Total}} - E_{\text{Atom}}$, where $E_{\text{Total}}$ is the total energy of the system, $E_{\text{Atom}}$ is the energy of a single carbon atom in graphene, and $N_{\text{Total}}$ is the total number of atoms in the system. Due to the mismatch between six membered rings and five (or eight) membered rings, residual forces drive the structures of zigzag chains to deviate from the ones in perfect graphene. In
order to study the variation of zigzag chains, we defined the differential energy of a zigzag chain between 585 ELDs and perfect graphene, \( \Delta E_{\text{zigzag-chain}} = E_{\text{chain-GR}} - E_{\text{chain-G}} \), where \( E_{\text{chain-GR}} \) (\( E_{\text{chain-G}} \)) is the energy of zigzag chain in zigzag-edged graphene ribbons (ZGRs; perfect graphene).

**III. RESULTS AND DISCUSSION**

The geometric structure of graphene embedded with 585 ELDs is formed by periodically connected ZGRs stabilized with carbon dimers (C₂), as shown in Fig. 1(a). By changing the width of the ZGRs, a series of allotropes were obtained. Here, we label the carbon allotropes with the total number of zigzag chains \( N \) between rows of C₂. The systems with \( N \) ranging from 2 to 12 were investigated. When \( N \) is larger than 12, the interaction between 585 ELDs can be ignored, so the 585 ELD embedded in graphene can be treated as an isolated defect and will not be discussed in this paper. Due to the mismatches between five, eight and six membered rings, residual strain exists along the edges of the 585 ELD, which results in a slightly larger C-C bond than that in the interior of ZGRs. Electronic effect also plays a role and will be discussed later in this paper. Figure 1(b) shows bond lengths of the 585 ELD as a function of \( N \). When \( N \) increases from 2 to 4, the bond lengths of the 585 ELD change markedly. For C₂, the bond length decreases rapidly from 1.48 to 1.45 Å. By further increasing \( N \) from 4 to 12, the differences between bond lengths becomes smaller. However, even for isolated ELD \((N \geq 12)\), the bond length of C₂ is still \( \sim 0.1 \) Å larger than that of the interior of ZGR. In the center of the 585 ELD, the angle \( \alpha \) deviates strongly from 120°, indicating that the typical \( sp^2 \) hybridization is partially destroyed. For the zigzag chain at the edges [denoted in Fig. 1(a)], clear distortion occurs due to the different strain induced by a pentagon and an octagon. A pentagon has a tensile effect on the hexagonal rings, while an octagon has a compressive effect on the hexagonal rings. For the systems with \( N = 2 \) and 4, the residual forces cannot be fully relaxed. Thus, large distortions of the zigzag chain occur. However, for the systems with \( N \geq 6 \), the zigzag chain next to the edge acts as a “buffer” chain [marked in Fig. 1(a)], which relaxes the forces in the 585 ELD. Therefore, the distortion of the zigzag chain at the edges almost disappears.

To evaluate the stability of the geometric structures of the systems, their formation energies were calculated. Since the carbon allotrope, which contains only five and eight membered rings, is energetically more unstable than graphene, a larger concentration of the five and eight membered rings inevitably possesses larger formation energy. Thus, \( E_{\text{formation}} \) monotonously increases with decreasing \( N \), as shown in Fig. 1(c). However, even the \( N = 2 \) system has a formation energy that is still lower by \( \sim 0.1 \) eV/atom than the case containing only five and eight membered rings. The carbon allotrope that only contains five and eight membered rings has been reported to be energetically more stable [29] than T graphene [42] and graphdiyne [43]. The formation energies of the systems we studied here are much lower than these carbon allotropes. Thus, there is great potential to synthesize them successfully in experiments.

As discussed previously, the buffer zigzag chain has the effect of relaxing the residual forces in the 585 ELD. Therefore, with increasing \( N \), the 585 ELD will be more stable. On the other hand, since the hexagonal rings should be modified to stabilize the 585 ELD, the energy of ZGRs will increase. Figure 1(d) shows the behavior of the increased energies of zigzag chains in ZGRs. The buffer chain \((n = 2)\) suffers from the largest energy increase due to its marked structural distortion. After the third zigzag chain, the chain energies almost converge, indicating much less distortion compared with the buffer chain.

Due to the appearance of nonhexagonal rings, a localized density of states may exist. To further understand the characteristics of such local states, the band structures of the systems were calculated. As shown in Fig. 2, independent of \( N \), flat bands are found close to the Fermi level around the \( \Gamma \) point. For large \( N \), the flat band is degenerate, but when \( N \leq 8 \), the flat band splits. Another feature of the band structures is the modified Dirac cone between the \( \Gamma \) and \( Y \) points. Compared with perfect graphene, the Dirac point shifts below the Fermi level for \( N \leq 8 \), acting as a doping of graphene. One branch of the Dirac cone is significantly modified and forms a flat band at the Fermi level. This flat band is mainly contributed by the edge A atoms. Due to the split of the flat band, ordered magnetic moments are localized at the edges of ZGRs (or the 585 ELD), as shown in Fig. 3. Interestingly, the systems show three stable magnetic configurations: ferromagnetic arrangement at ELD (FM state), antiferromagnetic arrangement at ELD (AFM state), and ferromagnetic arrangement at ELD but antiferromagnetic arrangement at neighboring ELDs (L-AFM state), as seen in Fig. 3.

To investigate the behavior of magnetism as well as the doping level with increasing \( N \), the magnetic moment and concentration of Dirac fermions were studied. On one hand, as presented in Fig. 4(c), the magnetic moment of the system (with FM state) first increases with \( N \) to a maximum value...
The stability of magnetic configurations is in the order L-AFM > FM > AFM > NM, which has a similar behavior as that of zigzag graphene ribbons. This is reasonable. In order to reduce the exchange interaction [44], the ferromagnetic arrangement is preferentially located at an ELD, while an antiferromagnetic arrangement prefers to be located at the neighboring ELDs. Thus, due to the exchange interaction between neighboring ELDs, the L-AFM state is the most stable one with \( N \leq 6 \). On the other hand, the energy of the Dirac point is also dependent on the width of ZGRs. As shown in Fig. 2, the Dirac point shifts close to the Fermi level, with increasing \( N \), and then is pinned at the Fermi level when \( N \geq 12 \). For application in electronic devices, the concentration of Dirac fermions [45] was calculated. As shown in Fig. 4(a), the concentration of Dirac fermions decreases rapidly with increasing \( N \). For \( N = 2 \), \( \sigma_{\text{Dirac-fermion}} \) is as high as \( \sim 2.3 \times 10^{13} \) cm\(^{-2}\). Interestingly, due to the split of the flat band, the degenerated Dirac point was separated, which results in different spin densities of Dirac fermions. Experimentally, based on field-effect transistors, the doping level can reach \( 3 \times 10^{13} \) cm\(^{-2}\) [33]. For the energetically stable carbon allotropes studied here, we demonstrate that high-level doped graphene can be achieved by controlling the distance between 585 ELDs. Because of the unequal spin densities of Dirac fermions, this suggests potential applications in spintronics.

The origin of the magnetism and doping of the system can be explained as follows. By analyzing the evolution of band structures with decreasing \( N \), clear changes can be found near the \( \Gamma \) and \( L \) points. For a system with a large \( N (N \geq 12) \), one flat band (\( \Gamma F \) band) is slightly above the Fermi level close to the \( \Gamma \) point, and the Dirac point is pinned at the Fermi energy, while near the \( L \) point, the other flat band (\( LF \) band) is slightly below the Fermi level. With decreasing \( N \), the \( \Gamma F \) band, as well as Dirac point, gradually shift below the Fermi level. In the meantime, the \( LF \) band rises above the Fermi level, becoming unoccupied. This indicates that the charges that previously occupied the \( LF \) band are transferred to the \( \Gamma F \) band with decreasing \( N \). By analyzing the wave functions, it was found that the \( LF \) band is mainly originates from \( C_2 \) and the \( \Gamma F \) band mostly originates from edge \( A \) atoms. Therefore, the shifts of the flat bands should be attributed to the charge transfer from \( C_2 \) atoms to edge \( A \) atoms. To further verify this conclusion, we calculated the Mulliken population of the systems. As shown in Fig. 5, with decreasing \( N \), a clear charge transfer can be found from the center to the edge of the 585 ELD, which decays rapidly to the bulk of ZGRs. This charge transfer can be considered as a self-doping process, as proposed in Ref. [18]. The doping level becomes larger with decreasing \( N \). Since both the interior of ZGR and \( C_2 \) show rigid \( \pi \) conjugation [46], the additional electrons at edge \( A \) cannot pair with surrounding electrons. Thus, spin polarization occurs there. The charge transfer becomes larger with decreasing \( N \), and as a result, the magnetic moment increases.

However, the value of the magnetic moment becomes zero for a system with \( N = 2 \). On one hand for this system, a ZGR consists of only a pair of edge zigzag chains. A large distortion of ZGRs causes the softening of the \( \pi \) conjugation. Therefore, the additional electrons can partially participate in the bonding with surrounding electrons. On the other hand, the Coulomb onsite repulsion between the local electrons was totally ignored in the above calculations. Due to its semilocal nature, the GGA functional always delocalizes the electron density of...
Theoretical value of a rigid shift of 2.5 eV for all the values of Fermi level. Due to the self-interaction error [47–51], the GGA can induce a very high localized density of states close to the Fermi level. As studied previously, a 585 ELD Coulomb onsite interaction between local electrons may result in a nonmagnetic stable state. Therefore, the underestimated density of states appears at the Fermi energy, implying a magnetic instability of the system. For the systems studied here, a large localized density of states at the 585 ELD, the values of \( U_{\text{eff}} \) are clearly greater than for ZGRs. Applying appropriate values of effective Coulomb onsite repulsion \( U_{\text{eff}} \) for the systems discussed above, the magnetic moment increases in different degrees, as shown in Fig. 4(c). Especially for the \( N = 2 \) system, magnetism is triggered with Coulomb onsite interaction.

Further, the behavior of \( U_{\text{eff}} \) at the 585 ELD was studied. As shown in Fig. 4(d), for systems from \( N = 4 \) to \( N = 12 \), \( U_{\text{eff}} \) at \( N = 12 \) system.

In summary, with first-principles calculations, we systematically studied the distance-dependent electronic structures of 585 ELDs embedded in graphene. By reducing the distance between 585 ELDs, the interaction between 585 ELDs became more evident. In going from “isolated” 585 ELDs to closely packed 585 ELDs, many interesting characteristics are observed. First, the strength of Coulomb onsite repulsion between the electrons at edge A decreases, which, in turn, reduces the onsite occupation energy. Therefore, more electrons are transferred to edge A atoms as \( N \) is reduced. As a result, the self-doping occurs at the edges of the 585 ELD.

### IV. CONCLUSIONS

In summary, with first-principles calculations, we systematically studied the distance-dependent electronic structures of 585 ELDs embedded in graphene. By reducing the distance between 585 ELDs, the interaction between 585 ELDs became more evident. In going from “isolated” 585 ELDs to closely packed 585 ELDs, many interesting characteristics are observed. First, the strength of Coulomb onsite repulsion between the electrons at edge A decreases, which, in turn, reduces the onsite occupation energy. Therefore, more electrons are transferred to edge A atoms. Due to the rigid \( \pi \) conjugation at \( C_2 \) and in the interior of ZGRs, the additional electrons at edge A atoms can hardly couple with the surrounding electrons. Therefore, magnetic ordering appears at the edges of 585 ELDs. Second, due to the charge transfer, the Dirac point gradually shifts below the Fermi energy, causing \( n \) doping of graphene. The carrier concentration increases in this process. Based on our previous paper [54] using molecular dynamics (MD) simulations, a highly concentrated 585 ELD can be obtained by linear adsorption of carbon atoms in graphene. Experimentally, by thermal reconstruction of polycrystalline graphene film, controlled 585 ELDs have been achieved [55]. Our finding provides a route for designing \( n \)-type spintronic devices in graphene.
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