Comprehensive mechanism of ferromagnetism enhancement in nitrogen-doped graphene

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Abstract

Realizing the strong ferromagnetism (FM) with both the Curie temperature above room temperature and high magnetization in graphene, is key for its real application in future spintronics. Nitrogen-doping has been confirmed to be one of the most promising ways for experimental realization of room temperature FM in graphene. However, the comprehensive mechanism, which needs to verify the enhancements of both the nitrogen complexes-induced magnetism and the FM coupling among them, remains to be completely explored, which impedes the experimental optimization of the FM in nitrogen-doped graphene (NG). Here, we theoretically perform a comprehensive analysis on the FM enhancement in NG. The enhancement of both the magnetic moments and FM coupling highly depends on the N concentration and relative geometric configuration of the N complexes. Especially, the magnetic moments and FM coupling are attributed to the \(\sigma-\pi\) magnetic interaction between the localized and itinerant moments, the band reconstruction originated from the proximity of N complexes, and the sublattice match/mismatch. The FM enhancement is high sensibility to the geometric configurations of the N complexes, and only the presence of graphitic-3N combined with trimerized pyridine can realize the sublattice-independent strong FM in the high N-concentration limit. Whereas the low N-concentration limit favors the substantial FM enhancement in all systems, but would unavoidably undergo both the low Curie temperature and low magnetization due to the relatively low N-concentration. We hope that the comprehensive mechanism of FM enhancement we offered can push the optimization of the FM in NG via tuning its N concentration and geometric configuration of the N complexes by the rational design of the specific experimental strategies.

1. Introduction

Witnessing the pioneering work on isolated individual graphene from graphite [1], researchers have shown great interest in this material for its unique properties. As the electronic degree of freedom, the spin in graphene possesses a long spin diffusion length [2], which offers it the potential application in spintronic devices [3]. Nevertheless, the perfect graphene is intrinsically non-magnetic due to the delocalized \(\pi\)-bonding network [4–6]. To generate the magnetic moments in graphene, some approaches have been explored through destroying the \(p_z\) electronic balance of bipartite hexagonal sublattice following Lieb’s theorem [7], such as zigzag edges [8, 9], vacancies [10, 11], \(sp^3\) functionalization [12], and substitutional doping [13–15]. Furthermore, it is the key to realize exchange couplings among these localized magnetic...
magnets for acquiring the robust ferromagnetism (FM) [14, 16–18]. In comparison with the strongly localized magnetic moments commonly found in the transitional material with 3d or 4f electrons, the FM of the sp-electron-only light-element materials most likely roots in the itinerant electrons, occupying the flat bands and yielding the sharp density of states (DOS) peaks at the Fermi energy. It was proposed previously that these materials would obey the sp-electron Stoner FM with relatively high Curie temperature [19].

Substitutional doping, an effective strategy to imprint magnetism in graphene, as experimentally and theoretically reported [13, 15, 20–23], has attracted extensive attentions. Particularly, the N element possesses rich electrons and the similar atomic size to C, so it can act as an effective substitutional doping method in graphene with the original plane structure. Through affecting the electronic characteristic of graphene, N-doping could dramatically change the physical properties of graphene [24]. Experimentally, these properties would be affected by the N concentration and geometric configuration [13, 22, 25–28]. When C atoms are substituted by N atoms, a great variety of N-doped graphene (NG) formations would be acquired [13, 27, 29, 30]. Apart from the substitution, the vacancies would inevitably exist, and thus forms the vacancy-containing N in NG during the real process of preparation [28]. Although the earlier literature demonstrated that the vacancy-containing N complexes are inclined to transform into the graphitic N complexes [27], this transformation is incomplete, which has also been confirmed by our recent experiment [31]. Consequently, the vacancy-containing and graphitic N complexes would coexist in the real case, and the origin of magnetism can be attributed to two sections, i.e. σ and π states. It has been reported that the localized magnetism occupies a vital portion of the former, which makes it difficult to form collective magnetism, whereas itinerant magnetism plays a dominant role in the latter [20]. Thus, utilizing the itinerant magnetism as a bridge to realize long-range couplings of localized magnetic moments triggers our interest. Using this strategy, our experiment realized the nearly pure FM at 2 K with a medium N concentration of 6.59 at. % [31], which provides a feasible perspective for the realization of ordered magnetism. Nevertheless, the specific enhancement dependences of both the magnetic moments and magnetic interactions on the influence factors of the N concentration and geometric configuration, are rarely known. Therefore, it is of great significance to afford a comprehensive analysis for the FM enhancement in NG and, thus to unveil the microscopic magnetic mechanism.

In this study, we theoretically perform a comprehensive analysis on the FM enhancement in NG by systematically investigating NG with the high (9.23 at. %) and low (3.87 at. %) N-concentration limits. The results unveil that the FM enhancement is determined by both the N concentration and geometric configuration. Based on the detailed analyses on the effect of the σ–π magnetic interaction, the band reconstruction, and the sublattice match/mismatch on the FM enhancement, we then obtain the comprehensive mechanism of the enhanced FM for NG. Additionally, we propose the bridge effect of the itinerant moments originated from the graphitic N complexes for the localized magnetic moment introduced by vacancy-containing N complexes, which favors the FM enhancement in NG.

2. Computational details

All calculations were carried out using the spin-polarized density functional theory (DFT) within the projector augmented wave formalism [32], as implemented in the Vienna Ab Initio Simulation Package [33, 34]. The description of exchange–correlation functional was based on the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) [35]. The kinetic energy cutoff was at 600 eV for plane wave expansion of the Kohn–Sham orbitals. The Monkhorst–Pack schemes \( 3 \times 3 \times 1 \) and \( 17 \times 17 \times 1 \) were performed in the Brillouin zone to guarantee the convergence of the Kohn–Sham eigenvalues for geometry optimization and electronic DOS, respectively. The N-doped structures were built with the \( 6 \times 6 \) (9.23 at. %) and \( 9 \times 9 \) (3.87 at. %) supercells, which respectively include 71 and 161 atoms with six C atoms substituted by six N atoms. To make the interactions between the periodic layers negligible, the vacuum region was set to 20 Å along the direction perpendicular to NG sheets. All atoms were ensured to fully relax until the Hellmann–Feynman forces on each atom drop below \( 5 \times 10^{-3} \) eV Å\(^{-1}\).

The total formation energy of NG can be obtained through [36–38]:

\[
E_t = E_{NG} + y\mu_C - (E_G + x\mu_N),
\]

where \( E_{NG} \) and \( E_G \) are respectively the total energy of NG and perfect graphene supercell; \( x \) and \( y \) are respectively the number of C atoms substituted by N atoms and C atoms removed from the perfect graphene; \( \mu_C \) and \( \mu_N \) are the chemical potential for C and N atoms, which can be respectively obtained from the total energy of perfect graphene per atom and a half of the total energy of N\(_2\) molecule in the gap phase. We follow the rule that higher (more positive) formation energies show a lower possibility for forming these defects in thermodynamic equilibrium.
3. Results and discussions

3.1. N geometric configurations and parameters

When N atoms are introduced into graphene, the mixed defects graphene becomes the key concern around researchers [13, 39]. Generally speaking, the trimerized pyridine (TPY), which is formed through three N atoms substituting the same sublattices around a vacancy, is more stable than the monomerized and dimerized pyridine [40], as shown in figure 1(a). Besides, it is common that the N atom bonding with C atoms forms a pentagon around the vacancy in the approximated ratio of 1:2 with hexagon [25, 26, 28, 31], referred as the trimerized pyrrolic (TPI) complex (figure 1(b)). Both the TPY and TPI are widespread as the types of vacancy-containing N complexes, and thus should be both considered in the following discussion.

Graphitic N defects, generated during the nonequilibrium process, also prefer to exist in the forms of three N atoms occupying the same sublattices around a C atom or in one hexagon [41], which constitutes two types of complexes, graphitic-3N (G3N) and triazine (T) complexes (figures 1(c) and (d)). Thus, to systematically investigate the bridge effect of graphitic N complex in vacancy-containing NG, we established four systems, i.e. TPY-G3N (T) and TPI-G3N (T). Considering the character of bipartite hexagonal structure in graphene, two defects in each of the four systems could occupy the same (AA) or different (AB) sublattices (labeled as A or B, respectively). Meanwhile, despite the effect of different sublattice occupations of TPI on the magnetism from the arbitrary direction was considered in previous work [31], one can note that the dangling N atoms in the pentagon for the TPI complex simultaneously occupy two sublattices. Therefore, the effects of sublattice occupation on magnetism for all TPI-G3N (T) configurations could actually not be considered. Based on the fact that the interaction between two vacancies would not be negligible when their distance is below 1 nm due to the nature of the localized magnetic moment [42], we focus on the configurations with the large enough supercell, which could exclude the possible interaction between two vacancies. The 6 × 6 supercell was firstly chosen to simulate the high N-concentration (9.23 at. %) case (figures 1(e)–(h)). In consideration of the investigative completeness, we also simulate the low N-concentration structures (3.87 at. %) in a 9 × 9 supercell. Considering the periodicity of these configurations, there exist two high symmetrical directions, corresponding to the armchair (a) and zigzag (z) orientations (labeled as a and z), respectively. Along the different directions, the spatial separations between two defects could change (labeled as n, n = 1, 2, 3, …). Although TPY/TPI may be closer to G3N/T in the neighboring supercell than that in the same supercell, due to the periodic boundary conditions, the...
magnetic interactions are considered in periodic structures, which guarantees that TPY/TPI closer with neighboring supercell would have no substantive impact on the calculated results. In a word, the configurations can be denoted by Aan, Ban, Azn, and Bzn with the consideration of sublattices, orientations, and spatial separations. After the structural optimization, different structural parameters for all TPY- and TPI-containing configurations are studied. For the TPY-containing configurations, the C–N bonds of TPY vary from 1.29 to 1.35 Å, and the formed equilateral triangle by N atoms is slightly broken with the 2.55–2.63 Å sides, which is commensurate with the previous report (C–N bond length of 1.33 Å and equilateral triangle sides of 2.61 Å, respectively) [20, 40]. This result means that the introduction of the graphitic N defect has little effect on the structures of TPY-containing configurations. In contrast, for the TPI-containing configurations, the pentagonal C–N bonds vary from 1.33 to 1.42 Å, and the bond lengths decrease apparently when two defects get close to each other. Notably, 1.33 Å is the value of hexagonal C–N bond length, as provided by references [19, 39], and one could infer that the structure of TPI-containing configurations is sensitive to the spatial separation of two defects. From the perspective of total energy differences, the discrepancies among these configurations are quite small, which reveals that they are likely to coexist (figure S1 (https://stacks.iop.org/NJP/23/103003/mmedia) and 2).

3.2. Mechanism of FM enhancement in NG

To begin, we briefly review the magnetic property of the individual complexes, which has been widely discussed in previous literature [20, 26, 28]. In the framework of PBE scheme, the weak σ magnetism, localized at the N atoms, is observed in the TPY complex. The magnitude of the total magnetic moment slightly depends on the selected supercell. The weak nature of the σ magnetism in the TPY complex means it is easily affected by other defects, as illustrated below. In comparison, the strong and well localized σ magnetism with the fixed moment of ∼0.94\(\mu_B\), irrespective of the selected supercell, is revealed at the N atoms in the TPI complex. On the other hand, the magnetism of the G3N/T complex is more itinerant and weakly depends on the supercell size due to its π nature. It should be noted that the main contributions of the magnetic moments in these individual complexes originate from the C atoms rather than the N atoms, and this feature plays a vital role in the magnetism of the TPY/TPI-containing configurations.
3.2.1. Mechanism of FM enhancement for the high N-concentration limit

Now we focus on the magnetic properties of high N-concentration-limit NG and explore the factors that affect the ordered magnetism. First, we discuss the magnetic properties of TPY-G3N (T), and the moments are shown in figures 2(a) and (b). Interestingly, the results possess several common trends. (i) Compared with the magnetic superimposition of isolated defects, the enhanced magnetism is induced in both of two systems (table S1). (ii) The magnetic moment with spatial separation shows a vibrational feature. It is analogous to the Friedel oscillation typically observed around impurities [43] and magnetic order oscillation predicted in graphene nanoribbon [44], suggesting the subtle interaction or interference between two defects. (iii) The total energy difference (relative to the configuration Aa1, figure S1) of the respective configuration exhibits the discrepant trend compared with the magnetic moment (figure 2), indicating the important role of the charge density fluctuations in stabilizing the configurations in NG. Unlike the vacancies in perfect graphene sheet, N doping introduces the additional charges transferring from carbon to nitrogen [20] and induces the charge density wave [44].

For the TPY-G3N configurations, the enhanced magnetism is found along the armchair direction, such as Ba1, Aa4, and Ba4 (figure 2(a)). In particular, the total energy in Aa4 configuration is substantially low among all the selected TPY-G3N configurations (figure S1(a)), which may be the favorable configuration in high-N-concentration NG. In contrast, all configurations fail to enhance magnetism along the zigzag direction. Although the total magnetic moment is related to the spatial separation and relative orientation between the two defects, the magnetism enhancement possesses a sublattice-independent feature. Herein, the sublattice-independent character is responsible for observing the effective long-range ferromagnetic order [31], and the promotion effect of G3N defect in magnetic couplings has been reported [20].

On the other hand, only when two defects situate on the different sublattices does the enhanced magnetism arise in the case of TPY-T, such as Ba3 and Ba4 (figure 2(b)). In other words, if T is introduced into TPY-containing NG, the magnetism is dictated by the spatial separation, the orientation, and particularly, the occupied sublattice. Considering that too many critical conditions should be satisfied to realize the enhanced magnetism in TPY-T, a statistically random distribution of the mixed TPY and T configuration goes against the robust FM. Moreover, those configurations with the enhanced magnetism are energetically unfavorable (figure S1(b)). Therefore, generated the G3N complex is more beneficial to a long-rang magnetic order than that of the T complex in the TPY-containing NG. In comparison, the introduction of both the G3N and T complexes are failed to enhance the magnetism of TPI-containing NG (figures 2(c) and (d), and table S2). These results mean that graphitic N complexes could bring quite different magnetic interactions for TPY- and TPI-containing NG, and we would respectively discuss the concrete mechanisms in the following parts.

To obtain a clear picture of the magnetism of the respective configuration, we focus on the spin-polarized charge densities of TPY-G3N. Considering the abundant configurations would bring a large amount of calculation, we take the enhanced-magnetism cases and the contrastive configurations as examples for detailed discussion, while the full results are attached in the supplemental material. For all configurations placed on the same sublattice, the net spin density mainly arises at N atoms of the G3N and C atoms, and it is almost entirely quenched at N atoms of the TPY (figures 3(a) and (b), S3(a)–(c), S4(a), and S4(b)). Moreover, the net spins of Aa4 are relatively larger compared with other configurations. Further, the obvious electron transfer from carbon to nitrogen can be verified through the Bader charge analysis, which could drive Lieb’s imbalance and thus cause the net magnetic moment. Specifically, the magnetic moment is $0.22 \mu_B$ in the N atoms of G3N, but $1.03 \mu_B$ in the C atoms for Aa4 configuration. The magnetic moments of the C atoms are delocalized, which are mostly motivated by the appearance of G3N and could maintain far away from it. Consequently, the itinerant magnetism derived by G3N, offering the medium for the magnetic interaction, plays a vital role in enhancing the exchange coupling of the localized magnetic moments. For the case of two defects occupying the opposite sublattices, although the localized magnetic moments on the N atoms around TPY are small, the substantial net spins can be seen from the spin-polarized charge densities (figures 3(c), S3(d)–(f), S4(c), and S4(d)). For Ba1 configuration, the magnetic moments are respectively 0.08 and 0.26$\mu_B$ for N atoms of TPY and G3N, while the main moments ($0.99 \mu_B$) still stem from the C atoms. This means that the proportion of three magnetic origins is discrepant between the configurations occupying the same or different sublattices. Interestingly, similar behaviors are observed in TPY-T, while only Ba3 and Ba4 represent enhanced magnetism. More information can be obtained from figures S5 and 6. Thus, the ferromagnetic alignment is believed to mainly evolve upon itinerant magnetism of both C atoms and localized N around graphitic N.

In principle, the magnetism of the system with mixed magnetic defects highly depends on the interaction between the two defects and the defects-induced band structure reconstruction. Both factors are associated with the spatial separation and relative orientation of defects. Moreover, the sublattice dependence is also non-negligible in the bipartite lattice, such as graphene.
Figure 3. Spatial distribution of the spin-polarized density \((\Delta \rho = \rho_\uparrow - \rho_\downarrow)\), where \(\rho_\uparrow(\downarrow)\) indicates spin-up (down) density, in the \(6 \times 6\) supercell of TPY-G3N. (a) Aa2, (b) Aa4, and (c) Ba1. The isosurface value of spin-polarized electron density is 0.0035 e Å\(^{-3}\). Yellow color represents the positive (up) spin density. (d) The schematic magnetic interaction between two defects. The gray line represents the unit cell. The blue (red) hollow circle represents the A (B) sublattice of graphene network, while the blue solid circle represents the N atoms of G3N fixed on the A sublattice. The dark triangle and light hexagon colored in yellow schematically illustrate the main magnetization density generated by the individual G3N with the periodic boundary condition (also see figures 3(b) and (c), S3, and S4), and the thickness of lines represents the relative magnitude of magnetization. The TPY complex denoted by the small blue and red triangles is introduced along the armchair (blue dotted line) or zigzag (red dotted line) direction. The small cyan and yellow triangles show magnetization density induced by the TPY complex. Three typical processes along the armchair direction discussed in the text, i.e. 1 (Aa2) with strong \(\sigma-\pi\) magnetic interaction, 2 (Aa4) with negligible \(\sigma-\pi\) magnetic interaction, and 3 (Ba1) with the remarkable sublattice match, together with the process along the zigzag direction, i.e. 4 (Az1) without direct \(\sigma-\pi\) magnetic interaction, are explicitly shown.

We show the schematic magnetic interaction between two defects in the TPY-containing configurations (figure 3(d)). In TPY-G3N, strong \(\sigma-\pi\) magnetic interaction is observed for Aa1/2 cases. In consideration of the weak magnitude of the \(\sigma\) magnetism in TPY, the magnetism of this system is foreseeable to be significantly suppressed. Moreover, the sublattice mismatch (the induced \(\pi\) magnetism mainly at B sublattice versus N atoms of TPY at A sublattice) prevents the emergence of the \(\pi\) magnetism on the N atoms of the TPY complex (figures 3(a) and S3(a)). In comparison, no evident \(\sigma-\pi\) magnetic interaction exists in Aa3/4/5, which means the magnetism changes little. Though the direct or indirect \(\sigma-\pi\) magnetic interaction is also presented in the Ba situations, the sublattice match induced \(\pi\) magnetism on N atoms of TPY compensates the possible magnetic reduction (figures 3(c) and S3(d)–(f)). These arguments clearly demonstrate the reason for the small magnetic change in the Ba cases discovered in the first-principle calculations. On the other hand, in consideration of the reduction of the total moments along the zigzag direction while in the absence of the \(\sigma-\pi\) interactions, the strong band reconstruction due to the smaller separation between two defects is substantial.

Such picture also accounts for the part of the results in TPY-T (figure S7). The \(\sigma-\pi\) magnetic interaction, together with the sublattice mismatch, strongly suppresses the magnetism of Aa1/2 configurations. In contrast, such interaction is absent in Ba cases (except for Ba1, in which the sublattice match is present), rendering the remarkable sublattice-dependent magnetism occurs in TPY-T. Similarly, the magnetism in the case along the zigzag direction cannot be explained within such picture due to the proximity of two defects, which will be further discussed below. However, the nearly full suppression of magnetism in the Aa3/4 cases remains elusive, where no direct interaction and the well separation between two defects are discovered.

To deeply understand the origin of magnetism, spin-polarized band structures together with the projected density of states (PDOS) (atom- and orbit-resolved) are further analyzed. Comparing the band structures of isolated defect (figures 4(a) and (b), and S8) with that of mixed defect for all configurations in NG, obviously, it is vulnerable to external interference. On the whole, the band structures of mixed defect
Figure 4. Spin-polarized band structures and PDOS in the 6 × 6 supercell. (a) TPY and (b) G3N. The results of the TPY-G3N system: (c) Aa2, (d) Aa4, and (e) Ba1. (f) The left (right) panel is strong (weak) magnetization. Red and blue arrows indicate the spin-up and spin-down states, respectively. The Fermi level is fixed at 0 eV.

exceed a simple superimposed of each component. This means that relatively strong magnetic coupling is introduced between the two defects, in accordance with the results mentioned above. The emergence of the exchange coupling between the two defects could provide prerequisites for long-range ferromagnetic order in NG, and further break the π–π bonding symmetry resulting in the enhanced magnetism.

For TPY-G3N, all configurations represent metallic features, which provides the possibility of being ferromagnetic. Comparing the band structures of TPY-G3N with that of the isolated defects (figures 4(a)–(e)), the unpaired π electrons from the G3N in the former case push the flat band from the vacancy-containing N downward, which restrains the σ moments. Such effect is robust in Aa1, where the σ band is pushed down to about −0.97 eV (compared with about −0.51 eV in most cases) (figure S9), in agreement with the strong σ–π magnetic interaction revealed above. Whereas the flat band of G3N still lies at the Fermi level, providing the possibility of generating the π moments. In particular, the flat bands at the Fermi level in Ba cases are more perfect than that in the Aa case, except for the Aa4/5. Combining the magnetic interaction and sublattice matching discussed above, the magnetism in Ba case is therefore robust.
against the separations. In comparison, the band flatness is much reduced in the configuration of TPY-G3N along the zigzag direction (figures S9(g)–(j)). Similar band flatness reduction is also found in the Aa2 case (figure 4(c)). According to the $sp$-electron Stoner FM criterion [4], the imprinting ferromagnetic alignment would be affected by the flat band, which has been widely employed, such as sulfur-doped graphene [21] and zigzag graphene nanoribbons [12]. Our results also show that the flat band at Fermi level indeed splits into two branches (figures 4(d) and (e)), which contributes to the itinerant magnetism. Due to the bridge effect of the itinerant magnetism, the localized magnetic moments are easier to couple with each other, which is beneficial to enhance the magnetism.

From another perspective, magnetism is associated with the charge difference between the majority and minority spin states below the Fermi level. Specifically, metallic characteristic results in weak magnetization, whereas half-metal feature drives the strong magnetization (figure 4(f)). Combining the band structures and PDOS, one can see that if the charge numbers of two spin states have a remarkable difference, it will lead to the enhanced magnetism. In contrast, if the exchange coupling causes the extension of band widths, which would induce the transform of charge from the majority spin state to the minority spin state, and thus appear the reduced magnetism.

Utilizing the PDOS, we further analyze the magnetic component of TPY-G3N in detail. In these cases, the $2p_{x+y}$ orbitals of N atoms around TPY provide the localized $\sigma$ state, which is far from the Fermi level and occupied by the surplus electron of N atoms. Consequently, the $\sigma$ component has no effect on the magnetism. Therein, the emerged moments entirely originate from the $2p_z$ orbitals of C atoms and N atoms (figures 4(d) and (e)), displaying $\pi$ feature.

We also further clarify the origin of magnetism in the case of TPY-T. The band reconstruction exhibits evident sublattice dependence. The original flat bands at the Fermi level contributed by the T complex are substantially destroyed in the Aa/Az cases, while they remain robust in the Ba/Bz cases (figures S10 and 11). These results are in agreement with the magnetism revealed before qualitatively. Along the armchair direction, when two defects occupy the same sublattices, the semiconductor characteristic emerges (figures S10(a)–(d)), which goes against the formation of FM. Indeed, the exchange split is suppressed or even disappears, corresponding to the reduced magnetism. In contrast, the metallic feature is captured when the defects occupy the different sublattices (figures S10(e)–(h)). The large splitting is induced by the incommensurable difference of charge emerges between two spin channels, contributing to the strong FM for Ba3 and Ba4 (figures S10(g) and (h)). Besides, the corresponding PDOS shows that the magnetism is attributed to the $2p_z$ orbitals of C atoms and all N atoms.

Combining the $\sigma$–$\pi$ magnetic interaction between two defects, the band reconstruction attributed by the proximity of two defects, and the sublattice match, the magnetism in TPY-containing graphene is well established.

Before the analysis of the ferromagnetic coupling for TPI-G3N (T), we also calculated its antiferromagnetic state. The resultant data show that the magnetic moments are nonzero, indicating that the antiferromagnetic state is unstable, and thus would not be the ground state. In consideration of the magnetic complexity of the triangular lattice system, the ferromagnetic coupling between two defects could be thus considered as relative dominating.

Further, the magnetic mechanism for TPI-G3N (T) is analyzed (figure 5). Different from the entirely quenched localized $\sigma$ magnetism in TPY-G3N (T), the moment of N atoms around TPI is remained in TPI-G3N (figures 5(a) and S12), which may be ascribed to the newly appeared pentagon. To our knowledge, the N atom in the pentagon belongs to $sp^3$ hybridization [25, 45], and thus more unpaired electrons ($\sigma$ feature) emerge compared to the $sp^2$-hybridized N atoms in the hexagon of TPY, which further gives rise to the larger localized magnetic moment in TPI. While the itinerant magnetism nearly disappears along the armchair direction except for the $a3$ configuration (figures 5(a) and S12(a)–(c)). This result can further be confirmed from the spin-polarized band structures and PDOS. As can be seen from figures 5(c), and S13(a)–(c), a narrow impurity band splits into two branches, but the $\pi$-band is non-degenerate only in $a3$ configuration. This reflects the mutual influence between the $\sigma$ and $\pi$ electrons is likely to obtain relatively larger moments. The $\sigma$ component originates from $2p_{x+y}$ orbitals of N atoms around TPI, and the $\pi$ character is contributed by $2p_z$ orbitals of C atoms and all N atoms. In contrast, along the zigzag direction, both C and all N atoms contribute to the observed magnetism for all configurations (figures S13(d)–(f)). The magnetic component is consistent with the armchair direction.

As for the case of TPI-T, apart from the magnetic behaviors mentioned above, i.e. the coexisting of itinerant and localized magnetism or the disappearance of itinerant magnetism, some interesting phenomenon arises (figures 5(b) and S14). Along the armchair direction, the orientations of major and minority spin are intrinsically opposite in the $a1$ and $a4$ configurations (figures 5(b) and S14(a)). Consequently, the negative coherence between two defects would lead to antiferromagnetic coupling due to the quantum interference. In the case of $z3$, the appearance of the occupied $\sigma$ state leads to the
Figure 5. Spatial distribution of the spin-polarized density (\(\Delta \rho = \rho_\uparrow - \rho_\downarrow\)), where \(\rho_\uparrow (\rho_\downarrow)\) indicates spin-up (down) density, in the 6 × 6 supercell. (a) a3 of the TPI-G3N system and (b) a4 of the TPI-T system. The isosurface value of spin-polarized electron density is 0.0035 e Å\(^{-3}\). Yellow and cyan colors represent the positive (up) and negative (down) spin density values. (c) and (d) Spin-polarized band structures and PDOS of the corresponding configurations. The Fermi level is set to zero.

disappearance of the localized magnetic moments (figure S14(f)). Moreover, the exchange splitting between majority and minority spins is pretty weak (figs 5(d) and S15). In a word, all these factors would cause reduced magnetism. Consequently, when the graphitic N complexes are generated into the TPI-containing NG, the mutual effect between the \(\sigma\) and \(\pi\) components is vital for the magnetic behavior.

In brief, compared with the complicated situations in the TPY-containing configurations, the magnetism in TPI is rather simple. Due to the strong and localized nature of TPI \(\sigma\) magnetism, it remains robust in all situations. The direct or indirect \(\sigma-\pi\) magnetic interaction simultaneously suppresses the itinerant \(\pi\) magnetism of the G3N/T complexes and the localized \(\sigma\) magnetism of the TPI complex more or less, especially in the cases with smaller separations between two defects. Furthermore, the sublattice balance nature of the pentagonal TPI naturally supports the sublattice-independent magnetism of TPI-containing configurations.

3.2.2. Mechanism of FM enhancement for the low nitrogen-concentration limit

According to the earlier literature, the appearance of FM is at a significant N concentration of about 5 at. %, and one failed to observe the magnetic order below this content both in experimental and theoretical studies [13, 20, 22]. Not surprisingly, the above results of high N-concentration configurations show the substantial FM, whereas the case of the low N-concentration (<5 at. %) configurations in graphitic and vacancy-containing N complexes coexisting graphene still keeps unclear, and also for the completeness of the study, so it is necessary to give a further discussion. To explore the influence of itinerant magnetism on
localized magnetism in the low N-concentration configurations (3.87 at. %), we restructure the TPY-G3N (T) and TPI-G3N (T) in a $9 \times 9$ supercell (figure S16).

Like the case of the TPY-containing configurations in the high N-concentration limit, the results also show the sublattice-independent magnetic enhancement, and the magnetism is related to the spatial separation and the directional selection between two defects figures 6(a) and (b), and table S3). Besides, it should be reminded that the averaged magnetization per site is relatively weaker than that in the high N-concentration limit due to the larger supercell size.

Basically, the magnetic mechanism in low N-concentration is similar to that in high N-concentration. The determinants of the magnetic property include the magnetic interaction and the sublattice match, as well as the band reconstruction. In particular, the larger supercell provides more opportunities to achieve the strong FM. As shown in the spin-polarized charge densities (figures S17–22), the strong $\sigma-\pi$ magnetic interaction is presented. Considering the computational cost and time, and the spaghetti picture, the band structures were not calculated. Observing the PDOS, the exchange split contributes to the itinerant magnetism near the Fermi level, which mainly stems from the $2p_z$ orbitals of the C and all N atoms (figures S23–27). A small part of magnetism is also contributed from the localized magnetic moment, which is originated from the $2p_{x+y}$ orbitals of the N atoms around TPY. Consequently, the long-range ferromagnetic order could be realized.

Unlike the strong suppression of the magnetism in TPI-containing configurations in the high N-concentration limit, the weak magnetic enhancement is also achieved in TPI-G3N (T) (figures 6(c) and (d), and table S4). The reasonable reason may originate from the interference between the itinerant $\pi$ magnetism of the G3N/T complex, and the presence of TPI defects would modify the band structure and charge fluctuations, etc, which potentially provides positive coherence between the G3N/T complexes. However, this is not easy to verify, so we just take it as one reason for discussion.

The origin of the magnetism shows intricacy in the TPI-G3N/T (figures 7, S28, and S29). Generally speaking, both the itinerant and localized moment (respectively donated by graphitic N and TPI complexes) occupy the significant proportion in generating the magnetism. Nevertheless, the magnetic origins in different configurations are discrepant. (i) Only the vacancy-containing N atoms (such as a1 configurations of TPI-G3N/T) are responsible for the magnetism (figures 7(a) and S29(a)). (ii) Only the graphitic N and C atoms (such as a4, a5, a6, z3, and z6 configurations of TPI-T) are responsible for the magnetism (figure S29). (iii) All the N and C atoms (the other configurations of TPI-G3N/T) are responsible for the

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**Figure 6.** The magnetic moments with different sublattices, orientation, and spatial separation calculated using the $9 \times 9$ supercell in NG. (a) TPY-G3N, (b) TPY-T, (c) TPI-G3N, and (d) TPI-T. The dashed lines indicate the superimpose of magnetic moments for isolated vacancy-containing and graphitic N complexes.
magnetism (figures 7(b), S28 and S29). Notably, the magnetism is more sensitive to the spatial separation between the two defects in TPI-T compared to TPI-G3N, which shows the appearance of antiferromagnetic couplings between the graphitic and vacancy-containing N complexes in a7 and z1 configurations (figures S29(g) and (h)). The rich magnetism with the spatial separation could be resulted from the competition of the positive correlation and frustration [46–48], while the more stable behavior in TPI-G3N might be ascribed to the advantage of G3N in introducing robust FM. Furthermore, the asymmetric 2px + y orbitals of the N atoms around TPI near Fermi level are also observed shown in the PDOS (figures 7(c) and (d), and S30–32), which provides the σ feature. The two incoordinate spin channels of C-pz and all N-pz contribute to the itinerant magnetism. The mutual interaction between the localized and itinerant magnetism promotes the acquisition of the long-rang ferromagnetic order.

Our numerical results are inconsistent with the previous studies in the low N concentration [13, 20]. This may be due to the fact that the formation energies are relatively high (6.00 to 9.90 eV) for all configurations with the low N concentration (shown in tables S5 and S6). The higher (more positive) formation energies show a lower possibility for forming these defects in thermodynamic equilibrium. Moreover, the average magnetization per site is relatively weak in low N-concentration limit. These factors may limit the experimental realization of FM in NG. While the theoretical study hardly considers the coupling between the graphitic and vacancy-containing N defects [20].

In previous work [20], the magnetic coupling between graphitic N defects or between vacancy-containing N defects has been well studied. The results reveal that (i) the coupling between vacancy-containing N defects presents sublattice-dependent behaviour regardless of the N concentration, and (ii) only in high N concentration does the sublattice-independent magnetic coupling between graphitic N defects would occur. By contrast, the coupling between the specific graphitic and vacancy-containing N defects (TPY-G3N) presents both the sublattice- and N-concentration-independent behaviour in our work. This configuration could contribute to the observed FM in both high and low N concentrations. Herein, graphitic N defects can act as a bridge to achieve the long-range magnetic coupling for vacancy-containing N defects.

Now, we can obtain the comprehensive picture of FM enhancement in NG, which is associated with the N concentration and geometric configuration. In the high N-concentration limit, the TPY-G3N system
represents the sublattice-independent behavior, which is responsible for the observed FM. Intriguingly, the low N-concentration allows all systems to achieve the sublattice-independent magnetism. Besides, our previous study revealed that, in the medium N-concentration case, both TPY- and TPI-containing NG show enhanced FM, while only the TPI-T system possesses the sublattice-independent characteristic [31]. Based on the above facts, one can reasonably give the following conclusions. From the perspective of the N concentration, all systems show enhanced FM except for the high-N-concentration case, which reveals that the positive coherence is concentration-dependent and the high N concentration (e.g. 9.23%) would suppress this effect. From the perspective of the geometry configuration, all TPY-containing NG presents enhanced FM, while the TPI-containing NG possesses this feature only in the case with obvious positive coherence. Notably, the weaker averaged magnetization per site in the low N-concentration graphene might hamper the acquisition of substantial FM during the real process. Therefore, the excellent magnetic behavior may be expectable if the two conditions are simultaneously satisfied: (i) the combination of the above enhancement effects on the magnetism and acquiring the abundant magnetization density; (ii) the positive synergistic effect among the individual enhancement effects. In a word, one can observe a robust FM through modulating the N concentration and geometry configuration in NG.

4. Conclusions

To summarize, we report a comprehensive framework of the FM enhancement in NG. The magnetic interactions between the itinerant and localized moments depend on both the N concentration and geometric configuration (defect type, sublattice occupation, orientation, and the spatial separation between two defects). Based on the visual results, the magnetic mechanism is mainly attributed to the $\sigma-\pi$ magnetic interaction, the band reconstruction due to the proximity of two defects, and the sublattice match/mismatch between two defects. In the high N-concentration case, only when graphitic-3N is induced into the TPY-containing NG does the sublattice-independent enhanced FM could be realized, which would be the situation of the obtained FM for the statistically random distribution of the defects. Interestingly, all systems represent the enhanced magnetism in the low N-concentration limit, which is prone to be the situation of emerging spontaneous magnetization. Notably, the high N-concentration case possesses high magnetization but with the remarkably restrained condition, while more opportunities for FM enhancement can be offered in the low N-concentration limit but with the lower Curie temperature and magnetization. Consequently, an appropriate concentration may support the FM optimization. Our theoretical investigation provides the available avenues for realizing the strong FM with both high Curie temperature and high magnetization, i.e. obtaining the certain geometric configuration (TPY-G3N) or an appropriate N-concentration graphene with coexisting graphitic and vacancy-containing N complexes, and further offers a reasonable explanation.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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