The mechanisms of impurity–impurity and impurity–matrix interactions in B/N-doped graphene

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1. Introduction

Graphene has attracted a great deal of attention due to its surprising physical and chemical properties in recent years [1–3]. Its distinguished properties make graphene a material which could be used in the fields of gas sensors [4], nanodevices [5] and so on.

In-plane heteroatom substitution of graphene is a potential strategy to tune the structure and electronic properties [6]. For graphene, B and N are the best candidates since they have similar covalent radius to C. The B and N atoms introduce holes and electrons to the lattice, leading to p- or n-type semiconductor nanostructure, respectively [7]. It is found that the B/N dopants in graphene sheets can modulate the chemical reactivity and the transport properties of the materials [3,8–11]. Many researches on B/N-doped graphene have been carried out due to its promising physical and chemical properties in recent years [1–3]. Its distinguished properties make graphene a material which could be used in the fields of gas sensors [4], nanodevices [5] and so on.

In the present Letter, we focus on the I–I and I–M interactions. Our results have revealed that the impurities interact with each other through the long-range screened Coulomb interaction, and the impurity–matrix interaction is understood from the orbital hybridization. The impurity-induced inter-valley interference only shows a minor modification on the Coulombic impurity–impurity interaction. The B impurity binds more strongly with the matrix than the N impurity. The variation of the Fermi-level energy relative to Dirac point with the itinerant carrier concentration, along with the delocalized distribution of the carriers, indicates the non-local doping effect of the impurities.

Using DFT calculations, we investigate mechanisms of the impurity–impurity and impurity–matrix interactions in B/N-doped graphene. Our results have revealed that the impurities interact with each other through the long-range screened Coulomb interaction, and the impurity–matrix interaction is understood from the orbital hybridization. The impurity-induced inter-valley interference only shows a minor modification on the Coulombic impurity–impurity interaction. The B impurity binds more strongly with the matrix than the N impurity. The variation of the Fermi-level energy relative to Dirac point with the itinerant carrier concentration, along with the delocalized distribution of the carriers, indicates the non-local doping effect of the impurities.

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2. Theoretical mode and calculation details

The DFT calculations are performed using Quantum ESPRESSO package [25]. The electronic exchange–correlation interaction is described by the Perdew–Burke–Ernzerhof (PBE) [26] in the scheme of a generalized gradient approximation (GGA) and an ultrasoft [27] pseudopotential has been used to model the ionic core. The periodic graphene supercells (2N² atoms per supercell), with sizes of \( N \times N \) \((N = 3, 4, \ldots, 12)\) times of the graphene unit cell, are used in our calculations. The vacuum between the graphene layers is set to 12 Å, which is regarded as large enough to avoid the interaction between the mirrors. The energy cutoffs for wave function and charge density are 30 Ry and 300 Ry, respectively. Uniform k-point grid is chosen to be Int(36/N) × Int(36/N) × 1 for a \( N \times N \) supercell. The Methfessel–Paxton smearing technique [28] is adopted, with an energy width of 0.01 Ry. The supercells are fully relaxed with the convergence criteria of \( 10^{-2} \) Ry/bohr for the force, \( 10^{-4} \) Ry for the energy, respectively.

To effectively study the I–I and I–M interactions, we use hexagonal supercells of graphene with the impurities occupying the high-symmetry sites. Figure 1a shows the periodic graphene supercell with a size of \( N \times N \), with the \( D_A \) and \( D_B \) being the doping positions and \( N_{A_0} \) (the C–C bond length in pure graphene) is the lattice constant of the supercell. Two doping methods are applied in our Letter. One case is the single B or N substitution of C (B–G or N–G) (Figure 1b), where the I–I distance \((R)\) is measured by \( N_{A_0} \). The other way is co-doping by using B–N pair to substitute two carbon atoms (BN–G) which are located at the vertex of supercell and the center in regular triangle composed of three vertexes, where \( R \) is measured by \( N_{A_0}/\sqrt{3} \). The periodic impurity lattice has the same hexagonal symmetry as the matrix lattice, thus, (1) the I–I interaction can be scaled by just one parameter \( R \) in this high-symmetry system and (2) the interaction mechanism will not be artificially contaminated by the lowering of the configurational symmetry. These superiorities of this structural model will be implied by the results in this Letter. On the other hand, we can also conduct the investigation on I–I interaction in a fixed-size supercell. However, the impurity lattice symmetry changes with doping sites of impurities and \( R \) is not a good scaling parameter due to the interference by other duplicates of impurities especially if long-range interaction among dopants is treated, which will produce the noise to performance of the perfect physical mechanisms.

To investigate the mechanisms of I–I and I–M interactions, we define the substitutional energy \( (E_{sub}) \) in mono-doping and co-doping cases as the difference of cohesive energy between the doped and pristine graphene. The corresponding \( E_{sub} \)s are expressed as

\[
E_{sub}(B) = E_{tot}^{(B+G)} - E_{tot}^{(G)} - E_{co}^{(B)} \tag{1a}
\]

\[
E_{sub}(N) = E_{tot}^{(N+G)} - E_{tot}^{(G)} - E_{co}^{(N)} \tag{1b}
\]

\[
E_{sub}(BN) = E_{tot}^{(BN+G)} - E_{tot}^{(G)} - E_{co}^{(BN)} \tag{1c}
\]

where \( E_{co}^{(i)} \) stand for the cohesive energy of B–G, N–G, BN–G and G with the size of \( i \) \times \( i \) supercell \((1 \leq i \leq 6)\) and \( n_i \) denotes the number of constituent \( i \) atom. Eqs. (1a–c) can be written as

\[
E_{sub}^{(B)} = E_{tot}^{(B+G)} - E_{tot}^{(G)} - E_{tot}^{(C)} - E_{co}^{(B)} \tag{2a}
\]

\[
E_{sub}^{(N)} = E_{tot}^{(N+G)} - E_{tot}^{(G)} - E_{tot}^{(C)} - E_{co}^{(N)} \tag{2b}
\]

\[
E_{sub}^{(BN)} = E_{tot}^{(BN+G)} - E_{tot}^{(G)} + 2E_{tot}^{(C)} - E_{co}^{(BN)} - E_{co}^{(B)} \tag{2c}
\]

where \( E_{co}^{(i)} \) represent the total energy of B–G, N–G, BN–G, G, single C atom, single B atom and single N atom, respectively. The total energy of defective supercell is the summation of the energy of the isolated defect (I–M interaction energy \( E_{int} \)) and the interaction energy of impurities with its periodic images \( (I–I) \) interaction energy \( E_{int} \) [29]. The definition of \( E_{int} \) in Eqs. (2a–c) reflects the total energy difference between doped and undoped systems, also emphasizing the fact of the I–I and I–M interactions.

3. Results and discussion

When foreign atoms (B/N) replace the atoms in sheet, they will both deform the lattice structure and change the distribution of electrons. For example, the B–C bond length is \( \sim 1.48 \) Å and the N–C bond length is \( \sim 1.41 \) Å, while the C–C bond length is \( 1.42 \) Å in pristine graphene, in agreement with previous studies [21,30,31]. In terms of electronic structure, the electrons in B/N doped system will redistribute due to the different electronegativities between the impurity atoms and C atoms. According to our

Figure 1. (a) The periodic graphene supercell with the size of \( N \times N \) and the lattice constant of \( N_{A_0} \) where \( D_A \) and \( D_B \) sites are the doping sites. The periodic supercell (b) with one B or N dopant and (c) one BN pair. Pink, blue and green balls stand for dopants (B or N) and gray balls stand for C.
Löwdin charge population, the charge accumulations at B and its three nearest C atoms are +0.18 e and −0.24 e, while ones at N and three C atoms neighbored to it are −0.21 e and +0.39 e, respectively. This fact has also been confirmed by previous theoretical analyses [32–34]. Moreover, the B/N dopant will introduce itinerant carriers (holes/electrons) onto the graphene matrix (shown later), which results in the local negative/positive charge around the B/N dopant for the charge conservation. Therefore, when summarizing the positive charges on the B (N) atom and negative (positive) charges on the three B–C (N–C) covalent bonds, the B (N) site can be viewed as a negative (positive) charge center, namely $I_q$. Thus, the above results imply that the $I$–$I$ interactions can be treated as $I_q$–$I_q$ interactions with screening effect from the C matrix with the itinerant carriers.

Figure 2 displays the dependence of substitution energy ($E_{sub}$) on the inter-impurity distance ($R$). In the mono-doping case, the $E_{sub}$ decreases with the increasing $R$ (Figure 2a and b), which indicates a repulsive interaction between substitutional dopants, while it increases in the co-doping case (Figure 2c), which exhibits that the performance is in an attractive form. Besides, $E_{sub}(B)$ is less than $E_{sub}(N)$, implying the B dopant binds more strongly to the matrix than the N dopant. These phenomena will be discussed later in more details. Previous Letter on the interaction between potassium adatoms on graphene surface has made a conclusion that they are dipole–dipole interaction and the interaction energy is $1/R^3$ dependence [35], where the type of $I$–$I$ interaction arising from the formation of ionic K–C bond and weak screening effect of the matrix. However, B–C and N–C bonds in B/N-doped graphene are polarized covalent bonds due to the small electronegativity difference between B/N and C atoms. In this situation, a charge center around the dopant $I_q$ can feel the electrostatic fields from its periodic images. Thus, we can describe the environmental electrostatic potential for a local $I_q$ using a multipole expansion, i.e. with monopolar ($\sim R^{-1}$), dipolar ($\sim R^{-2}$), and quadru-polar ($\sim R^{-3}$) electrostatic potentials. The electrostatic potential and the local $I_q$ are labeled as $\phi$ and $Q$ here, and the $I$–$I$ interaction energy $E_\phi$ can be described by $\phi \times Q$. Considering that $E_{sub}$ is the summation of $E_\phi$ and $E_{static}$, the dependence of $E_{sub}$ on $R$ can be expressed as

$$E_{sub}(R) = a/R + b/R^2 + c/R^3 + d.$$  

where fitting parameters $a$, $b$ and $c$ have the information of charges on images of $I_q$ and screening effect originating from the C matrix with the itinerant carriers. The constant $d$ represents the interaction energy of isolated defect with matrix, namely $E_{static}$. The first three terms are the multipole expansion of $\phi \times Q$. The $E_{sub}(R)$ curves obtained from DFT calculations are fitted by Eq. (3), and the fitting parameters for B–G, N–G and BN–G are listed in Table 1. Because of the large dopant concentration in BN–G, the three-period inter-valley ($K$–$K'$) interference has an observable modulating effect on the $E_{sub}(R)$ variation (Figure 2c), which results in the difficulty for fitting. Thus, only $\frac{1}{2}$ of the data are used for fitting in BN–G, as shown in Figure 2c.

Both the calculated $E_{sub}$s and the fitted curves are shown in Figure 2, from which three-period oscillations also can be observed in all the B–G, N–G, and BN–G systems. This kind of oscillation is a common phenomenon in graphene due to the interference of $K$ and $K'$ valleys [36,37]. However, compared with the Coulombic impurity–impurity interaction, such inter-valley interference only plays a minor modifying effect in $E_\phi$ (Figure 2 and the insets). The variation of $E_{sub}$ within a large $R$ range (Figure 2, insets) clearly shows the nature of long range impurity–impurity interaction, which also indicates the non-local screening effect of the graphene matrix on charged impurities. The decreasing trend in the $E_{sub}(R)$ curves for B/N mono-doping indicates the increase in the stability of the doped system, due to the decreased B–B or N–N repulsive force. On the contrary, the increasing trend in the $E_{sub}(R)$ curve for BN co-doping indicates the decrease in the stability of the system, due to the decreased B–N attractive interaction. Based on Eq. (3), it can be derived that $E_\phi = a/R + b/R^2 + c/R^3$. Since all the fitting parameters (Table 1) for B–G, N–G and BN–G have been obtained, the physical behavior of the $I$–$I$ interaction at any $R$ can be readily predicted, e.g. the curves shown in Figure 3. Both the B and N doping introduce itinerant carriers (holes and electrons) onto the graphene matrix, while effects introduced by the holes and
The partial density of states \( \rho \) can be calculated by the energy difference between \( E \) in the supercell with the size of 10 \( \times \times \) through influencing the \( \sigma \) orbitals of C atoms within the \( \pi \) \( = \) Fermi velocity \([1,2]\). In \( \pi \) \( \sigma \) \( \sigma \) \( \pi \) at the Dirac point (see \( \pi \) \( \sigma \) \( \pi \) \( \pi \)).

To understand the binding mechanism between the impurity and the matrix, we now turn to the electronic structure analysis of the B- and N-doped graphene. Generally, the stability of B-G and N-G depends on the strength of aromatic \( \Pi \) bonds and \( \sigma \) bonds. However, the effect of \( \Pi \) bonds on the large difference of \( \varepsilon_{\text{sub}} \) is not expected (shown latter). The partial density of states (PDOS) for N-G (in \( 4 \times 4 \) supercell) in Figure 4a shows that the majority of the N (2s) orbital is isolated from the C orbitals of the graphene matrix, implying the weak \( \sigma \) hybridization between the N dopant and the matrix. However, all B orbitals hybridize with the C orbitals of the matrix (Figure 4b). This difference in the orbital hybridization between B-G and N-G is caused by that in the energy matching between the atomic orbitals. The energy levels for the atomic orbitals are calculated using the all-electron method, which are \(-13.74, -5.29\) eV for C \( 2s \) and \( 2p \), \(-9.44, -3.61\) eV for B \( 2s \) and \( 2p \), and \(-18.56, -7.09\) eV for N \( 2s \) and \( 2p \). The larger energy mismatch \((4.82\text{ eV})\) for N \( 2s \) and \( 2p \) will lead to worse \( \sigma \) hybridization compared to that \((4.30\text{ eV})\) for B \( 2s \) and \( 2p \) (Figure 4a). This explains the reason why the N \( 2s \) orbital does not considerably participate in the impurity–matrix \( sp^2 \) hybridization as the B \( 2s \) orbital. Apart from the change in impurity–matrix orbital hybridization, the band filling caused by the B and N doping in graphene also can have effect on \( \varepsilon_{\text{sub}} \) through influencing the strength of the aromatic \( \Pi \) bond. However, this effect can be neglected, because the difference between the \( \varepsilon_{\text{sub}} \) \( \Pi \)-bond strength) is about 0.1 eV under holes-doping and electrons-doping with the same concentration \([39]\), which is far less than that in \( \varepsilon_{\text{sub}} \).

Table 1

<table>
<thead>
<tr>
<th></th>
<th>a (eV nm⁻³)</th>
<th>b (eV nm⁻³)</th>
<th>c (eV nm⁻³)</th>
<th>d (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B–G</td>
<td>4.7644</td>
<td>-51.4783</td>
<td>252.8520</td>
<td>2.2937</td>
</tr>
<tr>
<td>N–G</td>
<td>5.5155</td>
<td>-61.0332</td>
<td>272.6380</td>
<td>3.5670</td>
</tr>
<tr>
<td>BN–G</td>
<td>-11.5832</td>
<td>74.1494</td>
<td>-216.0050</td>
<td>6.3190</td>
</tr>
</tbody>
</table>

Figure 3. The I–I interaction energy \( E_n \) as a function of the \( R \) in B–G (blue line), N–G (red line), and BN–G (cyan line).

Figure 4. The PDOS (a) in N–G and (b) in B–G. Only one carbon atom from the nearest neighbor of dopant is shown. Vertical gray dashed and solid lines represent Fermi-level energy \( E_F \) (zero) and the energy \( E_n \) at the Dirac point.

between B–G and N–G \((-1.2\text{ eV})\). In a word, the phenomena above infer that the weaker \( \sigma \) hybridization between N and the matrix plays an important role in the larger substitution energy in N–G than that in B–G. Although the band filling is not important for the impurity–matrix hybridization and the difference between B–G and N–G, it will be important for the non-local impurity–impurity interaction. The carriers in the matrix introduced by the impurities will be analyzed in the following.

The B and N dopants introduce holes and electrons to the graphene sheet, respectively. And the Fermi level relative to Dirac point will downshift (upshift) with increasing the hole (electron) concentration. Pervious studies on the pure graphene under homogeneous charging by electric field have figured out that the shift of Fermi-level energy with respective to Dirac point, namely \( \Delta E_F \), is proportional to the square root of itinerant carrier concentration \( n \) \( \left( \Delta E_F = \sqrt{n} A \right) \), where \( A = \hbar v_F^2 \) and \( v_F \) is the Fermi velocity \([1,2]\). In our Letter, \( \Delta E_F \) can be calculated by the energy difference between the Fermi-level energy \( E_F \) and the energy \( E_n \) at the Dirac point (see Figure 4). However, it is still not clear whether the relative properties will hold in B/N–G. The correlation between \( \Delta E_F \) and \( n \) is shown in Figure 5, which exhibits the same dependence on \( n \) \( \Pi \)-behavior as the pure graphene subjected to an electric field for controllable \( n \). In our calculation, \( n \) in each B–G (N–G) supercell with various sizes is estimated by the formula \( n = N_c/S \), where \( N_c \) is the itinerant carrier number in \( p \) \( or \) \( C \) atoms within the energy range \( (E_F, E_0) \), and \( S \) is the area per doped supercell. We also find that the dopant concentration \( (\theta) \) has a consistent proportional relationship with \( n \), which is \( n = 0.50 \cdot \theta \). This means that each phosphoric N or B dopant contributes about 0.50 carriers to the graphene matrix, in agreement with experimental results \( (n = 0.60 \cdot \theta) \) \([19]\). The similarity in the \( \Delta E_F(n) \) variation between under homogeneous charging by electric field and local-impurity doping indicates the delocalized distribution of the carriers in B–G and N–G, which is proved in Figure 6, where the carriers between \( E_F \) and \( E_n \) in the supercell with the size of \( 10 \times 10 \) exhibit the distributions of holes (Figure 6a) in B–G and electrons (Figure 6b) in N–G. Local atomic impurities can induce itinerant carriers in graphene matrix, which is originated from the weak electronic screening in this two-dimensional lattice. The weak screening, as well as the resulted itinerant charges, determines the long-range character of the interaction between impurities in graphene. Lherbier et al. have pointed
in one sublattice, the carrier densities at the sites in the other sublattice of the graphene matrix will always be larger. This is exactly the Friedel oscillation arising from the inter-valley (K–K') interference [36,37], and it results in the three-period oscillation in the $E_{\text{F}}(R)$ variations (Figure 2). From both the carrier distributions (Figure 6) and the $E_{\text{F}}(R)$ variations (Figure 2), it can be seen that this oscillation has a long-range decay, which is also resulted from the weak electronic screening in graphene. Our findings have systematically revealed the non-local effect of B/N doping and the long-range I–I interaction, which are caused by the weak electronic screening in two-dimensional graphene.

4. Conclusions

Based on density functional theory, the mechanisms of the impurity–impurity (I–I) and impurity–matrix (I–M) interactions in B-, N-, and BN-doped graphene have been discussed. The impurities in graphene interact with each other through the long-range screened Coulomb interaction. The impurity-induced inter-valley interference only shows a minor modification on the Coulombic impurity–impurity interaction. The B dopant binds more strongly to the graphene matrix than N dopant, which is ascribed to the weaker N–C hybridization than B–C. Adjusting the itinerant carrier concentration $n$ through B or N doping level in graphene, the shift of Fermi-level energy relative to the Dirac point proportional to the square root of $n$, together with the delocalized distributions of the carriers, indicates that the doping effect is non-local. In a word, the I–I interaction is long-range Coulomb interaction in character and the doping effect is non-local in B/N-doped graphene. Therefore, it is expected that the conductivity and chemical reactivity of the sheet of graphene could be effectively tuned by the atomic impurities.

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References


Figure 5. The variation of the Fermi-level energy relative to Dirac point $\Delta E_{F}$ as a function of the itinerant carrier concentration $n$ in B–G (bottom) and N–G (top). $n$ can be tuned by the size of supercell doped with B or N atoms (see text). Solid curves (blue line for B–G and red line for N–G) stand for fitting curves. $A$ is the constant in fitting formula $\Delta E_{F} = \pm A n^{1/2}$, where + and − denote electron doping in N–G and hole doping in B–G, respectively.

Figure 6. The charge density distribution of (a) holes in B–G and (b) electrons in N–G.

out that B/N chemical doping of primitive graphene was a viable way to tailor the graphene properties without impeding its good conducting behavior [3]. This is also benefited from the delocalized effect of these impurities, because carriers can easily transport between delocalized impurity states. Apart from the delocalized carrier distribution, the long-range decaying Friedel oscillation is also reflected in the carrier distribution (Figure 6). There are two sublattices in graphene, and when an impurity substitute a site

$$E_{\text{F}}(R) = \frac{2}{\pi c} \frac{A}{4} \left( \frac{R}{\sqrt{E_{\text{F}}}} \right)$$

where $c$ is the speed of light and $A$ is a constant.
[38] L. Ci et al., Nat. Mater. 9 (2010) 430.