Nonlocal and Local Electrochemical Effects of Doping Impurities on the Reactivity of Graphene

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ABSTRACT: The chemical reactivity of graphene doped by B or N (B/N-G) toward H adatom has been studied systematically using density functional theory. From the site dependence of the adsorption energy of hydrogen adatom, the nonlocal and local charge-doping effects and local strain effect of B and N impurities on the chemical reactivity of graphene are derived. The nonlocal doping charges originate from nonlocal aromatic electron resonance, but the local doping charges are bonded to the vicinity of B/N dopant as a result of its high/low inherent chemical potential. Both of nonlocal and local charge-doping effects coexist in B-doped or N-doped graphene, while the nonlocal charge-doping effect will be largely suppressed in BN-codoped graphene. The nonlocally distributed doping holes/electrons in graphene enhance the stability of H adatom within the range of at least 9 Å away from the B/N dopants, while locally distributed holes/electrons in the vicinity of the B or N impurities only have a considerable stabilizing effect on the H adatom close (∼2 Å) to the dopants. These nonlocal and local electrochemical effects revealed here are useful for further doping-charge controlling and chemical engineering in doped graphene. Our results also clarify the issue of that the dopant-induced strain has a negligible effect on the enhanced stability of H adatom.

1. INTRODUCTION

Recently, graphene (G) has attracted extensive research interest due to its unusual physical and chemical properties as well as the vision in energy storage and electrode materials and so on.1,2 It has a perfect hexagonal structure with all valence electrons bonding with each other, resulting in its relative inert chemical reactivity under various environments. Improving the chemical reactivity of graphene, the uptake of adatoms as H, alkali metal, or transition metals (TM) can be increased, which is useful in the area of hydrogen storage or catalysis.3−5

Charge doping is an effective method to tailor the electronic properties and improves the reactivity of materials. It can be easily realized in graphene via charge transfer induced, for example, by substrate6−9 or adsorbate10,11 gate biasing12 and substitutional B/N dopants.13−17 Huang et al. have revealed that the chemical reactivity of graphene can be improved by both electron and hole doping, which enhances the thermodynamic stability of H adatom on graphene.6 Another method to realize charge doping in graphene is to introduce atomic impurities (e.g., B or N) with valence number smaller (hole doping) or larger (electron doping) than that of C atom.10,18−21 On the basis of the theoretical results, Muhich pointed out the fact that the binding energy between Pt and graphene substrates and the capacity of Pt on substrates can be effectively increased after the incorporation of impurities (B or N atoms) into substrates.3

To understand the charge-doping effect on the H-graphene binding strength, we have theoretically doped pristine and hydrogenated graphene with homogeneous artificial charges, and our simulation results indicated that the electron occupation in the bonding π and antibonding π* bands plays an important role in the chemical reactivity of graphene. Such homogeneous charge doping mimics the graphene under gate bias to some extent. However, the excess charges introduced by B or N dopants in graphene have a nonhomogeneous distribution, which has been well characterized by STM experiments and theoretical simulations.22−24 On the other hand, the strain field induced by dopants also has a tendency to influence the adatom stability.25−27 It has also been found that the adatoms attractively interact with vacancy-type defects in graphene within the range of 20−30 Å.25,26 Although this nonlocal attraction has been only ascribed to the combination of the strain field and strain-induced electronic effect of these defects,25,26 the vacancies also both nonlocally perturb the charge density around the defects and

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cause a self-doping in graphene,\textsuperscript{28–31} which will probably contribute to the nonlocal interaction between adatom and defected graphene. A clear physical picture for the strain and charge effects is required to solve this problem. B and N dopants both introduce doping charges (including local doping charges in the vicinity of B or N dopants and nonlocal doping charges in graphene matrix) and induce strain field in graphene matrix, which could affect its chemical reactivity. In order to disclose these electrochemical and elastochemical effects of B and N dopants in graphene, the interaction mechanism between the H adatom and B/N-doped graphene needs an in-depth investigation.

In the present work, the interaction mechanism between the H adatom and B/N-G has been studied systematically by density functional theory (DFT) calculations. In order to reveal the chemical reactivity of B/N-doped graphene, as well as to understand the effects of doping charges (nonlocal and local) and strain, the adsorption energy of H adatom on various sites of B/N-G substrate is calculated. It is found that the enhancement of adsorption stability of H adatom is contributed by both nonlocal and local electrochemical effects of B and N dopants. The dopant-induced strain effect (elastochemical effect) on the enhanced stability of H adatom is negligible. The related electronic mechanisms are thoroughly interpreted by detailed analysis.

2. COMPUTATIONAL DETAILS

Our first-principles calculation is based on density functional theory (DFT) using Perdew–Burke–Ernzerhof (PBE)\textsuperscript{32} functional within generalized gradient approximation (GGA) as implemented in the Quantum Espresso package.\textsuperscript{33} An ultrasoft pseudopotential\textsuperscript{34} has been used to describe the electron–ion interaction. The energy cutoffs for electron wave function and charge density are 30 and 300 Ry, respectively. The Methfessel–Paxton smearing technique\textsuperscript{35} is adopted, with an energy width of 0.01 Ry. All configurations considered in the calculations have been fully relaxed until the Hellmann–Feynman forces drop below 10^{-3} Ry/bohr and the self-consistence-field (SCF) convergence threshold for electronic energy is set to be 10^{-8} Ry. The chemical reactivity of doped and pristine graphene can be reflected by the adsorption energy of H adatom ($E_{\text{ads}}(X-G)$ and $E_{\text{ads}}^H(G)$), which are successively calculated according to the following equations:

$$E_{\text{ads}}(X-G) = E_{\text{tot}}^H + E_{\text{tot}}^{X-G} - E_{\text{tot}}^{H@X-G}$$

(1)

where $X-G$ stands for graphene with a single B dopant (B-G), graphene with a single N dopant (N-G), or graphene with a B-N dopant pair (BN-G). $E_{\text{tot}}^H$, $E_{\text{tot}}^{X-G}$, $E_{\text{tot}}^{H@X-G}$, $E_{\text{tot}}$ and $E_{\text{tot}}^{H@G}$ denote the total energy of an isolated H atom, X-G, H-adsorbed X–G, G, and H-adsorbed G, respectively.

In order to reveal the chemical reactivity of B/N-doped graphene as well as to understand the effects of doping charges and strain, a periodic graphene supercell of (17.06 Å × 17.26 Å) with a single B/N dopant (Figure 1a) or a B–N dopant pair (Figure 1b) is used. This relatively large supercell is necessary here because of the nonlocal distribution of the doping charges in B/N-doped graphene.\textsuperscript{22–24} The interlayer interaction diminishes when the separation between neighboring periodic layers is as large as 12 Å. In hydrogenated graphene, there is no observable direct interaction between different H adatoms, while the aromatic mesomeric effect\textsuperscript{36,37} (i.e., electronic resonance) in graphene will induce an indirect H–H interaction, resulting in the configuration dependence of adsorption stability and magnetism of hydrogenated graphene.\textsuperscript{38–41} However, the response of the strengths of the C–H and C–C bonds to charge doping does not qualitatively vary in different adatom configurations.\textsuperscript{4,42} It has also been indicated that if the H–H interaction is neglected, the B/N dopant has the same enhancing effect on the stabilities of single and multiple H adatoms on graphene.\textsuperscript{20} Therefore, the single H adatom is chosen here to study the electrochemical and elastochemical effects of B and N dopants.\textsuperscript{4,42} The adsorption sites considered here are categorized into two groups, i.e., the armchair path (AP) and zigzag path (ZP), which are respectively the A1-B2-A3-B4-A5-B6-A7-B8 and A1’-B2’-A3’-B4’-A5’-B6’-A7’-B8’ paths labeled in Figure 1a. For BN–G, only the C1-C2-C3-D3-D2-D1 path has been considered (Figure 1b). These paths also play important roles in the dynamic behavior of H adatom\textsuperscript{41,43} and the stability of graphene nanostructures.\textsuperscript{4,45} These adsorption-site groups are named as AP-H@B-G, ZP-H@B-G, AP-H@N-G, ZP-H@N-G, and AP-H@BN-G, respectively. To further clarify such nomenclature, the AP-H@B-G configuration, for instance, represents that the H atom is adsorbed on the carbon site within the AP of B-G.

The stability of H adatom on B/N-G ($E_{\text{ads}}^H(X-G)$) depends on the charge doping (i.e., electrochemical effect) and dopant-induced strain effect (i.e., elastochemical effect), which can be expressed as...
$E_{\text{ads}}^{H}(X-G) = E_{\text{ads}}^{H}(X-G) + E_{\text{ads}}^{Q}(G)$ \hspace{1cm} (3)

where $E_{\text{ads}}^{H}(G)$ is the adsorption energy of H adatom on neutral equilibrium G, and $E_{\text{ads}}^{Q}(X-G)$ and $E_{\text{ads}}^{Q}(G)$ are the contributions of dopant-induced strain and charge doping to $E_{\text{ads}}^{H}(X-G)$, respectively. In order to evaluate $E_{\text{ads}}^{Q}(X-G)$, the stability of H adatom on the pristine graphene $E_{\text{ads}}^{H}(G)$ with a homogeneous mechanical strain is calculated first (Figure 2). The dopant-induced strain of one C atom at S site ($\text{strain}(C_S)$), here S stands for the labeled C atom site in Figures 1a,b) within AP or ZP of B/N-G is defined as

$$\text{strain}(C_S) = \frac{l_1 + l_2 + l_3}{3} - l_0$$ \hspace{1cm} (4)

where $l_1$, $l_2$, and $l_3$ are the bond lengths of three nearest neighbors of $C_S$. $l_0$ is the C−C bond length in equilibrium pristine graphene (1.422 Å). Using the derived strain($C_S$) (eq 4) as an input data, we can obtain the $E_{\text{ads}}^{H}(X-G)$ from $E_{\text{ads}}^{H}(G)$ curve with the strain (Figure 2). Then, the corresponding $E_{\text{ads}}^{Q}(X-G)$ can be derived by eq 3. Only part of $E_{\text{ads}}^{H}(B-G)$ and $E_{\text{ads}}^{H}(N-G)$ is displayed in Figure 2.

Although B and N tend to bond with each other in graphene due to their Coulombic attraction,\(^{24}\) in order to reveal the underlying electrochemical mechanism, B and N are separated in BN-G (Figure 1b), which enables us simultaneously demonstrate the nonlocal and local natures of doping charges introduced by B and N. If setting B and N close to each other, the nonlocal nature cannot be derived from the short-range annihilation between holes and electrons. On the other hand, in BN-G, the B and N dopants can occupy the same or different sublattice with similar electrochemical effects. The former is chosen here due to its lower energy. These could be well verified by the carrier distributions in BN-G with (1) B and N bonding with each other and (2) B and N occupying the same sublattice (Figure S1 in the Supporting Information) as well as their comparison with Figure 4a−c.

3. RESULTS AND DISCUSSION

B and N not only introduce doping charges (holes or electrons) but also induce the strain in graphene matrix. Both charge doping and strain can affect the chemical reactivity of graphene, which can be reflected by the adsorption energy of H adatom ($E_{\text{ads}}^{H}$) on various carbon sites within the AP or ZP of B/N-G. As shown in Figures 3a−d, $E_{\text{ads}}^{H}(B/N-G)$ oscillatory decreases with increas-
neous charge doping by gate biasing to graphene can weaken the graphene reactivity (or stability of H adatom), we need further concentration on their significance. The energetic oscillation is related with the effect of Friedel oscillation in the charge distribution, which will be discussed in detail at the last paragraph of this section. In addition, the oscillation amplitude in $E_{\text{lat}}^{\text{H}}(B/N-G)$ along the AP (Figure 3a,c) is larger than that along the ZP (Figure 3b,d). These results indicate the adsorption-site dependence of $E_{\text{lat}}^{\text{H}}(B/N-G)$ as well as the nonlocal effect of B (N) dopant in B-G (N-G). Mechanisms will be analyzed later. $E_{\text{lat}}^{\text{H}}(B-G)$ is $\sim$0.1 eV larger than $E_{\text{lat}}^{\text{H}}(N-G)$, implicating that the effect of holes on the stability of H adatom exceeds that of electrons, which agrees well with Denis’s results and Huang’s results of doped and hydrogenated graphene with artificial charges. The same results demonstrate that the electrochemical effect of B/N dopants prevails over the interatomic orbital hybridization (B−C, N−C). When H is adsorbed on a site in the AP of BN-codoped graphene (BN-G), $E_{\text{lat}}^{\text{H}}(BN-G)$ has a fast decay down to the vicinity of $E_{\text{lat}}^{\text{H}}(G)$ (0.82 eV) within a range about 2.45 Å (Figure 3e,f). This indicates the local effect of a BN dopant pair in BN-G. The strain of B/N dopants in graphene can influence the stability of H adatom. The contribution from the strain of B/N dopants ($E_s(B/N-G)$) is displayed in Figure 3a−f; for a better view, $E_s(B/N-G)$ has been upshifted by 0.82 eV (the value of $E_{\text{lat}}^{\text{H}}(G)$), labeled by $E_s(B/N-G)$. In H-adsorbed B/N-G systems, the variation of $E_s(B/N-G)$ is only $\lesssim$40 meV, which demonstrates that strain contribution to $E_{\text{lat}}^{\text{H}}(B/N-G)$ is negligible. Our results are expected to deeply understand the effect of the strain of defects on the adatom. For example, the nonlocal enhancement of the adatom stability has been ascribed to the combination of the strain field and strain-induced electronic effect of these defects. However, the vacancies also both nonlocally perturb the charge density around the defects and cause a self-doping in graphene. Similar as to charge doping effect of B/N dopants, the self-doping effect of defects is also an electrochemical effect that will mostly contribute to the interaction between adatom and defective graphene since a biaxial strain of 2% only enhances $E_{\text{lat}}^{\text{H}}$ by $\sim$20 meV. Our results clarify the issue of that the dopant-induced strain has a negligible effect on the enhanced stability of H adatom. In the rest, the strain effect of B and N dopants on the chemical reactivity of B/N-doped graphene will not be involved, and the discussion will concentrate on their significant electrochemical effect.

To reveal the electrochemical effect of B and N dopants on the graphene reactivity (or stability of H adatom), we need further investigations on the related electronic mechanisms. Homogeneous charge doping by gate biasing to graphene can weaken the strength of an aromatic π bond ($\pi$ and $\pi^*$) via electron occupation in $\pi$ or $\pi^*$ bands, leading to the improved adsorption energy of H adatom. However, B or N dopants can introduce nonhomogeneous doping charges (holes or electrons), and the doping charges density differs from one site to another. These doping charges of B or N dopants include the nonlocally distributed holes/electrons in graphene matrix and the locally distributed holes/electrons close to dopants. The former originates from aromatic electron resonance (called mesomeric effect) and thus can easily spread in graphene matrix (i.e., nonlocal electrochemical effect), while the latter is bonded to the vicinity of B/N dopants as a result of their inherent chemical potential (i.e., local electrochemical effect). When H is adsorbed on a C atom, it needs to break the Π bond, the strength of which is in relationship with the distribution of doping charges (carriers). Holes in B-G (Figure 4a) and electrons in N-G (Figure 4b) clearly show the nonlocal distribution, along with the behavior of oscillatory decrease with the increased distance from B or N dopants. Moreover, the oscillation of carriers density in AP is much stronger than that in ZP. For BN-G, both electrons and holes coexist in graphene matrix, and the distribution is displayed in Figure 4c. It exhibits that the nonlocal doping charges are largely canceled out and only part of local doping charges persist, in contrast to doping charges (Figure 4a,b). We have also examined the electrochemical effect of BN-doped graphene with B and N occupying the same graphene sublattice (Figure S1 in the Supporting Information). In this case, the carriers distribution shows that the nonlocal charge-doping effect is also largely suppressed (similar as Figure 4c). Accordingly, the nonlocal nature of the electrochemical effect does not depend on the sublattice occupation. The above results indicate that both nonlocal electrochemical effect and local electrochemical effect do coexist in B-G or N-G, while the nonlocal electrochemical effect will be largely suppressed in BN-G. We can also derive the nonlocal electrochemical effect and local electrochemical effect in B-N-G from the behavior of $E_{\text{lat}}^{\text{H}}(B/N-G)$ with $R$ increasing. It can be seen that $E_{\text{lat}}^{\text{H}}(BN-G)$ has a fast decay down to the $E_{\text{lat}}^{\text{H}}(G)$ for pristine G within a range about 2.45 Å (Figure 3e,f), inferring the local electrochemical effect. However, $E_{\text{lat}}^{\text{H}}(B/N-G)$ in B-G or N-G has no obvious decaying variation within such short-range (Figure 3a,d) and instead has a long-ranged oscillatory decaying trend, with that the decaying range is at least 9 Å. In addition, the oscillation in $E_{\text{lat}}^{\text{H}}(B/N-G)$ is caused by the Friedel oscillation in charge density. Thus, the energy oscillation itself is also another proof for the nonlocal electrochemical effect of B and N dopants. These results have testified the local and nonlocal electrochemical effect in B-G and
N-G. The special distribution of carries indicates the different strength of H bond at a certain carbon site. If we carefully compare $n$ at each carbon site within AP or ZP (Figure 4) to $E_{fl}^H(B/N-G)$ (Figures 3a–f) at the corresponding site, they unexpectedly show the same behavior. We found the correlation between carriers density $n$ and the adsorption energy of H adatom on B/N-doped graphene, which reveals that the nature of chemical reactivity of B/N-G is dependent on $n$ induced by B or N dopants. The carriers distribution of BN-G (Figure 4c) absolutely reflects the electrochemical effect of B and N dopants. Thus, it is unnecessary to calculate the adsorption energy of H adatom in other paths (e.g., zigzag path). The $n$-$E_{fl}^H(B/N-G)$ correlation stresses that the local electrochemical effect and nonlocal electrochemical effect of B/N-G have a local stabilizing effect on H adsorption at a certain C site. In addition, our calculations show that B-doped and N-doped graphene are nonmagnetic, which is consistent with other reports.\(^{50,51}\) This is because the nonlocal carriers induced by B and N dopants are very itinerant and their electronic exchange interaction (driving force for spin polarization) is relatively small. The adsorption of H tends to induce spin polarization in graphene; however, the magnetic state also has a nonlocal characteristic, leading to a weak magnetism.\(^4\) This magnetic state can be easily annihilated by the nonlocal carriers from B and N dopants. Even in the pristine graphene with H adatom, the nonmagnetic–magnetic energy difference is only 0.04 eV, which is far less than the increase in $E_{fl}^H$ by the doping charge here (up to 1.0 eV). Thus, the perturbation from magnetism on the electrochemical effect of B and N dopants can be safely neglected. Recently, Denis pointed out that the 3p elements have a potential to modulate the bond strength of H adsorption on pristine graphene.\(^52\) Further investigation on electrochemical and elastochemical effect of 3p elements on the stability of H adatom will be done soon.

It has been illustrated above that the nonlocal and local charges induced by B and N dopant enhance the H adatom stability, and we will further show in the following that these two kinds of charges also can influence (be well probed by) the H-graphene electron transfer by Löwdin population\(^{53}\) analysis. The net charge of H atom ($Q^H$) adsorbed on various sites of B-G or N-G surfaces is plotted in Figure 5, where the dashed line denotes the net charge of H adsorbed on pristine graphene $Q^H(G)$ (0.2 e). Similar to $E_{fl}^H(B/N-G)$ (Figure 3a–d), $Q^H(B/N-G)$ also presents an oscillation behavior. This is related with the nonlocal Friedel oscillation\(^{46–48}\) of electronic states in defects graphene, resulting in the inhomogeneous distribution of holes/electrons in the two sublattices of graphene (Figure 4). The affinity of C to electron is dependent on its possessing charge density, which then influences the electron transfer between H adatom and graphene matrix. There are both nonlocal and local doping charges on the A1 site (Figure 1a), while only nonlocal ones on other farther sites; therefore, the oscillation amplitude of $Q^H(B/N-G)$ at the A1 site is much larger than that at other sites. In addition, $Q^H(B-G)$ increases as R increases when H is adsorbed on the B-G system, while the opposite result happens for H-adsorbed N-G. The value of $Q^H(B/N-G)$ approaches 0.2 e when H is far away from B or N dopants. On the other hand, our results indicate that holes (induced by B) at a C site enhance electron transfer from H to the substrate, while electrons (induced by N) weaken it. These phenomena arose from charge transfer are in accordance with previous results relative to charge doping by gate biasing to graphene with H adsorption,\(^4\) but not well explained yet. Here we could understand the charge transfer from the effect of holes/electrons density on the affinity of C to electron. For the B-G system, B introduces holes to C atoms of graphene matrix, leading to the increase of affinity of C atoms that makes electron transfer from H to the matrix when H is adsorbed on a certain C atom. However, N introduces electrons to C atoms of graphene matrix, leading to the decrease of affinity that makes electrons transfer from matrix to graphene. It should be pointed out that the charge transfer between H adatom and graphene is only a reflection of the doping-charge density of B/N-G systems, as well as its characteristics, while the adsorption stability is governed by the electrochemical effect of B and N dopants, but not by the H-graphene electron transfer.

4. CONCLUSIONS

By density functional theory (DFT) calculations, the interaction mechanism between the H adatom and B/N-doped graphene (B/N-G) has been investigated systematically. From the site dependence of the adsorption energy of hydrogen adatom, both nonlocal and local electrochemical effects of B and N impurities contribute to the enhanced chemical reactivity of graphene. The nonlocal doping charges originate from nonlocal aromatic electron resonance, and the local doping charges are bonded to the vicinity of B/N dopant as a result of its high/lowlow inherent chemical potential. Both nonlocal and local charge-doping effect do coexist in B-doped or N-doped graphene, whereas nonlocal charge-doping effect has been largely suppressed in BN-codoped graphene. The nonlocal electrochemical effect enhances the stability of H adatom within the range of at least 9 Å away from the B/N dopants, while the local electrochemical effect only has a considerable stabilizing effect on the H adatom close (≈2 Å) to the dopants. Our results also clarify the issue of that the dopant-induced strain has a negligible effect on the enhanced stability of H adatom. Finally, we have demonstrated that the adsorption stability of H adatom is independent of the H-graphene charge transfer, whereas the charge transfer reflects the doping-charge density of B/N-G systems and further confirms the existence of nonlocal and local electrochemical effects of B and N dopants.

**ASSOCIATED CONTENT**

Supporting Information

Figure S1. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b02812.

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