Band gap modulation in $\gamma$-graphyne by p-n codoping

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Abstract – The modulation of the band gap in the two-dimensional carbon materials is of importance for their applications as electronic devices. By first-principles calculations, we propose a model to control the band gap size of $\gamma$-graphyne. The model is named as p-n codoping, i.e., using B and N atoms to codope into $\gamma$-graphyne. After codoping, the B atom plays the role of p dopant and the N atom acts as n dopant. The Fermi energy level returns around the forbidden zone and the band gap of $\gamma$-graphyne becomes bigger or smaller. Moreover, the gaps exhibit an oscillating behaviour in the different codoping configurations. The proposed model serves as new insights for a better modulation of the electronic properties of 2D carbon materials.

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For decades, silicon semiconductor has been achieving great success in electronic technology. Making a field effect transistor smaller in volume is a development trend in the field of digital logic. However, its development process continuously meets theoretical and technical challenges. There are two urgent problems in front of us, i.e., thermal effect and quantum effect. Therefore, looking for new alternative materials has become an important research subject in physics, chemistry and material science. Graphene has been considered to be a hot candidate to replace silicon since its successful fabrication [1]. Such system with Dirac fermions [2] has been under focus in both theoretical and experimental fields [3–7] due to its intrinsic high electron mobility and large on/off ratio. However, pristine graphene does not have a nonzero band gap, a property which is mandatory for many electronic and optoelectronic applications, which greatly limits the applications on next-generation electronic devices. In recent years, graphene, another kind of carbon allotrope with Dirac points, is increasingly becoming attractive. Graphene and its expanded structures are similar to graphene and can be regarded as big hexagonal rings joined together by acetylenic linkages (C≡C≡C) in various construction forms [8–16]. These materials consist of layered carbon sheets containing $sp$ and $sp^2$ bonds [10,14]. In different construction forms, the geometries of graphene are various including $\alpha$, $\beta$ and 6, 6, 12 structures and so on [8,10,14,17]. Most of the structures of graphene are semimetals with zero gap. Malko et al. [8] even found that the structure of graphyne also possessed Dirac cones in the same way as graphene. As we known, In order to realize practical applications as electronic devices, a material must present a band gap competitive with silicon. Fortunately, one of the graphyne structures was proved to be a direct semiconductor and its band gap is about 0.5 eV at the $M$-point in the Brillouin zone (BZ) [10–12,14]. For the convenience of narration, this structure is named as $\gamma$-graphyne. Considering the underestimation of the band gap from the generalized gradient approximation (GGA) calculations, Guo et al. determined the gap of $\gamma$-graphyne to be 0.96 eV from hybrid functionals [13]. Therefore, from this perspective, $\gamma$-graphyne is more suitable for the use in electronic devices than graphene.

Band gap modulation is a research focus correlated to graphene and graphyne. Chemical doping, molecular adsorption, substrate doping and external stress are usually effective methods to change and control the electronic properties of carbon-related materials. Especially, the p-n codoping method is a well-established one [18,19], where an elemental doping plays the role of p doping and another
elemental doping acts as $n$ doping. After such codoping, the band gaps of graphene and graphyne are opened. In this work, we are aiming at the band gap modulation of $\gamma$-graphyne by the $p$-$n$ codoping method. We investigate in detail the effect of dopants B and N on the electronic properties and the band gap of $\gamma$-graphyne. In order to avoid the unsucces of additional GGA calculations in determining the band gap, we reproduce the band structures of $\gamma$-graphyne with hybrid functionals. The results show that the $p$-$n$ codoping method enormously expand the band gap of $\gamma$-graphyne even at the GGA level. After using the hybrid functionals, the change in band gap is more obvious. Moreover, in the same way as $\alpha$-graphyne, the band gaps exhibit periodic oscillations with increasing the distance of the dopants.

Our theoretical framework is based on first-principles calculations. The VASP package [20,21] is adopted to find the optimum geometries and determine the band structures of undoped, B(N)-doped and B/N-codoped graphyne. The projector augmented wave (PAW) [22,23] is used to describe the interaction between ions and electrons. GGA-type PBE functionals [24] are chosen as exchange-correlation functional. Careful tests for cutoffs of the wave function show that $500$ eV is enough for wave function expansion. The $5 \times 5 \times 1$ $k$-points for the representation of the BZ are taken to explore the optimum geometries of the considered systems. We optimize all geometries by reducing the Hellman-Feynman forces down to $0.01$ ev/Å$^2$. Based on the optimum geometries, we re-calculate the energy band structures by hybrid functionals HSE06 [25]. In both cases of band calculations from GGA-PBE and HSE06, the denser $11 \times 11 \times 1$ $k$-points are taken for the first self-consistent step. 120 special points along the high symmetry lines $\Gamma$-$M$-$K$-$\Gamma$ are chosen for band calculation and plotting. In order to address the dopant effect on the band structures of doped $\gamma$-graphyne, the electrostatic potential is first calculated and set to zero. Then the obtained eigenvalue and the Fermi energy are shifted with respect to the electrostatic potential. In the vertical direction of the sheet, periodic boundary conditions are also set with a vacuum region of 20 Å to avoid the interaction with adjacent layers. In order to quantify the stability and formation ability of the doped systems, we calculate the formation energy defined as $E_F = E_{DG} - E_{PG} + nE_C - \sum E_{dopant}$, where $E_{DG}$ is the total energy of single doped or codoped systems, $E_{PG}$ is the total energy of pristine graphyne, $E_C$ is the energy of one carbon atom in pristine graphyne, $n$ is the number of carbon atoms substituted by dopants, $\sum E_{dopant}$ is the total energy of dopant B, N or B/N pairs.

The two-dimensional crystalline structure for the primitive cell of $\gamma$-graphyne is hexagonal with $p6/mmm$ symmetry, as shown in fig. 1(a), which is the same as graphene and other hexagonal graphyne. In $\gamma$-graphyne, the bonds among C atoms belong to C-C single bond (a-b) or C≡C triple bond (b-c). Comparing with graphene, two extra C atoms are inserted into C-C bonds of $\gamma$-graphyne, forming a C≡C-C≡C chain (a-b-c-d). The optimized lattice constant $a$ (or $b$) is equal to 6.89 Å and the bond lengths of C-C and C≡C are 1.41 and 1.22 Å, respectively, in good agreement with previous works [10,12]. The calculated band structure of the pristine primitive cell is displayed in fig. 2(a) that shows that $\gamma$-graphyne has a direct band gap of 0.46 eV at the $M$-point, being consistent with the data of 0.46 eV [10] and 0.52 eV [12]. Most of graphyne have Dirac cones [8,10,14,17]. However, $\gamma$-graphyne exhibits semiconductor behaviour with a suitable band gap, which may promise some potential applications in semiconductor devices. It is well known that the band gap of semiconductor is underestimated in the pure GGA level. However, hybrid functionals such as HSE06 can give excellent description of the electronic structure of the semiconductor and reproduce the experimentally measured band gap quite well. The calculation of the band gap for $\gamma$-graphyne from hybrid HSE06 functional yields twice the gap value of 0.96 eV (fig. 2(b)). Therefore, it is necessary to adopt two functionals to confirm each other. In this paper, all the band structures for the considered systems are recalculated at the HSE06 level based on the optimized geometries determined by the PBE functional.

The single B- and N-doped graphyne are formed by one B or N atom substituting one C atom in graphyne. There are two inequivalent sites for single B or N doping, namely, a and b sites. The structure parameters in optimized B- and N-doped graphyne are listed in table I and are shown in fig. 1(b)–(e). For single B doping at the a site, the bond lengths of the three B-C are 1.46, 1.51, and 1.51 Å, longer than the $d_{C-C}$ (1.41 Å) in pristine graphyne. At the a site,
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Fig. 2: (Color online) The band structures of pristine and B or N singly codoped γ-graphyne along the \( \Gamma-M-K-\Gamma \) line. \( B_a, B_b, N_a \) and \( N_b \) mean B or N atom doping in the a or b site. Panels (a) and (b) are the PBE and HSE results, respectively. The vacuum level is set to zero and the Fermi energy level is marked by a blue dotted line.

Table 1: The distances between C and dopants (\( d_{C-B} \) and \( d_{C-N} \)), the formation energies \( E_F \), the vacuum energy level \( E_{Vacuum} \), and the Fermi energy level \( E_{Fermi} \) of B or N single doping. \( d_{C-B} \) or \( d_{C-N} \) indicate the shortest bond when the B or N atom binds with several C atoms. \( W \) means work function and \( W = E_{Vacuum} - E_{Fermi} \). \( E_{Vacuum} \), \( E_{Fermi} \), and \( W \) for pristine γ-graphyne are 1.15, 1.89 and 5.17 eV, respectively.

| \( d_{C-B(N)} \) (Å) | \( E_F \) (eV) | \( E_{Vacuum} \) (eV) | \( E_{Fermi} \) (eV) | \( W \) (eV) |
|----------------------|--------------|----------------|----------------|---------|
| a site               | b site       | a site | b site       | a site | b site       |
| \( d_{C-B} \)        | 1.46         | 1.33  | 1.35         | 1.19   |
| \( d_{C-N} \)        | 1.78         | 2.78  | 3.51         | 2.47   |
| \( E_F \)            | 1.12         | 1.12  | 1.16         | 1.16   |
| \( E_{Vacuum} \)     | −4.22        | −4.20 | −3.43        | −3.21  |
| \( E_{Fermi} \)      | 5.34         | 5.33  | 4.59         | 4.37   |

the long \( d_{C-B} \) (similar to the C-C bond) is 1.46 Å while the short bond one is 1.33 Å (similar to the C≡C bond). In the case of N doping at the a site, the three \( d_{C-N} \) are 1.35, 1.43, and 1.43 Å. At the b site, the long \( d_{C-N} \) (similar to the C-C bond) is 1.37 Å while the short bond (similar to the C≡C bond) is 1.19 Å. As mentioned above, one can find that the C-B (C-N) bonds are longer (shorter) than the corresponding C-C or C≡C bonds both in a and b sites. This can be attributed to the fact that the N atom has more valence electrons than the B atom, leading to a shorter C-N bond than the C-B bond. This also can be explained from the atomic radius \( r \) of B, C, N which are related as \( r_B > r_C > r_N \). When one B replaces one C, the B atom will repulse the adjacent C atoms to the outside, leading to longer C-B bond than the original C-C bond. When N replaces C, the N atom will approach the adjacent C atom due to its smaller atomic radius, leading to shorter C-N bond than the original C-C bond. The formation energies \( E_F \) of B-doped graphyne at a and b sites are 1.78 and 2.78 eV, smaller than those of N-doped graphyne of 3.51 and 2.47 eV. In a word, B-doped γ-graphyne is more easily synthesized in experiments than the N-doped one. To consider the doping site, the B doping prefers to select the a site while the N doping the b site.

The electronic energy band structures for B- and N-doped graphyne are shown in fig. 2, where the data for the vacuum energy level \( E_{Vacuum} \), and the Fermi energy level \( E_{Fermi} \) and the work function \( W \) are collected in table 1. For single B doping either at a or b site, the Fermi energy level \( E_{Fermi} \) becomes smaller comparing with pristine graphyne. Moreover, the valence band maximum (VBM) moves up and crosses the Fermi energy level. Therefore, B doping acts as \( p \)-type dopant. On
Fig. 3: (Color online) The band structures of B/N codoped γ-graphyne for the considered seven codoped configurations along the Γ-M-K-Γ line. Panels (a) and (b) are the results in PBE and HSE level, respectively. The vacuum level is set to zero and the Fermi energy level is marked by a blue dotted line.

Table 2: The distances between C and dopants ($d_{C-B}$ and $d_{C-N}$), the formation energies $E_F$, and the band gaps $E_{gap}$ for two configurations of B/N codoping. The $d_{C-B}$ or $d_{C-N}$ indicate the shortest bond when the B or N atom binds with several C atoms.

| Configuration | $d_{C-B}$ (Å) | $d_{C-N}$ (Å) | $E_F$ (eV) | $E_{gap}$ (PBE) (eV) | $E_{gap}$ (HSE) (eV) |
|---------------|---------------|---------------|-------------|----------------------|----------------------|
| ax            | 1.33          | 1.17          | 5.89        | 8.91                 | 1.01                 |
| ab            | 1.28          | 1.14          | 5.53        | 8.54                 | 1.00                 |
| ac            | 1.29          | 1.15          | 5.51        | 8.51                 | 1.00                 |
| ad            | 1.30          | 1.16          | 5.56        | 8.56                 | 1.00                 |
| ae            | 1.31          | 1.17          | 5.62        | 8.62                 | 1.01                 |
| af            | 1.32          | 1.18          | 5.67        | 8.67                 | 1.01                 |
| ag            | 1.33          | 1.19          | 5.72        | 8.72                 | 1.01                 |
| ah            | 1.34          | 1.20          | 5.77        | 8.77                 | 1.01                 |

The contrary, for single N doping either at a or b site, the Fermi energy level $E_{Fermi}$ becomes bigger comparing with pristine graphyne. Moreover, the conduction band minimum (CBM) moves down and crosses the Fermi energy level. Therefore, N doping behaves as n-type dopant. At the a site for B and N doping, the original band gap zones become obviously larger. In contrast, at the b site for B and N doping, the band gap zones slightly narrow. The band structures given by PBE and HSE06 exhibit the similar dispersion trend expected for the given gap width which is bigger from HSE06 than from PBE. As in the above discussions, B and N doping make the Fermi energy level move down and up relative to the forbidden band. Therefore, it will be very interesting and meaningless if the Fermi level can return to the original site using p-n codoping, and the exiting band gap will be modulated.

We further investigate the geometries and electronic properties of B/N codoping in γ-graphyne to modulate its band structures. Eight possible substitutional sites, noted in fig. 1(a), are considered. Two types of codoping configurations are investigated in detail. They are ax and xa ($x = b, c, \cdots, h$), which represent that the B (or N) atom substitutes the C atom in the a site and the N (or B) atom substitutes the C atom in b, c, d, e, f, g, and h sites, respectively. The geometry parameters and formation energies are listed in table 2. The planar structure remains after B/N codoping into graphyne. We think that the size effect plays an important role in these doped systems. B, N and C belong to the second-period elements and are nearest neighbors. They have comparable atomic radius. Therefore, it is unlikely that the C atom is pulled out of the graphene plane after B/N codoping. The $d_{C-B}$ and $d_{C-N}$ are almost the same as in single B and N doping. The C-B single bond covers the range of 1.46–1.55 Å and the C≡B triple bond, similar to C≡C, is about 1.33 Å. The C-N single bond covers the range from 1.35 to 1.42 Å and the C≡B triple bond is about 1.17 Å. The formation energies for the two configuration types change from 2.51 to 4.63 eV for ax and 3.56 to 5.89 eV for xa, indicating that the doped graphyne with the B atom at the a site is easier to synthesize than N doping at the a site. For the xa configuration, the ga is the most preferred codoped configuration. In the two configuration types, the ab case is the easiest to form and the ga case is the most difficult to realize. This means that the B-N pair induces the lowest energy in all codoped configurations owning to the charge...
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Finally, the electronic band structures are calculated at the PBE and HSE06 levels. Taking ax ($x = b, c, \cdots, h$) for example (as shown in fig. 3), the forbidden zone of pristine $\gamma$-graphyne returns back to the Fermi energy under the counteraction between B and N doping. More importantly, around $E_{\text{Fermi}}$, a different codoping site induces a different band gap after B/N codoping. Furthermore, the band gaps exhibit an oscillation behavior, changing in the big-small-big way. The situation of xa ($x = b, c, \cdots, h$) is similar to ax with the oscillating band gap. The periodic oscillation behavior exhibited in B/N codoped graphynes, shown in fig. 4, may be due to the collaborative effect between the the symmetry breaking [26] and energy level coupling [27,28]. The a-b and c-d sites are the two inequivalent sublattices. The a, d, e, and h sites are the equivalent sites. The b, c, g, and f sites are another group of equivalent sites. Doping at two random different sites will break the symmetry of two sublattices of $\gamma$-graphyne, and thus introduce different band gaps. On the other hand, the $p$-$n$ codoping from B and N atoms impose two opposite influences on the valence band (VB) and conduction band (CB) of undoped $\gamma$-graphyne. This coupling of VB and CB to each other also brings a different band gap size to the system.

The band gaps values for ax and xa are summarized in table 2. For the ax codoping configuration, the induced gaps in the PBE level lie in the interval [0.26 eV, 1.63 eV] while the gaps in the HSE06 level lie in [0.89 eV, 2.44 eV]. For the xa codoping configuration, the induced gaps in the PBE level lie in the interval [0.25 eV, 1.66 eV] while the gaps in the HSE06 level lie in [0.29 eV, 2.44 eV]. Generally, comparing to the PBE functional, the hybrid HSE06 functional introduces bigger gap values to the considered systems with the maximal amplitude of 242% (ae case). Therefore, the use of the HSE06 functional in this paper is essential to correct the the gaps from the PBE results. The maximum and the minimum of the gaps occur in the ah (or ha) and ea cases, respectively. It is exciting that the gap for the most stable codoping site of the ab case is 1.08 eV, close to the well-known band gap of semiconductor Si ($\sim$1.14 eV), which may promise potential applications of B/N codoping $\gamma$-graphyne in future.

In summary, the geometric and electronic structures for B or N single doping and B/N codoping in $\gamma$-graphyne are investigated from first-principles calculations. The pure GGA-type PBE functionals and the hybrid HSE06 functionals are adopted to determine the electronic properties of the considered doped systems. For single B or N doping, judging from the formation energy, the B doping is more easy to realize than the N doping in $\gamma$-graphyne. The B and N dopings prefer to select a different site of the two inequivalent sites. Furthermore, the Fermi energy level moves down or up after single B or N doping which gives us a chance to modulate the electronic properties of $\gamma$-graphyne. Therefore, we further investigate the geometric and electronic structures by B/N codoping into $\gamma$-graphyne. The results show the B-N pair is the most preferred codoping configuration. The Fermi energy level returns around the forbidden zone and the gaps exhibit an oscillating behavior with increasing distance between the B and N atoms. The oscillated band gap is caused by the collaborative effect between of the breaking of sublattice symmetry and energy level coupling in $\gamma$-graphyne.

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