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Communication: Oscillated band gaps of B/N-codoped α -graphyne

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The physical mechanism for the electronic structures tuning and band gap opening of α -graphyne are investigated from the first principles calculations. The pathway of using B and N atoms to codope into graphyne is proposed. After codoping, B atom plays a role of hole doping and N atom acts as electron doping. In codoped graphyne, the Fermi energy returns around the Dirac point and a gap is introduced. Interestingly, the opened gaps oscillate periodically with the increasing distances between B and N atoms with the gap from 0.07 eV to 0.50 eV, which is caused by the breaking sublattice symmetry. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4769354>]

Since its successful fabrication,¹ graphene has been exhibiting potential applications and interesting physics in many fields.^{2–6} The properties of graphene have been under focused investigations in both theories and experiments in recent years.^{7–12} One of the most attractive properties is how to control the linear band structure near the famous Dirac cones.^{7,9,13,14} Graphyne is a new carbon-based form that consists of planar carbon sheets containing *sp* and *sp*² bonds,^{15–18} which can be regarded as the big hexagonal rings joined together by the acetylenic linkages (C–C≡C–C) rather than the C–C=C–C in graphene. In experiment, although large graphyne structures have not been synthesized yet, graphdiyne (expanded graphynes) films and graphdiyne tubes have been already obtained.^{19,20} According to the construction form, the polymorphs of graphyne are various including α , β , and 6,6,12 structures. From first principles calculations, Malko *et al.*²¹ found that these three structures also possessed Dirac cones in the Brillouin zone (BZ). Therefore, graphynes have wonderful properties which can be comparable with graphene in the applications of electronics. However, similar to graphene, graphyne exhibits as semiconductor with zero band gap, which may limit its practical applications as electronic devices. In order to widely use graphyne into the field of electronics, the first step is to open a band gap in the order of 1 eV for graphyne.

Chemical doping, molecular adsorption, substrate doping, and external stress are usually the effective methods to change and control the electronic properties of carbon-related materials.^{17,22–28} For example, the band of bilayer graphene is opened when K atoms are adsorbed on graphene-SiC system.²⁴ This is due to that the SiC acts as hole doping and K atom acts as electron doping. Boron (B) and nitrogen (N) are the usual dopants for graphene because they are the neighbors of C in the periodic table of elements. Moreover,

after B and N doping into graphene, the planar honeycomb lattice remains unchanged and the B- or N-doped graphene is non-magnetic.^{6,12} For graphyne, Kang *et al.*¹⁷ found that the band gap of the system was tunable under uniform strain. Malko *et al.*³⁰ found that a band gap occurred at the Dirac point with heteroatoms H or B/N pair in 6,6,12-graphyne. Nowadays, B and N atoms are regarded as the typical hole and electron dopants, respectively.²³ For B doping, the Fermi energy level E_f is shifted below the Dirac point. In contrast to B doping, the N dopants shift the E_f above the Dirac point. The doping mechanism reminds us that the electronic structures can be modulated by hole or electron doping. In our previous work,²⁹ we found that a method to open the band gap of graphene by B and N (or Li adsorption) codoping into graphene, which can also be used for graphyne. However, because the structures of graphyne are different significantly from graphene, we expect some new physics can be shown.

In this work, we are aiming at the band gap opening of α -graphyne and propose hole/electron codoping to achieve this goal. Our model is using B/N codoping into graphyne. As expected, B atom plays a role of hole-type doping, while N atom electron-type doping. The obtained energy band structures show that B/N codoping can realize the opening of band gap with a range of 0.07–0.50 eV, depending on different codoping configurations. The oscillations of band gaps with the increasing distance between B and N atoms indicates new physics in these systems, which can be responsible for the breaking symmetry of sublattice of graphyne.

The geometries exploring and electronic energy bands calculations are performed by Quantum-ESPRESSO package³¹ within the framework of pseudopotential plane waves method. The generalized gradient approximation (GGA) proposed by Perdew *et al.*³² is used for the exchange-correlation functional. The Vanderbilt ultrasoft pseudopotential³³ is used to describe the interaction between ions and electrons. The cutoffs of 40 Ry for the wave function and 400 Ry for the charge density are adopted.

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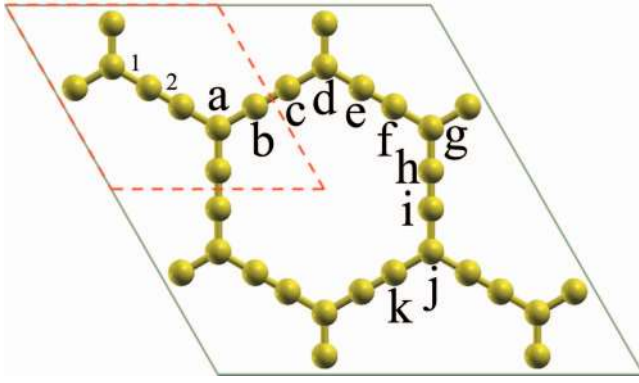


FIG. 1. The primitive cell (red dash parallelogram), the 2×2 supercell, and 11 substitutional positions for doping and codoping in graphyne. Numbers 1 and 2 denote C–C and C \equiv C bonds.

A 32-atomic 2×2 supercell as shown in Fig. 1 with $5 \times 5 \times 1$ k-points³⁴ for the representation of BZ is taken to simulate the related electronic properties. The periodical boundary conditions are employed in the vertical direction of the sheet with a vacuum region of 20 Å. Furthermore, Methfessel-Paxton³⁵ smearing of 0.01 Ry is used in all cases. To obtain accurate energy band structures, denser k -points of $11 \times 11 \times 1$ are taken. We optimize all geometries by reducing the Hellman-Feynman forces down to 0.001 a.u. In order to quantify the stability and formation ability of the doped systems, we calculate the formation energy defined as $E_F = E_{DG} - E_p + n \times E_C + \sum E_{\text{dopant}}$, where E_{DG} is the total energy of single doped or codoped systems, E_p 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 atom substituted by dopants, $\sum E_{\text{dopant}}$ is the total energy of dopant B, N, or B/N pairs.

Firstly, we verify the structural and electronic properties of primitive cell of α -graphyne shown in red dash parallelogram part in Fig. 1. Its crystalline structure is hexagonal in the atomic plane with $p6/mmm$ symmetry, which is the same as graphene. In α -graphyne, the bonds of C atoms have two types, i.e., C–C single bond and C \equiv C triple bond (denoted as number 1 and 2 in Fig. 1, respectively). Comparing with graphene, two extra C atoms are inserted into C–C bonds of α -graphyne, forming C–C \equiv C–C chain structures. The optimized lattice constants a (or b) is 6.97 Å. The bond lengths of C–C and C \equiv C are 1.40 and 1.23 Å, which are in agreement with recently reported results.³⁶ The energy band structures of the primitive cell also show that valence and conduction band meet in famous K or K' point (so-called Dirac point). The calculated first and second derivatives of the two involved bands in reciprocal space are $\pm 28.1 \text{ eV}\text{\AA}$ and $\pm 251.0 \text{ eV}\text{\AA}^2$, respectively, which are consistent with Malko's results and can be compared with the values of $\pm 34 \text{ eV}\text{\AA}$ and $\pm 130 \text{ eV}\text{\AA}^2$ in graphene.²¹

We study the properties of B- or N-doped graphyne by one B or N atom randomly substituting one C atom in graphyne. There are two inequivalent sites for single B or N doping. They are a and b site as shown in Fig. 1. After careful minimization of force and energy, the ground state geometries are obtained and their structural parameters are listed in

TABLE I. The distances between C and dopants ($d_{\text{C-B}}$ and $d_{\text{C-N}}$), the formation energies E_F of B or N single doping.

	B doping		N doping	
	a site	b site	a site	b site
$d_{\text{C-B(N)}} (\text{\AA})$	1.48	1.48, 1.35	1.37	1.37, 1.18
$E_F (\text{eV})$	2.07	3.28	2.32	0.69

Table I. In the case of B doping at a site, the lengths of three B–C bonds are 1.48 Å, longer than $d_{\text{C-C}}$ in pristine graphyne. For N doping, the lengths of $d_{\text{N-C}}$ decrease to 1.36 Å. In the case of b site, the long $d_{\text{C-B(N)}}$ distances (a–b bond) are same as those in a site cases. However, the short $d_{\text{C-B(N)}}$ bonds (similar to C \equiv C bonds) are 1.35 and 1.18 Å. In a word, the B–C (N–C) bonds are longer (shorter) than the C–C bonds in both in a site and in b site. The formation energy data (in Table I) show that the cases of a and b sites are the possibility to synthesize B- or N-doped graphyne, especially for N-doped graphyne. The electronic energy band structures for B- and N-doped graphyne are in good agreement the electronic structures of B- or N-doped graphene,²⁹ where the Fermi level E_f is shifted below the Dirac point for B doping and E_f is shifted above the Dirac point in the case of N doping. Furthermore, similar to B- or N-doped graphene, there are band gaps shown in the energy band structures. These gaps are above and below the E_f in the band structures for B- and N-doped graphyne,²⁹ which gives us a possibility to induce a semimetal-to-semiconductor transition. The band structure of B- and N-doped graphyne at b site is similar to that in a site. The changes of band structure of graphyne after doping are almost the same as the situations in graphene.^{23,29}

To reach the goal of band gap opening, we further investigate the electronic properties of B/N codoping. Eleven possible substitutional sites are considered. According to the notations in Fig. 1, we consider two types codoping configurations. One is ax or xa ($x = b, c, \dots, j$) which represent that B (or N) atom substitutes C atom in a site and N (or B) atom substitutes C atom in b, c, d, e, f, g, h, i, and j sites, respectively. The other is by or yb ($y = c, d, \dots, k$) which represent that B (or N) atom substitutes C atom in b site and N (or B) atom substitutes C atom in c, d, e, f, g, h, i, j, and k sites, respectively. The geometry parameters and formation energies are listed in Table II. The $d_{\text{C-B}}$ and $d_{\text{C-N}}$ are almost the same as the results of single B and N doping, keeping the planar structures. The formation energies for the two configuration types change from 1.06 eV to 3.96 eV for ax and 3.73 eV to 5.25 eV for xa, indicating that the doped-graphyne with B atom at a site is easier to synthesize than N doping at a site. In both the two configuration types, the ab case is the easiest to form and the ia case is most difficult to realize. The electronic band structures are calculated at last. Taking the nine configurations of ax ($x = b, c, \dots, j$) for example (as shown in Fig. 2), the Dirac point of pristine α -graphyne returns back to the Fermi energy. As mentioned above, B or N doping makes the Dirac point of pristine α -graphyne moving above or below the Fermi energy. The counteraction between B and N doping keeps Dirac point of pristine α -graphyne in the original

TABLE II. The C-dopants distances (d_{C-B} and d_{C-N}), the formation energy E_F , and the band gaps E_{gap} for four configurations of B/N codoping. It should be pointed out that d_{C-B} or d_{C-N} indicate the shortest bond when B or N atom bind with several C atoms.

ax	ab	ac	ad	ae	af	ag	ah	ai	aj
d_{C-B} (Å)	1.48	1.50	1.49	1.49	1.49	1.49	1.49	1.49	1.49
d_{C-N} (Å)	1.17	1.17	1.35	1.17	1.17	1.35	1.18	1.17	1.35
E_F (eV)	1.06	1.77	1.09	2.22	2.18	3.96	2.19	2.26	3.81
E_{gap} (eV)	0.29	0.17	0.48	0.16	0.34	0.07	0.33	0.15	0.50
xa	ba	ca	da	ea	fa	ga	ha	ia	ja
d_{C-B} (Å)	1.33	1.34	1.49	1.35	1.35	1.49	1.35	1.34	1.49
d_{C-N} (Å)	1.35	1.34	1.35	1.35	1.35	1.35	1.35	1.35	1.35
E_F (eV)	4.03	4.80	3.73	5.22	5.10	3.96	5.09	5.25	3.81
E_{gap} (eV)	0.39	0.13	0.45	0.10	0.44	0.08	0.49	0.08	0.49
by	bc	bd	be	bf	bg	bh	bi	bj	bk
d_{C-B} (Å)	1.48	1.35	1.35	1.35	1.34	1.34	1.35	1.34	1.34
d_{C-N} (Å)	1.34	1.35	1.17	1.17	1.35	1.17	1.18	1.35	1.18
E_F (eV)	1.33	4.79	3.17	3.28	5.10	3.52	3.50	5.24	3.46
E_{gap} (eV)	0.15	0.15	0.31	0.20	0.41	0.13	0.33	0.13	0.34
yb	cb	db	eb	fb	gb	hb	ib	jb	kb
d_{C-B} (Å)	1.49	1.48	1.34	1.34	1.49	1.34	1.34	1.48	1.34
d_{C-N} (Å)	1.34	1.17	1.17	1.17	1.17	1.17	1.17	1.18	1.18
E_F (eV)	1.33	1.77	3.23	3.29	2.18	3.52	3.50	2.25	3.46
E_{gap} (eV)	0.15	0.15	0.29	0.19	0.34	0.13	0.29	0.14	0.34

position on the Fermi level. More importantly, around the E_F , the band gaps are introduced to graphyne after B/N codoping and different configurations induce different band gaps. The electronic properties of xa ($x = b, c, \dots, j$), by and yb ($y = c, d, \dots, k$) are similar. The detailed band gaps are listed in Table II. The induced band gaps for all configurations types change from 0.07 eV to 0.50 eV. The maximum and minimum value occur in the aj and ag configures, respectively. It is exciting that the gap for the most stable configuration of the ab case is 0.29 eV and 0.39 eV for the ax and xa types, respectively. The symmetry breaking³⁷ and breaking of C-C \equiv C-C chains induced by B/N codoping may be responsible for the band gap opening. Furthermore, considering the underestimate of band gap from GGA calculations, the induced band gap of 0.5 eV can give us confidence to believe that the mechanism and the pathway to open the band gap of semimetal graphyne by electron-hole codoping are valid and meaningful in both theory and practical applications.

It is very interesting to note that with increasing the distance between B and N atoms, the band gaps exhibit periodic oscillations, as shown in Fig. 3. From the viewpoint of sublattice symmetry, a and d sites in Fig. 1 represent K and K' in reciprocal spaces. Therefore, we can consider that a-b and c-d are the two inequivalent sublattices in α -graphyne. According to this definition, we can distinguish two groups of doped sites for ax or xa: c-d-e and i-j-k are belonging to one group, f-g-h are the other group. Doping at these two different groups will induce different symmetry, and thus introduce different band gaps. From Fig. 3, we can find that the width of gaps oscillated periodically. We can explain these oscillations using the breaking symmetry of different sublattices, where c-d-e or i-j-k sites exhibit small-large-small gaps oscillations,

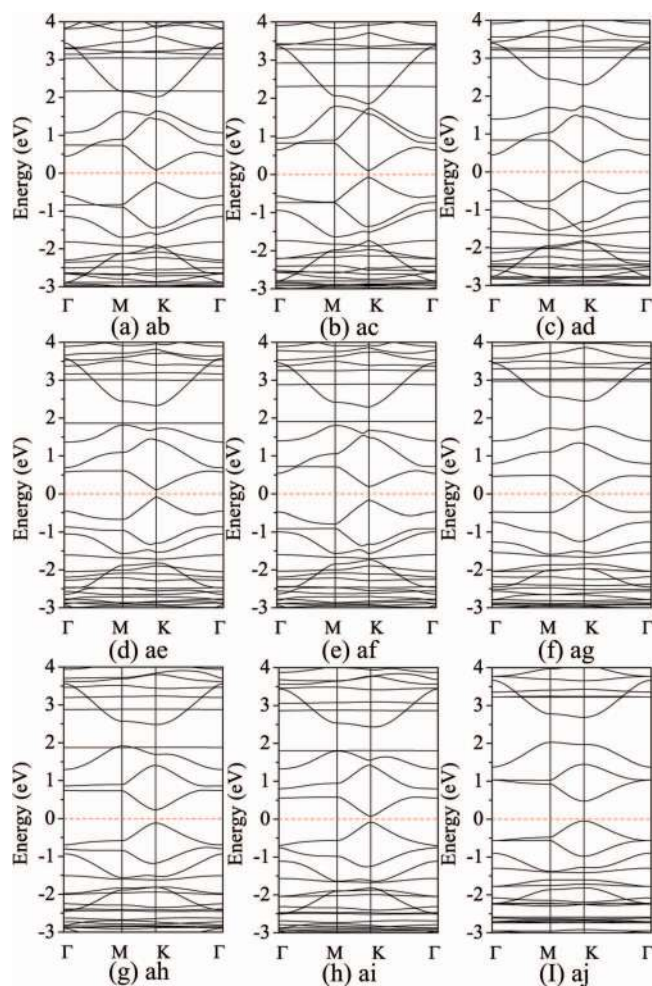


FIG. 2. The band structures of B/N codoped graphyne for nine codoped configurations. The band gaps for these nine corresponding configurations are listed in Table II. The Fermi E_F level is denoted by dash lines.

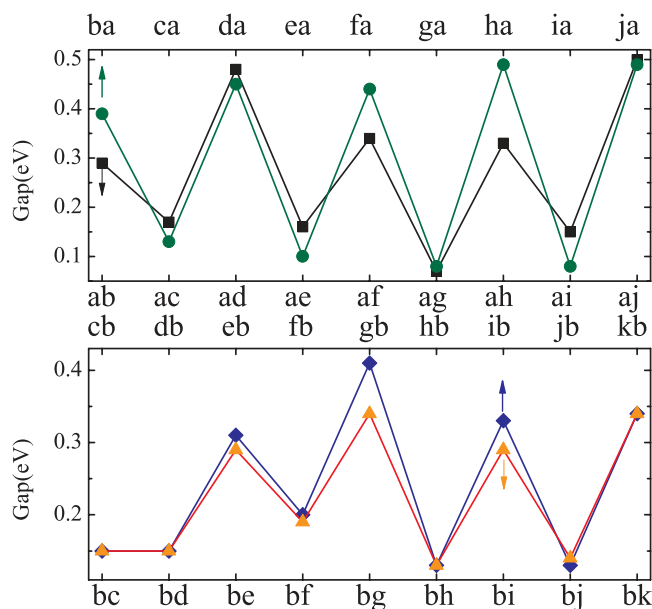


FIG. 3. The band gap variations at different B and N codoped sites. The upper panel shows the band gaps of ax and xa codoping, and the lower panel shows the by and yb codoping.

and f–g–h exhibit large-small-large oscillations. For by and yb codoping, the oscillations are similar.

In conclusion, we present first principles study on the geometries and electronic structures tuning of α -graphyne by B, N doping or codoping. We found the bands of graphyne can be opened by B/N codoping and introduce exciting width of band gaps for graphyne. With different codoped sites, the band gaps exhibit periodic oscillations by breaking the sublattice symmetry. The intrinsic physical mechanism for the opening of gap is the combination of the B acting as hole doping and N as electron doping. This work will enrich electronics investigations and present a way to realize the opening of band gap by elemental codoping.

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