# Journal of Materials Chemistry C

# PAPER



Cite this: J. Mater. Chem. C, 2016, 4, 7339

Received 27th May 2016, Accepted 8th July 2016 DOI: 10.1039/c6tc02184k

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### 1 Introduction

Carbon, as a basic element of life, has versatile flexibility in forming different hybridization states (*i.e.*, sp, sp<sup>2</sup> and sp<sup>3</sup>). Besides some naturally existing allotropes, such as sp<sup>2</sup>-hybridized graphite and sp<sup>3</sup>-hybridized diamond, many other carbon allotropes with low dimensions (D) have been prepared in experiments, such as 0-D fullerene,<sup>1</sup> 1-D nanotubes<sup>2</sup> and 2-D graphene.<sup>3</sup>

Due to the existence of Dirac cones, graphene has a variety of unique properties, such as the quantum Hall effect<sup>4</sup> and giant carrier mobilities,<sup>5</sup> which lead to its great applications in spintronics<sup>6</sup> and optoelectronics.<sup>7</sup> It stimulates great interest in other low dimensional materials, especially 2-D monolayer materials.<sup>8,9</sup> In the meanwhile, these sp<sup>2</sup>-hybridized carbon allotropes also inspired the imagination of other carbon allotropes with more hybridization states, such as sp states in view of the successful experimental realization of a carbon atomic chain.<sup>10</sup> Actually, Baughman and Eckhardt<sup>11</sup> proposed the family of graphyne (GY) for the first time a few decades ago. By replacing the C–C bonds in graphene with  $-C \equiv C$ – linkages, sp states

# Multiple Dirac cones in BN co-doped β-graphyne<sup>†</sup>

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BN co-doped  $\beta$ -graphyne ( $\beta$ -GY) was investigated using state-of-the-art theoretical calculations.  $\beta$ -GY with sp or sp<sup>2</sup> carbon pairs substituted by BN pairs was referred to as  $\beta$ -GY<sub>BN1</sub> or  $\beta$ -GY<sub>BN2</sub>, respectively. Their dynamic and thermal stabilities were confirmed by phonon spectrum calculations and *ab initio* molecular dynamics (AIMD) simulations. Interestingly, the ternary hybrid BCN monolayer  $\beta$ -GY<sub>BN1</sub> was predicted to be semimetallic with multiple distorted Dirac cones at the Fermi level, including crossed ones and gapped ones. Their infrared (IR) and Raman spectra were simulated to serve as fingerprints for experimental identification. It was also found that hydrogen atom adsorption would depress the energy bands of  $\beta$ -GY<sub>BN1</sub>, and made other isotropic Dirac cones crossed at the Fermi level. Our study not only indicates the potential applications of BN co-doped  $\beta$ -GY in future spintronics and optoelectronics, but also implies a possible approach to explore novel semimetallic Dirac materials.

were introduced. Based on the ratio of sp constituents, these graphene derivatives can be generally classified into  $\alpha$ -graphyne,<sup>11,12</sup>  $\beta$ -graphyne,<sup>11,12</sup>  $\gamma$ -graphyne,<sup>11,13</sup> graphdiyne,<sup>13,14</sup> 6,6,12-graphyne,<sup>11,12</sup>  $\delta$ -graphyne<sup>15</sup> and so on. Compared with graphene, some graphynes possess similar properties (*e.g.*, Dirac cones<sup>12</sup>), while some others exhibit quite different properties (*e.g.*, much lower stiffness<sup>16</sup> and much lower thermal conductance<sup>17</sup>) due to the existence of acetylenic bonds. These graphynes have great potential applications in nanoelectronics, energy storage,<sup>18</sup> anode materials,<sup>19</sup> gas separation,<sup>20</sup> water desalination,<sup>21</sup> and so on.

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A bottom-up approach to synthesize graphynes was proposed a few years ago,<sup>22</sup> and graphyne flakes were synthesized successfully.<sup>22–24</sup> Recently, graphdiyne (expanded  $\gamma$ -graphyne) based nanofilms,<sup>25</sup> nanotubes<sup>26</sup> and nanowalls<sup>27</sup> were obtained in experiments, which indicated that the experimental realization of monolayer graphynes was in the near future. A theoretical investigation on possible environments for the synthesis of graphynes ( $\alpha$ ,  $\beta$  and  $\gamma$ ) on transition metal surfaces was reported very recently.<sup>28</sup> Though the experimental data for graphynes were very limited up to now, theoretical studies have given much more knowledge, such as those potential applications listed above.

To explore wider applications of graphynes, property engineering plays a key role. Due to the close number of valence electrons and comparable atomic size, substitutional doping of B and/or N atoms is a common way to modulate the electronic and transport properties of carbon allotropes (*e.g.*, graphene and graphyne). For example, it was found that a hybrid graphenelike BCN monolayer with particular stoichiometry was ferromagnetic.<sup>29,30</sup> The band gap of the graphene-like BCN monolayer could be widely tuned by changing the concentration of carbon.<sup>31</sup> The successful synthesis of B/N mono-doped graphene,<sup>32–34</sup> BN co-doped graphene,<sup>35</sup> BN monolayers<sup>9</sup> and

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<sup>†</sup> Electronic supplementary information (ESI) available: The band structure of β-graphyne (β-GY), the geometry structure, phonon spectrum and band structure of the BN analogue of β-GY; comparison between the binding energies of graphene, β-GY, graphdiyne and BN co-doped β-GY; AIMD simulations of β-GY<sub>BN1</sub> and β-GY<sub>BN2</sub>; electron localization function (ELF) maps and two center two-electron bonding patterns of β-GY<sub>BN1</sub>; atomic displacements of the Raman-active phonons for β-GY<sub>BN1</sub>. See DOI: 10.1039/c6tc02184k

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other BCN nanotubes<sup>36</sup> implied the possibility of other hybrid BCN monolayer allotropes. The BN analogues of  $\alpha$ -graphyne,<sup>37</sup>  $\gamma$ -graphyne<sup>38,39</sup> and graphdiyne nanoribbons,<sup>40</sup> as well as BN co-doped  $\gamma$  graphyne<sup>38,39</sup> and 6,6,12-graphyne<sup>41</sup> were investigated using density functional theory (DFT) methods, and some interesting properties were predicted, such as Dirac cones and much wider band gaps.

To the best of our knowledge, studies on the BN co-doped or BN analogue of  $\beta$ -graphyne ( $\beta$ -GY) are scarce. A basic question is whether such  $\beta$ -GY derivatives have comparable properties to or even more interesting properties than the pristine one. In this study, we investigated the stability, electronic properties and band structures of BN co-doped and the BN analogue of  $\beta$ -GY using DFT calculations. Distorted Dirac cones crossed at the Fermi level were expected in the hybrid BCN monolayer, while it could transform into another semimetal with isotropic Dirac cones crossed at the Fermi level by hydrogen atom adsorption.

### 2 Methods

All calculations were performed using the Vienna ab initio simulation package (VASP)<sup>42,43</sup> with the projector augmented wave (PAW)<sup>44,45</sup> pseudopotential method. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)<sup>46</sup> exchange-correlation function was chosen. All structures were fully relaxed using a conjugate gradient method without symmetry constraints, until the Hellmann-Feynman force acting on each atom was less than 0.001 eV  $Å^{-1}$ . The kinetic energy cutoff for the plane-wave basis set was 500 eV. A large vacuum spacing (more than 15 Å) was used to prevent mirror interactions. The Brillouin zones were sampled with 0.12 and 0.1  $Å^{-1}$  spacing in reciprocal space by the Monkhorst-Pack scheme<sup>47</sup> for geometry optimizations and further property calculations, respectively. They corresponded to  $7 \times 7 \times 1$  and  $9 \times 9 \times 1$  *k*-point meshes for the primitive  $\beta$ -graphyne unit cell. The phonon spectra were calculated using the Phonopy program<sup>48</sup> combined with the VASP package. The off-resonance Raman activity and infrared (IR) intensities were calculated using other codes<sup>49-51</sup> using the VASP package as a back-end.

#### 3 Results and discussion

After DFT optimization, the lattice parameter of pristine  $\beta$ -GY was predicted to be 9.48 Å, which was in good agreement with previous studies (9.46 Å<sup>52</sup> or 9.50 Å<sup>53</sup>). The calculated band structure of  $\beta$ -GY (as shown in Fig. S1a, ESI†) also agreed well with previous calculations.<sup>12,52,53</sup> In order to understand the effect of BN co-doping on the properties of  $\beta$ -GY, sp-hybridized, sp<sup>2</sup>-hybridized or all carbon atoms were substituted by BN pairs. The structures, stabilities and properties of these derived systems were compared and discussed as follows.

How would the structure of  $\beta$ -GY change after BN co-doping? The structures of  $\beta$ -GY with sp, sp<sup>2</sup> or all carbon atoms substituted by BN pairs (referred to as  $\beta$ -GY<sub>BN1</sub>,  $\beta$ -GY<sub>BN2</sub> or  $\beta$ -GY<sub>BN3</sub>, respectively) are displayed in Fig. 1a and b and Fig. S1b (ESI†).

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Fig. 1 (a) The structure of  $\beta$ -graphyne ( $\beta$ -GY) with sp carbon pairs substituted by BN pairs ( $\beta$ -GY<sub>BN1</sub>). (b) The structure of  $\beta$ -GY with sp<sup>2</sup> carbon pairs substituted by BN pairs ( $\beta$ -GY<sub>BN2</sub>). Phonon spectra of (c)  $\beta$ -GY<sub>BN1</sub> and (d)  $\beta$ -GY<sub>BN2</sub>. The pink, grey and blue balls stand for B, C and N atoms, respectively.

The geometry of β-GY mainly remained unchanged after substitution, and the lattice parameter increased to 9.67, 9.63 and 9.66 Å. As shown in Fig. S2 (ESI†), their binding energies per atom are negatively correlated with these lattice parameters. As a result, from the point of view of thermodynamics,  $\beta$ -GY<sub>BN1</sub>,  $\beta$ -GY<sub>BN2</sub> and  $\beta$ -GY<sub>BN3</sub> were a little less stable than graphene and graphdiyne. So we examined their dynamic stabilities using phonon spectrum calculations, as displayed in Fig. 1c and d and Fig. S1c (ESI<sup>+</sup>). The high symmetry *k* points in the first Brillouin zone are  $\Gamma(0, 0, 0)$ , M(0.5, 0, 0) and K(1/3, 1/3, 0). The calculated phonon dispersion curves show that neither optical nor acoustical phonon frequencies are negative for  $\beta$ -GY<sub>BN1</sub>,  $\beta$ -GY<sub>BN2</sub> and  $\beta$ -GY<sub>BN3</sub>, which confirm their stabilities. There are three distinct acoustic modes in their phonon spectra, linear dispersion in-plane transverse modes (TA) and longitudinal modes (LA), as well as out-of-plane modes (ZA) with quadratic dispersion near the  $\Gamma$  point, as predicted in graphene.<sup>54</sup>

In order to investigate the effect of different doping sites on the properties, we will focus on  $\beta$ -GY<sub>BN1</sub> and  $\beta$ -GY<sub>BN2</sub> in the following discussion. Their thermal stabilities were also assessed by performing *ab initio* molecular dynamics (AIMD) simulations. As shown in Fig. S3 (ESI†), both of them are able to withstand temperatures as high as 1000 K without structure reconstruction, which implies that both of them are dynamically stable and separated by high energy barriers from other local minima on the potential energy surface (PES).

Different geometries are expected to give rise to different band structures, which lead to different transport properties. The band structures of  $\beta$ -GY<sub>BN1</sub> and  $\beta$ -GY<sub>BN2</sub> are displayed in Fig. 2a and b. Interestingly, two probable Dirac cones (A and A') are observed at the Fermi level for  $\beta$ -GY<sub>BN1</sub>, which are located on the lines from  $\Gamma$  to *M* and  $\Gamma$  to *K*. It is similar to the band



Fig. 2 The band structures of (a)  $\beta$ -GY<sub>BN1</sub> and (b)  $\beta$ -GY<sub>BN2</sub>. (c) The projected densities of states (PDOS) and (inset d) total DOS (TDOS) near the Fermi level for  $\beta$ -GY<sub>BN1</sub>.

structure of 6,6,12-graphyne<sup>12</sup> with two different Dirac cones at the Fermi level. If the symmetry is considered, there are six probable Dirac cones A and six probable Dirac cones A' in the first Brillouin zone of  $\beta$ -GY<sub>BN1</sub>. Besides probable Dirac cones A and A', linearly crossed bands were also observed at points B and C above or below the Fermi level. In contrast to the semimetallic characteristic of  $\beta$ -GY<sub>BN1</sub>,  $\beta$ -GY<sub>BN2</sub> is an indirect semiconductor with a large band gap of 2.0 eV (Fig. 2b), while  $\beta$ -GY<sub>BN3</sub> is an insulator with a gap of 4.1 eV (Fig. S1d, ESI<sup>+</sup>).

To further confirm the semimetallicity of  $\beta$ -GY<sub>BN1</sub>, the projected density of states (PDOS) and total density of states (TDOS) are presented in Fig. 2c and d. Obviously, the TDOS for points A (and A'), B and C are 0, which further indicates that these points may be Dirac points, at which two bands cross linearly. Furthermore, as shown in Fig. 2c, these probable Dirac cones are constituted by  $\pi$  bands (derived from  $p_{z}$  orbitals), which come from C atoms as well as B and N atoms.

The bands in the vicinity of points A, A', B and C are shown in Fig. 3. It shows that there are no gaps at points A, B and C, which indicates they are crossed Dirac points. In contrast, there is a small band gap (about 96 meV) at point A', which suggests gapped Dirac cones. Similar to 6,6,12-graphyne<sup>12</sup> and Pmmm boron,<sup>55</sup> the distorted Dirac cones at point A would exhibit different linear dispersions in  $k_x$  and  $k_y$  directions. The slope of the valence and conduction bands in the  $k_x$  direction is  $\pm 14.57$  eV Å, equivalent to a Fermi velocity  $v_{\rm F} = E/\hbar k = 0.35 \times 10^6 \text{ m s}^{-1}$ , where  $\hbar$  is the reduced Planck's constant. The corresponding values in the  $k_v$  direction are  $\pm 8.4$  eV Å and  $0.20 \times 10^6$  m s<sup>-1</sup>, so this slop is much smaller than that in the  $k_x$  direction. In contrast, the slope in the  $k_{\nu}$  direction for  $\beta$ -GY is much larger than that in the  $k_x$  direction.<sup>12</sup> Direction dependent transport properties are expected due to the anisotropy of the Dirac cones in the  $k_x$  and  $k_y$  directions. In the meanwhile, the Dirac cones at points B and C are isotropic, the Fermi velocities for which are 0.61  $\times$  10<sup>6</sup> and 0.45  $\times$  10<sup>6</sup> m s<sup>-1</sup>, respectively.



(d)

0.32

0.34 0.36

0.36

0.34 k

0.32

Fig. 3 Dirac cones in the vicinity of points (a) A, (b) A', (c) B and (d) C for β-GY<sub>BN1</sub>

0.36

0.32 0.34

-0.95

€ 1.05

-1.1

-1 15

-1.2

Energy (

-1

(a)

(c)

0.32

0.34 0.36

0.05

0 (eV) 0.02

-0.1

1.45

€ 1.35 0 1.3

1.15 1.1

1.4



Fig. 4 (a) Charge difference density (CDD) maps sliced in the atomic plane of  $\beta$ -GY<sub>BN1</sub> and (b) six center two-electron (6c-2e)  $\pi$  bonding patterns of  $\beta$ -GY<sub>BN1</sub> using the SSAdNDP method. In the CDD maps, the colors red and blue refer to 0.08 and -0.02 |e| bohr<sup>-3</sup>, respectively.

These Dirac cones also have potential applications, as they may be increased or depressed by some physical effects, such as a strain effect.56

In order to further explore the physical origin of the Dirac cones, the charge difference density (CDD) maps, electron localization function (ELF) maps and bonding patterns calculated using the solid state adaptive natural density partitioning (SSAdNDP) method are displayed in Fig. 4a and b and Fig. S4a-d (ESI<sup>†</sup>). As shown in Fig. 4a, there is high charge transfer from B atoms to N atoms, in detail, each B atom lost about 1.9 e while each N atom gained about 1.8 e from Bader charge analysis. In the meanwhile, there is heavy electron accumulation between B and N atoms (shown in Fig. 4a and Fig. S4a, ESI<sup>†</sup>), which comes from triple bonds in BN pairs (one  $\sigma$  and two  $\pi$  bonds in Fig. S4c and d from SSAdNDP analysis, ESI<sup>+</sup>). Besides 21 two center two-electron (2c-2e)  $\sigma$  bonds and 12 2c-2e  $\pi$  bonds in BN pairs, there are 3 six center two-electron (6c-2e)  $\pi$  bonds with an occupation number (ON) of 1.87 |e| in each unit cell (shown in Fig. 4b). As discussed above, the bands constituting Dirac cones are derived from p<sub>7</sub> orbitals of B, C and N atoms, so they corresponded to these 6c-2e bonds, for only these  $\pi$  bonds covered B, C and N atoms. In one word, these 6c-2e  $\pi$  bonds play a dominant role in the formation of Dirac cones.



Fig. 5 Simulated infrared (IR) and Raman spectroscopies for (a)  $\beta$ -GY<sub>BN1</sub> and (b)  $\beta$ -GY<sub>BN2</sub>. The symmetries and frequencies (cm<sup>-1</sup>) for characteristic IR and Raman peaks were labeled.

Infrared (IR) and Raman spectroscopies are widely used to identify the characteristic vibrational modes of materials. The simulated IR and Raman spectra for  $\beta$ -GY<sub>BN1</sub> and  $\beta$ -GY<sub>BN2</sub> are displayed in Fig. 5a and b. As shown in Fig. 5a, there are two characteristic Raman peaks for  $\beta$ -GY<sub>BN1</sub> at about 1232 and 1897 cm<sup>-1</sup>. They both come from in-plane vibrations with symmetry  $A_{g}$ , and lie between the characteristic Raman frequencies (1196 and 2157 cm<sup>-1</sup>) of  $\beta$ -GY.<sup>57</sup> Similar to  $\beta$ -GY,<sup>57</sup> these two peaks are mainly attributed to the breathing motion of big atomic hexagons and the bond stretching of sp BN pairs (as shown in Fig. S5a and b, ESI<sup>†</sup>). Two characteristic IR peaks at 1311 and 1985 cm<sup>-1</sup> for  $\beta$ -GY<sub>BN1</sub> were also predicted. In the meanwhile, there are two Raman peaks at 1078 and 2201 cm<sup>-1</sup> for  $\beta$ -GY<sub>BN2</sub>, which also come from the in-plane breathing motion of big atomic hexagons and bond stretching of sp C-C pairs. These characteristic IR and Raman peaks can serve as fingerprints for experimental identification.

Besides B, C and N atoms, graphynes containing other heteroatoms (e.g., H) can be imagined as well. In some cases, hydrogen atom adsorption would open the gap of graphyne,<sup>58</sup> while sometimes substitution of carbon atoms by hydrogen atoms has little effect on the band structure.<sup>41</sup> β-GY<sub>BN1</sub> with hydrogen adatoms was investigated to examine the effect of hydrogen atom adsorption on the band structure, especially on the Dirac cones. Given the electronegativity differences (2.04 for B, 2.55 for C and 3.04 for N) and symmetry, one hydrogen atom was placed on top of each N atom symmetrically. As we focused on the adsorption effect on the band structure, the atomic positions were optimized with the lattice parameters maintained (shown in Fig. 6a). Interestingly, the band structure for the optimized geometry mainly retains the shape after adsorption, though all the bands are depressed. In detail, the Dirac cones at A and A' lie below the Fermi level, while the Dirac point B is located at the Fermi level (shown in Fig. 6c). In other words, it transforms into a semimetal with isotropic Dirac cones at the Fermi level (shown in Fig. 6b) from an anisotropic one, which will lead to very different transport behaviors. The slope and



Fig. 6 (a) Geometry structure, (b) Dirac cones formed by the valence and conduction bands at the Fermi level and (c) band structure and density of states (DOS) for  $\beta$ -GY\_{BN1} with H adatoms. The pink, grey, blue and white balls stand for B, C, N and H atoms, respectively.

Fermi velocity at point B are  $\pm 16.77$  eV Å and  $0.40 \times 10^5$  m s<sup>-1</sup>, respectively, which are larger than the corresponding values of the Dirac point A in pristine  $\beta$ -GY<sub>BN1</sub>.

As discussed above, when sp hybridized C–C pairs in  $\beta$ -GY were substituted by BN pairs, crossed Dirac cones were maintained, while other gapped Dirac cones appeared. As a result, a novel semimetallic Dirac monolayer was obtained, which implied that substituting sp hybridized C–C pairs by other atoms in  $\beta$ -GY, or assembling sp<sup>2</sup> C–C pairs and other atoms into a hexagonal lattice, may be a possible way to explore novel semimetallic Dirac materials.

#### 4 Conclusions

Density functional theory calculations were carried out to investigate the geometries, stabilities and band structures of BN-coped β-GY. β-GY with sp, sp<sup>2</sup> or all carbon atoms substituted by BN pairs were referred to as β-GY<sub>BN1</sub>, β-GY<sub>BN2</sub> or β-GY<sub>BN3</sub>, respectively. Their dynamic and thermal stabilities were confirmed by phonon spectrum calculations and ab initio molecular dynamics (AIMD) simulations. All of them do not have imaginary frequencies. Furthermore,  $\beta$ -GY<sub>BN1</sub> and  $\beta$ -GY<sub>BN2</sub> are able to maintain their configurations at temperatures as high as 1000 K. Interestingly, multiple crossed Dirac cones and gapped Dirac cones at the Fermi level were predicted in the ternary hybrid BCN system β-GY<sub>BN1</sub>, which indicated its semimetallicity. From our analysis, six center two-electron (6c-2e)  $\pi$  bonds play a dominant role in the formation of these Dirac cones. In contrast,  $\beta$ -GY<sub>BN2</sub> and  $\beta$ -GY<sub>BN3</sub> were predicted to be a wide-bandgap semiconductor and an insulator, respectively. The infrared (IR) and Raman spectra of  $\beta$ -GY<sub>BN1</sub> and  $\beta$ -GY<sub>BN2</sub> were simulated to serve as fingerprints for experimental identification. The effect of hydrogen atom adsorption on  $\beta$ -GY<sub>BN1</sub> was also studied, and it was found that the

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original distorted Dirac cones at the Fermi level were depressed while the other isotropic Dirac cones crossed at the Fermi level. So its transport properties were tuned. In a few words, BN-coped  $\beta$ -GY is a promising material in future spintronics and optoelectronics. Furthermore, our study implies that substitution or adsorption on appropriate hosts may be a possible way to explore novel semimetallic Dirac materials.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 11504213, 21373130 and 21473106) and the Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase). We greatly acknowledge the computing resources provided by the Network Center of Shanxi University and the National Supercomputing Center in GuangZhou.

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