Design of Two-Dimensional Graphene-like Dirac Materials $\beta_{12}$-XBeB$_5$ ($X = H, F, Cl$) from Non-graphene-like $\beta_{12}$-Borophene

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ABSTRACT: Two-dimensional (2D) Dirac materials and boron sheets have attracted intense interest recently. However, 2D Dirac materials remain rare and difficult to be realized experimentally, and 2D boron sheets generally have high dynamical instability. Stimulated by the experimental observation of Dirac cones in non-graphene-like $\beta_{12}$ boron sheets and based on the understanding of boron sheet electronic organization, we theoretically design new 2D Dirac materials $\beta_{12}$-XBeB$_5$ ($X = H, F, Cl$) with high stability. We confirm $\beta_{12}$-HBeB$_5$ as the global energy minimum among its 2D allotropes based on global structure search methods, a strong indication of its experimental feasibility. Our designed $\beta_{12}$-HBeB$_5$ has not only a high Fermi velocity, but also a Dirac state very robust against extraordinary large tensile strains, an advantage for flexible electronics applications. Our work opens a new avenue to designing feasible 2D Dirac materials and stabilizing borophene sheets.

Ever since the discovery of graphene, many 2D materials have been extensively studied both experimentally and theoretically. Among them, two-dimensional (2D) Dirac materials, characterized by linear energy dispersion near the Fermi level, have shown potential for applications in next-generation nanoscale devices, thanks to their unique electronic properties such as ballistic charge transport, high carrier mobility, and quantum Hall effect. Despite the abundance of 2D materials, 2D Dirac materials are relatively rare due to the rigorous requirements on the symmetry, parameters, Fermi level, and band overlap in the materials to achieve Dirac cone features. So far, only the Dirac state of graphene has been experimentally realized, while the experimental feasibility and practical applications of the other theoretically predicted 2D Dirac materials such as $\alpha$, $\gamma$, and $\beta$-graphene are still beyond reach. It is therefore important to identify, through experimental serendipity or sentient design, new 2D Dirac materials that are more likely to be realizable.

Among various potential systems, graphene-like boron sheet has attracted much interest as a good platform to design new 2D Dirac materials with fascinating properties. In graphene-like boron sheet, each boron atom has three valence electrons, and the Dirac states can be obtained by adding two electrons to each boron hexagonal ring. This can be achieved by embedding a metal atom of a suitable size, donating two electrons to the boron framework, as shown in Figure 1a. This strategy has been demonstrated in several systems like FeB$_2$, TiB$_2$, and strained BeB$_2$ monolayers. Similarly, as shown in Figure 1b, a triangular atomic layer of tetravalent metal like Mo sandwiched by two boron hexagonal layers can also form a Dirac state with double Dirac cones, because each tetravalent metal atom can donate two electrons to each of the two boron hexagonal lattices. Additionally, the electron deficiency in boron leads to its novel bonding characters, i.e., boron can behave both covalently and ionically. Consequently, boron itself can also donate electrons to the hexagonal boron sheets and induce the Dirac states. For example, as shown in Figure 1c, in P6/mmm boron bilayers, two boron hexagonal layers are vertically connected by B–B pairs. Each B–B pair has six valence electrons, two of which form a B–B covalent bond, leaving the other four electrons donated to the two boron hexagonal lattices and resulting in the double Dirac cone states. Similarly, in Figure 1d, Pnmm-boron can be seen as the boron chains attached above or below and parallel to the distorted graphene-like boron sheet. In the chains, each boron atom forms two covalent-like bonds with two electrons left for each B–B pair. Then the B–B pair, which is ionic-like, donates the left two electrons to the distorted boron hexagonal lattices, resulting in the tilted Dirac state with ultrahigh and anisotropic carrier mobility. Despite the great promise of those above systems in achieving Dirac states, the graphene-like boron sheet has not been realized yet due to its higher energy. Instead, recent theoretical and experimental works have demonstrated the realization of non-graphene-like 2D boron sheets composed of triangular and hexagonal boron motifs. Some other boron sheets like M-boron, which is entirely composed of B$_{20}$ clusters in a hexagonal arrangement with magnetic properties, are also predicted. Straightforwardly, it would be more...
We notice that, among all the nongraphene-like boron sheets, some still preserve the honeycomb hexagonal lattice with the hollow sites (centers of the hexagon rings) being partially or fully filled with additional B atoms, like \( \beta_{12} \) (Figure 2a), \( \alpha \) (Figure S1a), and \( \delta_k \) (Figure S1b) boron sheets.\(^{19}\) Consequently, these sheets also have Dirac cones composed of the \( p_z \) electrons of the B atoms in the honeycomb hexagonal lattices, as seen in Figure 2b and Figure S1c,d, respectively. Due to the electron deficiency of B atoms compared to C atoms, the Dirac cones in boron sheets deviate from the Fermi levels. Additionally, those additional ionic-like B atoms can donate electrons to the honeycomb hexagonal lattices, leading to the additional shifts of Dirac cones. To realize these Dirac states, the Fermi levels need to cross the Dirac cones by filling or removing the electron states between the red and the green dashed lines in Figures 2b and S1c,d. Recently, Feng et al. have experimentally and theoretically determined \( \beta_{12} \) boron sheets grown on Ag(111) substrate as the first monolayer Dirac material beyond the honeycomb graphene-like structure,\(^{26} \) thus demonstrating the feasibility of realizing Dirac states in nongraphene-like boron sheets. However, whether isolated 2D Dirac materials based on non-graphene-like boron sheets can stably exist, still remains unknown.

In our work, we show that, by rationally designing the nongraphene-like \( \beta_{12} \) boron sheets via the electron-accepting atoms like H, F, and Cl and the electron-donating atoms like Be, we identify several new isolated 2D Dirac materials based on non-graphene-like monolayer boron sheets with tetravalent ions in between, (c) P6/mmm boron bilayer predicted in ref\(^\text{17} \), and (d) Pmmn-boron predicted in ref\(^\text{18} \). Small green balls are boron atoms in hexagonal lattices, large light blue balls are divalent ions, large purple balls are tetravalent ions, and small blue balls are ionic-like boron atoms. Additionally, we notice that, among all the nongraphene-like boron sheets, some still preserve the honeycomb hexagonal lattice with the hollow sites (centers of the hexagon rings) being partially or fully filled with additional B atoms, like \( \beta_{12} \) (Figure 2a), \( \alpha \) (Figure S1a), and \( \delta_k \) (Figure S1b) boron sheets.\(^{19}\)

Figure 1. Top and side view of structures of (a) graphene-like monolayer boron sheet with divalent ions absorbed at hollow sites, (b) two graphene-like monolayer boron sheets with tetravalent ions in between, (c) P6/mmm boron bilayer predicted in ref\(^\text{17} \), and (d) Pmmn-boron predicted in ref\(^\text{18} \). Small green balls are boron atoms in hexagonal lattices, large light blue balls are divalent ions, large purple balls are tetravalent ions, and small blue balls are ionic-like boron atoms.

HBeB\(_5\) can have very robust Dirac states against tensile strains, i.e., 12% biaxial tensile strain or 18% uniaxial tensile strain along the \( y \) direction, possibly an advantage for flexible electronic applications. Our work opens a new avenue to designing feasible 2D Dirac materials and stabilizing borophene sheets.

To shift the Fermi levels in these nongraphene-like boron sheets to Dirac cone positions, we follow two considerations. On one hand, the ionic-like boron atoms at the hollow sites can donate electrons to the hexagonal lattice. Because each hexagon ring only needs two electrons to form the Dirac state as discussed for the graphene-like 2D Dirac materials, one of the three electrons of the ionic-like boron atom thus should be taken away by electron-accepting atoms such as H, F, and Cl. On the other hand, for the hexagon ring without an additional boron atom at the center, two electrons need to be donated using a divalent atom such as Be. By considering the combination of the electron-accepting atoms and the electron-donating atoms, we investigate the feasibility of obtaining Dirac states in nongraphene-like boron sheets that still preserve the honeycomb hexagonal lattices, including \( \beta_{12} \), \( \alpha \), and \( \delta_k \) boron sheets. After careful check of the electronic properties and the stabilities, we find that functionalized \( \alpha \) and \( \delta_k \) boron sheets do not have stable Dirac states (Figures S2 and S3 in the Supporting Information), and therefore we mainly focus on the design of Dirac states based on \( \beta_{12} \) boron sheets during the following discussions.

We perform our first-principles calculations using density-functional theory (DFT)\(^27\) as implemented in the VASP code.\(^28,29\) The global structure search in 2D space is performed using the IM2ODE package based on the differential evolution (DE) method.\(^31,32\) Detailed calculation methods can be found in the Supporting Information.

The structure of our designed \( \beta_{12}-\text{HBeB}_5 \) monolayer is shown in Figure 2c, where a H atom serves to take one extra electron away from the ionic-like boron atom [B(5)], while a Be atom donates two electrons to the empty hexagonal boron ring. The electron accepting and donating atoms can be attached to the same side or two sides of the \( \beta_{12} \) boron sheet. Our calculations show that the system with the electron-accepting and the electron-donating atoms on opposite sides has a lower energy by 0.06 eV/atom than the case with electron accepting...
and donating atoms on the same side (Figure S4). We further confirm the structure of \( \beta_{12} \)-HBeB\(_5\) by performing global structure search. We have performed a DE search at least two times with different sizes of HBeB\(_5\) cells up to 21 atoms. It shows that \( \beta_{12} \)-HBeB\(_5\) is the global energy minimum among its allotropes in the 2D space.

Due to the interactions between the attached atoms and boron atoms, all five boron atoms in \( \beta_{12} \)-HBeB\(_5\) do not lie in the same plane as they are in the \( \beta_{12} \) boron sheet. Instead, B(5) is pulled up by the electron-accepting atom, and the hexagonal boron ring gets buckled, as seen in Figure 2c with atomic positions provided in the Supporting Information. The \( \beta_{12} \)-HBeB\(_5\) sheet has a cohesive energy of 5.26 eV/atom. The total binding energy between \( \beta_{12} \) boron sheet, H atom and Be atom is 6.99 eV according to our calculations. Such large cohesive and binding energies indicate that \( \beta_{12} \)-HBeB\(_5\) is strongly energetically stable. Phonon spectrum calculation shows that \( \beta_{12} \)-HBeB\(_5\) is dynamically stable, without imaginary frequencies (Figure 2e). We further perform Ab-initio Molecular Dynamic simulation for \( \beta_{12} \)-HBeB\(_5\) using a 4 \times 6 supercell at a temperature of \( T = 800 \) K. After a running time of 10 ps, the structure of \( \beta_{12} \)-HBeB\(_5\) is still well kept, as seen in Figure 2f, suggesting that \( \beta_{12} \)-HBeB\(_5\) is also thermally stable at high temperatures. The robust stability of \( \beta_{12} \)-HBeB\(_5\) combined with the earlier reported synthesis of \( \beta_{12} \) boron sheet strongly indicates the experimental feasibility of this new 2D Dirac material.

To further understand the stability of \( \beta_{12} \)-HBeB\(_5\), we analyze the chemical bonding between atoms by calculating the electron localization function (ELF).\(^{33}\) In Figure 3, the ELF isosurface at 0.75 shows that H atom indeed takes electrons from the B(5) atom, and the Be atom donates electrons to the
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From nearest neighbor hopping approximation, the Letter $i = \sum_{t}$. Using bonding in graphene, thus stabilizing this structure. For example, the B(5) atom is actually not completely ionized. Instead, a small amount of electrons lie between them and other boron atoms, indicating that the weak covalent bonding. The overall bonding in $12$-HBeB$_5$ mimics carbon bonding in graphene, thus stabilizing this structure.

The calculated band structure of $12$-HBeB$_5$ is shown in Figure 2d. Due to the combined effects of the electron accepting and donating atoms, the Dirac bands in $12$ boron sheet are shifted, and the Fermi level crosses no other bands but exactly the Dirac point, which is around (0, 1/3) in the reciprocal space, forming a Dirac state. We also sample the whole first Brillouin zone and confirm the Dirac state, as shown in Figure 4a. Spin–orbital coupling effect is checked, and no band gap opening is observed (Figure S5).

To understand the origin of the Dirac state in $12$-HBeB$_5$, we plot the partial charge densities for the valence band maximum (VBM) and the conduction band minimum (CBM) at the Dirac point. As a mimic of graphene, $12$-HBeB$_5$ shows similar electronic characters around the Dirac point, i.e., both the VBM and the CBM mainly correspond to $p_z$ orbitals from the hexagonal boron rings. However, due to the buckling in $12$-HBeB$_5$, the Dirac state also have some $p_x$ orbitals for the VBM and some $p_y$ orbitals for the CBM from B(5) atom, as shown in Figure 4b,c. We further confirm the electronic characters of the Dirac states in $12$-HBeB$_5$ by plotting the orbital-projected band structure (Figure S6).

It is interesting to note that, due to the existence of B(5), electron hopping among the boron atoms in the hexagonal rings can be strengthened, which could lead to a high Fermi velocity near the Dirac cone. Our calculation shows that the Fermi velocity in $12$-HBeB$_5$ can reach $0.73 \times 10^6$ m/s, which is comparable to that of graphene (0.82 $\times 10^6$ m/s). Using maximally localized Wannier function methods, we derive the electron hopping parameters between atomic orbitals (Table S1). In graphene, it is known that Fermi velocity is derived as $v_F = \frac{e \hbar}{m^*}$ from nearest neighbor hopping approximation, where $a$ is the nearest carbon–carbon distance, and $t$ is the hopping parameter. Here in $12$-HBeB$_5$, the hexagonal lattice becomes distorted, and accurate derivation of the Fermi velocity from tight binding models is difficult. Nevertheless, we can still get Fermi velocity by averaging the results through all the nearest neighbor bonds, i.e., $v_F = \frac{e \hbar}{m^*} = \frac{1}{12} \sum_{i,j} \frac{3}{\sqrt{2}} a t_{ij}$. Using our calculated hopping parameters and the atomic distances, we get a Fermi velocity of $0.79 \times 10^6$ m/s, in good agreement with our result from direct first-principles calculations. Note that, in graphene, the Fermi velocity decreases when graphene lattice is stretched, and Fermi velocity is dropped by more than 40% when the lattice is expanded by 20%. In $12$-HBeB$_5$, while the average B–B distance in the hexagonal boron ring is about 20% larger than the C–C distance in graphene, the Fermi velocity is only 10% smaller due to the increased hopping parameters in $12$-HBeB$_5$ from additional hopping contributions through B(5) atom. This idea might be used while engineering Dirac materials to increase their Fermi velocities.

We note that, the eigen-energy of the highest occupied state at $\Gamma$ point is about 0.1 eV smaller than that at the Dirac cone position. As a result, the robustness of the Dirac state against strain needs to be examined. We consider both biaxial and uniaxial strain effect on the Dirac state of $12$-HBeB$_5$. Figure 5 shows that the Dirac state is sustained under the biaxial strain between −0.5% and 12% (Figure 5a,b), or under the uniaxial strain between −5% and 12% along the $x$ direction (Figure 5c,d), or under the uniaxial strain between −1% and 18% along $y$ direction (Figure 5e,f). Larger compressive or tensile strain will make $12$-HBeB$_5$ metallic, either due to the increase of the eigen-energy of the highest occupied state at $\Gamma$ point or due to the decrease of the eigen-energy of the lowest unoccupied state at $\Gamma$ and $\Gamma$ points. We find that the highest occupied state at the $\Gamma$ point mainly has $p_z$ character of B(4) atoms. Consequently, small compressive strain will easily push this state up to be higher than the state at the Dirac cone, resulting in the semimetal-to-metal transition. With this point in mind, we further check the Dirac state of $12$-HBeB$_5$ using the pseudopotential of local density approximation (LDA) functional, which yields lattice constants of about 1% ~ 2% smaller than the PBE results. Nevertheless, our calculation shows that,
the existence of Dirac state is independent of the selected functionals (see LDA band structure of $\beta_{12}$-HBeB$_5$ in the Supporting Information). Different from the highest occupied state at the $\Gamma$ point, the lowest unoccupied state at te R or $\Gamma$ point mainly corresponds to $p_z$ characters. The tensile strain, which can largely push down the highest occupied state at the $\Gamma$ point, slowly decreases the eigen-energy of the lowest unoccupied state at the R or $\Gamma$ point. Consequently, the Dirac state of $\beta_{12}$-HBeB$_5$ can sustain extraordinary large tensile strain, i.e., the 12% biaxial and 18% uniaxial tensile strain, which might be a promising property of $\beta_{12}$-HBeB$_5$ for flexible electronic applications.

In summary, we show that, by rationally designing the nongraphene-like $\beta_{12}$ boron sheets, we identify new isolated 2D Dirac materials $\beta_{12}$-XBeB$_5$ ($X = H, F, Cl$). Using $\beta_{12}$-HBeB$_5$ as an example, we demonstrate that $\beta_{12}$-HBeB$_5$ has very robust stability. Based on the recently reported successful synthesis of $\beta_{12}$ boron sheets, we expect the experimental feasibility of this new 2D Dirac material as well. Our designed $\beta_{12}$-HBeB$_5$ not only has a high Fermi velocity of $0.73 \times 10^6$ m/s due to additional hopping through the ionic-like boron atoms, but also has very robust Dirac state against extraordinary large tensile strains, thus advantaging it for flexible electronic applications. Our designed $\beta_{12}$-FBeB$_5$ and $\beta_{12}$-ClBeB$_5$ show similar properties (Supporting Information). This work thus opens an avenue to designing feasible 2D Dirac materials and stabilizing borophene sheets. We note that the recently proposed Dirac boron hydride sheet with $P_{bcm}$ symmetry agrees with our design principles.

**ASSOCIATED CONTENT**

*Supporting Information*
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b02163.

Calculation methods, structures, and band structures of $\alpha$ and $\delta$ boron sheets; structures, band structures, and stabilities of functionalized $\alpha$ and $\delta$ boron sheets; atomic position information on $\beta_{12}$-HBeB$_5$; spin–orbital coupling and LDA band structure of $\beta_{12}$-HBeB$_5$; band structures of $\beta_{12}$-FBeB$_5$ and $\beta_{12}$-ClBeB$_5$ (PDF)

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