Ultra-stable metallic freestanding multilayer borophene with elevated work function

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Abstract:

Understanding the structural stability of freestanding multilayer borophene is crucial because the interlayer interaction effect can lead to a new stabilized mechanism that can play a key role in determining the probability of its experimental realization, as evidenced by two recent experimental studies (substrate-supported bilayer $\alpha$- [Nat. Mater. 2021, 21, 35] and $\beta_{12}$-like borophene [Nat. Chem. 2022, 14, 25]). This study examines the structural stability of 1–3-layer structures of five typical borophene classes ($\alpha$, $\chi_3$, $\beta_{12}$, $\delta_6$, and $\delta_3$), and the results obtained indicate that $\alpha$-borophene (BBP) exhibits the most favorable stability in the 1–3-layer series. Accordingly, the structural stabilities, electronic structures, and work functions of 1–5-layer BBP are investigated systematically. The reduced interlayer bonds, as well as increased binding and interlayer interaction energy with an increasing layer number, demonstrate that both the interlayer interaction and stability are enhanced, as confirmed by ab initio molecular dynamics simulations. Moreover, metallicity and in-plane multi-centered bonding remain in the four multilayer structures. Remarkably, the interlayer bonding shifts from the isolated covalent dominant B–B bonds (2-/3-layer) to 5- or 6-centered localized bonds with mixed covalent and ionic components (4-/5-layer) via electronic localization function and bond population analyses. The interlayer and in-plane multi-centered bonds lead to the formation of an unprecedented interconnected 2D tubular geometry ($\alpha$-type boron nanotubes), which significantly enhances the interlayer bonding strength, resulting in highly stable 4- and 5-layer BBP. The work functions of 4- and 5-layer BBP, in particular, are similar to those of the frequently used Pt anode
material; therefore, they are considered highly attractive anode materials for applications in electronic devices.

**Keywords:** multilayer borophene, stability, work function, binding energy, interlayer interaction, electronic structure
1. Introduction

The discovery of borophene in a triangular lattice, an atomic-thick boron layer that can be fabricated on an Ag substrate [1], has demonstrated a series of surprising physical and chemical properties, and thus, the discovery of other new two-dimensional (2D) boron nanomaterials has attracted significant attention [2-5]. Interestingly, the electron-deficient characteristic of boron and resulting versatile bonding features lead to the rich structural diversity of borophene, unlike other Xenes [4-7]. Borophene polymorphs are characterized as triangular boron lattices comprising periodically arranged hollow polygons (e.g., α-, β-, and χ-type) with two exceptions: hexagonal (δ3-type) and triangular (δ6-type) lattices [8]. To date, a wide range of monolayer borophene polymorphs with various atomic structures, including α-, β-, β8-, β12-, δ3-, δ6-, and χ3-types, have been experimentally realized using molecular beam epitaxy (MBE) [9], atomic layer deposition [1], and chemical vapor deposition (CVD) [10] on various metal surfaces under different growth conditions [11]. These borophene nanostructures feature excellent mechanical, electronic, and optical properties, including topologically non-trivial electron bands and, in certain heterostructures, might even host high-temperature superconductivity [12]. Therefore, they have triggered remarkable research interests in the fields of chemistry, physics, material science, and condensed matter [2, 13], and are promising for applications in electronic devices, nanotechnology, energy conversion, and photonics [14, 15].

The growth of substrate-supported borophene commonly requires interfacial coupling with 2D metal templates, such as Ag(111)/(110)/(100) [1, 9, 16], Al(111) [17], Au(111) [18], Cu(111) [19], and Ir(111) [20], to stabilize its 2D form. Unfortunately, as-synthesized borophene has been limited to only single atomic layers for quite a long time, despite its rich polymorphs. Until recently, Hersam and Chen et al. realized
bilayer borophene structures on Ag(111) and Cu(111) surfaces via MBE under ultrahigh vacuum conditions, consistent with two covalently bonded α-phase and β_{12}-like layers, respectively, as evidenced using scanning tunneling microscopy and density functional theory (DFT) calculations [21, 22]. However, these substrate-supported borophene materials inevitably encounter instabilities in their structures when exfoliated from 2D metal templates or exposed to the atmosphere [23]; hence, the synthesis of freestanding borophene materials is critical for realizing their practical applications in electronic devices. Both the liquid- and solid-phase exfoliation techniques, where thin boron flakes are peeled from the boron bulk by ultrasonic or micromechanical energy, have been effective for producing freestanding 2D boron sheets. Massive and stable borophene materials have been prepared using the exfoliation technique, facilitating their large-scale application in nanoelectronic devices [23]. Thus far, freestanding monolayer β_{12}- and χ_{3}-borophene materials have been experimentally realized through low-temperature [23] or sonication-assisted liquid-phase exfoliation [24, 25] using various solvents, e.g., acetone, N-methyl pyrrolidone, dimethylformamide, and isopropyl alcohol, and micromechanical exfoliation aided by a double-sided foam tape [26].

However, atomically well-defined freestanding multilayer borophene materials including bilayer configurations have remained elusive. It is not a clear priori whether a freestanding bilayer borophene, or one with even more layers, could be formed experimentally. Unambiguously, a more exigent task, other than experimental exploration of these materials, is to explore the structural stabilities and bonding features of the freestanding multilayer borophene materials by theoretical prediction, especially for the theoretically highly stable and experimentally available (monolayer
or bilayer) borophene structures, which will provide significant guidance for the rational design of such materials experimentally.

This study investigated the structural stabilities of five typical 1–3-layer borophene (α-, χ3-, β12-, δ6-, and δ3-borophene) structure using first-principles DFT techniques, based on their experimentally available monolayer configurations. According to the calculation results of 1–3-layer borophene structures and the fact that monolayer and bilayer α-borophene materials have been experimentally realized, a systematic theoretical study was further conducted on the (i) geometries and stabilities, (ii) electronic structures, and (iii) work functions of 1–5-layer α-borophene nanostructures. First, the thermodynamic and dynamic stabilities of the investigated multilayer borophene systems were confirmed by combining the binding energy results and *ab initio* molecular dynamics (AIMD) simulations. Second, in addition to the systematic analysis of the electronic structures and work function changes with respect to the layer number from 1 to 5, the intrinsic mechanisms underlying their structural stabilities variations are primarily discussed herein. The present study provides a better understanding of the evolution of the stability and work function of borophene with increasing layer numbers and the role of the unique interlayer interaction in promoting their stabilities, as well as extends the advanced applications of borophene in anode materials and prompts more research attention to this outstanding and emerging multifunctional 2D material.

2. *Computational methods*

Ground-state total energy and work function calculations were conducted based on first-principles DFT methods as implemented in the DMol³ code. Exchange-correlation interactions were treated using the generalized gradient approximation (GGA) in the
Perdew–Burke–Enzerhof (PBE) form [27] with a real-space global orbital cutoff radius of 5.1 Å. All electron core treatments, double numerical basis sets including the polarization functions on all atoms, and unrestricted spins were applied. The DFT-D3 method was utilized to consider the van der Waals interaction in the first-principles calculation [28]. A large vacuum space of 35 Å was included in the supercell along the z-direction to avoid image-image interactions. In this study, 2 × 1 (16 atoms), 1 × 2 (16 atoms), 3 × 1 (15 atoms), 3 × 3 (18 atoms), and 3 × 2 (12 atoms) supercells were adopted to investigate monolayer α-, χ3-, β12-, δ6-, and δ3-borophene systems, respectively. The Brillouin zone was sampled using 18 × 18 × 1 mesh points in k-space according to the Monkhorst-Pack scheme. The convergence criteria for a residual force, energy, and atomic displacement were set to 2 × 10^{-3} Hartree/Å, 1.0 × 10^{-5} Hartree, and 5 × 10^{-3} Å, respectively.

The electronic localization function (ELF), Bader charge, and density of states (DOS) results were acquired using the Vienna ab initio simulation package (VASP) with the projector augmented wave method in the MedeA® software environment. GGA-PBE [27] and DFT-D3 [28] were used for the functional correction of van der Waals forces, which may be contained in the investigated systems. The plane-wave cutoff was set as 450 eV, and 18 × 18 × 1 k-points were used. The CASTEP module based on the ultrasoft pseudopotential method was used to obtain bond population results. The exchange-correlation energy was described by the GGA and PBE formulas [33]. The first Brillouin zone was sampled on an 18 × 18 × 1 k-point grid, and a cutoff energy of 400 eV was chosen to expand the Kohn–Sham wave functions.

3. Results and discussion

3.1 Geometries and stabilities
In this study, five experimentally available single-layer borophene, namely \( \alpha \)-[10, 29], \( \chi_3 \)-[9, 16], \( \beta_{12} \)-[9, 24], \( \delta_6 \)-[1], and \( \delta_3 \)-borophene [17]) models were constructed (Fig. 1). The lattice parameters utilized in this study, which are shown in Table S1, were consistent with those in previous studies [30-32]. The binding energy \( (E_b) \), which was obtained using Eq. 1, was used to determine the thermodynamic stability of the different multilayer borophene structures.

\[
E_b = -\frac{1}{n} E_{\text{total}} + E_{\text{atom}}
\]

(1)

where \( n \) is the number of boron atoms in one borophene system, and \( E_{\text{total}} \) and \( E_{\text{atom}} \) represent the total energies of a borophene system and a free and isolated boron atom, respectively.

The binding energies of monolayer \( \alpha \)-, \( \chi_3 \)-, \( \beta_{12} \)-, \( \delta_6 \)-, and \( \delta_3 \)-borophene are 6.295, 6.041, 6.034, 6.025, and 5.231 eV/atom, respectively, which are in accordance with those reported previously using the PBE functional (6.08–6.28 eV/atom, \( \alpha \)-borophene [30, 33, 34], 6.160 eV/atom, \( \chi_3 \)-borophene [32], 6.150 eV/atom, \( \beta_{12} \)-borophene [32]; 6.110 eV/atom, \( \delta_6 \)-borophene [32]; and 5.290 eV/atom, \( \delta_3 \)-borophene [32]). \( \alpha \)-Borophene exhibits the highest binding energy among the five single-layer borophene systems, confirming its best thermodynamic stability, which is consistent with results obtained in previous study using the PBE and PBE0 functional [9, 10]. Moreover, the binding energies of monolayer \( \chi_3 \)-, \( \beta_{12} \)-, and \( \delta_6 \)-borophene are in the narrow range of 6.025–6.041 eV/atom, which suggests that the synthesized \( \chi_3 \)-, \( \beta_{12} \)-, and \( \delta_6 \)-borophene nanostructures tend to form mixtures of the three configurations but not single crystal phases. This was confirmed by the recent experimental studies on Ag(111) using MBE
and low-temperature [23] or sonication-assisted liquid-phase exfoliation [24, 25], wherein both $\chi_3$- and $\beta_{12}$-borophene were obtained simultaneously. However, the graphene-like honeycomb $\delta_3$-borophene has the lowest binding energy (5.231 eV/atom), which is lower than those of other borophene systems by 13.2% (0.79 eV/atom, $\delta_6$-borophene)–16.9% (1.06 eV/atom, $\alpha$-borophene), suggesting the worst thermodynamic stability among the five investigated monolayer systems. The relatively lower thermodynamic stability of $\delta_3$-borophene can be mainly attributed to the electron deficiency characteristic of boron, as compared with carbon in a similar honeycomb-like hexagonal graphene, wherein the synergy of the in-plane $sp^2$-bonded $\sigma$ covalent bonds and out-of-plane delocalized $\pi$-bonds results in an excellent stability. Thus, monolayer $\delta_3$-borophene is unstable because no electrons occupy the $\pi$ bond [2].

Despite its undesirable thermodynamic stability, the synthesis of $\delta_3$-borophene is extremely beneficial owing to its specific characteristics, such as superconducting nature, Dirac fermions [11], and in particular, its higher surface activity than the other borophene materials. Accordingly, the key issue in the experimental design of $\delta_3$-borophene is to increase the number of electrons in the $\delta_3$-borophene plane to satisfy the demand of the abovementioned graphene-like bonding. This strategy was confirmed by the experimental study of Li et al., wherein honeycomb $\delta_3$-borophene was successfully realized on an Al(111) surface using MBE under ultrahigh vacuum conditions; herein, the Al substrate acted as an electron donor, supplying almost one electron to each boron atom [17]. This electron donating ability was more prevalent in the Al(111) substrate than in the Ag(111) substrate [11].
Fig. 1. Binding energies and geometrical structures of five different types of optimized monolayer structures: (a) α- (α-1L), (b) χ3- (χ3-1L), (c) β12- (β12-1L), (d) δ6- (δ6-1L), and (e) δ3-borophene (δ3-1L).

The geometries of bilayer borophene are rather complicated, and thus, mainly six typical stacking configurations (AA, AB, AAp, ABp, AAb, and ABb) with high symmetry were considered in this study [35, 36], as shown in Figure S1 with α-borophene as the example. The initial lattice constants for the bilayer structures are based on those of the abovementioned optimized monolayer borophene configurations. The top layer of the AA stacking mode is stacked directly on the bottom layer without any deviation in the z-axis direction (Figure S1a). The AB stacking mode refers to the misplacement of AA between the top and bottom layers at a 1/2 hexagonal (B6) distance along the B1→B3 direction (Figure S1b). The AAp (ABp) and AAb (ABb) stacking modes (Figure S1c–f) can be viewed as the shifting of the AA and AB stacking modes at half of the B–B bond length along, either in the B1→B2 or B1→B3 direction,
respectively; all the interlayer distances of the sublayers are initially set as approximately 3.0 Å [8]. Five bilayer borophene structures, namely α-AB, χ3-AA, β12-AA, δ6-ABp, and δ3-AA, are the equilibrium configurations with the highest $E_b$ in each optimized borophene species, as shown in Figure S2–S6 and Fig. 2, wherein the α-AB [35, 37], χ3-AA [38], β12-AA [38], and δ6-ABp [37] configurations are consistent with those in previous studies.

![Fig. 2. Binding energies and geometrical structures of five optimized bilayer structures of (a) β12-, (b) α-, (c) χ3-, (d) δ6-, and (e) δ3-borophene; carmine and cyan spheres represent the top and bottom layer, respectively.](image)

Table 1 lists the interlayer distances ($D$), average interlayer distances ($D_a$), minimum interlayer bond lengths/distances ($L_{\text{min}}$), and maximum interlayer bond lengths/distances ($L_{\text{max}}$) of 2–3-layer borophene systems. $D$ and $D_a$ were computed using Eqs. (2) and (3), respectively.
\[ D = Z_{n,\text{min}} - Z_{m,\text{max}} \]  
\[ D_a = Z_{n,\text{aver}} - Z_{m,\text{aver}} \]

where \( Z_{n,\text{min}} \) refers to the lowest \( z \)-axis value among all the boron atoms in the \( n \)th layer of a multilayer borophene system, while \( Z_{m,\text{max}} \) corresponds to the highest \( z \)-axis value among of the boron atoms in the \( m \)th layer of the corresponding multilayer borophene (\( n = m + 1 \), the \( m \)th layer refers to the bottom layer relative to the \( n \)th layer). \( Z_{n,\text{aver}} \) and \( Z_{m,\text{aver}} \) refer to the average \( z \)-axis values of the boron atoms in the \( n \)th and \( m \)th layers of the corresponding multilayer \( \alpha \)-borophene, respectively. Herein, \( D_{mn} \) and \( D_{amn} \) indicate the interlayer distance and average interlayer distance between the \( m \)th and \( n \)th layers (\( n = m + 1 \)), respectively.

Table 1: Interlayer distances (\( D \)), average interlayer distances (\( D_a \)), minimum interlayer distances (\( L_{\text{min}} \)), and maximum interlayer distances (\( L_{\text{max}} \)) of 2–3-layer borophene systems; \( D_{mn} \) and \( D_{amn} \) represents \( D \) and \( D_a \) between the \( m \)th and \( n \)th layer (\( n = m + 1 \)), respectively. \( L_{\text{min}} \) and \( L_{\text{max}} \) in both 1–2 layer (1–2L; 1-layer indicates the bottom layer) and 2–3 layer (2–3L) are provided for 3-layer \( \delta_6 \)-borophene system (3L-\( \delta_6 \)).

<table>
<thead>
<tr>
<th>Structure</th>
<th>( D (\text{Å}) )</th>
<th>( D_a (\text{Å}) )</th>
<th>( L (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D_{12} )</td>
<td>( D_{23} )</td>
<td>( \bar{D} )</td>
</tr>
<tr>
<td>2L-( \beta_12 )</td>
<td>2.547</td>
<td>–</td>
<td>2.547</td>
</tr>
<tr>
<td>2L-( \alpha )</td>
<td>1.544</td>
<td>–</td>
<td>1.544</td>
</tr>
<tr>
<td>2L-( \chi_1 )</td>
<td>2.779</td>
<td>–</td>
<td>2.779</td>
</tr>
<tr>
<td>2L-( \delta_6 )</td>
<td>1.732</td>
<td>–</td>
<td>1.732</td>
</tr>
<tr>
<td>2L-( \delta_3 )</td>
<td>0.113</td>
<td>–</td>
<td>0.113</td>
</tr>
<tr>
<td>3L-( \alpha )</td>
<td>1.505</td>
<td>1.527</td>
<td>1.516</td>
</tr>
<tr>
<td>3L-( \beta_12 )</td>
<td>2.841</td>
<td>2.835</td>
<td>2.838</td>
</tr>
<tr>
<td>3L-( \chi_1 )</td>
<td>2.969</td>
<td>2.978</td>
<td>2.973</td>
</tr>
<tr>
<td>3L-( \delta_6 )</td>
<td>1.734</td>
<td>2.562</td>
<td>2.148</td>
</tr>
<tr>
<td>3L-( \delta_3 )</td>
<td>1.208</td>
<td>1.208</td>
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</table>
From the interlayer distance perspective, the D and Da for bilayer β₁₂-borophene (2L-β₁₂) are 2.547 and 2.663 Å, respectively, which is consistent with those reported previously for 2-layer β₁₂-borophene (2.65 Å, PBE) [38]. Moreover, its interlayer B–B distance varies from 2.547 to 2.994 Å, indicating the van der Waals interlayer interaction for freestanding bilayer β₁₂-borophene. In sharp contrast, the interlayer interaction in the substrate-supported bilayer β₁₂-like borophene is a covalent bond in nature [21]. Similarly, D and Da for bilayer χ₃-borophene (2L-χ₃; 2.779 Å and 2.887 Å, respectively) are consistent with the previous theoretical result (2.80 Å, PBE) [38], suggesting the van der Waals interlayer interaction in freestanding bilayer χ₃-borophene, which can also be confirmed by its interlayer bond distance range (2.846–2.965 Å; Table 1). Additionally, both the D values of bilayer α-, δ₆-, and δ₃-borophene (1.544 Å, 1.732 Å, and 0.113 Å, respectively) and interlayer B–B bond lengths (1.646–1.886 Å, 1.912–3.697 Å, and 1.660–1.739 Å, respectively) indicate that interlayer B–B bonds are formed for the three bilayer systems, consistent with the bilayer α- and δ₃-borophene cases in previous studies [8, 32, 35]. The bilayer δ₆-borophene with van der Waals interlayer bonding has been theoretically reported with an interlayer distance of 3.072 Å [36], which was also obtained from our optimization results (Figure S5e and S5f). However, the binding energies of the van der Waals interlayer bonded bilayer δ₆-borophene (6.292–6.294 eV/atom) are lower than that of the interlayer covalently bonded one (6.406 eV/atom, Figure S5a and Fig. 2d) by approximately 0.11 eV, thereby indicating that the van der Waals interlayer bonded bilayer δ₆-borophene is not the ground-state configuration.

Bilayer β₁₂-borophene possesses the highest binding energy (6.442 eV/atom) among the five series of bilayer structures (Fig. 2), thus indicating the most favorable thermodynamic stability. However, according to the AIMD simulation results (Figure
S7 and S8), a phase transition occurs for the bilayer $\beta_{12}$-borophene, and the bilayer structure separates into two isolated monolayer sheets with an interlayer distance of approximately 6 Å after a 6 ps dynamic process at 300 K. The unstable interlayer binding between the two layers originates from the weak van der Waals interaction, thereby suggesting that bilayer $\beta_{12}$-borophene is dynamically unstable. This conclusion was indirectly confirmed by a recent experimental result, wherein only covalently bonded $\beta_{12}$-like bilayer borophene, but not van der Waals connected bilayer $\beta_{12}$-borophene, was realized by MBE [22]. Apart from the dynamically unstable bilayer $\beta_{12}$-borophene, bilayer $\alpha$-borophene exhibits the highest binding energy (6.430 eV/atom) between the remaining four series of bilayer structures (Fig. 2). According to the AIMD simulation results (Figure S9 and S10), freestanding bilayer $\alpha$-borophene is both thermodynamically and dynamically stable, which can also be indirectly verified by the experimentally realized covalently bonded bilayer $\alpha$-phase boron layers on the Ag(111) surface using MBE [22]. Moreover, substrate-supported bilayer $\chi_3$-borophene was prepared via the CVD method [39]. In contrast, freestanding $\chi_3$-borophene cannot be effortlessly realized experimentally. Although the binding energy of bilayer $\chi_3$-borophene (6.418 eV/atom; Fig. 2c) is more significant than that of bilayer $\delta_6$-borophene (6.406 eV/atom), it is dynamically unstable because a phase transition occurs for bilayer $\chi_3$-borophene, and the bilayer structure separates into two isolated monolayer sheets with an interlayer distance of approximately 8 Å after a 6 ps dynamic process at 300 K (Figure S7 and S8). However, bilayer $\delta_6$-borophene maintains its structure after a 6 ps dynamic process at 300 K (Figure S7 and S8), suggesting that it is thermodynamically and kinetically stable. Additionally, a lack of significant substrate support, for example on Al(111), and substrate-assisted electron transfer to the boron layer [11, 17], distorts the optimized freestanding bilayer $\delta_3$-borophene structure but
preserves the hexagonal structure (Fig. 2e); however, its lowest binding energy (6.159 eV/atom) among the five investigated structures and unfavorable dynamic stability (Figure S7 and S8) make it exceedingly difficult to prepare experimentally. Therefore, only bilayer α- and δ6-borophene can be realized among the five investigated bilayer structures based on the primary combined thermodynamic and dynamic analytic results, which is closely related to their in-plane and interlayer structural stability, particularly to their covalent bonded interlayer features.

The preset configurations for 3-layer borophene systems were constructed using various stacking modes based on the thermodynamically most favorable bilayer borophene models and the test results are shown in Figure S11–S15 and Fig. 3. Clearly, α-ABA, β12-AAA, χ3-AAA, δ6-AAAp, and δ3-AAA are thermodynamically most favorable configurations in each type of borophene structure. Among them, the 3-layer δ6-borophene configuration is consistent with the ground-state configuration of previously reported 3-layer δ6-borophene [36]. The D (1.505–1.527 Å (α) and 1.208 Å (δ3)), Dα (2.462–2.569 Å (α) and 1.473 Å (δ3)), and interlayer B–B bond lengths (1.633–1.966 Å (α) and 1.632–1.909 Å (δ3)) of the 3-layer α- and δ3-borophene (3L-α and 3L-δ3, Table 1) show that covalent bonds are formed in these two 3-layer systems, in agreement with the 3-layer δ3-borophene case in a previous study [32]. However, the D (2.835–2.841 Å (β12) and 2.969–2.978 Å (χ3)), D4 (2.879–2.881 Å (β12) and 3.002 Å (χ3)), and B–B distances (2.838–2.942 Å (β12) and 2.985–3.029 Å (χ3)) of 3-layer β12- and χ3-borophene (3L-β12 and 3L-χ3; Table 1) suggest that interlayer interactions can be attributed to van der Waals forces. Interestingly, the D and interlayer bond lengths between the first (bottom layer) and the second layer of 3-layer δ6-borophene (3L-δ6) are 1.734 Å and 1.915–3.677 Å, respectively, indicating a covalent interlayer interaction. In sharp contrast, the D and interlayer bond lengths between the second and
third layer of 3-layer δ₆-borophene are 2.562 Å and 3.422–3.481 Å, respectively, indicating a van der Waals interaction. Unambiguously, covalent bonds and van der Waals interlayer interactions coexist in the 3-layer δ₆-borophene systems.

**Fig. 3.** Binding energies and geometrical structures of five different series of the optimized 3-layer structures of (a) α-, (b) χ₃-, (c) β₁₂-, (d) δ₆-, and (e) δ₃-borophene; carmine and cyan spheres represent the middle, and top and bottom layer, respectively.

A 3-layer α-ABA configuration with covalent interlayer interactions and a binding energy of 6.475 eV/atom is the thermodynamically most favorable 3-layer configuration among the five series of borophene (Fig. 3), consistent with the monolayer system. Moreover, the AIMD simulation results (Figure S9b and S10b) indicate that the 3-layer α-borophene is dynamically stable, which shows that it is the most promising freestanding 3-layer borophene structure that can be realized.
experimentally. Following the decreasing binding energy sequence, 3-layer $\beta_{12}$-AAA (6.470 eV/atom), $\chi^3$-AAA (6.444 eV/atom), and $\delta_6$-AAAp (6.383 eV/atom) exhibit lower thermodynamic stabilities than the 3-layer $\alpha$-ABA configuration, with a decrease of 0.005, 0.031, and 0.092 eV/atom, respectively. However, only the 3-layer $\delta_6$-borophene is dynamically stable, thereby maintaining mixed covalent and van der Waals interlayer interactions, between the three structures after an AIMD course of 6 ps at 300 K; the 3-layer $\beta_{12}$-borophene separated into three parts with interlayer distances of approximately 6 Å (1–2 layer) and 8 Å (2–3 layer), whereas the $\chi^3$-borophene separated into two parts with interlayer distances of approximately 8 Å (1–2 layer) after a 6 ps dynamic process at 300 K (Figure S16a–c and S17a–c). Additionally, the 3-layer $\delta_3$-AAA configuration exhibits the lowest binding energy of 6.313 eV/atom among the five different series of borophene structures, which is in accordance with the cases in monolayer and bilayer systems. Unexpectedly, the freestanding 3-layer $\delta_3$-borophene is dynamically stable, that is, it maintains its fundamental atomic configuration after a 6 ps AIMD process at 300 K (Figure S16d and S17d), which is in significant contrast to its bilayer case. This implies that the increased layer number (1→3) plays a vital role in increasing the stability of $\delta_3$-borophene not only from the thermodynamic (5.231 eV (1-layer)→6.159 eV (2-layer)→6.313 eV (3-layer), $E_b$), but also kinetic perspective, though it is still the thermodynamically most unstable one among the five investigated borophene structures. Therefore, it is possible to realize $\alpha$-, $\delta_6$-, and $\delta_3$-borophene in 3-layer borophene systems.

Encouraged by the successful realization of substrate-supported monolayer [10] and bilayer $\alpha$-borophene [22] structures using MBE, the abovementioned result that $\alpha$-
borophene has the most favorable stability among the five investigated freestanding configurations for 1–3-layer cases, which indicates the highest potential to be experimentally realized, motivated the authors to further explore the stabilities, thermodynamic possibility of their existence, bonding characteristics, and properties of freestanding multilayer α-borophene structures with more than three layers. Accordingly, 4- and 5-layer α-borophene was geometrically optimized according to the configuration and stacking mode of the thermodynamically most favorable 1–3-layer α-borophene. In total, eight configurations, including ABAB, BABA, BAAB, AABA, ABBA, AAAB, ABBB, and BAAA, were considered before the geometrical optimization calculation. The results clearly show that the α-ABAB configuration possesses the highest binding energy (6.521 eV/atom), indicating that it is the thermodynamically most favorable structure among the tested 4-layer models (Figure S18). Similarly, the 5-layer α-ABABA stacking mode had the largest binding energy (6.579 eV/atom) among all the optimized structures (Figure S19), indicating that it is the ground-state configuration of 5-layer α-borophene. This stacking mode (ABAB…, Fig. 4) is exceedingly similar to that of other multilayer 2D nanostructures, such as graphene [40], silicene [41], and phosphorene [42]. Therefore, the cross-bedded AB stacking mode is the most favorable one for multilayer α-borophene systems (1–5 layer). Figure 4 shows the optimized equilibrium structures of the 1–5-layer α-borophene systems.
Table 2 provides the average in-plane B–B bond lengths (\( \bar{L}_n \)) of multilayer \( \alpha \)-borophene systems. The average B–B bond length (1.702 Å) of monolayer \( \alpha \)-borophene is in accordance with that obtained previously (1.66–1.70 Å) using the PBE functional [33, 34], whereas the average in-plane B–B bond length (1.736 Å) in bilayer \( \alpha \)-borophene is similar to the bilayer \( \alpha_1 \)-AB (1.700 Å) case [35]. Moreover, as the number of layers increases from 1 to 5, the average in-plane B–B bond length of \( \alpha \)-borophene exhibits an increasing tendency in the range of 1.702 (1 layer)–1.822 Å (5 layers), suggesting that the borophene plane grows increasingly relaxed.

To understand the bonding between different layers in multilayer \( \alpha \)-borophene systems, the interlayer B–B bond distances (\( L_i \)) were calculated. The range of \( L_i \) (\( L_{i,\text{min}} \)–
L_{i,max}) and average L_{i} (\bar{L}_{i}) are provided in Table 2. Table S2 lists the L_{i} data of all the multilayer α-borophene systems (2–5 layer). The L_{i} and \bar{L}_{i} of all the multilayer α-borophene systems are 1.759–1.950 Å and 1.837–1.874 Å, respectively, implying that these interlayer bonds have an identical natural characteristic, that is, covalent bonding (for more details, see Section 3.2). These interlayer B–B bond length values are slightly higher than those of the in-plane B–B bond lengths in 1–3-layer α-borophene systems (1.702–1.770 Å) and become increasingly approximate to the \bar{L}_{p} in 4–5-layer α-borophene systems (1.797–1.822 Å). This indicates that in-plane and interlayer B–B bonds are inclined to be identical as the number of α-borophene layers increases. In contrast, the average bond length for all the in-plane and interlayer B–B bonds in a borophene system (\bar{L}_{p}) increases gradually from 1.702 to 1.833 Å as the number of layers increases (Table 2). Whether the abovementioned variations of in-plane and interlayer B–B bonds accompany a change in the thermodynamic stability of the corresponding system or not will be discussed later on.

Table 2 Average in-plane B–B bond lengths (\bar{L}_{p}), minimum (L_{i,min}), maximum (L_{i,max}), and average interlayer B–B bond lengths (\bar{L}_{i}), and average values of the sum of in-plane and interlayer B–B bond lengths (\bar{L}_{p}) of 1–5-layer BBP systems.

<table>
<thead>
<tr>
<th>Structure</th>
<th>L_{p} (Å)</th>
<th>L_{i,min}</th>
<th>L_{i,max}</th>
<th>\bar{L}_{i}</th>
<th>\bar{L}_{p} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L-BBP</td>
<td>1.702</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.702</td>
</tr>
<tr>
<td>2L-BBP</td>
<td>1.736</td>
<td>1.803</td>
<td>1.906</td>
<td>1.837</td>
<td>1.741</td>
</tr>
<tr>
<td>3L-BBP</td>
<td>1.770</td>
<td>1.811</td>
<td>1.923</td>
<td>1.874</td>
<td>1.777</td>
</tr>
<tr>
<td>4L-BBP</td>
<td>1.797</td>
<td>1.759</td>
<td>1.939</td>
<td>1.848</td>
<td>1.813</td>
</tr>
<tr>
<td>5L-BBP</td>
<td>1.822</td>
<td>1.801</td>
<td>1.950</td>
<td>1.858</td>
<td>1.833</td>
</tr>
</tbody>
</table>

Furthermore, the calculated L_{i} values for the 2-, 3-, 4-, and 5-layer α-borophene are 1.803–1.906, 1.811–1.923, 1.759–1.939, and 1.801–1.950 Å, respectively, all of which are slightly higher than the in-plane bond lengths in monolayer BBP (1.668–
1.722 Å). Additionally, these L₄ values are consistent with those in bilayer α-borophene (1.8–1.9 Å) [8, 22] and bilayer β₁₂-like borophene (1.82 Å) [21], from which the formation of covalent interlayer bonds between the four-coordinated boron atoms have been confirmed. Therefore, these multilayer α-borophene systems should have similar covalent interlayer bonds (discussed further in Section 3.2).

To characterize the variation in the interlayer distances of the multilayer α-borophene systems, the interlayer distance (D) and average interlayer distance (Dₐ) were computed using Eqs. (2) and (3), respectively (Table 3). The D in the 2-layer α-borophene system (1.544 Å) is consistent with that in a previous study (1.54 Å) [34]. Moreover, the average D values in multilayer α-borophene systems (2–5-layer) are 1.516 (3-layer)–1.566 Å (5-layer), which is evidently lower than that (1.702 Å) in monolayer α-borophene, indicating the formation of interlayer bonds in some interlayer regions, consistent with the preceding interlayer bond length results. Furthermore, the Dₐ values present a decreasing tendency as the number of layers increases (2.863→2.465 Å), indicating that the interlayer interactions in multilayer α-borophene systems become increasingly enhanced.

Table 3 Interlayer distances (D) and average interlayer distances (Dₐ) of 2–5-layer α-borophene (BBP) systems; Dₘₙ and Dₘₙₙ represent D and Dₐ between the mᵗʰ layer and nᵗʰ layer (n = m + 1), respectively.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2L-BBP</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.544</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.863</td>
</tr>
<tr>
<td>3L-BBP</td>
<td>1.527</td>
<td>1.505</td>
<td>–</td>
<td>–</td>
<td>1.516</td>
<td>2.569</td>
<td>2.462</td>
<td>–</td>
<td>–</td>
<td>2.516</td>
</tr>
<tr>
<td>4L-BBP</td>
<td>1.518</td>
<td>1.525</td>
<td>1.505</td>
<td>–</td>
<td>1.516</td>
<td>2.484</td>
<td>2.440</td>
<td>2.537</td>
<td>–</td>
<td>2.487</td>
</tr>
<tr>
<td>5L-BBP</td>
<td>1.555</td>
<td>1.577</td>
<td>1.578</td>
<td>1.553</td>
<td>1.566</td>
<td>2.466</td>
<td>2.464</td>
<td>2.464</td>
<td>2.466</td>
<td>2.465</td>
</tr>
</tbody>
</table>
To comprehensively explore the interlayer interaction strength in these multilayer borophene systems, the interlayer interaction energy ($\Delta E_m$) and average interlayer interaction energy ($\Delta E_i$) were rationally defined to describe the interlayer interaction from two different aspects. $\Delta E_m$ and $\Delta E_i$ can be defined as:

\[
\Delta E_m = (E_D + E_T) - E_{\text{total}}
\]

\[
\Delta E_i = \frac{1}{n-1} \left[ \sum_{n=1}^{n} (E_n) - E_{\text{total}} \right]
\]

where $E_{\text{total}}$ is the single-point total energy of a multilayer borophene system; $E_D$ and $E_T$ are the total energies of the models below and above an interlayer area, respectively; n (2–5) refers to the layer number of multilayer borophene ($m = n - 1$); and $E_n$ is the total energy of the $n^{th}$ layer in an n-layer system. The calculation details of $\Delta E_m$ are provided in the Supplementary material. $\Delta E_m$ distinctly displays every interlayer interaction strength in a multilayer borophene system; however, $\Delta E_i$ can be conveniently utilized to compare the average interlayer interaction strength variation in various multilayer borophene systems.

Table 4 lists the binding energies of multilayer $\alpha$-borophene (1–5-layer), and the $\Delta E_m$ (m = 1–4) and $\Delta E_i$ of multilayer $\alpha$-borophene (2–5-layer). The binding energies of multilayer $\alpha$-borophene exhibit an increasing tendency in the range from 6.295 (1-layer) to 6.579 eV/atom (5-layer), thus indicating an enhanced thermodynamic stability. Clearly, the enhancement in the interlayer interaction plays a key role in increasing the thermodynamic stability of multilayer $\alpha$-borophene. The elevated binding energies of the 2–5-layer $\alpha$-borophene configurations investigated herein, the excellent dynamic stabilities according to our AIMD results (Figure S9 and S10), as well as the successful experimental realization of monolayer [10] and bilayer $\alpha$-borophene [22] demonstrate
that the realization of 3–5 layer α-borophene can be highly anticipated, particularly for 5-layer α-borophene.

Table 4 Binding energies ($E_b$) of 1–5-layer α-borophene (BBP) systems, and interlayer interaction energies ($\Delta E_m$) and average interlayer interaction energies ($\Delta E_i$) of 2–5-layer BBP systems.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_b$ (eV)</th>
<th>$\Delta E_1$ (eV)</th>
<th>$\Delta E_2$ (eV)</th>
<th>$\Delta E_3$ (eV)</th>
<th>$\Delta E_4$ (eV)</th>
<th>$\Delta E_i$ (eV)</th>
<th>$\Delta E_m$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L-BBP</td>
<td>6.295</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2L-BBP</td>
<td>6.430</td>
<td>7.617</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7.617</td>
<td>7.617</td>
</tr>
</tbody>
</table>

From the interlayer interaction intensity perspective, both $\Delta E_m$ and $\Delta E_i$ present the same increasing tendency as the number of layers increases ($7.617 \rightarrow 13.175$ eV, $\Delta E_m$; $7.617 \rightarrow 11.625$ eV, $\Delta E_i$), indicating an enhanced interlayer interaction which also confirms the abovementioned increasing thermodynamic stability. This is consistent with the interlayer distance analytical results. Combining the binding energy and interlayer interaction energy results demonstrates that 5-layer α-borophene has the highest binding energy and interlayer interaction energy among the multilayer structures, suggesting that it has the most favorable thermodynamic stability and the highest probability of being experimentally prepared. Moreover, the middle interlayer interaction in 4- (13.917 eV) and 5-layer (14.566 eV and 14.556 eV) systems are stronger than those in the bottom and top layers (11.64–11.80 eV), indicating that the bindings between the middle layers are greater than those between the marginal layers.
3.2 Electronic structures

To further investigate the electronic properties and bonding features of multilayer BBP systems, the Bader charge, bond population, ELF, and DOSs were calculated. Table 5 provides the Bader population of the interlayer bonded boron (IB), neighboring boron (NB), and remote boron (RB) atoms ($Q_{\text{IB}}$, $Q_{\text{NB}}$, and $Q_{\text{RB}}$, respectively) in each layer of 2–5-layer α-borophene (BBP) systems. NBs refer to the boron atoms adjacent to the interlayer bonded boron atoms, and RBs are the boron atoms other than NBs and the interlayer bonded boron atoms; 1-layer corresponds to the bottom boron plane in a multilayer borophene system.

In a 2-layer BBP system, the interlayer bonded boron atoms in 1- and 2-layer lost 0.404 e and 0.457 e, respectively, whereas the NBs in the 1- and 2-layer gain 0.399 e and 0.432 e, respectively. Therefore, the formation of interlayer B–B bonds in the 2-layer BBP is mainly due to the contribution of the interlayer bonded boron atoms. Similarly, for a 3-layer BBP system, the interlayer bonded boron atoms in the top, middle, and bottom layers lost 0.032 e, 0.302 e, and 0.041 e, respectively, and the corresponding NBs acquire 0.146 e, 0.131 e, and 0.029 e, respectively, and the RBs in the bottom layer gained 0.036 e, also indicating that the interlayer bonded boron atoms contribute a dominant part in the interlayer B–B bonds.

For 4-layer BBP system, the interlayer bonded boron atoms in the 2-, 3-, and 4-layer obtain 0.009 e, 0.047 e, and 0.053 e, respectively; the interlayer bonded boron atoms in the 1-layer lost 0.068 e. The NBs in 2- and 4-layer lose 0.152 e and 0.116 e, respectively. This suggests that the interlayer B–B bond mainly originates from the contribution of NB atoms (lose 0.238 e), and the contribution of the interlayer bonded boron atoms is marginal. In a 5-layer BBP system, the interlayer bonded boron atoms in the 2-, 3-, and 4-layer gain 0.009, 0.028 e, and 0.087 e, respectively. The top and
bottom layer lose 0.087 e and 0.119 e, respectively, in which one part of electrons transfer to NB (0.07 e and 0.09 e for the top and bottom layer, respectively) and the other part participates in the formulation of interlayer B–B bond (approximately 0.03 e). Moreover, the NBs in the 4-layer lose 0.114 e, in which one part transfers to the interlayer bonding B atoms (0.087 e) and the other participates in the formulation of the interlayer B–B bond (approximately 0.03 e). Thus, the interlayer B–B bond in a 5-layer BBP system originates from the joint contribution of the interlayer bonding boron atoms and NBs. Consequently, the interlayer bonded boron atoms in 2- and 3-layer BBP systems contribute significantly to the interlayer B–B bonds formation, and interlayer covalent bonding for 4- and 5-layer BBP systems is due to the contribution of interlayer bonding boron atoms and NBs.

Table 5 Numbers of interlayer-bonded boron atoms (nIB), neighboring boron atoms (NBs) adjacent to interlayer-bonded boron atoms (nNB), remote boron atoms (nRB), and their Bader population ($Q_{IB}$, $Q_{NB}$, and $Q_{RB}$, respectively) in each layer of 2–5-layer α-borophene (BBP) systems (1-layer refers to the bottom layer in a multilayer system).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Layer</th>
<th>nIB</th>
<th>$Q_{IB}$</th>
<th>nNB</th>
<th>$Q_{NB}$</th>
<th>nRB</th>
<th>$Q_{RB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2L-BBP</td>
<td>1-layer</td>
<td>3</td>
<td>0.457</td>
<td>13</td>
<td>−0.432</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>2-layer</td>
<td>3</td>
<td>0.404</td>
<td>13</td>
<td>−0.399</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>1-layer</td>
<td>2</td>
<td>0.041</td>
<td>10</td>
<td>−0.029</td>
<td>4</td>
<td>−0.036</td>
</tr>
<tr>
<td>3L-BBP</td>
<td>2-layer</td>
<td>6</td>
<td>0.302</td>
<td>10</td>
<td>−0.131</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>3-layer</td>
<td>4</td>
<td>0.032</td>
<td>12</td>
<td>−0.146</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>1-layer</td>
<td>6</td>
<td>0.068</td>
<td>10</td>
<td>−0.030</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>2-layer</td>
<td>13</td>
<td>−0.009</td>
<td>3</td>
<td>0.152</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>3-layer</td>
<td>16</td>
<td>−0.047</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>4-layer</td>
<td>8</td>
<td>−0.053</td>
<td>8</td>
<td>0.116</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>1-layer</td>
<td>6</td>
<td>0.119</td>
<td>10</td>
<td>−0.090</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>2-layer</td>
<td>13</td>
<td>−0.009</td>
<td>3</td>
<td>−0.0004</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>5L-BBP</td>
<td>3-layer</td>
<td>16</td>
<td>−0.028</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>4-layer</td>
<td>15</td>
<td>−0.087</td>
<td>3</td>
<td>0.114</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>5-layer</td>
<td>6</td>
<td>0.087</td>
<td>10</td>
<td>−0.073</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>
Figure S20 and S21 show the normalized total densities of states (TDOSs) and partial densities of states (PDOSs) of the s, p$_x$, p$_y$, and p$_z$ orbitals of boron atoms in 1–5-layer BBP, respectively. All the DOS curves for 1–5-layer BBP structures across the Fermi level (Figure S20) indicate that the increased layer number cannot open the BBP gap and all the multilayer BBP systems investigated herein are metallic. This favors the application of BBP in electronic devices, which is similar to the multilayer $\alpha_1$- [35], $\eta_{4/28}$- [35], and $\delta_6$-borohene [36, 43] cases. Moreover, the states in the Fermi level are p$_z$ orbital dominant for monolayer BBP systems and the in-plane PDOS can be ignored, which is the typical feature for mixed hexagonal and triangular borohene with the highest stability, that is, to place E$_F$ precisely at the zero-point of the in-plane PDOS, filling all available in-plane bonding states and none of the antibonding ones (Figure S21a) [33]. This feature is maintained for 2- and 3-layer BBP (Figure S21b and S21c), although the interlayer chemical bonding has formed. However, the contribution of the p$_z$ orbital to the Fermi state reduces considerably for the 4–5-layer BBP, i.e., the contribution from the in-plane PDOS (p$_x$, p$_y$, and s orbital) becomes comparable to the p$_z$ orbital, especially for the p$_z$ orbital (pink lines) (Figure S21d and S21e), implying that the interlayer bonding of 4–5-layer BBP plays more important roles in the structural stability than that in 2–3-layer BBP systems. Additionally, the hybridization between the s and p orbitals was identified in the five multilayer BBP systems. To further understand the interlayer bonding, the PDOS of the interlayer bonded boron atoms were plotted, as shown in Fig. 5. It is interesting to note that p$_z$ and p$_x$ dominant and p$_z$ dominant Fermi states are formed in 4–5-layer and 2–3-layer BBP, respectively, thereby showing the remarkably diverse interlayer bonding between the two which will be further discussed hereafter.
Fig. 5 PDOSs of the s, pₓ, pᵧ, and pₑ orbitals of the interlayer bonded boron atoms for 2–5-layer BBP systems.

Figure 6 provides top and slice views of the ELF for the in-plane hexagonal hole (B₆) in each layer of 1–5-layer BBP systems; Fig. 6a shows the three-dimensional (3D) top view of the 1-layer BBP system and the three boron atoms (B₁, B₃, and B₅) are the three points to determine the slice plane for Fig. 6a–6p, that is, Slice B₁B₃B₅. For monolayer BBP (Fig. 6b), ELF is mainly distributed in the region between the neighboring boron atoms in the B₆ hexagonal hole, indicating that the B–B bond in the B₆ hole is covalent in nature. Moreover, the ring-like green ELF at the middle region in the B₆ hole confirms the formation of the localized 6c-2e π-bond in B₆ [6]. As the number of layers increases, a multi-centered 6c-2e bonding feature is maintained for all the multilayer BBP systems (Fig. 6c–6p). However, the covalent feature of the in-plane
B$_3$–B$_4$ bonds reduces for 4- and 5-layer systems (Fig. 6h–6p), which is due to their contribution of some p electrons to the interlayer bonding in the system.

Fig. 6 (a) 3D top views of the ELF for monolayer BBP; (b)–(p) slice views (slice B$_1$B$_3$B$_5$) of ELF for the in-plane B$_6$ hexagonal hole with an isovalue of 0.2 for each layer of the 1–5-layer BBP systems. nL-$m$ (n = 1–5; m = 1–5) indicates the $m^{th}$ layer in a n-layer BBP system.
Fig. 7 (a) 3D top views of the ELF for monolayer BBP; (b)–(p) slice views (slice B₁B₃B₅) of the ELF for the in-plane B₆ hexagonal hole with an isovalue of 0.2 for each layer of the 1–5-layer BBP systems; nL-m (n = 1–5; m = 1–5) indicates the mᵗʰ layer in the n-layer BBP system.

Figure 7 shows the top and slice views of ELF for the in-plane filled hexagonal hole (B₇) in each layer of 1–5-layer BBP systems, in which Fig. 7a is the 3D top view of the monolayer BBP system and B₁, B₃, and B₅ are the three points to identify the slice plane for Fig. 6a–6p, that is, slice B₁B₃B₅. For monolayer BBP, the ELF is mainly distributed in the region between the neighboring boron atoms in the vertex of the hexagon, indicating a covalent bonding character (Fig. 7b). Additionally, the ring-like olivine ELF around the central boron atom in the B₇ hole, which connects the central boron atom and other six atoms in B₇, suggests the formulation of localized 7c-2e π-
bonds in B$_7$ [6]. As the number of layers increases, the multi-centered 7c-2e bonding feature remains for all the multilayer BBP systems (Figs. 7(c)–(p)), in contrast to the B$_6$ case in which the covalent feature reduces for in-plane B$_3$–B$_4$ bonds for 4- and 5-layer systems. The unchanged in-plane bonding features of the B$_7$ hole for multilayer BBP systems, as compared to monolayer BBP, mainly stems from the abundant valence electrons in B$_7$ than in B$_6$, in spite of their p electrons also participating in the interlayer bonding.

Table 6 Number of interlayer B–B bonds ($n$), number of interlayer bonded boron atoms (m), and interlayer B–B bond populations of multilayer α-borophene (BBP) systems.

<table>
<thead>
<tr>
<th>Structure</th>
<th>n</th>
<th>m</th>
<th>Interlayer B–B bond population</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>I (0.00–0.30)</td>
</tr>
<tr>
<td>2L-BBP</td>
<td>3</td>
<td>6</td>
<td>–</td>
</tr>
<tr>
<td>3L-BBP</td>
<td>6</td>
<td>12</td>
<td>–</td>
</tr>
<tr>
<td>4L-BBP</td>
<td>42</td>
<td>43</td>
<td>0.24–0.30 (10)</td>
</tr>
<tr>
<td>5L-BBP</td>
<td>56</td>
<td>59</td>
<td>0.26–0.29 (10)</td>
</tr>
</tbody>
</table>

To characterize the bonding interaction between various layers in multilayer α-borophene systems, the calculated interlayer B–B bond population values (Table 6) were rationally divided into three series, namely type (I) (0.00–0.30), type (II) (0.31–0.50), and type (III) (0.51–1.00). The type (I), (II), and (III) bond populations correspond to the ionic dominant bonding, the covalent bonding with a relatively strong ionic component, and the covalent-dominant bonding, respectively. As shown in Table 6, as the layers increases, the number of interlayer B–B bonds increases rapidly from 3 (2-layer) to 56 (5-layer), accompanied by a dramatic increase in type (I) and (II) B–B bonds (0 (2-layer)–10 (4- and 5-layer), type (I); 0 (2-layer)–32 (5-layer), type (II)). Moreover, the average interlayer B–B bond population decreases from 0.73 (2-layer) to 0.38–0.41 (4- and 5-layer). These abovementioned results demonstrate that the ionic
component increases, and the covalent component decreases gradually as the number of layers increases for interlayer B–B bonds of multilayer BBP systems; the interlayer interaction shifts from covalent dominant bonding (2 layer) to mixed covalent and ionic bonding (5 layer).

Furthermore, the typical interlayer B–B bonds were selected to plot the ELF slice views to further understand the interlayer bonding natures of these multilayer BBP systems, as shown in Figure S22 and 8. The ELF of a 2-layer BBP system is mainly distributed over the middle region between two bonded interlayer boron atoms (B7–B8 and B10–B11 in Figure S22a and S22b, respectively), confirming the typical covalent features, which is in accordance with the case in previous studies [22, 41, 43-45]. The ELF slice views for the B13–B14 bond (0.44, bond population; type (II)) and B16–B17 bond (0.83, bond population; type (III)) of 3-layer BBP systems were plotted, as shown in Figure S22c and S22d, respectively. The ELF accumulates between the bonded interlayer boron atoms, rather than around them, thus confirming that the interlayer B–B bonds for 3-layer BBP exhibit a covalent feature. In contrast, the covalent bond in B13–B14 is weaker than that in the B16–B17 bond, as verified by the bond population results (0.44, B13–B14; 0.83, B16–B17). Therefore, the interlayer B–B bonds for the 3-layer BBP show covalent dominant bonding with only a small ionic component.
Fig. 8 (a)–(d) Slice views of the ELF for interlayer B–B bonds of 2–5-layer BBP systems; (e) enlarged top and side views of a boron nanotube-like motif in 4- and 5-layer BBP systems. Yellow and green spheres represent interlayer bonded boron atoms as shown in the ELF slice views.

The interlayer bonds of the 4- and 5-layer BBP are remarkably different from those of the 2- and 3-layer BBP, as indicated by the abovementioned DOS and bond population analyses. Clearly, the interlayer bonded B atoms are all isolated and not bonded with each other, that is, there is little interaction between different interlayer B–B bonds in 2- and 3-layer BBP systems (Fig. 8a and 8b). In sharp contrast, substantial interlayer bonded boron planes with five or six boron atoms (B₅ or B₆) as an elementary unit form in the interlayer regions of 4- and 5-layer BBP systems in the 2 × 1 supercell (Figs. 8c and 8d). Remarkably, the nanotube-like geometry, consistent with previously reported α-type boron nanotube (derived from the α-borophene) [46], is observed for the “motif” of 4- and 5-layer BBP from their side views (Fig. 8e), which is formed by
the interlayer bonded $B_5$ and $B_6$ units and their adjacent in-plane boron atoms. The interlayer ELF distributes in the middle region of the five or six boron atoms in the interlayer $B_5$ or $B_6$ unit for 4- or 5-layer BBP systems (Figs. 8c and 8d), rather than only being located between the two interlayer bonded boron atoms (2- or 3-layer BBP) (Figs. 8a and 8b). This indicates the formation of 5- or 6-centered localized bonds that delocalize between five or six bonded interlayer boron atoms. The interconnected tubular structure and multi-centered interlayer bonding character significantly enhance the interlayer bonding strength and stabilities of 4- and 5-layer BBP systems, thus leading to an enhanced interlayer interaction energy and more favorable thermodynamic stability than those of 1–3-layer BBP systems.

### 3.3 Work functions

The work functions ($\phi$) of the investigated multilayer BBP systems were computed using Eq. (9), which indicates the minimum energy required to draw an electron from the $E_F$ to the vacuum level ($E_{\text{vac}}$).

$$\phi = E_{\text{vac}} - E_F$$  \hspace{1cm} (6)

Fig. 9 shows the calculated work functions of the plane $\alpha$-borophene (PBP), multilayer BBP, and graphene systems. The following important features can be identified in Fig. 9. The calculated $\phi$ of PBP (4.08 eV) is consistent with previously reported theoretical (4.08–4.11 eV, PBE) [47, 48] and experimental values (4.02 eV) [49]. The work function of BBP (4.14 eV) is similar to those in previous studies (4.14 eV, PBE [47]; 4.16 eV, PW91 [50, 51]). The work function of BBP increases from 4.14 eV (1-layer) to 5.69 eV (4-layer) and 5.66 eV (5-layer); that is, the work functions of multilayer BBP systems (2–5-layer) are higher than that of the monolayer BBP. Among the investigated multilayer BBPs, the work function of 2-layer BBP (4.79 eV) is similar
to that of graphene (4.60 eV) and the work functions of 3-, 4-, and 5-layer BBP systems (5.42, 5.69, and 5.66 eV, respectively) are higher than graphene by 17.8, 23.7, and 23.0%, respectively. The work functions of 4- and 5-layer BBP (5.66–5.69 eV) are similar to that of the frequently used Pt anode material (5.60 eV) [52]. Therefore, 2-layer BBP and 3–5-layer BBP can be utilized as alternative materials for graphene and candidates of anode materials for electric devices, respectively, particularly the highly stable 4- and 5-layer BBP with a high potential as a substitute material for Pt. One can experimentally prepare needed work function favorable multilayer BBP materials according to the evolution of the work function with the layer number of BBP.

![Graph showing work functions, Fermi levels, and vacuum energy levels of multilayer BBP systems.](image)

**Fig. 9.** Work functions ($\phi$), and Fermi ($E_F$) and vacuum energy levels ($E_{vac}$) of multilayer BBP systems.

Based on the work function definition, both the decrease in the $E_F$ and increase in the $E_{vac}$ contribute to the increase in the work function. To evaluate the proportion of the contribution of these two factors, the $E_F$ and $E_{vac}$ are shown in Fig. 9. The values of $E_F$ (orange bar) are obviously higher than those of $E_{vac}$ (green bar), indicating the predominant contribution of $E_F$ to the work function of the multilayer BBP. Moreover,
the reduction in $E_F$ (1.98 eV) relative to that of monolayer BBP predominantly contributes to the increase in the work function of multilayer BBP with an increasing number of layers, whereas the contribution of the $E_{\text{vac}}$ change (0.45 eV) is minor.

4. Conclusions

Herein, based on the initial exploration of the structural stabilities of the 1–3-layer $\alpha$-, $\chi_3$-, $\beta_{12}$-, $\delta_6$-, and $\delta_3$-borophene systems, we focused on geometries, stabilities, electronic structures, and work functions of the 1–5-layer $\alpha$-borophene systems using first-principles DFT calculations. The main conclusions are as follows:

(1) $\alpha$-Borophene exhibits the most favorable thermodynamic and kinetic stability among the five investigated 1–3-layer configurations. The interlayer bindings for 2-/3-layer $\alpha$- and $\delta_3$-borophene, and bilayer $\delta_6$-borophene are attributed to the covalent bond, while van der Waals interlayer interactions are confirmed for bilayer $\beta_{12}$- and $\chi_3$-borophene. In particular, mixed covalent bonds and van der Waals interlayer interactions are observed in the 3-layer $\delta_6$-borophene.

(2) AB-type stacking is the most thermodynamically favorable mode for 2–5-layer $\alpha$-borophene (BBP) systems, and they are all dynamically stable based on AIMD simulation results. As the number of layers increases (1–5), the BBP plane becomes increasingly relaxed, and the binding energy and interlayer binding energy both increase, indicating an enhanced interlayer interaction and thermodynamic stability.

(3) All multilayer BBP systems investigated herein are metallic, indicating that the increased layer number cannot open the BBP gap. The $p_z$ orbital plays a pivotal role in the Fermi states in 1–3-layer BBP systems, and the in-plane orbital also contributes considerable portions to the Fermi states in 4–5-layer BBP systems. As the layer number accumulates, the multi-centered bonding feature in in-plane B$_6$ and B$_7$
hexagons remains. Additionally, the covalent component reduces and the ionic component increases in interlayer B–B bonds for multilayer BBP systems; the interlayer interaction shifts from the covalent dominant bonding (2-layer) to mixed covalent and ionic bonding (5-layer) via ELF and bond population analyses. In the interlayer regions, isolated and scattered interlayer B–B bonds form in the 2- and 3-layer BBP; impressively, 5- or 6-centered localized bonds have been observed in 4- and 5-layer BBP, thus leading to the interconnected tubular structure with α-type boron nanotubes as the “motif,” which significantly enhances the interlayer bonding strength and stabilities of 4- and 5-layer BBP systems.

(4) The work functions of 2–5-layer BBP are higher than that of monolayer BBP, wherein the work functions of 2-layer BBP and 4- and 5-layer BBP systems are similar to those of graphene and the frequently used Pt anode material, respectively.

These predictions provide new insight into the stability and bonding nature of multilayer borophene structures and highlight the potential applications of these work function tunable materials in important nanoelectronic devices, thus inspiring the development of multilayer 2D boron nanomaterials.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org

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