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Flat Boron: A New Cousin of Graphene

*Sheng-Yi Xie, Yeliang Wang, and Xian-Bin Li**

The mechanical exfoliation of graphene from graphite provides the cornerstone for the synthesis of other 2D materials with layered bulk structures, such as hexagonal boron nitride, transition metal dichalcogenides, black phosphorus, and so on. However, the experimental production of 2D flat boron is challenging because bulk boron has very complex spatial structures and a rich variety of chemical properties. Therefore, the realization of 2D flat boron marks a milestone for the synthesis of 2D materials without layered bulk structures. The historical efforts in this field, particularly the most recent experimental progress, such as the growth of 2D flat boron on a metal substrate by chemical vapor deposition and molecular beam epitaxy, or liquid exfoliation from bulk boron, are described.

1. Introduction

Crystalline materials are important components of the physical world. Some crystalline materials, such as graphite, have very strong interactions in one plane, and very weak interactions in the third orientation, thus allowing these materials to form layered structures. Some other crystalline materials, which are more common, however, lack the anisotropy of bonding in orientations and favor the formation of 3D bonding structures. In 2004, Novoselov et al. experimentally obtained an atomically thin crystal, which was named “graphene” afterward, by the mechanical exfoliation of layered graphite.[1] Since then, 2D materials have gained huge research interest due to their unprecedented physical or chemical properties, which are usually absent in their bulk forms.[2] In addition to graphene, hexagonal boron nitride (h-BN),[3] transition metal dichalcogenides (TMDs),[4] black phosphorus,[5] MXene,[6] silicene,[7] germanene,[8] and stanene[9] have been successively realized in later experiments. With the increased members of the 2D materials family,[3–10] the question arises whether any crystalline materials, either having a layered structure or not, can be fabricated into 2D crystal.

The answer to this question would be yes for all layered materials, which only need to overcome weak van der Waals interactions between the adjacent layers. Additionally, the experimental synthesis of graphene has effectively built the paradigm for fabricating other 2D crystals, which also have layered bulk structures. As a neighbor of carbon in the periodic table, boron has a rich variety in chemistry and thus, forms more than ten bulk polymorphs, but none of them exhibit layered structures.[11] Consequently, the production of atomically thin flat boron crystals, or borophene, becomes a difficult experimental challenge. Almost within two decades of continual theoretical and experimental efforts since 2D flat boron (we define the strictly atomically thin 2D boron crystals as borophene, yet 2D flat boron extends to few-layers thin 2D boron crystals with certain thickness throughout the whole paper) was first proposed in 1997,[12] this challenge was finally overcome in recent experiments.[13] The experimental production of 2D flat boron, like that of graphene, has dramatically promoted the related research. As shown in **Figure 1**a, the number of published papers (searched with the key words “2D boron crystal” in the database of the Web of Science), has experienced a sudden increase since 2014 and 2015 when 2D flat boron was synthesized. The experimental production of 2D flat boron not only adds a new member with novel properties into the family of 2D materials, but also further builds a paradigm to synthesize other chemically or structurally complex 2D materials without any corresponding layered bulk forms. Some comprehensive reviews or perspectives,[14] with varying degrees of generality, have summarized the significant progress of this area. We refer the reader to the papers on the latest and rapid experimental progress on flat boron or metal-boron clusters.[14a–c,15] For 2D flat boron, three papers[14d–f] provide the profound understanding of the inherent chemical and structural variety, the fine tuning by the substrate, and the prospects for future research. More information about γ-icosahedral boron sheets can be gained from a recent review.[14g] However, the latest experimental progress[13c,d,16] achieved is not included in the above reviews due to the rapid development of this field.

Here, we retrospectively describe the milestones to realize 2D flat boron and, different from previous reviews, especially present a historical research review of this area. Starting from introducing the progress of boron clusters and theoretical proposals to realize 2D flat boron, we focus on the latest experimental efforts, including chemical vapor decomposition on a metal substrate, molecular beam epitaxy, and liquid exfoliation, to produce 2D flat boron. Additionally, the fascinating properties offered by borophene, such as Dirac fermions,

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superconductivity, topological properties, and energy applications, are discussed. Future potential applications of borophene and its inspiration to benefit other complicated 2D crystal production are discussed in the final section. Figure 1b chronologically illustrates the above related research works.

2. Planar Boron Clusters

The research of planar boron clusters or boron sheets starts from the pioneering work of Boustani.[12,17] By using density functional calculations (DFT) and quantum chemical methods, Boustani proposed a series of boron clusters composed of hexagonal pyramids to be quasi-planar.[12] He further suggested the construction of the quasi-planar boron surfaces, which are the embryonic form of the concept of 2D flat boron, to use the hexagonal pyramids of planar boron clusters as a basic unit. Additionally, he proposed the “Aufau principle” to construct relatively stable boron quasi-planar structures by hexagonal or pentagonal pyramids.[17a] In an experiment, the production of small boron clusters was reported in 1988,[18] yet the first spectroscopic confirmation of the structure did not come until 2002.[19] With the combination of photoelectron spectroscopy (PES) and ab initio calculations, the structures of B_5^- and B_5, as well as their electronic structures and chemical bonds, were deduced experimentally.[19] The PES, combined with ab initio calculations, provides the strong power to investigate the structures and bonding for clusters. By this means, immediately afterward in 2003,[20] Zhai et al. substantiated B_8^- and B_9^- to be perfectly planar molecular wheels with double (both σ and π) aromaticity.[20a] Furthermore, B_{11}^-, B_{12}^-, and B_{15}^- were proposed to be aromatic clusters while B_{13}^- and B_{14}^- were proposed to be antiaromatic clusters.[20b] After that, numerous boron clusters (B_{16}^-, B_{19}^-, B_{20}^-, B_{22}^-, and B_{23}^-) were also experimentally indicated to be planar.[21] In 2014, Piazza et al. discovered the planar B_{36}^- cluster with a central hexagonal hole, which provides the first indirect evidence of the experimental viability of 2D boron with hexagonal holes.[22] Hence, analogous to graphene, the word “borophene” was coined and accepted in this study[22] (a similar term “boraphene” was suggested earlier for the flat boron honeycomb layers[23]). Very quickly in the same year, Li et al. showed the B_{35}^- cluster, which contains a double hexagonal hole, to be a more flexible building block to construct borophene.[24] **Figure 2** displays the structures of the above planar boron clusters and more deeper understanding about these clusters can be gained from the recent comprehensive reviews.[14a–c] Apart from the wonderful planar clusters, other boron nanostructures such as boron rings and nanotubes have also been observed in experiments[25] and discussed in theory,[26] and further details about this area were summarized in a previous review.[27]

3. Theoretical Exploration of 2D Flat Boron Sheets

With increasing the size, boron clusters will transform from planar/quasi-planar to cage-like structures.[28] In 2007, Szwacki et al. creatively proposed the B_{80} buckyball[29] which is analogous with the structure as well as the symmetry of the well-known C_{60}. Interestingly, despite its metastability compared to some other proposed isomers,[30] unfolding the B_{80} in one plane will construct the famous boron α-sheet,[31] as elucidated in a later study.[32] Thus, the proposal of B_{80} helps to bridge the research between the boron clusters and 2D flat boron. The 2D flat boron exhibits very complicated structures due to the rich chemistry of boron. Graphene presents a honeycomb structure with carbon sp^2 hybridization to form three strong in-plane σ covalent bonds and one out-of-plane π bond. In contrast, boron lacks one electron, and thus, the honeycomb of boron is unstable because no electrons occupy the π bond. To adjust for the electron deficiency, the bonding mechanism

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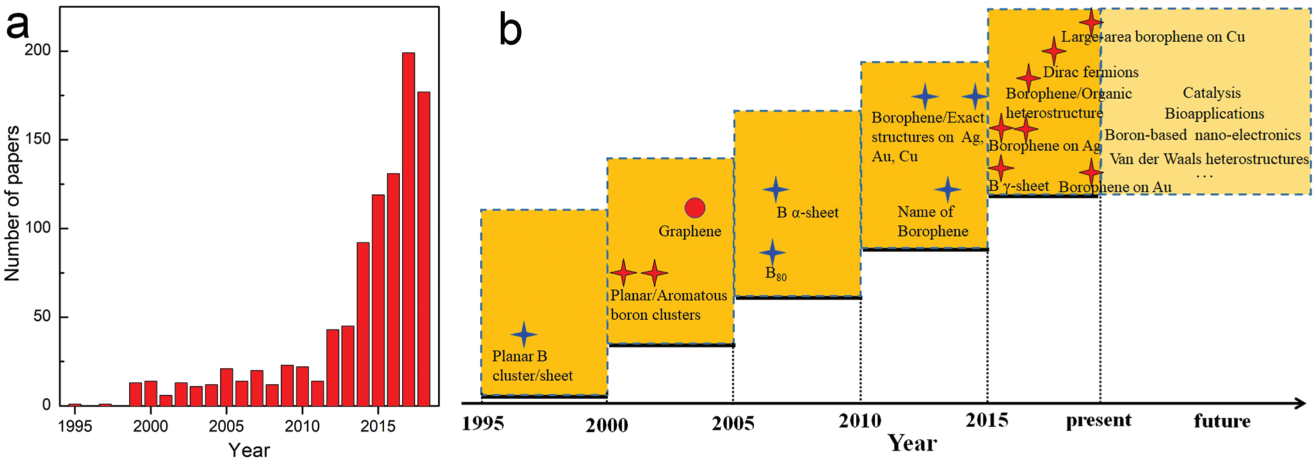

Figure 1. a) The number of papers with the keywords "2D boron crystal" searched in the Web of Science, Clarivate, in 2019. b) Breakthroughs in 2D boron research. Blue and red indicate theoretical and experimental investigations, respectively. The red circle marks the experimental production of graphene in 2004 as a reference.

of boron is changed. Besides ordinary two-electron-two-center bonds, boron also possesses multicenter bonds, in which three or more atoms share two electrons.[33] Thus, boron favors the formation of multicoordinated structures in bulk with the indication of a large challenge to fabricate boron into an atomically monolayered structure despite the efforts over the last two decades. To stabilize the boron monolayer, extra electrons are needed. Usually, there are two approaches to compensate for the electrons lacking in the boron honeycomb. First, Tang and Ismail-Beigi suggested that a combination of boron honeycomb motifs (which are electron-deficient) and boron triangle motifs (which are electron-excessive) provides a way to balance electrons and to stabilize the boron monolayer.[31a] By this means and the stimulation of the B_{80} buckyball, they predicted the boron α-sheet and shed light on the origin of its stability. With the help of crystal structure prediction method, numerous 2D boron structures[34] with different ratios and arrangements of boron vacancy in a triangle lattice, were proposed with competitive energy. This structural polymorphism,[35] in contrast with the specific honeycomb structure of graphene, is an intrinsic property of 2D flat boron. Moreover, 2D flat boron can also gain energy by the buckling[36] or forming layers within a certain thickness.[37] Second, an alternative way is that the deficient electrons can be supplied by a foreign substance such as metal layers[38] or metal substrates.[39] In 2013, using first-principles calculations, Liu et al. explored that borophene, strictly atomically thin 2D boron crystals, can survive to form on a metal substrate such as Cu, Ag, and Au or metal boride (MgB_2, TiB_2) substrates.[39] This study guided the subsequent experimental synthesis of borophene[13] because metal substrates not only support the deposition of boron atoms or clusters, but also provide the source of electronic balance,[38d] both of which are essential for the final production of borophene in experiments. In 2013, Zhao and co-workers proposed the growth picture of borophene from boron clusters on the Cu (111) surface.[40] They discovered that the formation energy of deposited boron clusters monotonically decreased with increasing cluster size, which is accompanied by the low diffusion barrier for a boron atom on Cu (111), to ensure the continuous growth of planar boron clusters. Moreover, the essential hexagonal holes, can facilely occur at the edge of planar boron clusters and then diffuse in, to help the growth of large-scale borophene.[13c] In 2015, using the cluster expansion method and the surface structure search method, Zhang et al. systemically studied the preferred possible structures of borophene on Au, Ag, Cu, and Ni substrates.[41] They indicated that metal substrates can lift the polymorphic energy degeneracy of isolated borophene and select a special one as the most favorable. As simply illustrated in **Figure 3**, the theoretical efforts over the past two decades, not limited to those mentioned above, helped to guild the final experimental production of 2D flat boron.

4. Experimental Synthesis

4.1. Growth of 2D Flat Boron by Chemical Vapor Deposition (CVD)

With more than a decade of intensive research, several methods have been considered to synthesize graphene. Mechanical exfoliation can produce very high quality freestanding graphene, which can be used to research the exotic properties of graphene in the laboratory. Chemical vapor deposition can grow large-area uniform graphene on a metal substrate and could be used in the future in the nanoelectronics industry. High quality graphene can also be produced by the SiC surface with thermal vaporization of Si atoms.[42] Additionally, liquid-phase exfoliation[43] or chemical exfoliation[44] can produce graphene with a low cost. However, experimental progress of true 2D flat boron was still rare until very recently, in comparation to the prosperous developments of theoretical simulations and predictions over a long period of time. Xu et al. tried a chemical vapor deposition method to grow 2D boron sheets.[45] They chose diborane as the boron source, which was then thermally decomposed in a furnace, and Si wafer as the substrate on which the boron atoms deposited and grew. The CVD experiment was performed under a pressure of 8 Pa and a temperature of 950°. The obtained boron nanosheet was single-crystalline with high quality and

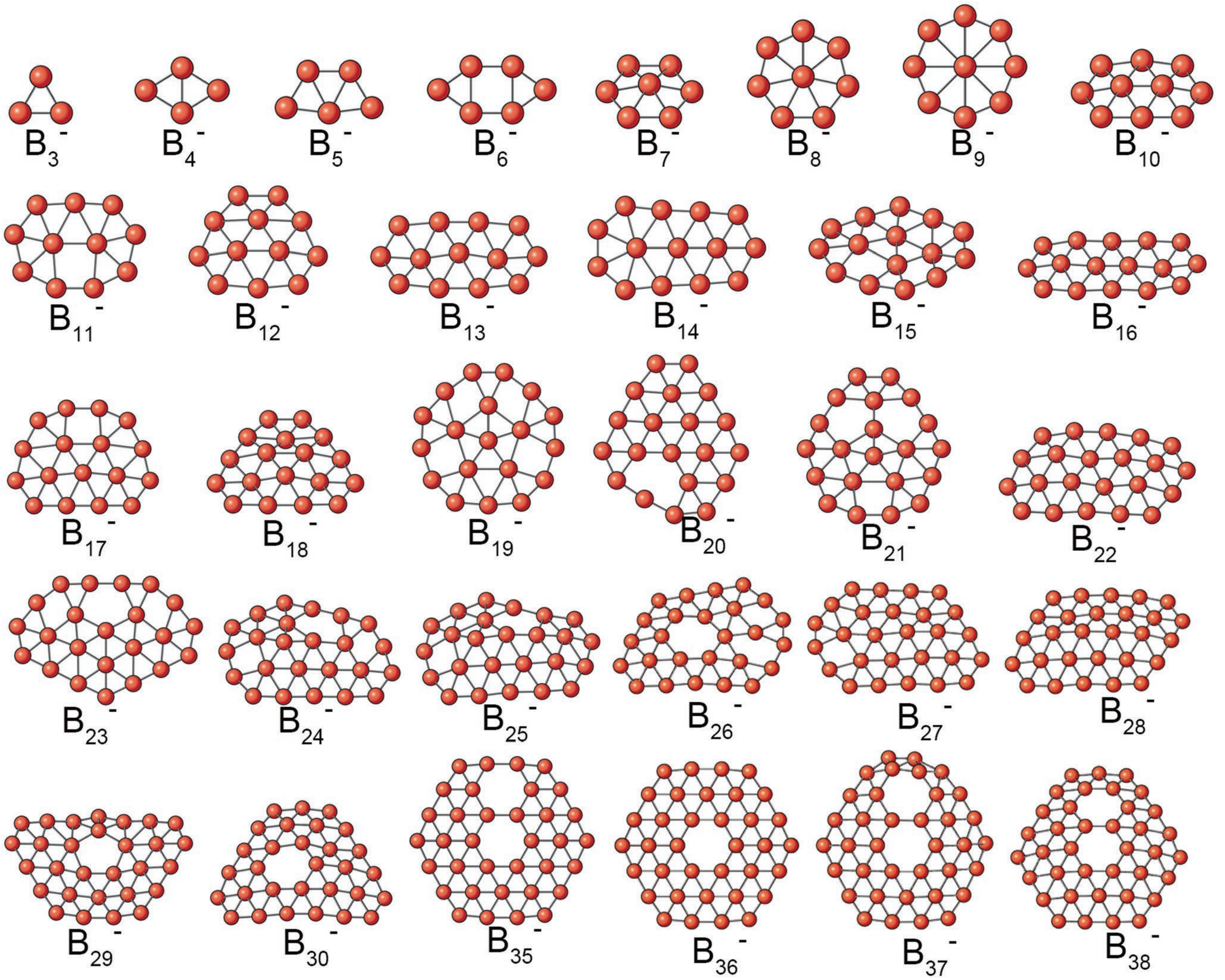

Figure 2. The structures of size-selected planar/quasi-planar boron clusters determined by photoelectron spectroscopy and first-principles calculations. Triangles of B_3 generally appear in all the boron clusters, but some tetragonal, pentagonal, and hexagonal holes appear with increased size. Reproduced with permission. Copyright 2017 Nature Publishing Group.[14a]

has the same crystal structure as the bulk α-boron,[45] verified by their high-resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAFD) patterns. The width of these boron sheets ranges from tens of nanometers to 3 µm and the length varies from 3 to 20 µm, as determined by scanning electron microscopy (SEM) images. However, the thicknesses of the boron sheets are still up to 10 nm, indicating that the sheets contain more than 20 atomic layers of bulk α-boron.[45] In their experiment, the Si wafer substrate is catalyst-free and has weak interactions with the deposited boron atoms, which causes the boron sheet to grow thick and favors the bulk α-boron structure. Moreover, the remained dangling bonds on the Si substrate may limit the size of the boron sheet from growing large. In addition, the diborane may introduce the doping of hydrogen into the boron sheets, which may be the origin of their boron sheets displaying the transport behavior of an intrinsic p-type semiconductor, as the role of hydrogen in other semiconductors.[46]

To decrease the thickness, Tai et al. further developed the CVD method and synthesized thin boron films on Cu foil,[47] as illustrated in **Figure 4**a. In their experiment, boron powder and boron oxide (B_2O_3) were taken as the sources and were reacted at temperatures up to 1100° to form vaporized B_2O_2 molecules, which then were deposited on the Cu substrate and further reduced by introducing H_2 gas to gain the desirable 2D boron sheet. During the process, they found that proper low-pressure conditions ranging from 18 to 100 Pa were necessary to facilitate the growth of the 2D boron sheet. The size of the produced boron sheet reaches up to 2×3 cm^2, and the thickness decreases to only 0.8 nm, as determined by the atomic force microscopy (AFM) images. By the HRTEM technique, the atomic structure of the boron sheet was assigned to be the complex orthorhombic γ-B_{28} cell composed of icosahedral B_{12} units and B_2 dumbbells,[47] as shown in Figure 4b. Here, the Cu foil served both as the catalyst (to accelerate the reaction of B_2O_2 with H_2) and the substrate (to support the growth of the

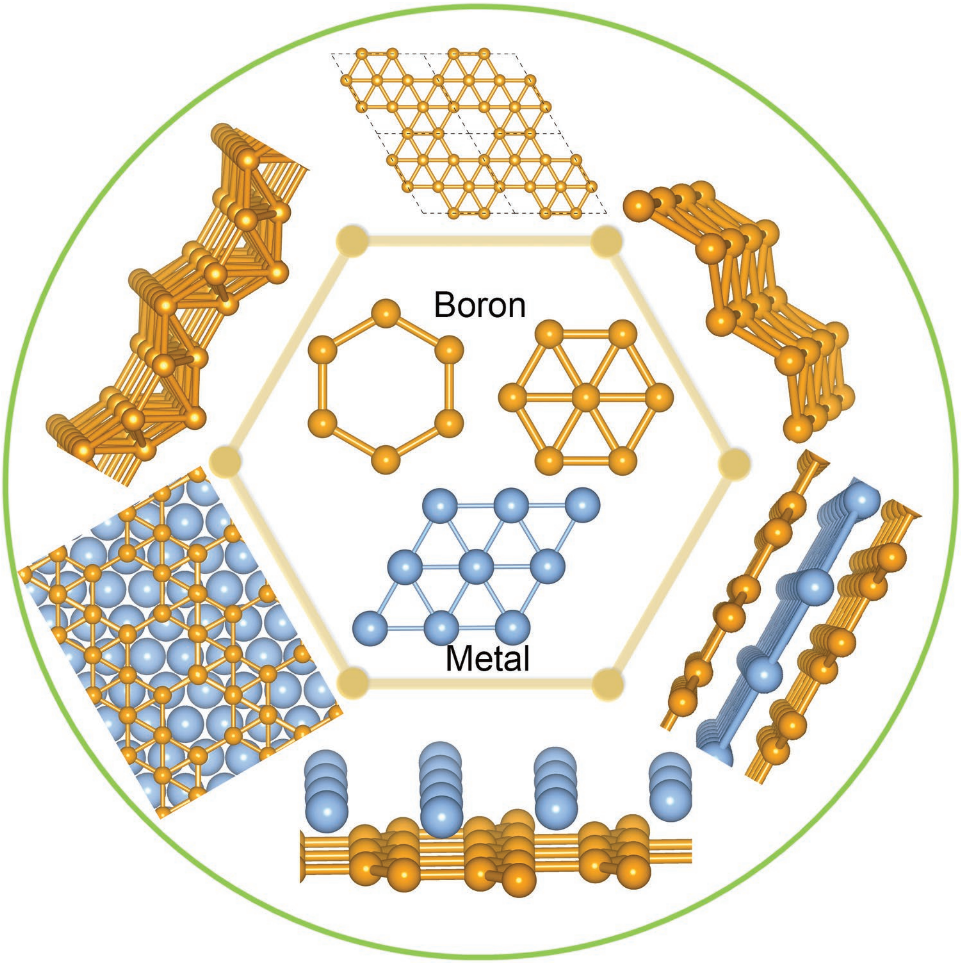

Figure 3. Theoretical sketch of the stabilization of 2D boron sheets and their structures. Boron honeycomb with typical two-center bonds combined with boron triangle motifs with multicenter bonds are the basic building blocks for the 2D boron sheet.[31a] The boron honeycomb lacks electrons, whereas the boron triangle motif has additional electrons, and the mixing of the two shapes in a proper ratio stabilizes the boron sheet.[31a] Moreover, boron sheets can achieve lower energy through buckling[36a] or the formation of multilayers.[14g,51a] Finally, metals can serve as both the electron donor[38b,c] and the substrate[41] to stabilize the 2D boron sheets.

boron sheet). In contrast to the Si wafer, the Cu substrate can effectively increase the interaction with the deposited boron, and thus, the boron sheet has the γ-B_{28} structure instead of bulk α-boron structure as in the experiment of Xu et al.[45] Interestingly, the obtained boron film can be easily transferred to a SiO_2/Si substrate through dissolving the Cu substrate, suggesting that the γ-B_{28} sheet is chemically stable and may survive in a freestanding form. Additionally, the γ-B_{28} sheet is expected to have a promising direct bandgap up to 2.25 eV (estimated from the optical bandgap measurement, see Figure 4c) or 2.07 eV (determined by first-principles calculations). Thus, the γ-B_{28} sheet will serve as a competing candidate in future nanoelectronics and nanodevices. A more detailed description of the γ-B_{28} sheet was summarized in a recent review.[14g]

4.2. Growth of 2D Flat Boron by Molecular-Beam Epitaxy (MBE)

However, the two experiments above did not fill the gap of realizing strictly atomically thin boron layer analogous to graphene. In 2015, Mannix et al. adopted a molecular-beam epitaxy method to grow a true atomic layer of 2D boron (or borophene) on a silver substrate under ultrahigh vacuum conditions (smaller than 5×10^{-8} Pa).[13a] They used an electron beam evaporator to deposit boron atoms from a very pure boron source (99.9999%) on the atomically clean Ag (111) substrate, as illustrated in **Figure 5**a. The high temperatures from 450° and 700° were helpful for the growth of borophene in their experiment. By using high-resolution scanning tunneling microscope (STM) techniques, two distinct boron phases including a homogenous phase and a more corrugated stripped phase were also unfolded.[13a] Both the deposition rate and annealing temperature were altered to tune the relative concentrations of the two phases. A low deposition rate favors the formation of the stripped phase while a high deposition rate facilitates the formation of the homogenous phase. By ab initio crystal structure searching method, the crystal structure of the stripped phase was proposed to be an anisotropic buckled sheet with a rectangular unit cell (space group: *Pmmn*), as shown in Figure 5b, matching with the experimental STM images. However, the

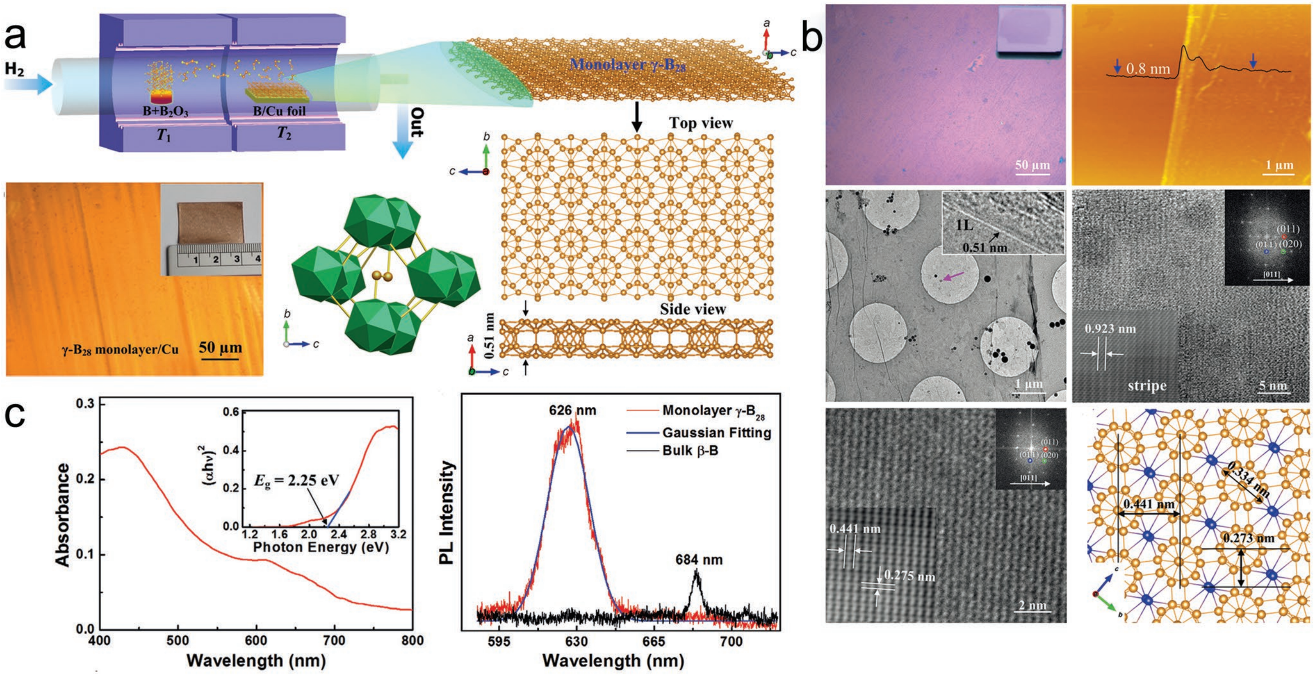

Figure 4. Experimental synthesis of a thin 2D γ-B_{28} sheet (0.8 nm in thickness) by CVD on a Cu substrate. a) Schematic of the growth process, optical image of the obtained sheet, and the basic polyhedral structure and atomic structure of the γ-B_{28} sheet. b) Experimental characterization of the γ-B_{28} sheet on a SiO_2/Si substrate demonstrated with optical, AFM topographical, TEM, and HRTEM images. c) Optical bandgap and photoluminescence spectral measurements of the monolayer γ-B_{28} sheet. Reproduced with permission. Copyright 2015 Wiley.[47]

detailed crystal structure of the homogenous phase remains unsolved, although some boron chains clearly appear in the STM images. The cross-sectional aberration-corrected scanning transmission electron microscopy (AC-STEM), verifies that the stripped phase is atomically thin, as shown in Figure 5c. Furthermore, the scanning tunneling spectroscopy (STS) shows the metallic conduction characteristics of the two phases of borophene, as shown in Figure 5d.

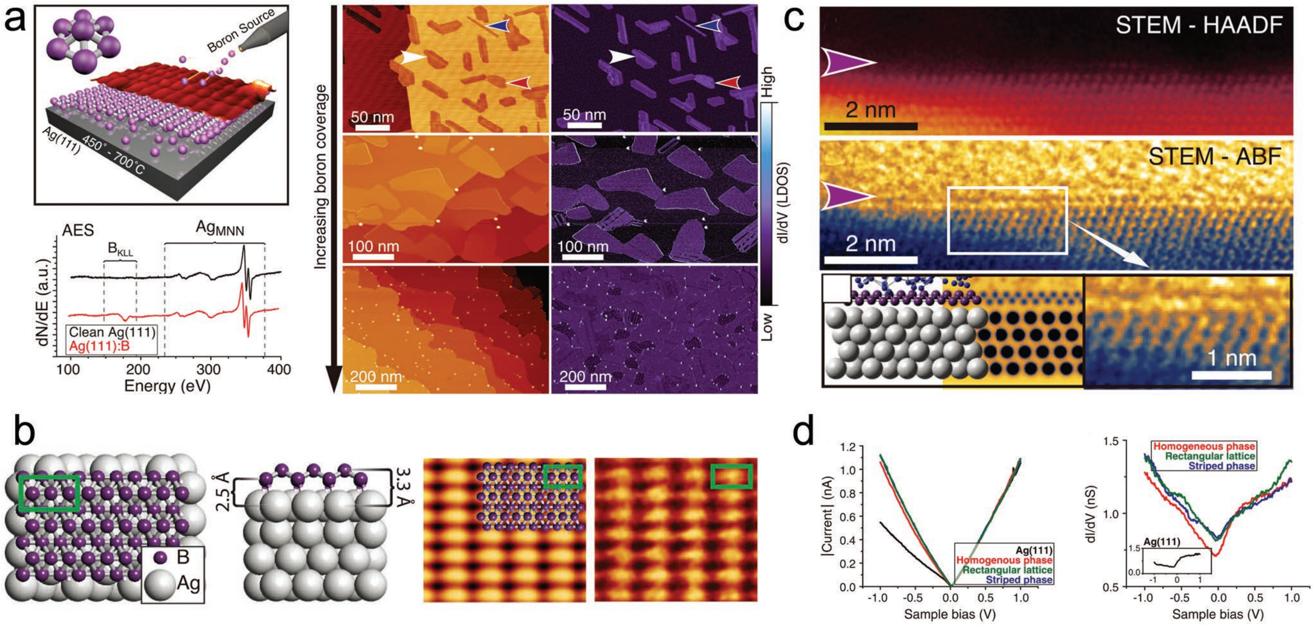

Figure 5. Experimental formation of borophene on a Ag (111) substrate by MBE epitaxial growth performed at Argonne National Laboratory. a) Growth schematics and experimental characterization of borophene by Auger electron spectroscopy and STM. b) Simulated borophene structure and related STM images obtained through first-principles calculations. c) Experimental characterization of the structure of borophene by aberration-corrected scanning transmission electron microscopy. d) Scanning tunneling spectroscopy of borophene. Reproduced with permission. Copyright 2015 American Association for the Advancement of Science.[13a]

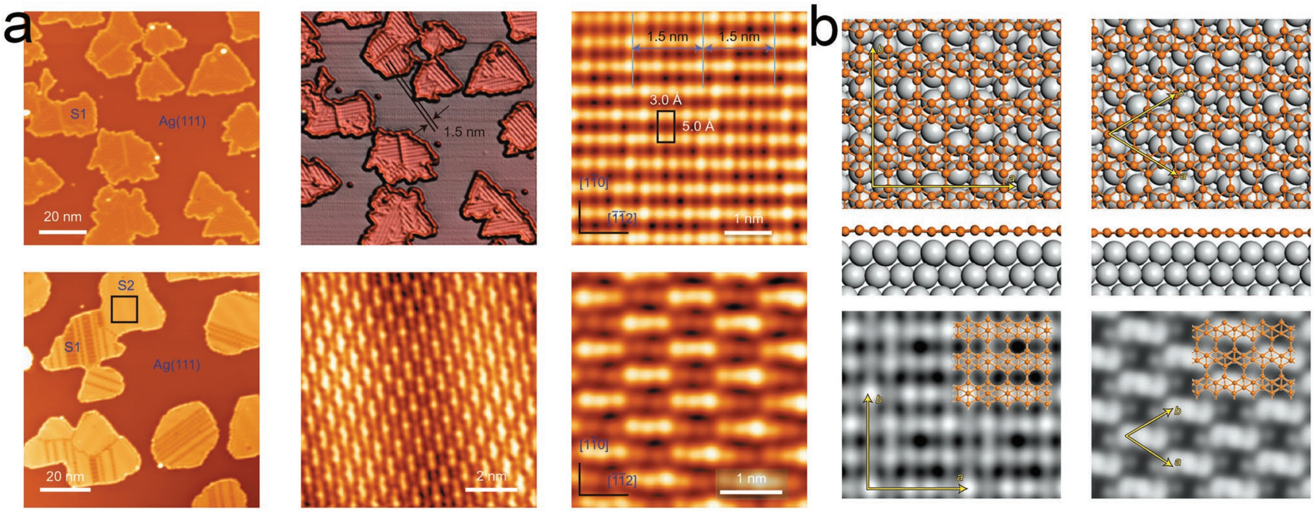

Figure 6. Experimental realization and related structural characterization of borophene on a Ag (111) substrate by MBE epitaxial growth performed at the Institute of Physics, CAS. a) Experimental STM images of boron structures on a Ag substrate. Two phases (S1 phase in the top panel and S2 phase in the bottom panel) are obtained with annealing temperatures of 570 and 650 K, respectively. b) The atomic structures and related simulated STM images of the two phases (S1 and S2 phases are shown in the left and right panels, respectively) of borophene on the Ag substrate, determined by first-principles calculations. Reproduced with permission. Copyright 2016 Nature Publishing Group.[13b]

Independently, almost at the same time, Feng et al. reported another MBE epitaxial growth of borophene on a Ag (111) substrate under ultrahigh vacuum conditions (6×10^{-11} Torr, or 8×10^{-9} Pa).[13b] The growth temperature is very critical for the structure of borophene. Below 500 K, only some boron clusters or disordered structures appear on the Ag surface. As the temperature increases to 570 K, boron monolayer islands start to form in order, as shown in the top panel of **Figure 6**a. Through the high-resolution STM study and first-principles calculations, the observed monolayer structure (defined as the S1 phase in their report) is proposed to be the β_{12} sheet, as predicted by theory.[41] By continually annealing the sample at temperatures up to 650 K, part of the S1 phase will transform to another phase called the S2 phase with a χ_3 structure[34a] (see the bottom panel of Figure 6a). The observed S2 phase can also be directly realized by increasing the substrate temperature above 680 K during the growth. The atomic models of the S1 and S2 phases are shown in Figure 6b. Here, both the studies of Mannix et al.[13a] and Feng et al.[13b] mainly used STM studies as well as first-principles calculations to determine the structures of borophene on the Ag (111) substrate. However, more experimental efforts (direct or indirect) should be undertaken. For example, the experimental STM images for the stripped phase in the work of Mannix et al. and the S1 phase in the work of Feng et al. are very similar, and the unit cells of the two phases derived from the images are also very close (both are rectangular cells, $a = (5.1 \pm 0.2)$ Å, $b = (2.9 \pm 0.2)$ Å for Mannix's study; $a = 5$ Å, $b = 3$ Å for Feng's study). Despite (at first glance) the agreement between the first-principles calculations and STM images for the two works, further experimental techniques should still be undertaken to reconfirm the structures, considering the multitude of phases with close energies and structures in previous predictions.[35] Feng et al. also evaluated the chemical stability of borophene on a Ag (111) substrate that was exposed to air by an XPS study.[13b] Approximately 20% of boron atoms were oxidized under a coverage of 0.7 monolayer, indicating the chemical stability and that the transfer from the metal substrate of borophene still faces challenges. In this sense, the γ-B_{28} sheet[47] is better since it was successfully transferred from Cu foil to a Si substrate. However, from the view of the synthesis of 2D materials, the two parallel experiments by Mannix et al.[23] and Feng et al.[24] have gained great success because they both produced strictly atomically thin 2D boron sheets. This marks a milestone to synthesize chemically or structurally complex 2D materials without corresponding layered bulk forms. For the two experiments,[13a,b] the substrate and growth temperature are two crucial factors to produce the borophene. In fact, the single-crystal Ag (111) substrate provides an atomically smooth platform to facilitate the growth of borophene. More importantly, the interaction between the Ag substrate and boron is appropriate, which not only suppresses growth into 3D form but also benefits the annealing on the substrate to form flat boron due to a small boron diffusion barrier.

The crystal domains of borophene grown on the Ag (111) surface in the above two experiment are still limited to nanoscale sizes, which are too small for future device fabrication, Wu et al. most recently reported the production of large-area borophene up to 100 µm^2.[13c] They grew borophene on a single-crystal Cu (111) surface in an ultrahigh vacuum (2×10^{-10} Torr or 2.67×10^{-8} Pa) Low-energy electron microscopy (LEEM) system augmented with an MBE capability to realize the real-time monitoring of in situ growth. Notably, they cleaned the Cu surface by repeated cycles of argon ion sputtering and postannealing at 870 K to produce a clean and broad terrace on the Cu surface, on which they grew borophene at the temperature of 770 K. As shown in **Figure 7**a, the domain length of borophene along the terrace direction can exceed 10 µm, yet the domain width is limited to the terrace width (≈1–3 µm). Figure 7b reveals the structure of borophene on the

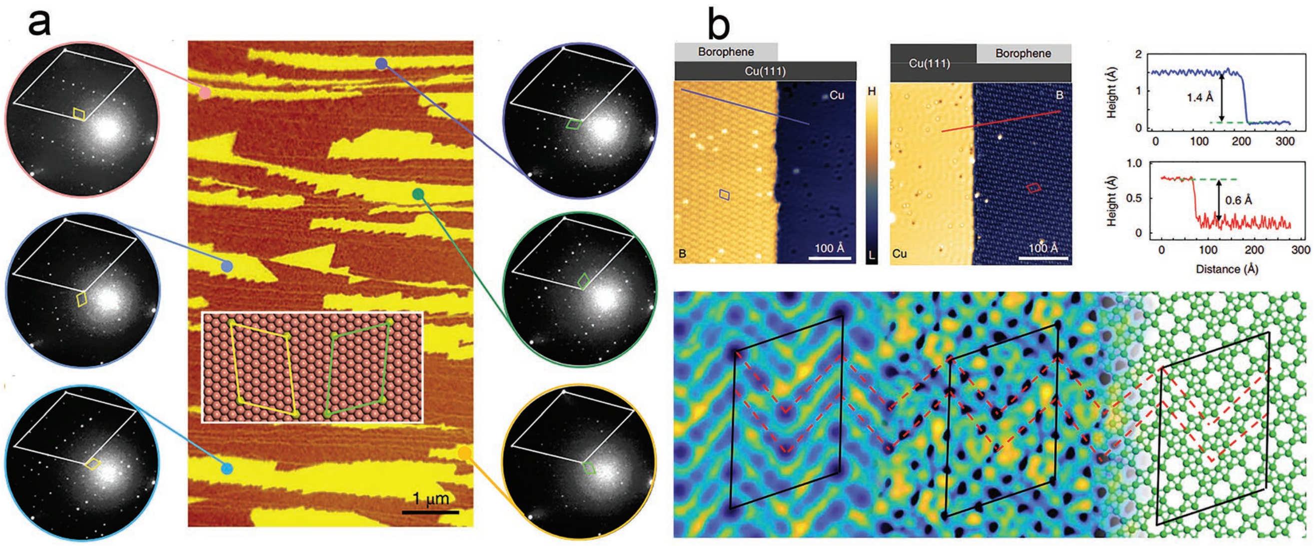

Figure 7. Experimental production of borophene on a Cu (111) substrate by MBE performed at Yale University. a) Domain structure of borophene. The middle panel shows a bright-field LEEM image of borophene (yellow area) on the Cu surface. The left and right panels show selected-area LEED patterns of borophene with two types of unit cells in a mirror symmetry (see the inset). b) The atomic model of borophene on Cu (111). The top panel shows STM images and the height of the profiles for two borophene–Cu step edge stacking styles. The bottom panel shows experimental (left) and theoretical (middle) ultrahigh-resolution STM data and the atomic structure (right) of borophene. Reproduced with permission. Copyright 2019 Nature Publishing Group.[13c]

Cu (111) surface by experimental STM and DFT simulations. Although the observed borophene has a much larger unit cell (21.84 Å × 15.96 Å), the experimental results generally coincide well with previous theoretical findings[40,41] ($\eta = 1/6$ for theory[41] and $\eta = 1/5$ for this experiment;[13c]z undulation of 0.3 for theory[41] and 0.43 for this experiment;[13c] the growth of large-area borophene as predicted[40,41]). Interestingly, the phase of borophene on the Cu surface, despite with different chirality and rotations (Figure 7a), is unique and can be preserved from 760 to 5 K, in contrast with the two competing phases (β_{12} and χ_3) of borophene on Ag (111). As suggested by precious theoretical work,[41] Cu (111) surface has a strong interaction with borophene and thus, helps to remove the degeneracy of the polymorphous borophene, which should be one significant reason for the experimental large-area growth of borophene. Subsequently, Kiraly et al. synthetized borophene on a Au (111) surface.[13d] Distinct from the direct deposition of boron on Ag or Cu surfaces, the formation of borophene on the Au surface occurs via two steps: boron atoms first dissolve into bulk Au at a temperature of 823 K and then segregate to the surface to form the borophene during the cooling of the substrate, as revealed by their first-principles calculations and time-of-fight secondary ion mass spectrometry. Like that grown on Ag (111), the obtained borophene on Au (111) is still limited to a nanoscale size, which requires more experimental attempts to be scaled up.

Very interestingly, in 2018, a very attractive honeycomb structure of borophene, was successfully prepared on an Al (111) surface with the MBE technique.[48] The large electron transfer from the Al surface and the strong interaction between the boron sheet and the substrate are considered to be significant to stabilize the honeycomb structure, as theoretical works predicted.[49] The production of boron honeycomb structure indicates that plenty of 2D boron structures can be prepared via controlling the interaction with metal substrates. In addition, recently Zhong et al. synthesized borophene nanoribbons on a Ag substrate also by the MBE method.[50] In the experiment, they used a Ag (110) surface, instead of a Ag (111) surface, as the substrate and produced four types of nanoribbons (χ_3, β, β_8, and β_{12}).[34a]

4.3. Growth of 2D Flat Boron by Liquid Exfoliation

The synthetic methods in the above experiments, including CVD and MBE, require some severe conditions such as high temperature or/and ultrahigh vacuum, which limit the massive and low-cost production required for industrial applications. Very recently, Li et al. reported the production of 2D boron sheets by sonication-assisted liquid-phase exfoliation at room temperature.[16] They used boron powder dissolved in dimethylformamide (DMF) and isopropyl alcohol (IPA) (see the fabrication process in **Figure 8**a). The thickness and size of the boron sheets can be controlled by changing the exfoliating solvent type and centrifugation speed. The average thickness and area for the DMF-exfoliated boron sheets are ≈1.8 nm (4 boron layers) and 20 000 nm^2, in contrast with the IPA-exfoliated boron sheets, which have a thickness and area of 4.7 nm (11 boron layers) and 1800 nm^2. The obtained boron sheets have a well-defined crystal structure of β-rhombohedral boron according to the HRTEM images shown in Figure 8b,c, and they show a wide optical bandgap up to 4 eV. These boron sheets show excellent performance for use as supercapacitor electrode materials. However, the mechanism of the exfoliation of the boron sheets from the covalent connections in bulk boron is still unclear at present. It deserves additional experimental and theoretical efforts to uncover this mystery.

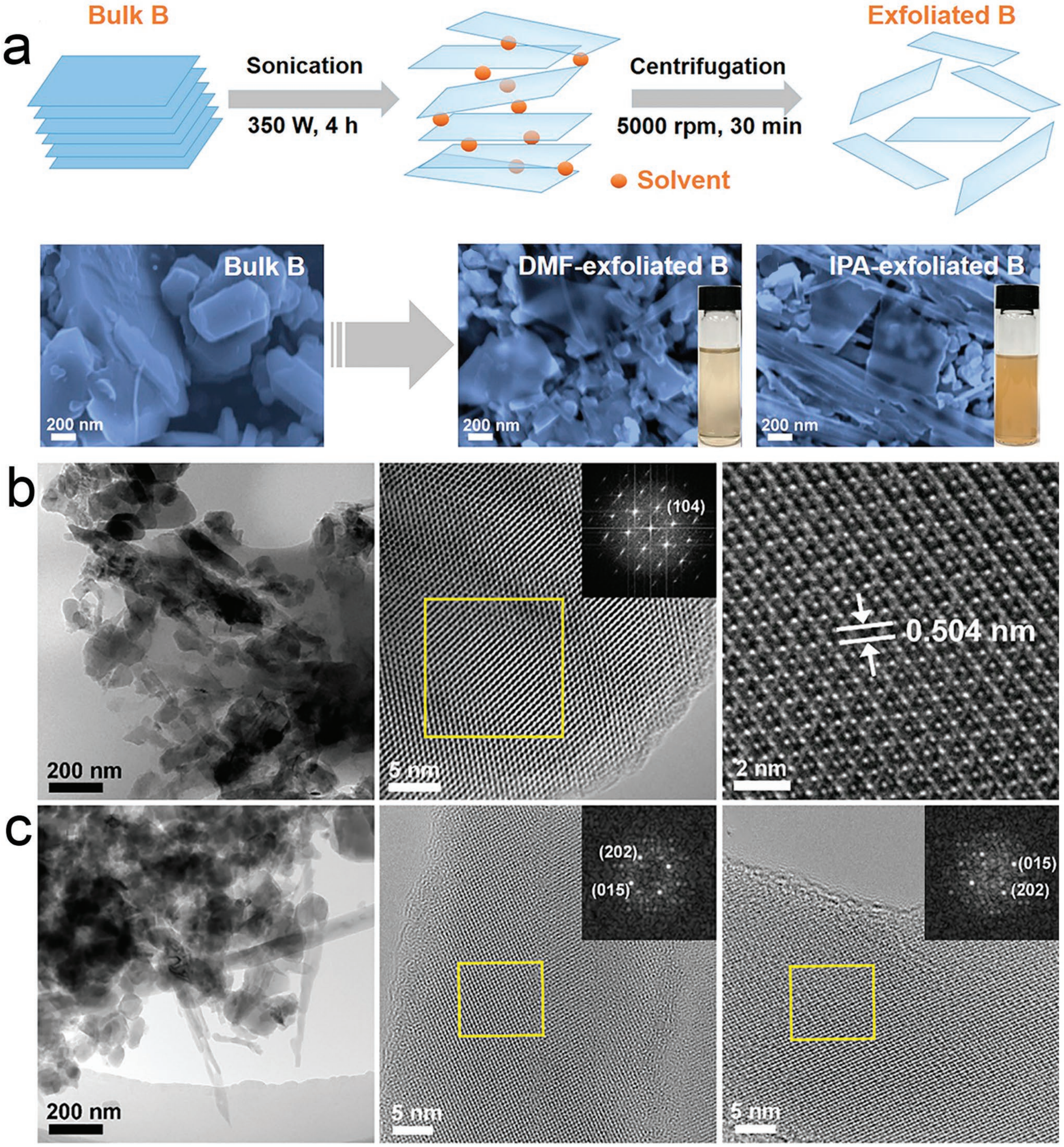

Figure 8. a) Schematic diagram of sonication-assisted liquid-phase exfoliation of few-layer boron sheets for possible mass production. (b) and (c) show typical TEM images of the obtained boron sheets prepared in DMF and IPA solvents, respectively. The insets in (b) and (c) are the related FFT patterns for the chosen areas. Reproduced with permission. Copyright 2018 American Chemical Society.[16]

5. Properties and Applications of 2D Flat Boron

Many exotic properties of borophene have been predicted in theory, yet the experimental confirmation of these properties is critical at this stage. Dirac fermion behavior is one of the outstanding properties for borophene that was proposed by theoretical predictions.[51] With angle-resolved photoemission (ARPES) measurements, Feng et al. have carefully investigated the β_{12} borophene sheet structure and found that this boron sheet can be decomposed into two triangular sublattices to hold the Dirac cone band structures.[52] The Dirac cones appearing in the β_{12} borophene sheet are split into pairs due to

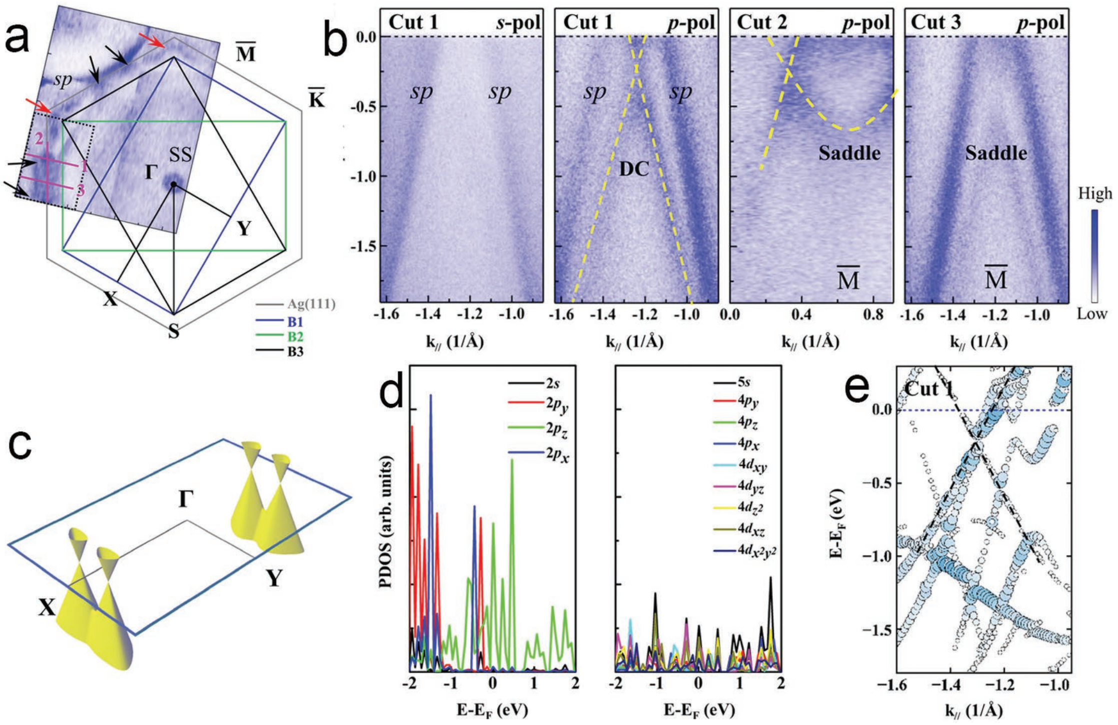

Figure 9. Band structures for β_{12} borophene on Ag (111). a) Fermi surface for the β_{12} boron sheet on Ag (111) system. b) ARPES intensity plot measured with different slices along the route of (a). c) Schematic of the Dirac cones in the Brillouin zone. d) Calculated PDOS of B and Ag atoms and the e) band structure for β_{12} borophene on the Ag surface. Reproduced with permission. Copyright 2017 American Physical Society.[52a]

the interaction between the boron layer and Ag (111) substrate. They also found that Dirac cone features can arise in lattices with large unit cells. The Fermi surface of the β_{12} borophene/Ag (111) measured by ARPES is shown in **Figure 9**a. Furthermore, in Figure 9b, they used ARPES with s and p polarized light along different cuts in the Brillouin zone to verify the Dirac fermions of the system of the borophene/Ag (111). The related schematic drawing of the Dirac cones in the system is shown in Figure 9c. First-principles calculations also confirm the experimental results of the Dirac fermions (see Figure 9d,e). This work not only verifies the topological property of borophene, but also strengthens the identification of the atomic model of β_{12} borophene apart from the previous STM images.[24]

Since electronic devices and systems require the integration of multiple materials with well-defined interfaces, it is therefore of high interest to identify chemical methods to form atomically abrupt heterostructures between borophene and electronically distinct materials. Recently, Liu et al. demonstrated the self-assembly of lateral heterostructures between borophene and an organic molecule PTCDA.[53] The process was also proven by their molecular dynamic (MD) simulations. They further used in situ X-ray photoelectron spectroscopy to confirm the weak chemical interaction between borophene and PTCDA. In addition, an electronically abrupt interface was revealed by molecular-resolution ultrahigh vacuum STM and STS (see **Figure 10**a). The lateral heterostructure is schematically shown in Figure 10b, which is also proven by the measurement of high resolution STM images as illustrated in Figure 10c. This borophene/PTCDA heterostructure forms a metal/semiconductor lateral heterojunction and could be used for future nanoelectronics.

In addition to the Dirac fermions and device-like heterostructures, other novel properties and applications of borophene have also been continually uncovered. Zhang et al. found that the intrinsic resistivity of borophene could be easily tuned by adjusting the carrier density.[54] Penev et al. reported the phonon-mediated superconductivity of borophene with a critical transition temperature T_c of ≈10–20 K,[55] which is close to the case of the lithium-intercalated graphene.[56] The mechanical properties of 2D boron sheets have been predicted to rival those of graphene.[57] 2D boron sheets have also been proposed to be applied for visible plasmonics according to their high free charge carrier concentration of the metallic phases.[58] Moreover, one kind of 2D boron has been predicted to have antiferromagnetic properties.[59] The novel properties shown by 2D flat boron, including superconductivity,[55,60] topological properties,[51,61] and magnetism,[59] as well as its application in energy storage,[16] make it a competitive candidate for future nanodevices.

6. Conclusion

Since Boustani et al. first proposed planar boron clusters in 1997, many significant research efforts have attempted to realize 2D flat boron over the last two decades. **Table 1** lists some chosen representative research works of flat boron during this period. In the beginning, researchers mainly cared about the clusters. The successful production of graphene in 2004,[1] however, stimulated the interests in 2D flat boron sheets. After that, numerous theoretical studies[31a,34a,35,39,51a] investigated

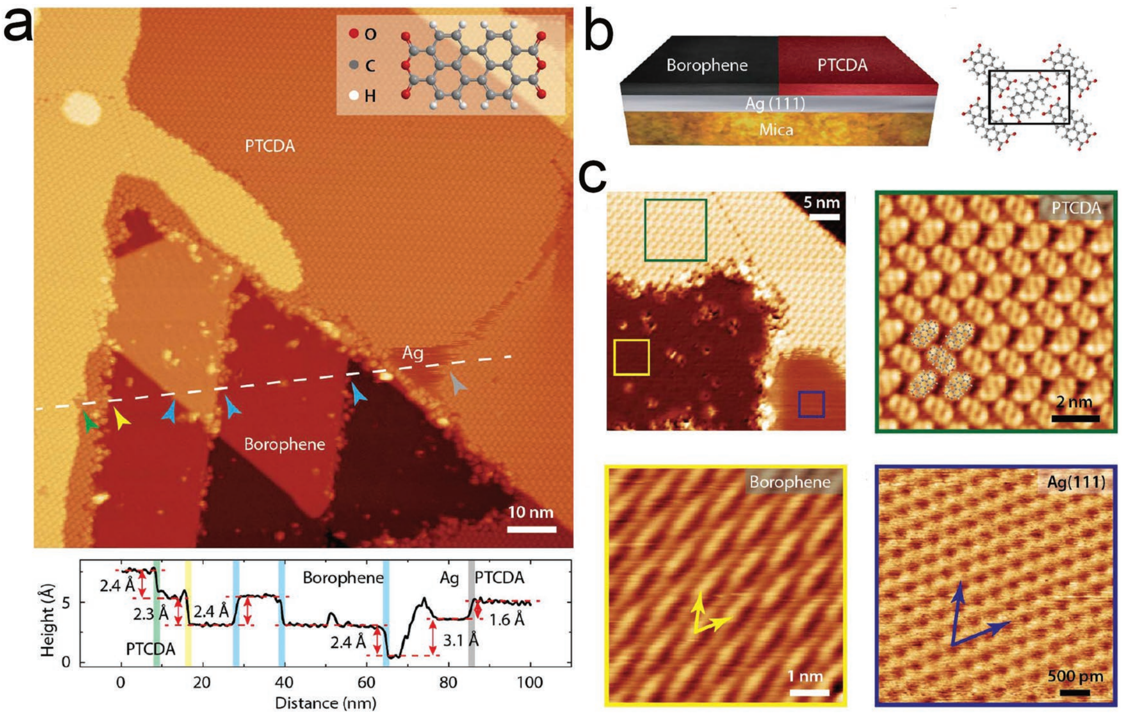

Figure 10. Prototype device: borophene/organic lateral heterostructure. a) STM image of a borophene/organic lateral heterostructure and a cross-sectional profile along the dashed white line. b) Schematic of the borophene/organic lateral heterostructure and the unit cell of the organic crystal structure. c) High-resolution STM image of the borophene/organic lateral heterostructure with feature positions. Reproduced with permission. Copyright 2017 American Association for the Advancement of Science.[53]

Table 1. Some representative research works of flat boron or borophene for the past two decades.

Year	Main affiliation	Finding	Method
1997	Bergische University, Germany	Proposal of planar boron clusters, idea of boron sheet,[12] and "Aufbau principle"[17a]	DFT
2002	Washington State University, USA	First spectral experiment on the structure of boron cluster[19]	PES and DFT
2003	Washington State University, USA	Discovery of the planarity and aromaticity in small boron clusters[20a]	PES and DFT
2007	Rice University, USA	Proposal of the B_{80} fullerene[29]	DFT
2007/2008	Yale University, USA/Tsinghua University, China	Proposal of the 2D boron α-sheet:[31] unfolded B_{80} in a plane	DFT
2013	Rice University, USA	Prediction of the synthesis of borophene on Ag, Au, and Cu surfaces[39]	DFT
2013	Dalian University of Technology, China	Proposal of the growth mechanism of borophene from boron clusters on Cu (111)[40]	DFT
2014	Brown University, USA	Synthesis of B_{36}^{-} with a hexagonal hole and proposes the name of borophene[22]	PES and DFT
2015	Rice University, USA	Prediction of the detailed borophene structures on Ag, Au, Cu, and Ni surfaces[41]	DFT
2015	Huazhong University of Science and Technology, China	Synthesis of single-crystalline ultrathin boron nanosheets to be fabricated into photodetector devices[45]	CVD growth on silicon wafer
2015	Nanjing University of Aeronautics and Astronautics, China	Synthesis of γ-B_{28} sheet[47]	CVD growth on Cu foil
2015/2016	Argonne National Laboratory, USA/Institute of Physics, China	Synthesis of borophene on Ag[13a,b]	MBE on Ag (111)
2017	The University of Tokyo, Japan	Discovery of the Dirac fermions in borophene[52a]	ARPES and DFT
2017	Northwestern University, USA	Production of borophene/organic lateral heterostructure[53]	PES and MD
2018	Nanyang Technological University, Singapore	Scalable production of few-layer boron sheets[16]	Liquid-phase exfoliation
2019	Yale University, USA	Synthesis of large-area (100 μm^2) single-crystal borophene on Cu[13c]	MBE on Cu (111)
2019	Argonne National Laboratory, USA	Synthesis borophene on Au[13d]	MBE on Au (111)

the possible crystal structures and proposed strategies to synthesize the 2D flat boron sheets. The final experimental realization, progressing from a few layers[45,47] to an atomically thin layer,[13a,b] greatly spurred the research, and many corresponding papers were published at that time. The growth of 2D flat boron by CVD[32,33] and MBE[13a,b] methods marks a milestone for the synthesis of 2D materials. The successful synthesis of 2D flat boron, accompanied by the fabrication of other 2D crystals without a layered bulk form, such as hafenene[62] and 2D GaN,[63] opens a door for the willful synthesis of 2D materials via controlling the complicated chemistry of materials. These results indicate that any element in the periodic table and any compound could also be possibly fabricated into 2D forms. Besides the synthesis area, a recent experiment showed the electronic properties of borophene can be tuned by line defect.[64] In the future, whether all-boron electronics could be realized in a manner similar to all-carbon electronics, should be explored. Additionally, the fundamental research within these physical platforms and the potential applications in energy, catalysis, or biology also deserve great theoretical, experimental, and industrial efforts focusing on this brand-new 2D flat boron, a new cousin of graphene.

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Note: Referring to the work in ref. [13c], described on page 7, the temperature for gowth of borophene in the following sentence was corrected on September 3, 2019 after initial publication online:

“Notably, they cleaned the Cu surface by repeated cycles of argon ion sputtering and postannealing at 870 K to produce a clean and broad terrace on the Cu surface, on which they grew borophene at the temperature of 770 K.”

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, borophene, borophene synthesis

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