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Boron based two-dimensional crystals: theoretical design, realization proposal and applications

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The successful realization of free-standing graphene and the various applications of its exotic properties have spurred tremendous research interest for two-dimensional (2D) layered materials. Besides graphene, many other 2D materials have been successfully produced by experiment, such as silicene, monolayer MoS₂, few-layer black phosphorus and so on. As a neighbor of carbon in the periodic table, element boron is interesting and many researchers have contributed their efforts to realize boron related 2D structures. These structures may be significant both in fundamental science and future technical applications in nanoelectronics and nanodevices. In this review, we summarize the recent developments of 2D boron based materials. The theoretical design, possible experimental realization strategies and their potential technical applications are presented and discussed. Also, the current challenges and prospects of this area are discussed.

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Introduction

With a simple arrangement of carbon atoms in a 2D honeycomb lattice, graphene has attracted large research interest

since it holds many exotic and superexcellent properties which are rare in other materials.^{1–3} Graphene has ultrafast carrier transport ability,^{4–6} excellent optical transmittance,⁷ high Young's modulus⁸ and thermal conductivity.⁹ Based on these extraordinary properties, applications based on graphene in many areas have been investigated, including high-speed transistors,^{10,11} transparent electrodes,¹² optical devices,¹³ and sensors,¹⁴ and energy generation and storage.^{15,16} The fundamental research interest and application prospect aroused by graphene also encouraged people to explore other 2D materials beyond graphene. As an isoelectronic system with graphene, 2D BN was successfully prepared by experiment on

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a large scale and used in many areas.^{17,18} Further, as the congeners of carbon, silicon and germanium also can be produced in 2D forms with the help of substrates.^{19–22} Recently, transition metal dichalcogenides, as a typical example of MoS₂,^{23,24} have been experimentally realized in monolayer structures. Few-layer black phosphor has also been produced by mechanical exfoliation and applied in high-speed transistors with a considerable energy gap.^{25–27}

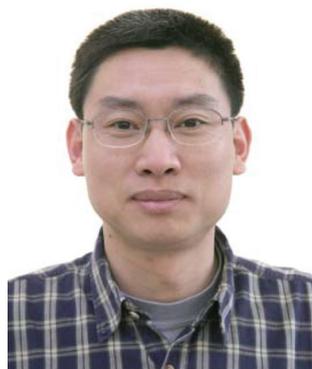
Different from the huge success of graphene, a 2D boron sheet meets a large challenge in experimental preparation. The possible origin may be because the element boron lacks an electron.²⁸ Compared with the typical sp² or sp³ hybridization of carbon, boron has a more complex bonding mechanism.²⁹ Thus, boron has an extremely complicated chemistry and structural behavior in its bulk allotropes.^{30–33} For example, α-B₁₂ is built with the icosahedra B₁₂ positioned at the rhombohedral lattice site. The neighboring B₁₂ have strong interactions and form bonds with each other to stabilize the system. The absence of layered bulk materials makes it difficult to mechanically exfoliate the corresponding 2D sheet, as successfully realized in other 2D materials. As a result, thermal evaporation deposition, chemical vapor deposition and molecular beam epitaxy should be the potential techniques to experimentally produce a 2D boron sheet. Moreover, the electron deficiency of boron (compared to that of carbon) makes the ground state of 2D boron sheet still unclear. A lot of theoretical works have been devoted to discuss the possible structures of 2D boron sheets.

In this review, we focus on the recent developments of boron based 2D materials. First, the theoretical discussion on 2D boron based structures and related properties will be presented. Then, the experimental effort will be introduced. Finally, the possible application and potential challenges will be provided as the final part of this review.

Theoretical design

Design of α-sheet

Carbon-based nanostructures have gained great success in recent years, including zero-dimensional (0D) fullerene, one-dimensional (1D) carbon nanotube and 2D graphene. These nanostructures vary in long range symmetry but have very similar local structures and can be transformed with some operations. Graphene can be wrapped up into 0D fullerene or rolled into 1D carbon nanotubes. The development of carbon-based nanostructures also provokes the research interest in boron nano-materials. Different from the exclusive honeycomb lattice structure of graphene, the structure of the 2D boron sheet is more complicated. Compared with carbon valence electron configuration of 2s²2p², boron lacks one electron with 2s²2p¹. Thus, the ultrastable honeycomb lattice of graphene becomes unstable for the 2D boron sheet. Boustani first predicted some quasi-planar boron clusters by the first-principles calculation method,³⁴ which opened the door for the research of the 2D boron sheet. Further, layered boron sheets and boron nanotubes were investigated.³⁵ The 2D honeycomb boron sheet has much smaller binding energy than that of the planar triangle network, while the buckled triangle lattice has a larger one.³⁵ Thus, the buckled triangle network was thought to be the best choice to construct a 2D boron sheet.^{34–38} Lau *et al.* predicted a new planar 2D boron sheet mixing the triangular and quadrangular motifs through which the binding energy increased although it is still smaller than that of the buckled triangular lattice.³⁹ Tang *et al.* did some pioneering work to predict the energetically stable 2D boron sheet with hexagonal holes embedded in the planar triangle lattice.^{40–42} The famous α-sheet with one hexagonal hole in every nine boron triangular atoms was proposed to have a larger binding energy than the buckled triangular lattice. In order to explain



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the exotic stability of the suggested α -sheet, a detailed study of the bonding character of boron was undertaken. They divided the bonding state of the boron sheet into the in-plane part and out-of-plane part, as shown in Fig. 1(a). The in-plane states are composed of the sum of s , p_x and p_y states while the out-of-plane state is merely contributed to by the p_z states. In-plane states form the σ bond and the out-of-plane states form the π bond. Generally, the σ bond of the in-plane part is stronger than the π bond of the out-of-plane part. Furthermore, the bonding states gain energy while the antibonding states cost energy. So, it is valuable to analyze the exact position of the Fermi level compared with the position of the bonding state. The graphene-like honeycomb boron sheet is clear. Similar to graphene, it forms normal two-center bonds with the two neighboring boron atoms. Besides, an energy gap emerged between the in-plane bonding and antibonding states, and the Dirac point derived by the crossing of the π band and the π^* band is located in the gap. However, different from graphene where the Fermi level is across the Dirac point, the Fermi level of the honeycomb boron sheet is far below the Dirac point. The empty occupation on the σ bonding state makes the honeycomb boron sheet unstable. On the contrary, the flat triangular lattice has the Fermi level over the crossing point of σ bonding and antibonding states. The over-occupied σ antibonding states also make this sheet unstable. The proposed α -sheet balanced the cases of the honeycomb and triangular sheet, and it's to be stable. Moreover, a detailed model of three-center bonds⁴³ against the traditional two-center bonds is used to describe the stability of this α -sheet.⁴⁰ Derived from their image and model, the hexagonal sheet should be stable

by accepting electrons while the flat triangular structure should remove the electrons in its antibonding states in order to be stable. Galeev *et al.* also provided a similar picture of electron balance in detail to explain the stability of the α -sheet. In their model, the hexagonal holes serve as scavengers of extra electrons from the surrounding filled hexagons.⁴⁴ The α -sheet combined these two phases in the right proportion, and presents the stability for the both sub-structures. The model was also used to explain the stability of B_{80} fullerenes.⁴⁵ The suggested α -sheet can be considered as the precursor of B_{80} as graphene is the precursor of carbon fullerenes.^{40,46} In addition, a self-doping image, in which adding or removing boron atoms is equivalent to adding or removing electrons from a system, was proposed to generally design some other stable pure boron 2D sheets,⁴¹ as illustrated in Fig. 1(b). Their work demonstrates a novel bonding mechanism in pure boron compounds and it has significant implication in designing stable structures of 2D boron sheets.

Proposal of polymorphism of the 2D boron sheet

According to Tang's strategy, an 2D planar boron sheet can be considered as the combination of a hexagonal hole and a triangular boron lattice, which will lead to a very large number of possible configurations. The direct use of first-principles calculation methods will be very difficult to deal with the large combinatorial problem of the possible structures. Penev *et al.* successfully solved this problem with the combination of the cluster expansion method^{47,48} and first-principles calculations to thoroughly and systematically explore the configuration space of 2D boron sheets.⁴⁹ They treated the 2D boron sheet as the pseudoalloy constituted by closed-pack triangular boron atoms and hexagonal vacancy, as shown in Fig. 2. It was predicted that a number of stable 2D boron polymorphs with

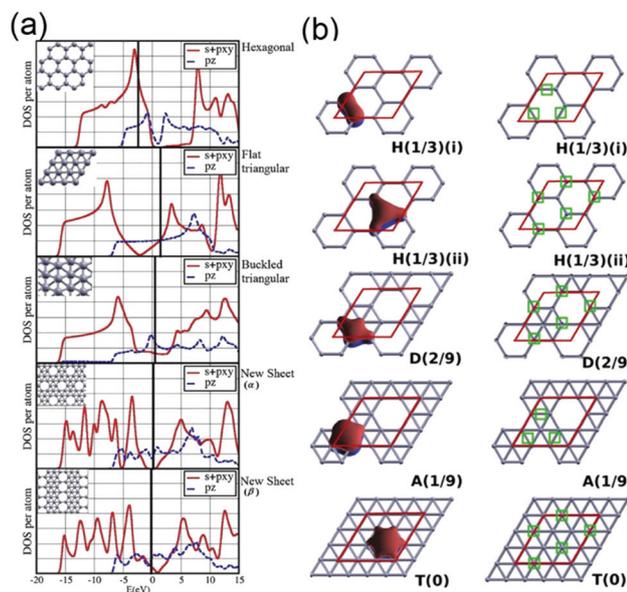


Fig. 1 (a) Projected density of state (PDOS) for different boron sheets. In-plane states and out-of-plane states are divided. (b) Isosurface contour plots of π maximally localized Wannier functions for different boron sheets. Taken from ref. 40 and 41. Reproduced with permission. Copyright 2007 and 2009, American Physical Society.

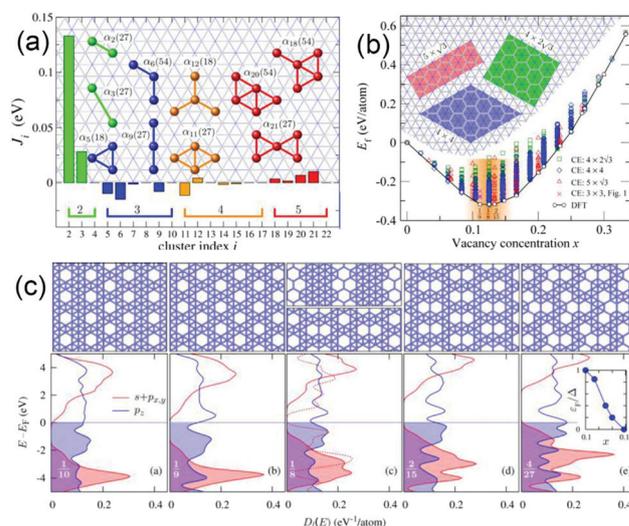


Fig. 2 Cluster interactions and formation energy of various building blocks of 2D boron sheets. (a) Effective cluster interactions J_i . (b) Formation energies of structures. (c) PDOS of some most stable B layers. Reproduced with permission. Taken from ref. 49. Copyright 2012, American Chemical Society.

closely similar cohesive energies emerge in the configuration space. Though those structures are obviously different, they have a similar vacancy concentration in the range 10–15%. The various potential structures whose cohesive energies are very near makes the 2D boron sheets tend to form polymorphs. This is completely distinct with the hexagonal BN sheet. For the BN sheet, N can transfer an extra electron to B to form a honeycomb lattice with typical two-center bonds. The electron deficiency of boron drives it to form various intricate multi-center bonds which make the boron sheets display complex chemical structures.

Global minimum searching boron sheet

Various 2D boron sheet structures with close energies have become a challenge for determining their ground state. An efficient structure prediction method with global minimum optimization provides a powerful tool to search for the complex ground state of a 2D boron sheet. Recently, Oganov *et al.* developed an *ab initio* evolutionary algorithm^{50,51} and Ma *et al.* designed a particle swarm optimization package^{52–54} to predict stable structures under given conditions. Wu *et al.* firstly used the *ab initio* global minimum optimization method to explore stable 2D boron structures.⁵⁵ The α -sheet with the hexagonal hole concentration of 1/9 proposed by Tang *et al.*, indeed was a low-energy structure among their search results but it was not a dynamically stable structure since some imaginary frequencies appeared in the Brillouin zone, as shown in Fig. 3(b). However, their predicted buckled α -sheet (defined as α' -sheet) is shown in Fig. 3(a), although it is not completely planar, it has larger cohesive energy according to both PBE and PBE0 functional than that of the original α -sheet and is with dynamical stability. Several other low-energy structures were also predicted with very similar cohesive energy of the α -sheet (less than 10 meV), which also supported the polymorphous 2D boron sheet proposed by Penev. The work also revealed that the α -sheet and α' -sheet should be semiconductors with the PBE0 functional since PBE underestimated the band gap.

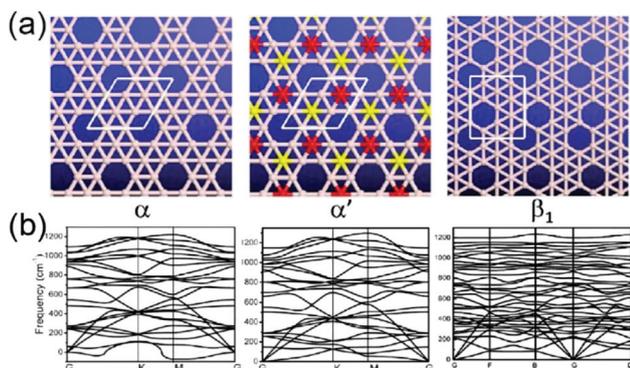


Fig. 3 The structures of α -sheet, buckled α -sheet and β_1 -sheets and the corresponding phonon dispersions. The colorful atoms in the middle of (a) indicating the buckled boron atoms. Taken from ref. 55. Reproduced with permission. Copyright 2012, American Chemical Society.

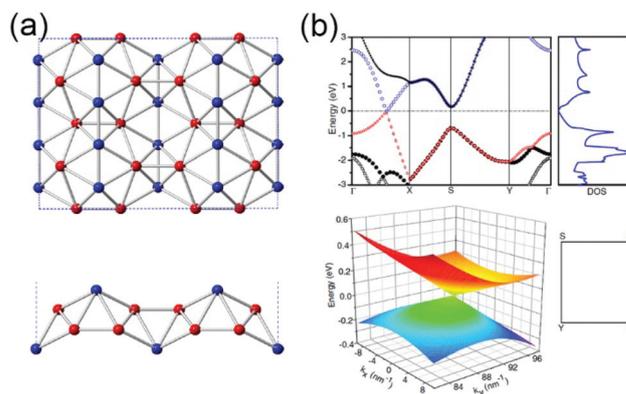


Fig. 4 Structure of $Pmmn$ boron sheet ($2 \times 2 \times 1$ supercell) with nonzero thickness and its related distorted Dirac cone. The different colors indicate nonequivalent boron atomic positions. Taken from ref. 58. Reproduced with permission. Copyright 2014, American Physical Society.

Besides, other works of global minima crystal searching were also undertaken to obtain the low energy phases of the 2D boron sheet. Yu *et al.* predicted 1/8 and 2/15 structures with close energy with the α -sheet.⁵⁶ Lu *et al.* found two low-energy structures which are composed of the isolated-hexagon and twin-hexagon holes.⁵⁷ Zhou *et al.* found that the non-zero thick boron sheet structure will decrease in energy compared with planar structures.⁵⁸ Their suggested $Pmmn$ and $Pmmm$ boron sheet structures gained energy of 50 meV and 80 meV respectively compared with the α -sheet from the GGA functional. The non-zero thick 2D boron sheet, which was similar to the bulk α -boron in geometry and bonding, reflects the frustration of the pure boron system.^{32,58} Interestingly, this $Pmmn$ structure in Fig. 4(a) has exotic electronic properties with a distorted Dirac point located at the Fermi level of the system. The electronic structure of this $Pmmn$ boron sheet is similar to graphene though the Dirac cone is orientation dependent while that of graphene is isotropical, see Fig. 4(b). The occupation of the electron leads to the stability of this structure. All the bonding states are fully occupied while the antibonding states are fully empty, which pushes the energy lower to make the structure stable. Besides, the origin of the Dirac point in this $Pmmn$ boron sheet is from the hybridization of the in-plane and out-of-states, which is also different from graphene¹ or graphyne⁵⁹ where the Dirac points completely arise from the crossing of π and π^* bands.

B₁₂ icosahedral sheet

Very recently, Kah *et al.*⁶⁰ designed several novel boron sheets constructed by icosahedra B₁₂ as the building blocks with the semi-empirical Hamiltonian simulation method.^{61,62} Their proposed icosahedral δ_6 sheet, arraying B₁₂ in a triangular lattice, even has larger cohesive energy (76 meV per atom) than the buckled α sheet. Moreover, the δ_6 sheet has a semiconductor character, which is different from most predicted metallic boron sheets.

Metal layer stabilization boron sheets

A stable boron sheet can be considered as a self-doping balance in a frustrated system, where some sub-parts transfer electrons to others.⁴¹ From the doping viewpoint, a metal can be thought as the external-doping to stabilize the boron sheet. Tang *et al.* used this idea to design a stable atomically thin MgB₂ sheet.⁴¹ Moreover, in order to maintain the Dirac Fermions of the boron honeycomb sheet, some metal doped-boron based 2D sheets were also proposed.^{63–66} According to the electron deficiency of boron, a sandwich structure containing a metal Mo layer was proposed to stabilize the boron honeycomb sheet.⁶³ This structure is dynamically stable without an imaginary frequency in the phonon spectrum. Also, the electronic structure was interesting. There are two Dirac cones which approach the Fermi level. Interestingly, the two Dirac cones are almost isotropical even the d orbital of Mo contributes to the formation of Dirac cones, as shown in Fig. 5. Furthermore, another similar structured MnB₄ system which has both strong electron–phonon interaction and ferromagnetic properties, makes this 2D structure rather significant. Besides, some studies have explored potentially stable 2D boron-metal structures, as shown in Fig. 6. Zhang *et al.* predicted a monolayer TiB₂.⁶⁴ The metal Ti layer was located on one side of the boron honeycomb. This structure also was predicted with a Dirac point across the Fermi level. However, the Dirac cone states are mainly derived from the

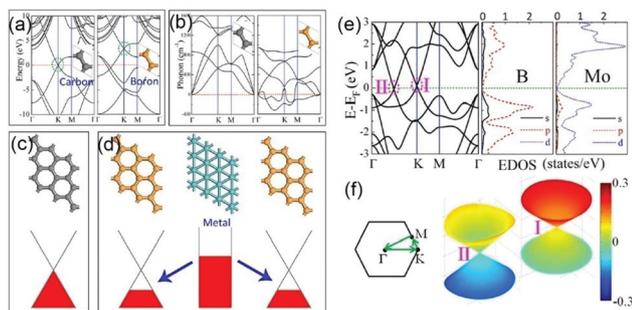


Fig. 5 The sketch of a metal stabilization boron honeycomb sheet (Here, MoB₄ as a typical model) and its electronic structure. Taken from ref. 63. Reproduced with permission. Copyright 2014, American Physical Society.

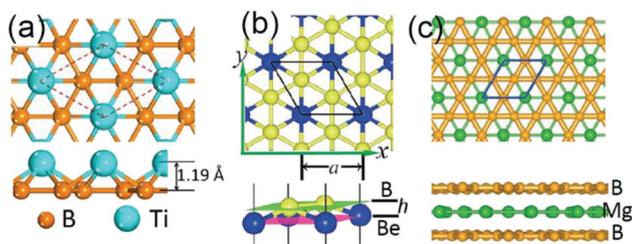


Fig. 6 Some structures of 2D metal-boron structures. (a), (b) and (c) are 2D TiB₂, BeB₂ and MgB₆ separately; taken from ref. 64–66. Reproduced with permission. Copyright 2014, American Physical Society; 2015, Royal Society of chemistry.

d orbital of Ti. Furthermore, the Dirac point can be maintained even on the BN substrate. Mu *et al.* proposed another case of BeB₂ with the Dirac point if the isotropical strain is added in this structure.⁶⁶ Besides, a boron-kagome 2D MgB₆ is also predicted to be with dynamical stability.⁶⁵

Realization proposal

Thermal decomposition in experiment

Compared with other 2D materials such as graphene, BN, and monolayer MoS₂, the realization of an atomically thin 2D boron sheet in experiment still faces a huge challenge. However, some other nanostructures of boron are successfully produced, including boron nanowires^{67–69} and nanobelts.^{70,71} Ciuparu *et al.* firstly synthesized single-wall boron nanotubes by the chemical reaction of CCl₃ and H₂ with the help of a catalyst.⁷² The diameter of these boron nanotubes was about 36 Å. Liu *et al.* successfully fabricated multi-wall boron nanotubes which were metallic and had field emission properties.⁷³ However, at present production of large-scale 2D boron sheets is still a big challenge. Very recently, Xu *et al.* adopted a vapor–solid process *via* thermal decomposition of diborane under low pressure conditions of 0.5 Pa with gas cleaning and then heating at a temperature of 950 °C, acquired about 10 nm thick single-crystalline boron nanosheets which have excellent field emission performance and a good thermal stability,⁷⁴ see Fig. 7. From the SEM images in Fig. 7a–c, the boron sheets uniformly grow over the substrate and have a width ranging from tens of nanometers to 3 μm and with a length of several micrometers. These boron sheets are smooth and almost transparent, which is good for optoelectronic applications. Patel *et al.* synthesized boron nanosheets using the thermal vapor decomposition method.⁷⁵

Laser vaporization of quasi-planar boron clusters

Wang *et al.* used laser vaporization of boron-enriched target experimental technology to produce boron clusters and analyzed the results by photoelectron spectra and DFT global minimum search.^{76–88} It is found that some of those boron clusters have quasi-planar structures and even have hexagonal vacancies surrounded by triangular motifs, which was similar to the previously predicted 2D boron sheet. They produced a planar hexagonal B₃₆ cluster with one hexagonal vacancy⁸⁶ and a B₃₅ cluster with double hexagonal vacancies,⁸⁴ which is shown in Fig. 8. These planar boron clusters were proposed to serve as the building blocks for the extended single-atom layer 2D boron sheet. However, it still has a long way to go to construct these planar boron clusters into the 2D boron sheet. Their study provides the first experimental evidence of the existence of boron nanostructures with hexagonal vacancies.

Grow boron sheet on the substrates

Amsler *et al.* employed the *ab initio* minima hopping method to systematically study the low energy surface reconstruction structure on the α-boron (111) surface.⁸⁹ It was found that a

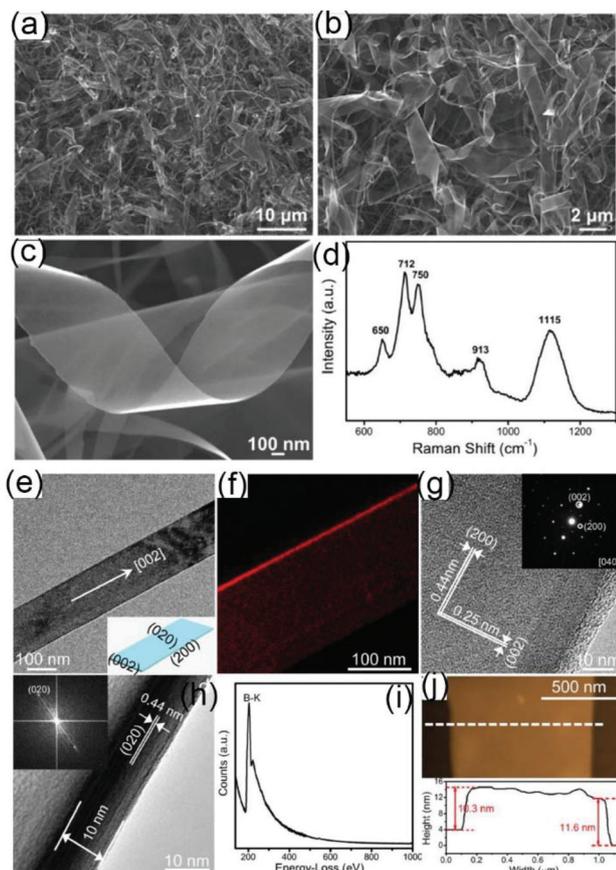


Fig. 7 Ultrathin single-crystalline boron nanosheets realized in experiment. (a)–(c) SEM pictures of the boron nanosheets; (d) micro-Raman spectrum of the boron nanosheet at room temperature; (e) TEM picture; (f) energy-filtering mapping of boron element; (g) HRTEM picture of the growth direction; (h) HRTEM picture of the side facet; (i) EELS spectrum and (j) AFM picture for the boron nanosheets. Taken from ref. 74. Reproduced with permission. Copyright 2015, Wiley publish group.

planar and conductive monolayer sheet would form on the surface. Zhou *et al.* also found a similar quasi-planar boron sheet on bulk boron.⁹⁰ But considering the strong covalent interaction with the substrate, it would be very difficult to exfoliate these boron sheets from the bulk substrate. Liu *et al.* explored the possible synthesis method of the 2D boron sheet on other substrates by first-principles calculations.⁹¹ Various substrates were considered in their work, including metals (Cu, Ag, Au) and metal borides (MgB_2 , TiB_2). It was found that the metal, Au or Ag(111), surface can react as a good substrate and boron atoms decomposed from precursors can be driven by the gradient of chemical potential to assemble into 2D clusters and further grow into a large sheet. It is also indicated that a high nucleation barrier would exclude the formation of boron 3D-structures on the two metal substrates. More importantly, the boron sheets are predicted to be weakly bound to the substrates, which is much favorable to be separated from the substrate. Liu *et al.* systematically researched the detailed growth mechanism of the 2D boron sheet on the Cu sub-

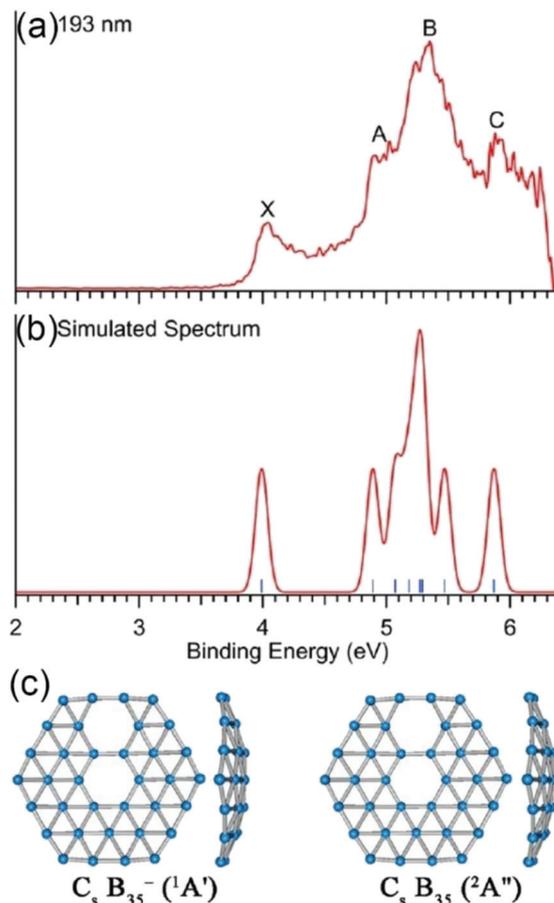


Fig. 8 Experimental and simulated photoelectron spectroscopy for the B_{35} cluster. Taken from ref. 84. Reproduced with permission. Copyright 2014, American Chemical Society.

strate.⁹² Their results revealed that boron monolayers should be very stable on the Cu(111) surface due to the substrate passivation. Besides, boron clusters have low diffusion barrier on the substrate and also their formation energy can be decreased with increasing their size. Thus, the continuous growth of the 2D boron sheet could be realized in experiment, as shown in Fig. 9. Moreover, their results also proved that the hexagonal holes will easily arise at the edge of a triangular boron cluster and diffuse inside the cluster. Thus, a boron monolayer sheet with the suggested mixed hexagonal-triangular geometry could be realized on the Cu substrate. Their study gave a clear picture of the growth mechanism of the boron monolayer on the Cu substrate and will be very helpful for further experimental synthesis of 2D boron sheets.

Successfully fabricated boron nanotubes may become a source to produce boron nanoribbons. Previous experiments have successfully unzipped graphene nanotubes into nanoribbons by oxidative⁹³ or Ar plasma cutting.⁹⁴ Compared with the C–C bond in graphene, the B–B bond in the boron sheet is weaker. Thus, it should be easier to break boron bonds. However, the complex structure of boron nanotubes may meet the challenge to be unzipped into boron ribbons. Thus, more

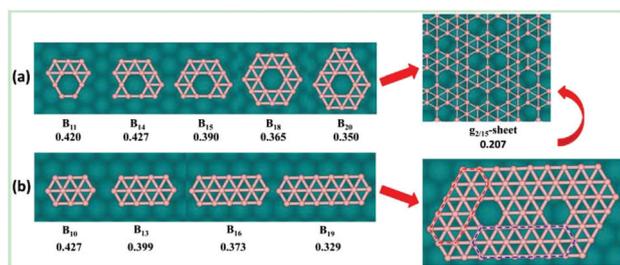


Fig. 9 (a), (b): two potential growth paths of 2D boron monolayer sheet from boron clusters in Cu substrate. Reproduced with permission from ref. 92. Copyright 2013, Nature publishing group.

experimental and theoretical efforts are required to verify this proposal.

Application

Xu *et al.* used their boron nanosheets obtained through decomposition of diborane to fabricate FET devices and photo-electronic devices. The turn-on electric field in their field emission experiment was $3.6 \text{ V } \mu\text{m}^{-1}$ and the threshold electric field was $5.08 \text{ V } \mu\text{m}^{-1}$. The boron nanosheets also hold a high photosensitivity and fast photoresponse, as shown in Fig. 10(a) and (b). Some calculations are required to explore the potential application of 2D boron sheets. Wang *et al.* suggested that the 2D boron sheet can be used as the potential hydrogen storage material by decorating metal anions,⁹⁵ as shown in Fig. 10(c). Zheng *et al.* investigated the adsorption geometries, binding energy, electronic structures and work functions of Li clusters on a 2D boron α -sheet.⁹⁶ Their simulation proved that the clustering effect of Li on the boron α -sheet is suppressed and Li-

absorbed 2D boron sheets could be promising candidates for electrode materials in electronic devices. Banerjee *et al.*, with the *ab initio* molecular dynamic method, proved that 2D-boron sheets could act as an anode material in lithium ion batteries.⁹⁷ In Fig. 10(d), Peng *et al.* studied the mechanical properties of α -boron sheets under strain and predicted a high in-plane stiffness (about 2/3 of that of graphene) of α -boron sheet.⁹⁸ The simulation results imply that α -boron sheets have advanced mechanical properties with high strength and high flexibility and might be used in surface acoustic wave sensors.

Conclusion and outlook

In this review, we present the recent developments of a boron based 2D sheet. Compared with graphene, the biggest challenge for the 2D boron sheet is the realization in experiment. At present, a free-standing 2D boron sheet is hard to obtain, but the growth on the metal substrate, such as on Cu, may be possible *via* the experimental route. The designing rule of the 2D Boron structure should obey the electron-occupation balance. Similar to graphene, a pure boron monolayer sheet can display interesting electronic properties, such as Dirac cone band dispersion. A metal-boron compound is possibly another choice to realize the 2D boron based system, where the Dirac cone, ferromagnetism, or even superconductivity has been theoretically proposed. Thus, a 2D boron based crystal holds potential applications in future nanoelectronic devices and the platform to study nanophysics. Besides, theoretical studies have approved that the 2D boron sheet can also be used as a hydrogen storage material or a good choice of electrode materials.

Acknowledgements

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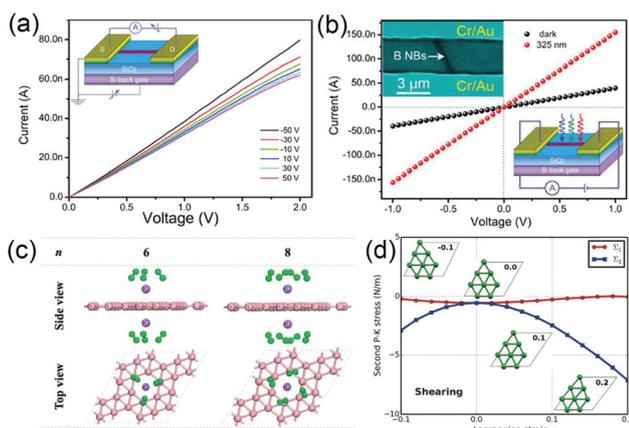


Fig. 10 (a), (b): I - V curves of boron nanosheets based FET and photo-electronic devices. (c) Li (purple balls) decorated 2D boron sheet used for hydrogen (small green balls) storage. (d) Mechanical properties of the α -sheet. Taken from ref. 74, 95 and 98. Reproduced with permission. Copyright 2015, 2014 Wiley publication group and 2015, Royal Society of chemistry.

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