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FEATURE ARTICLE

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 in experiment, such as silicene, monolayer MoS_2, few-layer black phosphorus and so on. As a neighbor of carbon on 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 technique application of 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 prospective of this area are discussed.

Introduction

With a simple arrangement of carbon atoms in 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 modulus[8] 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 electrode[12], optical devices,[13] sensors,[14] energy generation and storage.[15, 16] The fundamental research interest and application prospect aroused by graphene also encourage people to explore other 2D materials beyond graphene. As an isoelectronic system with graphene, 2D BN was successfully prepared in experiment with large-scale and used in many areas.[17, 18] Further, as the congeners of carbon, silicon and germane also can be produced in 2D forms with the help of substrate.[19-22] Recently, transition metal dichalcogenieds, as an typical example of MoS_2,[23, 24] has been experimentally realized in monolayer structure. 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, 2D boron sheet meets large challenge in experiment preparation. The possible origin may be from that element boron lack electron[28]. Compared with the typical sp^2 or sp^3 hybridization of carbon, boron has more complex bonding mechanism[29]. Thus, boron has extremely complicated chemistry and structure behavior by its bulk allotropes[30-33]. For example, α-B_{12} is build with by the icosahedra B_{12} positioned at the rhombohedral lattice site. The neighboring B_{12} have strong interaction and form bonds with each other to stabilize the system. The absence of layered bulk materials make it hard 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 produce 2D boron sheet in experiment. Moreover, the electron deficiency character of boron makes the ground state of 2D boron sheet still in debate. A lot of theoretical works have been devoted to discuss the possible structures for 2D boron sheet.

In this review, we focus on the recent developments of boron based 2D materials. First, the theoretical discussion on 2D boron based structure and related property will be present. Then, the experimental effort will be introduced. Finally, the possible application and potential challenge 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) fullerence, one-dimensional (1D) carbon nanotube and 2D graphene. These nanostructures are various in long range symmetry but have very similar local structures and can be transformed with some operations. Graphene can be wrapped up into 0D fullerence or rolled into 1D carbon nanotubes. The development of carbon-based nano-structures also provokes the research interest of

boron nano-materials. Different from the exclusive honeycomb lattice structure of graphene, 2D boron sheet is more complicated. Compared with carbon valance electron configuration of $2s^2 2p^2$, boron lacks one electron with $2s^2 2p^1$. Thus, the ultrastable honeycomb lattice of graphene becomes unstable for 2D boron sheet. Boustani firstly predicted some quasi-planar boron clusters by first-principles calculation method,[34] which opened a door for the research of 2D boron sheet. Further, layered boron sheets and boron nanotubes were investigated.[35] 2D honeycomb boron sheet has much smaller binding energy than the planer triangle network, while the buckled triangle lattice has a larger one.[35] Thus, buckled triangle network was thought to be best choice to construct 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 the buckled triangular lattice.[39] Tang *et al*., did some pioneering work to predict energetically stable 2D boron sheet with hexagonal holes embedding 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 larger binding energy than the buckled triangular lattice. In order to explain the exotic stability of the suggested α-sheet, a detailed study of the bonding character of boron is taken. They divided the bonding state of boron sheet into the in-plane part and out-of-plane part, as shown in Fig. 1 (a). The in-plane states are composed by the sum of s, p_x and p_y states while the out-of-plane state is merely contributed by the p_z states. In-plane states form σ bond and out-of plane form π bond. Generally, σ bond of in-plane part is stronger than the π bond of 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 Fermi level compared with position of bonding state. The graphene-like honeycomb boron sheet is clear. Similar with 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 π band and π* band is located in the gap. However, different from graphene that the Fermi level is across the Dirac point, the Fermi level of honeycomb boron sheet is far below the Dirac point. The empty occupation on the σ bonding state makes 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 honeycomb and triangular sheet to be stable. Moreover, a detailed model of three-center bonds[43] against traditional two-center bonds is used to describe the stability of this α-sheet.[40] Derived from their picture and model, the hexagonal sheet should be able to lower its energy by accepting electrons while the flat triangular structure should remove the electrons in its antibonding states to be stable. Galeev et al., also provided similar picture of electron balance in detail to explain the stability of α-sheet. In their model, the hexagon holes serve as scavengers of extra electrons from the surrounding filled hexagons[44]. The α-sheet combined these two phases in the right proportion, presents the stability by 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 the precursor of B_{80} as graphene is the precursor of carbon fullerenes.[40, 46] In addition, a self-doping picture, 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 to design stable structures of 2D boron sheets.

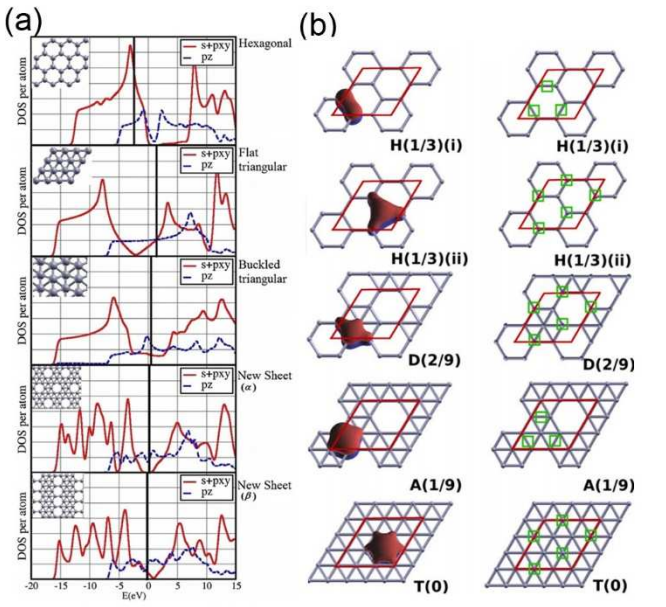

Fig. 1 (a) Projected density of state (PDOS) for different boron sheets. In-plane states and out-of-plane states are divided. (b) Isosurface contour plots of π maximally localized Wannier functions for different boron sheets. Taken from ref. 33 and 34. Reproduced with permission. Copyright 2007 and 2009, American Physical Society.

Proposal of polymorphism of 2D boron sheet.

According to Tang's strategy, an 2D planar boron sheet can be considered as the combination of hexagonal hole and 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 pseduoalloy 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 closely similar cohesive energies emerge in the configuration space. Though those structures are obviously different, they have a similar vacancy concentration ranged in 10-15%. The

various potential structures whose cohesive energies are very near makes 2D boron sheets tend to form polymorphs. This is completely distinct with hexagonal BN sheet. For BN sheet, N can transfer an extra electron to B to form honeycomb lattice with typical two-center bonds. The electron deficiency of boron drive it forming various intricate multi-center bonds which makes boron sheets display complex chemical structures.

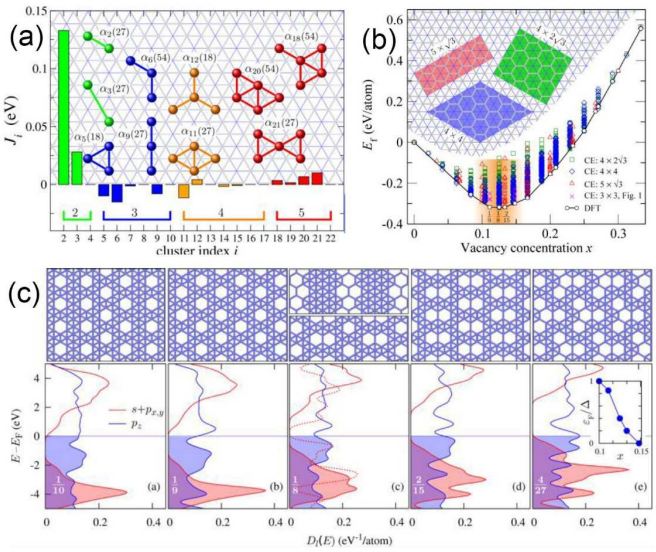

Fig. 2 Cluster interactions and formation energy of various bluiding blocks of 2D born sheets. (a) Effective cluster interactions J_i. (b) Formation energies of structures. (c) PDOS of some most stable B layers**.** Reproduced with permission. Taken from ref. 40. Copyright 2012, American Chemical Society.

Global minimum searching boron sheet

Various 2D boron sheet structures with closed energies become a challenge to determine the ground state. An efficient structure prediction method with global minimum optimization provides a powerful tool to search for the complex ground state of 2D boron sheet. Recently, Oganov *et al*., developed *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 *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 searching 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) in Fig. 3 (a), although it is not completely planar, has larger cohesive energy according to both PBE and PBE0 functional than original α-sheet and with dynamical stability. Several other low-energy structures were also predicted with very similar cohesive energy of α-sheet (less than 10 meV), which also supported the polymorphous 2D boron sheet proposed by Penev. The work also revealed that α-sheet and α'-sheet should be semiconductors with the PBE0 functional since PBE underestimated the band gap.

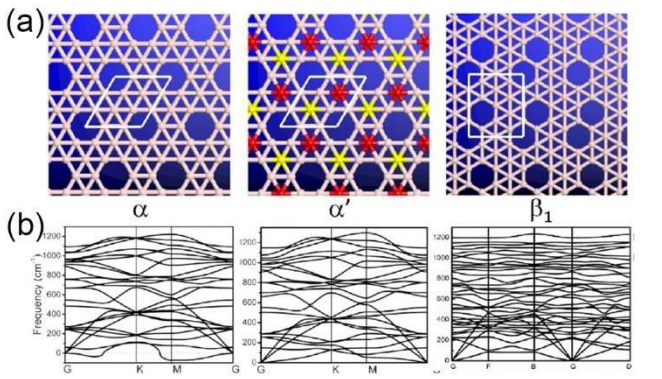

Fig. 3 The structures of α-sheet, bulcked α-sheet and β1-sheets and the corresponding phonon dispersions. The colorful atoms in the middle of (a) indicating the buckled boron atoms. Taken from ref. 46. Reproduced with permission. Copyright 2012, American Chemical Society.

Besides, other works of global minima crystal searching are also taken to get low energy phases of 2D boron sheet. Yu *et al*., predicted 1/8 and 2/15 structures with closed energy with α-sheet.[56] Lu *et al*., found two low-energy structures which are composed by the isolated-hexagon and twin-hexagon holes.[57] Zhou *et al*., found that non-zero thick boron sheet structure will decrease energy compared with planar structures.[58] Their suggested *Pmmn* and *Pmmm* boron sheet structures gained energy of 50 meV and 80 meV compared with α-sheet from the GGA functional. The non-zero thick 2D boron sheet, tended to be similar with bulk α-boron in geometry and bonding, reflects the frustration of pure boron system.[32, 58] Interesting, 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 with graphene though the Dirac cone is orientation dependent while that of graphene is isotropical, see Fig. 4(b). The occupation of electron leads to the stability of this structure. All the bonding states are fully occupied while antibonding states are fully empty, which pushes the energy lower to make the structure stable. Besides, the origin of Dirac point in this *Pmmn* boron sheet is from the hybridization of in-plane and out-of-states, which is also different from graphene[1] or graphyne[59] where the Dirac points completely arise from the crossing of π and π* bands.

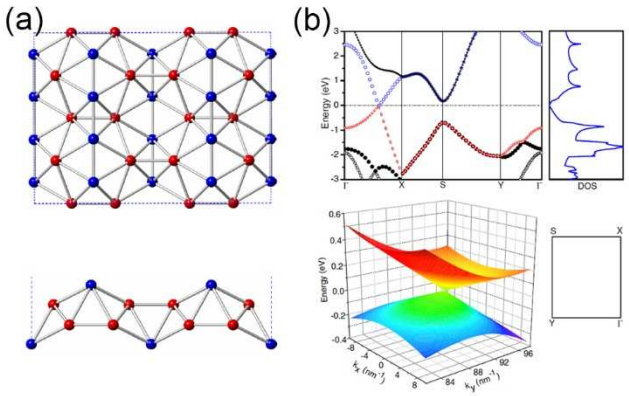

Fig. 4 Structure of Pmmn boron sheet (2x2x1 supercell)with nonzero thickness and its related distorted Dirac cone. The different colors indicate nonequivalent boron atomic positions. Taken from ref. 49. Reproduced with permission. Copyright 2014, American Physical Society.

B_{12} icosahedral sheet.

Very recently, Kal *et al*., [60] magically designed several novel boron sheets constructed by icosahedra B_{12} as the building blocks with semi-empirical Hamiltonian simulation method[61, 62]. Their proposed icosahedral δ_6 sheet, arraying B_{12} in a triangle lattice, even has larger cohesive energy (76 meV per atom) than the buckled α sheet. Moreover, the δ_6 sheet behaves in a semiconductor character, which is different from most predicted metallic boron sheet.

Metal layer stabilization boron sheets

Stable boron sheet can be considered as a self-doping balance in a frustrated system, where some sub-part transfer electrons to others.[41] From the doping view, metal can be thought as the external-doping to stabilize boron sheet. Tang *et al*., used this idea to design a stable atomically thin MgB_2 sheet. Moreover, in order to keep the Dirac Fermions for 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 boron honeycomb sheet.[63] This structure is dynamically stable without imaginary frequency in phonon spectrum. Also, the electronic structure was interesting. There are two Dirac cones approach the Fermi level. Interesting, the two Dirac cones are almost isotropical even *d* orbital of Mo contributes the formation of Dirac cones, as shown in Fig. 5. Furthermore, another similar structured MnB_4 system has both strong electron-phonon interaction and ferromagnetic properties, which makes this 2D structure rather significant. Besides, some work has explored potentially stable 2D boron-metal structures, as shown in Fig. 6. Zhang *et al*., predicted a monolayer TiB_2.[64] The metal Ti layer was located in one side of 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 d orbital of Ti. Furthermore, the Dirac point can be kept even on the BN substrate. Mu *et al*., proposed another case of BeB_2 with the Dirac point if the isotropical strain is added in this structure.[66] Besides, a boron-kagome 2D MgB_6 is also predicted to be with dynamical stability.[65]

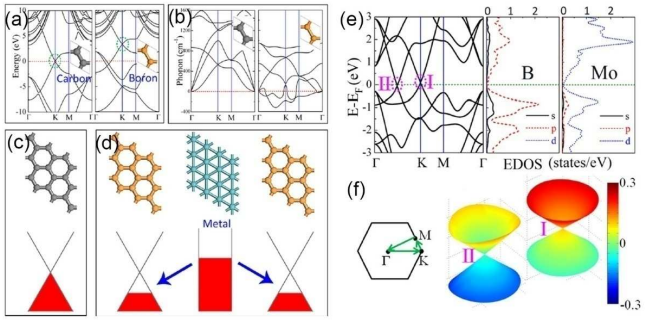

Fig. 5 The sketch of metal stabilization boron honeycomb sheet referenced the stable carbon honeycomb and electronic structure of MoB_4 as a typical model. Taken from ref. 52. Reproduced with permission. Copyright 2014, American Physical Society.

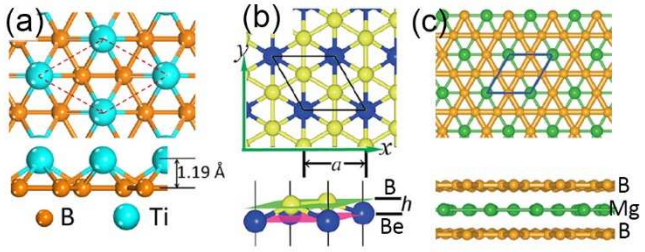

Fig. 6 Some structures of 2D metal-boron structures. (a), (b) and (c) are 2D TiB_2, BeB_2 and MgB_6 seperately; Taken from ref. 53-55. Reproduced with permission. Copyright 2014, American Physical Society; 2015, Royal Society of chemistry.

Realization Proposal

Thermal decomposition in experiment

Compared with other 2D materials as graphene, BN, monolayer MoS_2, the realization of atomically thin 2D boron sheet in experiment still faces huge challenge. However, some other nano-structures of boron are successfully produced, including boron nanowires,[67-69] nanobelts.[70, 71] Ciupara, *et al*., firstly synthesized single-wall boron nanotubes by the chemical reaction of CCl_3 and H_2 with the help of catalyst.[72] The diameter of these boron nanotubes were about 36 Å. Liu *et al*., successfully fabricated multi-wall boron nanotubes which were metallic and had field emission properties.[73] However, large-scale 2D boron sheet is still a big challenge to be produced at present. Very recently, Xu *et al*., took a vapor-solid process via thermal decomposition of diborane under low pressure conditions of 0.5 Pa with gas cleaning and then heating at the temperature of 950 ℃, acquired about 10 nm thick single-crystalline boron nanosheets to be hold up excellent field emission performance and a good thermal stability,[74] see Fig. 7. From the SEM images in Fig.7 a-c, the boron sheets uniformly grow over the substrate and has a width ranging from tens of nanometers to 3 um and with a length of several ums. These boron sheets are smooth and almost transparent, which is good

for optoelectronic applications. Patel *et al*., synthesized boron nanosheets using a thermal vapor decomposition method.[75]

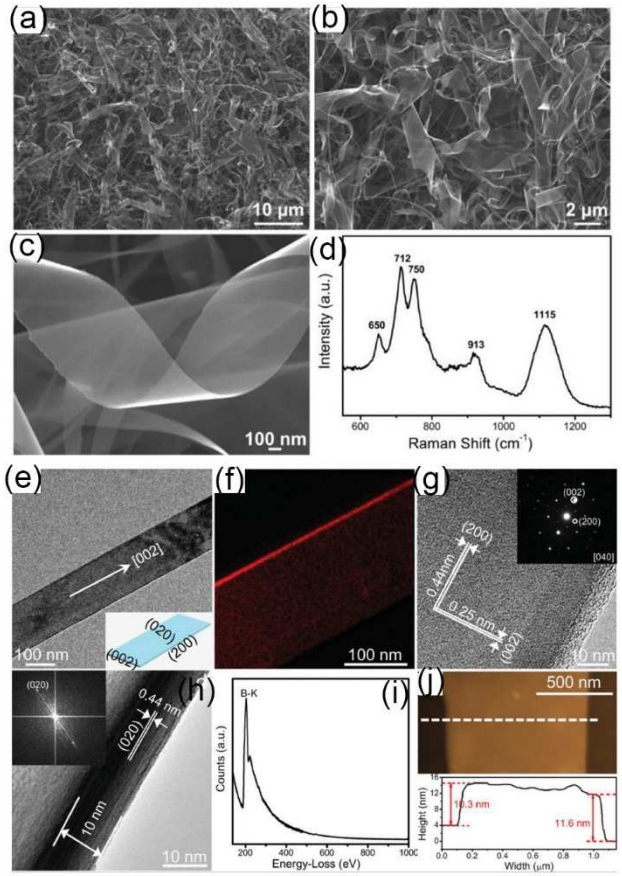

Fig. 7 Ultrathin single-crystalline boron nanosheets realized in experiment. (a)-(c) SEM pictures for the boron nanosheets; (d) micro-Raman spectrum of the boron nanosheet at room temperature; (e) TEM picture; (f) energy-filtering mapping of boron element; (g) HRTEM picture of the growth direction; (h) HRTEM picture of the side facet; (i) EELS spectrum and (j) AFM picture for the boron nanosheets. Taken from ref. 63. Reproduced with permission. Copyright 2015, Willy publish group.

Laser vaporization of quasi-planar boron clusters

Wang *et al*., used laser vaporization of boron-enriched target experimental technology to produce boron cluster and analyzed the results by photoelectron spectra and DFT global minimum search.[76-88] It is found that some of those boron clusters are with quasi-planar structures and even with hexagonal vacancy surround by triangle motifs, which was similar with previous predicted 2D boron sheet. They produced a planer hexagonal B_{36} cluster with one hexagonal vacancy[86] and B_{35} 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 extended single-atom layer 2D boron sheet. However, it still has a long way to construct these planar boron clusters to 2D boron sheet. Their study provides the first experimental evidence for the existing of boron nanostructures with hexagonal vacancies.

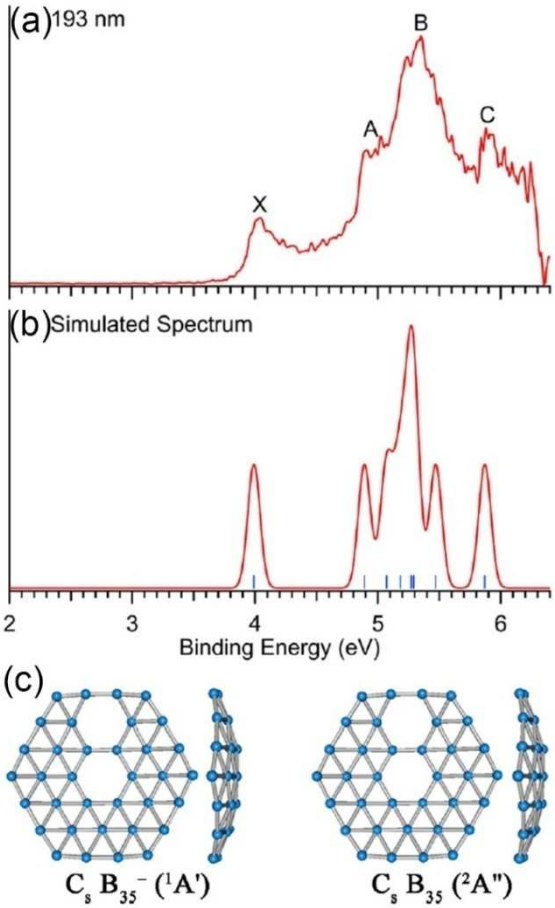

Fig. 8 Experimental and simulated photoelectron spectroscopy for the B_{35} cluster. Taken from ref. 73. Reproduced with permission. Copyright 2014, American Chemical Society.

Grow boron sheet on the substrates

Amsler *et al*., employed *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 planar and conductive monolayer sheet would form on the surface. Zhou *et al*., also found similar quasi-planar boron sheet on bulk boron.[90] But considering the strong covalent interaction with the substrate, it should be very difficult to exfoliate these boron sheets from the bulk substrate. Liu *et al*., explored the possible synthesis method of 2D boron sheet on other substrates by first-principles calculations.[91] Various substrates were considered in their work, including metal (Cu, Ag, Au) and metal boride (MgB_2, TiB_2). It is found that 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 important, 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 2D boron sheet on Cu substrate.[92] Their results revealed that boron monolayers should be very stable on Cu(111) surface due to the substrate passivation. Besides, boron clusters has a low diffusion barrier on the substrate and decrease of formation energy with the increase of cluster size. Thus, the continuous growth of 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, boron monolayer sheet with suggested mixed hexagonal-triangular geometry should be realized on Cu substrate. Their study gave a clear picture for the growth mechanism of boron monolayer on Cu substrate and will be very helpful for further experimental synthesis of 2D boron sheet.

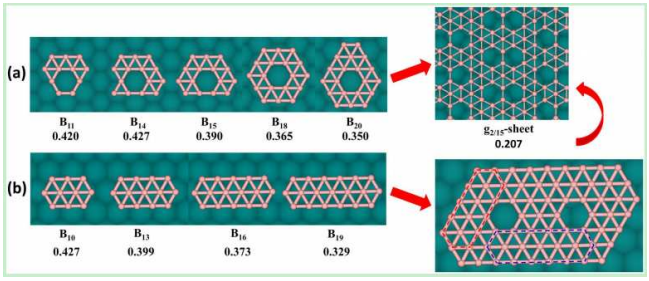

Fig. 9 (a) Surface modification of GO with POSS, and photographs of original GO in water and the synthesized POSS-graphene in $CHCl_3$. (b) SEM image of the POSS-grafted GO film, the inset is the image of water droplet CA, ~111.2°. (c) SEM image of a rough POSS-graphene film prepared from POSS-graphene particles, the corresponding water CA is 157°. Reproduced with permission.[47] Copyright 2012, American Chemical Society.

Successfully fabricated boron nanotubes may become a source to produce boron nanoribbons. Previous experiments have successfully unzipped graphene nanotubes into nanoribbons by oxidative[93] or Ar plasma cutting.[94] Compared with C-C bond in graphene, B-B bond in boron sheet is weaker. Thus, it should be more easier to break boron bonds. However, the complex structure of boron nanotubes may meet challenge to be unzipped into boron ribbons. Thus, more experimental and theoretical efforts should be contributed to verify this proposal.

Application

Xu *et al*., used their boron nanosheets obtained through decomposition of diborane to fabricate FET devices and photoelectronic devices. The turn-on electric field in their experiment is 3.6 V/μm and the threshold electric field is 5.08 V/μm. The boron nanosheets also hold a high photosensitivity and fast photoresponse, as shown in Fig. 11 (a) and (b). Some calculation works are taken to explore the potential application of 2D boron sheet. Wang *et al*., suggested 2D boron sheet can be used as the potential hydrogen storage materials by the decorating of metal anions,[95] as shown in Fig. 11(c). Zheng *et al*., investigated the adsorption geometries, binding energy, electronic structures and work functions of Li clusters on 2D boron α-sheet.[96] Their simulation proved that the clustering effect of Li on boron boron α-sheet is suppressed and Li-absorbed 2D boronsheet could be promising candidates for electrode materials in electronic devices. Banerjee *et al*, with the ab-inito molecular dynamic method, proved that 2D-boron sheets could be act as anode material in lithium ion battery.[97] Peng *et al*., studies the mechanical properties of α-boron sheet under strains and predicted a high in-plane stiffness (about 2/3 of that of graphene) of α-boron[98]. The simulation results imply α-boron sheets have advanced mechanical properties with high strength and high flexibility and might to be used in surface acoustic wave sensors.

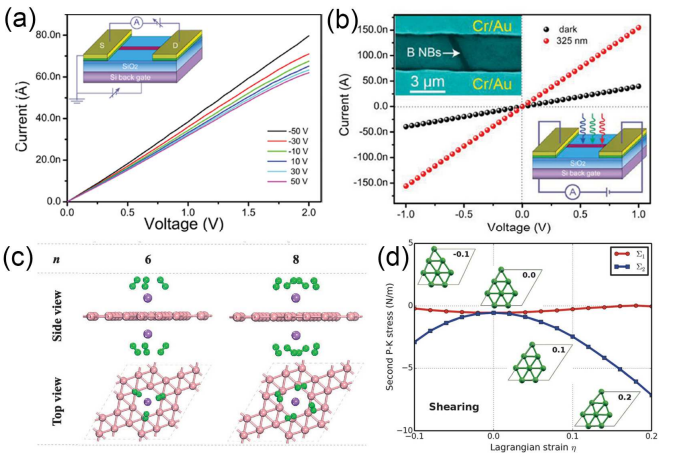

Fig. 10 (a), (b): I-V curves of boron nanosheets based FET and photo-electronic devices. (c) Li (purple balls) decorated 2D boron sheet used for hydrogen (small green balls) storage. (d) mechanical property of α-sheet. Taken from ref. 63 and ref. 84. Reproduced with permission. Copyright 2015, 2014 Willy publication group and 2015, Royal Society of chemistry. .

Conclusion and outlook

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

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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