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Review

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Emerging applicability of two-dimensional boron for energy catalysis

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Abstract: Due to their unique physical and chemical properties, two-dimensional (2D) boron nanosheets have received tremendous research attention and demonstrated substantial value in electronic devices, biomedicine, and energy conversion. In the preparation of boron nanosheets, compared with the bottom-up synthesis predominantly employed for electronics, the top-down synthesis route offers more facile and scalable production. In this mini-review, we mainly discuss the recent advances in the synthesis of boron nanosheets using the top-down strategy and the relevant applications in energy catalysis. Finally, inspired by our recent works on the novel applications of 2D silicon, we put forward prospects for designing boron nanosheets, providing insights into developing viable techniques for high-performance heterogeneous catalysis.

Key words: Two-dimensional (2D) boron nanosheets; Top-down method; Catalytic applications

1 Introduction

Two-dimensional (2D) nanomaterials have received significant research interest in recent years owing to their unique physical and chemical attributes different from their bulk structure, such as large surface area, high carrier mobility, and excellent mechanical properties (Fan et al., 2021). During the past decade, various 2D nanomaterials were successfully synthesized, including silicene, MXenes, black phosphorus, graphene, and transition metal dichalcogenides (TMDs) (Han et al., 2022). These 2D nanomaterials found important application in sensors, biomedicine, electronics, and energy conversion and storage (Hou et al., 2023). Therefore, the continuous development of novel 2D materials is a fascinating prospect for researchers.

Boron (B) is a neighbor of carbon in the periodic table, thus the two share many similarities. Consequently, the question arises whether boron-based materials can be fabricated into 2D nanomaterials. In 2013, using first-principles calculations, Liu et al. (2013) predicted that B sheets can be synthesized on Ag (1 1 1) or Au (1 1 1) surfaces by deposition. In 2015, for the first time, Mannix et al. (2015) employed the molecular beam epitaxy (MBE) method to experimentally grow boron sheets on silver surfaces under ultra-high vacuum conditions. Subsequently, 2D boron was successfully synthesized on different metal substrates (including Cu, Au, and Al) (Hou et al., 2020). Although these bottom-up methods for the synthesis of 2D boron have achieved great progress, the harsh preparation conditions and the limited production yield have impeded their large-scale application. By contrast, top-down strategies, including chemical exfoliation, cation exchange, and physical exfoliation, have been found promising for preparing 2D boron in high quality and yield (Ji et al., 2018; Ou et al., 2021; Sun et al., 2023).

In this mini-review, we firstly discuss the top-down strategies for preparing 2D boron and its applications in energy catalysis from recent years. Then, the challenges and perspectives for future developments on 2D boron materials are outlined. Different from previous reviews focusing on bottom-up methods for 2D boron devices, this mini-review aims to provide useful insights into synthesizing scalable 2D boron and promote new fields of application.

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2 Synthesis of 2D boron using top-down strategies

2.1 Chemical exfoliation

Compared with epitaxial growth methods, the chemical exfoliation strategy is more extensive in preparing 2D nanomaterials owing to its simplicity, low cost, and high-yield characteristics. To date, most reported 2D nanomaterials obtained via chemical exfoliation have originated from materials with layered structures. Etching solvents (such as HCl and HF) can be used to break the interlayer bonding between the adjacent layers and thus obtain layered structures. For example, our group has successfully prepared various 2D silicon nanosheets by the chemical exfoliation method (Qian et al., 2018; Wang CH et al., 2022). Furthermore, $CaSi_2$ was employed as a precursor and then the Ca^{2+} was deintercalated by concentrated hydrochloric or $CuCl_2$ (Wang SH et al., 2022; Su et al., 2023).

MgB_2 is another layered ionic solid in which magnesium layers are sandwiched between two boron layers. The superconducting properties of this compound were reported in 2001, triggering huge research interest (Nagamatsu et al., 2001). The layered structure makes MgB_2 an excellent precursor for 2D boron synthesis. To extract the inter-layer magnesium (Mg) cations, as shown in Fig. 1a, James and Jasuja (2017) employed ethylene diamine tetraacetic acid (EDTA) as a chelating agent to exfoliate the Mg atoms from bulk MgB_2 under magnetic stirring for 1 h. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) of boron-based nanosheets indicated a stoichiometric ratio (Mg: B) of 0.48: 2.00, confirming the selective extraction of 52% Mg atoms. As shown in Fig. 1b, atomic force microscopy (AFM) images revealed the 1.0–1.7 nm thickness of the obtained nanosheets. It is noteworthy that various functional groups (such as hydride, hydroxy- and oxy-functional) were easily decorated on the surface of boron sheets due to the loss of Mg atoms (Fig. 1c). Das and Jasuja (2018) subsequently synthesized lamellas resembling "nanoaccordions" with a thickness in the range of 300–400 nm using sulfuric acid (H_2SO_4) and tetramethylammonium hydroxide (TMAOH) as exfoliation solvents in an ice bath for 72 h. The purpose of applying TMAOH was to facilitate the expansion of layered crystals and then promote the delamination of MgB_2. Under ultrasonication in water, these nanoaccordions could be further transformed into few-layer thick (3–5 nm) 2D boron-based nanosheets. The obtained nanosheets were examined by ICP-AES and exhibited a stoichiometry of $Mg_{0.6}B_2$, suggesting that 40% of Mg atoms were excluded. To further extract Mg atoms from MgB_2, Zhang et al. (2022) added I_2 into a mixture system composed of CH_3CN, HCl, and MgB_2, and stirred the mixture for 14 d under nitrogen gas protection to prepare few-layer Mg-deficient borophene nanosheets (FBN). HCl played an important role in etching Mg atom layers, and the negative charge of boron layers was reduced by oxidation with I_2, so that Mg layers could be deintercalated to the maximum extent (78%). Furthermore, based on the density functional theory (DFT), Zhang et al. (2022) proposed that the structure of 2D boron could not be maintained when the Mg atoms in the bulk MgB_2 were completely extracted, owing to the electron deficiency of boron atoms. Our research group employed concentrated HCl to etch MgB_2 under protective nitrogen gas atmosphere at room temperature for 24 h (Zhang et al., 2024). The obtained boron-based nanosheets exhibited a stoichiometry of $Mg_{0.12}B_2$, which is by far the highest deintercalation rate of Mg atoms compared to other reported boron-based nanosheets. This result may be attributed to the high concentration of HCl for extracting Mg atoms. Transmission electron microscopy (TEM) imaging showed that the thickness of the nanosheets was about 5 nm (Fig. 1d).

AlB_2 has a similar layered structure to MgB_2, indicating its potential value as a precursor for 2D boron synthesis. Xie et al. (2022) employed different acids to selectively etch the AlB_2 precursor. After HCl etching, the 2D boron nanosheets with 4 nm thickness were obtained. As shown in Fig. 1e, the main peak at 6° is the boron product in the X-ray diffraction pattern, suggesting that Al atoms were exfoliated. By contrast, the main XRD peaks are AlF_3 and Al_2O_3 after HF etching, indicating that this step could completely remove the B element, leaving Al, O, and F behind. These results indicate that HCl is a suitable etching agent to exfoliate the AlB_2 precursor. Except for acid etching, an alkali solution is also a suitable etching agent to exfoliate bulk AlB_2 due to the strong binding ability between hydroxide radicals and the element Al. Cai et al. (2022) employed a concentrated NaOH solution to etch AlB_2 under stirring at 70 °C in a water bath for

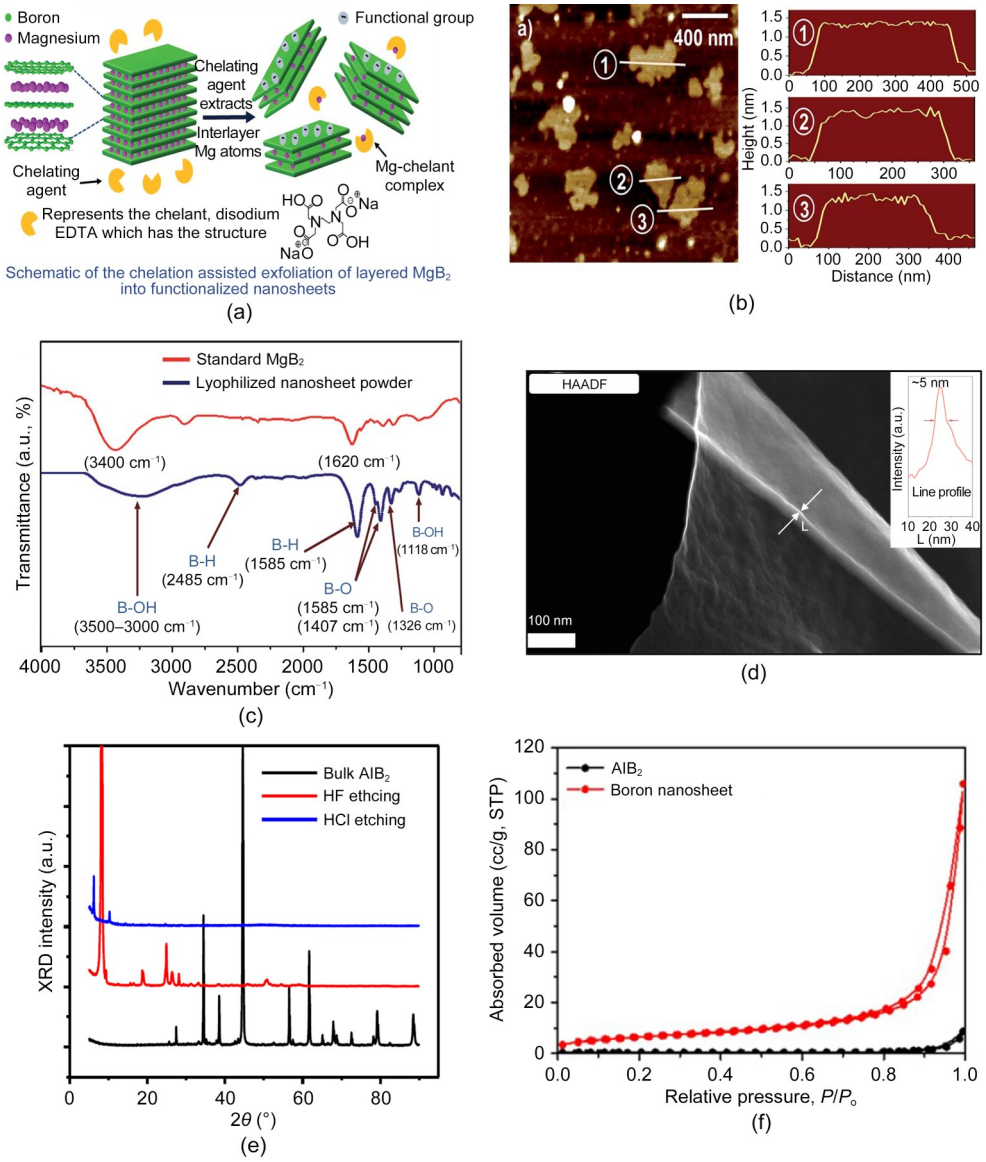

Fig. 1 (a) Schematic depicting the process of ethylene diamine tetraacetic acid (EDTA) chelating a substantial fraction of interlayer Mg atoms; (b) AFM images of the obtained boron nanosheets; (c) Fourier-transform infrared (FT-IR) spectra of standard MgB_2 and boron nanosheets; (d) TEM image of the boron nanosheets. The inset image is the line profile at position "L"; (e) XRD patterns of bulk AlB_2, the boron product after HCl etching, and the aluminum product after HF etching; (f) Nitrogen absorption-desorption isotherms of boron nanosheets and their precursor AlB_2. Figs. 1a–1c are reprinted from (James and Jasuja, 2017), Copyright 2017, with permission from the Royal Society of Chemistry; Fig. 1d is reprinted from (Zhang et al., 2024), Copyright 2024, with permission from the Royal Society of Chemistry; Fig. 1e is reprinted from the supplementary information of (Xie et al., 2022), Copyright 2022, with permission from Springer Nature; Fig. 1f is reprinted from (Cai et al., 2022), Copyright 2022, with permission from the Royal Society of Chemistry. References to color refer to the online version of this figure

12 h. The obtained boron nanosheets with a thickness of 4 nm had a higher surface area (140.4 m^2/g) than pristine AlB_2 particles (4.1 m^2/g) (Fig. 1f).

2.2 Cation exchange with resin

2D boron nanosheets are easily furnished with many functional groups in the liquid phase exfoliation process. These can improve the stability of boron nanosheets and tune their properties at the same time. Among them, hydrogen atom is a common element that attaches to the surface of boron sheets. After hydrogenation, the bonding of boron nanosheets can be restructured, so that the formed hydrogen boride (HB) will be stable in air or water.

Nishino et al. (2017a) prepared HB sheets (Fig. 2a) by the cation exchange method in methanol (or acetonitrile) at 343 K under an inert atmosphere for 3 d. Using an ion-exchange resin, the Mg atoms of MgB_2 were completely exchanged by protons, and the average yield of HB sheets as a yellow powder was 43.2%. The obtained HB sheets were estimated to have a thickness of approximately 0.5 nm. According to the results of thermal desorption spectroscopy (TDS), the B/H ratio in HB sheets was determined as 1:1 (Fig. 2b). It is noteworthy that the presence of $B(OH)_3$ as a by-product could be detected during the synthetic process. To obtain unoxidized layered HB sheets, Tominaka et al. (2020) developed an improved Schlenk method and obtained a pure HB sheet by ion-exchange reaction. Most importantly, the improved Schlenk method could effectively increase the yield of HB sheets from 43.2% to 60.2%, as shown in Fig. 2c, a significant step toward for the mass production of boron nanosheets. Furthermore, to reduce the synthesis time of HB sheets while maintaining a high yield, Kawamura et al. (2020) added formic acid to the acetonitrile solution including MgB_2 powder and cation-exchange resin. As shown in Fig. 2d, the formic acid acts as a mediator to facilitate ion exchange between protons in the ion-exchange resin and Mg atoms in MgB_2. Thus, this method took only 2 h of reaction time to achieve 50% yield, significantly faster than the conventional process taking 3 d.

2.3 Physical exfoliation

A convenient strategy to obtain 2D materials from bulk materials is the mechanical exfoliation method, which utilizes shear forces to overcome the weak van der Waals interactions between the connecting layers. Novoselov et al. (2004) successfully synthesized monolayer and few-layer graphene from graphite by employing this method for the first time. Subsequently, various 2D materials were prepared by this approach, such as MoS_2, BP, and WS_2 (Radisavljevic et al., 2011; Zhao et al., 2013; Liu et al., 2014). However, it was not

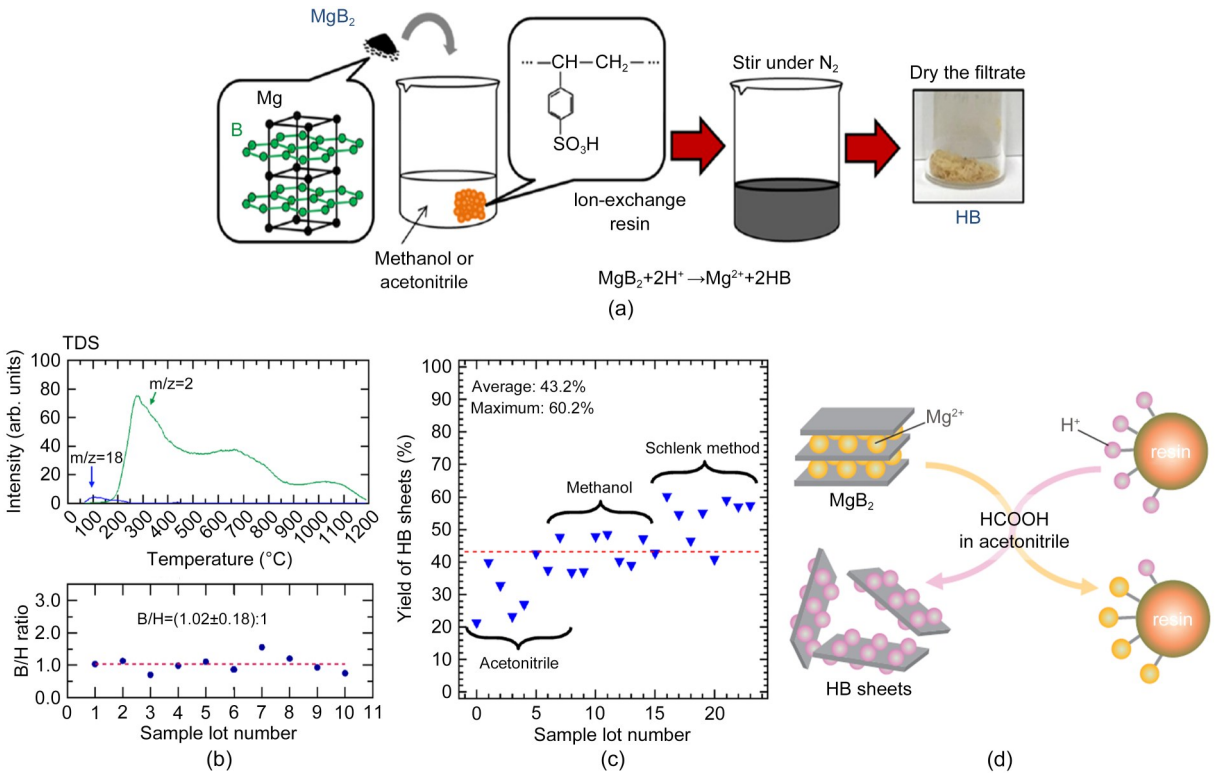

Fig. 2 (a) Schematic illustration of HB nanosheet preparation by a cation exchange process; (b) TDS of HB nanosheets; (c) Yields of HB nanosheets using the conventional ion-exchange method with acetonitrile or methanol, and the Schlenk method with methanol; (d) Schematic illustration of the synthesis of HB nanosheets facilitated by formic acid. Figs. 2a is reprinted from (Nishino et al., 2017a), and Fig. 2b is adapted from (Nishino et al., 2017a) with some modifications, Copyright 2017, with permission from the American Chemical Society; Fig. 2c is reprinted from (Tominaka et al., 2020), Copyright 2020, with permission from Elsevier; Fig. 2d is reprinted from (Kawamura et al., 2020), Copyright 2020, with permission from The Chemical Society of Japan

until 2021 that Chahal et al. (2021) adopted it for the synthesis of 2D boron owing to the misunderstanding of the crystal structure of boron. The authors proposed that the failure of using scotch tape was due to the higher exfoliation energy of boron crystal than other bulk crystals (including MoS_2, Gr, and BP) calculated by DFT as shown in Fig. 3a. Therefore, they employed double-sided foam tape as an alternative to exfoliate the boron crystal (Fig. 3b). Field-emission scanning electron microscopy (FESEM) indicated that the lateral dimensions of the obtained boron sheets were a few micrometers, but the straightened stiff sheets also seemed relatively thick (Fig. 3c).

Despite the simplicity and cost-efficiency of mechanical exfoliation to prepare 2D materials, it has some shortcomings, such as large thickness and low yield, which fails to meet the demands of many technological applications. By contrast, the ultrasonication liquid exfoliation method has been recognized as an appealing route to produce 2D materials, due to its advantage that the size, quality, and yield of 2D materials can be controlled by the sonication solvent and time. Li et al. (2018) prepared few-layer boron sheets from bulk boron by the ultrasonication liquid method, as shown in Fig. 3d. They found that the obtained boron sheets had an average thickness of 1.8 nm by using dimethylformamide (DMF) as the exfoliation solvent. When isopropyl alcohol (IPA) was used instead, the thickness of boron sheets was 4.7 nm. Most importantly, the obtained boron nanosheets exhibited excellent stability in the exfoliating solvent over 50 d under ambient conditions, suggesting the enormous potential of this strategy for practical applications. Subsequently, Ma et al. (2020) combined probe sonication and water bath sonication to prepare boron sheets from bulk boron precursor in IPA solvent. As shown in Fig. 3e, the high resolution transmission electron microscope (HRTEM) image confirmed the high crystalline nature of the

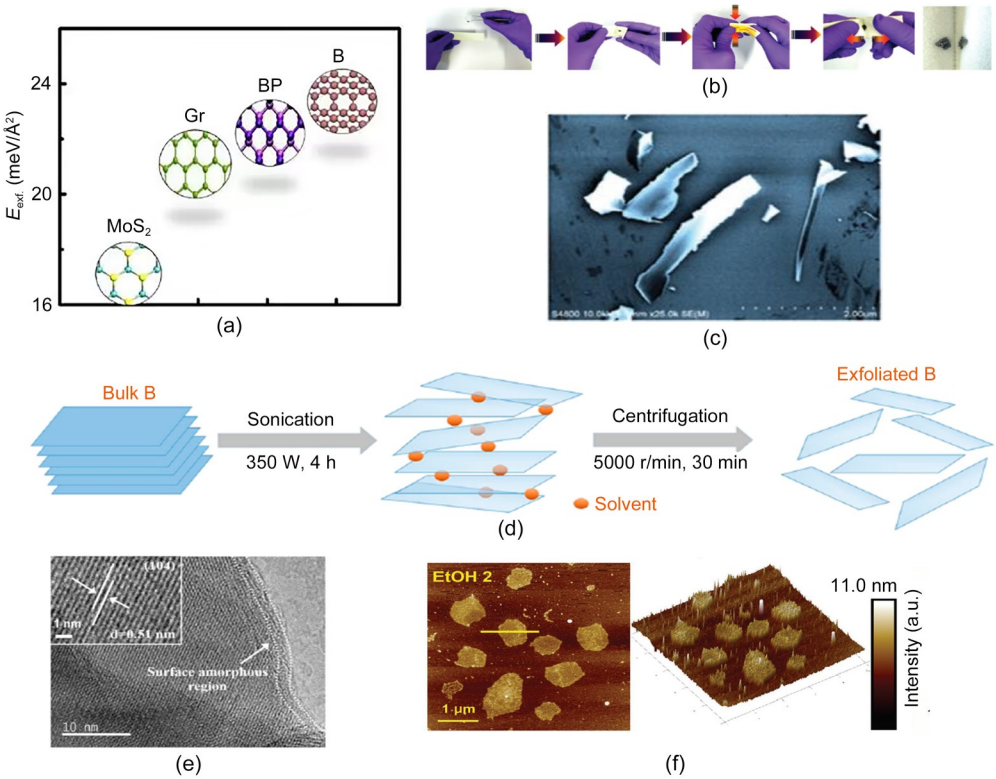

Fig. 3 (a) Exfoliation energy of different materials (including MoS_2, Gr, BP, and B); (b) Digital images of the steps of the mechanical exfoliation of boron nanosheets using double-sided foam tape; (c) FESEM image of the obtained boron nanosheets; (d) Schematic illustration of the ultrasonication liquid exfoliation process; (e) HRTEM image of the exfoliated boron nanosheets; (f) AFM image of the exfoliated boron nanosheets in ethanol solvent. Figs. 3a–3c are reprinted from (Chahal et al., 2021), Copyright 2021, with permission from John Wiley and Sons; Fig. 3d is reprinted from (Li et al., 2018), Copyright 2018, with permission from the American Chemical Society; Fig. 3e is reprinted from (Ma et al., 2020), Copyright 2020, with permission from the Royal Society of Chemistry; Fig. 3f is reprinted from (Chand et al., 2022), Copyright 2022, with permission from John Wiley and Sons

exfoliated boron nanosheets. In addition, these sheets maintained good structural integrity and had a thickness of 2.1 nm and a lateral size of 82 nm. Meanwhile, in the above-mentioned works, ultrafine pure boron powder was used as the precursor, increasing the cost. Recently, Chand et al. (2022) prepared ultrathin boron nanosheets from low-cost bulk boron chunks by combining mechanical grinding and ultrasonication liquid exfoliation methods. The yield of boron sheets from the ethanol solvent was 15 mg per 300 mg bulk boron, showcasing its efficiency and low cost to synthesize boron sheets. The AFM results showed that the obtained boron nanosheets had a thickness of 5.5 nm in ethanol solvent (Fig. 3f).

In addition to bulk boron as the precursor, the layered compound of MgB_2 can also be exfoliated into boron-based sheets by the ultrasonication liquid method. Das et al. (2015) found that 2D boron-based nanosheets could be synthesized from MgB_2 in the presence of water by ultrasonication for 30 min. The obtained nanosheets exhibited a magnesium-deficient stoichiometry and were functionalized with hydroxyl groups, thus they were not pure boron nanosheets. To explore the reaction mechanism between MgB_2 and water, Nishino et al. (2017b) revealed that there are mainly two steps in this reaction. First, there is an ion-exchange between protons and Mg cations. Second, the Mg-deficient boron hydride sheets and water undergo a hydrolysis reaction to produce H_2 and Mg-deficient hydroxyl-functionalized boron nanosheets.

3 Catalytic functions of 2D boron

Many reviews have summarized the relevant applications of 2D boron in electronic devices, biomedicine, and energy storage (Han et al., 2022; Fan et al., 2023; Hou et al., 2023). However, the catalytic application mechanism has not been systematically discussed. In this section, we focus on 2D boron as the harbor of active sites and supports for catalysis. We hope that this perspective will shed light on how to develop high-performance catalysts based on 2D boron materials.

3.1 2D boron as catalytic sites

Recently, Fujino et al. (2019) explored the catalytic activity of HB nanosheets obtained from MgB_2 precursor in the ethanol-reforming reaction. The HB catalyst exhibits a distinct ethanol conversion, which increases with the temperature (Fig. 4a). By contrast, the precursors MgB_2 and B_2O_3, the main byproducts during the process of HB synthesis, do not show any catalytic performance. In addition, the main product is ethylene (C_2H_4) at various reaction temperatures (Fig. 4b), indicating that ethanol reforming by HB nanosheets is a dehydration reaction, as shown in Fig. 4c. To further explore the reaction mechanism, Fujino et al. (2021) confirmed the lattice H of HB participating in the dehydration reaction of ethanol by using isotope ethanol with in situ Fourier transform infrared (FT-IR) techniques. Subsequently, Goto et al. (2022) found that the HB nanosheets as catalysts could also convert CO_2 into CH_4 and C_2H_6 at 423 K under a moist atmosphere. These results indicate that the HB nanosheets have huge potential as heterogeneous catalysts for energy conversion.

Beyond the above utility 2D boron, it has been proven beneficial for N_2 activation by DFT calculation (Lu et al., 2018). Zhang et al. (2019) prepared boron nanosheets (BNS) from a bulk boron precursor by the ultrasonication liquid exfoliation method. The prepared BNS was deposited dropwise on carbon paper (BNS/CP) and, for the first time, experimentally employed in the N_2 reduction reaction (NRR). As shown in Fig. 4d, the BNS/CP exhibited the highest NH_3 yield of 13.22 μg/(h·mg_{cat}) in 0.1 mol/L Na_2SO_4 among the reported NRR catalysts. Besides, after 2 h of NRR electrolysis, the amount of produced NH_3 for BNS/CP was 2.64 μg, significantly larger than blank CP (0.13 μg) and bulk B/CP (0.17 μg) (Fig. 4e). The superior NRR performance of BNS/CP is possible because the catalyst has more active sites and lower charge transfer resistance. Furthermore, the authors confirmed by DFT calculations that the rate-determining step was the desorption process of the second NH_3 molecule (Fig. 4f).

Recently, our group prepared boron nanosheets with a few Mg atoms by the chemical exfoliation method, denoted as Mg-BNSs (Zhang et al., 2024). We explored the catalytic performance of Mg-BNSs in the oxidation dehydrogenation of propane. As shown in Fig. 4g, the catalysts yielded 39.8% propane conversion, and the propene and ethene selectivities were as high as 63.5% and 18.4%, respectively, at 530 °C. Most importantly, the catalysts maintained good stability at 530 °C even after testing for 100 h (Fig. 4h). Based on FT-IR, we identified that the B-H groups on the

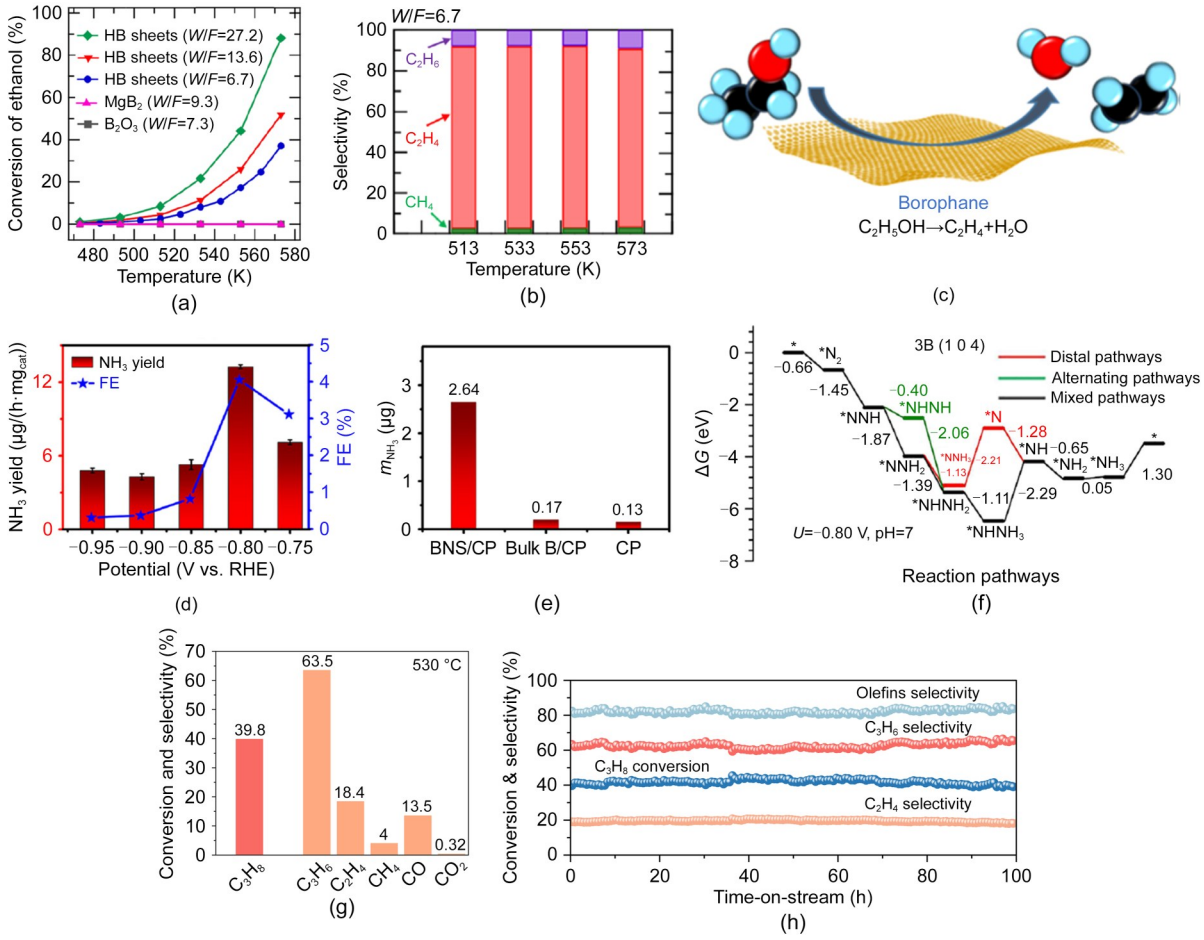

Fig. 4 (a) Ethanol conversion of HB sheets, MgB_2, and B_2O_3 at different temperatures (*W*/*F* (g·min/mmol) is the weight of the catalyst (g) divided by the flow rate of C_2H_5OH (mmol/min)); (b) Selectivity of ethanol reforming by HB as a function of temperature; (c) Schematic illustration of ethanol dehydration on HB sheets; (d) NH_3 yields and Faraday efficiencies (FEs) for BNS/CP under the corresponding potential (RHE means reversible hydrogen electrode); (e) Yields of NH_3 produced with different electrodes at −0.8 V after 2 h of electrolysis; (f) Free-energy diagram of NRR on the B (1 0 4) surface; (g) Catalytic performance of Mg-BNS at 530 °C; (h) Stability test of Mg-BNSs at 530 °C. Figs. 4a–4c are reprinted from (Fujino et al., 2019), Copyright 2019, with permission from American Chemical Society; Figs. 4d–4f are reprinted from (Zhang et al., 2019), Copyright 2019, with permission from American Chemical Society; Figs. 4g and 4h are reprinted from (Zhang et al., 2024), Copyright 2024, with permission from Royal Society of Chemistry. References to color refer to the online version of this figure

catalysts converted into B-O groups as the active site during the reaction process.

3.2 2D boron as catalytic supports

Our team has identified abundant Si-H groups on the surface of 2D silicon by chemical exfoliation, which can react with metal ions (Cu^{2+}, Pd^{2+}, and Ag^{2+}) to form metal nanoparticles for catalysis (Wang et al., 2021). Recent research has revealed the similarity of B-H on 2D boron in such reaction. Ito et al. (2020) confirmed that the prepared HB nanosheets had a redox potential between −0.277 and −0.257 V versus standard hydrogen electrode (SHE) by employing ultraviolet-visible spectroscopy. Hence, metal ions with redox potentials larger than −0.257 V can be reduced by HB nanosheets, such as Ni^{2+}, Cu^{2+}, Fe^{3+}, Ag^{+}, Pd^{2+}, and Pt^{2+}. For example, the Cu^{2+} from $Cu(CH_3COO)_2$ was reduced by HB nanosheets in acetonitrile solution, and the obtained highly dispersive Cu nanoparticles were approximately 2 nm in size (Fig. 5a). Therefore, HB nanosheets may be a useful option for constructing nanocomposite catalysts by acting as both the chemical reductant and the support.

Using HB nanosheets, Gao et al. (2020) reduced noble metal ions, such as $PtCl_4^{2-}$, $PdCl_4^{2-}$, and $AuCl_4^{-}$, to construct electrocatalysts containing noble metal

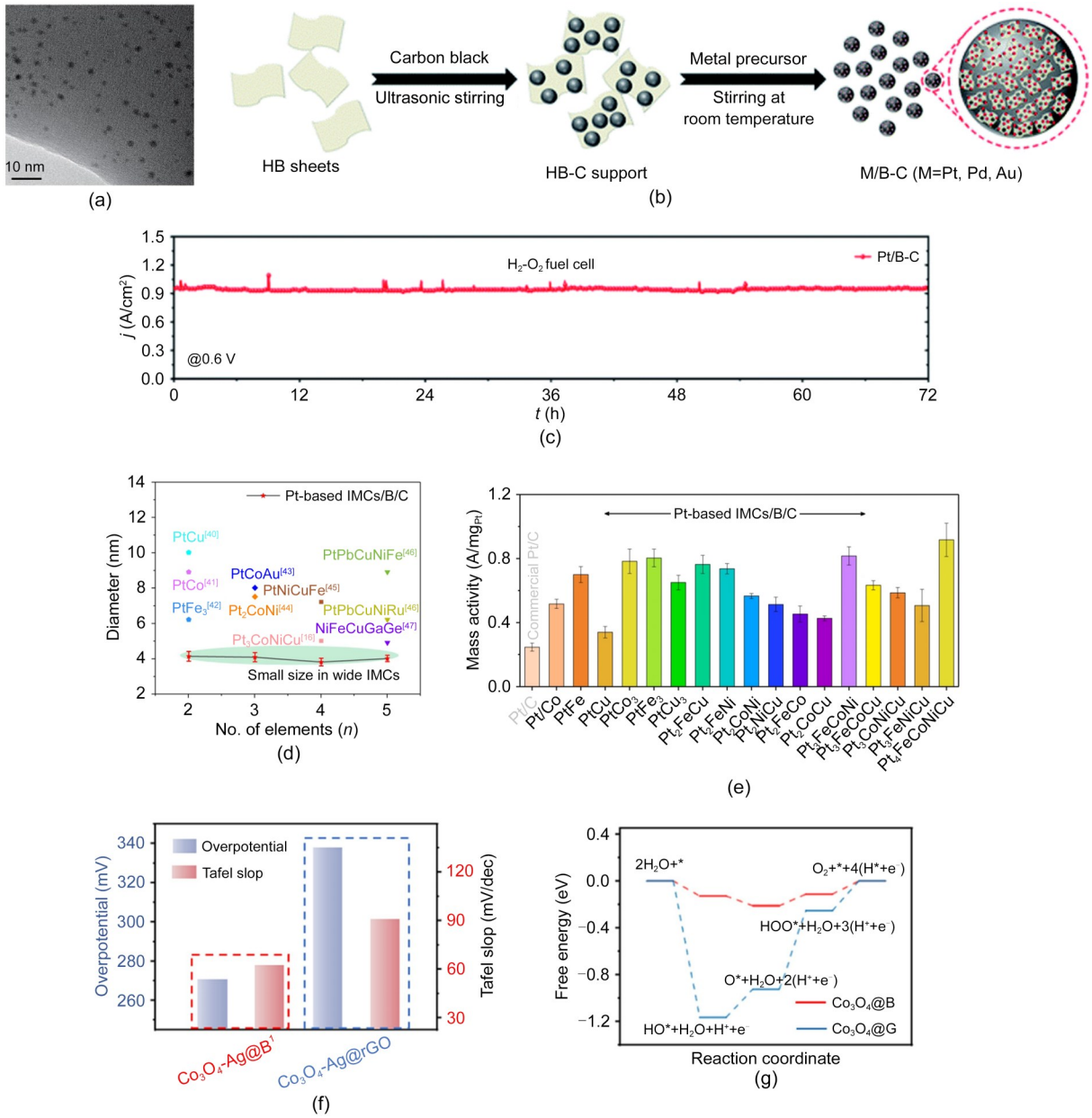

Fig. 5 (a) TEM image of Cu nanoparticles on an HB nanosheet; (b) Schematic illustration of the synthetic process of M/B-C; (c) H_2-O_2 fuel cell durability test of Pt/B-C at 0.6 V for 72 h; (d) Comparison of intermetallic alloy size between Pt-based intermetallic compounds with the reported studies; (e) Mass activity of commercial Pt/C and Pt-M/B-C for ORR; (f) Overpotentials and Tafel slopes to achieve 10 mA/cm^2 for Co_3O_4-Ag@B and Co_3O_4-Ag@rGO catalysts; (g) Reaction free energy diagram for oxygen evolution reaction (OER) on Co_3O_4@B and Co_3O_4@graphene. Fig. 5a is reprinted from (Ito et al., 2020), Copyright 2020, with permission from The Chemical Society of Japan; Figs. 5b and 5c are reprinted from (Gao et al., 2020), Copyright 2020, with permission from Royal Society of Chemistry; Figs. 5d and 5e are reprinted from (Zeng et al., 2023), Copyright 2023, with permission from Springer Nature; Figs. 5f and 5g are reprinted from (Saad et al., 2021), Copyright 2021, with permission from Elsevier. References to color refer to the online version of this figure

nanoparticles (M/B-C, M=Pt, Pd, and Au), as shown in Fig. 5b. It is noteworthy that the amount of noble metal loading reached 52.9% (mass fraction), and the particles were ultrafine-sized ((2.9±0.7) nm) and highly dispersed, so that the electrocatalysts exhibited excellent catalytic performance. In addition, they were also highly durable owing to the stronger interaction between noble metal nanoparticles and 2D boron nanosheets. For example, the catalytic performance of Pt/B-C was higher than that of commercial Pt/C catalyst in the

oxygen reduction reaction (ORR), methanol oxidation reaction (MOR), and hydrogen evolution reaction (HER) systems. It also maintained the potential of 0.6 V over 72 h in the H_2-O_2 fuel cell (Fig. 5c). Zeng et al. (2023) confirmed by DFT calculation that the strength of the Pt-B bond was more than 5 times of Pt-C. Based on the robust Pt-B bonds, the authors modulated the metal precursors to synthesize the binary, ternary, quaternary, and quinary Pt intermetallic compound nanocatalysts. Compared with the reported carbon-supported intermetallic PtM nanoparticles, the PtM/B/C catalysts had smaller nanoparticle sizes at around 4 nm (Fig. 5d). Such small size enables higher ORR activity than commercial Pt/C (Fig. 5e).

Beyond the above strategies, Saad et al. (2021) employed HB nanosheets as a support for OER catalysts. The B-H groups on the surface of HB reduced Ag^+ to form Ag nanoparticles with an average size of 7 nm. The as-formed Ag nanoparticles were used as seeds to grow Co_3O_4 nanoplates on the surface of HB support, denoted as Co_3O_4-Ag@B. The authors discovered that the interaction between boron nanosheets and Co_3O_4 could enhance the stability and activity of Co_3O_4-Ag@B in the OER reaction. Compared with the control sample with reduced graphene oxides (rGO) as the support, Co_3O_4-Ag@B showed a lower overpotential of 60 mV and a lower Tafel slope of 27 mV/dec (Fig. 5f). Besides, the overpotentials (η) for Co_3O_4-Ag@B to deliver 30 and 100 mA/cm^2 current density were small, 307 and 350 mV, respectively, lower than those for Co_3O_4-Ag@rGO (380 and 440 mV). The result of DFT calculation further indicated that the Co_3O_4@B had a lower energy barrier with 0.10 eV for the intermediate conversion process than the Co_3O_4@graphene, owing to the formation of Co-B and B-O bonds with the HB nanosheet support (Fig. 5g).

Overall, it is a promising approach to synthesize nano-compound catalysts by employing boron nanosheets as support. The strong interaction between boron nanosheets and metal nanoparticles promotes the stability and activity of catalysts, providing huge potential value and wide application prospects in energy conversion and catalysis.

4 Summary and perspective

This mini-review summarizes the synthesis of 2D boron nanosheets by using the top-down method, including chemical exfoliation, cation exchange, and physical exfoliation. The obtained 2D boron nanosheets have been successfully applied in energy conversion and catalysis. Thanks to the added functional groups, 2D boron nanosheets exhibit excellent catalytic performance in ethanol conversion, CO_2 conversion, N_2 reduction reaction, and the oxidation dehydrogenation of propane as active sites. In addition, B-H groups on the surface of 2D boron nanosheets have been demonstrated to be direct reductants for several metal ions. The interaction between the thus formed metal nanoparticles and 2D boron nanosheets can increase the stability of nano-compound catalysts and enhance their activities. Therefore, 2D boron nanosheets can be considered ideal catalytic supports and catalysts (Table 1). Inspired by these pioneering research studies on 2D boron nanosheets, we propose some perspectives to broaden this field.

Firstly, although chemical exfoliation is a facile strategy to synthesize 2D boron nanosheets, it cannot prepare nanosheets with pure boron. For instance, the obtained boron nanosheets have many residual metal atoms when employing acid etching of MgB_2 or AlB_2. To further extract metal ions, it may be a promising route to combine the acid etching method with chelation-assisted and oxidizing strategies. Chelation agents with high affinity for Mg^{2+} or Al^{3+} may facilitate the exsolution

Table 1 Summary of 2D boron heterogeneous catalysts in recent studies

Entry	Catalyst	As catalytic support	As catalytic site	Reference
1	HB nanosheets	–	Ethanol conversion	Fujino et al., 2019
2	HB nanosheets	–	CO_2 conversion	Goto et al., 2022
3	BNS/CP	–	N_2 reduction reaction	Zhang et al., 2019
4	Mg-BNSs	–	Oxidation dehydrogenation of propane	Zhang et al., 2024
5	Pt/B-C	Oxygen reduction reaction	–	Gao et al., 2020
6	PtM/B/C	Oxygen reduction reaction	–	Zeng et al., 2023
7	Co_3O_4-Ag@B	Oxygen evolution reaction	–	Saad et al., 2021

of these cations, while oxidizing agents (e. g., metal ions used for exfoliating $CaSi_2$ for the synthesis of 2D Si nanosheets) may help break the ionic Mg-B bonds by annihilating the negative charges of boron. In addition, many metal borides (such as Ni_2B, Cu_2B, and Mo_2B) also have huge potential for preparing 2D boron as the precursors. What is more, some metal borides with layered structures can be directly used for high-performance catalysis (Li et al., 2023).

Secondly, many functional groups (including hydride, hydroxyl, and oxy-functional groups) can be simultaneously attached to the surface of boron sheets by top-down approaches from bulk boron or MgB_2. These functional groups can not only stabilize the boron nanosheets but also tune their properties. For instance, the OH group can tune the band gap of boron nanosheet due to the hybridization of the oxygen *p* orbital with the boron *p* orbital, which renders the B-OH nanosheets potential value in photo-detection (Wang et al., 2020). In addition, Zhang et al. (2019) prepared boron nanosheets from bulk boron in IPA solvent. They found that the oxidized and H-deactivated boron nanosheets could catalyze the NRR more effectively than pristine boron nanosheets. Therefore, it is worth exploring suitable target reactions that can maximize the functions of these groups and identify their specific roles in more versatile energy conversion and catalytic applications.

Finally, the emerging strong metal-support interaction (SMSI) between boron nanosheets and metal nanoparticles is a distinct class from traditional SMSI systems that often involve reducible oxides. This results in exceptionally high loading capacity, stability and dispersion of nanoparticles, conducive to high-performance catalysis. Our recent success in embedding metal nanoparticles into 2D Si nanosheets for highly stable reversed water gas shift reaction also suggests that such SMSI structure has an innate catalytic advantage (Wang SH et al., 2022). However, the mechanism of SMSI formation between boron and metal remains unknown. It is certainly of interest to illustrate the evolutionary process of metal-B bonds (and metal-O, B-O bonds when oxygen is involved in the reaction), which deserves further exploration through in-situ characterization and theoretical simulation.

To conclude, 2D boron is a treasure trove for energy catalysis. Its potential for the advanced catalytic systems has just emerged but has been underpinned by recent demonstrative works. Its sustainable development and further exploitation will be contingent on judicious design of the materials synthetic methods that likely involve the facile and productive top-down approaches. Bearing both the functional groups and metal sites that can participate in the reactions, the obtained boron nanosheets may be excellent options for boosting catalytic performance.

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Author contributions

Wei SUN and Dake ZHANG proposed the topic of the review. Wei SUN and Dake ZHANG wrote and revised the manuscript. Chengcheng ZHANG applied for the copyrights of figures. Shenghua WANG summarized these figures. All authors contributed to discussion and manuscript review.

Conflict of interest

Dake ZHANG, Chengcheng ZHANG, Shenghua WANG, and Wei SUN declare no competing interests.

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