BORON 9(2), 82 - 95, 2024

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JOURNAL OF BORON
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Review of properties, synthesis, and energy applications of borophene, a novel boron-based 2D material

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ARTICLE INFO

Article history:
Received February24, 2024
Accepted May 31, 2024
Available online June 28, 2024

Review Article

DOI: 10.30728/boron.1442569

Keywords:
Boron
Borophene
Energy applications
Two-dimensional material

ABSTRACT

At least 16 bulk polymorphs of linked icosahedrons exist in boron that are not found in other materials, due to the low covalent radius and sp^2 hybridization capacity of boron atoms. One of them is borophene, an exciting new nanomaterial with a wide range of possible energy uses. The existence of borophene, a two-dimensional (2D) material, has been proven by both theoretical and experimental studies. Borophene's high magnetic conductivity, theoretical specific capacities, and ion transport properties make it a promising candidate in energy applications (EAs). In this study, firstly, the structure, chemical, and physical properties of borophene were mentioned. Then, in terms of synthesis approaches, both top-down and bottom-up techniques such as ultra-high vacuum (UHV), chemical vapor deposition (CVD), exfoliation by sonochemistry (ExS), molecular beam epitaxy (MBE) and multi-step thermal decomposition (MTD) were discussed. Finally, its use as a catalyst in high-metal-ion batteries, hydrogen storage (HS), nanoelectronics applications hydrogen evolution reaction (HER) was mentioned.

1. Introduction

Over the past ten years, active energetic elements including, sulfur, nitrogen, zinc, molybdenum, phosphorus, halogens, and boron have caught the attention of researchers. Due to the increasing need for green chemistry and renewable energy, boron is becoming increasingly important in energy research. Boron's adaptable chemistry makes energy applications (EAs) easier [1,2]. Atomic, physiochemical, and other properties of boron are listed in Table 1. Figure 1 depicts the location of boron in the periodic table [2-5]. A boron atom has three valence electrons in its outermost layers, scattered in the 2s^2 and 2p^1 orbitals. The boron atom has an electron deficiency because it possesses four bonding orbitals, one more than the valence electron. Therefore, boron is capable of sp^2 hybridization, which facilitates the development of low-dimensional structures and produces a wide range of characteristics. Moreover, boron may form various compounds due to its location halfway between metals and nonmetals [5-7]. Boron atom, due to its similarity to nearby carbon, fullerenes, nanotubes, and 2D films can develop as well as other low-dimensional allotropes. It is sensitive to chemical reactions that saturate the valence shell and coordination sphere. Due to the many ways that boron may be bound, at least 16 bulk polymorphs consisting of linked icosahedrons exist in boron that are not present in other base materials [8]. The capacity of boron to create stable molecular networks with covalent bonds makes it comparable to carbon. Regular boron icosahedra are seen in amorphous boron. Crystalline boron forms four primary allotropes: γ-orthorhombic, β-tetragonal, α-rhombohedral, and β-rhombohedral [5].

Table 1. Structural properties of boron.

	B
Atomic number	5
Phase	Solid
Atomic weight	10.81
Allotropes	α-tetragonal, α-rhombohedral, β-rhombohedral, γ orthorhombic, β-tetragonal, borophene, cubic boron, borospherene, amorphous boron
Isotope	^{10}B, ^{11}B
Melting point	2076°C
Density (liquid)	2.08 g/cm^3
Molar heat capacity	11.087 J/(mol·K)
Thermal conductivity	27.4 W/(mK)
Electronegativity	2.04

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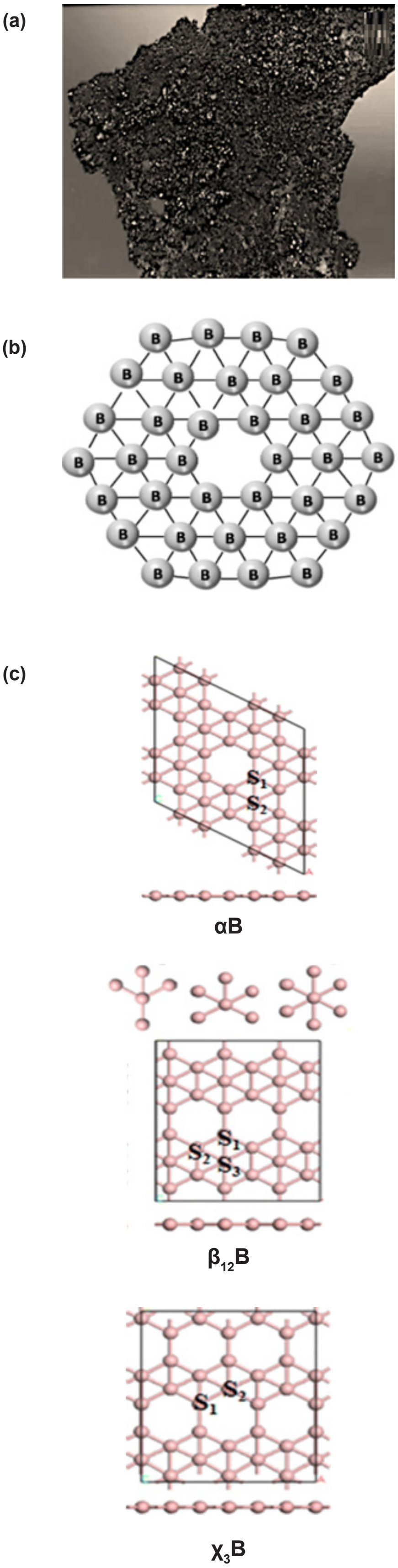

Figure 1. a) The real image of borophene, b) Structure of smallest atomic-cluster scale borophene (B_{36}), c) Top and side views of atomic structures of αB, β_{12}B, and χ_3B [Open access 27].

At room temperature, the most prevalent and stable phase is β-rhombohedral. In 2014, it was discovered that elemental boron has new allotropes called borospherene (B40 molecules similar to fullerene) and borophene (a structure similar to graphene) icosahedra [9]. Due to their extremely 2D electron quantum confinement, these 2D nanomaterials have considerable promise for many uses, including biomedicine, electronics, catalysis, and energy storage [10]. Of these nanomaterials, graphene is one of the most well-known. Its zero-band gap and semi-metallic structure, however, restrict its application, especially in semiconductor apparatuses that need a suitable energy gap. Recent research has focused on black phosphorus and antimony because of their low thermal conductivities, high carrier mobilities, and adjustable band gaps. However, these materials degrade rapidly when exposed to air, limiting their use in photoelectric and photovoltaic devices [11]. It has become possible to artificially synthesize 2D borophene from boron atoms recently. Unlike 3D objects generated by specific production processes, pure bulk boron clusters such as B7, B13, or B36 are planar or quasi-planar structures that may form 2D nanostructures like borophene [10].

Borophene and its 2D materials display a wide range of electronic features, including topology, superconductivity, charge density wave, magnetism, and other rich physical properties [13]. Both graphene and borophene have a huge specific surface area and a 2D planar structure. Furthermore, the B atom has a lower relative atomic mass than the C atom. This fact makes borophene superior to graphene in applications such as hydrogen storage (HS) [14]. In brief, the crystalline form of boron's atomic monolayer is called borophene. This current review of borophene research focuses on new developments in EAs. Firstly, the chemical and physical characteristics of borophene were covered. The thermal, optical, mechanical, electrical, elastic, and mobile characteristics of borophene have been compared with those of other 2D materials. Then, recent advancements in the synthesis of borophene are explained in various stages. Subsequently, the possible uses of borophene were explored, including supercapacitors, metal ion batteries, catalytic behavior, and HS. Large-scale applications in the fields of energy, green chemistry, catalysis, nanocomposites, nanohybrids, heterolayer devices, and sensors can all benefit from this review. Lastly, a summary of borophene is provided, considering its significant contribution to materials science and applications. Even after borophene was realized experimentally, most of the literature on the subject still focuses on theoretical studies. More work is needed to uncover more novel and intriguing physical features of crystalline and semiconductor borophene [15]. This brief analysis will lead to a fresh perspective on the matter.

2. Structure, Chemical and Physical Properties of Borophene

Comprehensive research of 2D boron materials was prompted by the proposal of Boustani et al. [16,17] that the most stable boron structure might form by bucking triangular motifs. Lau and Pandey [18] demonstrated that the buckled triangular boron may be stabilized by combining delocalized three-center-two-electron bonds and localized two-center-two-electron σ bonds. In a study conducted by Yakobson et al. in 2007 [19], the B80 buckyball, consisting of 20 hexagons and 12 pentagons, was found to be similar to the well-known C60 fullerene in terms of form and symmetry. Figure 1a displays the real image of borophene. Whereas the next element of boron, carbon, favors a bulk two-dimensional layered graphite, borophene is well-known for the presence of B12 icosahedral lattices, which serve as the building blocks for several boron compounds. Since there are only three electrons in the outer shell of borophene, and since the electrons are highly confined, and limited to each boron atom and its neighbor, the honeycomb of borophene is unstable. However, both the basic unit of the bulk boron molecule and the icosahedral B12 cluster [20-22] are very reactive. In addition to the above structures, three more pure B, B7, B13, and B36, have been reported, but their existence is still entirely hypothetical. B7, B13, or B36 (see Figure 1b) are planar or quasi-planar structures that can form 2D nanostructures like borophene. Planar and quasi-planar structures, usually constructed as pentagonal pyramid B6 or hexagonal pyramid B7 units, have been experimentally proven [17]. Unlike graphene, which has a higher relative atomic quality, borophene has an anisotropic structure that gives it outstanding mechanical qualities. Furthermore, borophene outperforms Pt and MoS_2, which are readily accessible on the market, as a feasible choice for hydrogen evolution reaction (HER) in H_2 fuel batteries, according to recent research. Graphene is not as efficient at storing H_2 gravimetrically as borophene [23]. The atomic structure, typical of electron-deficient elements like boron, is created via polycentric and bicentric in-plane bonding. The two-dimensional boron sheet borophene also exhibits this structural diversity. A further examination reveals that the borophene synthesizes in three phases, specifically 2Pmmn, β12, and χ3 [24]. Furthermore, χ3 and β12 both show a triangular lattice that is identified by various periodic hole configurations. Scanning tunneling microscopy has demonstrated that they are likewise flat, lacking any observable vertical undulation. Finally, the hole densities of the β12 and χ3 sheets are quite close together [4]. The borophenes β12 and χ3 are metallic. Tight hole densities in the β12 and χ3 sheets explain the simple exchanges between the two structures during annealing. They are both flat and free of vertical undulation [4]. One of these is the fully flat χ3 phase, whereas β12 is an atomic sheet with atomic ridges [24-27]. Figure 1c shows the atomic structures of αB, β12B, and χ3B borophene. Higher electron densities are observed along the ridges with the χ3 phase [25,26]. The gaps between the ridge lines can serve as ion transport channels in use for energy storage. It is predicted that the atomic bonding of gaseous molecules on the borophene surface will be better at the ridge line, as this may provide better stabilization. In a similar vein, more catalytic activity is anticipated [24]. Borophene is a remarkable material because of its special qualities and enormous potential for technological applications. Nevertheless, before it can be marketed, more research on its structural traits and qualities is needed. A vacancy defect in borophene that affects the mechanical characteristics was proposed by Zhou and Jiang [28]. The synthesized χ3 and sheets were found to have Young's modulus up to 198.5 N/m and 179.0 along the armchair direction. Additionally, 2-Pmmn displays a negative Poisson's ratio that is entirely distinct from all known 2D materials. The Young's modulus of the 2-Pmmn phase is 398 N/m. This value is larger than that of β12 and χ3. According to Penev et al.'s [29] prediction, the 2px and 2py states gave rise to the metallic states of β12 and χ3 sheets, which caused a band gap to develop in the boron sheets at η=10~15%, almost exactly at the Fermi level. Further theoretical calculations show that borophenes such as α, β12, χ3 and δ6, boron layers can achieve structural planarity and greater stability by intermixing hollow hexagons and triangular lattice instead of just triangular lattice [7]. Interestingly, the hollow hexagons of the triangular lattice contribute significantly to the structural diversity of borophene. After hydrogenation, the γ-B28 and α′-borophene have been effectively studied by Hou et al. [30], who discovered that the boron may widen up the bandgap to generate semiconducting materials. In the meantime, photoluminescence spectroscopy and UV-vis absorption were also studied to work the optical characteristics of the boron sheets. In borophene, thermal conductivity has been investigated as an additional significant physical characteristic. The many kinds of thermal conductivity are a result of the diversity of borophene structures. The heat conductivity of α-sheet borophene was found to be 1.43 $nWK^{-1}nm^{-2}$ [13]. Furthermore, the majority of other borophenes have anisotropic heat conduction. In the zigzag and armchair directions, the thermal conductivities of β12 are approximately 10.97 and 3.30 $nWK^{-1}nm^{-2}$, respectively. As a result, it was discovered that borophene has almost as remarkable thermal conductivity as graphene. Furthermore, employing first-principles calculations, Yakobson et al. [31,32] have methodically examined the superconducting property of borophene. Amazingly, they discovered that superconductivity was present in every kind of stable borophene. Nonetheless, there are currently few experimental studies on the advantageous characteristics of borophenes. It is critically anticipated that further impacts on experimental realization would enhance and validate the features of borophene [31-34]. Figure 2 shows the top view of χ3-borophene along the (a) c-axis (b) a-axis and (c) b-axis [25].

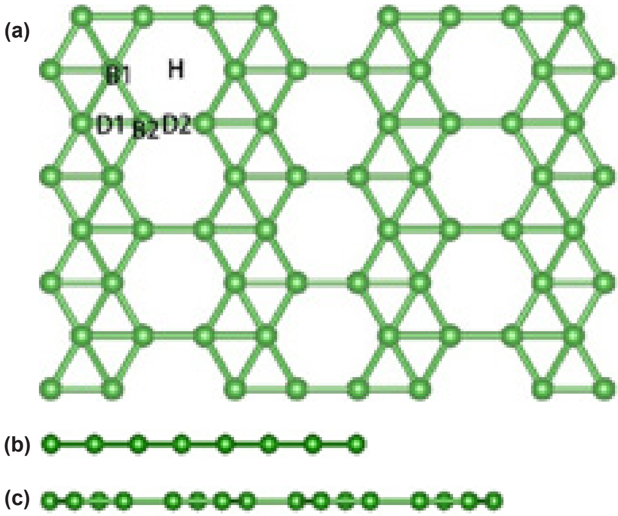

Figure 2. Top view of χ_3-borophene along the (a) c-axis (b) a-axis, and (c) b-axis (Open access [25]).

3. Synthesis of Borophene

Because of its distinct chemical and physical characteristics, borophene has accelerated many applications in optoelectronics, nanoelectronics, energy conversion, and energy storage [32].

However, because of the material's reactivity, borophene is prone to oxidation. These factors make borophene costly to produce and challenging to handle. This makes borophene less useful in general. A few review papers on the synthesis and uses of borophene have surfaced recently. Their primary synthesis methods are ultra-high vacuum (UHV), chemical vapor deposition (CVD), exfoliation by sonochemistry (ExS), and molecular beam epitaxy (MBE) for borophene. What is important in the structure and quality of the synthesized borophene are the materials that provide the kinetically preferred growth. A suitable metal substrate, such as Cu or Ag stabilizes the formation of 2D boron clusters. Second, the temperature needs to be carefully regulated, as extremely low temperatures prevent boron growth from exceeding the nucleation barrier of the 2D structure. In such cases, boron aggregates are formed. When temperatures are very high, growth is encouraged to overcome the 3D boron nucleation barrier, resulting in the development of 3D structures. As a result, the temperature must be maintained at the temperature between the development of 2D and 3D structures [12,30]

3.1. Ultra High Vacuum Conditions

By forcing the gas out of a UHV chamber, ultra-high vacuum conditions are produced. The gas is in free molecular flow at these low pressures. Before a gas molecule collides with another gas molecule, it will collide with the chamber walls several times. As a result, nearly every molecular interaction occurs on different chamber surfaces. The focus of borophene has been on its varied polymorphism and anticipated characteristics, such as phonon-mediated high mechanical strength, superconductivity, and flexibility. However, borophene oxidizes quickly in air, making it difficult to integrate borophene into useful devices and restricting experimental characterization to UHV conditions. Liu et al.'s [34] work involved hydrogenating borophene with atomic hydrogen under an extremely high vacuum to create "borophene" polymorphs. Borophene was hydrogenated by subjecting it to atomic hydrogen under UHV conditions. In an ultrahigh vacuum preparation room (~1×10^{-10} mbar), a solid boron rod was evaporated onto Ag (111) sheets on mica. The pristine Ag (111) surface was prepared for borophene development by repeatedly sputtering Ar ions for 30 minutes at 1×10^{-5} mbar and then annealing for 30 minutes at 550°C. According to the findings, the most prevalent borophene polymorph has a mixture of three-center-two-electron boron-hydrogen-boron and two-center-two-electron boron-hydrogen connections. Kiraly et al. [22] synthesized and characterized nanoscale borophene structures on Au (111) at UHV. Spectroscopic measurements revealed that borophene grown on Au (111) has a metallic electronic structure. A statistical examination of island size revealed that, at low boron concentration, borophene islands were composed of one to eight rhombohedral units with a typical area of 1 nm2. It was verified that borophene on Au (111) had metallic electrical characteristics. Mannix et al. [35] produced thin borophene layers on the inert Ag (111) single-crystal surface. Solid boron was used as a source of atoms under an extremely high vacuum to create the sheets. To circumvent the difficulties presented by hazardous precursors, it was produced as atomically thin sheets of borophene under UHV conditions utilizing a solid supply of boron atoms. The findings demonstrated that at the substrate temperature of 550°C, three phases of borophene the scrapped phase, the homogenous phase, and the nanoribbons were produced. The substrate was kept at between 450°C and 700°C during development, with a boron flow rate of between 0.01 and 0.1 monolayers per minute. The conjugated striped phase appeared as the temperature rose; however, both phases exhibited metallic characteristics. However, due to significant material consumption and energy loss, maintaining UHV conditions in laboratories is expensive and difficult. It also takes a lot of time.

3.2. Molecular Beam Epitaxy

Recently, boron nanosheets on an Ag substrate were successfully manufactured using MBE, as shown above. However, the method's applicability as a manufacturing technique was constrained by the poor yield, which led to a tiny sample at a high cost. MBE is a concentrated kind of physical vapor deposition or vacuum evaporation that allows for exact control over doping concentrations, alloy compositions, material cleanliness, and interface formation [36]. To confirm the 2D structure of borophene, Feng et al. [37] grew atomic borophene layers on silver substrates with the UHV chamber combining an MBE. Elemental boron, used as a precursor to borophene, was evaporated on a pure silver substrate at temperatures ranging from 550 to 800 K. As a result, β12 and χ3 phase borophene were obtained. Zhu and colleagues [38] used ab initio calculations to evaluate the enhanced stability of the MBE method for effectively producing honeycomb borophene onto an aluminum substrate. Analysis of the structural, electrical, and lattice energy factors yielded results indicating a strong adhesion between the metal substrate and honeycomb borophene that was significantly higher than that of graphene and metal. Li et al. [39] have successfully synthesized graphene-like borophene, a pure honeycomb, by growing MBE in an ultrahigh vacuum on an Al (111) surface. Images obtained using scanning tunneling microscopy show that borophene is a perfect monolayer with a flat, non-buckled honeycomb structure, similar to graphene. Liu et al. [40] experimentally demonstrated the synthesis of an atomically well-defined borophene on Ag (111) via MBE in a UHV. The structure of this bilayer (BL) borophene is consistent with two covalently bonded α-phase layers (referred to as BL-α borophene), according to the results of its characterization. A heightened local work function surpassing 5 eV and significant interfacial charge transfer doping are shown by field-emission resonance spectroscopy, whereas the electronic density of states around the Fermi level of BL-α borophene is identical to that of SL borophene polymorphs. Van der Waals epitaxy is considered to be a highly effective method for growing perfect 2D materials on large functional substrates; however, there are currently no reports on the stable and controlled synthesis of borophene on non-metallic substrates. Wu et al. [41] have formed borophene films on a mica substrate using van der Waals epitaxy, where H_2 and sodium borohydride ($NaBH_4$) served as carrier gases and boron sources. The lattice structure of the synthesized borophene was found to match the expected α′-boron layer. Under the light of a 625 nm light-emitting diode, the borophene photodetector exhibits good photosensitivity of 1.04 $A\,W^{-1}$ at a reverse bias of 4 V.

3.3. Chemical Vapor Deposition

CVD is a technique commonly used to produce graphene. It has been tried to use this technique to produce more 2D borophene at a reduced cost while also increasing its efficiency and yield. However, the substrates selected, and the various conditions used for various applications remain to be studied extensively. Therefore, more research into borophene synthesis techniques and related circumstances is crucial. The vacuum deposition method, known as CVD, is used to produce solid materials with excellent performance. In the semiconductor sector, this process is widely used to make thin sheets. In conventional CVD, one or more volatile precursors are introduced to the wafer (substrate); thereafter, they react and/or decompose to generate the target deposit on the substrate surface. Gas passage across the reaction chamber regularly produces and eliminates volatile byproducts. In microfabrication procedures, CVD is commonly utilized to deposit materials in a range of morphologies, including amorphous, polycrystalline, and monocrystalline. Borophene, carbon nanotubes, diamond, graphene, tungsten, filaments, fluorocarbons, titanium nitride, and various high dielectrics are among these materials [42]. Tai et al. [43] successfully grew a borophene-like material on Cu using the CVD technique. The process was performed at 1100°C with a B: B_2O_3 ratio of 1:1, conditions like those utilized in the production of graphene. To create borophene, the CVD process involves injecting diborane onto a flat surface that has been warmed, cleaned atomically, and subjected to a high vacuum. The surface was then selectively filtered from borazine using a liquid nitrogen-cold trap in a freeze-thaw cycle. Hou et al. [30] used a handmade CVD to build the boron monolayer. Throughout the experiment, hydrogen gas was utilized as a carrier gas, and a combination of B and B_2O_3 powders as a boron source to create diboron dioxide vapor. A temperature of 1100°C was set. A big area of boron monolayer was produced on Cu foil at 1000°C for one hour. The analysis results unmistakably demonstrated that the monolayer structure consisted of icosahedral B12 units and B2. Furthermore, considerable photoluminescence was seen, suggesting that the monolayer is a promising semiconductor. The optical band gap of the produced borophene determined by UV-vis was found to be around 2.25 eV, which is close to the predicted value (2.07 eV).

3.4. Exfoliation via Sonochemistry or Liquid Phase Exfoliation

2D materials can be ultrasonically prepared, cleaned, and diluted using sonochemistry [44]. It is difficult to produce borophene sheets without defects, as they generally require extremely low pressure and highly advanced production equipment. ExS synthesis can result in the production of the desired layer, depending on the solvent type and sonication period. Figure 3 shows illustrates the sonication-assisted liquid-phase exfoliation process of borophene. Massive lateral monolayer sheets may emerge if the solvent interacts with the material in the right way. If it does not interact properly, it sonicates for the same length of time and forms sheets with many stacking layers; on the other hand, extended sonication causes fragmentation and little borophene dots. Due to the inherent limitation of borophene growth via UHV and MBE to tiny regions, industrial-scale production is challenging and expensive [21]. Chowdhury and colleagues [45] investigated the electrochemical exfoliation approach used generally to produce graphene. Figure 3 shows borophene production by exfoliation via sonochemistry. This method was utilized to validate the creation of borophene from elemental boron. The generated borophene's Raman spectrum was assessed, and the zeta potential was used to gauge the borophene's stability. When compared to other methods in use, this one may be regarded as the most prospective

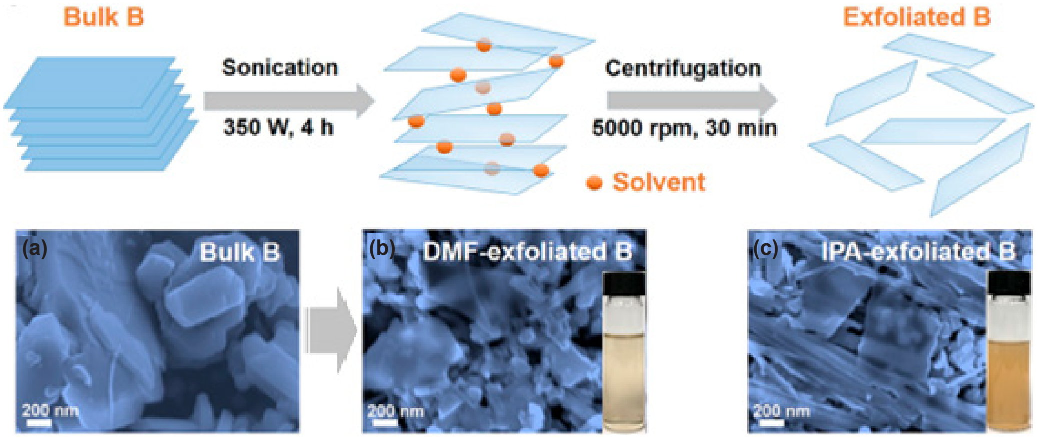

Figure 3. (a) Illustrates the sonication-assisted liquid-phase exfoliation process, (b) SEM images of bulk B. The insets of (c) and (d) show the corresponding photographs of a B sheet dispersion in DMF and IPA, respectively. Reproduced with permission from Ref. [46], ©American Chemical Society, 2018.

and promising approach. Li et al. [46] established a more efficient method of liquid-phase exfoliation for synthesizing high-grade boron sheets by adjusting the concentrations of the solvents dimethylformamide and isopropyl alcohol and the centrifugation rates. Exfoliated few-layer B sheets have been fabricated for the electrode materials of supercapacitors. Exceptional cycle stability with an energy retention of 88.7% was demonstrated by this capacitor, which also displayed exceptional energy density as high as 46.1 Wh/kg at a power density of 478.5 W/kg. It has also been proven to have excellent electrochemical performance with a wide potential of up to 3.0 V. Ranjan et al. [47] stated a simple and flexible technology for the synthesis of borophene utilizing an inventive ExS technique. In contrast to its reduction, which produces free-standing borophene, modification of Hummer's approach resulted in the chemical production of borophene oxide. By using ExS of boron powder in a variety of solvents, including, ethylene glycol, acetone, water, isopropyl alcohol, and dimethylformamide, freestanding borophene was created. The existence of interphases of β12, χ3, and borophene, phase purity, and metallic nature were supported by the analysis results. They found that borophene oxide has a specific capacity of ≈4941 mAh g^{-1}, which is far higher than that of current 2D materials and their hybrids.

Zhang et al. [48] produced a new borophene preparation methodology with several layers and large flake sizes using an ExS approach involving probe ultrasonic and ball milling-thinning. The surface tension of some solvents is correlated with the exfoliating action of B precursors. When utilizing solvents, a comparatively low surface tension is appropriate for exfoliating bulk B. Four thick layers of borophene with an average lateral dimension of 5.05 μm were created using acetone as the peeling solvent. Large-flake-size exfoliated few-layer borophene exhibits minimal surface composition change. On the other hand, surface contamination both before and during exfoliation causes a certain amount of chemical state

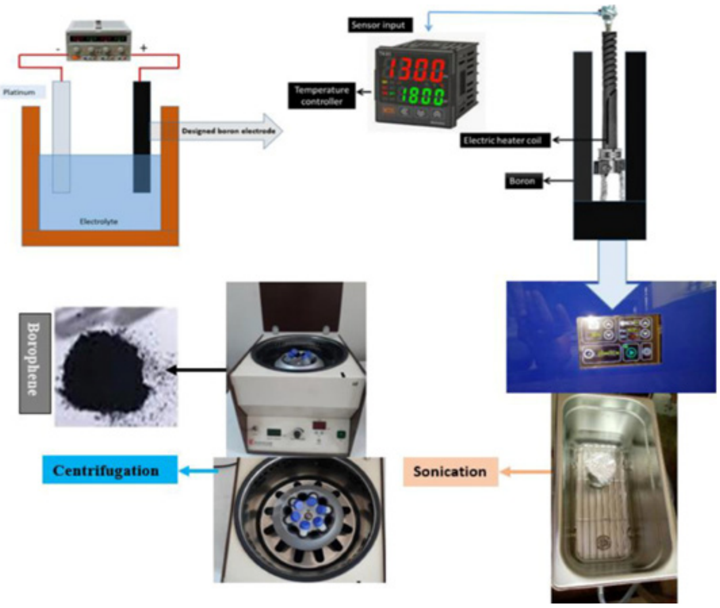

Figure 4. Borophene production by ExS (Open access [45]).

alteration in B. This liquid-phase-exfoliation process with acetone solvothermal assistance can provide enormous horizontal sizes of high-quality borophene. This is a straightforward and efficient way to create large-scale, few-layer borophene flakes, and it may be applied to other 2D materials without comparable bulk layer allotropes.

3.5. Multi-Step Thermal Decomposition

IIn recent years, the in-situ MTD of $NaBH_4$ has been used to manufacture freestanding, large-scale, ultra-stable hydrogenated borophene layers. By using in-situ MTD of $NaBH_4$ powder in an atmosphere rich in hydrogen, Wu et al. [49] created metal matrix composites consisting of borophene. By using spark plasma sintering, 3D borophene sheet network/ copper (BSN/Cu) composites have been created. The synthesized samples' structure and chemical bonding properties were assessed using a variety of analytical techniques. In conclusion, the addition of borophene greatly enhances the mechanical characteristics of the composites. Because borophene and copper have a greater interfacial attraction than graphene and copper, they can bond to the material without breaking [49]. Hou et al. [30] synthesized hydrogenated borophenes using in situ MTD of sodium borohydride. Crystalline borophenes rewritable memory devices, which become ultra-stable upon application of strong acid or base, have been found to have impressive switching properties such as a high ON/OFF current ratio, a low operating voltage, and strong stability. In the study, they showed that by using hydrogen as a carrier gas and gradually in situ MTD of sodium borohydride, hydrogenated borophenes can be produced in large quantities without the need for any metal substrate. Table 2 shows the comparison of borophene synthesis methods.

As the newest member of the 2D nanomaterial family, borophene still has a knowledge gap to fill. This can be achieved using an easy, cost-effective, scalable, and repeatable manufacturing process. Therefore, efforts are ongoing to obtain bulk quantities of several-layered borophene and produce bulk amounts of borophene for further fundamental studies and practical potential evaluation. For this purpose, a new method, different from the synthesis methods mentioned above, appears in the literature. Zielinkiewicz et al. [50] investigated the effectiveness of using mechanical energy in a planetary ball mill to exfoliate bulk boron into a few-layered borophene. The conditions under which β-rhombohedral, γ-orthorhombic, and τ-B structures occur have been characterized. It was discovered that the length of the ball-milling process, the mass rotation speed, and the bulk boron loading could all be used to regulate the thickness and distribution of the final flake. In-depth examinations employing microscopic and spectroscopic methods demonstrate that the phase shift brought about by mechanical energy during ball milling aids in the exfoliation process in the borophene sample that is produced. The XRD diffraction patterns of boron before and after ball milling are displayed in Figure 5. For an easy comparison, rotational speed (Figure 5a), time (Figure 5b), and mass loading (Figure 5c) are displayed. All samples exhibited the typical reflections of volumetric boron.

4. Using Borophene as an Energy Material

Applications of borophene in energy have gained a lot of interest due to its ionic conductivity, high surface activity, and metallic band structure suitable for electronic conductivity. Unlike graphene, which has a higher relative atomic quality, borophene has an anisotropic structure that gives it outstanding mechanical qualities. Borophene has been tested in applications related to chemical sensors, voltaic devices, supercapacitors, storage devices, photodetectors, and sensors. Furthermore, the ability to store energy makes borophene a potentially useful electrode material. This section will explain borophene's EAs, such as HS, electronic and optical devices, metal-ion batteries, oxygen, and hydrogen evolution reactions.

4.1. Storage of Hydrogen

Since, hydrogen is a renewable and clean energy source, its development and use are critical for society. One of the most significant technological issues facing the development of H_2 energy sources is HS. The optimal physical HS technique should have average adsorption energy that falls between physical and chemical adsorption energies (0.1-08 eV) [51]. Borophene has attracted attention among physical HS molecules due to its good adsorption kinetics and large specific surface areas. The enormous surface area of the atomic layers and the ease with which hydrogen atoms stick to borophene's monolayer structure make it a promising material for storing hydrogen. According to theoretical research, borophene outperforms other materials in its ability to store hydrogen, being able to store almost 15% of its weight in hydrogen [51-53].

Table 2. Comparison of borophene synthesis methods

Methods	Temperature (°C)	Boron Source	Structure of Borophene	Ref.
Ultrahigh vacuum	400-750	Solid boron	Freestanding monolayer	[35]
Chemical Vapor Deposition	500-1000	Boron rod, B, B_2O_3	γ-phase, rhombohedral	[22]
Exfoliation by Sonochemistry	5-100	Boron powder	β12, X3, and intermediate phases	[24]
Molecular beam epitaxy	150-500	Pure boron, Borax	β_{12} and X_3 phases	[41]
Multi-step thermal decomposition	490-800	$NaBH_4$ powder	3D-borophene network	[49]

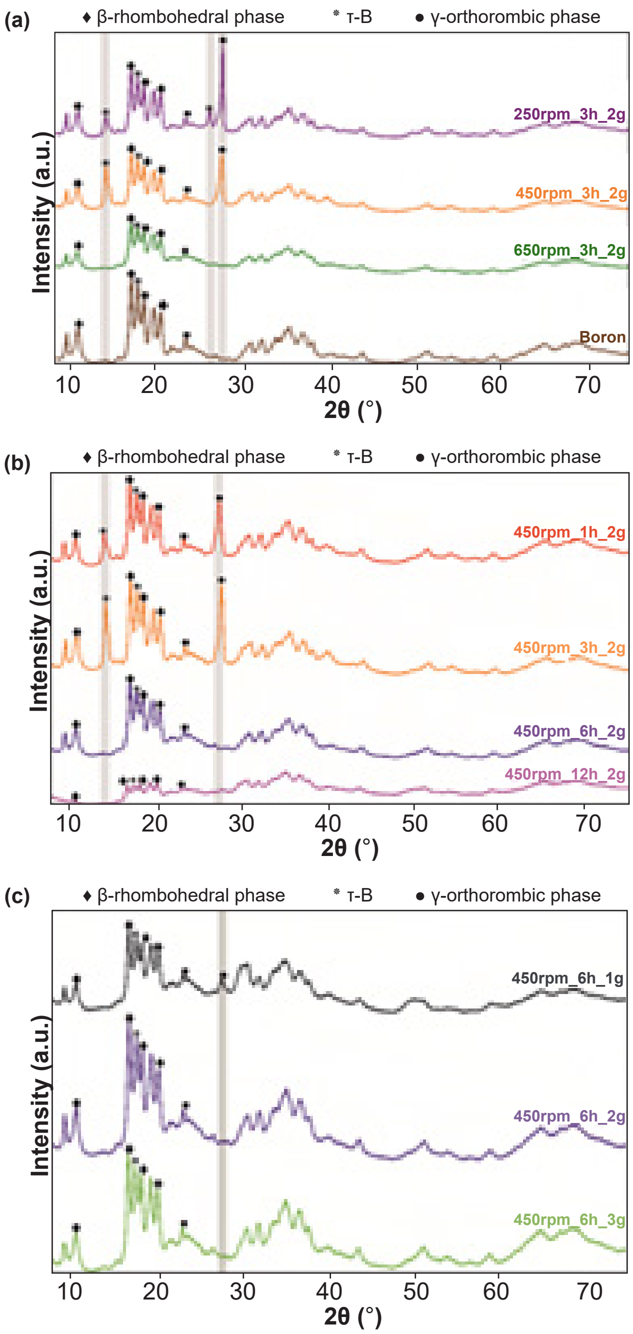

Figure 5. XRD of bulk boron and borophene flakes after the ball-milling process comparing (a) rotation speed, (b) time, and (c) mass loading (Open access [50]).

Baraiya and colleagues [23] utilized density functional theory (DFT)-based first-principles calculations to examine the HS capacity of nitrogen-doped and pure nitrogen-decorated borophene. The work includes a detailed discussion of the adsorption site, charge transfer, electronic structure, adsorption energy, and HS ability of borophene layers that are pristine, nitrogen-doped, and pure nitrogen-decorated. Without clustering, the N atom forms a strong bond with the borophene layer. When an N atom is added, the borophene layer's ability to adsorb H_2 is increased in comparison to its pure state. Nitrogen-doped and pure nitrogen-decorated layers attain gravimetric densities of 6.22 wt% and 1.51 wt%, respectively, according to calculations for HS. Cabria et al. [54] used a quantum thermodynamic model, and Van der Waals-corrected DFT performed the HS capacity of confined Li-decorated borophene layers in a stable configuration. They demonstrated the remarkable volumetric HS capacity, particularly at low temperatures, of borophene's small Li-decorated slit pores. Thus, in low-temperature applications, nanoboron sheets would be perfect for storing H_2. Liu et al. [51] conducted a theoretical investigation into the HS characteristics of β12-borophene and β12-borophene decorated with Li. The results show that H_2 molecules are first totally split into H atoms, which are then adsorbed on the B-B bridge areas. They then modified the HS capacity of β12-borophene and enhanced the HS performance using Li atoms. Numerical simulations show that the 2Li-β12 system has an HS capacity of 10.85 weight percent and can adsorb up to H_2 molecules, compared to the Li-β12 system's maximum capacity of seven H_2 molecules. Consequently, the reversible HS ability was enhanced, and the amount of hydrogen stored was greatly increased by the physical adsorption of H_2 on Li-β12. Using theoretical calculations, Wang et al. [55] looked into the HS characteristics of a novel Ca-decorated boron sheet. One Ca atom has been shown to be able to trap up to six H_2 molecules at 0 K, with an improved binding energy of -0.20 to -0.32 eV/H_2. When the boron plate is adsorbed with Ca on both sides, a gravimetric H_2 density of 12.68 weight percent is attained. It was also determined how temperature and pressure affected the Ca-decorated boron plate's ability to store H_2. The findings indicate that a possible HS medium for use in vehicles is the Ca-decorated boron layer.

4.2. Nanoelectronics Applications

Owing to the extraordinary qualities that were just discussed, borophene has available prospective uses in the many domains of optoelectronics, and nanoelectronics. For these applications, a useful technique to open the band gap of borophene and stabilize the structure of 2D materials is hydrogenation. For instance, graphene, silicene, and germanene can undergo hydrogenation to go from excellent conductors to semiconductors with a large bandgap. Similarly, theoretical studies have demonstrated that hydrogenation is a useful strategy for adjusting the electrical characteristics of boron layers and stabilizing their structure. Large-scale hydrogenated borophenes were successfully produced by Hou et al. [30] using hydrogen as the carrier gas. They created a process for the in situ MTD of $NaBH_4$ in order to generate borophenes under controlled circumstances without the need for a metal substrate. The memory device that was built showed good stability, a small working voltage of less than 0.35 V, and a high ON/OFF current ratio of 3×10^3 [30]. The tunability of the band gap of two-dimensional (2D) semiconductor few-layer borophene was experimentally investigated by Wang et al. [11]. Using EvS, functionalized borophene (borophene-OH) was created for this purpose. Consequently, by adjusting the centrifugation rates, borophene-OH with the desired thickness was achieved. Smooth borophene was created during exfoliation by surface energy matching and breaking the B-B bond between boron and 2-butanol. Borophene-OH has an adjustable band gap ranging from 0.65 to 2.10 eV. When compared to other 2D monoelemental materials, it demonstrates a considerable increase in photosensitivity (58.5 μAW^{-1}) and photocurrent intensity (5.0 μAcm^{-2}) with the introduction of borophene-OH. As a result, borophene-OH has high optoelectronic potential and is a promising semiconductor. For usage in lasers, Ma et al. [56] looked into the photonic qualities of borophene. They used LPS to create 2D borophene. The produced borophene's shape and structure were thoroughly examined, and a Z-scan was utilized to quantify its nonlinear optical characteristics. It has been discovered that borophene is a highly effective broadband optical switch that is widely employed in mid-and near-infrared laser systems for mode-locking. At center wavelengths of 1560 and 1063 nm, respectively, pulses with durations as short as 693 and 792 fs have been effectively transmitted.

4.3. Catalytic Capabilities

The researchers claim that borophene's exceptional catalytic abilities in the CO_2 electroreduction process, as well as the evolution reactions of hydrogen and oxygen, possess the ability to bring forth a new era for water, including energy cycles. Numerous applications exist for borophene in the HER. The lightest HER catalyst is borophene [49]. There is an excessively strong contact between the H atom and borophene due to its high surface activity. Water splitting might be greatly accelerated by Ni-doped α-borophene, according to Wanga and Zheng's [27] calculations. They showed that decoration or doping with different transition metals, such as Ni or Co, has a profound effect on the catalytic activity of χ3, α, and β12 borophenes. Ni-doped α-borophene exhibited low Gibbs free hydrogen adsorption energy (ΔGH~0.055 eV) for the HER and a worthwhile overpotential (0.455 V) for the OER. According to Wang et al. [27], borophene is a good HER catalyst with many active sites, metallic conductivity, and almost negligible free energy resulting from hydrogen adsorption. However, the free energy of borophene hydrogen adsorption was found to be only 0.02 eV. This is considerably lower than the ΔGH on the mostly used Pt catalyst (0.09 eV). Moreover, a silver substrate has no effect on borophene's strong catalytic activity. Negatively charged borophene has a maximum CO_2 collection capacity of 6.731014 cm^2. Wang and others [26], investigated the catalytic performance of borophene nanoribbons (BNRs) using first-principles calculations. Calculations indicate that BNRs can be highly active edge-dependent catalysts for the hydrogen evolution reaction. The effects of nanoribbon width and strain engineering on the catalytic performance of BNRs were investigated and it was found that the width did not affect the catalytic activity of armchair BNRs (ABNRs). A Gibbs free energy of ΔGH ≈ 0 was reached at a critical pressure strain of εC = -2%. This concludes that ABNRs may be a catalyst for an ultrafast HER through modulation of strain engineering. Figure 6 a and b show the energy-strain diagram of ABNRs and the stress-strain diagram of ABNRs. The figure suggests that the elongation at break for ABNRs is above 5%.

The CO_2 electroreduction of Cu-supported borophene structures was studied by Shen, H., and collaborators. The lowering of the CO_2 electroreduction overpotential is mostly due to the distinct chain architectures of Cu atoms [57]. The researchers found that by offering secondary adsorption sites and producing tiny overpotentials in the favored reaction pathway CO_2-CH_3OH, borophene-based copper chains exhibit strong catalytic activity for CO_2 electroreduction. Cu's outstanding CO_2 consumption performance motivates the distribution of Cu's 2D characteristics for improved catalysis. They investigated the catalytic characteristics of Cu atom chains on β-borophene layers for the first time, motivated by cutting-edge research on novel 2D-protected B-layers. They discovered that by disrupting the cross-sectioning connection, the Cu-B layer would remain safe.

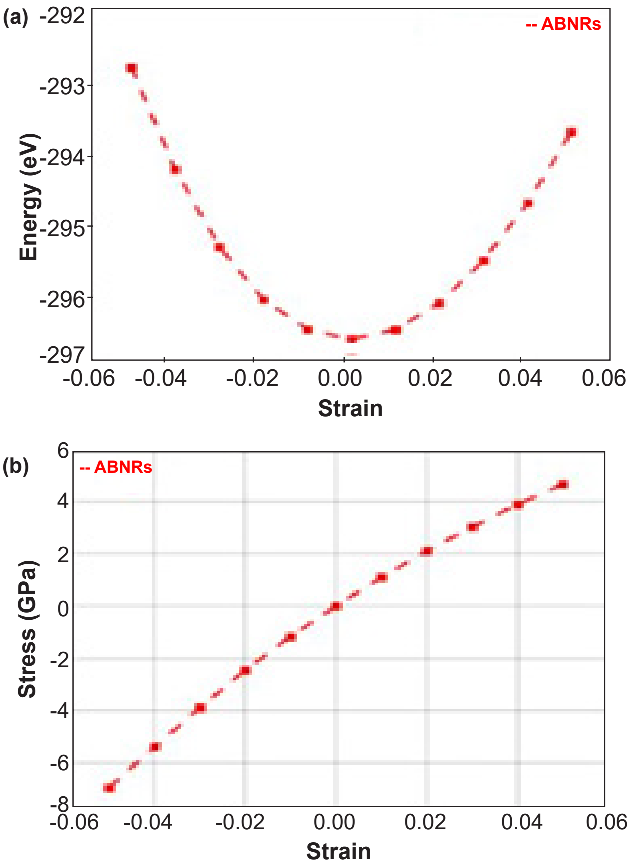

Figure 6. (a) The energy-strain diagram of ABNRs, and (b) the stress-strain diagram of ABNRs. Reproduced with permission from Ref. [26], ©American Chemical Society, 2021.

4.4. Metal-Ion Batteries

Borophene is considered a viable anode material for Na, Li, and Mg ion batteries because of its exceptional ion transport capabilities, high theoretical specific capacities, and good electrical conductivity. The outstanding electronic conductivity and ionic conductivity of borophene ensure the seamless operation of the charging and discharging processes. Borophene film studies in the literature have generally been done from a theoretical perspective. The use of flat borophene films (BFs) in the construction of lightweight, high-capacity, improved rechargeable ion batteries has been investigated [14,20]. Mortazavi et al. [58] investigated the use of distinct flat BFs as anode materials for Li-ion, Al, Mg, and Na batteries using comprehensive first-principles DFT simulations. The charge transfer between the BFs was assessed via Bader charge analysis. The study of ion diffusions was also conducted using the nudged elastic band approach. Profiles of open-circuit voltage and average atom adsorption energies as a function of adatoms coverage were calculated. The results imply that flat borophene films can serve as thermally stable, electrically conductive anode materials for Al, Li-ion, Mg, and Na batteries, with ultra-high capacities of 1640 mAh/g, 2480 mAh/g, and 2040 mAh/g, respectively. Xia and associates [59] suggested halogen decorating as an experimentally workable way to promote the Li-ion transition in χ3 borophene, using χ3 borophene as the prototype system. It is anticipated that borophenes, which are synthetic polymorphs of boron with three different forms (T, β12, and χ3), could one day be used as anode materials for Li-ion batteries that have extraordinary capacity. In the study, potential adsorption sites and binding interactions between halogens and χ3 borophene were examined. The most common diffusion paths have energy barriers of less than 0.2 eV, making iodine the ideal dopant. However, the use of these borophenes in the rapid charging area is hindered by their sluggish hopping of Li into β12 and χ3 borophenes with high energy barriers (about 0.6 eV). Strong binding of halogens to χ3borophene resulted in a large electron transfer from the second to the first, which caused a local electron shortage in χ3borophene. The findings suggest that in borophene-based anode materials, halogen inclusion can promote Li-ion intercalation and deintercalation.

4.5. Supercapacitors

Unlike other 2D materials, borophene's edges can regenerate at low temperatures and low chemical energies. The production of borophene nanomaterials with innovative morphologies, such as ultra-thin borophene nanoribbon, is now possible and is anticipated to enhance electronics performance for a range of applications [18]. It has been proposed that borophene might be a viable material for flexible electronics, such as supercapacitors, when combined with polymers and advanced composites [17]. α-borophene was synthesized by Göktuna and Taşaltın [60] using a simple and inexpensive ultrasonic exfoliation method. The synthesized α-borophene exhibited enough electrostatic repulsion, as indicated by the zeta potential profile, resulting in acceptable physical stability. It was observed that even after 1000 cycles, the synthesized borophene's specific capacitance remained at 95%, measuring 960 F.g^{-1}. This demonstrated that α-borophene might enhance polyaniline's functionality. It has been suggested that the developed PANI/Borophene electrode is a promising material for supercapacitors. Large-scale several-layer B sheets were made via sonication-assisted liquid-phase exfoliation by Hongling Li, Lin Jing, and others [61] and their capacitive performance was assessed.

Additionally, exfoliated few-layer B sheets showed exceptional stability and excellent dispersion in organic solvents without aggregates for more than 50 days under ambient conditions. This was made possible by the solvent residue shell that forms an excellent barrier against air oxidation on the B sheet surface. With an impressive energy density of up to 46.1 Wh/kg at a power density of 478.5 W/kg, an energy retention of 88.7%, and an extensive potential window up to 3.0 V, this device as designed delivers excellent electrochemical performance that is demonstrated steadily throughout the cycle. This work provided evidence of a successful method for the regulated synthesis of B-sheets. In addition, the synthesized B shows promise for energy storage and next-generation optoelectronics application. In addition to the energy applications mentioned above, borophene has rarely been studied in other applications. These include photoelectrochemical cells and water separation applications. For a type-II heterojunction, complementary surface-charged, nanoscale 0D-0D hybrids of borophene and phosphorous nitride dots with advantageous band alignments are suggested by Mohanta and Qureshi [62]. For improved photoelectrochemical water oxidation, this hybrid model offers quick carrier separation and resistance to carrier recombination. The two processes in the synthesis of borophene dots were hydrothermal and sonication. To create the 2D sheets, 30 mL of dimethylformamide solution containing 30 mg of boron powder was ultrasonically sonicated at 400 W for 5 hours. The findings demonstrate that improved photoelectrochemical performance is supported by surface charge-directed borophene phosphorous nitride nanodot heterojunction. Zhang et al. [63] studied the effects of two-dimensional boron sheets on solar thermal water evaporation. In this work, they hydrogel-based solar vapor generators enhanced with novel 2D boron nanosheets. Under 1 sun irradiation, the resultant solar vapor generators showed an exceptional evaporation rate of 4.03 kg m^{-2} h^{-1}. The remarkable enhancement is ascribed to the two-dimensional boron nanosheets, which resulted in an increased intermediate water content and a decreased water evaporation enthalpy of 845.11 kJ kg^{-1}. High salt resistance and durability were also displayed by the solar vapor generators into which boron nanosheets were included, indicating their enormous potential for desalination applications.

5. Conclusion

In this review, theoretical and experimental progress in borophene research, especially the prospects for its chemical synthesis, was analyzed. Unlike others, research on borophene as a two-dimensional material was dominated by preliminary theoretical research. However, after more than ten years of persistent theory, the discovery of single-atom layer borophene, which has been successfully experimentally synthesized on silver substrates, has stimulated a great deal of research on borophene in the international academic community. There are inherent disadvantages to both top-down and bottom-up techniques in terms of synthesis approaches. Although borophene substrate growth synthesis is made possible by CVD and MBE technologies, which also provide hurdles for real-world borophene applications, these methods are costly, time-consuming, and produce materials that have little.

The further advancement of borophene energy applications inevitably requires many considerations. Previously mentioned methods have been tried to grow large-area, high-quality borophene, but there is still a big challenge in this field. More robust and effective methods must be created to boost production and quality. Phase stability analyses revealed that the 2-Pmmn, χ3, and β12 phases exhibited relatively greater stability on Ag substrates, whereas the production of honeycomb borophene was limited, especially when grown on an Al substrate. One can synthesize borophene in a single phase on a given metal substrate. On the other hand, the wet chemical process leads to the formation of β12 and χ3-phases. Qualitative analysis of the effects of substrate, growth temperature, growth precursors, and other factors on the nucleation of borophene and the inhibition of three-dimensional borophene nucleation needs to be investigated. Borophene's high surface activity is a major synthesis problem as well as a contributing factor to its instability. One way to stabilize them could be to alter their surface in a way that lowers the borophene's surface energy. Hydrogenation is a further strategy for borophene stabilization. Borophene can be used with other 2D materials to lower surface energy and provide a more stable solution. The author hopes that this article can stimulate further theoretical and experimental research and shed light on borophene research, which will ultimately help achieve large-area, high-quality results.

Authorship contribution statement

Gülbahar Bilgiç Tüzemen: Methodology, investigation, writing-original draft, review & editing.

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