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Uluslararası Doğu Anadolu Fen Mühendislik ve Tasarım Dergisi ISSN: 2667-8764, 5(1), 126-142, 2023 <u>https://dergipark.org.tr/tr/pub/ijeased</u>



Derleme Makalesi / *Review Article* Doi: <u>10.47898/ijeased.1232358</u>

Production Methods and Energy Applications of Borophene

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Yazar Kimliği / Author ID (ORCID Number)	Makale Süreci / Article Process	
*Sorumlu Yazar / Corresponding author:	Geliş Tarihi / Received Date :	11.01.2023
halilekici@kilis.edu.tr	Revizyon Tarihi / Revision Date :	15.04.2023
D https://orcid.org/0000-0002-8750-5591, H. Ekici	Kabul Tarihi / Accepted Date :	03.06.2023
	Yayım Tarihi / Published Date :	15.07.2023
Alunti / Cite : Ekici, H. (2023). Production Methods and Energy Applications of Borophene, International Journal of		

Alinti / *Cite* : Ekici, H. (2023). Production Methods and Energy Applications of Borophene, International Journal of Eastern Anatolia Science Engineering and Design, 5(1), 126-142.

Abstract

Two dimensional materials have unique physical, chemical and electrical properties. Many theoretical studies on borophene revealed important possible properties, such as metallicity, transparency, conductivity and chemical activity; due to vacancies present in its structure. It was first synthesized in 2015 and experimental studies on this new exciting 2D material is few in number. It was found that many of these studies still focus on expensive and sophisticated production methods such as Molecular Beam Epitaxy (MBE) and Chemical Vapor Deposition (CVD). Although graphene, first of these 2D materials, is being studied more than two decades, it could not do the expected impact on energy industry due to lack of production methods in industrial scale. In this review, it was intended to build a narrative on the experimental production methods and resulting structures of borophene rather than theoretical background. It was found that liquid phase exfoliation method to synthesize borophene sheets might be the most promising method to upscale borophene production. Theoretical, computational and experimental studies suggested that β_{12} and χ_3 borophene structures were stable and could be produced by sonochemical exfoliation method. In addition, possible uses in energy applications and some future prospects were also discussed. Borophene produced this way, might be used in batteries, supercapacitors hydrogen evolution (HER) and oxygen evolution (OER) reactions.

Keywords: Borophene, 2D materials, Energy storage.

ISSN: 2667-8764 <u>https://dergipark.org.tr/tr/pub/ijeased</u> © 2023 IJEASED. All rights reserved.

Borofen Üretim Teknikleri ve Enerji Uygulamaları

Özet

İki boyutlu malzemeler benzersiz fiziksel, kimyasal ve elektriksel özelliklere sahiptir. Borofen üzerine yapılan birçok teorik çalışma, yapısında bulunan boşluklar nedeniyle metaliklik, şeffaflık, iletkenlik ve kimyasal aktivite gibi önemli olası özellikleri ortaya çıkarmıştır. İlk olarak 2015 yılında sentezlenen bu yeni ve heyecan verici 2B malzeme üzerine yapılan deneysel çalışmaların sayısı oldukça azdır. Halihazırdaki çalışmaların çoğunun hala Moleküler Işın Epitaksi (MBE) ve Kimyasal Buhar Biriktirme (CVD) gibi pahalı ve sofistike üretim yöntemlerine odaklandığı görülmüştür. 2 boyutlu malzemelerden ilki olan grafen, yirmi yılı aşkın süredir üzerinde çalışılmasına rağmen, endüstriyel ölçekte üretim yöntemlerinin eksikliği nedeniyle enerji endüstrisinde beklenen etkiyi yapamamıştır. Bu derlemede, teorik arka plandan ziyade borofenin deneysel üretim yöntemleri ve ortaya çıkan yapıları üzerine bir anlatı oluşturulması amaçlanmıştır. Borofen tabakalarını sentezlemek için sıvı faz eksfoliyasyon yönteminin borofen üretimini endüstriyel ölçekte gerçekleştirmek için en umut verici yöntem olabileceği bulunmuştur. Teorik, hesaplamalı ve deneysel çalışmalar, β_{12} ve χ_3 borofen yapılarının kararlı olduğunu ve sonokimyasal eksfoliyasyon yöntemiyle üretilebileceğini göstermiştir. Ayrıca, enerji uygulamalarındaki olası kullanımları ve gelecekteki bazı beklentiler de tartışılmıştır. Bu şekilde üretilen borofen, bataryalarda, süperkapasitörlerde hidrojen evrimi (HER) ve oksijen evrimi (OER) reaksiyonlarında kullanılabileceği öngörülmüştür.

Anahtar kelimeler: Borofen, 2B malzemeler, Enerji depolama.

1. Introduction

2D materials draw a great deal of interest from the researchers, due to their unique and promising chemical, physical and electrical properties. Graphene, which consists of a single layer of carbon atoms placed in a hexagonal manner, is the first one of these materials.(Razaq et al., 2022)-(A. Gupta et al., 2015) Various theoretical and experimental studies propose other 2D materials such as silicene, germanene, borophene, stanene, phosphorene, arsenene, antimonene, bisthumene, selenene and tellurene.(L. Zhang et al., 2021) In addition, similar polyatomic 2D materials, such as graphene oxide, boron nitride and two dimensional transition metal dichalcogenides (e.g. molybdenum disulfide, tungsten disulfide, molybdenum diselenide and tungsten diselenide) were also extensively studied.(Choi et al., 2017)

Borophene was first synthesized at 2015 on the Ag(111) substrate (Mannix et al., 2015). Since its materialization in the laboratory, interest on this fairly new material gradually increased throughout the years. The number of studies about borophene was given in Figure 1.



Figure 1. Number of borophene studies throughout the years; Data from Web of Science (Access date: April 2023).

Density functional theory (DFT) calculations and simulations on this subject point out it is possible to obtain various borophene sheet structures. Electron deficiency, different bonding situations and many compounds indicate that boron is a chemically active element. Basic structure of borophene is a β_{12} icosahedron and crystals are formed through different connections and bonding styles.(J. Jiang et al., 2018)-(Albert & Hillebrecht, 2009) The comprehensive review by Ou et al, (2021) on borophene and its biomedical applications presents a good summary of theoretical borophene structures throughout the years and were given in

Figure 2.(Ou et al., 2021)



Figure 2. Development of borophene structure models in theoretical studies throughout the years. Printed under creative commons license.(Ou et al., 2021)

Borophene forms a triangular structure unlike the hexagonal structure of graphene; however, unlike graphene, there are vacant locations present in borophene sheet. This special layout is also called hollow hexagons and due to their presence, borophene sheet exhibits unique physical and chemical properties such as anisotropy, flexibility, transparency, conductivity and polymorphism. The placement of vacancies determine the aforementioned properties of borophene.(Mannix et al., 2018) Highly anisotropic crystal structure of borophene may lead to metallic and semi metallic behavior. Occurrence of Dirac cones near or at the Fermi level leads to possibility of anisotropic conductivity due to their anisotropic bonding configuration.(Xie et al., 2020) Anisotropic borophene sheets have strong optical transparency and have less than 1% absorbance in the visible light spectrum. Conductivity and transparency properties make borophene possible to be used as a transparent electrode and a complement for optoelectronic devices. Theoretical study on borophene sheets with χ_3 and β_{12} structure suggest that anisotropic single gap superconductivity is possible between the temperature values of 27.0 and 33.0 K.(Zhao et al., 2018) In another study, β_{12} and γ_3 borophene sheets were grown on Ag(111) substrate through direct evaporation of a pure boron source. The superconducting transition temperatures were found to be 18.7 and 24.7 K respectively. Proposed values are higher than graphene, which exhibits superconductivity theoretically at 8.1 K and experimentally at 7.4 K.(Gao et al., 2017)

Due to borophene's multiple exciting and promising properties, plenty of theoretical and experimental studies were conducted and many reviews were written on this subject in recent years. Batteries, supercapacitors, hydrogen storage, gas sensing and biomedical applications were suggested as possible utilization fields for borophene. In this brief review, it was intended to build a narrative on the experimental production of borophene and inform about its possible uses in energy storage applications.

2. Experimental Production of Borophene

2.1. Molecular Beam Epitaxy:

Borophene was first experimentally produced by MBE method on Ag(111) substrate (Mannix et al., 2015). Feng et al.(Feng et al., 2016) deposited borophene on a clean Ag(111) substrate under ultrahigh vacuum($6x10^{-11}$ torr). Ag(111) substrate was cleaned by repeated argon ion sputtering. Pure (99.99%) boron was deposited by an electron-beam evaporator. Through high resolution scanning

tunneling microscopy (STM), they observed β_{12} and γ_3 types of borophene sheets. Also, single atom thick borophene nanoribbons were successfully synthesized by Zhong et al. (Zhong et al., 2017) on Ag(110) substrate under the similar conditions. Li et al. (W. Li et al., 2018) synthesized single layer honeycomb borophene by using an Al(111) substrate. They reported that although honeycomb borophene exhibits superconducting abilities, it is also highly unstable. According to their theoretical calculations Li et al. argued that electron transfer from Al(111) substrate to each boron atom stabilized the borophene structure. They verified the realization of graphene like honeycomb borophene through scanning tunneling microscopy measurements. Kiraly et al. (Kiraly et al., 2019) considered that Au has a lower chemical reactivity than other metals and deposited boron atoms under ultrahigh vacuum at room temperature on an Au(111) surface, and found that boron atoms formed islands of 1 nm^2 area. When they raised the temperature to 550 °C, they observed that boron dissolves in substrate and segregates back to the surface as the medium temperature cools back to room temperature. Although Borophene was synthesized over various metals; the size of boron sheets ranged in nanometers. These dimensions were not acceptable for any practical use, therefore a more reactive substrate than Ag(111) metal was needed. For that purpose, Cu(111), which facilitated the borophene growth more than other metals but not too reactive to form metal borides, was used by Wu et al., as a substrate.(Wu et al., 2019) They maintained 770 K substrate temperature and utilized low energy electron microscopy (LEEM) to monitor the Dynamics of borophene growth. They combined the LEEM and STM results and proposed that χ_3 type of borophene sheets, with up to 100 μ m² area, were formed on Cu(111) surface. Ir(111) is another substrate that is used in borophene production. Vinogradov et al.(Vinogradov et al., 2019) deposited boron on Ir(111) surface in a temperature range from 300 °C to 600 °C. Their STM images and DFT calculations indicated that χ_6 type of borophene sheets were formed.

Molecular Beam Epitaxy (MBE) is a powerful way to synthesize 2D materials. MBE process involves the deposition of atoms from a pure elemental vapor source on a suitable substrate, under a ultrahigh vacuum environment. Diffusion and deposition are adjusted by the temperatures of the elemental source and substrates respectively. It is theorized that catalytic effect of the substrate might suppress the formation of 3D clusters, even though energy levels favor them. MBE is also used to synthesize 2D silicene and germanene.(Vogt, 2018) Therefore, MBE is the preferred way to produce borophene, in many studies.

2.2. Chemical vapor deposition:

Bhowmik and Rajan.(Bhowmik & Govind Rajan, 2022) concluded that graphene, hexagonal boron nitride and hexagonal metal dichalcogenides and as well as silicene posphorene and borophene can be produced with chemical vapor deposition (CVD) method. Tai et al.(Tai et al., 2015) obtained atomically thin borophene sheets on copper films, with CVD method. They prepared boron source by mixing pure boron powder (99.99%) with boron oxide (B₂O₃) powder at equal weight amounts. They placed boron mixture in heating zone and put a Cu foil (3x2 cm², 25 μ m) substrate in reaction zone. Initially, they produced boron vapor in the heating chamber at 1100 °C (T₁) and transferred pure H₂ carrier gas to the reaction chamber, where the temperature was at 1000 °C(T₂). They conducted the deposition process for one hour and obtained γ -B₂₈ borophene films. Schematic representation of their process was given in

Figure .



Figure 3. γ -B28 borophene synthesis with CVD method. Printed with permisson from John Wiley and Sons. (Tai et al., 2015)

Thermal decomposition of diborane is another approach to produce 2D borophene sheets via CVD method. For this process, Mazaheri et al.(Mazaheri et al., 2021) used Aluminum coated Silisium wafer as substrate in a single zone CVD system, where chamber pressure was set to 10^{-3} mbar. They set the CVD chamber temperature to 830 K to anneal the substrate surface with H₂. They introduced

diborane (B₂H₆) and carrier gas (H₂) mixture to the deposition chamber, where B₂H₆ decomposed to B_(s) and H₂. They obtained χ_3 borophene on the quasi-liquid Aluminum substrates, at the end of the process.

CVD reactors are comprised of a quartz cylinder with a diameter of 2-5 centimeters and placed in a heated furnace, which may contain one or more heated zones. The temperature at each zone is individually programmed and controlled. The reason why quartz is selected as a construction material for a CVD reactor chamber was to sustain higher temperatures that might reach up to more than a thousand Celsius degrees. The deposition process occurred in two ways: reactants were introduced to reaction chamber in gas phase or solid phase reactants were placed in the chamber and sublimated with a carrier gas. Either way, substrate material was placed in the chamber at an appropriate position. Generally atmospheric pressures are used in reactor chamber but it is also possible to attain low pressures with vacuum pumps.

2.3. Sonochemical exfoliation:

Coleman (2013) described the enthalpy of mixing for graphene flakes dispersed and exfoliated in solvents with the equation below (Coleman, 2013):

$$\frac{\Delta H_{mix}}{V} \approx \frac{2}{T_{NS}} \left(\sqrt{E_{S,S}} - \sqrt{E_{S,G}} \right)^2 \phi_G$$

where, ΔH_{mix} is mixing enthalpy, V is mixture volume, T_{NS} is nanosheet thickness and φ_G is volume fraction of dispersed graphene. $E_{S,S}$ and $E_{S,G}$ represent the surface energies of solvent and graphene respectively. When the surface energies are close to each other, enthalpy of mixing gets smaller. Coleman's study was focused on solvents such as N-methyl-pyrrolidone (NMP) and dimethylformamide (DMF) that are used to exfoliate carbon nanotubes. Similarly, Ranjan et al. (Ranjan et al., 2019) studied the exfoliation of pure boron powder, boron nitride, molybdenum disulphide (MoS₂) and polyvinylidene fluoride. They mixed 150 mg of boron in 40 mL of six different solvents; namely acetone, deionized water, isopropyl alcohol, di-methyl formamide and ethylene glycol. Mixtures were ultrasonicated with a 40 Khz ultrasonic bath up to 24 hours. Samples from each container was taken at regular intervals in order to examine borophene sheet formation. Mixtures were centrifuged afterwards. Characterization was made by obtaining High Resolution Tunnelling Electron Microscopy (HRTEM), Tunnelling Electron Microscopy (TEM) and scanned area electron

diffraction (SAED) with tunnelling electron microscopy. These measurements confirmed the presence of β_{12} and χ_3 borophene sheets. According to their findings, acetone and ethylene glycol yielded monolayer sheets after 12 and 20 hours respectively, meanwhile water and isopropyl alcohol were good at down to few monolayers however with small sheet sizes. HRTEM and Fast Fourier Transform images of borophene sheets in acetone were given in

Figure . Fast Fourier Transform (FFT) images (top-right corner) exhibited three parallel rows of dot patterns, where brighter central row originates from atomic ridges while the other two rows represent atoms situated between the ridges. They argued that this was the proof for the formation of the β_{12} phase in synthesized borophene sheets. FFT image b showed a similar pattern. Image from another sheet (Figure 4c), showed boron atoms situated ≈ 2.5 Å apart and other part show narrowly positioned boron atoms ≈ 1.8 Å apart. They deduced that the left part was Moire's pattern and the right part resembled the χ_3 phase.



Figure 4. a) β_{12} , b) intermediate and c) χ 3-like borophene phases. Yellow brackets indicate magnified visuals Printed with permisson from John Wiley and Sons.(Ranjan et al., 2019)

Acetone was used by Zhang et al.(F. Zhang et al., 2020) as a solvent for exfoliation to obtain larger sheet sizes. Boron powder acetone mixture was solvothermally treated in teflon autoclaves at 200 °C for 24 hours. Following that, the suspension was sonicated at 225 W for 4 hours. They obtained four-layer thick borophene with an average lateral size of $5.05 \,\mu\text{m}$. Similar sonochemical exfoliation procedures using NMP or DMF as solvent were used in various studies that examine the different aspects of borophene. This method is not only used to synthesize borophene but other boron nanosheet related materials as well. Wang et al. (2020) initially synthesized borophene from boron powder with sonochemical exfoliation and created borophene-hydroxide with defined thickness, where surface functionalization was done by ice-bath sonication. Their aim was to determine the photo-electrochemical performance of semiconducting borophene-OH(Wang et al., 2020).

As a result, MBE and CVD methods for borophene production has disadvantages such as requirement of sophisticated equipment, very high process temperatures, vacuum environment and need for substrates. In addition, the amount of produced borophene and surface area was very small for practical uses. Although these methods are suitable for scientific studies, they are not scalable, sufficient nor efficient for large scale production. On the other hand, Ranjan et al. (Ranjan et al., 2020) concluded sonochemical exfoliaton process might yield a monolayer or multilayer sheet based on the solvent used and sonication time during exfoliation process. If solvent-boron interaction occurs properly; laterally large and monolayer sheets can be obtained. However, when the interaction is not proper, large number of stacking layers are obtained. As the sonication time increased, tiny sheets (borophene dots) were formed due to fragmentation. Therefore, it is imperative to optimize the sonication process to obtain good quality borophene sheets.



Figure 5. Borophene structures. Green circles represent the boron atoms in the borophene sheet; a) β_{12} borophene b) χ_3 borophene

3. Borophene in Energy Storage Applications

3.1. Batteries:

Batteries hold a significant place in modern electronics. They are extensively being used in communication, computation, transportation and renewable energy production. In order to make these operations cheaper and more accessible, issues in battery technology such as energy density, low performance under various environmental conditions and charge-discharge cycle life should be addressed. 2D materials offer promising solutions to energy density and battery lifecycle problems.

Mortazavi et al. (2016) employed a first-principles DFT calculations study in order to investigate the interaction of free-standing monolayer borophene with Ca, Mg, Na and Li ions.(Mortazavi et al., 2016) Their calculations predicted strong binding energies around 4.03 eV, 2.09 eV, 2.92 eV and 3.28 eV between borophene and adsorbed Ca, Mg, Na or Li ions, respectively. They also found that binding energy decreases by increasing the ion concentration. In addition, they acquired significant charge capacites of 800 mA hg⁻¹, 1960 mA hg⁻¹, 1380 mA hg⁻¹ and 1720 mA hg⁻¹ ¹ for Ca, Mg, Na and Li ion adsorption on borophene, respectively. They concluded that fast diffusion, low energy barriers between adsorbed ions and borophene and resistance to high temperatures up to 750 K makes borophene an excellent anode material in rechargeable ion batteries. Similar ab-initio molecular dynamics (AIMD) study by Jiang et al. (2016) determined that borophene has an adsorption energy of 1.12 eV. Their theoretical result for specific capacity for lithiated borophene was 1860 mAhg⁻¹. They reported the energy barrier for diffusion as 2.6 meV and argued that this value is much lower than other anode materials such as Ti₃C₂ and phosphorene.(H. R. Jiang et al., 2016) Another AIMD study about Na-ion batteries argued that the energy barrier for Na diffusion on monolayer borophene is lower than of graphene and MoS₂; therefore a better choice to be used as an anode material in Na-ion batteries.(Liang et al., 2017) The AIMD study by Zhang et al.(2016) on stable borophene structures of β_{12} and γ_3 in Na-ion and Li-ion batteries proposed similar findings. Borophene structures maintained good electric conductivity before and after adsorption, had small energy barriers, low average open-circuit voltages. β_{12} and χ_3 have storage capacites up to 1984 mAhg⁻¹ in and 1240 mAhg⁻¹ respectively. (X. Zhang et al., 2016) Borophene sheets might find themselves in lithium sulfur batteries as well according to a study that investigated the electrocatalytic activity of few-layer β_{12} crystalline sheets. Resulting Li-S battery had an areal capacity of 5.2 mAh cm⁻² at a sulfur loading of 7.8 mg cm⁻². Capacity fading rate was found to be 0.039% in 1000 cycles, which means their battery outperformed other battery types in terms of charge-discharge life cycle (Lin et al., 2021).

3.2. Supercapacitors:

Supercapacitors are another group of devices that are used to store energy. Although they are similar to batteries, there are several key differences in their working principle. Batteries use chemical reactions, mainly oxidation reduction; meanwhile supercapacitors store energy in an electrical field. Supercapacitors consist of two conductive plates, an electrolyte and an insulator. When a current, in other words, charging is applied, uniformly distributed positive and negative ions in the electrolyte are separated and adsorbed to the surface of the respective plates, therefore storing potential energy. Since there is not a chemical reaction, no surface wear, no side products that lead to dendrite or gas formation inside the device, supercapacitors have much longer charge-discharge cycle lives. Supercapacitors can be charged and discharged much faster than batteries, perform better at low and high temperatures but they are not without drawbacks. They have higher specific power W/kg but their specific energy Wh/kg is significantly lower than batteries. In addition they lose energy much faster when they are idle and can't supply constant voltage, they are used together with batteries or for power intensive applications like acceleration of an electric vehicle. 2D materials might significantly improve the supercapacitor performance if they are used on the conductive plates inside supercapacitors.

Li et al. (2018) investigated producing few-layer boron sheets by liquid-phase exfoliation and their supercapacitive performance.(H. Li et al., 2018) Electrode was prepared by mixing borophene nanosheets with active carbon and poytetrafluoroethylene and used 1-butyl-3-methylimidazolium hexafluorophosphate as electrolyte. Their device exhibited up to 46.1 Wh/kg and 478.5 W/kg energy and power densities respectively. They also reported the cycling stability as 88.7 % for 6000 chargedischarge cycles. Polyaniline (PANI) is another supercapacitor electrode that exhibits good capacitance.(V. Gupta & Miura, 2006) Goktuna and Tasaltın (2021) studied the performance of PANI α borophene electrodes. They reported the specific capacitance as 960 F/g and capacitance retention as 95 % after 1000 cycles.(Göktuna & Taşaltın, 2021) Similarly, Türkmen et al. (2022) prepared a liquid phase exfoliated β_{12} borophene poly(3,4-ethylenedioxythiophene) polystyrene-sulfonate (PEDOT:PSS) electrode. They mixed borophene with (PEDOT:PPS) at different amounts and found

specific capacitances change from 230 to 853 F/g and capacitance retention as 95 % after 1000 cycles.(Türkmen et al., 2022)

3.3. Borophene as a catalyst:

Simple, active, stable and cost-effective catalysts are necessary for efficient hydrogen production via hydrogen evolution reaction(HER) in order to successfully deploy hydrogen based energy technologies.(Strmcnik et al., 2016) Several studies indicate that different borophene and related materials are efficient catalysts. α -MoB₂, simply a borophene-molybdene-molybdene structure that maintains high catalytic activity at high hydrogen coverage, can deliver large current densities and has excellent catalytic stability.(Chen et al., 2017) DFT study α -borophene revealed that if Ni and Pd are doped with α -borophene sheets, they display high catalytic activity towards oxygen evolution reaction and when Fe, Co, Cu, Ag and Pt doped with α -borophene, they exhibit high catalytic activity towards HER. Therefore bimetal-doped α -borophene might be an excellent catalyst to facilitate water splitting process.(P. Zhang et al., 2020) First principles study on Boron nanoribbons suggested that armchair borophene nanoribbons are energetically stable and highly active edge-dependent (catalytic activity on the edges) HER catalysts.(Wang et al., 2021) Computational study on transition metal borophene monolayer catalysts revealed that Ni doped α , α_1 and β_1 bor0phene show remarkable bifunctional (HER/OER) catalytic activity.(Xu et al., 2020)

4. Conclusion

In this review, the experimental methods to produce borophene and its potential in energy applications were briefly summarized. Based on the given conclusions, free standing borophene has excellent chemical and physical properties due to its unique structure. Theoretical studies suggest many different borophene structures such as alfa, beta and pmmn are possible, however experiments coupled with electron microscopy views and DFT calculations, β_{12} and χ_3 structures of borophene (Figure 5) are stable, display the desired properties and can be readily produced. Borophene can be turned into battery anodes and supercapacitor electrodes, improving their performance significantly and in some cases out performing other 2D materials. Borophene can be used as a non-precious bifunctional HER and OER catalyst. In addition, it can be used in many other applications such as cancer treatment, drug delivery, bioimaging, gas sensing, CO₂ capture and hydrogen storage. Therefore, If this promising material ever to be produced in an industrial scale, further research should be conducted. MBE and CVD cannot be utilized since these methods are already too expensive in

laboratory scale. These methods require metal substrates, very high temperatures, sophisticated equipment and vacuum. Equipment and energy costs would be astronomical, thus unfeasible for industrial scale production. Sonochemical exfoliation on the other hand, is a much simpler and cheaper method. Sonochemical reactors are already working in the industrial applications. Many studies about borophene production by sonochemical methods suggested using different solvents, centrifuging times and temperatures to design mono or multilayer borophene. It is easier to fine tune a process at miligram levels however, when these milligrams wanted to be turned into kilograms, other different, unknown challenges will appear. From an engineering perspective, designing and optimizing a sonochemical reactor specific for liquid exfoliation of boron powders to obtain brophene might help to overcome these challenges. Focusing on cheaper and proven organic solvents such as acetone instead of DMF or NMP could help making the production of this wonder material industrially feasible. Despite being studied for several years, graphene could not deliver its expected impact on energy industry due to aforementioned challenges about large scale production. Borophene is a fairly new material and its experimental realization is just 7-8 years old. Thus, the possible use of borophene can be studied in other fields such as solid-state batteries (SSB), implementation of 3D printing into the production process of supercapacitors and SSB's. Graphene was thoroughly investigated but there isn't any study concerning the 3D printing application in the production and use of borophene in the literature.

Conflict of Interest:

The authors declare no conflict of interest.

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