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A Short Review of Two-Dimensional Metal Borides: Structure and Synthesis

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Abstract: Two-dimensional transition metal borides (MBenes) pose significant advantages in various applications owing to their high oxidation resistance and stability, tailorable surface properties, and large surface area. MBenes, two-dimensional transition metal borides, was discovered in 2017 and showed similar structural properties with transition metal carbides and nitrides known as MXenes. MBenes display great potential in various applications, including sensing and catalysis, due to their high electrical conductivity, the rich content of surface functional groups, the easy modification of surface functional groups and/or surface chemistry, the large physical surface area, and the hydrophilic surface properties. Despite its great potential, the research focused on MBenes is in the infant stage, and further research should be conducted to unravel the real potential of those new material families, especially in advanced materials science. This review briefly defines the structure and synthesis of MBenes.

Keywords: 2D materials, MBenes, synthesis, etching.

Boyutlu Metal Borürlerin Kısa Bir İncelemesi: Yapısal Özellikler ve Sentez

Özet: İki boyutlu geçiş metali borürleri (MBenes), yüksek oksidasyon direnci ve stabilitesi, uyarlanabilir yüzey özellikleri ve geniş yüzey alanı nedeniyle çeşitli uygulamalarda önemli avantajlar sağlamaktadır. İki boyutlu geçiş metali borürleri olarak adlandırılan MBene' ler, 2017 yılında keşfedilmiş ve MXene olarak bilinen geçiş metali karbürleri ve nitrürlerle benzer yapısal özellikler göstermektedir. MBene'ler, yüksek elektriksel iletkenlikleri, yüzey fonksiyonel gruplarının zengin içeriği, yüzey fonksiyonel gruplarının ve/veya yüzey kimyasının kolay modifikasyonu, geniş fiziksel yüzey alanı ve hidrofilik özellikleri nedeniyle sensör ve katalizör uygulamaları dahil olmak üzere çeşitli uygulamalarda büyük potansiyel sergilemektedirler. Bu büyük potansiyellerine rağmen MBene üzerine yapılan araştırmalar başlangıç aşamasındadır ve bu yeni malzeme ailesinin gerçek potansiyelini ortaya çıkarmak için daha fazla araştırma yapılmalıdır. Bu derleme çalışmasında, MBene'lerin yapısı ve sentezi kısaca tanımlanmaktadır.

Anahtar Kelimeler: İki boyutlu malzemeler, MBene, sentez, dağlama.

Review

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1.Introduction

Two-dimensional (2D) materials are used extensively in many different areas, including sensors, energy production and storage (Yang et al., 2024), and biomedical and electronic applications (Chen et al., 2010; Xue et al., 2015; Yang et al., 2020; Zazoum et al., 2021). Intensive studies have been carried out on the discovery and applications of materials with a 2D layer structure similar to graphene, starting with successfully isolating a 2D graphene sheet in 2004. These materials have attracted great interest in different research areas, such as energy storage and production, electrochemistry, sensors and biosensors, and electronic devices due to their distinct physical and chemical properties compared to their bulk equivalents. Different 2D layered structures such as transition metal sulfide dichalcogenides (TMDs), hexagonal boron nitride (hBN), transition metal carbides, and nitrides (MXene), which are analogous to 2D graphene in terms of layered structure, exhibit large physical surface area (Novoselov et al., 2005; Geim 2009; Chhowalla et al., 2013; Sinha et al., 2018). The fact that MXene-based materials exhibit particularly low oxidation resistance which in turn significantly reduces the stability of electrochemical and electronic systems developed with the use of these materials (Soomro et al., 2023). In this context, synthesizing innovative 2D structures with high electrical conductivity, mechanical strength, high dispersibility in liquid media, abundant surface functional groups, and high oxidation resistance is essential for practical applications.

Two-dimensional transition metal borides (MBenes) have been discovered; therefore, their properties and performance in electrochemical applications should be studied more. MBenes were first reported by Ade and Hillebrecht (Ade and Hillebrecht, 2015) in 2015. MBenes exhibit better physicochemical properties than MXenes, especially for electrochemical applications, in terms of physical and chemical properties (Ozkan, 2024). MBenes have metallic electrical and thermal conductivity (50-80 W/mK), large surface area (4-5 m^2/g), rich surface functional groups, and higher oxidation resistance than MXenes, which allows the development of more stable systems and products in practical applications. The potential of MBenes in diverse applications is schematically displayed in Figure 1. MBenes have been used in energy storage and catalysis applications due to their excellent mechanical and electrical properties and high electrical conductivity. They are intriguing candidates for a variety of energy storage devices, including batteries and supercapacitors, due to their high surface area, superior conductivity, and customizable electrical characteristics (Tripathy, 2024). Additionally, MBenes can also be used biosensor application (Gurbuz et al., 2025). Because of their high carrier mobility and optical response, these nanostructures may find application in field-effect transistors, sensors, and photodetectors in electronics (Figure 1). The high surface-to-volume ratio and chemical reactivity of 2D nanostructures present chances to improve reaction kinetics and selectivity in energy conversion and catalysis (Ramachandran et al., 2024).

The schematic showing the structures and compositions of MBene obtained is given in Figure 2 (Zhang et al., 2022). As the composition shifts from the metal-rich regime to the boron-rich regime, Figure 2 illustrates the evolution of the metal-boride structure. This review defines MBenes first, and information about their unique properties and application areas is given. Then, experimental synthesis methods of MBenes are summarized and discussed. Finally, discussions and perspectives on current issues, significant challenges, and future development of MBenes are presented.

2.Structure of MBenes

Except for having boron atoms instead of carbon or nitrogen, the structure of MBene is similar to the MXenes. MBenes are produced from MAB phases (layered ternary M_2AlB_2 phases, $M_2Al_2B_2$ phases, and bulk layered binary boride phases with a M_xB_y composition) and consist of transitional metal borides (Miao et al., 2024). 2D transition metal borides have two different crystallographic orientations, including hexagonal and orthorhombic arrangements, and are represented by the formula M_nB_{2n-2} (M: transition metal, B: boron, and n: 2, 3, or 4). MBenes are synthesized by the selective etching of MAB phases and exhibit a sandwich-like structure with an M–B_2–M stacking sequence (Tripathy, 2024). Based on the structure of the starting MAB phase, two different MBenes with orthorhombic and hexagonal structures can be obtained. In this context, orthorhombic MBenes originate from orthorhombic MAB (orth-MAB) precursors. In contrast, hex-MBenes originate from hexagonal MAB (hex-MAB) precursors (Khan et al., 2024). The reported MBene compositions and their structures are displayed in Figure 3.

Compared to the Mxenes, MBenes are expected to have broader application potential, especially in energy storage and generation applications, owing to their higher mechanical strength, oxidation stability, and higher electronic conductivity (Tripathy, 2024). The computational results also confirmed those expectations, which shows that MBenes show diverse properties for energy storage applications (Javed et al., 2024). One of the main advantages of MBenes over MXenes is their oxidation stability. The oxidation resistance of MBenes is higher than that observed in MXene structures, rendering them suitable for practical applications, especially in humid environments (Ozkan, 2024). On the other hand, in the case of restacking, which is widely encountered in 2D layered materials with weak Van der Waals bondings, MBenes also experience significant challenges, especially in electrochemical applications. The restacking of the 2D layered MBenes results in the loss of the electrochemically active surface area and ion accessive catalytic centers, which decreases the system's overall performance (Yang et al., 2024). Therefore, some alternative methods, including the use of 0D, 1D, and 3D spacers between the layers, should be implemented, as in the case of MXenes and other 2D materials.

3.Synthesis of MBenes

So far, we have discussed the properties of MBenes, such as their high oxidation resistance and, hence, high stability compared to MXenes despite having similar structures (Gurbuz et al., 2024). Synthesis methods of MBenes in high yields will be presented in this section. Figure 4 shows a schematic representation of the synthesis methods for binary borides and ternary MAB phases.

3.1 Chemical reduction

One of the simplest methods for obtaining MBenes is chemically reducing metal salts with a strong borohydride (Zhang et al., 2024). Compared to replacing expensive platinum group metal catalysts, this spontaneous and exothermic reaction approach is more cost-effective. Following a rapid reaction, the majority of metal salts leave behind black residues that can be cleaned and dried (Wang et al., 2014). The borohydride salt serves as a source of boron and a reducing agent. The amorphous structure of TMB-based nanosheets (Co_2B, Fe_2B, etc.) produced by chemical reduction changes to a crystalline form upon high-temperature annealing. This method has been reported to be very efficient for using MBenes as electrode materials (Sharma et al., 2022).

3.2 Chemical exfoliation

The liquid phase exfoliation is another method to transform the 3D MAB phases into a 2D layered structure (Björk et al., 2023). The AlB_2 structure of metal borides of the MB_2 type can often be exfoliated. In recent years, several metal borides of the AlB_2 type, such as MgB_2, AlB_2, TiB_2, ZrB_2, HfB_2, NbB_2, TaB_2, CrB_2, and MnB_2, have undergone chemical exfoliation to produce the corresponding 2D metal boride-based nanosheets. Only a few MBene morphologies—nanodots, nano granules, nanoflakes, nanosheets, and nano wreaths—can be produced by altering the recrystallization time during the synthesis (Zhang et al., 2017). The proper solvent environment is necessary for exfoliation procedures to create MBene in high yield and quality. New methods for producing perfect MBene in high yield are being developed by closely analyzing the solvent selection (Zhang et al., 2017).

3.3 Mechanical exfoliation

Solid-state mechanical exfoliation is a simple and high-yield method for producing 2D nanostructures from metal-borides (Liu et al., 2023). Thus far, ball milling metal borides like TiB_2, NbB_2, MgB_2, Ni_2B, and VB_2 have only produced submicrometer particles. Current research indicates metal borides can be mechanically exfoliated to produce 2D nanoforms using ball milling or mechanical grinding (Zhang et al., 2024). Using appropriate high-energy ball milling equipment with ideal milling parameters (time, power, etc.) will significantly increase the production of MBenes (pristine form) (Yang et al., 2024). Ball milling can be readily scaled for commercial uses as well, given the ease of use of the synthesis equipment. There are several studies investigating the synthesis of 2D MBene via ball milling. Wang et al. (2022), synthesized MoB2 using the ball milling approach and obtained MoB_2 nanoplatelets with good mechanical properties. In particular, it is worthwhile to investigate using MBenes produced by mechanical grinding or ball milling in electronics, catalysis, and energy storage (Jiang et al., 2022).

3.4 Other methods

A few studies suggest that electroless deposition, which uses a reduction process to form coatings, is a better option for metal diborides (Sharma et al., 2022). in the majority of the electroless deposition techniques, a reducing agent such as $NaBH_4$ is used to create metal boride-based two-dimensional nanostructures, or MBenes. Additionally, more hybrid synthetic approaches must be developed to synthesize ultrathin film. It is necessary to adjust several variables that impact the MBenes' film thickness and quality, including substrate, pressure, temperature, reaction time, and precursor flow rates. The ability to create high-quality ultrathin films that can be used or customized for various future applications will be brought about by tuning and optimizing these properties. The research suggests that all of the known synthesis procedures, including MBE (molecular-beam epitaxy), CVD (chemical vapor deposition), PVD (physical vapor deposition), and HPCVD (hybrid physical-chemical vapor deposition), may be scaled up if practical techniques for producing high-quality MBenes (with control over their thickness and tunable structural shape) could be explored (Wen et al., 2019; Sharma et al., 2022).

4.Conclusions and Future Perspectives

Research has demonstrated that two-dimensional MBenes's large surface area, exceptional reactivity, mechanical strength, and high electrical conductivity can be exploited to develop electrochemical systems with high activity. MBenes are more complex than MXenes due to their crystallographic configurations, polymorphisms, and structural changes. Because of this, it is challenging to synthesize them and then separate them. This will be possible if this bottleneck is removed—a new functional system into individual flakes. Rational control over the material-structure-property relationship of MBenes and devices with multi-purposes can be designed thanks to recent advancements in MBene manufacture and use, which bodes well for the thoughtful creation of high-performance 2D materials. Because of their increased mechanical strength, MBenes have a high Young's modulus and strong anisotropy, which makes them appropriate for use in the manufacturing of medical equipment such dental implants, artificial joints, and bone repair materials. Therefore, in the future, MBenes will be used not only in the energy field, but also in medicine, implantation, environment and sensors.

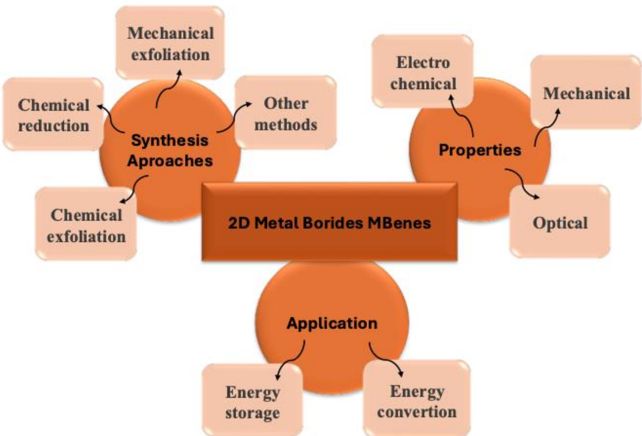

Figure 1. Applications of the 2D Transition Metal Borides (MBenes).

Şekil 1. İki boyutlu metal brorürlerin (MBene) uygulamaları.

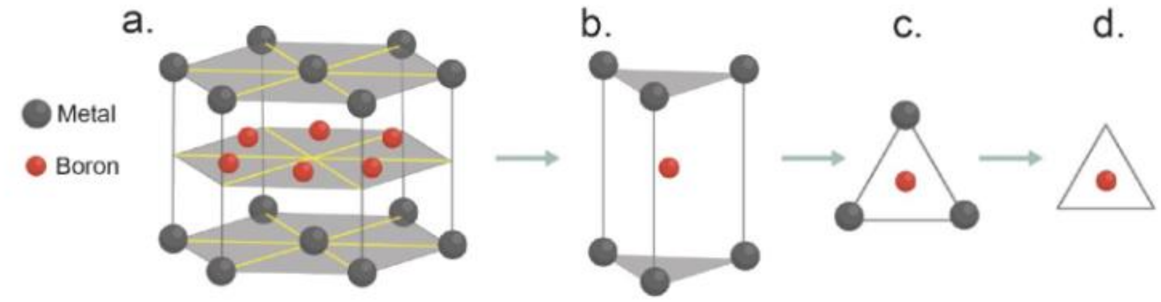

Figure 2. Structural unit of metal borides a. Structure consisting of AlB2 type metal diboride and b. triangular prism, c. top view of the triangular prism, d. view of the pressed metal atoms at the corners of the triangle. (Gunda et al., 2021).

Şekil 2. Metal brorürlerin yapıları, a. AlB2 tipi metal diborür ve b. üçgen prizmadan oluşan yapısı, c. üçgen prizmanın üstten görünümü, d. üçgenin köşelerindeki bastırılan metal atamlarının görünümü. (Gunda vd., 2021).

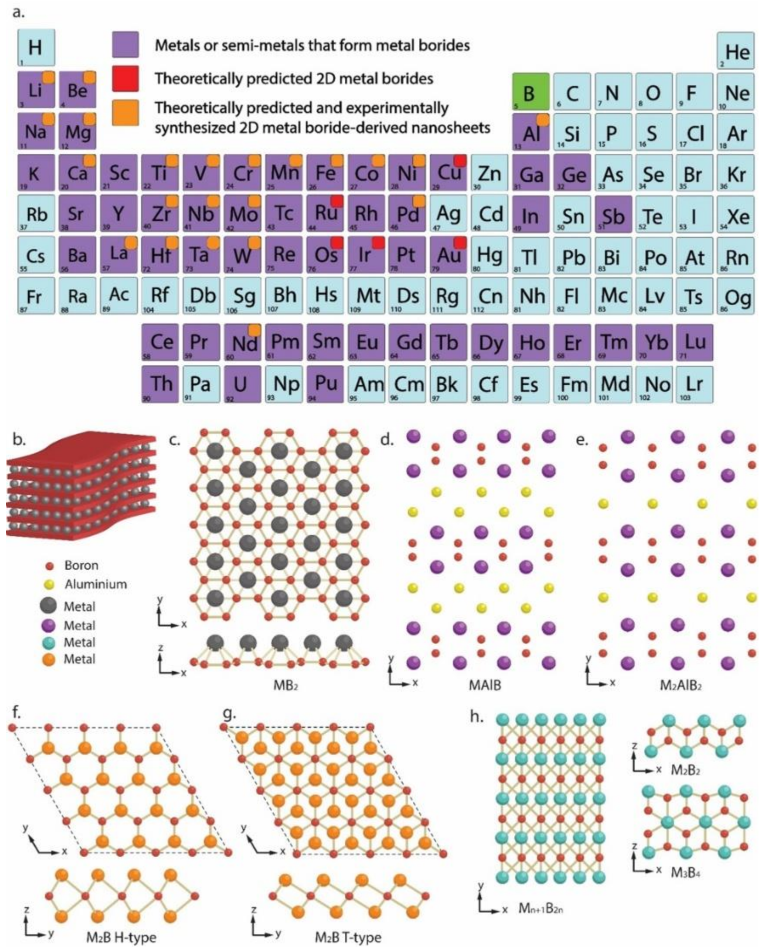

Figure 3. Metals that form borides and their structural motifs. (a) Metals or semimetals that create borides are indicated in purple in the periodic table. The orange-marked metals are anticipated and experimentally realized as 2D nanostructures formed from metal-borides. Although they have not yet been empirically verified, the metals shown in red are theoretically anticipated to exist as metal-boride generated 2D nanostructures. Crystal structures of metal borides include (b) layered metal borides, (c) MB_2 type, (d) MAlB-type MAB phase, (e) M_2AlB_2-type MAB phase, (f) H-type M_2B, (g) T-type M_2B, and (h) $M_{n+1}B_{2n}$ type showing M_2B_2 and M_3B_4 phases (Gunda vd., 2021).

Şekil 3. Borürler oluşturan metaller ve yapısal motifleri. (a) Mor renkle vurgulanan borürler oluşturan metalleri veya yarı metalleri gösteren periyodik tablo. Turuncu renkle işaretlenen metaller hem metal-borür türevi 2B nanoyapılar olarak öngörülmekte hem de deneysel olarak gerçekleştirilmektedir. Kırmızı renkle işaretlenen metallerin teorik olarak metal-borür türevi 2B nanoyapılar olarak var olduğu öngörülmektedir ancak henüz deneysel olarak doğrulanmamıştır. Metal borürlerin kristal yapıları şunları içerir: (b) katmanlı metal borürler, (c) MB2 tipi, (d) MAlB tipi MAB fazı, (e) M_2AlB_2 tipi MAB fazı, (f) H tipi M_2B, (g) T tipi M_2B ve (h) M_2B_2 ve M_3B_4 fazlarını gösteren $M_{n+1}B_{2n}$ tipi. (Gunda vd., 2021).

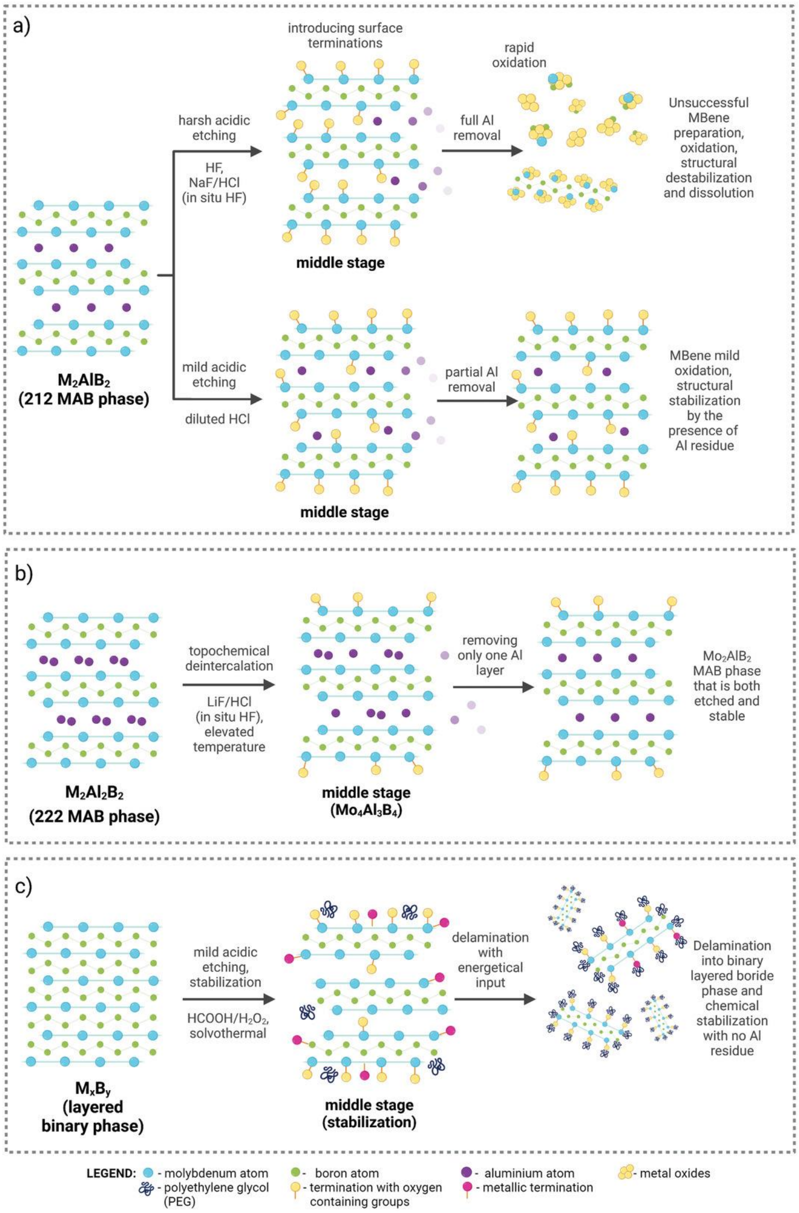

Figure 4. Diagrammatic representation of the many synthesis pathways that were tested and produced different outcomes for the synthesis of MBenes. When aluminum is used as the A interleaving element, the process may begin, a) layered, ternary M_2AlB_2 MAB phases, or b) $M_2Al_2B_2$ phases, c) with bulk layered binary boride phases with a M_xB_y composition (Nair et al.,2022).

Şekil 4. MBene'lerin sentezi için test edilen ve farklı sonuçlar üreten birçok sentez yolunun diyagramatik gösterimi. Alüminyum, A ara eleman olarak kullanıldığında, işlem, a) katmanlı, üçlü M_2AlB_2 MAB fazları veya b) $M_2Al_2B_2$ fazları, c) M_xB_y kompozisyonlu yığın katmanlı ikili borür fazları ile başlayabilir (Nair et al.,2022).

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