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Review

Theoretical Advances in MBenes for Hydrogen Evolution Electrocatalysis

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Abstract: Two-dimensional transition metal borides (MBenes) have emerged as promising electrocatalysts for hydrogen evolution reactions (HERs), attracting significant research interest due to theoretical computations that enhance the understanding and optimization of their performance. This review begins with a comprehensive summary of HER mechanisms, followed by an in-depth examination of the geometric and electronic properties of MBenes. Subsequently, this review explores MBene-based electrocatalysts for HERs, employing free-energy diagrams and an electronic structure analysis to assess both the intrinsic catalytic activity of MBenes and the theoretical performance of single-atom modified MBenes. Finally, the prospects and challenges associated with MBenes are discussed, providing valuable insights to guide future research in this area. Overall, this topic holds significant relevance for researchers in the HER field, and this review aims to deliver theoretical insights for the optimal design of advanced MBene electrocatalysts.

Keywords: 2D MBenes; hydrogen evolution reaction; density functional theory

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1. Introduction

The over-exploitation of traditional fossil fuels and significant ecological degradation have made energy and environmental issues major obstacles to sustainable global development. Consequently, exploring and utilizing renewable energy sources is a promising solution to these crises, ensuring the security of human society and the planet [1–3]. Hydrogen (H_2) energy is regarded as a future energy source due to its outstanding characteristics, including zero pollution, high efficiency, abundant availability, and diverse applications [4–6]. Particularly, hydrogen production via water electrolysis powered by renewable energy is considered one of the most promising methods due to its minimal pollutant emissions, zero carbon dioxide output, and environmental benefits [7,8]. Therefore, advancing hydrogen production technology is both crucial and highly significant. Platinum (Pt) exhibits optimal surface adsorption properties and exceptional catalytic activity, making Pt-based catalysts the most effective for HERs [9,10]. However, the high cost and limited availability of Pt impede large-scale production and widespread application. Therefore, it is essential to develop low-cost catalysts with excellent activity and stability.

Since the exfoliation of graphene in 2004 [11], a new class of materials with sheet-like structures has emerged. Numerous two-dimensional (2D) materials have since been developed, such as hexagonal boron nitride (*h*-BN) [12], transition metal dichalcogenides (TMDs) [13,14], layered double hydroxides (LDHs) [15], black phosphorus (BP) [16], and MXenes [17]. Notably, 2D MXenes have attracted significant research interest and application in catalysis due to their diverse structures, varied elemental compositions, and scalable

synthesis. Boron analogs of MXenes, called transition metal borides (MBenes), are considered promising next-generation catalysts due to their unique optoelectronic and mechanical properties. MBenes provide advanced structural and topological features attributed to the multicentric bonding characteristics of boron, which support the formation of various metal borides [18,19]. Several excellent reviews on MBenes have been published [20–22], primarily focusing on their synthesis, experimental characterization, and electrocatalytic performance. However, while experimental research provides macroscopic insights into catalyst performance, theoretical studies explore the surface chemistry, electronic structure, and reaction mechanisms at the atomic scale. These theoretical insights are crucial for understanding electrochemical reaction processes and predicting ideal electrocatalysts.

In this review, we aim to systematically explore the theoretical advancements in MBenes as electrocatalysts for HERs. First, a brief introduction to the mechanism of hydrogen evolution reaction is provided, outlining the key steps involved in the reaction. Following this, the unique geometric and electronic properties of MBenes are analyzed, highlighting their potential for efficient and cost-effective hydrogen production. Subsequently, the discussion focuses on the intrinsic catalytic activity of MBenes, with particular emphasis on their electronic structure and surface chemistry. The impact of single-atom modifications on the catalytic performance of MBenes is then assessed, with attention to the theoretical mechanisms that enhance HER activity. Finally, this review outlines the current challenges and future directions in the theoretical investigation of MBenes, offering insights to guide future experimental and computational efforts in the development of high-performance HER catalysts.

2. Mechanism of Hydrogen Evolution Reaction

A standard electrolyzer consists of three main components: an electrolyte and two catalyst-coated electrodes (cathode and anode) [23]. The HER at the cathode is a multi-step process influenced by the pH of the electrolyte [24]. Currently, the HER mainly considers the Volmer–Tafel and Volmer–Heyrovsky mechanisms, determined by the relative rates of each reaction (Figure 1 and Table 1).

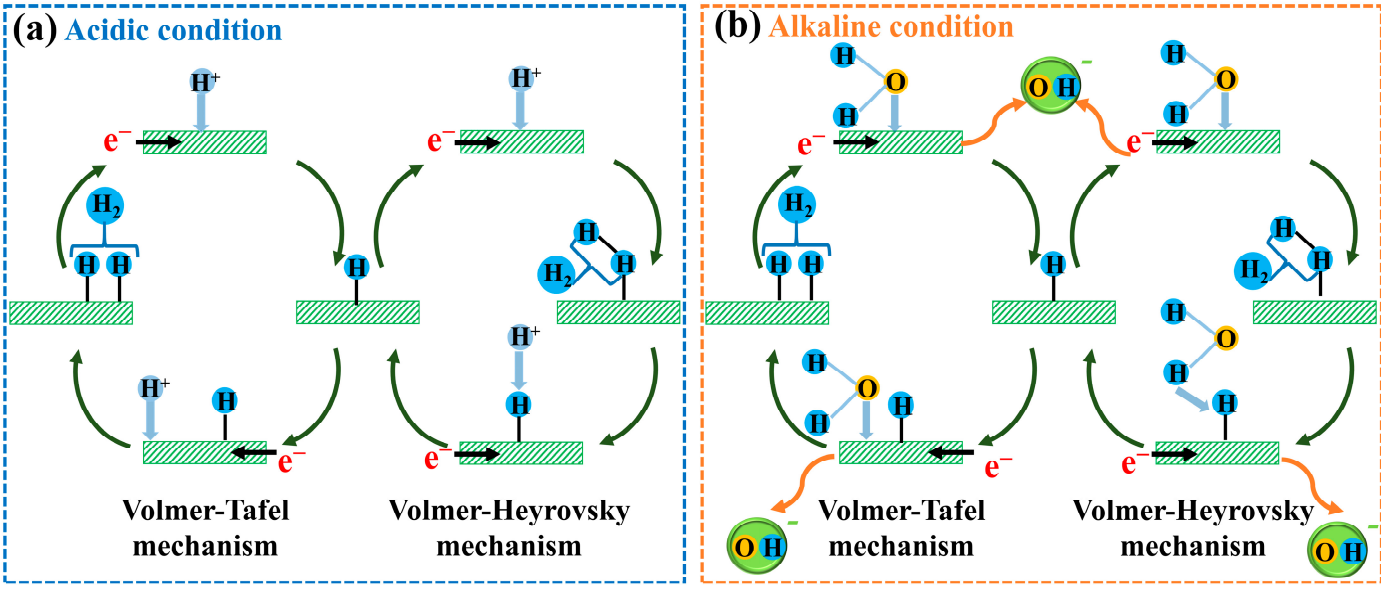


Figure 1. Schematic depiction of the hydrogen evolution reaction (HER) mechanism in (**a**) acidic conditions and (**b**) alkaline conditions.

Table 1. HER mechanisms in acidic and alkaline electrolytes and the corresponding Tafel slopes.

Mechanism	Acidic Condition	Alkaline Condition	Tafel Slop (mv dec^{-1})
Volmer reaction	$H^+ + e^- \rightarrow H^*$	$H_2O + e^- \rightarrow OH^- + H^*$	120
Heyrovsky reaction	$H^* + H^+ + e^- \rightarrow H_2$	$H^* + H_2O + e^- \rightarrow OH^- + H_2$	40
Tafel reaction	$H^* + H^* \rightarrow H_2$	$H^* + H^* \rightarrow H_2$	30

Under acidic conditions, the initial step in the HER is the Volmer reaction, where hydrogen protons combine with active sites on the electrode surface to form adsorbed hydrogen intermediates (H*). Depending on the coverage of H*, the second step can proceed via either the Heyrovsky or Tafel reaction. When H* coverage is low, the H* species are widely spaced and do not easily combine. In this case, H* on the catalyst surface reacts with protons from the electrolyte to produce hydrogen gas in a process known as the Heyrovsky reaction [25]. Conversely, at high H* coverage, two H* species directly couple to form hydrogen gas without electron transfer, known as the Tafel reaction. Under alkaline conditions, the first step in HER is also the Volmer reaction. Nevertheless, unlike in acidic conditions where the proton source is H^+, in alkaline conditions, water molecules provide the protons [26]. In this step, water molecules combine with electrons to form OH^- and H*. The higher energy barrier required to break the O-H bond in water molecules restricts the efficiency of alkaline HER in industrial applications. Similarly, the Heyrovsky reaction in alkaline media involves H* combining with water molecules to produce hydrogen gas. However, the Tafel reaction is not affected by pH and still involves the direct coupling of two H* species to form hydrogen gas.

According to the widely accepted Sabatier principle [27], an ideal electrocatalyst for HERs should have a moderate hydrogen adsorption strength, ensuring it is neither too strong nor too weak. As described in the aforementioned chemical reactions, adsorbed H* is a crucial step. The Gibbs free energy (ΔG_{H^*}) of hydrogen adsorption is the critical factor and rate-determining step for initiating the reaction [28]. In 2006, computational chemist Nørskov and colleagues employed theoretical simulations to determine a series of ΔG_{H^*} values [29], which they combined with experimentally measured exchange current densities to construct a classic HER activity volcano curve (Figure 2). This plot illustrates that noble metals such as Pt, Pd, and Rh are located near the peak, indicating their high efficiency in HER activity. Consequently, the HER activity volcano plot serves as a valuable reference in the development of new, cost-effective, and efficient HER electrocatalysts, guiding the selection of catalysts that ideally lie at the peak of the plot. Understanding the detailed mechanisms of HERs under different conditions is crucial for advancing the design of effective electrocatalysts. Insights from the Sabatier principle and the HER activity volcano plot enable researchers to strategically develop materials that optimize hydrogen adsorption and overall reaction efficiency. By leveraging these principles, researchers can design electrocatalysts that enhance the sustainability and scalability of hydrogen production technologies.

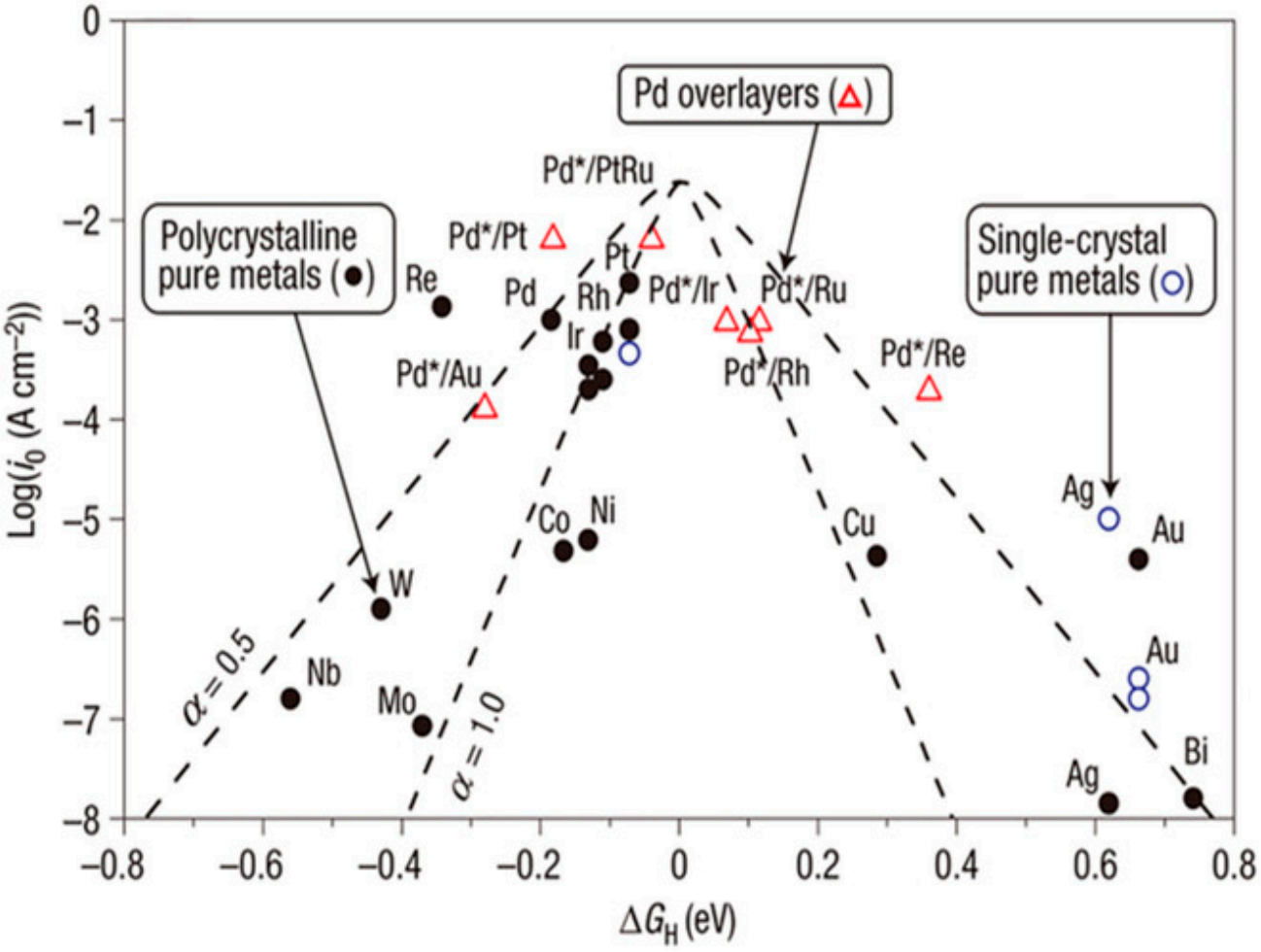


Figure 2. Volcano curve of HER activity. Reproduced with permission from [29], Springer Nature, 2006.

3. Properties of MBenes

Due to the limited valence electrons of boron (B), B atoms exhibit diverse covalent bonding patterns within different MBene lattices, resulting in extensive and varied surface interactions. MBenes are widely used in energy storage and catalysis owing to their excellent chemical properties, stability, mechanical strength, and electrical conductivity. Additionally, the properties of MBenes can be tailored for specific applications by modifying the composition of the "M" and "B" elements and altering the surface terminations. However, research on MBenes is still in its early stages, and their properties require further exploration. The main geometric and electronic properties of MBenes are outlined below.

3.1. Geometric Properties

MBenes represent a novel category of 2D materials, characterized by their unique structural and chemical properties. These materials are a subset of transition metal borides, but differ significantly due to their distinct layered "sandwich" structure [30,31]. They are derived from the MAB phases, which exhibit variable chemical formulas, such as M_2AB_2, $M_3A_2B_2$, and M_4AB_6. In these formulas (Figure 3a), M denotes an early transition metal, while A represents an element primarily from either the IIIA or the IVA group [32]. In 2015, Ade and Hillebrecht introduced MAB phases as layered ternary structures and characterized MBenes as derivatives of MXenes [33]. Figure 3b shows six orthorhombic MAB phases, M_2AB_2, $M_2A_2B_2$, $M_3A_2B_2$, M_4AB_4, M_3AB_4, and M_4AB_6, as well as two hexagonal phases, M_2AB_2 and M_3AB_4, characterized by alternating layers of transition metal borides and A or A_2M layers [34]. Using aluminum as a representative for the

alternating element A, the MAB phases can be categorized based on their crystal space group: MAlB and M_2AlB_2 belong to the Cmcm space group, whereas M_3AlB_4 and M_4AlB_6 are classified under the Pmmm space group [35,36].

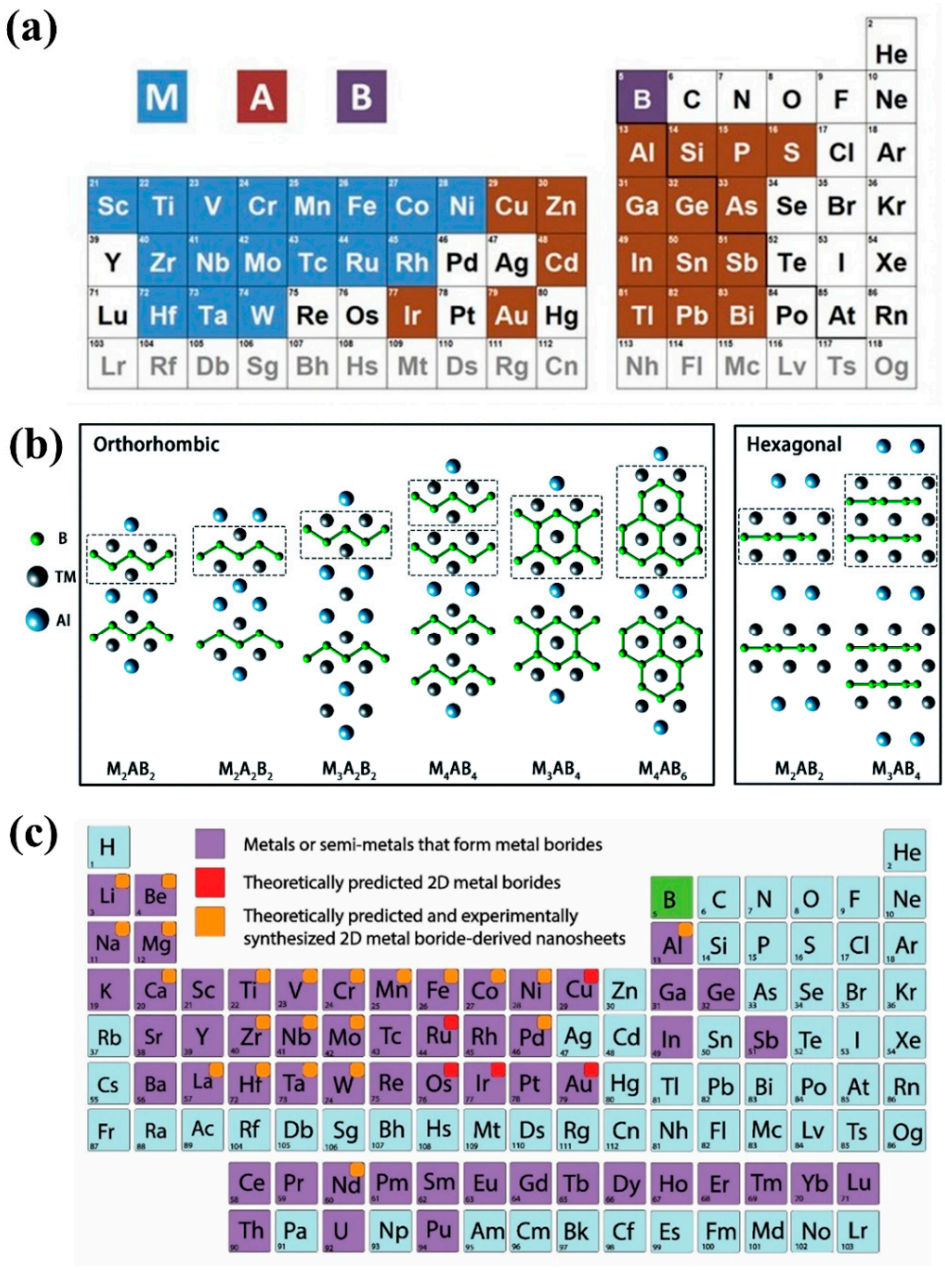


Figure 3. (**a**) The composition of elements in the MAB phase. Reproduced with permission from [32], Wiley-VCH, 2022. (**b**) Configurations of MAB phases in orthorhombic and hexagonal forms. Reproduced with permission from [34], Royal Society of Chemistry, 2022. (**c**) Depictions of elements capable of forming MBenes. Reproduced with permission from [18], American Chemical Society, 2021.

In recent years, MBenes have seen rapid advancements in both theoretical and experimental research. For instance, theoretical studies have predicted that 2D hexagonal M_2B_2 (M = Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta, W, Gd) and M_3B_4 (M = Zr, Hf) exhibit excellent stability [37–42]. To synthesize MBenes, the precursor MAB phase is indispensable. Wang et al. were the pioneers of successfully synthesizing hexagonal Ti_2InB_2, making it the first synthesized hexagonal MAB phase. Figure 3c, informed by recent experimental and theoretical reports on MBene formation, identifies the metals and semimetals that have been studied and those that can form metal borides [18]. Despite these advancements,

the experimental applications of MBenes face significant challenges primarily due to the complexities in synthesis methods [20,43,44]. Issues such as oxidation, incomplete etching, and phase transformation hinder both top-down and bottom-up approaches, while limited experimental verification restricts exploration of their practical properties and applications. Thus, the exploration of MBenes holds significant promise for future research and applications. Their unique structural properties could lead to advancements in various fields, including electronics, catalysis, and materials science. The stability and versatility of these materials make them promising candidates for next-generation technologies.

3.2. Electronic Properties

The excellent conductivity of electrocatalysts is crucial for ensuring efficient electron transport, which is a key factor in optimizing their overall catalytic performance. To date, researchers have conducted extensive and detailed studies on the energy band structure, density of states (DOS), Fermi level, and magnetic properties of MBenes using density functional theory (DFT) [34,45,46]. These studies aim to deepen the understanding of the relationship between the composition, structure, and electronic properties of electrocatalysts, thereby providing valuable guidance for the development of new electrocatalytic materials that are efficient, stable, and cost-effective. For instance, Tang et al. conducted a theoretical study on the band structure and projected density of states (PDOS) of a two-dimensional TiB monolayer. The results indicated that the TiB monolayer possessed metallic properties, with its electrical conductivity predominantly driven by Ti-3d electrons near the Fermi level (Figure 4a) [47]. Additionally, the electron localization function (ELF) analysis identified a weak nucleus-free two-dimensional electron gas in free space (2DEG-FS) within the TiB monolayer. This 2DEG-FS could potentially improve electron transport efficiency by minimizing heat generation and electrical resistance. However, the 2DEG-FS state disappeared when the TiB monolayer surface was functionalized with O and OH groups (Figure 4b). Furthermore, Aarti Shukla demonstrated the metallic properties of Ti_2B and showed that doping the system with a single transition metal atom (TM-Ti_2B) enhances its stability, as evidenced by the calculated adsorption energy [48]. Consequently, the TM-Ti_2B systems retained both the metallic properties and magnetic state of the pristine Ti_2B. Wang et al. examined the electronic properties of Nb_2B and NbB *h*-MBenes, focusing on the effects of oxygen functionalization [49]. The ELF analysis (Figure 4c) demonstrated a transition from Nb-associated lone pair electrons in the bare structures to strong ionic Nb-O interactions upon functionalization. The band structures (Figure 4d,e) further revealed the intrinsic metallicity of these MBenes, primarily due to delocalized d orbitals of Nb. These findings underscore the tunability of electronic properties in *h*-MBenes through targeted surface and compositional modifications. Based on first-principles calculations combined with machine learning, Lu et al. investigated the electronic properties and density of states of MBene/Si_3N_4 van der Waals superlattices, finding that stacking variations significantly influence band structure and electronic properties, while machine learning predictions achieve high accuracy when local atomic environments are incorporated [50].

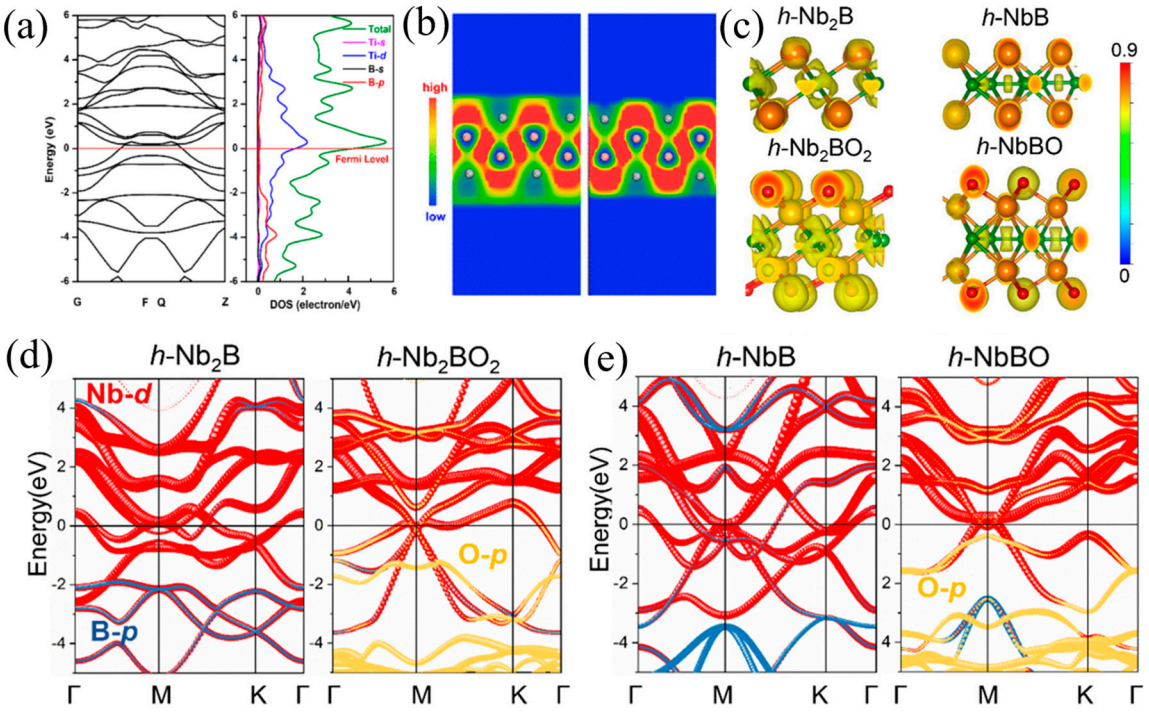


Figure 4. (**a**) Band structure and partial density of states (PDOS) for a TiB single-layer. (**b**) ELF maps for the TiB single layer and $[TiB]^+$. Reproduced with permission from [47], American Chemical Society, 2019. (**c**) 3D isosurfaces of the electron localization function (ELF) for *h*-Nb_2B and *h*-NbB, both with and without O functionalization, plotted at the isosurface value of 0.75. (**d**) Band structures of *h*-Nb_2B and *h*-Nb_2BO_2. (**e**) Band structures of *h*-NbB and *h*-NbBO. Reproduced with permission from [49], American Chemical Society, 2024.

The magnetic properties of MBenes significantly influence their electron transport dynamics and play a crucial role in determining the adsorption energies of reaction intermediates, thereby impacting overall catalytic performance [51,52]. For example, Sun et al. calculated the total density of states and band structures of several MBenes, demonstrating that 2D Mo_2B_2, Fe_2B_2, Cr_2B_2, and W_2B_2 all exhibited metallic characteristics with excellent electronic conductivity [53]. The conductive properties of Mo_2B_2 were primarily attributed to the 4D orbitals of Mo atoms (Figure 5a,b). Meanwhile, 2D Fe_2B_2 was characterized by a spin-polarized ground state, with its magnetic properties mainly arising from the 3D orbitals of Fe atoms (Figure 5c,d). Similarly, Guo et al. conducted a comparative study on the total energies of one ferromagnetic (FM) phase and four distinct antiferromagnetic (AFM) phases using a 2×2 supercell, ultimately determining the magnetic ground states of these materials [54]. Their findings suggest that magnetic states play a critical role in regulating the adsorption of reaction intermediates, which could significantly affect the catalytic activity for HERs.

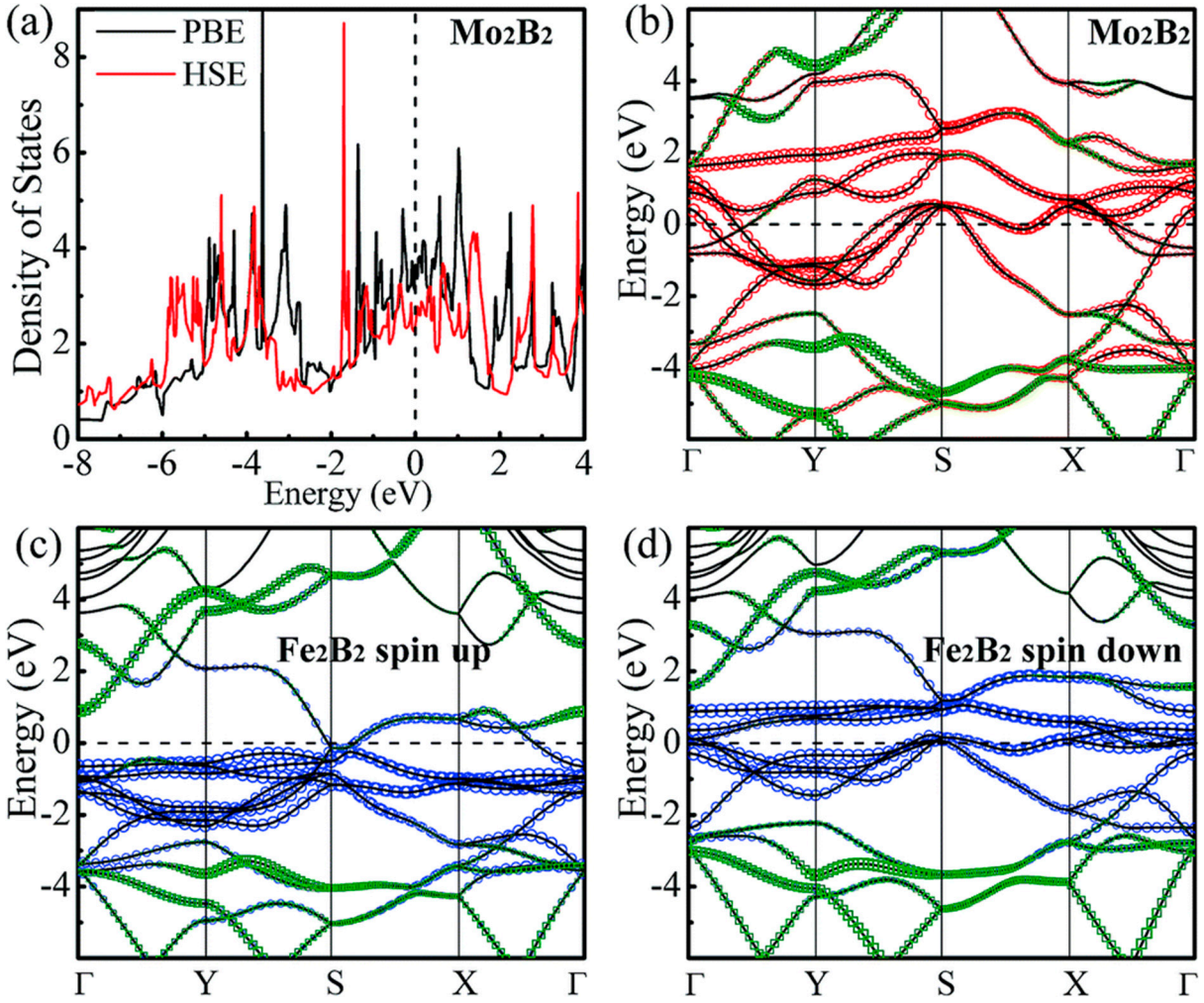


Figure 5. (**a**) Computed density of states for 2D Mo_2B_2. (**b**–**d**) Band structures for 2D Mo_2B_2 and Fe_2B_2, where the sizes of the red/blue circles and green squares indicate the projected contributions of Mo/Fe d orbitals and B atom p orbitals, respectively. Reproduced with permission from [53], Royal Society of Chemistry, 2017.

4. MBene-Based Electrocatalysts for Hydrogen Evolution Reactions

4.1. Intrinsic Catalytic Theoretical Activity of MBenes

The unique layered sandwich structure, diverse surface functionalization, and excellent electron conductivity of MBenes show extraordinary potential in the field of HERs. Up to now, theoretical calculations have extensively explored the design and optimization of 2D MBene structures to evaluate their potential in electrocatalysis, particularly for HERs. Among these studies, Sun et al. conducted a systematic study using first-principles calculations to investigate the Gibbs free energy (ΔG_{H^*}) changes in Fe_2B_2 under varying hydrogen coverages (1/8, 1/4, 3/8, and 1/2) [53]. The corresponding calculated ΔG_{H^*} values were −0.007 eV, −0.001 eV, 0.038 eV, and 0.059 eV (shown in Figure 6a), all of which were significantly more favorable than that of Pt (−0.09 eV). Furthermore, they found that $Fe_2B_2O_2$ exhibited a near-zero ΔG_{H^*} value of −0.133 eV at a hydrogen coverage of 1/2, indicating that the oxygen-functionalized Fe_2B_2 MBene possessed remarkable HER activity from a thermodynamic standpoint (Figure 6b). Two years later, the Sun team proposed a series of Cr-based MBenes ($Cr_{n+1}B_{2n}$, n = 1–3) and demonstrated their structural stability and metallic conductivity using ab initio calculations [55]. They further investigated the HER catalytic activity of $Cr_{n+1}B_{2n}$ using 2 × 2 supercells under varying hydrogen coverages, as depicted in Figure 6c–e. Notably, Cr_4B_6 maintained near-zero ΔG_{H^*} values across all cover-

ages, with ΔG_{H^*} values of −0.129, 0.099, and −0.003 eV at 1/2, 3/4, and 1 ML coverages, respectively, demonstrating exceptional HER catalytic activity compared to Pt. Building on these findings, Xu et al. evaluated the HER performance of various two-dimensional MBenes by calculating the corresponding ΔG_{H^*} values [56]. Their analysis revealed that Cr_2B_2 and Mo_2B_2 monolayers displayed relatively weak HER catalytic activity. In contrast, the Mn_2B_2 monolayer stood out for its excellent HER performance, characterized by very small $|\Delta G_{H^*}|$ values. Specifically, the ΔG_{H^*} values for Mn_2B_2 at hydrogen coverages of 1/8 and 3/4 were found to be 0.002 eV and 0.001 eV, respectively, as depicted in Figure 6f. These findings highlight the strong potential of Mn_2B_2 as a highly efficient catalyst for HER. Recently, Wang et al. combined ab initio calculations with experimental research to evaluate the stability of functionalized *h*-MBenes using surface Pourbaix diagrams [49]. Their work identified O-terminated *h*-MBenes as optimal candidates for HER electrocatalysis, with *h*-ZrBO and *h*-Nb_2BO_2 emerging as particularly active HER catalysts. Both materials exhibit $|\Delta G_{H^*}|$ values approaching the ideal 0 eV, underscoring their considerable potential in HER applications (Figure 6g,h).

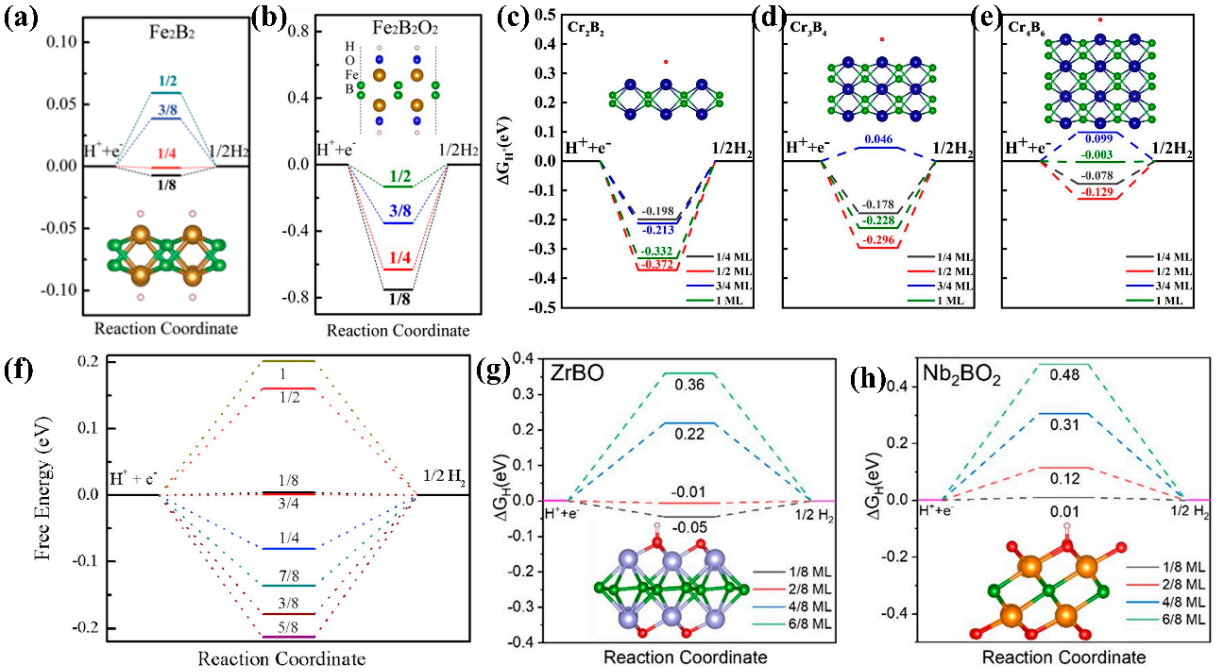


Figure 6. Calculated H adsorption Gibbs free energy ΔG_{H^*} of (**a**) Fe_2B_2 and (**b**) $Fe_2B_2O_2$ under varying hydrogen coverages. Reproduced with permission from [53], Royal Society of Chemisry, 2017. The free-energy diagram for the HER at different hydrogen coverages on the surfaces of (**c**) Cr_2B_2, (**d**) Cr_3B_4, and (**e**) Cr_4B_6. Reproduced with permission from [55], Elsevier, 2020. (**f**) The ΔG_{H^*} of Mn_2B_2 under varying hydrogen coverage. Reproduced with permission from [56], Elsevier, 2020. The ΔG_{H^*} with different hydrogen coverage on (**g**) ZrBO and (**h**) Nb_2BO_2. Reproduced with permission from [49], American Chemical Society, 2024.

Expanding on the understanding of hydrogen coverage effects, Sun et al. employed spin-polarized density functional theory to investigate the influence of hydrogen coverage on the HER catalytic activity of MBenes [54]. Their results revealed that MBenes such as Mn_2B_2, Fe_2B_2, Co_2B_2, Co_3B_4, and Mn_4B_6 exhibited outstanding HER properties ($|\Delta G_{H^*}| < 0.2$ eV) across various hydrogen coverage levels, underscoring their robustness and versatility (Figure 7a–c). The study further explored the relationship between hydrogen coverage and the interaction strength between hydrogen atoms and MBene surfaces, using Fe-based and Co-based MBenes as prototypes (Figure 7d–f). To provide a comprehensive comparison, Table 2 summarizes the ΔG_{H^*} values for various 2D MBenes, highlighting the materials that demonstrated particularly favorable HER activity. As hydrogen coverage

increased, a slight elongation of the Fe–H and Co–H bond lengths was observed, likely due to perturbations in the surrounding Fe or Co atoms induced by hydrogen adsorption. Interestingly, Wang et al. utilized high-throughput first-principles calculations combined with machine learning to screen quaternary *h*-MAB phases, efficiently identifying 47 stable candidates from a chemical space of 15,771 compounds [57]. Their bond strength analysis suggested that some of these quaternary *h*-MAB phases have the potential to be exfoliated into bimetallic *i*-MBenes. Guided by these theoretical insights, the team successfully synthesized the two-dimensional bimetallic *i*-MBene $Mo_2ErB_3T_{2.5}$, which exhibited outstanding catalytic activity and stability in the electrochemical HERs. These studies collectively underscore the immense potential of MBenes as next-generation HER catalysts, driven by their unique structural and electronic properties. The systematic theoretical approaches outlined in these works highlight promising avenues for the development of highly efficient and stable electrocatalysts for sustainable hydrogen production. Beyond their application as HER catalysts, theoretical studies have demonstrated that MBenes possess significant potential in a range of electrocatalytic reactions [51]. These findings not only confirm the exceptional HER performance of MBenes, but also emphasize their broader potential as multifunctional catalysts, solidifying their role as emerging materials in the field of electrocatalysis [58,59].

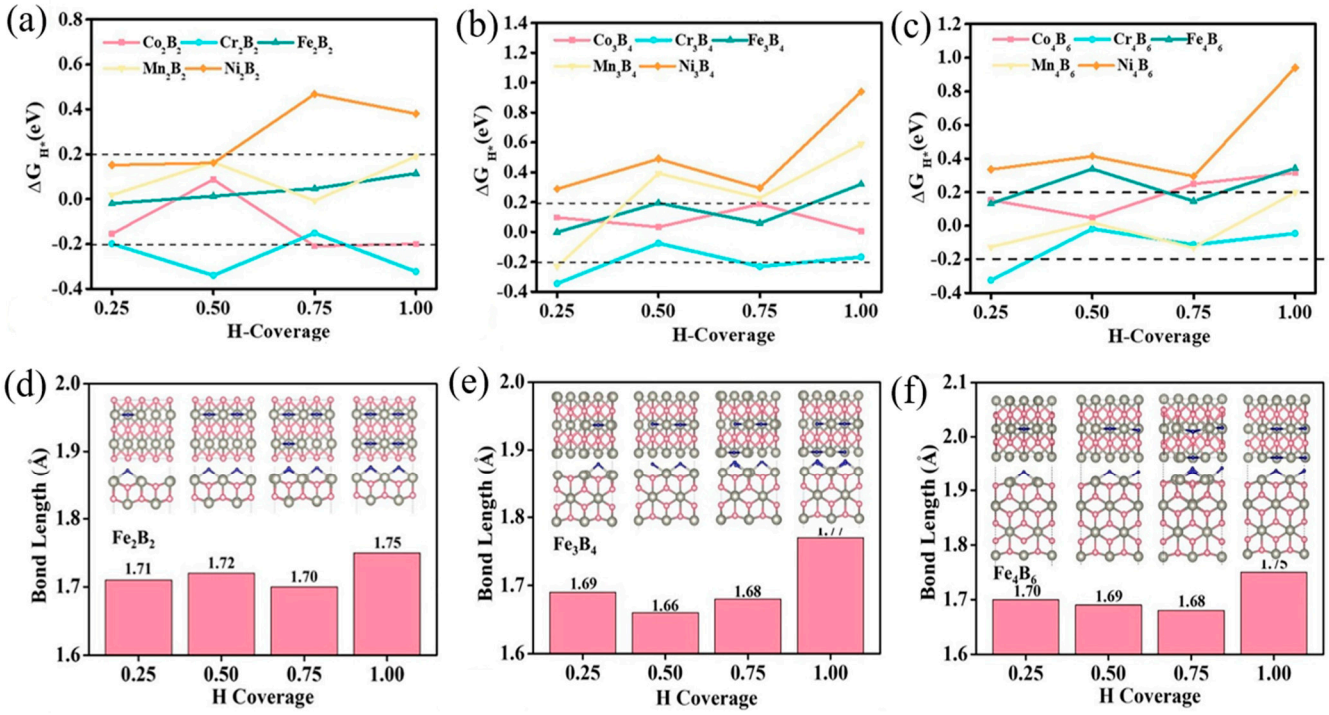


Figure 7. The ΔG_{H^*} of (**a**) M_2B_2, (**b**) M_3B_4, and (**c**) M_4B_6 at varying hydrogen coverages; atomic configurations of (**d**) Fe_2B_2, (**e**) Fe_3B_4, and (**f**) Fe_4B_6 at their optimal adsorption sites under different H coverage levels. Reproduced with permission from [54], Elsevier, 2023.

Table 2. ΔG_{H^*} values for various 2D MBenes in HERs.

2D MBenes	ΔG_{H^*} (eV)	Reference
TiB-O *	0.03	[47]
h-ZrBO	−0.01	[49]
h-MoBO	0.01	[49]
h-ScBO	0.03	[49]
h-Zr_2BO_2	0.06	[49]
h-Nb_2BO_2	0.01	[49]
Fe_2B_2	−0.001	[53]

Table 2. *Cont.*

2D MBenes	ΔG_{H^*} (eV)	Reference
Mn_4B_6	0.02	[54]
Fe_2B_2	0.02	[54]
Co_2B_2	0.09	[54]
Co_3B_4	0.01	[54]
Mn_2B_2	0.001	[54]
Fe_3B_4	0.02	[54]
Fe_4B_6	−0.06	[54]
Co_4B_6	0.15	[54]
Cr_4B_6	−0.078	[55]
Mn_2B_2	0.002	[56]

* indicates O-termination.

4.2. Theoretical Activity of Single-Atom Modified MBenes

Single-atom catalysts (SACs), known for their 100% atom utilization and uniform active sites, typically exhibit high catalytic activity [60–62]. Utilizing MBene-based materials as substrates for heteroatom doping has emerged as a promising strategy to enhance the performance of HERs. For example, embedding Ni atoms into Mo vacancies in Mo_2B_2 MBenes ($Ni@Mo_2B_2$) as SACs provided excellent structural stability and metallic conductivity. $Ni@Mo_2B_2$ had the potential to serve as a bifunctional electrocatalytic performance for water splitting, with a low $|\Delta G_{H^*}|$ value of 0.09 eV for HERs [63]. Li et al. reported that introducing various transition metal atoms into MBene materials ($Mo_2B_2O_2$ and $W_2B_2O_2$) significantly modulated their catalytic properties (Figure 8a,b) [64]. Notably, vanadium (V) atom doping significantly improved the catalytic performance of $W_2B_2O_2$, reducing the $|\Delta G_{H^*}|$ from 0.67 to 0.013 eV. Their research highlights that electron transfer between the metal atoms and the MBenes is crucial in altering HER performance. In fact, electron transfer can significantly modulate the electronic structure of metal atoms (Figure 8c), thereby affecting their catalytic activity and reaction pathways. This provides new insights into the design of efficient HER electrocatalysts, underscoring the importance of controlling the interfacial properties between the metal and the MBenes. Additionally, Sun et al. utilized machine learning models combined with density functional theory to identify metal atom-doped MBenes [65], such as Co/Ni_2B_2, Pt/Ni_2B_2, Os/Co_2B_2 and Mn/Co_2B_2, as efficient HER SACs with ΔG_{H^*} values close to zero: 0.089, −0.082, −0.087, and −0.044 eV, respectively. This finding demonstrates that machine learning models are powerful tools for accelerating the screening of HER catalysts, significantly reducing computational costs and enabling more extensive studies. Aarti Shukla conducted a comprehensive computational study using density functional theory to investigate the potential of single-atom embedded on novel Ti_2B MBenes for HERs [48]. As shown in Figure 8d, the elevated adsorption energies of H* at the T_H and T_B sites on pristine Ti_2B hinder hydrogen desorption, negatively affecting electrocatalytic activity. To mitigate this issue, the doping of transition metals at the Ti site enhanced hydrogen adsorption. Following the incorporation of transition metals as SACs, the ΔG_{H^*} value for the TM-Ti_2B system was reduced to within 0.2 eV (Figure 8e). This decrease signifies substantial orbital overlap between the d orbitals of the transition metals and the hydrogen orbitals, indicating strong interactions between the transition metal atoms and hydrogen. Notably, the Pd-Ti_2B system exhibited the highest catalytic activity, with a ΔG_{H^*} value approaching thermal neutrality at −0.057 eV. These results highlight the significant potential of transition metals as SACs in MBenes, emphasizing their essential role as promising candidates for high-performance HER catalysts. Recent studies indicate that, while SACs exhibit unique catalytic properties, their practical application is significantly hindered by stability challenges [66,67]. Due to the high surface energy of individual metal atoms, SACs are susceptible to aggregation during catalytic reactions, which leads to deactivation. Therefore, developing synthetic strategies that enhance stability while allowing for high metal loading is essential, along with integrated experimental–theoretical approaches to verify SAC structures.

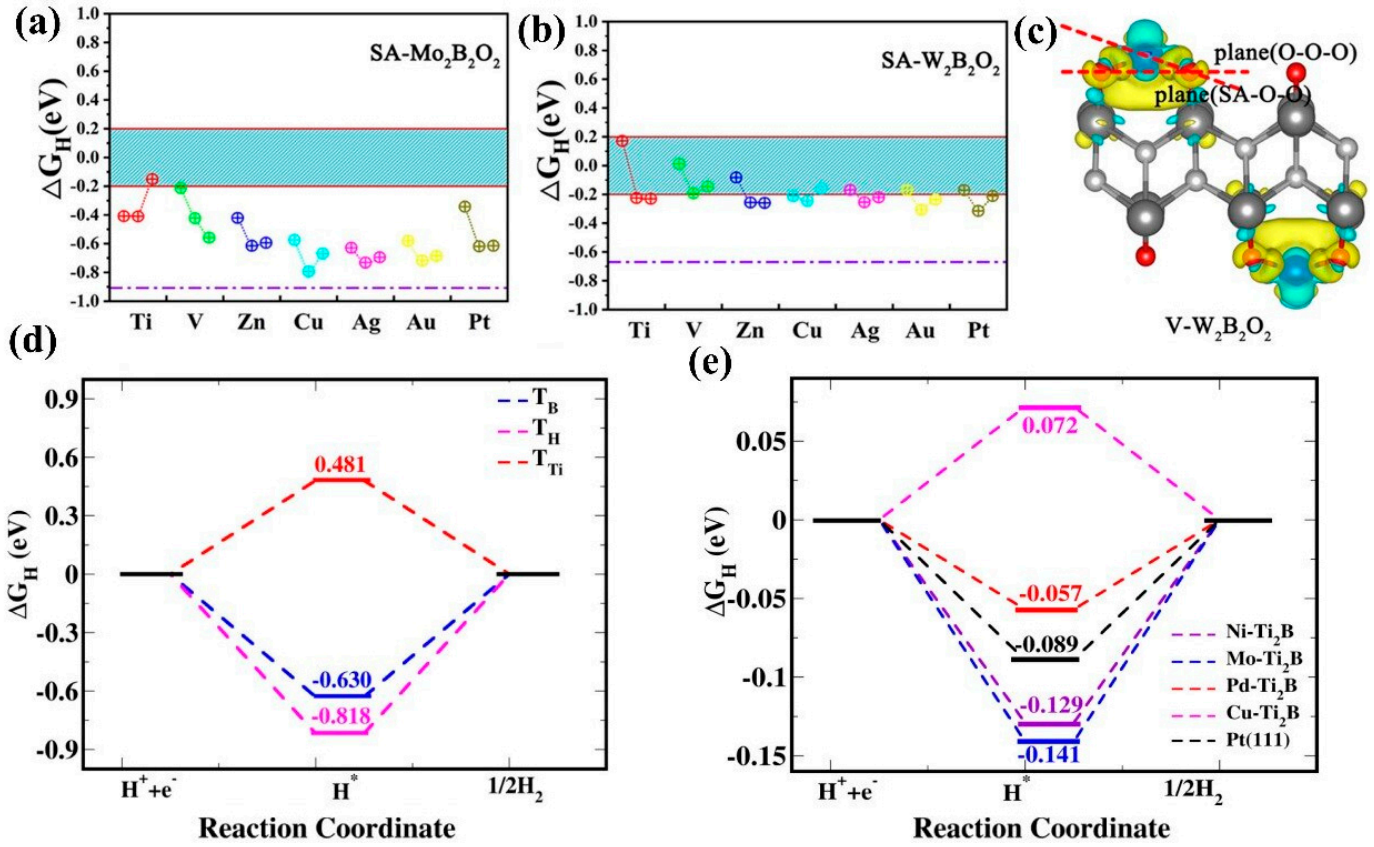


Figure 8. The ΔG_{H^*} values following the introduction of different metal single atoms into (**a**) $Mo_2B_2O_2$ and (**b**) $W_2B_2O_2$. (**c**) Three-dimensional structure of V-$W_2B_2O_2$. Reproduced with permission from [64], American Chemical Society, 2020. The ΔG_{H^*} of (**d**) pristine Ti_2B and (**e**) TM-Ti_2B. Reproduced with permission from [48], Elsevier, 2024.

Experimental studies combined with theoretical calculations have further explored various single-atom doping strategies and substrate modifications to enhance the electrocatalytic HER activity of MBenes. For example, Kim et al. anchored Pt single atoms onto the $MoAl_{1-x}B$ material, demonstrating that the strong interaction between $MoAl_{1-x}B$ and Pt atoms enhances the charge density and alters the d-band electron properties of the Pt sites [68]. Their results indicated that Pt-$MoAl_{1-x}B$ achieved more favorable free energies for H_2O dissociation and H* adsorption under both alkaline and acidic conditions, outperforming other catalysts (Figure 9a,b). These findings suggest that single-atom modified MBenes effectively facilitate water dissociation into intermediates, leading to the production of H_2 and significantly enhancing HER activity. Tan and colleagues employed both experimental and computational methods to explore the electrocatalytic performance of transition metal single-atom modified MoB_2 (TM-MoB_2) SACs for HERs [69]. They successfully synthesized a series of TM-MoB_2 SACs (where TM = Ni, Co, Fe), with Ni-MoB_2 exhibiting exceptional activity under both alkaline and acidic conditions. DFT calculations revealed that the incorporation of Ni atoms significantly altered the electronic structure of the Mo sites, achieving an optimal balance between water dissociation and hydrogen adsorption. Figure 9c presented the Gibbs free energy profile for water dissociation on the (100) surface of Ni-MoB_2, illustrating a low-energy barrier at the Mo sites. Figure 9d further confirms that hydrogen adsorption is more favorable at the Mo sites compared to the Ni sites, establishing Mo as the primary active center for HERs. This study highlights the pivotal role of single-atom modification in enhancing the catalytic efficiency of MoB_2, offering valuable insights for high-performance designs.

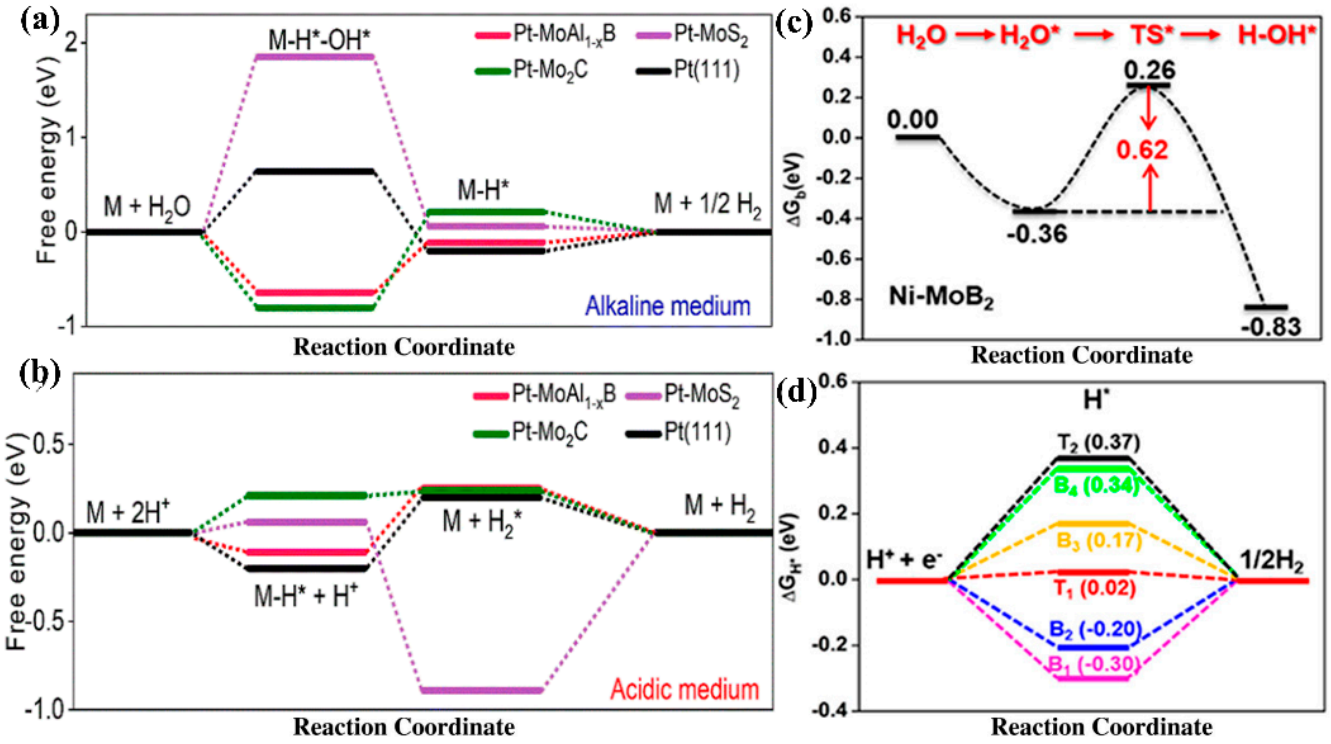


Figure 9. Free energy of H* intermediates adsorbed on Pt (111), Pt-MoS_2, Pt-Mo_2C, and Pt-$MoAl_{1-x}B$ in (**a**) alkaline and (**b**) acidic environments. Reproduced with permission from [68], Royal Society of Chemistry, 2023. (**c**) Gibbs free energy profile for water dissociation on the (100) surface of Ni-MoB_2. (**d**) The ΔG_{H^*} of Ni-MoB_2 on various sites. Reproduced with permission from [69], American Chemical Society, 2023.

5. Conclusions and Outlook

In recent years, a considerable number of pivotal theoretical studies have focused on MBenes to expedite the discovery of new materials. This review offers a comprehensive summary of the latest developments in MBenes for HER applications, with an emphasis on their structural properties and catalytic activity. Methods such as single-atom doping and surface loading have proven to be effective in boosting the intrinsic HER activity of MBenes. These advancements have been instrumental in developing more reliable MBenes-based electrocatalysts, with performance metrics approaching those of commercial platinum catalysts. Despite substantial theoretical advancements in MBenes for electrochemical HER, several key challenges still need to be addressed.

(i) Most earlier theoretical studies on MXenes have relied on simplified CHE model calculations. Although these methods provide valuable insights, they often overlook key factors like the effects of applied potential and the complexities of interfacial electron transfer, which are crucial for accurately understanding electrochemical performance. Future studies could focus on developing more comprehensive models that integrate these variables, allowing for a more accurate simulation of real experimental conditions. Overcoming these modeling challenges is crucial for advancing the theoretical foundation of MBene research.

(ii) Although surface doping with heteroatoms and single-atom loading has been applied to enhance the HER activity of MBene-based electrocatalysts, the practical limitations of stability remain a significant barrier. Future research could explore the construction of heterostructures within MBene-based nanomaterials. Additionally, dual-atom or metal-cluster surface modification strategies may help further improve the stability and efficiency of MBenes in HER applications. Experimental validation of these modified structures will be essential to verify theoretical predictions and bridge the gap between theory and application.

(iii) The current descriptors for evaluating the activity of MBenes-based electrocatalysts require deeper investigation. With the rapid development of machine learning, combining machine learning with DFT calculations presents a promising, cost-effective alternative to relying solely on DFT. This approach can help extract physically meaningful descriptors, providing crucial theoretical guidance for the design of highly active electrocatalysts. Additionally, incorporating machine learning-driven predictions into experimental studies could expedite the identification of optimal MBene configurations for HER, addressing the challenge of linking theoretical advances with practical applications.

Overall, theoretical simulations are essential for advancing HER electrocatalysts and providing valuable guidance for experimental synthesis. Although MBenes remain a relatively underexplored class of catalysts or co-catalysts, theoretical insights into materials design are poised to pave the way for significant breakthroughs in clean energy research.

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