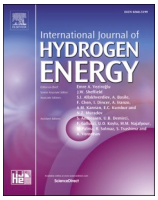
International Journal of Hydrogen Energy 221 (2026) 154099



Contents lists available at ScienceDirect

International Journal of Hydrogen Energy

journal homepage: www.elsevier.com/locate/he





Multidimensional engineering of MoS_2 electrocatalysts: Bridging edge-site activation, phase modulation, and defect control for efficient hydrogen evolution

Xuexue Pan [a,b,c,*], Yi Zhao [a], Dinmukhambet Baimbetov [d], Yevgeniy Muralev [d], Samal Syrlybekkyzy [d], Berik Bakhytzhanovich Akhmetov [d], Qian Liu [e], Qamar Abbas [c,f,**]

[a] Zhongshan Advanced Functional Materials Engineering Technology Research Center, Guangdong Engineering Research Center of New Energy Materials and Devices, Zhongshan Polytechnic, Zhongshan, 528400, China
[b] School of Energy Science and Technology, Henan University, Kaifeng, 475004, China
[c] Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, 60-965, Poznan, Poland
[d] Yessenov University, 130000, Aktau, Kazakhstan
[e] Zhongshan Power Supply Bureau of Guangdong Power Grid Co., Ltd., Zhongshan, 528405, China
[f] Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010, Graz, Austria

ARTICLE INFO

Keywords:
Defect engineering
Nanostructure
MoS_2
Electrocatalytic hydrogen evolution reaction
Edge site
HER

ABSTRACT

Molybdenum disulfide (MoS_2) is a transition metal compound with a layered structure and unique physical and chemical properties, which has been widely explored as a catalyst for the electrocatalytic hydrogen evolution reaction (HER). The crystal structure of MoS_2 consists of an S–Mo–S layer, in which the edge sites are considered to be catalytically active. However, challenges are still faced regarding the defect control, stability, electrical conductivity, and large-scale synthesis of MoS_2. This review summarizes the use of MoS_2 in HER and explores its advantages as a catalyst for hydrogen generation, as well as outlines challenges and strategies to improve its catalytic efficiency. Particular focus has been given to summarizing various methods for the activation of edge sites to improve the electrocatalytic performance of MoS_2. In addition, nanostructuring of MoS_2, doping and heterostructures, phase transition control, surface modification, and advanced synthesis technologies to improve edge site activation and overall catalytic performance have been reviewed. Further, the potential of MoS_2 in practical HER applications, future research directions, and comparison with other electrocatalytic reactions have been elaborated. Although MoS_2 is widely regarded as a competitive electrocatalyst for hydrogen production, further research work is needed to harness its potential in the electrolyzes for hydrogen energy.

1. Introduction

Electrolysis of water to produce hydrogen and oxygen dates back to the 19th century. Initially, direct current generators were used for small-scale electrolysis applications. Michael Faraday discovered in the 1850s that water could be broken down into oxygen and hydrogen by passing an electric current through it, laying the foundations of electrolysis technology. This straightforward reaction could solve some of the most significant issues of the modern world: 'green' energy supply and sustainable materials. One of the first applications of this process was chlor-alkali electrolysis which was developed in the early 20th century to produce chlorine gas and sodium hydroxide through seawater electrolysis. However, a more promising application of electrolysis is the production of hydrogen. Hydrogen is the key fuel to achieving sustainable development and low-carbon economy in the global energy transition due to its high energy density and zero carbon emissions [1–3]. With the continuous increase in energy demand and the increasingly severe environmental pollution problems, finding efficient and clean energy alternatives has become an urgent issue in scientific research [4–6]. As an essential exploration direction in this field, the bottleneck for the commercial application of hydrogen energy mainly lies in its efficient and low-cost production technology [7,8]. Electrocatalytic hydrogen

* Corresponding author. Zhongshan Advanced Functional Materials Engineering Technology Research Center, Guangdong Engineering Research Center of New Energy Materials and Devices, Zhongshan Polytechnic, Zhongshan, 528400, China.
** Corresponding author. Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, 60-965, Poznan, Poland.
E-mail addresses: panxuexue@zspt.edu.cn (X. Pan), qamar.abbas@tugraz.at (Q. Abbas).

https://doi.org/10.1016/j.ijhydene.2026.154099
Received 31 July 2025; Received in revised form 8 February 2026; Accepted 14 February 2026
Available online 25 February 2026
0360-3199/© 2026 The Authors. Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

evolution reaction (HER) directly affects the energy efficiency and economy of the entire process of hydrogen production through the performance of its catalyst. For instance, state-of-the-art commercial electrolyzers utilizing platinum-group catalysts can achieve energy efficiencies of ~60-70% and operate at low overpotentials (<50 mV) to drive high current densities, setting a high-performance benchmark [9–11]. Among numerous candidate catalytic materials, molybdenum disulfide (MoS_2) exhibits significant catalytic potential in electrocatalytic hydrogen evolution reactions due to its unique physical and chemical properties, especially the abundant active edge sites in its layered structure [12–14]. The electrolysis of water can be described by the following reactions: $2H_2O+2e^- \rightarrow H_2+2OH^-$ and MoS_2 as a catalyst can promote the decomposition of water to produce hydrogen and oxygen [15].

MoS_2 offers a low-cost and abundant resource compared to traditional platinum catalysts. Quantitatively, the raw material cost of MoS_2 is a few orders of magnitude cheaper than that of platinum, making it an economically attractive alternative for large-scale applications [16]. In addition, it also can adjust its electronic structure through doping, phase transition control, and other means to further enhance its catalytic performance [17,18]. By optimizing the nanostructure of MoS_2, it is possible to maximize the exposure of its active edge sites and enhance charge transfer, thus improving the kinetics of the hydrolysis reaction [19]. For example, MoS_2 prepared by the hydrothermal synthesis method has a high specific surface area and uniform nanostructure, which contributes to improving its catalytic activity and stability. However, MoS_2 still faces challenges regarding electronic conductivity, stability, and large-scale synthesis technology, which limits its practical application in hydrogen energy [20,21]. These challenges manifest as a performance gap where optimized MoS_2 catalysts can achieve overpotentials as low as 75-200 mV to reach a current density of 10 mA cm^{-2}, while lagging behind the exceptional performance of platinum-based catalysts (<20 mV). Bridging this performance gap while leveraging the significant cost advantage is the central technological challenge driving current research efforts [22].

Numerous reviews have summarized the progress of MoS_2 for HER, however, a cohesive analysis that centralizes the “edge site” as the fundamental framework for rationalizing and integrating diverse performance enhancement strategies is notably lacking [23]. This review distinguishes itself by adopting this edge-site-centric perspective to critically synthesize recent advances.The cataloging modifications explicitly explore the synergy between defect engineering, heterostructure construction, and phase engineering in modulating the electronic structure and increasing the density of active edge sites [24]. Furthermore, this article places a specific emphasis on establishing quantitative structure-activity relationships, linking atomic-scale configurations and material properties directly to macroscopic catalytic metrics, which is crucial for guiding the rational design of next-generation catalysts [25].

This article also aims to comprehensively review the fundamental research progress of MoS_2 in electrocatalytic hydrogen evolution reactions and explore its catalytic advantages, challenges, and performance improvement strategies. An in-depth analysis is conducted of the relationship between the edge sites of MoS_2 and its catalytic activity, as well as the latest research progress in optimizing the properties of MoS_2 through methods such as nanostructuring, doping, and surface modification. This article also includes future development directions and outlook for MoS_2 in the hydrogen evolution reaction, as well as the key issues that need to be solved to achieve its commercial application, aiming to provide guidance and practical reference for promoting the use of MoS_2 in sustainable energy systems.

2. Structural characteristics of MoS_2

MoS_2 exists in different structural forms, including monolayers, nanoparticles, nanotubes, and multilayer structures [14,26,27]. Monolayer MoS_2 is a two-dimensional material with a layered structure of a hexagonal honeycomb [28]. This structure allows MoS_2 to exhibit high electron mobility and tunable bandgap properties in electronic devices.

2.1. Crystal structure of MoS_2

MoS_2 is a typical transition metal sulfide possessing a layered structure, and its unique crystal properties provide the theoretical basis for its application in many fields, especially in the electrocatalytic hydrogen evolution reaction (HER) [14,29,30]. The crystal structure of MoS_2 consists of a three-atom-layer arrangement, with a layer of molybdenum (Mo) atoms sandwiched between two layers of sulfur (S) atoms [31]. This unique stacked structure plays a crucial role in determining the physical and chemical properties of MoS_2, such as its semiconducting behavior and catalytic activity [32,33]. As depicted in Fig. 1a, the structure of MoS_2 can vary from bulk to monolayer forms, with each morphology having distinct geometric arrangements: trigonal, octahedral, and distorted octahedral [34]. These structures significantly influence the energetics of the active sites embedded within the bulk material, which are critical for its performance in various applications [32]. Fig. 1b presents the band structures for different layers of MoS_2, including bulk, quadrilateral, bilayer, and monolayer forms [35]. The band structures illustrate how the electronic properties change as the layer thickness is reduced, with the monolayer MoS_2 showing a direct bandgap, which is a desirable feature for many electronic and optoelectronic applications [36].

Advances in synthesis methods, such as the use of magnetron sputtering followed by sulfurization in a confined space to create wrinkled MoS_2 thin films [31] and the epitaxial growth of wafer-scale single--crystal MoS_2 monolayers via buffer layer control [32], have further highlighted the importance of understanding and optimizing the structural properties of MoS_2 for improved functionality. These methods allow for precise layer thickness and structure control, which can tailor the material's properties for specific applications. The layered structure of MoS_2, as shown in Fig. 1a [34], also offers opportunities for further creating heterostructures and composites to enhance its performance [37]. For instance, combining MoS_2 with other materials can produce synergistic effects that improve its catalytic efficiency and stability. The ability to manipulate the structure of MoS_2 at the nanoscale opens up new possibilities for designing materials with tailored properties for energy conversion, storage, and other advanced technologies.

However, the structural discussion of MoS_2 often relies on idealized models that overlook practical challenges [38]. For example, while theoretical models describe perfect 2H and 1T phases, real-world syntheses frequently yield mixed-phase systems with uncontrolled defects, leading to inconsistencies in catalytic performance [39]. Recent studies highlight that the phase stability of 1T-MoS_2 is compromised under operational conditions due to spontaneous transition to the 2H phase, which is rarely critically addressed in foundational texts [40]. Furthermore, the impact of interfacial strain and defect propagation during layer stacking—often ignored in textbook descriptions—can significantly alter electronic properties, as evidenced by discrepancies between DFT calculations and experimental observations of bandgap modulation [41]. This gap between idealized structures and practical realities underscores the need for a more nuanced interpretation of MoS_2 crystallography in electrocatalytic applications [42].

2.1.1. Structure of S–Mo–S layer

In the S–Mo–S layered structure, each molybdenum atom is surrounded by six sulfur atoms to form an octahedral coordination structure [43,44]. The molybdenum atoms are centrally located between the two layers of sulfur atoms, while the sulfur atoms are located at the top and bottom, forming a layered structure (Fig. 1c and d) [45]. The atoms inside each S–Mo–S layer are connected by covalent bonds, guaranteeing stability and a high degree of structural integrity [46]. The

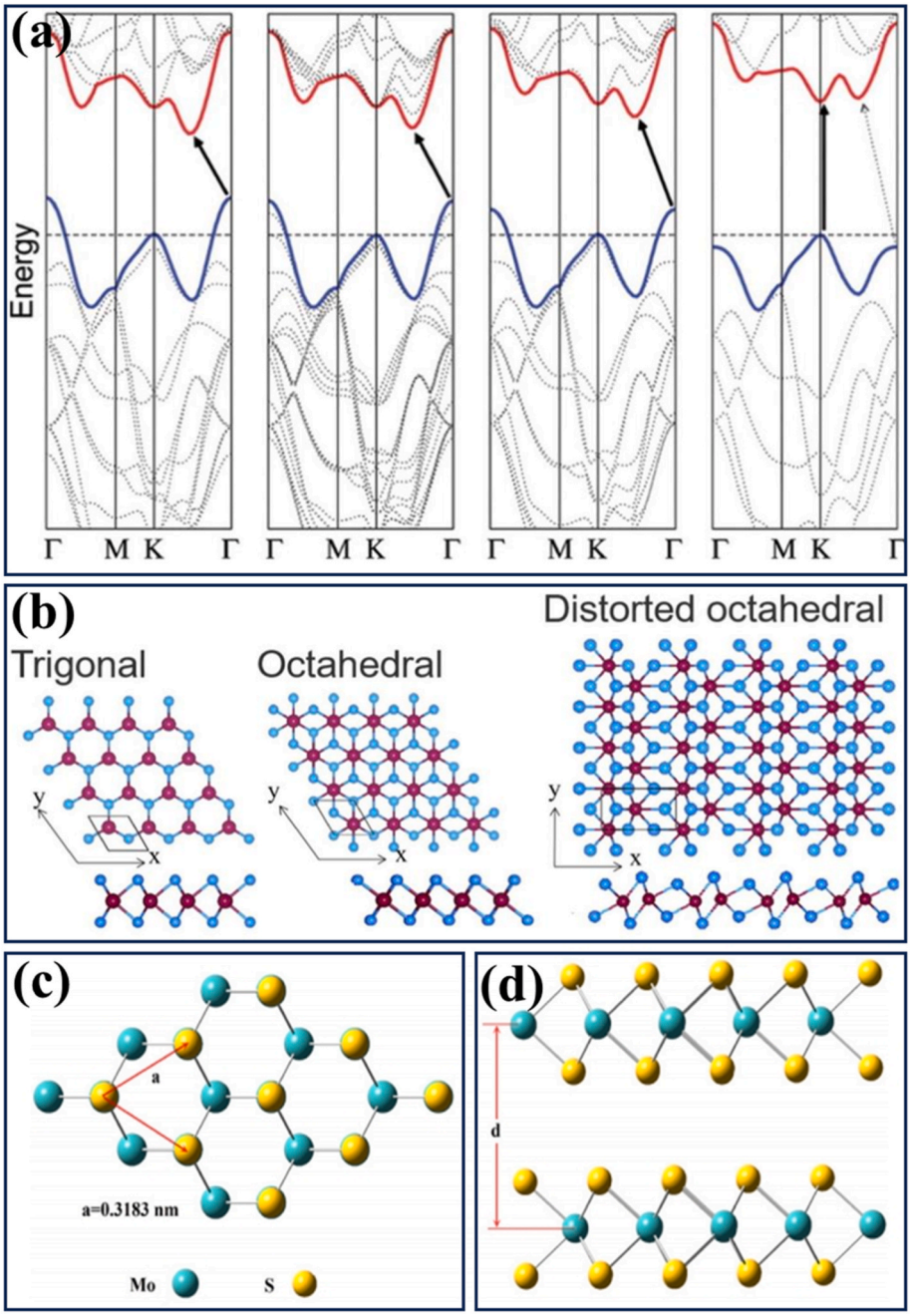


Fig. 1. (a) Three crystalline phases of MoS_2 presented in a sequence. From left to right: trigonal, octahedral, and its strained version elaborated on a similar scale [34]. (b) Top and side views of various phases of TMDs: trigonal prismatic (H), octahedral (T), and distorted octahedral (Td) coordination geometries. Purple spheres indicate the transition metal, whereas blue spheres indicate chalcogen atoms. The box in the figure indicates a unit cell size for each phase of TMDs (H, T, or Td phase) [35]. (c) One Mo atom is connected to six S atoms, and the Mo–S bond is covalent [45]. (d) Molybdenum disulfide has an interlayer spacing of d = 0.65 nm, with only weak van der Waals interactions [45]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

characteristics of this structure give MoS_2 excellent chemical stability and mechanical properties [14,47–49].

Despite the apparent robustness of the S–Mo–S layer, critical analysis reveals that covalent bonding within the layer is susceptible to disruption under electrochemical conditions [50]. Sulfur vacancies or molybdenum substitutions—common in synthetic samples—can lead to localized electronic states that deviate from idealized models, affecting catalytic activity [51]. For instance, literature reports conflicting values for Mo–S bond strengths under strain (ranging from 2.31 Å to 2.41 Å), indicating that structural perfection is rarely achieved in practice [52]. This variability highlights the limitations of static structural descriptions in predicting dynamic behavior during HER [53].

2.1.2. *van der Waals interaction*

The different S–Mo–S layers are tightly stacked through weak van der Waals interactions [54–57]. This van der Waals force is originated by instantaneous dipolar interactions between atoms with distant interlayer distances [58,59]. Since this interaction is relatively weak, the layers can be slipped or separated relatively quickly, this property allows MoS_2 to be used as a lubricant or as a two-dimensional material in electronic devices (Fig. 1c and d) [45]. However, such interlayer van der Waals forces may limit charge transfer, enhancing the catalytic

efficiency [14,45,55,57,60–62].

In the layered structure of MoS_2, adjacent sulfur-molybdenum-sulfur (S–Mo–S) sandwich layers are stacked by weak van der Waals force interactions, and this weak bonding property between the layers has a dual regulatory effect on the exposure of edge sites. On the one hand, the interlayer slip (sliding movement) behavior caused by the van der Waals force can be controlled by mechanical stress to achieve the relative displacement between layers, thereby changing the geometric configuration and electronic state of the edge sites. On the other hand, the shear strain generated by interlayer slip can induce suspended bond reconfiguration of sulfur atoms, which dynamically regulates the density and distribution of active sites at the edge. The physical mechanism of interlayer slip: When the shear deformation occurs between MoS_2 layers, the adjacent layers reach the lowest energy AB stacking configuration through slippage. Theoretical calculations show that the interlayer slip energy barrier is only ~0.03 eV/atom, which leads to slippage during mechanical peeling or electrochemical cycling [63]. During the slip process, the relative positions of sulfur atoms at the edges of the upper and lower layers change, exposing the edge sites that were originally covered by the upper layers Through in-situ TEM observation, it was found that the interlayer slip angle of more than 10° could increase the density of edge active sites by 3-5 times [64].

Interlayer slip not only affects the physical exposure of edge sites but also alters their intrinsic activity through strain-electron coupling. The in-plane shear strain ($\varepsilon > 2\%$) due to slippage can lead to an upward shift in the Mo 4d orbital energy level and a decrease in hydrogen adsorption free energy (ΔG_{H^*}). The experimental TOF value of the MoS_2 edge site increased from 0.15 s^{-1} to 0.38 s^{-1} after slippage, indicating a synergistic effect between strain regulation and site exposure. At industrial-grade current densities (>500 mA/cm^2), the intense impact of hydrogen bubbles can trigger an irreversible accumulation of interlayer slip, resulting in the collapse of edge structures [65,66]. By introducing gold nanoparticle intercalation, the slip amplitude can be effectively anchored, and the initial current density of more than 90% can be maintained in the 100-h stability test. In addition, the vertically oriented nanosheet array design can limit the slip direction to the in-plane dimension, and enhance the structural stability through geometric confinement [64].

2.1.3. Atomic configuration and activity of edge sites

The electronic state properties of the Mo/S coordination unsaturated site at the edge of molybdenum disulfide (MoS_2) are the key to understanding its catalytic performance. The electronic states of these unsaturated sites are closely related to their catalytic activity, which can be analyzed in depth by using theories such as the D-band center theory. From the perspective of the d-band center theory, the center position can intuitively predict the interaction strength between the surface adsorbate and the catalyst surface. At the coordination unsaturated site of the Mo atom at the edge of MoS_2, the distribution of d electron orbitals changes due to the change of the surrounding coordination environment, resulting in the shift of the center of the d band. The position of the center of the d-band affects the strength of the chemical bonding of the Mo atom at the edge of the hydrogen atom. When the center of the d band moves upwards close to the Fermi level, the interaction between the d orbital of the Mo atom and the 1s orbital of a hydrogen atom is enhanced, which is conducive to the adsorption of hydrogen atoms. Conversely, when the center of the d-band is far away from the Fermi level, the adsorption capacity of hydrogen atoms decreases [67,68]. This change in electronic state not only affects the strength of hydrogen adsorption but also has an important impact on the subsequent steps of hydrogen atom combination to form hydrogen. Similarly, the coordination unsaturated site of the marginal S atom also has a unique electronic state. The 3p orbital electron distribution of the S atom is rearranged in the coordination unsaturated state, which makes its adsorption behavior to the hydrogen atom different from that of the Mo atom. The electron cloud density of the S atom and its interaction with surrounding atoms drive it to play an important role in hydrogen evolution reactions [69]. In some cases, S atoms may participate in the hydrogen adsorption process as proton acceptors and subtle changes in their electronic states will affect the transfer and adsorption kinetics of protons.

There are significant activity differences at the edges of different crystal planes (Mo - edge/S - edge) of MoS_2. The edge of Mo-terminated is theoretically predicted to have a ferromagnetic ground state. In experimental observations, Mo-edges often exist in a zigzag structure, and their sulfur atomic coordination numbers are low, which makes sulfur vacancies more likely to form. For example, sulfur atoms in the edge planes of MoS_2 [70] and its composites [7,8,71] exhibit high mobility due to binding to less than three molybdenum ions, and the formation of sulfur vacancies promotes the adsorption of reactants. On the other hand, sulfur-terminated structures (e.g., (100)-S_2) have low surface energy but may be limited in catalytic activity due to the saturation of sulfur atoms. However, the dynamic generation of sulfur vacancies can still increase activity, especially at high temperatures or under reaction conditions.

Mo-edge showed outstanding activity in electrocatalytic hydrogen evolution reactions. From an atomic structure point of view, the Mo atoms on the Mo-edge have a high electron density and a proper coordination environment, which allows them to form chemical bonds of moderate strength with hydrogen atoms [72]. In the hydrogen adsorption process, the Mo atom on the Mo-edge can effectively accept the electrons of the hydrogen atom to form a relatively stable adsorption state. At the same time, due to the special structure of Mo-edge, there is a suitable spatial distance between the adsorbed hydrogen atoms, which is conducive to the subsequent combination of hydrogen atoms to form hydrogen molecules. Moreover, the electronic structure of the Mo-edge is closer to the metal state, and it has good electronic conduction ability, which can quickly transfer electrons to the adsorbed hydrogen atoms and promote the hydrogen evolution reaction [73,74].

In contrast, the activity of the S-edge is relatively weak. The S atom on the S-edge has a strong electronegativity and a strong attraction to the electron, which makes the chemical bond formed by the S atom and the hydrogen atom stronger, resulting in the desorption of hydrogen to form hydrogen molecules. Thus, on the S-edge, the hydrogen adsorption process is relatively easy to occur, but the desorption step of hydrogen generation becomes the rate-limiting step of the reaction [74,75]. However, it is possible that the activity of the S-edge can be increased to a certain extent under specific reaction conditions, with appropriate surface modification or modification of the reaction environment. The metallic 1T phase edge site has higher intrinsic activity than the semiconductor 2H phase. In the 1T phase, due to its unique electron band structure and atomic arrangement, the electron cloud distribution at the edge site is more uniform and the electron migration rate is faster, which makes the whole process of hydrogen adsorption and hydrogen evolution more efficient. However, due to its semiconducting properties, the edge site of the 2H phase has relatively poor electron conduction ability, which restricts the kinetic process of the hydrogen evolution reaction, resulting in its activity being inferior to that of the edge site of the 1T phase. In conclusion, the electronic state analysis of the Mo/S coordination unsaturated sites at the edge and the study of the activity differences at the edges of different crystal planes (Mo-edge/S-edge) are important foundations for an in-depth understanding of the hydrogen evolution reaction mechanism of MoS_2-based electrocatalysts and have important guiding significance for improving the performance of catalysts through nanoengineering strategies and edge-specific control techniques [74,75].

Critical interpretation of edge site activity reveals significant discrepancies between theoretical predictions and experimental observations [38]. For instance, while D-band center theory optimistically predicts $\Delta G_H \approx -0.08$ eV for Mo-edge sites, experimental measurements often report values ranging from −0.08 eV to −0.25 eV, indicating oversimplification in models that ignore dynamic factors like surface

reconstruction or adsorbate coverage. Additionally, the presumed superiority of 1T-phase edges is challenged by their metastability [76]; under operational conditions, phase transition to 2H can nullify activity gains, a caveat rarely emphasized in textbook discussions [77]. These contradictions underscore the need for in-situ studies to bridge theory and practice.

2.2. Major phase of MoS_2

MoS_2 is a heterogeneous material that gives it different physical and structural characteristics and impacts its catalytic activity in the electrocatalytic HER [30,45,70,71,78]. There are two main crystal phases in MoS_2, namely 2H–MoS_2 and 1T-MoS_2, both of which have different symmetries and electronic structures [79–83].

2.2.1. Hexagonal symmetry of 2H–MoS_2

2H–MoS_2, as the thermodynamically stable phase of molybdenum disulfide, exhibits unique structural and electronic properties that make it highly versatile for various applications. Its hexagonal symmetry contributes to its stability and influences its electronic band structure [84,85], which is characterized by an indirect bandgap in bulk form and a direct bandgap in monolayer form [86–88]. This transition in electronic properties with thickness reduction is critical for optoelectronic applications, as highlighted in Refs. [89,90]. Furthermore, the covalent bonding within the S–Mo–S layers and the van der Waals interactions between layers allow for easy exfoliation into monolayers, enabling the exploration of its two-dimensional properties [91,92].

The semiconducting nature of 2H–MoS_2 is particularly advantageous for applications in field-effect transistors (FETs), photodetectors, and other electronic devices, where its high on/off current ratio and low leakage currents are desirable [93]. Additionally, the anisotropic thermal conductivity 2H–MoS_2, which is higher within the basal plane than the cross-plane direction, is another critical property for thermal management in nanoelectronics [87,94]. In catalysis, while the basal plane of 2H–MoS_2 is less active, recent studies have focused on engineering defects and doping to enhance its catalytic performance. For instance, doping with transition metals or introducing sulfur vacancies can significantly improve the hydrogen evolution reaction (HER) activity by increasing the number of active sites [92]. Moreover, phase engineering strategies, such as transforming 2H–MoS_2 into the metallic 1T phase, have been explored to enhance its catalytic properties further [91,92]. Lastly, the mechanical flexibility and chemical inertness of 2H–MoS_2 make it a promising candidate for flexible and wearable electronics and for protective coatings in harsh environments [93,95]. Combined with its tunable electronic and optical characteristics, these properties continue to drive research into its integration into next-generation technologies.

2.2.2. Octahedral symmetry of 1T-MoS_2

Due to its unique octahedral symmetry structure [96] 1T phase of molybdenum disulfide (T-MoS_2) exhibits metallicity characteristics that are significantly different from those of 2H semiconductors, which provides a physicochemical basis for improving the intrinsic catalytic activity of edge sites. As shown in Fig. 1a [34], the Mo atoms in the 1T phase are in an octahedral coordination environment to form the [MoS_6] octahedral structural unit, and their symmetry leads to a significant reorganization of the d orbital energy level of Mo. Theoretical calculations show that the center of the d-band of the Mo atom at the edge of 1T-MoS_2 is about 0.3-0.5 eV lower than that below the 2H phase Fermi level [96], and this electronic state control effectively reduces the hydrogen adsorption free energy (ΔG_{H^*}) and brings it closer to the ideal value ($\Delta G_{H^*} = 0$ eV). Density functional theory (DFT) simulations show that the ΔG_H of the 1T phase edge Mo site can be optimized to −0.08 eV, which is closer to the thermodynamically neutral adsorption state than the 2H phase edge site ($\Delta G_H \approx -0.25$ eV).

Octahedral symmetry-induced metallicity features significantly enhance the charge transport capacity of edge sites [96]. Angle-resolved photoelectron spectroscopy (ARPES) confirmed that the 1T-MoS_2 edge state showed a continuous electronic state distribution near the Fermi level, and its carrier concentration could reach more than 10^3 times that of the 2H phase. This high conductivity significantly reduces the electron transfer barrier during the electrocatalytic reaction, and the charge transfer resistance (R_{ct}) at the edge site of the 1T phase is about 2 orders of magnitude lower than that of the 2H phase. The synchrotron radiation X-ray absorption fine structure (XAFS) analysis further revealed that there was obvious lattice distortion of the Mo atom at the edge of the 1T phase, and the Mo–Mo bond length was shortened to 2.75 Å (3.15 Å for the 2H phase) [97,98], and this structural compression led to the formation of a highly active metastable surface at the edge site [99,100].

At the level of atomic-scale catalytic mechanism, the 1T phase edge exhibits unique bifunctional catalytic characteristics. Mo-edge site forms a strong coupling effect with the hydrogen 1s orbital through the d^2_{yz} orbital, which promotes the efficient progress of the Volmer step ($H^+ e^- \rightarrow H^*$). However, adjacent S-edge sites are involved in the kinetic optimization of the Heyrovsky/Tafel step ($H^*H^+ e^- \rightarrow H_2$) through p orbitals. In-situ Raman spectroscopy showed that the intensity of the S–H vibration peak (~2500 cm^{-1}) at the edge of the 1T phase was about 3 times stronger than that of the 2H phase at the potential of −0.2 V vs. RHE, confirming the more efficient adsorption/desorption capacity of hydrogen intermediates. This synergistic effect increases the intrinsic activity of the 1T-MoS_2 edge site by two orders of magnitude compared with the 2H phase, and the overpotential can be as low as 75 mV at a current density of 10 mA/cm^2 [97,101,102]. It is worth noting that the structural stability of the 1T phase has a dual regulatory effect on the edge activity. Transmission electron microscopy (TEM) showed that part of the octahedral structure would relax to the triangular prism structure during the electrochemical cycle, forming a local 1T′/2H mixed-phase interface. This phase transition-induced strain field (~3-5%) further activates the edge site to optimize hydrogen adsorption energy by modulating the Mo–S bond length (±0.05 Å) [103]. Theoretical simulations show that the moderate structural distortion can control the fluctuation range of ΔG_{H^*} within ±0.05 eV, ensuring the dynamic stability of catalytic activity. This finding provides a new research direction for the precise regulation of edge activity through controllable phase engineering.

2.2.3. Rationale for focusing on 2H and 1T phases

The selection of 2H and 1T phases for detailed discussion in this review is based on their predominant role in electrocatalytic HER applications [104]. These phases have been extensively studied due to their distinct electronic properties and catalytic activities. The 2H phase exhibits semiconducting behavior with high stability, while the 1T phase offers metallic conductivity and enhanced edge site activity [105]. In contrast, other phases such as 3R, T_1, and T_2 are less explored in HER research due to challenges in synthesis, stability, and limited catalytic performance data [106]. For instance, the 3R phase is naturally scarce and shows intermediate HER activity without significant advantages over 2H/1T systems, whereas T_1 and T_2 phases (e.g., 1T′) are metastable derivatives of 1T-MoS_2 with poor durability under operational conditions [107]. Thus, focusing on 2H and 1T phases aligns with the current understanding and practical relevance in optimizing MoS_2-based electrocatalysts.

3. Physico-chemical properties of MoS_2

3.1. Edge sites in MoS_2

The catalytic activity of molybdenum disulfide (MoS_2) is mainly due to the special atomic coordination environment and electronic structure characteristics of its edge site. Compared with the basal surface, the edge site has higher intrinsic catalytic activity, which is closely related to its unique electronic state distribution and adsorption energy regulation

[67,103,108].

3.1.1. Structural characteristics and coordination unsaturation of edge sites

There are two main types of edge structures in MoS_2: Mo-edge, which terminates with Mo atoms, and S-edges, which terminates with S atoms. High-resolution transmission electron microscopy (HRTEM) and scanning tunneling microscopy (STM) studies have shown that the typical coordination number of Mo-edge is 4 (compared to 6 coordination of basal Mo), forming a jagged structure covered by two sulfur trimers [109,110]. This coordination unsaturation results in a rearrangement of the d orbital electrons of the marginal Mo atoms, resulting in an unoccupied DMSO-d_6 orbital vacancy. X-ray absorption spectroscopy (XAS) of synchrotron radiation confirmed that the center of the d-band of Mo-edge shifted to the Fermi level by about 0.3 eV, which significantly enhanced its adsorption capacity for reaction intermediates [111].

3.1.2. Application of D-band center theory to active sites

Based on density functional theory (DFT) calculations, the catalytic activity of the Mo-edge is significantly correlated with the d-band center position of the Mo atom [14]. Hämmerli et al. found that when the d-band center of the Mo-edge moves up to −2.1 eV (relative to the Fermi level), its hydrogen adsorption free energy (ΔG_{H^*}) reaches an optimal value of −0.08 eV [112,113], which is close to the ideal value for the Pt (111) surface. This regulation is because the position of the center of the d-band directly affects the occupation of the anti-bond orbital: the upward shift of the d-band center leads to a stronger hybridization between the H 1s orbital and the Mo 4d orbital, but the excessive adsorption (>-1.8 eV in the center of the d-band) will reduce the catalytic efficiency due to the increase of the hydrogen desorption energy barrier. It is worth noting that the activity regulation of S-edge depends more on the p-orbital characteristics of sulfur vacancies, and its theoretical applicability of d-band needs to be modified in combination with the 3p orbital of sulfur [112–114].

3.1.3. Quantitative correlation between edge state density and hydrogen adsorption free energy

Projected density of states (PDOS) analysis shows that the conductive band density of states at the edge of the metallic 1T phase MoS_2 is 2 orders of magnitude higher than that of the semiconductor 2H phase near the Fermi level. This property significantly alters the electron transport path of hydrogen adsorption: the local density of states peaks at the edge of the 1T phase (in the range of −0.5 to 0.5 eV) forms a resonant tunneling effect with the H 1s orbital, reducing the ΔG_{H^*} by about 120 meV [115]. Specifically, when the dz^2 orbital density of states of the edge Mo has a characteristic peak at −0.2 eV, the corresponding ΔG_{H^*} reaches a minimum value of 0.06 eV, which can realize the directional modulation of the density of states by adjusting the stacking angle between the layers (15°-30°).

3.1.4. Mechanism of activity differentiation at the edge of crystal plane

The difference in activity at the edges of different crystal planes is due to the anisotropy of their electronic structures. First-principles calculations show that the activity of Mo-edge is about 3 orders of magnitude higher than that of S-edge, which is mainly attributed to: 1) the d-band width of Mo-edge (4.2 eV) is wider than that of S-edge (2.8 eV), which is conducive to electron delocalization; 2) The charge transfer ability of Mo-edge (Bader charge 0.32 e^-) was significantly better than that of S-edge (0.15 e^-). 3) The lattice strain caused by the long contraction of the edge Mo–S bond (2.31 Å vs 2.41 Å at the base) increases the orbital energy level of dz^2 by 0.15 eV [116].

3.2. Conductivity

The electrical conductivity of MoS_2 is an essential physical property in its electrocatalytic applications [84,117,118]. 2H–MoS_2, as a semiconductor, has a relatively low conductivity due to the low concentration of charge carriers (electrons and holes) due to its bandgap width [119]. However, the conductivity of MoS_2 can be significantly improved by introducing defects, doping, or forming metallic phases such as 1T-MoS_2 [33,120–122]. Due to its metallicity, electrons can move freely within the layer, resulting in a higher conductivity of 1T-MoS_2 [123–128]. The low intrinsic conductivity of 2H–MoS_2 directly limits electron transfer kinetics in the hydrogen evolution reaction (HER), leading to increased charge-transfer resistance (R_{ct}) and higher overpotentials, particularly at industrial current densities (>500 mA cm^{-2}) [129]. For instance, energy losses due to poor conductivity can reduce overall efficiency by 20–30% compared to metallic catalysts [130]. Moreover, conductivity degradation under long-term operation is often linked to electrochemical phase transitions (e.g., 1T to 2H) or oxidative processes at edge sites, which exacerbate performance decay [131]. These degradation mechanisms are critical to address for practical applications. The provided strategies demonstrate the enhanced catalytic performance of MoS_2-based composite catalysts, particularly MoS_2@nanoporous gold (NPG), for electrocatalysis of water splitting to produce hydrogen provides a schematic representation of the catalytic reaction, where water molecules (H_2O) are split into hydrogen (H_2) and oxygen at the catalyst surface (Fig. 2a-f) [84]. The layered structure of MoS_2, combined with the conductive gold substrate, facilitates this reaction by providing active edge sites for the hydrogen evolution reaction (HER) and ensuring efficient electron transport [119]. The polarization curves in Fig. 2b highlight the superior catalytic activity of MoS_2@NPG compared to annealed NPG and even approach the performance of platinum (Pt), a benchmark catalyst [84]. This improvement is attributed to the synergy between the high conductivity of the gold substrate and the catalytic activity of the MoS_2 layers [124,132].

In particular, MoS_2@NPG exhibits excellent catalytic activity in the electrocatalytic splitting of water to produce hydrogen. Fig. 2a vividly depicts the catalytic reaction mechanism: water molecules (H_2O) adsorb on the surface of the catalyst and dissociate into hydrogen (H_2) and oxygen at the active site [84]. Fig. 2b–c shows the polarization curves and the Tafel slopes of platinum, pure NPG, and MoS_2@NPG, respectively, and quantitatively compare their catalytic activity [84]. These graphs reveal the advantages of MoS_2@NPG catalysts in electrocatalytic water splitting for hydrogen production in all aspects [84]. These graphs reveal the advantages of MoS_2@NPG catalysts in electrocatalytic water splitting for hydrogen production in all aspects [83].

3.3. Chemical stability

The chemical stability of MoS_2 is the key to its long-term operation in the electrocatalytic hydrogen evolution reaction [71,133–135]. It is stable in most environments at room temperature and atmospheric pressure, and it is not easy to react with most chemicals [136,137]. This stability is mainly attributed to the strong covalent bonds within its S–Mo–S layer [138]. However, under practical HER conditions (e.g., high voltages, acidic/alkaline electrolytes, and dynamic current densities), MoS_2 faces significant electrochemical degradation challenges that can compromise its structural integrity and catalytic performance [139]. Key degradation mechanisms include: (i) *Oxidative dissolution of edge sites*: Sulfur atoms at Mo-edge or S-edge sites are susceptible to oxidation at potentials above 0 V vs. RHE [140], forming soluble sulfates (e.g., SO_4^{2-}) and creating vacancies that reduce active site density [141]. This process is accelerated by bubble-induced mechanical stress and electrolyte impurities. (ii) *Phase instability*: The metastable 1T phase tends to revert to the semiconducting 2H phase under electrochemical bias, leading to a drastic drop in conductivity and activity [142]. In-situ Raman studies confirm that this transition follows first-order kinetics, with rates increasing at elevated temperatures or high current densities [143]. (iii) *Interfacial corrosion*: In chloride-containing electrolytes (e.g., seawater), pitting corrosion occurs at defect sites, accelerating layer detachment [144]. These degradation pathways highlight the need for robust stability engineering to bridge the gap between laboratory

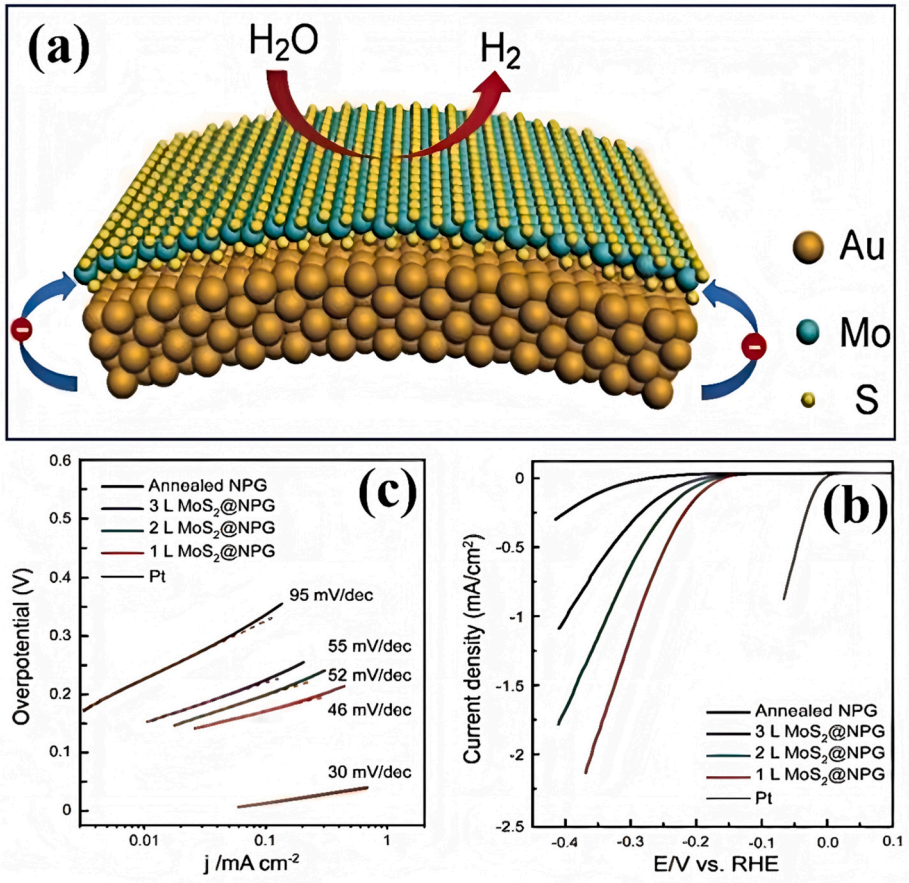


Fig. 2. (a) Schematic HER catalyzed by the monolayer MoS_2@nanoporous gold hybrid material [84]. (b) Polarization curves [84], and (c) corresponding Tafel slopes of pt, pure NPG, and MoS_2@nanoporous gold [84]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

performance and industrial application [145]. During HER process, catalysts such as MoS_2 are often exposed to extreme conditions, including high voltage and acidic or alkaline environments, which can significantly impact their stability [146,147].

Improving the chemical stability of MoS_2 has become a critical focus in current research. Strategies such as surface modification, the preparation of composite materials, or forming protective layers on the MoS_2 surface have been shown to effectively enhance the chemical stability of the catalyst during the catalytic process, thereby extending its service life [134,148–150]. For instance, nitrogen-doped carbon coatings on MoS_2 edges can suppress sulfur oxidation by acting as a physical barrier and electron donor, reducing vacancy formation Similarly, heterostructures with conductive substrates (e.g., graphene or carbon nanotubes) not only improve charge transfer but also mitigate phase transitions by providing epitaxial stabilization [151,152]. Optimizing synthesis conditions and post-processing methods has proven effective in producing MoS_2 catalysts with improved stability and performance [153,154]. For example, heterostructures like MoS_2/CoS_2 grown on carbon nanotubes [71] or integrating Pt atomic clusters with MoS_2 nanosheets and Co-doped carbon nanofibers [146] have enhanced catalytic efficiency and durability. Furthermore, advanced designs such as MoS_2 nanoflowers grown on plasma-induced W-anchored graphene have shown promise for stable hydrogen production in challenging environments like seawater electrolysis (Fig. 3a-c) [147]. Long-term stability tests (e.g., the 24-h chronoamperometry in Fig. 3b) demonstrate that such engineered catalysts maintain over 90% of initial activity by resisting electrochemical degradation, underscoring the effectiveness of these strategies [155].

In terms of improving the performance of hydrogen production by water electrolysis, researchers have made remarkable progress by carefully designing the material structure. For example, the growth of heterostructures such as MoS_2/CoS_2 on carbon nanotubes, or the integration of Pt clusters with MoS_2 nanosheets and cobalt-doped carbon nanofibers, are innovative structures that can effectively improve catalytic efficiency and durability. In addition, advanced designs, such as MoS_2 nanoflowers grown on plasma-induced W-anchored graphene, show great potential for stable hydrogen production, even in challenging environments such as seawater electrolysis. Fig. 3a shows the LSV curve and the corresponding Tafel slope plot, indicating that the material has excellent electrocatalytic activity [147]. Fig. 3b displays the I-t curve recorded over 24 h, reflecting the stability of the material over a long period of time [147]. In a mixed electrolyte of 0.5 M H_2SO_4 and natural seawater, the catalyst was held at −0.086 V vs. RHE (corresponding to 10 mA cm^{-2}) for 24 h chronoamperometric testing. The current density remained steadily around 10 mA cm^{-2}, retaining ≥9 mA cm^{-2} (>90 % of its initial activity) after 24 h with no discernible decay; fluctuations were < ±3 %. These results demonstrate that the MoS_2/W-graphene nanoflower architecture exhibits exceptional electrochemical stability for hydrogen evolution in the harsh seawater environment. Fig. 3c illustrates the Faraday efficiency achieved in use, further demonstrating its high efficiency in real-world applications [147].

Fig. 3d presents a volcano plot that relates the exchange current density (j_0) with the free energy change (ΔG_{H^*}) for hydrogen adsorption on various catalysts [156]. This plot is instrumental in identifying the optimal catalysts for HER, as it shows the relationship between the thermodynamic barrier for hydrogen adsorption and the catalytic activity. Catalysts like Pt and Ir exhibit high activity due to their low ΔG_{H^*}

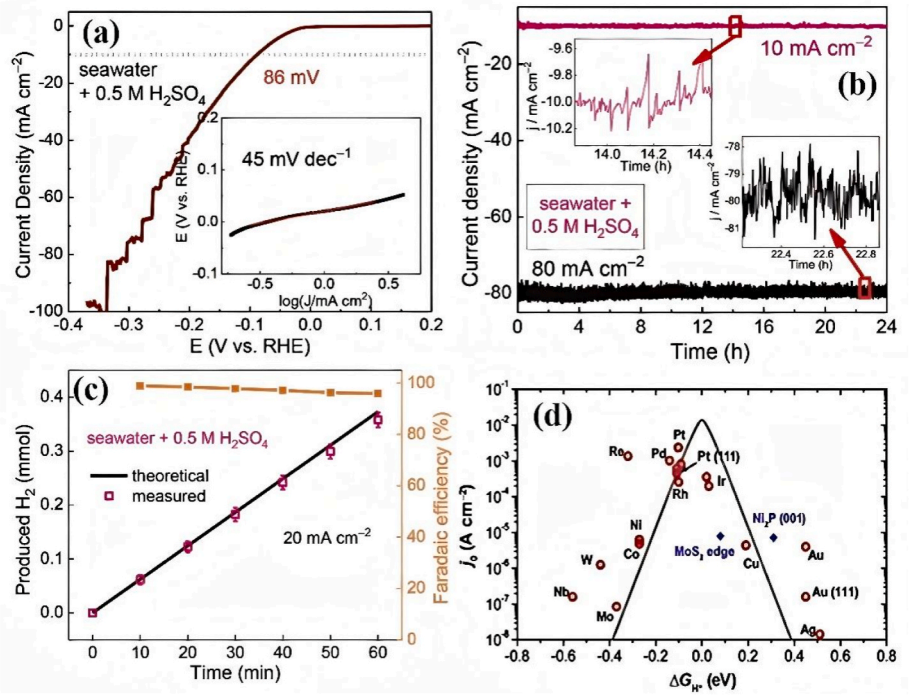


Fig. 3. (a) LSV and corresponding Tafel slope plots, (b) 24 h chronoamperometric curve recorded at −0.086 V vs. RHE (10 mA cm^{-2}) in 0.5 M H_2SO_4 + natural seawater. The time-dependent current density remained unchanged at both 10 and 80 mA cm^{-2} in the selected section of the illustration. (c) Faradaic efficiencies obtained when using [147]. (d) The activity of the electrocatalysts towards HER has a volcano plot relationship with the free energy change of adsorbed atomic hydrogen [156].

values but are also more expensive and less abundant. MoS_2 and its derivatives, on the other hand, offer a balance between activity and stability under harsh conditions, making them promising candidates for large-scale applications. However, achieving long-term stability requires addressing electrochemical degradation head-on [157]. By integrating degradation-resistant designs (e.g., edge passivation, phase stabilization) with activity optimization, MoS_2-based catalysts can overcome durability bottlenecks [158]. These efforts underscore the importance of conductivity and chemical stability in determining the performance of MoS_2 in HER. Through the continuous optimization of these strategies, the catalytic performance of MoS_2 can be further enhanced (Fig. 3d) [156], paving the way for its broader application in the field of hydrogen energy [14,71,159–161].

4. Catalytic activity of MoS_2 at its edge sites, stripping, and basal planes

4.1. Edge sites

The edge site is a key region where MoS_2 exhibits high catalytic activity in electrocatalytic hydrogen evolution (HER). Compared with the basal plane, the edge site can provide better hydrogen adsorption-free energy (ΔG_{H^*}) due to its coordination unsaturation characteristics and unique electronic structure, thereby significantly improving the catalytic performance. The geometry and local electronic states of edge sites have an important impact on their catalytic activity, especially the edge step sites, and edge curvature effects (such as nanocoiled structures) have shown unique advantages in regulating HER performance. This section will focus on these new findings and the mechanisms by which they affect catalytic performance.

4.1.1. Special catalytic activity of edge step sites

Edge step sites refer to step-like structures formed at the edge of MoS_2 crystals due to irregular growth or defects, and these step sites usually have higher coordination unsaturation and stronger local electron rearrangement capabilities (Fig. 4a and b) [162]. Specifically, due to the irregularity of the atomic arrangement, the coordination environment of some atoms at these sites is changed, and their coordination unsaturation is higher than that of the conventional sites inside the crystal, which makes the electron cloud distribution of the edge ladder sites more likely to change, and can show stronger local electron rearrangement ability in the process of chemical reactions. Fig. 4a and b shows SEM images of edge step sites in MoS_2 crystals, from which these special step-like structures can be observed, providing an intuitive visual basis for further research and application [162].

Compared with the conventional Mo-edge and S-edge, the edge step site can provide more active sites, and its electronic structure is more conducive to the adsorption and dissociation of hydrogen molecules. Step sites typically have higher surface energies due to their geometric irregularities, which makes it easier to adsorb reactant molecules (e.g., H^+). Further, coordination unsaturation of the step site leads to a shift in the center of the d-band, which optimizes the hydrogen adsorption free energy (ΔG_{H^*}). In addition, Mo and S atoms near the step site may form a synergistic effect, further enhancing the kinetic performance of HER. Through experimental and theoretical calculations, it has been confirmed that the energy barrier of hydrogen adsorption and desorption process is significantly reduced at the step site [163]. For example, atomic force microscopy (AFM) and scanning tunneling microscopy (STM) characterization showed that the local current density at the step site was much higher than that at the common edge site [164]. In addition, the formation of step sites can also be achieved by introducing specific defect engineering, such as ion bombardment or plasma treatment, to further improve the catalytic performance of MoS_2.

4.1.2. Edge curvature effect or nanocoil structure

The edge curvature effect refers to the change in the electronic structure and geometry of the edge due to the bending or curling of the MoS_2 crystal [165]. In recent years, the catalytic activity of edge sites has been significantly enhanced by designing MoS_2 with a nanocoiled structure. This enhancement is mainly attributed to stress-induced

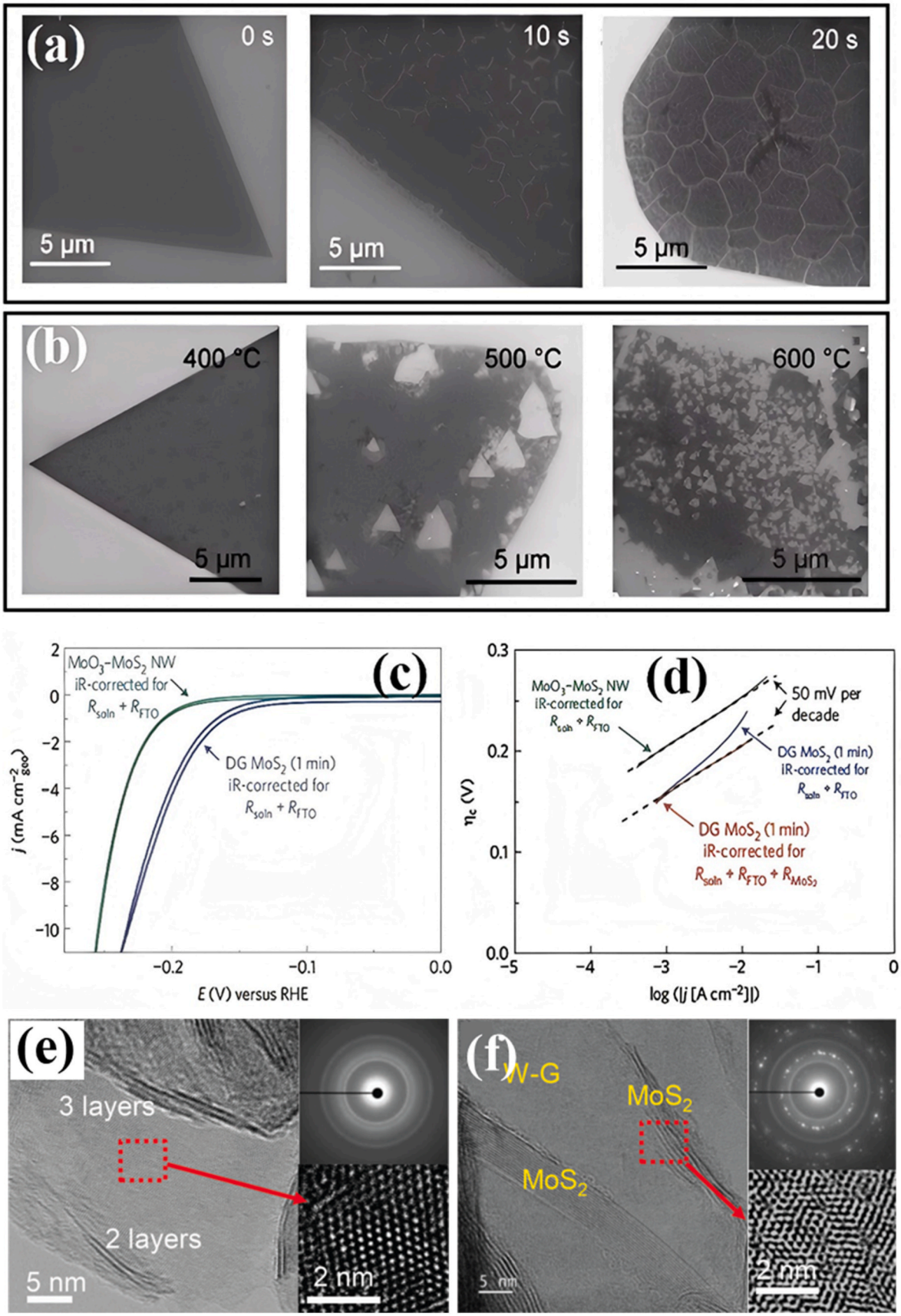


Fig. 4. (a-b) SEM images [162], (c) cyclic voltammogram of DG MoS_2 (1 min sample) versus core-shell MoO_3 -MoS_2 nanowires (NW) at 5 mV s^{-1} [163]. (d) Tafel plot of DG MoS_2 (1 min sample) versus core-shell MoO_3–MoS_2 NW [163]. (e) TEM, and (f) HRTEM images of the MoS_2@W-G composite (insets to (f): SAED pattern and higher-magnification image) [147].

regulation of electronic states. In nanocoiled structures, the bond length and bond angle between Mo and S atoms change due to the presence of curvature, resulting in the rearrangement of local electronic states. Theoretical calculations show that the crimped structure can effectively regulate the center position of the d-band at the edge site, making it closer to the ideal state of HER [165]. Further, the formation of curly structures significantly increases the exposure density of edge sites. The curly structure has a longer edge length as compared to the planar structure, thus providing more active sites. Enhancement of geometric effects: Regions of high curvature in the crimped structure generally have higher surface energy, which makes it easier for hydrogen molecules to adsorb in these regions. In addition, the curvature effect may also induce an enhancement of the local electric field, thereby accelerating the charge transfer process [166]. In experimental studies, MoS_2 nanosheets or nanotubes with curly edges can be fabricated by manipulating the synthesis conditions (e.g., atmosphere and temperature in CVD). These crimped structures exhibit lower overpotentials and higher current densities in the HER test. For example, the HER performance of MoS_2 nanotubes prepared by template-assisted method in acidic electrolytes is significantly better than that of traditional planar MoS_2 films (Fig. 4c and d) [163]. As shown in Fig. 4c, the cyclic voltammetry of DG MoS_2 (1 min sample) and core-shell MoO_3–MoS_2 nanowires (NW) at a sweep velocity of 5 mV s^{-1} shows that DG MoS_2 has superior electrochemical activity [163]. The Tafel diagram in Fig. 4d further confirms that the hydrogen evolution kinetics of DG MoS_2 are more efficient [163]. This performance improvement is mainly attributed to the fact that the nanotube structure can effectively increase the exposure of active sites and optimize the electron transport pathway, thereby improving its electrocatalytic hydrogen evolution ability under acidic conditions. Furthermore, high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images provide direct visualization of the curvature or crimped structures of MoS_2, offering stronger experimental evidence for the edge curvature effect. The HRTEM image in Fig. 4e confirms the presence of single-layer to few-layer MoS_2 with clearly active edge sites. The corresponding selected-area electron diffraction (SAED) pattern (upper inset to Fig. 4e) demonstrates that the basal plane of the MoS_2 nanoflower was the (001) plane. In addition, the nearest Mo–Mo distance in the trigonal lattice region was ≈0.27 nm, corresponding to the (100) plane of 1T-MoS_2, while the lattice spacing of ≈0.27 nm in the hexagonal lattice region corresponded to the (010) and (100) planes of 2H–MoS_2 (higher-magnification view in the lower inset to Fig. 4e). The STEM image in Fig. 4f indicates the edge structure of MoS_2 in the hybrid MoS_2@W-G catalyst. The upper inset to Fig. 4f reveals that the corresponding SAED rings arose from the stacking of MoS_2, W, and G with different crystallographic orientations [147]; they were composed of four diffraction rings of pure MoS_2 mixed with a multiphase crystalline structure for W-G. In the lower inset to Fig. 4f, a slight change in the d-spacing of the (002) plane of MoS_2 in the hybrid is observed, possibly due to compression of the in situ–grown stacked MoS_2 nanoflowers and W-G nanosheets. These structural insights corroborate the nanoscale bending and coiling discussed above, highlighting how curvature optimizes edge site activity.

4.2. Stripping

Stripping or exfoliation technology is one of the important methods for the preparation of high-quality MoS_2 nanomaterials, especially in obtaining single or few-layer MoS_2. Through the stripping technology, the interlayer stacking can be effectively reduced, the exposure density of the edge site can be significantly increased, and the electron transport performance can be optimized, so as to improve its catalytic activity in the electrocatalytic HER. However, the problems involved in the stripping process, such as layer control, defect introduction, yield improvement, and large-scale preparation, are still the focus of current research. This section discusses the main approaches to stripping, its benefits, and the challenges it faces.

(1) Mechanical stripping

Mechanical stripping was one of the earliest methods used to prepare monolayer MoS_2, usually by tape or other mechanical force to strip bulk MoS_2 into a monolayer or few-layer structure. This method has the advantage of being simple to operate, does not require chemical reagents, and results in high-quality monolayer MoS_2 with little to no additional defects introduced into the material. However, the yield of mechanical stripping is extremely low, making it difficult to meet the needs of large-scale preparation. In addition, precise control of the number of layers during the peeling process is difficult, and the resulting material is often small in size, limiting its application in practical catalysis [167,168].

(2) Liquid-phase stripping

Liquid-phase stripping is a widely used technique for the preparation of MoS_2, in which bulk MoS_2 is dispersed in a solvent with ultrasonic-assisted assistance to achieve the exfoliation of monolayer or few-layer structures. Commonly used solvents include N-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), and surfactant solutions [169]. Liquid phase stripping has the advantages of simple operation, low cost, and can achieve a certain degree of layer control. In addition, this method is suitable for large-scale preparation and has high practical application potential. However, ultrasound during liquid-phase exfoliation may introduce structural defects, which may affect the electronic structure and catalytic performance of the material [170]. In addition, the peeling efficiency and yield still need to be further improved, and a more environmentally friendly solvent system needs to be developed.

(3) Chemical peeling

Chemical peeling involves the introduction of intercalation agents (such as lithium ions, sodium ions, etc.) [171] into the interlayer of MoS_2 through a chemical reaction, thereby weakening the van der Waals force between the layers and achieving the peeling of single or few layers. For example, the lithium-ion intercalation method can be used to efficiently peel off MoS_2 and obtain the metallic structure of the 1T phase, thereby significantly improving its HER performance. However, the chemical stripping process often requires the use of strong reducing agents (such as n-butyllithium), which can bring environmental pollution and safety hazards. In addition, the intercalation of lithium ions may lead to lattice distortion and defect introduction of materials, affecting their structural stability and long-term catalytic performance. Therefore, how to optimize the chemical peeling process to reduce defect introduction while improving yield and environmental friendliness is the focus of current research [172].

(4) Electrochemical stripping

Electrochemical exfoliation is an emerging stripping technique that achieves interlayer stripping by introducing ions or gas molecules between MoS_2 layers through an electrochemical reaction. This method has the advantages of simple operation, environmental friendliness, and less defect introduction. For example, by electrochemical intercalation of hydrogen or oxygen, MoS_2 can be efficiently stripped and its original crystalline structure can be maintained. In addition, parameters during electrochemical stripping (e.g., voltage, electrolyte type, etc.) can be precisely manipulated to optimize the number of layers and edge sites. However, the efficiency and scale of electrochemical stripping still need to be further improved [173].

(5) Hot peeling

Thermal peeling enables interlaminar peeling of MoS_2 by introducing thermal stress or gas expansion through high-temperature treatment. The introduction of gas molecules (e.g., nitrogen, hydrogen) into the MoS_2 layer by high-temperature treatment can effectively peel off a single or few-layer structure. For example, thermal annealing results in layer-by-layer thinning of MoS_2 flakes, leading to a monolayer structure. During this process, the upper layer is gradually peeled off due to sublimation, and the optical contrast, Raman spectroscopy, and atomic force microscopy (AFM) characterization reveals that the crystal quality and surface roughness are less changed [171, 174]. Thermal peeling has the advantages of simple equipment and convenient operation, but high-temperature treatment may lead to lattice distortion or passivation of edge sites of the material, thus affecting its catalytic performance. In addition, the accuracy of layer control for hot peeling is low, making it difficult to meet the demand for high-quality MoS_2 [175].

(6) Comprehensive comparison of stripping technologies

Different stripping techniques have their advantages and disadvantages in terms of operational complexity, yield, layer control, and defect introduction. Mechanical exfoliation is suitable for the preparation of high-quality monolayer MoS_2, but the yield is extremely low; Liquid phase stripping has high practical application potential, but the solvent

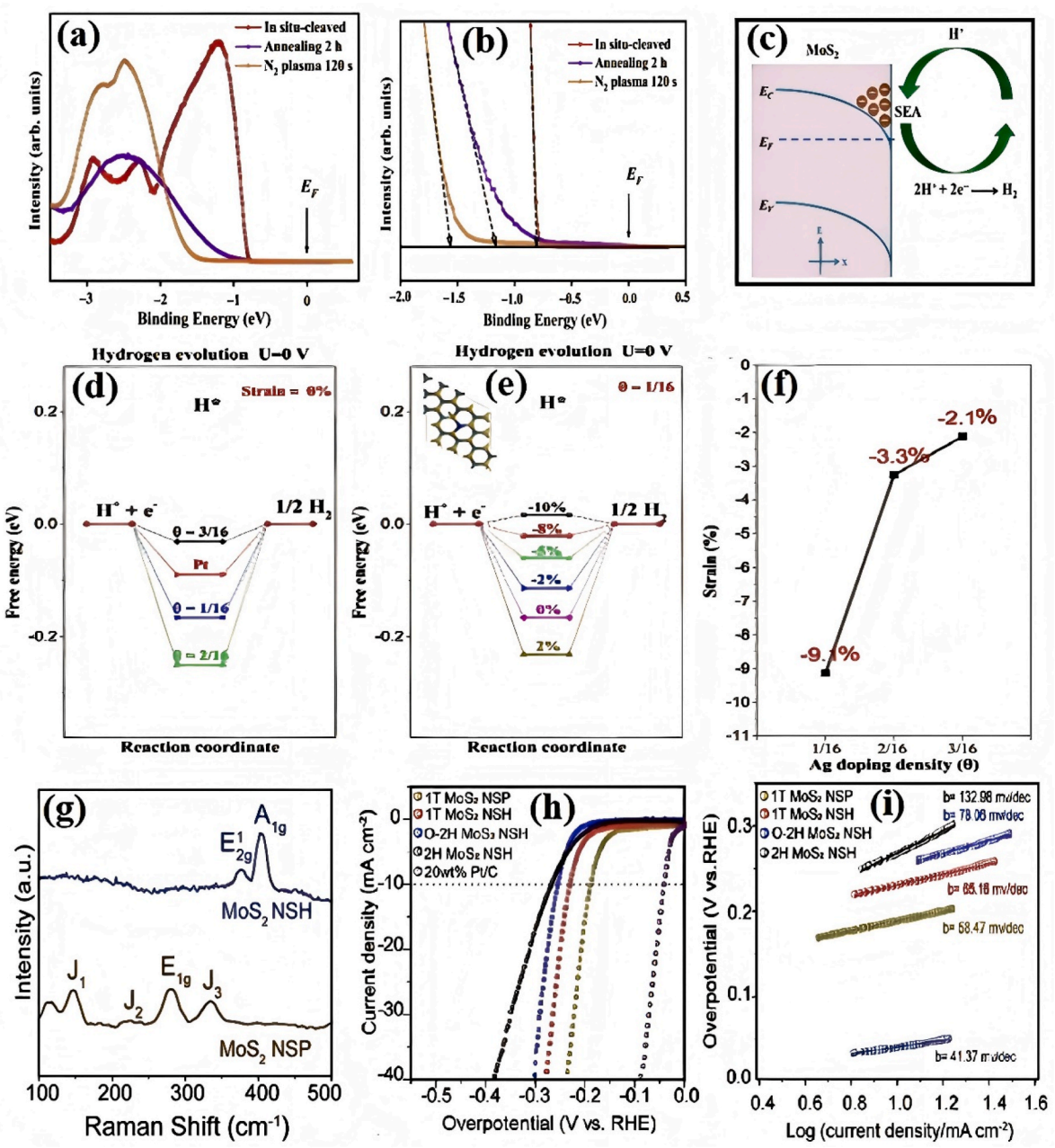


Fig. 5. (a) The normal emission spectra [178], and (b) magnified normal emission spectra of in situ-cleaved, annealed for 2 h, and N_2-plasma-treated for 120 s MoS_2 surfaces [178]. (c) Schematic diagram of SEA and its effect on HER in MoS_2. Surface band bending and SEA are produced by the donor-like surface states [178]. (d) Free energy at Ag doping density from $\theta = 1/16$ to $\theta = 3/16$ [180]. (e) Free-energy diagram for hydrogen evolution on Ag-doped MoS_2 ($\theta = 1/16$) under different strains [180]. (f) Strains required to optimize the hydrogen binding free energy (ΔG_{H^*} 0) on MoS_2 to zero at different Ag-doping densities [180]. (g) Raman spectra of the 1T MoS_2 NSP and 2H MoS_2 NSH [187]. (h) Polarization curves [187], and (i) corresponding Tafel slopes of 1T MoS_2 NSP, 1T MoS_2 NSH, O–2H MoS_2 NSH, and 2H MoS_2 NSH in 0.5 M H_2SO_4 [187].

system needs to be optimized to improve efficiency and environmental protection. Chemical exfoliation can obtain 1T phase MoS_2 but may introduce more defects. Electrochemical and thermal stripping have certain advantages in terms of environmental friendliness and large-scale preparation, but the process needs to be further optimized to improve material quality and yield. Therefore, future research should combine the advantages of multiple stripping technologies to develop efficient, green, and controllable stripping methods.

(7) Challenges and prospects of stripping technology

Although stripping technology has made significant progress in the preparation of MoS_2, there are still many challenges. Achieving precise control of the number of layers in the peeling process while avoiding excessive introduction of defects is a difficult point in current research. In addition, the efficiency and yield of the stripping technology still need to be further improved to meet the needs of large-scale preparation. Future research should focus on the following directions: developing green stripping methods to reduce environmental impact; combined with advanced characterization techniques, the structural evolution mechanism in the peeling process can be deeply understood; through multi-technology collaborative optimization, the precise control of the number of MoS_2 layers, edge sites, and crystalline phases can be realized. These efforts are expected to promote the wide application of stripping technology in the preparation of efficient and stable MoS_2-based HER catalysts [125,176,177].

4.3. Basal plane

Although the edge site of MoS_2 has attracted much attention in HER due to its high catalytic activity, the low intrinsic activity of its basal surface seriously limits the improvement of the overall catalytic performance. The base surface of MoS_2 occupies most of the surface area of the material, and activating the base surface and making full use of its potential catalytic ability is an important research direction in the overall catalytic performance of MoS_2. In this section, strategies have been discussed for improving the catalytic activity of the basal plane, including the regulation of the electronic structure of the basal plane, the introduction of defects, doping modification, and functionalization (Fig. 5a-c) [178].

Fig. 5a shows the magnified normal emission spectra of MoS_2 surfaces after in-situ cutting and annealing for 2 h, while Fig. 5b displays the magnified normal emission spectra of MoS_2 surfaces treated with N_2 plasma for 120 s [178]. From these two figures, the effect of different treatments on the surface properties of MoS_2 can be observed. Further, Fig. 5c provides a schematic diagram of sulfur-evaporation-assisted activation (SEA) in MoS_2 and illustrates its mechanism of action on HER (Hydrogen Evolutionary Reaction) [178]. Studies have shown that surface bending and SEA generation result from donor-like surface states, which are important for improving catalytic activity.

(1) Regulation of the electronic structure of the basal plane

The intrinsic activity of the MoS_2 substrate is low, mainly due to the deviation of its hydrogen adsorption free energy (ΔG_H) from the zero point, resulting in the kinetic limitation of hydrogen adsorption and desorption processes. By manipulating the electronic structure of the substrate, the ΔG_H can be effectively optimized, thereby improving the catalytic activity of the substrate. For example, by introducing stresses or strains, the electronic state distribution of the MoS_2 base can be changed, and its catalytic performance can be adjusted [178–180]. In addition, theoretical calculations show that the base surface of the 1T phase MoS_2 has higher metallicity and a closer to zero ΔG_H, so the partial conversion of the 2H phase to the 1T phase through phase engineering is an effective strategy to activate the catalytic property of the substrate [181]. However, the 1T phase has poor thermodynamic stability and is prone to phase transition, which poses a challenge for practical applications (Fig. 5d-f) [180].

Fig. 5d shows the change in free energy of the Ag doping density from $\theta = 1/16$ to $\theta = 3/16$, indicating that the change in doping density affects the stability of the system [180]. Fig. 5e demonstrates the free energy of hydrogen evolution in Ag-doped with MoS_2 ($\theta = 1/16$) under different strains, revealing the regulatory effect of strain on strain energy [180]. Fig. 5f further depicts the strain required to optimize the hydrogen-binding free energy (ΔGH^*) on MoS_2 to zero at different Ag doping densities, which provides key information for manipulating doping and strain to improve material stability and catalytic performance [180].

(2) Defect introduction

Defect engineering is another important strategy to activate the catalytic activity of the MoS_2 substrate. By introducing sulfur vacancies, Mo vacancies, or other structural defects on the basal surface, the chemical inertness of the basal surface can be effectively broken and a new active site can be formed. For example, the introduction of sulfur vacancies can alter the electronic state distribution of the substrate to achieve better HER performance, Bringing the ΔG_H^+ (free energy of hydrogen adsorption) of the substrate surface close to zero [182,183]. In addition, the introduction of defects can also promote the interfacial reaction between the substrate and the electrolyte. However, high defect concentrations can lead to a decrease in the structural integrity of the material and even lead to catalyst deactivation. Studies have shown that the sulfur vacancy concentration needs to be controlled within a reasonable range. Theoretical calculations indicate that a 12.5% sulfur vacancy concentration can reduce ΔG_H^+ to 0.02 eV, which is close to the ideal value. In this case, the vacancy distribution is dominated by discrete forms to avoid the aggregation-induced localization of electronic states. At low concentrations (e.g., $<$12.5%), the sulfur vacancies tend to aggregate to form chain-like structures, leading to a decrease in the energy gap and overly strong Mo–H adsorption, which is rather unfavorable for hydrogen desorption. Excessive defects (e.g., $>$12.5%) can destroy the structural integrity of MoS_2 and trigger catalyst deactivation. For example, excessive vacancy density may lead to substrate collapse or decreased electrical conductivity [183–186]. Therefore, achieving precise control of concentration and distribution in the process of defect introduction is an important research direction.

(3) Doping modification

By doping heteroatoms (such as metal or non-metal elements) on the MoS_2 base plane, its electronic structure can be effectively manipulated and the catalytic activity can be enhanced. For example, doped transition metals (e.g., Ni, Co, Fe) can introduce additional electronic states to optimize the ΔG_H of the base surface. The doping of non-metallic elements (such as N, P, O) can change the chemical environment of the substrate and enhance its interaction with intermediates. In addition, doping may also cause local lattice distortion on the substrate, which further improves the catalytic performance. However, inhomogeneities or side phases may be introduced during the doping process, which poses a challenge to the stability and reproducibility of the material (Fig. 5g–5i) [187].

To visualize this and the corresponding performance, Fig. 5g shows the Raman spectra of 1T MoS_2 NSP and 2H MoS_2 NSH [187]; Fig. 5h displays the polarization curves of 1T MoS_2 NSP, 1T MoS_2 NSH, O–2H MoS_2 NSH, and 2H MoS_2 NSH at 0.5 M H_2SO_4 [187]. Fig. 5i shows the Tafel slope for each of these materials [187]. Overall, this set of charts provides a clear understanding of the multifaceted impact of the factors introduced into the doping process on the performance of the material, and then the reasons behind the challenges to the stability and repeatability of the material.

(4) Functional modification

Functionalization is another effective strategy to improve the catalytic activity of MoS_2 basal surface. For example, by modifying organic molecules, metal nanoparticles, or other functional materials on the basal surface, additional active sites can be introduced or electron transport properties can be enhanced. In addition, the functionalization can also improve the hydrophilicity of the substrate, thereby improving the permeability and interfacial reaction efficiency of the electrolyte [188]. For example, studies have shown that Pt nanoparticles can be significantly improved by modifying them on the MoS_2 substrate. However, interfacial instability or material agglomeration may be triggered during functionalization, which poses a challenge to the long-term stability of catalysts.

(5) Synergistic effect between the base surface and the edge

Although the intrinsic activity of the basal surface is low, there may be a synergistic effect with marginal sites. For example, the basal surface can serve as a channel for electron transport, providing electronic support for edge sites [189]. At the same time, the interface region between the basal surface and the edge may form new active sites, thereby improving the overall catalytic performance. Therefore, a complete use of the synergistic effect between the basal surface and the edge in material design is an important research direction to improve the catalytic performance of MoS_2 [103].

(6) Challenges and prospects of basal surface activation

Although a variety of strategies have been used to activate the MoS_2 base, there are still many challenges. For example, maintaining the structural stability and conductivity of materials while activating the substrate is a difficult point in current research. In addition, defects or uneven distribution of doped atoms that may be introduced during basal surface activation may lead to instability in catalytic performance. Future research should focus on the development of precise basal surface manipulation techniques to achieve precise control of electronic structure, defects, and doping. Combined with theoretical calculations and advanced characterization techniques, the microscopic mechanism of basal surface activation can be understood.

5. Challenges of MoS_2 in electrocatalytic hydrogen evolution

MoS_2 is considered a promising catalyst for electrocatalytic HER, but it still faces a series of challenges in practical applications [50,190]. These challenges mainly involve the number and accessibility of the active sites [14,191–193], conductivity [14,194,195], defect control [196,197], stability [198,199], and large-scale synthesis [55,200,201]. In particular, the number and accessibility of active sites directly affect their catalytic efficiency [202,203].

5.1. Reaction mechanism of MoS_2 in electrocatalytic hydrogen evolution

The reaction mechanism of MoS_2 in HER involves the following main aspects.

5.1.1. Edge- or vacancy-deficient sites of MoS_2 for active sites of HER

In the electrocatalytic hydrogen evolution reaction based on MoS_2, edge or vacancy sites are widely considered the main active sites. The high catalytic activity of these sites is attributed to their unique electronic structure and chemical properties. Compared to the basal plane of MoS_2, edge or vacancy sites can significantly reduce the hydrogen adsorption free energy (ΔG_{H^*}), thereby promoting the HER reaction [204].

(1) Structural characteristics and activity of edge deficient sites

The edge sites of MoS_2 are divided into two types: Mo edge (molybdenum edge) and S-edge (sulfur edge) [205]. These edge sites, due to coordination unsaturation, have high chemical activity and are the main active regions for HER reactions. Due to the lack of sufficient sulfur atom coordination, molybdenum atoms on Mo edge exhibit strong electron affinity and can effectively adsorb hydrogen atoms (H*), thereby promoting the first step of HER reaction ($H^+ + e^- \rightarrow H^*$). The sulfur atoms on the S-edge can also provide suitable adsorption sites and participate in HER reactions due to coordination unsaturation. Theoretical calculations and experimental studies have shown that the activity of Mo edge and S-edge depends on their electronic state distribution and hydrogen adsorption free energy (ΔG_{H^*}). Among them, the sites with ΔG_{H^*} close to zero are considered the optimal catalytic active sites. In contrast, the basal plane of MoS_2 exhibits lower chemical activity due to the complete filling of d-electrons, making it difficult to effectively adsorb hydrogen atoms [179,206].

(2) Formation and activity of vacant sites

In addition to edge deficient sites, vacancies in MoS_2 are also considered important HER active sites. Vacancy defects mainly include sulfur vacancies (S-vacancies) and molybdenum vacancies (Mo-vacancies), among which sulfur vacancies are the most widely studied. The formation of sulfur vacancies leads to changes in the local electronic structure, exposing surrounding molybdenum atoms and increasing their electron density, thereby enhancing the adsorption capacity of hydrogen atoms. The presence of sulfur vacancies can effectively reduce ΔG_{H^*}, thereby enhancing HER activity [204,207]. The formation of molybdenum vacancies can significantly alter the local crystal structure and electronic state distribution, but their contribution to HER activity is usually small, mainly because molybdenum vacancies may disrupt the overall structural stability of MoS_2 [204]. By introducing an appropriate amount of vacancy defects, the HER performance of MoS_2 can be significantly improved. However, excessive vacancies may lead to structural collapse or excessive localization of electronic states in the material and reduce catalytic activity. Therefore, the concentration of vacancies needs to be precisely controlled.

(3) Synergistic effect of missing edge sites and vacant sites

The synergistic effect of missing edge sites and vacancy defects can further improve the HER performance of MoS_2. For example, sulfur vacancies at the edge site can enhance the electron density distribution at the edge, thereby optimizing hydrogen adsorption-free energy. In addition, the combination of missing sites and vacancy defects can provide more uncoordinated atoms and active centers, significantly increasing the active site density of the catalyst [207,208].

(4) Characterization of missing edge sites and vacant sites

To study the formation of missing margins and vacant sites and their effects on HER activity, researchers have used a variety of characterization methods. High-resolution transmission electron microscopy (HRTEM) gives direct observation of the edge structure of MoS_2 and the distribution of vacancy defects. Scanning tunneling microscopy (STM) reveals local structural features of missing edges and vacancies through atomic-resolution imaging. Electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) are used to detect the presence of sulfur vacancies and their changes in electronic state. Whereas, Raman spectroscopy indirectly characterizes the density of edge-missing sites through the change of edge characteristic peaks.

(5) Regulation strategies for missing edges and vacant sites

In order to maximize the exposure density of missing edge and vacant sites, a series of regulatory strategies have been proposed. Plasma

etching selectively removes sulfur atoms by plasma treatment, forming sulfur vacancies and increasing edge exposure. Chemical etching by chemical reagents (such as H_2O_2 or $NaBH_4$) to accurately regulate the formation of missing edges and vacancies of etched MoS_2. Through electrochemical cycling, more defect sites are induced to form on the surface of MoS_2. Further, by introducing heterogeneous atoms (such as Ni, Co, or N), the electronic structure of missing edges and vacant positions is regulated to enhance HER activity [167,209].

(6) Limitations of missing edges and vacant sites

Although missing edges and vacant sites can significantly increase the HER activity of MoS_2, they also have certain limitations. The formation of missing edges and vacancies can lead to a decrease in the structural stability of the material, especially under conditions of long operation or high current density. Excessive defects may cause overlocalization of the electronic state, resulting in a decrease in catalytic activity. The formation of missing edges and vacancies is usually random, and it is difficult to achieve precise control at the atomic level. Missing edges and vacancy sites are the main sources of MoS_2 HER activity, and its high catalytic activity is due to the coordination of unsaturated atoms and optimized hydrogen adsorption-free energy. However, future research needs to further develop precise defect control technology and solve the stability problem caused by defects, so as to provide new ideas for the design of efficient and stable MoS_2-based HER catalysts.

(7) Influence of Pore Size Distribution on Edge Site Accessibility and Hydrogen Adsorption Free Energy

The pore size distribution in MoS_2-based catalysts plays a critical role in modulating the hydrogen adsorption free energy (ΔG_H) and HER activity by affecting both the mass transport efficiency and the electronic structure of edge sites [38]. An optimized pore size distribution enhances the accessibility of edge sites by providing interconnected channels for reactant (H^+) diffusion and product (H_2) desorption, thereby reducing diffusion limitations and improving the kinetics of HER [210]. This geometric effect ensures efficient utilization of active sites, particularly at high current densities [211]. Moreover, the local curvature and strain induced by porous structures can tailor the electronic properties of MoS_2, such as shifting the d-band center position, which optimizes ΔG_H to values closer to zero (ideal for HER) [212]. For instance, controlled porosity can introduce tensile strain that adjusts the Mo–S bond lengths and enhances the metallicity of edge sites, further facilitating hydrogen adsorption and desorption processes [52]. Thus, pore size distribution serves as a key engineering parameter to synergistically improve both the thermodynamic (ΔG_H) and kinetic aspects of HER on MoS_2 catalysts.

However, the current understanding of MoS_2 edge and vacancy sites remains subject to significant limitations [213]. Theoretical models, such as d-band center theory, often rely on idealized structures and overlook dynamic factors like surface reconstruction or adsorbate coverage under operational conditions [214]. For instance, reported ΔG_H values for edge sites vary widely (e.g., −0.08 eV to −0.25 eV in literature), highlighting discrepancies between theoretical predictions and experimental measurements [215]. Moreover, vacancy engineering faces challenges in precise control of concentration and distribution [213]; excessive vacancies may lead to structural instability or catalytic degradation. The microscopic mechanisms underlying synergistic effects are not fully elucidated, necessitating in-situ studies to unravel site behaviors under dynamic reaction environments [216]. Future research should focus on atomic-level precision control strategies to address the trade-off between stability and activity.

5.1.2. The electronic structure of MoS_2 in HER

The electronic structure of molybdenum disulfide largely determines its catalytic performance in electrocatalytic HER. Its unique layered structure and electronic state distribution make MoS_2 exhibit significant catalytic activity differences in different crystal phases, crystal planes, and defect states. A better understanding of the electronic structure properties of MoS_2 and its impact on HER performance is essential to optimize its catalytic performance and design efficient catalysts.

(1) Crystalline phase and electronic structure of MoS_2

The main crystalline phases of MoS_2, semiconductor 2H phase, and metallic 1T phase possess significantly different electronic structures, which directly affects their catalytic performance. 2H– MoS_2 is an indirect bandgap semiconductor with a bulk bandgap of about 1.2 eV and a monolayer bandgap of about 1.8 eV. Due to its complete filling of d electrons, the base surface of the 2H phase exhibits low chemical activity, making it difficult to effectively adsorb hydrogen atoms (H*) [172,217]. However, the edge sites of the 2H phase, such as Mo-edge and S-edge, have uncoordinated atoms that provide high catalytic activity. Overall, the catalytic performance of the 2H phase mainly depends on the exposure density and electronic state distribution of the edge site.

On the other hand, 1T- MoS_2 is a metallic crystalline phase with partially filled d-electrons in the conduction band, exhibiting high conductivity and metallicity. Compared with the 2H phase, the base surface of the 1T phase has a higher electron density and a more suitable hydrogen adsorption free energy (ΔG_{H^*}), thus exhibiting significant intrinsic catalytic activity. In addition, the edge site of the 1T phase further enhances the kinetics of the HER reaction due to its metallic electronic structure. Converting the 2H phase to the 1T phase by chemical or physical methods (e.g., lithium intercalation, ion doping, etc.) can significantly increase the conductivity and basal activity of MoS_2, thereby improving its HER performance [217].

(2) D-band center theory and electronic state regulation

The catalytic performance of MoS_2 is closely related to the center position of its d-band. According to the d-band center theory, the shift of the d-band center position of the catalyst relative to the Fermi level affects the interaction strength of the adsorbate (e.g., H*) with the catalyst surface, thus determining the catalytic activity. In MoS_2, the d-band center of edge sites (e.g., Mo-edge and S-edge) is usually closer to the Fermi level, exhibiting strong metallicity and high catalytic activity. In contrast, the center of the D-band of the basal surface is farther away, resulting in weak adsorption capacity and low catalytic activity. An ideal HER catalyst should have near-zero hydrogen adsorption-free energy ($\Delta G_H \approx 0$) to balance the hydrogen adsorption and desorption processes. In MoS_2, the ΔG_H of the edge site is usually close to zero, while the ΔG_H of the base plane is far from the zero point. By manipulating the electronic structure of MoS_2 (e.g., doping, defect introduction, or phase transition), the d-band center position can be optimized, resulting in improved ΔG_{H^*} and its catalytic performance.

(3) Effect of defects on the electronic structure

Defects in MoS_2, such as sulfur vacancies [204,207], molybdenum vacancies [162,204], and edge defects, can significantly alter their electronic structure, affecting catalytic performance. The formation of sulfur vacancies leads to a redistribution of local electron density, exposing the surrounding molybdenum atoms and exhibiting higher electron affinity. This change in electronic structure optimizes the hydrogen adsorption free energy (ΔG_{H^*}), thereby enhancing its activity. The formation of molybdenum vacancies will significantly change the local crystal structure and electronic state distribution but may lead to a decrease in the overall stability of the material. As a result, molybdenum vacancies typically contribute less to HER performance. The synergistic effect of the defects, such as the combination of edge defects and sulfur

vacancies, can further enhance the electron density distribution and catalytic activity of MoS_2. For example, the introduction of sulfur vacancies can enhance the electronic state of the edge site, thereby improving its catalytic performance (Fig. 6a and b) [163].

This improvement is demonstrated in Fig. 6a, which shows the free energy as a function of the HER reaction coordinates and varies from 0% to 25% of the S vacancy [163]. At the same time, Fig. 6b further illustrates the polarization curves of the strain, vacancy, and strain-vacancy MoS_2 of the HER, which visually reflect the specific effect of sulfur vacancies on the catalytic performance [163].

(4) Heterostructure and electronic coupling effects

By constructing the heterostructure of MoS_2 and other materials, its electronic structure can be further manipulated and the catalytic performance can be improved. In the heterostructure of MoS_2 and conductive materials such as graphene, carbon nanotubes, or metal nanoparticles, electron transfer at the interface can significantly

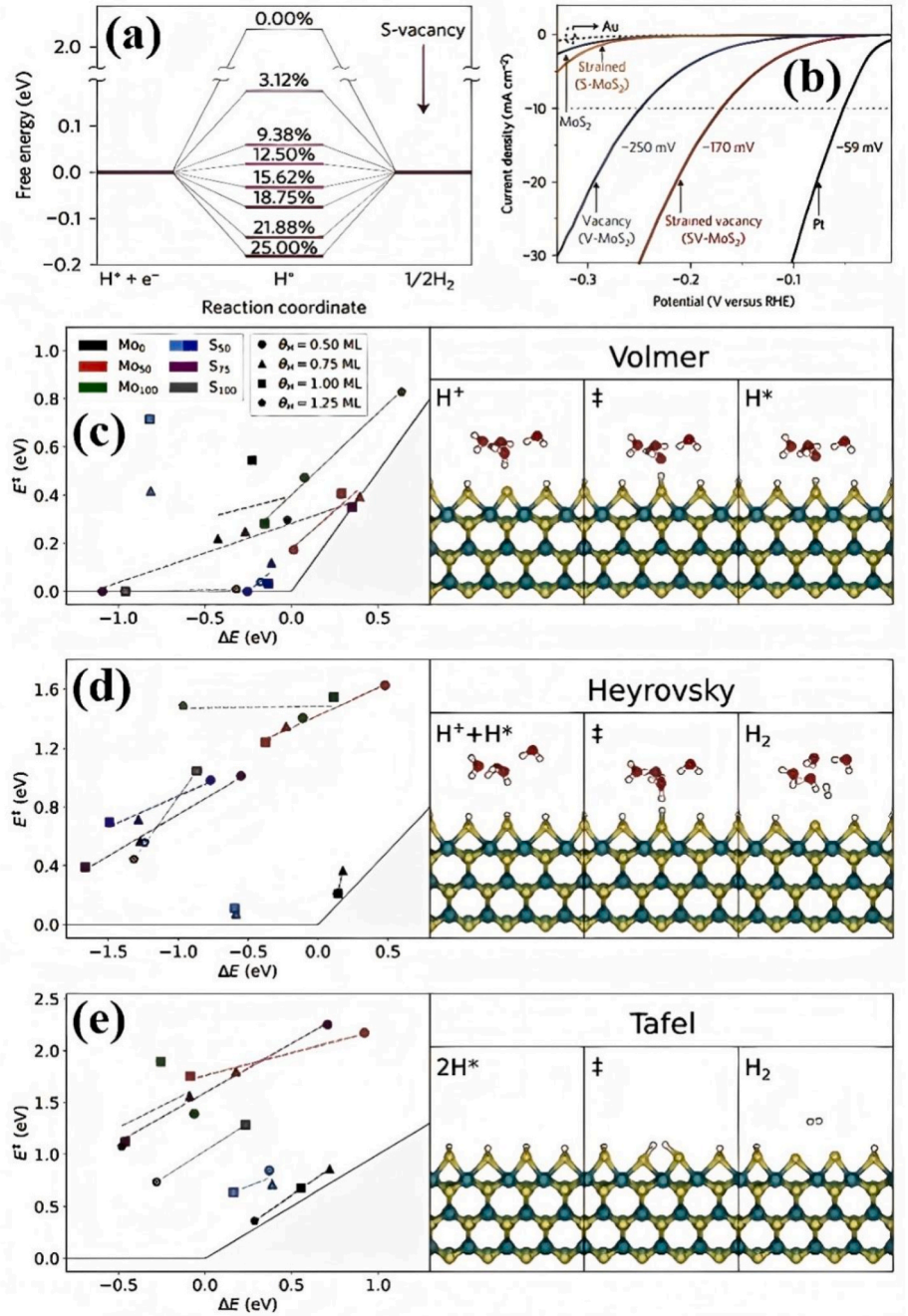


Fig. 6. (a) Free energy versus the HER reaction coordinates for the S-vacancy range of 0–25% [163]. (b) Polarization curves for the strained, vacancy, and strained vacancy MoS_2 for the HER [163]. (c-e) Scaling relations and reaction mechanisms for the (c) Volmer, (d) Heyrovsky, and (e) Tafel steps of hydrogen evolution, obtained with neutral supercells. The mechanism is visualized for the Mo50 edge at coverage yH = 1 ML [102]. The sided area marks the region of impossible values, defined by the limiting cases of E‡ = 0 (purely downhill pathway) and E‡ = DE (purely uphill pathway). For the S50 edge, light blue represents filling the Mo-sites first, while dark blue represents direct filling of the less favorable but more kinetically accessible S-sites. Within each system the activation energy generally scales linearly with the reaction energy, with some exceptions. The Mo0 and S50 edges (Mo-sites) display significantly lower activation barriers for the Tafel and Heyrovsky steps than that of the general trend (S-sites) [102]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

increase the conductivity and electron density of MoS_2, thereby improving HER performance. By introducing strain into MoS_2, the lattice constant and electronic state distribution can be manipulated [218]. For example, tensile strain can bring the center of the d-band closer to the Fermi level, thus optimizing the hydrogen adsorption free energy (ΔG_{H^*}). Further, in MoS_2 quantum dots, the electronic structure changes significantly due to the quantum confinement effect caused by size reduction, showing a higher proportion of edge sites and better electronic state distribution, thereby improving the catalytic performance.

The electronic properties of MoS_2 influence its HER performance. The electronic structure determines the conductivity of MoS_2, and the introduction of metallic 1T phase and heterostructure can significantly improve the efficiency of electron transport. The electronic state distribution of edge sites and defects directly affects the hydrogen adsorption-free energy (ΔG_{H^*}), thereby determining catalytic activity. The optimization of electronic structure can accelerate the electron-proton coupling process and reduce the overpotential of the HER reaction. The electronic structure of MoS_2 has an important influence on its catalytic performance. By manipulating the crystalline phase, defects, heterostructure, and strain, the electronic state distribution and hydrogen adsorption free energy of MoS_2 can be significantly optimized, thereby improving its HER performance. Future research should further combine theoretical calculations and experimental verification to explore the quantitative relationship between electronic structure and catalytic performance, so as to provide new theoretical guidance and technical routes for the design of high-efficiency MoS_2-based catalysts [218].

5.1.3. Reaction mechanism of MoS_2 in HER from Volmer-Tafel and Volmer-Heyrovsky routes

Electrocatalytic hydrogen evolution reaction is a key half-reaction in hydrogen production, and its reaction mechanism usually includes two main pathways: the Volmer-Tafel path and the Volmer-Heyrovsky path. As a potential high-efficiency HER catalyst, the catalytic performance of molybdenum disulfide is closely related to the HER reaction mechanism [218]. A better understanding of the reaction pathways and key steps of MoS_2 in HER is of great significance for optimizing its catalytic activity and designing efficient catalysts [160,219,220].

(1) Basic reaction pathways of HER

The reaction of HER in acidic electrolytes can be divided into three basic steps (Fig. 6c-e) [102].

i) Volmer step ($H^+ e^- \rightarrow H$)

On the surface of the catalyst, protons (H^+) combine with electrons to form adsorbed hydrogen atoms (H). This step is the initiation reaction of HER and involves electron transfer and hydrogen adsorption processes.

ii) Tafel step ($H\ H \rightarrow H_2$)

Two adsorbed hydrogen atoms (H*) combine on the surface of the catalyst to form a hydrogen molecule (H_2), which is desorbed from the surface of the catalyst. This step is a chemical reaction without electron transfer.

iii) Heyrovsky step ($H^+ e^- H \rightarrow H_2$)

An adsorbed hydrogen atom (H) combines with protons (H^+) and electrons in solution to directly form hydrogen molecules (H_2).

Depending on the reaction pathway, HER can be carried out through the following two main mechanisms: The Volmer step generates adsorbed hydrogen atoms (H*) followed by hydrogen molecules (H_2) through the Tafel step (Volmer-Tafel route). The Volmer step generates adsorbed hydrogen atoms (H*) followed by hydrogen molecules (H_2) through the Heyrovsky steps (Volmer-Heyrovsky path).

Fig. 6c illustrates the scaling relationship and reaction mechanism of the Volmer step of hydrogen evolution, Fig. 6d corresponds to the Heyrovsky step, and Fig. 6e is the Tafel step. When the coverage yH = 1 ML, the mechanism is visualized as the edge of Mo50 [102]. The sd ed region marks the area where the impossible value is marked, which is defined by the constraints of E = 0 (pure downhill path) and E = DE (pure uphill path). For the S50 edge, the light blue area indicates that the Mo site is filled first, while the dark blue area indicates that the S site is directly filled, although this path is less favorable, but is more dynamically closer. In general, in each system, the activation energy is linearly related to the reaction energy, although there are some exceptions. Of particular note is that the activation barriers at the Mo0 and S50 margins (Mo loci) in the Tafel and Heyrovsky steps are significantly lower than those at the S loci as indicated by the general trend.

(2) Reaction pathways of MoS_2 in HER

The catalytic performance of MoS_2 in HER is mainly determined by its edge sites (e.g., Mo-edge and S-edge), and the behavior of different reaction pathways on the MoS_2 surface depends on its electronic structure, hydrogen adsorption free energy (ΔG_{H^*}), and reaction kinetics.

i) Behavior of the Volmer step on the MoS_2 surface

The Volmer step is the initial step of HER, and its rate depends mainly on the adsorption capacity of hydrogen atoms on the MoS_2 surface. Theoretical calculations and experimental studies have shown that the edge sites of MoS_2 have uncoordinated atoms that provide suitable adsorption sites [221]. The ideal catalyst should have near-zero hydrogen adsorption-free energy ($\Delta G_{H^*} \approx 0$) to balance the hydrogen adsorption and desorption processes. The study showed that the ΔG_H of the Mo-edge was close to zero, while the ΔG_H of the S-edge was slightly away from the zero point, which made the Mo-edge exhibit higher activity in the Volmer step.

ii) Behavior of the Tafel step on the MoS_2 surface

The Tafel step involves the binding of two adsorbed hydrogen atoms (H*) and the generation of hydrogen molecules, the rate of which depends mainly on the surface density and interaction energy of the adsorbed hydrogen atoms. In MoS_2, the high-density distribution of the edge sites helps to increase the surface concentration of adsorbed hydrogen atoms, thus facilitating the Tafel step. However, too high hydrogen adsorption intensity may lead to difficulty in the desorption of H*, thus inhibiting the Tafel step. Therefore, optimizing the electronic structure of the MoS_2 edge site to balance hydrogen adsorption and desorption is the key to increasing the Tafel step rate [218,222].

iii) Manifestation of the Heyrovsky step on the MoS_2 surface:

The Heyrovsky step involves the combination of protons (H^+) in solution with adsorbed hydrogen atoms (H*) and electrons, the rate of which depends mainly on the electron transfer efficiency and proton supply capacity. The metallic 1T phase is able to significantly accelerate the electron transfer process of the Heyrovsky step due to its high conductivity and electron density. The 2H phase of the semiconductor has a low conductivity, which may limit the rate of the Heyrovsky step. Therefore, the reaction kinetics of the Heyrovsky step can be effectively improved by phase transition (e.g., 2H → 1T) or construction of heterostructures (e.g., MoS_2/graphene composites) [218].

(3) Reaction pathway selection of MoS_2

The specific reaction path of MoS_2 in HER (Volmer-Tafel or Volmer-

Heyrovsky) depends on its surface electronic structure, the distribution of active sites, and the reaction conditions. In cases where highly active edge sites (e.g., Mo-edge) predominate, the Volmer-Tafel path may be the main reaction mechanism, as the high density of adsorbed hydrogen atoms (H*) favors the Tafel step. Under conditions with higher electron transfer rates, such as in the 1T phase or heterostructures, the Volmer-Heyrovsky path may be dominant because the Heyrovsky step has a faster electron transfer process [97,223].

(4) Key factors influencing the reaction pathway

ΔG_H is a key parameter that determines the HER reaction pathway. The ideal catalyst should have a moderate ΔG_{H^*} that facilitates both hydrogen adsorption in the Volmer step and hydrogen desorption in the Tafel or Heyrovsky steps [97]. The conductivity of MoS_2 directly affects the efficiency of electron transfer in the Heyrovsky step. The metallic 1T phase is more conducive to the progress of the Volmer-Heyrovsky path due to its high conductivity [97]. The high density of the edge site increases the surface concentration of adsorbed hydrogen atoms, thus facilitating the Tafel step. Therefore, the exposure density of the edge site is an important factor affecting the Volmer-Tafel pathway. Under conditions of high current density or high proton concentration, the Heyrovsky step may be dominant, while at low current density or low proton concentration, the Tafel step may be more important. The kinetic performance of the HER reaction can be significantly improved by manipulating the crystalline phase of MoS_2 (e.g., 2H → 1T), optimizing the electronic state of edge sites (e.g., doping or defect engineering), and constructing heterostructures (e.g., MoS_2/conductive matrix composites). Future research should further combine theoretical calculations and experimental verification to further explore the selection of MoS_2 reaction paths under different reaction conditions, so as to provide new theoretical guidance and technical support for the design of high-efficiency MoS_2-based HER catalysts [97].

5.1.4. Structural engineering and modification strategies of MoS_2 in HER

The intrinsic catalytic performance of MoS_2 is limited by low basal activity, insufficient conductivity, and low utilization of edge sites. Therefore, the optimization of MoS_2 through structural engineering and modification strategies has become a key way to improve its electrocatalytic HER performance. In recent years, a series of innovative structural design and modification methods have been proposed focusing on edge site exposure, electronic structure manipulation, and hydrogen adsorption-free energy optimization, which have significantly improved the HER performance of MoS_2.

(1) Construction of vertically oriented nanosheet arrays

Due to the interlayer stacking effect, the exposure density of the edge sites of the traditional two-dimensional MoS_2 is insufficient, which limits the catalytic activity. By constructing vertically oriented MoS_2 nanosheet arrays, the exposed area of the edge sites can be effectively increased and their active sites can be maximized. For example, vertically oriented MoS_2 nanosheets prepared by chemical vapor deposition (CVD) or hydrothermal methods can not only significantly increase the edge density, but also improve the electron transport path, thereby reducing the overpotential of the HER reaction [224]. In addition, the design of the vertically oriented structure can effectively alleviate the retention of bubbles on the surface of the catalyst and improve the reaction rate and stability [225].

(2) Design of porous structure

The introduction of a porous structure is another important strategy to improve the catalytic performance of MoS_2. By manipulating the porosity and pore size distribution of MoS_2, the exposure of edge sites can be further increased, while providing more transport channels for reactant molecules. For example, porous MoS_2 structures prepared by template-assisted or etching techniques can optimize hydrogen adsorption free energy (ΔG_{H^*}) while maintaining a high specific surface area, thereby increasing HER activity. In addition, the porous structure can also effectively alleviate the mechanical stress of the catalyst in long-term use and improve its stability [226].

(3) Selective functionalization of edges

The electronic structure of the edge site has a decisive influence on the performance of HER, so selective manipulation of the edge site through functionalization is an effective means to improve the catalytic performance of MoS_2. For example, by introducing heteroatom doping (such as N, P, O), the electronic state distribution of the edge Mo/S site can be changed, and the center position of its d band can be optimized, thereby enhancing the adsorption and dissociation ability of hydrogen molecules. In addition, the loading of metal or non-metal nanoparticles has also been shown to significantly increase the catalytic activity of edge sites. For example, MoS_2 composites loaded with Pt nanoparticles take advantage of the synergistic effect of the high intrinsic activity of Pt with the high edge density of MoS_2 to achieve efficient HER performance [226].

(4) Plasma etching and electrochemical activation

Plasma etching and electrochemical activation have attracted extensive attention in recent years as effective means for the specific regulation of edge sites. By plasma etching, a large number of defects and edge sites can be introduced on the surface of MoS_2, thereby significantly increasing its catalytic activity. In addition, the electrochemical activation process can further optimize the electronic structure of the edge site, enhancing its metallicity and conductivity. For example, the exposure of the edge site of MoS_2 is significantly increased by electrochemical cycling, while its hydrogen adsorption free energy is optimized, resulting in a lower HER overpotential and a higher current density.

(5) Quantum dot edge proportion optimization and defect collaborative engineering

MoS_2 quantum dots exhibit excellent HER performance due to their high edge proportion and unique quantum confinement effect. By manipulating the size and morphology of quantum dots, the utilization rate of their edge sites can be further improved. In addition, defect collaborative engineering, as an emerging modification strategy, can effectively manipulate the electronic structure of edge sites and enhance their catalytic activity by introducing sulfur vacancies, Mo vacancies, or other defects. For example, the introduction of sulfur vacancies can significantly reduce the free energy of hydrogen adsorption while promoting the charge transfer rate, thereby improving HER performance.

(6) Heterostructure design

The construction of heterostructures provides a new research direction for the optimization of HER performance of MoS_2. By constructing heterojunctions with other 2D materials (e.g., graphene, MXene, g-C_3N_4) or metal compounds (e.g., NiS_2, CoP), electron transfer and synergistic effects at the interface can be achieved, resulting in significantly improved catalytic activity. For example, MoS_2/graphene composites significantly improve conductivity and edge site activity through the interfacial electron coupling effect. In addition, the design of the heterostructure can also improve the mechanical stability and corrosion resistance of the catalyst, further enhancing its application potential under practical working conditions.

(7) Strain engineering

By changing the lattice constant of MoS_2, strain can effectively regulate its electronic structure, especially the position of the d-band center, thereby optimizing the hydrogen adsorption free energy (ΔG_H), which is the core mechanism for enhancing the catalytic activity of HER [227]. For example, theoretical research suggests that applying a strain of approximately 1.5-2% to Ag doped MoS_2 can effectively optimize ΔG_H (Fig. 5e and f) [180]. In a vertically oriented nanosheet array, local strain fields are introduced due to lattice mismatch with the substrate or inherent curvature of the nanocoil structure [228]. This strain can synergistically increase the exposure density of edge sites and optimize their electronic structure, achieving a synergistic enhancement of "geometric effects" and "electronic effects" (Fig. 4c and d) [229]. In addition, the transition from 1T to 2H phase in 1T-MoS_2 is accompanied by lattice distortion (about 3-5% strain). The strain field induced by this phase transition can further activate the edge sites, forming a highly active metastable surface [230]. Strain engineering can also generate synergistic effects with other strategies such as defect engineering and heterostructure construction [231]. For example, the strain field can guide the formation and distribution of sulfur vacancies (S-vacancies), while the presence of vacancies can also locally release or introduce strain [232]. The synergy of the two can more effectively regulate the electron local density, thereby significantly reducing the HER overpotential [233]. As shown in Fig. 6b, the MoS_2 sample with strain and vacancies exhibits the optimal polarization curve [229].

Optimization of MoS_2 through structural engineering and modification strategies can significantly improve its HER performance. Vertically oriented nanosheets, porous structures, edge functionalization modifications, plasma etching, electrochemical activation, quantum dot edge optimization, heterostructure design and strain engineering have shown great potential in improving the exposure density of edge sites, optimizing the electronic structure, and improving the free energy of hydrogen adsorption. However, there is still a need to further explore the methods of precise control of edge sites at the atomic level, as well as the stability and durability of catalysts under dynamic conditions. By combining theoretical calculations and experimental verification, the deep correlation of "structure-electronic state-catalytic activity" can be established, which will provide clearer theoretical guidance and technical support for the design of efficient and stable MoS_2-based HER catalysts.

The theoretical models underlying structural engineering strategies (e.g., strain-induced ΔG_H optimization, edge site activation via doping) require experimental validation to establish their practical relevance [231]. Techniques such as high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) directly confirm the structural and electronic changes induced by modifications [234]. For instance, HRTEM images of vertically oriented MoS_2 nanosheets reveal increased edge density, correlating with reduced overpotentials in HER polarization curves [235]. Similarly, XPS analysis of doped MoS_2 (e.g., N or Co doping) validates shifts in d-band center positions, aligning with DFT-predicted enhancements in hydrogen adsorption free energy [236]. Electrochemical methods like linear sweep voltammetry (LSV) and Tafel analysis provide performance metrics (e.g., overpotential @ 10 mA cm^{-2}, Tafel slope) that quantitatively link theoretical predictions to experimental outcomes [237]. To systematically bridge theory and experiment, Table 1 summarizes key parameters: theoretical descriptors (e.g., ΔG_H, d-band center), experimental characterization techniques, and HER performance indicators [238]. This comparative framework demonstrates consistency between theoretical models and empirical data, reinforcing the reliability of structural engineering strategies [239].

Table 1 integrates theoretical predictions (e.g., ΔG_H from DFT), experimental techniques (e.g., HRTEM for morphology, XPS for electronic structure), and HER performance metrics (e.g., overpotential, Tafel slope). For example, the theoretical ΔG_H for Mo-edge sites (~0.08 eV) correlates with experimental overpotentials of ~150 mV, while strain engineering predictions align with observed reductions in Tafel slopes. This table highlights the synergy between theory and experiment, validating the structural strategies discussed in Section 5.1.4.

5.2. Parameters of MoS_2 in electrocatalytic hydrogen evolution

In the electrocatalytic HER process, the evaluation parameters of MoS_2-based catalysts primarily include overpotential, Tafel slope, current density, and stability [241–243].

5.2.1. Overpotential

Overpotential is one of the important parameters to measure the performance of an electrocatalyst, which reflects the additional voltage drive required to achieve a specific current density (e.g., 10 mA cm^{-2}). For electrocatalytic hydrogen evolution, a lower overpotential means that the catalyst has higher activity and lower energy consumption, so reducing the overpotential is one of the core goals of designing high-efficiency HER catalysts.

(1) Overpotential characteristics of MoS_2

As a potential HER catalyst, the overpotential properties of molybdenum disulfide (MoS_2) are significantly affected by the material structure, electronic properties, and active site distribution. The results show that the base surface of MoS_2 exhibits low intrinsic catalytic activity due to the deviation of hydrogen adsorption free energy (ΔG_{H^*}), resulting in a high overpotential. Edge sites (e.g., Mo-edge and S-edge) have a closer to zero ΔG_{H^*} due to their unsaturated coordination environment and unique electronic structure, which significantly reduces the HER overpotential. Therefore, increasing the exposure of the MoS_2 edge site and optimizing its electronic structure are the keys to reducing the overpotential (Fig. 7a) [244].

In addition, the phase structure of MoS_2 also has an important influence on the overpotential. The MoS_2 of the 2H phase of a semiconductor typically exhibits a higher overpotential due to lower conductivity and fewer active sites. However, the MoS_2 of the metallic 1T phase can significantly reduce the overpotential due to its higher conductivity and better electronic state distribution. For example, the overpotential of the 1T phase MoS_2 is as low as 100 mV, while the overpotential of the 2H phase MoS_2 is typically above 200 mV [128].

(2) Regulation of overpotential in structural engineering

Improving the exposure density and electron transport performance of MoS_2 at the edge site through structural engineering is an effective

Table 1
Comparative table linking theoretical parameters, experimental methods, and HER performance metrics for MoS_2-based catalysts modified via structural engineering.

Theoretical Parameter	Experimental Characterization Method	Performance Metric (HER)	Example System	Reference
ΔG_{H^*} (theoretical)	DFT calculations	Overpotential @ 10 mA cm^{-2}	Mo-edge site	[97]
ΔG_{H^*} (experimental)	LSV/Tafel analysis	Tafel slope (mV dec^{-1})	1T-MoS_2 nanosheets	[218]
d-band center position	XPS/STS	Current density @ fixed overpotential	N-doped MoS_2	[240]
Edge site density	HRTEM/SEM	Exchange current density (j_0)	Vertically oriented MoS_2	[224]
Sulfur vacancy concentration	EPR/Raman spectroscopy	Stability (cyclic retention)	Defect-engineered MoS_2	[207]
Strain-induced ΔG_{H^*} shift	In-situ XRD/Raman	Activation energy (E_a)	Strained MoS_2/graphene	[218]

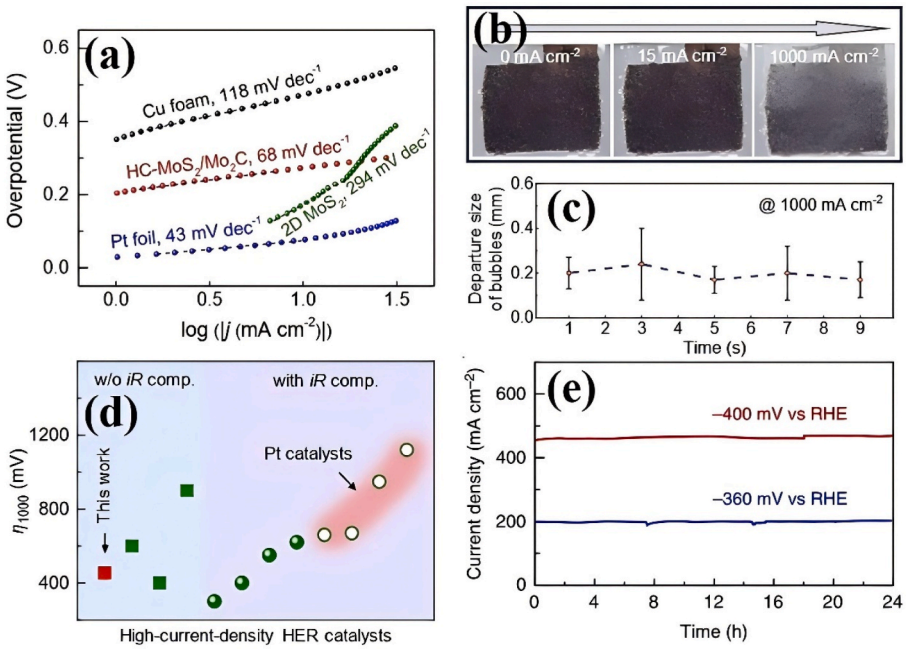


Fig. 7. (a) Tafel plots of different catalysts in 0.5 M H_2SO_4 at a scan rate of 5 mV s^{-1} [244]. (b) Photos and (c) corresponding size distribution of H_2 bubbles leaving the surfaces of HC-MoS_2/Mo_2C catalysts [244]. (d) A comparison of the HER performance of HC-MoS_2/Mo_2C catalysts [244]. (e) Chronoamperometric response (i-t) curves for HER using HC-MoS_2/Mo_2C at current densities of 200 and 500 mA cm^{-2} for 24 h [244].

strategy to reduce overpotential. For example, vertically oriented MoS_2 nanosheet arrays can maximize the utilization of edge sites while shortening the electron transport path, thereby significantly reducing the HER overpotential. In addition, the design of the porous structure not only increases the specific surface area but also provides more channels for the mass transfer of reactants and products, further reducing the reaction resistance and overpotential.

(3) Optimization of overpotential by electronic structure regulation

The electronic structure of MoS_2 plays a decisive role in its HER performance. By manipulating the electronic state distribution of MoS_2 by doping or defect engineering, the d-band center position of the edge site can be optimized to be closer to the ideal value of hydrogen adsorption free energy ($\Delta G_{H^*} \approx 0$ eV). For example, the doping of heteroatoms such as N and P can effectively adjust the electronic structure of MoS_2 and reduce the overpotential. In addition, the introduction of sulfur vacancies has also been shown to significantly enhance the catalytic activity of the edge site, thereby reducing the HER overpotential [162].

(4) The quantitative relationship between overpotential and edge density

In recent research efforts, a quantitative relationship has been established between MoS_2 edge density and HER overpotential through theoretical calculations and experimental verification. Studies have shown that the higher the density of the edge site, the lower the overpotential of the catalyst. For example, when the proportion of edge sites increases from 10% to 50%, the overpotential can be reduced by more than 50 mV. This relationship provides clear guidance for improving the catalytic performance of MoS_2 through structural design [101,245].

(5) Synergistic regulation of overpotential by heterostructure

The construction of heterostructures provides a new idea for further reducing the overpotential of MoS_2 (Fig. 7b-e) [244]. By constructing heterojunctions with highly conductive materials (e.g., graphene, carbon nanotubes) or other catalytically active materials (e.g., NiS_2, CoP), electron transfer and synergistic effects at the interface can be achieved, resulting in a significant reduction in overpotential. For example, MoS_2/graphene composites not only improve the conductivity but also optimize the electronic structure of the edge site through the interfacial electronic coupling effect, resulting in a significant reduction in the overpotential. Reducing the overpotential is a core goal to improve the performance of MoS_2-based HER catalysts. Through strategies such as edge site exposure, electronic structure optimization, defect engineering, and heterostructure design, the overpotential of MoS_2 has been significantly reduced. However, to further reduce the overpotential, it is still necessary to start from the precise regulation at the atomic level and explore the stability and activity changes of edge sites under dynamic reaction conditions. In the future, by combining theoretical calculations and experimental studies, the deep correlation between overpotential, material structure and electronic state could be established, for achieving a clearer direction and technical support for the design of high-efficiency and low-overpotential-based MoS_2-based HER catalysts.

The construction of heterostructures opens up a new path to reduce the overpotential of MoS_2. Fig. 7b shows a photograph of H_2 bubbles leaving the surface of the HC-MoS_2/Mo_2C catalyst, and Fig. 7c shows the size distribution [244]. Fig. 7d compares the HER performance of HC-MoS_2/Mo_2C catalysts [244]. Further, Fig. 7e presents the results of a 24-h chronometric ampere response (i-t) for HER at current densities of 200 and 500 mA cm^{-2} using HC-MoS_2/Mo_2C [244]. These charts provide a comprehensive view of the performance of HC-MoS_2/Mo_2C catalysts in the HER process from different perspectives, providing strong evidence of the effectiveness of heterostructures in reducing MoS_2 overpotential.

5.2.2. *Tafel slope*

The Tafel slope is one of the important parameters to evaluate the kinetic properties of the electrocatalyst hydrogen evolution reaction, which reflects the electron transfer rate of the catalyst in the HER process and the dominant step of the reaction mechanism [246]. By analyzing the Tafel slope, the reaction path of the catalyst and its

limiting steps can be deeply understood, so thata theoretical basis can be provided for optimizing the performance of the catalyst [247]. For molybdenum disulfide (MoS_2)-based HER catalysts, the study of the Tafel slope is the key to revealing the characteristics of the active site and the regulatory mechanism of electronic structure [139].

(1) The physical significance of the Tafel slope

In acidic media, HER typically follows a three-step reaction mechanism, as follows [219,248,249]:

Volmer step (electrochemical adsorption):$H^+ + e - \rightarrow H_{ads}$

In this step, protons (H^+) are adsorbed to the surface of the catalyst by electron reduction, forming hydrogen atoms in an adsorbed state (H_{ads}).

Heyrovsky step (electrochemical desorption):$H_{ads} + H^+ + e- \rightarrow H_2$

In this step, the hydrogen atoms (H_{ads}) in the adsorbed state combine with the protons (H^+) and electrons to directly generate hydrogen (H_2) and desorb from the surface.

Tafel step (chemical desorption):$2H_{ads} \rightarrow H_2$

In this step, two adsorbed hydrogen atoms (H_{ads}) undergo a chemical reaction on the surface of the catalyst to form hydrogen (H_2) and desorb [250,251]. Together, these three reaction pathways constitute the complete mechanism of hydrogen evolution reactions in acidic media. The Tafel slope value is a key indicator of the rate-determining step in the HER process [252]. The typical ranges of Tafel slope values for the three fundamental reaction mechanisms are as follows: when the Volmer step is the rate-determining step, the Tafel slope is typically around 120 $mV{\cdot}dec^{-1}$ [253]; when the Heyrovsky step is the rate-determining step, the Tafel slope typically falls within the range of 40 $mV{\cdot}dec^{-1}$ [254]; and when the Tafel step is the rate-determining step, the Tafel slope is typically around 30 $mV{\cdot}dec^{-1}$ [255]. The size of the Tafel ramp depends on the HER quick control steps:

If the Volmer step is a quick-control step, the Tafel slope is about 120 $mV{\cdot}dec^{-1}$; If the Heyrovsky step is a quick-control step, the Tafel slope is about 40 $mV{\cdot}dec^{-1}$; If the Tafel step is a quick control step, the Tafel slope is about 30 $mV{\cdot}dec^{-1}$ [256]. Therefore, the determination of the Tafel slope can help determine the main limiting steps of HER and provide an optimal direction for the design of catalysts.

(2) Tafel slope characteristics of MoS_2

Conventional MoS_2-based catalysts usually exhibit a high Tafel slope (>120 $mV{\cdot}dec^{-1}$) due to their low basal activity, indicating that the HER process is mainly limited by the Volmer step, i.e., hydrogen proton adsorption is difficult. This is related to the deviation of the hydrogen adsorption free energy (ΔG_{H^*}) of the MoS_2 base surface from zero, which makes it difficult for the base surface to effectively participate in the reaction during the HER process [257]. In contrast, edge sites of MoS_2 (e.g., Mo-edge and S-edge) are able to provide a closer to zero ΔG_{H^*} due to their unsaturated coordination environment and unique electronic structure, thereby significantly reducing the Tafel slope [23]. For example, studies have shown that the Tafel slope of MoS_2 nanosheet catalysts exposed to more edge sites can be reduced to 40-60 $mV{\cdot}dec^{-1}$, suggesting that the HER process may be controlled by the Heyrovsky step and the electron transfer rate is significantly increased [258]. In addition, the phase structure of MoS_2 also has an important influence on the Tafel slope [259]. The metallic 1T phase MoS_2 can further reduce the Tafel slope due to the higher conductivity and better electronic state distribution. For example, the Tafel slope of the 1T phase MoS_2 is typically closer to 40 $mV{\cdot}dec^{-1}$ than the 2H phase MoS_2 of semiconductors, indicating that the HER process has faster kinetic properties [222,260].

(3) Structural engineering regulation and control of Tafel slope

By optimizing the edge site exposure and electronic structure of MoS_2 through structural engineering, the Tafel slope can be significantly reduced and the HER kinetic performance can be improved [261]. For example, vertically oriented MoS_2 nanosheets are able to maximize the utilization of edge sites while shortening the electron transport path, thereby lowering the Tafel slope [262]. On the other hand, the introduction of porous structures can increase the specific surface area and edge site density, while providing more channels for mass transfer of reactants and products, thereby accelerating reaction kinetics and lowering the Tafel slope [263].

(4) Optimization of Tafel slope by electronic structure control

The electronic structure of MoS_2 has an important influence on its Tafel slope. Through doping, defect engineering, or heterostructure design, the electronic state distribution of MoS_2 can be optimized and its HER kinetic performance can be improved [215]. The introduction of heteroatoms such as N and P can adjust the electronic structure of the edge site, so that the center position of the d-band is closer to the ideal value, thereby reducing the Tafel slope [238]. Additionally, defect engineering by the introduction of sulfur vacancies can significantly enhance the catalytic activity of edge sites, promote hydrogen adsorption and dissociation processes, and reduce the Tafel slope [264].

(5) Synergistic regulation of heterostructure on Tafel slope

By constructing heterostructures with other materials, the Tafel slope of MoS_2 can be further reduced. For example, MoS_2/graphene composites not only improve the conductivity but also optimize the electronic structure of the edge site through the interfacial electronic coupling effect, resulting in a significant reduction of the Tafel slope [142]. In addition, the construction of heterojunctions with other transition metal compounds (e.g., NiS_2, CoP) can achieve synergistic effects at the interface and accelerate the electron transfer process, thereby further reducing the Tafel slope [265].

(6) The quantitative relationship between Tafel slope and edge density

Studies have shown that the Tafel slope of MoS_2 is closely related to the density of edge sites [266]. The higher the density of the edge site, the lower the Tafel slope of the catalyst. For example, when the proportion of marginal loci increases from 10% to 50%, the Tafel slope can be reduced by more than 30 $mV{\cdot}dec^{-1}$ [267]. This relationship provides clear guidance for improving the catalytic performance of MoS_2 through structural design.

The lowering of the Tafel slope is the key to improving the kinetic performance of MoS_2-based HER catalysts [129]. Through strategies such as edge site exposure, electronic structure optimization, defect engineering, and heterostructure design, the Tafel slope of MoS_2 has been significantly reduced [23]. However, to further reduce the Tafel slope, it is still necessary to start from the precise regulation at the atomic level to explore the activity changes of the edge site under dynamic reaction conditions [268].

5.2.3. *Current density*

Current density is one of the important parameters to evaluate the performance of electrocatalysts, which directly reflects the catalytic activity of catalysts under specific overpotentials [269]. For HER, higher current densities mean that the catalyst is able to achieve higher reaction rates at lower energy inputs [270]. Therefore, increasing the current density is one of the key goals for designing efficient HER catalysts. MoS_2 exhibits good HER potential due to its unique electronic structure and high activity at the edge site [191]. However, how to further

improve the current density through structural optimization and electronic regulation is still a hot topic in current research.

(1) Current density characteristics of MoS_2

The HER performance of MoS_2 is mainly determined by the activity of its edge site, while the base surface is almost not involved in the reaction due to the deviation of hydrogen adsorption free energy (ΔG_{H^*}) [257]. Therefore, the current density of MoS_2 is highly dependent on the exposure density and electronic structure of the edge site. Studies have shown that conventional MoS_2 thin film or particle catalysts can only achieve a current density of 10 mA cm^{-2} at high overpotential, which is mainly due to their low edge site utilization, insufficient conductivity, and limited hydrogen adsorption kinetics [271]. In contrast, by optimizing the structural and electronic properties of MoS_2, its current density can be significantly improved. For example, vertically oriented MoS_2 nanosheet arrays, porous structure design, and edge functionalization can effectively increase the exposure density of edge sites and reduce the hydrogen adsorption free energy, so as to achieve higher current density at lower overpotential [271].

(2) Improvement of current density in structural engineering

Optimizing the geometry and edge site distribution of MoS_2 through structural engineering is an effective means to improve the current density [23]. Conventional MoS_2 has a limited exposure density at edge sites due to the interlayer stacking effect, resulting in low current densities [272]. By constructing vertically oriented MoS_2 nanosheet arrays, the exposed area of edge sites can be significantly increased, and the electron transport path can be shortened, thereby increasing the current density [273]. The results show that vertically oriented MoS_2 nanosheets can achieve a current density of 10 mA cm^{-2} at low overpotential [274]. The porous structure can further improve the specific surface area and edge site density of MoS_2 while providing more channels for mass transfer of reactant molecules, reducing diffusion resistance, and thus significantly increasing the current density. For example, a porous MoS_2 catalyst prepared by a template-assisted method can achieve high current densities at low overpotentials [271,275].

(3) Optimization of current density by electronic structure control

The electronic structure of MoS_2 has a decisive influence on its current density. The electronic state distribution of MoS_2 can be optimized by doping, defect introduction, or phase structure manipulation, and its conductivity and edge site activity can be improved [258]. For example: Phase structure control: The metallic 1T phase MoS_2 can significantly increase the current density due to higher conductivity and better electronic state distribution [105]. Compared to the 2H phase MoS_2 of semiconductors, the current density of the 1T phase MoS_2 at the same overpotential is usually several times higher [276]. Heteroatom doping: By introducing heteroatoms such as N, P, and O, the electronic structure of the MoS_2 edge site can be adjusted to make the center position of the d-band closer to the ideal value, thereby enhancing the hydrogen adsorption and dissociation ability and increasing the current density [38]. Defect engineering: The introduction of sulfur vacancies or Mo vacancies can significantly enhance the catalytic activity of edge sites, promote the electron transfer process, and thus increase the current density [277].

(4) Synergistic improvement of current density by heterogeneous structure

By constructing heterostructures with other highly conductive materials or highly active catalytic materials, the current density of MoS_2 can be further improved [278]. For example: MoS_2/Graphene Composites: The high conductivity and large specific surface area of graphene can significantly improve the electron transport performance and edge site utilization of MoS_2, resulting in higher current density at lower overpotentials [279]. MoS_2/transition metal compound heterostructure: By constructing heterojunctions with NiS_2, CoP, and other materials, electron transfer and synergistic effects at the interface can be realized, and the current density can be further improved [280].

(5) Quantitative relationship between current density and edge density

Studies have shown that the current density of MoS_2 is positively correlated with the density of its edge sites [281]. The higher the edge site density, the greater the current density of the catalyst at the same overpotential. For example, when the proportion of edge sites increases from 10% to 50%, the current density can be increased by several times [270]. This relationship provides clear guidance for improving the catalytic performance of MoS_2 through structural design.

(6) Stability of current density under dynamic conditions

In practical applications, the current density stability of a catalyst is an important indicator to measure its performance. The current density of MoS_2 can be affected by edge site passivation, structural collapse, or electrolyte corrosion in long-term operation [282]. Therefore, the long-term stability of the current density can be effectively improved by introducing stability enhancement strategies (such as surface modification and heterostructure design) [283]. Current density is one of the core parameters to measure the performance of MoS_2-based HER catalysts. Through strategies such as edge site exposure, electronic structure optimization, defect engineering, and heterostructure design, the current density of MoS_2 has been significantly improved [23]. However, to further improve the current density, it is still necessary to start from the precise control at the atomic level to explore the stability and activity changes of the edge sites under dynamic reaction conditions [284]. In the future, by combining theoretical calculations and experimental studies, the deep correlation between current density, material structure and electronic state could be establishedfor a clearer direction and technical support for the design of MoS_2-based HER catalysts with high efficiency and high current density.

To specifically address the catalytic activity of MoS_2 at high current densities such as 100 mA cm^{-2}, key conditions include the use of metallic 1T phase MoS_2 for enhanced conductivity, vertically oriented nanosheet arrays to maximize edge site exposure and mass transfer, and defect engineering (e.g., sulfur vacancies) to optimize hydrogen adsorption free energy [142]. Heterostructure construction with conductive materials like graphene further improves interfacial charge transfer, as demonstrated by the HC-MoS_2/Mo_2C catalyst which maintains stability at 500 mA cm^{-2} for 24 h (Fig. 7e) [244]. Doping with elements like Co or N also enhances electronic structure and durability. Thus, through synergistic phase control, nanostructuring, and interface engineering, MoS_2 achieves efficient performance at industrial-level current densities.

5.2.4. Electrochemical stability

Electrochemical stability is one of the important indicators to evaluate the practical application potential of electrocatalysts, which reflects the ability of catalysts to maintain efficient catalytic performance under long-term operation and dynamic working conditions [285]. For MoS_2-based electrocatalytic HER catalysts, their electrochemical stability directly affects their feasibility in industrial-scale applications [286]. However, due to the activity and structural properties of the edge site, MoS_2 may face problems such as active site passivation, structural collapse, corrosion, and insufficient mechanical stability during long-term electrochemical operation [287]. Therefore, improving the electrochemical stability of MoS_2 is one of the key challenges to achieving its practical application.

(1) Problems and challenges of the electrochemical stability of MoS_2

The electrochemical stability of MoS_2 is mainly affected by the passivation of edge sites. The edge sites of MoS_2 are the main active regions of HER, but in long-term operation, edge sites may be passivated due to the formation of by-products such as oxides or sulfides, resulting in a decrease in catalytic activity [287]. Structural collapse and insufficient mechanical stability are some of the other factors influencing stability. The two-dimensional layered structure of MoS_2 may collapse due to bubble accumulation, mechanical stress, or electrolyte corrosion during electrochemical reactions, resulting in the loss of active sites [287]. In addition, under dynamic conditions, the conductivity of MoS_2 may decrease due to a change in phase structure (e.g., from a metallic 1T phase to a semiconductor 2H phase) or a decrease in the interfacial charge transfer efficiency, which can affect HER performance [288]. Furthermore, in acidic or alkaline electrolytes, MoS_2 can lead to loss of edge sites or catalyst deactivation due to chemical corrosion.

(2) Strategies to improve the electrochemical stability of MoS_2

In order to solve the above-mentioned issues, a series of strategies to improve the electrochemical stability of MoS_2 through structural design, surface modification, and electronic structure manipulation have been proposed.

i) Edge site protection and functional modification Surface modification: Passivation and corrosion of edge sites can be effectively prevented by introducing a protective layer (such as a carbon layer, polymer coating, or oxide coating) on the MoS_2 surface [287]. For example, studies have shown that modifying MoS_2 with carbon-based materials, such as graphene or carbon nanotubes, not only improves its electrical conductivity but also enhances its resistance to corrosion, thereby significantly improving electrochemical stability [287]. Functionalization: By introducing heteroatoms (e.g., N, P, O) or metal nanoparticles, the electronic structure of the edge site can be manipulated, reducing the rate of by-product formation, and thereby extending the lifetime of the catalyst [289]. ii) Structural engineering to improve mechanical stability Vertically oriented nanosheet array: The vertically oriented MoS_2 nanosheet structure can effectively alleviate the retention of air bubbles on the surface of the catalyst, reduce the damage of mechanical stress to the catalyst, and thus improve the electrochemical stability [290]. Porous structure design: The porous structure can not only increase the exposure density of the edge site, but also provide more mass transfer channels, reduce the influence of bubble accumulation on the catalyst structure, and thus improve its stability.

iii) Stabilization of phase structure 1T phase stabilization: The metallic 1T phase MoS_2 has higher conductivity and intrinsic activity, but the transition to the 2H phase can occur during long-term operation, resulting in performance degradation [142]. By introducing stabilizers (e.g., Li^+, Na^+) or constructing heterostructures, the transition of the 1T phase can be effectively inhibited and its electrochemical stability can be improved [291]. Heterostructure design: By constructing heterostructures with other materials (e.g., graphene, carbon nanotubes, transition metal compounds), the electronic coupling effect at the interface can be enhanced, and the structural stability and corrosion resistance of MoS_2 can be improved [292].

iv) Electrochemical activation and self-healing mechanisms Electrochemical activation: Through electrochemical cycling, the electronic structure of the MoS_2 edge site can be optimized and its resistance to passivation can be enhanced [293]. For example, the electrochemical activation process can remove surface unstable by-products while enhancing the metallicity of the edge sites, thereby improving electrochemical stability [294]. Self-healing mechanism: By introducing materials with self-healing functions, such as dynamic covalent bonds or reversible coordination bonds, self-healing can be achieved when the catalyst structure is damaged, thereby extending its service life [295].

(3) Characterization and evaluation of electrochemical stability

Electrochemical stability is typically characterized and evaluated by the long-term electrolysis test: Run the catalyst under constant current or potentiostatic conditions and record its current density or overpotential over time to assess its stability [296]. Cyclic voltammetry test: Through multiple cyclic voltammetry scans, observe whether the electrochemical performance of the catalyst is attenuated. Electrochemical Impedance Spectroscopy (EIS): Evaluates the electrochemical stability of a catalyst by measuring its change in charge transfer resistance and interface resistance [297]. Structure and composition characterization: X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and other techniques were used to analyze the structure and composition changes of catalysts before and after long-term operation [298].

(4) Research progress on the electrochemical stability of MoS_2

In recent years, a series of advances have been made in the study of the electrochemical stability of MoS_2. For example: Edge modification and doping: By introducing the doping of heteroatoms such as N and P, the anti-passivation ability and long-term stability of MoS_2 are significantly improved [299]. Heterostructure design: MoS_2/graphene composites exhibit excellent stability in long-term electrolytic tests, with almost no attenuation of current density over 100 h. Porous structure and vertically oriented design: Porous MoS_2 nanosheets and vertically oriented nanosheet arrays exhibit excellent mechanical stability and corrosion resistance in long-term operation [300]. Electrochemical stability is one of the key challenges in the practical application of MoS_2-based HER catalysts. The electrochemical stability of MoS_2 has been significantly improved through strategies such as edge site protection, structural engineering, phase structure stabilization, and heterostructure design. However, to further improve its stability, it is still necessary to focus on the mechanism of activity change and stability of edge sites under dynamic conditions, development of catalyst materials with self-healing function, and combined theoretical studies and experimental efforts [131].

At high current densities like 100 mA cm^{-2}, maintaining electrochemical stability is critical [283]. Strategies such as vertical nanosheet arrays and porous structures reduce bubble accumulation and mechanical stress, while heterostructures (e.g., with graphene) enhance corrosion resistance. Phase stabilization of 1T-MoS_2 through doping or interfacial engineering prevents degradation, and edge site functionalization (e.g., with N or Co) improves durability [301]. These approaches ensure long-term performance under industrial conditions.

5.3. *Number and accessibility of the active sites*

The number and accessibility of the active site are key factors in determining the catalytic efficiency of MoS_2 [191]. In the electrocatalytic hydrogen evolution reaction, hydrogen formation can only be performed efficiently in the active site of the catalyst [302,303]. Therefore, increasing the number of active sites and improving their accessibility are essential approaches to improving the catalytic properties of MoS_2. The number and accessibility of the active site are key factors in determining the catalytic efficiency of MoS_2 [203,302]. In the electrocatalytic HER, hydrogen generation can be initiated efficiently only at the catalyst's active site [302,304]. Therefore, increasing the number of active sites and improving their accessibility are essential approaches to improving the catalytic properties of MoS_2 [305]. The number of active sites can be increased by multiple means. For example,

by growing graphene on MoS_2 nanoparticles, the number of exposed edge sites can be significantly increased, thereby improving the catalytic activity [218,306].

Furthermore, using a ligand regulation strategy and cobalt doping can facilitate the exposure of the active site in the 1T-MoS_2 catalyst, accelerate hydro dissociation, and optimize the adsorption and desorption processes of H^- [307,308]. It has also been shown that vertical growth on MoS_2 nanosheets significantly reduces resistance while increasing the number of active edge sites [309,310]. Improving the accessibility of the active site is also the key to improving the catalytic efficiency [311]. For example, by introducing nitrogen heteroatoms or oxide impurities to the MoS_2 surface, changing the electronic structure can thus improve the accessibility and catalytic activity of the active site (Fig. 8a and b) [43,84].

Fig. 8a illustrates the mechanism of action of the MoS_2-NiMOF hybrid during hydrogen evolution, which provides critical insight into how hybrids improve catalytic performance [43]. At the same time, Fig. 8b presents a schematic diagram of the band structure of MoS_2, clearly showing the six valleys of the valence band at the K and -K points and the opposite spin-orbit splitting, which is of great significance for revealing the electronic behavior of MoS_2 and the improvement of its catalytic activity [84]. These results together suggest that the construction of heterostructures by chemical modification of MoS_2 surfaces is an effective strategy to reduce overpotential, which provides valuable theoretical support for promoting the application of MoS_2 in the field of electrocatalysis.

Moreover, by introducing the doping of metal atoms or transition metal elements into the MoS_2, the electronic structure and band gap can be effectively regulated, thereby improving the accessibility and catalytic activity of the active site [240,312–316]. Therefore, the catalytic performance of MoS_2 in electrocatalytic hydrogen precipitation can be significantly improved by increasing the number of active sites and improving its accessibility [317]. This includes nanostructure design, ligand regulation, doping strategies, and the introduction of transition metal elements [34,318]. These strategies enhance the catalytic activity and optimize the charge transport dynamics and electronic structure,

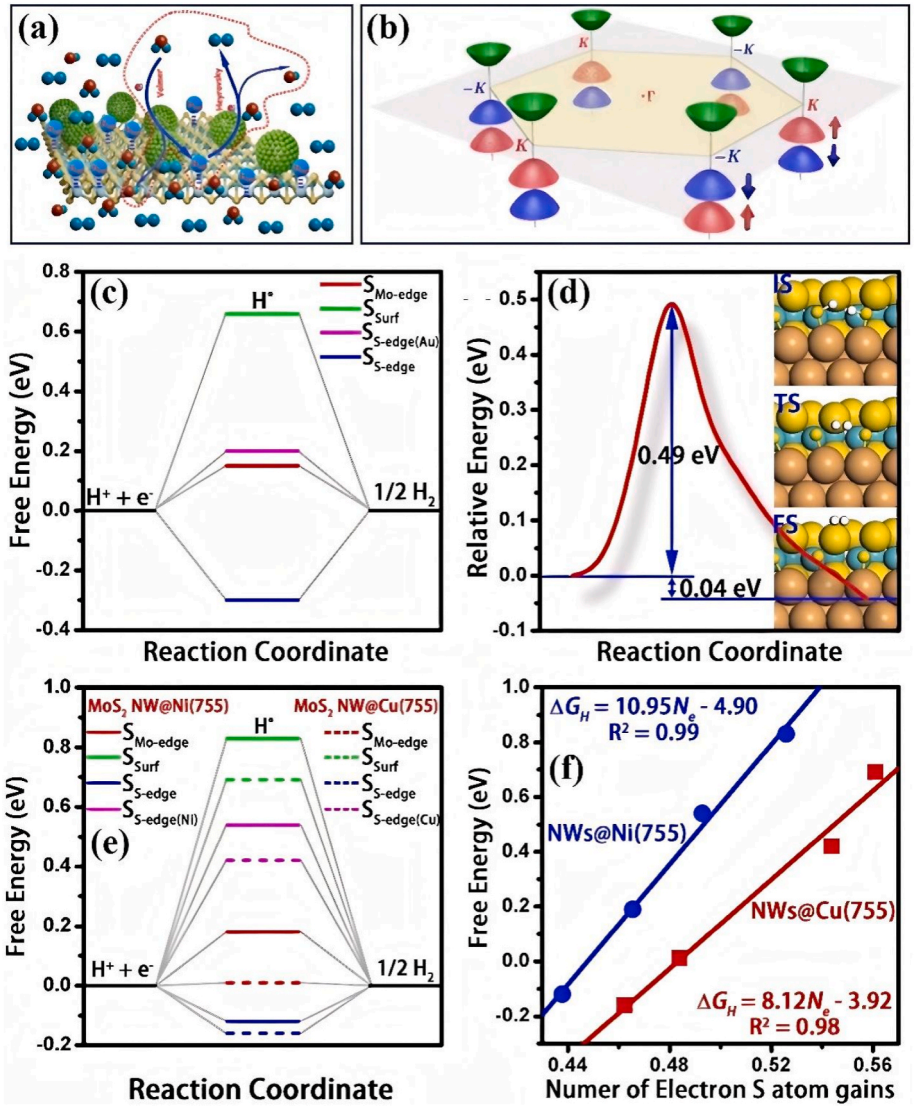


Fig. 8. (a) Mechanism of hydrogen evolution of MoS_2-NiMOF hybrids [43]. (b) Schematic diagram of the band structure of MoS_2 showing six valleys and opposite spin-orbit splitting of the valence band at the K and -K points [84]. (c) Calculated ΔG_H diagram for hydrogen adsorption for different S sites in MoS_2 NWs@Au (755), MoS_2 NWs@Ni (755) and MoS_2 NWs@Cu (755) [43]. (d) Minimum energy for Tafel reaction on SMo-edge sites at initial state (IS), transition state (TS), and final state (FS) [43]. (e,f) Calculated ΔGH as a function of number of electron S atom gains (Ne) for MoS_2 NWs@Ni (755) and MoS_2 NWs@Cu (755). Golden, blue, bronze, yellow, cyan, and white spheres represent Au, Ni, Cu, S, Mo, and H atoms [43]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

providing new approaches for developing efficient and low-cost clean energy technologies [130].

5.3.1. Catalytic activity of the edge site

The catalytic activity of the edge site is central to the efficient performance of MoS_2 in electrocatalytic HER [319]. Compared with the basal plane, the edge site of MoS_2 exhibits significantly higher catalytic activity due to its unique electronic structure and unsaturated coordination environment [320]. A better understanding of the structural characteristics, electronic state distribution, and their influence on HER performance at the edge sites is the key to designing efficient MoS_2--based catalysts.

(1) Structural characteristics of marginal sites

The edge sites of MoS_2 mainly include Mo-edge and S-edge, and their catalytic activity is derived from the unsaturated coordination environment and exposed active atoms [23]. Mo-edge: The Mo atom usually appears in a coordination unsaturated state at the edge and has a high d-electron density, which can effectively adsorb hydrogen ions (H^+) and promote their reduction to hydrogen (H_2). S-edge: The unsaturated coordination environment of the S atom at the edge allows it to participate in hydrogen adsorption and dissociation, but its activity is generally lower than that of the Mo-edge. Theoretical calculations show that the hydrogen adsorption free energy (ΔG_{H^*}) of the Mo-edge and S-edge is close to zero, which makes them the main active sites of HER [23]. In contrast, the basal surface of MoS_2 exhibits lower catalytic activity due to the deviation of ΔG_{H^*} from zero.

(2) Effect of electronic structure on the activity of edge sites

The catalytic activity of the edge site is closely related to its electronic structure. The edge site of MoS_2 has a unique distribution of d-electronic states, and its catalytic performance can be explained by the d-band center theory: D-band center theory: The d-band center position of the edge site determines the strength of its interaction with hydrogen adsorption [321]. When the center of the d-band is close to the Fermi level, the hydrogen adsorption capacity of the edge site is optimal ($\Delta G_{H^*} \approx 0$), resulting in the best HER performance. The results show that the center of the d-band of the Mo-edge is closer to the Fermi level, so its catalytic activity is higher than that of the S-edge [322]. In addition, the phase structure of MoS_2 also has a significant effect on the electronic state distribution of the edge sites. For example, the MoS_2 edge site of the metallic 1T phase exhibits higher intrinsic catalytic activity due to higher electron density and better d-band center position [323]. However, the edge site of the 2H phase of the semiconductor has relatively weak catalytic activity due to its low electron density [23].

(3) Differences in activity of different marginal sites

There are significant differences in the catalytic activity of Mo-edge and S-edge in HER, which is mainly due to their electronic structure and hydrogen adsorption properties: Mo-edge: Mo-edge is active from its unsaturated d-electronic state, which can effectively adsorb and activate hydrogen ions [324]. Theoretical and experimental studies have shown that the ΔG_{H^*} of the Mo-edge is closer to zero, so its HER activity is significantly higher than that of the S-edge. S-edge: The activity of the S-edge mainly depends on its unsaturated sulfur atoms, but because its electronic state distribution is not as ideal as that of the Mo-edge, its hydrogen adsorption capacity is weak, resulting in relatively low HER activity [325]. In addition, the activity of the edge site is also affected by the orientation of the crystal plane. For example, theoretical studies have shown that the (10-10) and (10-11) planes of MoS_2 exhibit superior HER performance due to higher edge site density.

(4) Regulation strategy of marginal site activity

In order to further improve the catalytic activity of the MoS_2 edge site, researchers have proposed a series of regulatory strategies, including structural engineering, electronic structure optimization, and surface modification [23]. i) Structural engineering: Vertically oriented nanosheet arrays: By constructing vertically oriented MoS_2 nanosheets, the exposure density of edge sites can be maximized, thereby improving catalytic activity. Surface finishing Functionalization: The catalytic activity of functional molecules or metal nanoparticles can be further enhanced by the introduction of functional molecules or metal nanoparticles at the edge sites. For example, the MoS_2 edge site loaded with Pt nanoparticles exhibits significantly enhanced HER performance [264].

(5) Association between edge site activity and HER performance

The activity of the edge site directly determines the HER performance of MoS_2. The results show that the density of the edge site is positively correlated with the performance of the HER: the higher the density of the edge site, the lower the overpotential of the catalyst and the greater the current density [326]. In addition, the optimization of the electronic structure of the edge site (e.g., the manipulation of the center position of the d-band) can significantly reduce the hydrogen adsorption free energy, thereby further improving the HER performance.

The edge site of MoS_2 exhibits excellent HER catalytic activity due to its unique structural and electronic properties [327]. Through strategies such as structural engineering, electronic structure optimization, and surface modification, the activity of edge sites can be further improved. However, there are still some challenges in the current research on the activity of edge sites, such as the activity change and stability of edge sites under dynamic conditions [23]. In addition, the development of atomic-level precision control technology could provide important guidance for the design of efficient and stable MoS_2-based HER catalysts.

5.3.2. Methods to increase the amount of edge sites

Several methods have been developed to increase the number of edge sites in the MoS_2. Nanostructuring of MoS_2 is an effective strategy to enhance its electrochemical performance by significantly increasing the material's specific surface area, thereby exposing more active edge sites [14,328]. Various nanoscale morphologies, such as MoS_2 nanosheets, nanowires, and nanotubes, have been developed to maximize the exposure of these edge sites, which are critical for catalytic and electrochemical activities [328,329]. The given images further illustrate the impact of nanostructuring on the electrochemical performance of MoS_2. Fig. 8c shows the free energy profile for the HER on different sites of MoS_2 [43], highlighting the lower free energy barrier at the edge sites compared to the surface sites [330]. This suggests that edge sites are more active for the HER. Fig. 8d-f compares the free energy profiles for HER on MoS_2 supported on different metal substrates (Ni and Cu) [43]. The results indicate that metal substrates can further lower the free energy barrier, particularly at the edge sites, enhancing the catalytic activity of MoS_2.

Specifically, by comparing the free energy distribution of MoS_2 to HER loaded on different metal substrates (Ni and Cu), it can be found that the metal substrate can further reduce the free energy barrier, especially at the edge, thereby enhancing the catalytic activity of MoS_2. Fig. 8d shows the minimum energy of the SMo-edge site in the initial state (IS), transition state (TS), and final state (FS) of the Tafel reaction [43]. Fig. 8e and f calculates the relationship between ΔG_H and the number of electron S atoms gain (Ne) for MoS_2 NWs@Ni (755) and MoS_2 NWs@Cu (755), respectively. Among them, gold, blue, bronze, yellow, cyan, and white spheres represent the Au, Ni, Cu, S, Mo, and H atoms, respectively [43]. These results reveal the mechanism of the influence of metal substrates on the catalytic activity of MoS_2, especially the enhancement of the activity of edge sites, and provide an important basis for optimizing the performance of MoS_2-based catalysts.

For instance, exfoliated MoS_2 nanosheets interspersed with MoS_2 quantum dots have been shown to exhibit enhanced activity due to their increased surface area and edge site density [329]. Similarly, selective activation of MoS_2 grain boundaries has been demonstrated to further improve its electrochemical performance by targeting specific active sites [328]. Fig. 8f presents a linear relationship between the free energy change (ΔG_{H^*}) and the number of electrons gained by sulfur atoms in MoS_2 supported on Ni and Cu [43]. The high correlation coefficients ($R^2 = 0.99$ and 0.98) indicate that the number of electrons gained by sulfur atoms is a critical factor in determining the HER activity of MoS_2. These advancements highlight the potential of nanostructured MoS_2 in applications requiring high surface area and active site accessibility [328–330].

Introducing defects, such as MoS_2 or dislocation, can create new edge sites and enhance their catalytic activity. Besides, using an intercalation agent or chemical expansion agent, the distance between MoS_2 layers can be expanded to make the internal edge sites more accessible [331–333]. Morphology in MoS_2 structures with open-edge sites can be directly affected by controlling the conditions in the synthesis process [334]. Furthermore, the chemical stripping method can produce single or few-layer MoS_2, while the epitaxial growth technology can be used to grow MoS_2 films with specific crystal surface exposure [335,336]. MoS_2 can effectively increase the number of edge sites through these methods, thus improving its performance in the electrocatalytic hydrogen evolution reaction [337,338]. However, implementing these strategies requires precise control and optimization to ensure that the prepared materials have high stability and excellent catalytic properties [339]. Moreover, further research and technological innovations are needed to overcome these challenges to achieve the widespread application of MoS_2 in hydrogen energy.

5.3.3. Deep encapsulation of edge sites

Edge sites of MoS_2 typically have high catalytic activity, but in actual materials, these sites may be difficult to effectively utilize by reactants due to deep embedding. Deep embedding mainly stems from the following two aspects: first, during the synthesis of MoS_2, the edge sites may be covered or shielded by inactive materials (such as residual precursors and surface adsorbents) [340]; The second is that the microstructure of the material is not properly designed, such as too close stacking or irregular topography, resulting in some edge sites being embedded in the material and unable to directly contact the reactant molecules in the electrolyte. This deep embedding significantly reduces the actual utilization of the edge site, thus limiting the overall performance of the catalyst [341]. In response to this problem, some effective solutions have been proposed in recent years. For example, techniques such as plasma etching or electrochemical activation can selectively remove the inactive material that overlays the edge sites, thus exposing more active sites [342]. In addition, the rational design of nanostructures (such as porous structures or hollow structures) can also effectively reduce the embedding phenomenon of edge sites. For example, porous MoS_2 nanosheets prepared by the template method can significantly increase the exposure density of edge sites and enhance the mass transfer capacity of reactants [343].

5.3.4. Limitations of 2D interlayer stacking on edge exposure

The two-dimensional layered structure of MoS_2 has a strong van der Waals force, which leads to the formation of multi-layer stacked structures during the synthesis process [344]. This interlayer stacking not only reduces the specific surface area of the material but also severely limits the exposure of edge sites, thereby weakening HER performance. Specifically, interlayer stacking results in some edge sites being buried in the interlayer interface, making it difficult to contact the reactants [345]. In addition, the stacked structure can create a bottleneck in electron transport, further reducing the overall conductivity and activity of the catalyst. In order to address the limitation of interlayer stacking on edge exposure, researchers have proposed a variety of nanoengineering strategies. For example, vertically oriented MoS_2 nanosheet arrays are an effective structural design that can significantly reduce interlayer stacking effects while maximizing the exposure density of edge sites by growing MoS_2 nanosheets vertically on the substrate [346]. In addition, the use of intercalation strategies (such as the introduction of metal ions or organic molecules) can effectively control the layer spacing and reduce the effect of interlayer stacking, thereby improving the accessibility of edge sites.

5.4. Electrical conductivity of MoS_2

Electrical conductivity is one of the key physical properties that affect the performance of MoS_2 as a catalyst for electrocatalytic HER [347,348]. Different MoS_2 crystal phases exhibit significantly different conductance directly related to their catalytic activity and efficiency [279,349].

5.4.1. Conductivity limitation of 2H–MoS_2

2H–MoS_2 is the most common crystalline phase of MoS_2, characterized by a lamina-like structure with hexagonal symmetry, as depicted in Fig. 9a [350]. This phase is a semiconducting material with a wide band gap, typically ranging from 1.2 to 1.8 eV [351], which results in low intrinsic conductivity. The enormous energy required to excite electrons from the valence band to the conduction band limits the number of charge carriers (electrons and holes) [350,352–354]. This low conductivity poses a challenge for electrocatalysis, as it hinders efficient electron transport and reduces catalytic performance despite the superior catalytic activity of 2H–MoS_2 at its edge sites [355–357]. Phase engineering, such as the transformation between the semiconducting 2H phase and the metallic 1T/1T' phase, has been explored to address these limitations. Optical reflectance spectra, shown in Fig. 9b [350], reveal that the 2H phase exhibits excitonic features. In contrast, the 1T/1T' phase displays a flat spectral profile, with the latter being generally less reflective, although sample-to-sample variations exist [85–87,358].

In situ Raman spectroscopy measurements, depicted in Fig. 9c [350], demonstrate the dynamics of the 1T/1T' to 2H phase transformation during laser annealing at 364 K, with characteristic Raman modes of the 1T/1T' phase (e.g., the 155 cm^{-1} mode) decreasing in intensity, while those of the 2H phase increase. The evolution of Raman spectra highlights the transition from the initial state (black) to the intermediate state (blue) and finally to the 2H phase (red), with the background continuum also increasing during annealing [350,352–355]. The Kinetics of the phase transition, shown in Fig. 9d [350], align with a first-order rate law, while the Arrhenius plot in Fig. 9e [350], provides insights into the temperature dependence of the transformation rate [350,352–355]. These results collectively underscore the importance of understanding the phase transformation dynamics and conductivity limitations of MoS_2 to optimize its structure and properties for enhanced electrocatalytic applications.

The poor intrinsic conductivity of 2H–MoS_2 directly impacts its commercial viability for HER. In industrial-scale electrolysis, high overpotentials resulting from low conductivity lead to significant energy losses, increasing the operational costs of hydrogen production [359]. For instance, at current densities exceeding 500 mA/cm^2, the energy efficiency of MoS_2-based electrolyzers may fall short of competitors like platinum-based catalysts, hindering economic feasibility [360]. Thus, addressing conductivity limitations is critical to reducing the levelized cost of hydrogen (LCOH) and enabling widespread commercialization.

5.4.2. High conductivity of 1T-MoS_2 and its stability

In contrast to 2H–MoS_2, 1T-MoS_2 is a metastable metallic phase with octahedral symmetry [43,357,361]. Its electronic structure leads to high conductivity because the band gap of the 1T phase is minimal and can even be approximately zero, which allows the electrons to move freely, thus providing higher conductivity [362,363]. This high conductance is

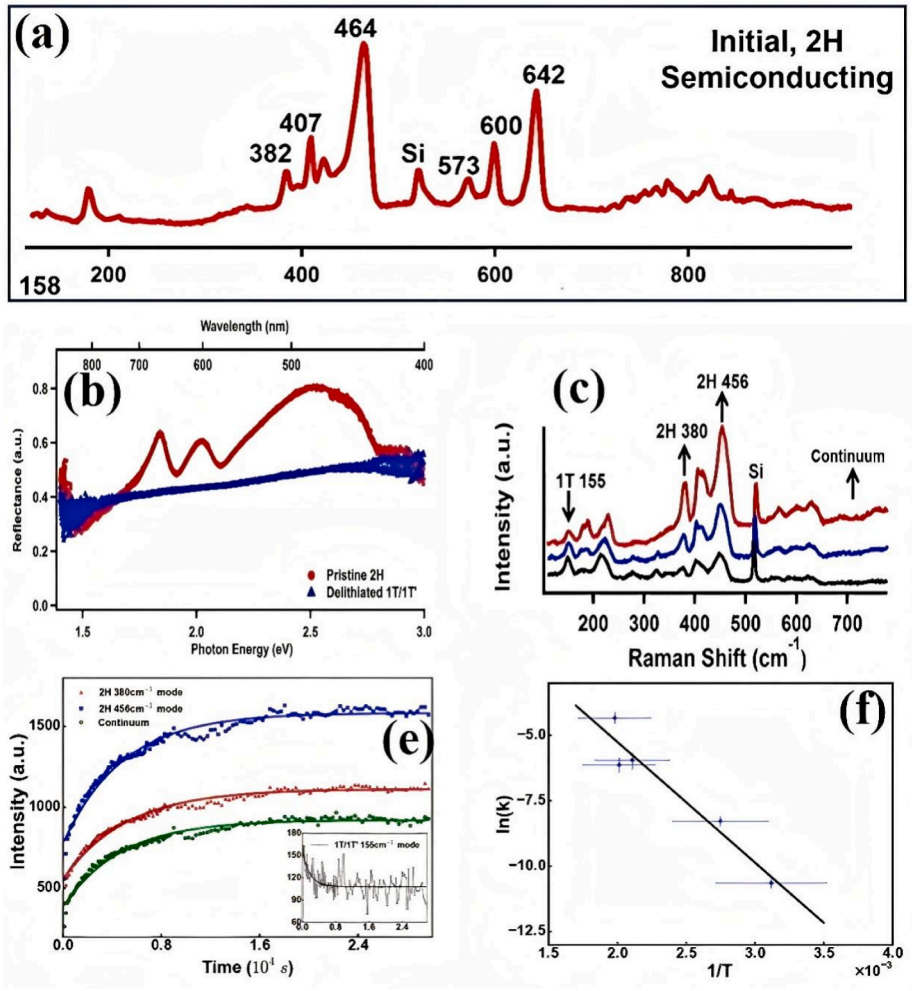


Fig. 9. (a)Raman spectra of MoS_2 polymorphs for Stokes scattering induced by weak laser excitation at 633 nm. Initial 2H MoS_2 [350]. (b) In situ Raman spectroscopy measurements of MoS_2 crystals during the 1T/1T′ to 2H phase transformation [350]. (c) Evolution of Raman spectra during 633 nm laser annealing at a calculated temperature of 364 K: initial state (black), intermediate state (blue), and final state (red) [350]. (d) Examples of phase transition kinetics based on different Raman modes for annealing at 364 K and a comparison with a first-order rate law [350]. (e) Arrhenius plot for the rate of the 1T/1T′ to 2H MoS_2 structural phase transformation [350]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

very advantageous for HER because it facilitates the rapid transport of electrons from the electrode to the catalyst's active site [357,364]. However, the stability of the 1T-MoS_2 is a crucial issue. At room temperature and atmospheric pressure, 1T-MoS_2 is often less stable than 2H–MoS_2 and is prone to transition back to the 2H phase in the environment [86,91]. This transition leads to decreased conductivity and diminished catalytic activity [365]. Critically, the metastability of the 1T phase originates from its higher surface energy due to octahedral coordination and lattice distortions (e.g., shortened Mo–Mo bonds ~2.75 Å vs. 3.15 Å in 2H–MoS_2), which create a low energy barrier (~0.03 eV/atom) for phase transformation [366]. This makes 1T-MoS_2 susceptible to even minor environmental fluctuations (e.g., temperature changes or electrolyte interactions) [367]. Existing stabilization strategies, such as chemical doping or heterostructure construction, often introduce unintended defects (e.g., interfacial stress or reduced active site density) and face challenges in scalability and cost-effectiveness for industrial applications [368]. For instance, doping may compromise structural integrity, while heterostructures can suffer from interface instability under long-term operational conditions. However, despite the high conductivity of 1T-MoS_2, its stability problems in practical applications limit its potential as an HER catalyst [329]. To address this issue, researchers are exploring various ways to stabilize 1T-MoS_2, including chemical doping [279,369], surface modification [370–373], preparation of 1T/2H heterostructures [86], and preparation of 1T-MoS_2 under specific synthetic conditions [43,374]. Through these strategies, the high conductance 1T-MoS_2 can be maintained to some extent while improving its stability and catalytic activity in HER [375,376]. Future solutions should prioritize atomic-level precision engineering, such as developing interface strain control (e.g., core-shell structures) to suppress phase transition, integrating in-situ characterization techniques (e.g., operando TEM or XAS) to monitor real-time phase dynamics, and exploring self-healing mechanisms (e.g., electrochemical regeneration) [377]. Additionally, machine learning-assisted screening of novel stabilizers (e.g., rare-earth dopants) and standardized testing protocols (e.g., accelerated aging at >500 mA cm^{-2}) are essential to bridge the gap between laboratory research and commercial deployment [378]. Advances in these studies are crucial to bringing MoS_2 to practical applications, but further innovation and research are still needed to overcome these challenges.

Despite its high conductivity, the metastable nature of 1T-MoS_2 poses severe challenges for long-term commercial application. The tendency to revert to the semiconducting 2H phase under operational conditions causes rapid degradation of catalytic activity, necessitating frequent catalyst replacement or regeneration [379]. This instability increases maintenance costs and compromises system reliability, which are paramount for industrial electrolyzers requiring continuous

operation over thousands of hours [380]. Therefore, enhancing the stability of 1T-MoS_2 is essential to achieving durable and cost-effective hydrogen production technologies.

5.5. Defect engineering

Defect engineering is an effective strategy to improve the catalytic performance of MoS_2 in the electrocatalytic HER [215]. By consciously introducing and controlling defects, the electronic structure and surface properties of MoS_2 can be significantly altered, thereby enhancing its catalytic activity [196,381]. Defect types include vacancies [186,347,382,383], doping [240,384,385], dislocations [386–388], etc. These can serve as active sites or change the electron density to improve the catalytic efficiency.

The quantification of defects is crucial for understanding their impact on catalytic performance. Defect concentration, such as sulfur vacancy density, can be quantified using various characterization techniques [389]. For instance, X-ray photoelectron spectroscopy (XPS) can analyze the chemical states and relative concentrations of defects, while electron paramagnetic resonance (EPR) is sensitive to paramagnetic defects like sulfur vacancies [390]. Raman spectroscopy can indirectly assess defect density through changes in peak positions and intensities. As shown in Fig. 10a–b, the HER performance of MoS_2 with different sulfur vacancy concentrations (MoS_2-n) demonstrates a quantitative correlation between defect density and catalytic activity. Theoretical calculations, such as density functional theory (DFT), can also predict optimal defect concentrations, e.g., a sulfur vacancy concentration of 12.5% minimizes the hydrogen adsorption free energy (ΔG_H) [391]. Advanced methods like scanning tunneling microscopy (STM) allow atomic-scale imaging of defects, enabling precise quantification of their distribution [392]. By combining these techniques, defect engineering can be systematically optimized for enhanced HER performance.

5.5.1. Introduction of defects to enhance catalytic activity

In the electrocatalytic HER, introducing defects in MoS_2 has effectively increased the number of catalytic active sites and altered the electronic structure, thereby significantly improving HER performance [347,393,394]. As illustrated in Fig. 10a [395], MoS_2 with varying sulfur vacancy concentrations (denoted as MoS_2-0, MoS_2-0.5, MoS_2-1.0, MoS_2-1.4, MoS_2-2.0) exhibits distinct catalytic activities, with MoS_2-1.4 demonstrating the lowest overpotential, indicating its optimal HER performance. Similarly, Fig. 10b shows the Tafel slopes of MoS_2 with different sulfur vacancy concentrations, where MoS_2-1.4 achieves the lowest Tafel slope of 105.2 mV dec^{-1}, highlighting its superior electrocatalytic kinetics [395].

Sulfur vacancies are crucial in increasing the active sites on the MoS_2 surface, facilitating the adsorption and reaction of hydrogen atoms on the catalyst [383,395–397]. Additionally, introducing non-metallic elements, such as nitrogen or carbon, through doping strategies can further regulate the electronic properties of MoS_2 [207]. This regulation enhances catalytic activity by providing additional electrons or creating new active centers and improving charge distribution and migration [398,399]. For instance, carbon-nitrogen deposition has been shown to create partial sulfur vacancies, resulting in enhanced HER performance [400]. These structural modifications increase the density of active sites and optimize charge transfer and electronic conductivity, thereby boosting the overall electrocatalytic performance of MoS_2-based materials [394,401]. The combination of sulfur vacancies, metal nanoparticle decoration, and non-metal doping provides a powerful strategy for achieving highly efficient HER catalysts [347,383,393,395–397,399].

5.5.2. Challenges of controlling defect types, quantities, and distributions

Although introducing defects is an effective means to improve the catalytic performance of MoS_2, controlling defects' type, number, and distribution can still be a technical challenge [387,402]. Introducing non-randomness of defects requires precise synthetic methods and conditional control to ensure that the defects can exist in a manner conducive to the catalytic reaction. For example, excessive defects may destabilize the material structure, reducing its stability and lifetime in practical applications [34,331]. Furthermore, different types of defects may have different effects on the catalytic activity, so experimental and theoretical studies are needed to optimize the introduction of the defects (Fig. 10c) [387].

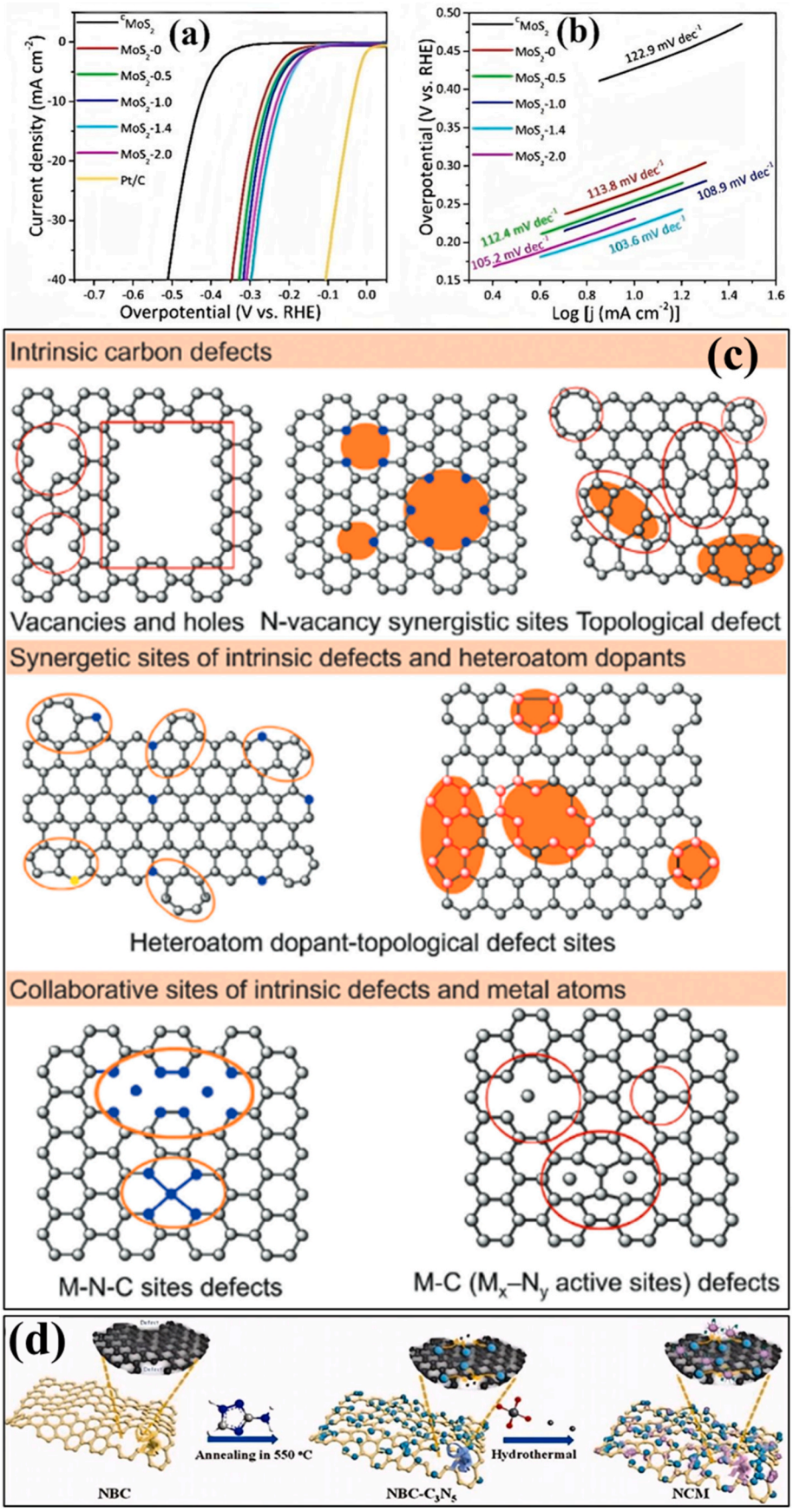
Temperature, pressure, chemical dose, and environment during the synthesis can all influence defect formation [14,404]. For example, chemical vapor deposition (CVD) techniques can be used to precisely control the introduction of defects in layered materials, while methods such as ion injection or plasma processing have also been used to introduce specific types of defects in MoS_2 [405]. In addition, advanced characterization techniques such as transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) are key tools for understanding and controlling the distribution of defects [79,406]. Therefore, defect engineering provides a promising approach to improve the performance of MoS_2 in electrocatalytic hydrogen evolution reactions, but further studies are needed to control the precise introduction and distribution of defects. Through these studies, an understanding of the specific effects of defects on the catalytic properties of MoS_2 can be better obtained to design more efficient catalysts [387,407,408].

5.5.3. The role of edge defects

An edge defect is an abnormal or absent arrangement of atoms in the MoS_2 edge site, usually manifested as a vacancy, rearrangement, or alteration of the coordination environment of the marginal Mo or S atoms. The introduction of edge defects can significantly alter the electronic state and chemical reactivity of edge sites. For example, marginal Mo vacancies lead to a redistribution of local electron density, making the surrounding Mo atoms exhibit stronger metallicity, thereby enhancing their adsorption capacity for H^+. In addition, the introduction of marginal S vacancies can expose more Mo atoms, making them new active sites, thereby improving the overall catalytic activity of the edge. From a theoretical calculation point of view, edge defects can optimize HER performance by adjusting the hydrogen adsorption free energy (ΔG_{H^*}). For example, studies have shown that the introduction of marginal Mo vacancies can bring ΔG_{H^*} closer to zero, thereby significantly reducing the HER reaction energy barrier. In addition, edge defects can also enhance the conductivity and electron migration capacity of the edge site, which has important implications for improving the overall performance of the catalyst.

5.5.4. Role of in-plane defects

In-plane defects refer to the absence, substitution, or lattice distortion of atoms on the MoS_2 base plane, mainly including S vacancies, Mo vacancies, doped atoms, and lattice dislocations. Although the intrinsic activity of the MoS_2 base surface is low, the introduction of in-plane defects can significantly change its electronic structure, making it exhibit certain catalytic activity. For example, the introduction of S vacancies in the plane will lead to the reconstruction of the local electronic state, so that the originally inert Mo atoms on the base surface have a certain catalytic ability. In addition, in-plane defects can also be used as channels for electron transfer, facilitating the electron coupling between the edge site and the substrate, thereby improving the overall catalytic performance. Another important role of in-plane defects is to enhance the adsorption capacity of MoS_2 and the chemical reactivity of the surface. For example, the in-plane S vacancy can be used as an adsorption site for reactant molecules, thereby promoting the activation and reduction of H^+. In addition, by introducing doped atoms (such as Ni, Co, Fe, etc.) or constructing heterostructures, the electronic state distribution of in-plane defects can be further optimized, thereby improving HER performance.



(caption on next page)

Fig. 10. (a) LSV curves [395], and (b) Tafel curves of the synthesized MoS_2 and MoS_2-n (n = 0, 0.5, 1.0, 1.4 and 2.0) catalysts. Electrocatalytic HER performance of different MoS_2 samples [395]. (c) Schematic illustration of typical carbon defects involving intrinsic carbon defects (such as vacancies and holes, edge defects, and topological defects); intrinsic defect and heteroatom dopant synergetic sites (N-vacancy and heteroatom-topological defect sites); collaborative sites of intrinsic defects and metal atoms (M—N—C defective sites, and M − C sites) [387]. (d) Fabricating process of NCM [403].

5.5.5. Synergistic mechanism of edge defects and in-plane defects

Although edge defects and in-plane defects each have a significant impact on the HER performance of MoS_2, the synergy between them can significantly improve the overall performance of the catalyst. The synergistic mechanism of edge defects and in-plane defects is mainly reflected in the following aspects.

(1) Coordinated regulation of electronic structure

Edge defects and in-plane defects can jointly regulate the electronic structure of MoS_2 through interaction. For example, the introduction of in-plane S vacancies can alter the electronic state distribution of the edge site, making it exhibit stronger metallicity and higher catalytic activity. In addition, in-plane defects can act as a bridge for electron transfer, promoting the electronic coupling between the edge site and the substrate, thereby improving the overall electron migration capacity.

(2) Synergistic enhancement of active sites

The introduction of in-plane defects can increase the exposure density of edge sites, thereby significantly improving the overall activity of MoS_2. For example, in-plane S vacancies can induce the remodeling of edge sites, so that more Mo atoms are exposed at the edges and become new active sites. In addition, the synergistic effect of edge defects and in-plane defects can optimize hydrogen adsorption free energy (ΔG_{H^*}), which can further improve HER performance.

(3) Synergistic promotion of reactant mass transfer

In-plane defects often introduce porous structures or channels, which can significantly improve the mass transfer capacity of reactants. For example, in-plane defects can promote the diffusion of H^+ in the electrolyte to the edge site, thereby improving the efficiency of the catalytic reaction. In addition, the synergistic effect of edge defects and in-plane defects can enhance the hydrophilicity of MoS_2, thereby further improving its dispersion and stability in the electrolyte.

(4) Synergistic improvement of stability

The synergistic effect of edge defects and in-plane defects can also enhance the structural stability of MoS_2. For example, the introduction of in-plane defects can alleviate the stress concentration of edge sites, thereby reducing the reconstitution or inactivation of edge sites during reactions. In addition, the synergistic effect of edge defects and in-plane defects can enhance the antioxidant capacity of MoS_2, thereby improving its stability in long-term operation.

5.6. Electrochemical limitations

The stability of MoS_2 in electrocatalytic HER is a critical factor in determining its feasibility for practical applications [133,192,409]. Advances in synthesis techniques and material engineering are essential to address these stability challenges and unlock the full potential of MoS_2 as an electrocatalyst for HER applications [133,192,410].

The electrochemical degradation of MoS_2 under operating conditions involves complex interplay between conductivity loss, chemical instability, and structural phase transitions [142]. Key degradation mechanisms include: (i) Anodic oxidation of sulfur edges at potentials above 0.2 V vs. RHE, leading to sulfate formation and active site loss [411]; (ii) Proton intercalation-induced lattice expansion and layer detachment during cathodic polarization [412]; (iii) Conductivity degradation through 1T-to-2H phase transition under electrical bias; and (iv) Interfacial corrosion accelerated by bubble-induced mechanical stress. These processes collectively contribute to performance decay, particularly at industrial current densities (>500 mA cm^{-2}) where operational stability remains a major challenge.

5.6.1. Oxidation issues at the edge sites

In the electrocatalytic process, the edge sites of MoS_2 play a critical role in determining its catalytic activity; however, these sites are highly susceptible to oxidation during the catalytic process, which can lead to a significant decrease in activity (Fig. 10d) [403]. During the HER, MoS_2 is exposed to the electrolyte. At high potentials, the sulfur atoms at the edge sites are vulnerable to attack by oxidizing species, forming sulfates or other oxides [413]. This oxidation process not only reduces the number of effective catalytic sites [414], but can also detach the catalytic layer, further compromising the material's performance, as depicted in Ref. [414]. Such degradation of the edge sites is a major challenge for maintaining the long-term stability of MoS_2-based catalysts. The oxidation kinetics follow a potential-dependent pathway where sulfur vacancies act as initiation sites for oxidative etching [415]. In-situ Raman studies reveal that edge oxidation accelerates above 0.3 V vs. RHE, with complete sulfur removal occurring within 100 cycles at 0.5 V [416]. This process is exacerbated by poor charge dissipation in semiconducting 2H–MoS_2, highlighting the conductivity-stability interdependence.

To address this issue, several strategies have been proposed to protect and stabilize the edge sites of MoS_2. These include introducing protective layers, such as nitrogen-doped carbon coatings, at the edge sites [314], using antioxidants to prevent oxidation [185,417], or employing advanced synthetic methods to enhance the intrinsic stability of the edge sites. Designing the electrolyte composition and optimizing operating conditions can also help suppress the oxidation of edge sites to a certain extent [185]. For example, Fig. 10d illustrates a process where nitrogen-doped carbon nanotubes (NBC) are combined with MoS_2 to form an NBC-C_3N_5 composite material through annealing at 550 °C followed by hydrothermal treatment, resulting in nitrogen-doped carbon-coated MoS_2 (NCM) [403]. The oxidation of edge sites poses a severe threat to the commercialization of MoS_2-based HER catalysts [158]. In industrial electrolyzers operating at high current densities (>500 mA/cm^2), oxidative degradation leads to rapid catalyst deactivation, necessitating frequent replacement or regeneration. This increases maintenance costs and system downtime, directly impacting the levelized cost of hydrogen (LCOH). For MoS_2 to compete with noble metal catalysts like Pt, its stability must exceed 10,000 h under dynamic conditions [418]; otherwise, the economic viability of large-scale hydrogen production is compromised [419]. Thus, addressing edge oxidation is not merely a materials science challenge but a critical barrier to market adoption.

5.6.2. 1T to 2H phase transition

The phase transition of MoS_2 significantly impacts its electrocatalytic properties [154]. The 1T phase MoS_2 is a metastable state with high electrical conductivity and catalytic activity, while the 2H phase is the most stable structural morphology [154,420]. During electrocatalysis, the 1T phase may gradually change to the 2H phase, and this transition will cause a decrease in electrical conductivity and a reduction of the active site, thus affecting the catalytic performance [154,421–423]. The phase transition follows first-order kinetics with an activation energy of 0.8-1.2 eV, accelerated by both electrochemical cycling and temperature

[424]. In-situ TEM studies show that phase initiation begins at grain boundaries and propagates inward, forming core-shell structures that impede charge transport [377]. The conductivity degradation correlates directly with phase transition extent, with 50% 1T-to-2H conversion resulting in 3-order-of-magnitude conductivity loss. Strategies to prevent the 1T to 2H phase transition include chemical doping, applied strain engineering, construction of composites, etc. [34,425,426]. Chemical doping can stabilize the lattice structure of the 1T phase by introducing foreign atoms [427,428]. Strain engineering changes the lattice parameters by applying mechanical stress to stabilize specific phase states [429,430]. Building composites such as MoS_2 heterostructures of the 1T/2H phase can exploit the synergistic effect between the two phases to improve the overall stability and catalytic properties [97,190,431]. Therefore, improving the stability of MoS_2 in HER requires comprehensively solving problems such as edge site oxidation and phase state transformation through material design and process optimization [159]. The practical implementation of these strategies will provide a solid foundation for applying MoS_2 in electrocatalytic hydrogen evolution reactions.

The instability of the metallic 1T phase during operation is a major commercialization hurdle for MoS_2. The transition to the semiconducting 2H phase under industrial conditions (e.g., fluctuating voltages or elevated temperatures) causes an irreversible loss in conductivity and activity, increasing overpotential and energy consumption [432]. In continuous electrolysis systems, this phase instability leads to performance decay, requiring costly catalyst regeneration or electrode replacement [130]. For MoS_2 to be viable in gigawatt-scale hydrogen production, strategies to stabilize the 1T phase must ensure longevity over years of operation, as even a 10% efficiency drop can render the technology economically unfeasible compared to alternatives [433]. Therefore, phase stability is not just a performance metric but a determinant of commercial scalability.

5.6.3. Interfacial degradation and chemical stability mechanisms

Beyond oxidative and phase instability, MoS_2 suffers from chemical degradation at catalyst-electrolyte interfaces. In acidic electrolytes, proton intercalation induces lattice expansion and layer separation, while alkaline conditions promote Mo dissolution through hydroxide complex formation [412]. Accelerated testing shows 40% activity loss after 100 h at pH 1, versus 25% loss at pH 13, indicating stronger acid vulnerability [434]. The degradation follows a logarithmic time-dependence, suggesting surface-passivation limited kinetics. Chemical stability is further compromised by sulfur mobility under operating potentials. In-situ XPS analyses reveal that sulfur vacancies migrate to form extended defects above −0.1 V vs. RHE [435], creating percolation paths for accelerated corrosion. This vacancy-driven degradation is particularly severe in 1T-MoS_2 due to its higher intrinsic sulfur mobility. Composite formation with conductive carbons or metal oxides can reduce vacancy migration rates by 70%, significantly extending operational lifetime [436]. These electrochemical degradation mechanisms collectively underscore the need for holistic stability engineering approaches that address both conductivity preservation and chemical stability enhancement simultaneously.

6. Synthesis methods for MoS_2

The synthesis method of MoS_2 has a decisive influence on its structure, performance, and application. Currently, researchers have developed various methods to synthesize MoS_2, including CVD [437,438], mechanical exfoliation [153,439], hydrothermal synthesis [440,441], solvent thermal synthesis [55], etc. Each method has unique advantages and limitations and is suitable for different application needs [442]. The synthesis of high-quality MoS_2 is the key to realizing its efficient application in the electrocatalytic HER.

6.1. Synthetic challenges of high-quality MoS_2

MoS_2 is a potential candidate to replace noble metal catalysts due to its unique layered structure and excellent HER performance [139]. However, the synthesis of high-quality MoS_2 still faces many challenges, including crystal phase control, layer number control, edge site optimization, defect engineering introduction, and large-scale fabrication [432]. These challenges have a direct impact on the structure, electronic properties, and catalytic performance of MoS_2 [443]. This section is dedicated to systematic analysis of difficulties in synthesizing high-quality MoS_2.

(1) The challenge of crystal phase control

MoS_2 has a variety of crystalline phases, among which the semiconductor 2H phase and the metallic 1T phase are the focus of research [142]. The 2H phase has high thermodynamic stability, but its basal intrinsic activity is low. The 1T phase is of interest due to its metallicity and high-edge activity. However, the 1T phase is easily converted to the 2H phase during the synthesis process, resulting in poor structural stability [444]. Therefore, the efficient synthesis and stability improvement of the 1T phase are the main difficulties at present. For example, chemical exfoliation and lithium-ion intercalation methods can obtain 1T phase MoS_2, but these methods are often accompanied by uncontrollable phase transitions and structural defects [445]. In addition, the mechanism of the influence of the proportional regulation of different crystalline phases on the catalytic performance is not fully understood, which further increases the complexity of crystalline phase control [446].

(2) The challenge of layer control

The catalytic performance of MoS_2 is closely related to the number of layers. Monolayer or multilayered MoS_2 typically exhibits superior HER performance due to its higher specific surface area and edge site density. However, in actual synthesis, it is still very challenging to precisely control the number of layers of MoS_2. For example, although the liquid phase exfoliation method can obtain single or few layers of MoS_2, its yield is low and the number of layers is unevenly distributed [447]. Although the CVD method can achieve controllable growth of layers, its growth process is complex and requires high equipment [448]. In addition, as the number of layers decreases, the thermodynamic stability of MoS_2 decreases, and it is prone to agglomeration or structural collapse.

(3) Challenge of marginal site optimization

The catalytic activity of MoS_2 is mainly derived from its edge site, while the intrinsic activity of the basal surface is low [449]. Therefore, how to maximize the number of edge sites during synthesis is the key to improving catalytic performance. However, the optimization of edge sites involves multiple challenges: on the one hand, traditional synthesis methods (such as hydrothermal or solvothermal) often result in interlayer stacking of MoS_2, which limits the exposure of edge sites [368]; On the other hand, the chemical environment of the edge site (such as the ratio of Mo-edge and S-edge) has a significant impact on the catalytic performance, but the regulatory mechanism is still not fully understood. In addition, the high activity of the edge site may cause it to dissolve or passivate during the reaction, which can affect the stability of the catalyst [450].

(4) Challenges introduced by defective engineering

Defect engineering is an important strategy to control the electronic structure of MoS_2 and improve the catalytic performance. For example, by introducing sulfur vacancies or doping heteroatoms, the electronic

state distribution and hydrogen adsorption-free energy of MoS_2 can be effectively controlled [451]. However, the introduction of defects is often accompanied by a compromise of structural integrity, which can lead to a decrease in the mechanical stability and conductivity of the catalyst [452]. In addition, precise regulation of the type, concentration, and distribution of defects remains a challenge. For example, too high a defect concentration can lead to catalyst deactivation, while an uneven defect distribution can lead to instability in performance [453].

(5) Challenges of large-scale preparation

Although high-quality MoS_2 can be prepared under laboratory conditions by a variety of methods (e.g., CVD, hydrothermal, liquid phase stripping, etc.), these methods still face many limitations in large-scale preparation [454]. For example, although the CVD method can achieve the controllable growth of high-quality monolayer MoS_2, its equipment cost is high and the preparation cycle is long, which makes it difficult to meet the needs of industrialization [455]. Although the hydrothermal method and the liquid phase stripping method are simple processes, their yields are low and the product uniformity is poor [456]. In addition, how to take into account the high edge site density, high conductivity, and structural stability of the material at the same time in the large-scale preparation process is also an urgent problem to be solved.

(6) Challenges in environmentally friendly synthesis processes

Many current synthesis methods of MoS_2 (e.g., lithium-ion intercalation) require the use of organic solvents or strong reducing agents, which may bring environmental pollution and safety hazards [457]. Therefore, the development of green and environment-friendly synthesis methods is an important direction in the future. For example, the synthesis of MoS_2 by hydrothermal or electrochemical methods is more environmentally friendly, but the precise control of the crystalline phase, number of layers, and edge sites in these methods is still a challenge [142].

(7) Challenges of structural uniformity and repeatability

In practice, the structural homogeneity and reproducibility of MoS_2 have an important impact on its catalytic performance [458]. However, due to the complexity of synthesis conditions (e.g., temperature, reaction time, precursor concentration, etc.), the structure and properties of MoS_2 tend to vary greatly from batch to batch. For example, a small change in the growth temperature in the CVD method may lead to a significant difference in the crystalline phase ratio, while a change in the reaction time in the hydrothermal method may affect the number of layers and the exposure of edge sites in the MoS_2 [459]. Therefore, how to achieve precise control of the synthesis process and high reproducibility of results are the key difficulties in the preparation of high-quality MoS_2.

(8) Challenge of stability under dynamic working conditions

In practical applications, MoS_2 catalysts need to maintain high efficiency and stable performance under dynamic conditions (e.g., high current density, long operation, etc.). However, due to the high activity of the edge site and the introduction of defects, MoS_2 may undergo dissolution, passivation, or structural reconstitution during the reaction, resulting in a decrease in catalytic performance [460]. Therefore, how to optimize the structural stability of MoS_2 while maintaining its high catalytic activity during the synthesis process is an urgent problem to be solved. Therefore, the synthesis of high-quality MoS_2 faces many challenges, such as crystalline phase control, layer number control, edge site optimization, defect engineering introduction, large-scale preparation, and stability improvement [319]. Future research should focus on the development of green, efficient, and controllable synthesis methods, combined with advanced characterization techniques and theoretical calculations, to deeply understand the structure-property relationship of MoS_2, and provide theoretical guidance and technical support for the design of high-performance HER catalysts [139].

6.2. Effect of different synthesis methods on defect type and concentration

The catalytic performance of MoS_2 is largely dependent on the number and properties of its edge sites, and the formation of these edge sites is closely related to the synthesis method of the material. By designing a rational synthesis strategy, the edge orientation, defect type, and distribution of MoS_2 can be effectively controlled, so as to optimize its electronic structure and catalytic activity.

6.2.1. Directional growth method regulating the edge orientation

Directed growth is an effective method to regulate the edge orientation of MoS_2 by controlling the direction of crystal growth. Due to the significant differences in the electronic structure and catalytic activity of MoS_2 edge sites (such as Mo-edge and S-edge) on different crystal planes, the directed growth method can improve the catalytic performance by selectively exposing the highly active edge sites. For example, by manipulating reaction conditions (e.g., temperature, precursor concentration, and atmosphere), vertically oriented growth of MoS_2 nanosheets can be achieved, exposing more edge sites to the catalytic reaction interface [461]. The results show that vertically oriented MoS_2 nanosheet arrays can not only significantly increase the density of edge sites, but also reduce the shielding of edge activity by the interlayer stacking effect, thereby enhancing the kinetic performance of hydrogen adsorption/desorption [462]. In addition, directed growth methods can selectively expose specific types of edge sites by manipulating the growth rate and direction of crystals. For example, under certain conditions, preferential growth of crystal planes with highly active Mo-edges can significantly improve catalytic performance [463]. This method provides new possibilities for the precise regulation of edge sites.

6.2.2. Edge site density control in vapor deposition

CVD is a common method for the preparation of high-quality 2D materials, and the edge site density of MoS_2 can be effectively controlled by controlling the key parameters in the deposition process [464]. Specifically, the reaction temperature, precursor concentration, carrier gas velocity, and substrate type in the CVD method have important effects on the crystal growth morphology and edge site distribution of MoS_2 [465]. At high temperatures, the growth of MoS_2 typically follows a "spiral growth" or "island growth" mechanism, both of which significantly affect the density of the edge sites. For example, by reducing precursor concentrations or regulating gas flow rates, interlayer stacking can be inhibited and the growth of monolayer or few-layer MoS_2 can be promoted, thereby increasing the exposure of edge sites [466]. In addition, the selection of substrates with specific lattice matches, such as sapphire or graphene, can induce ordered growth of MoS_2, further improving the density and uniformity of the edge sites. In recent years, researchers have also developed a multi-step CVD process that enables precise control of edge sites by introducing defect conditioning steps during the growth process, such as plasma treatment or atmosphere conditioning. For example, the introduction of hydrogen or hydrogen sulfide atmospheres during CVD growth can introduce specific defect types (e.g., sulfur vacancies or Mo vacancies) into MoS_2 crystals, thereby regulating the electronic structure and catalytic activity of edge sites [460].

Moreover, CVD techniques can be extended to synthesize one-dimensional (1D) MoS_2 nanostructures, such as nanorods and nanotubes, which exhibit unique geometric properties that further enhance edge site density and catalytic performance [467]. For instance, by optimizing CVD parameters (e.g., using template-assisted growth or

controlled gas-phase reactions), 1D MoS_2 nanotubes can be fabricated with high curvature edges, as discussed in Section 4.1.2. These curved structures induce local electronic state reorganization and strain effects, which optimize the hydrogen adsorption free energy (ΔG_H) and improve hydrogen evolution reaction (HER) activity. Additionally, 1D MoS_2 nanorods or nanowires provide directional electron transport pathways, as highlighted in Section 7.1, reducing charge transfer resistance and increasing the accessibility of active sites. The enhanced catalytic behaviour of 1D MoS_2 structures, such as the superior HER performance of MoS_2 nanotubes compared to planar films (Fig. 4c–d), demonstrates the importance of nanostructural engineering in vapor deposition methods for maximizing edge site utilization [467].

6.3. Standardization and laboratory to large-scale application

Scaling is successfully transferring materials from a laboratory scale to industrial-grade applications. For MoS_2, this process is crucial because it determines the practical application potential of the material in the electrocatalytic HER [468,469]. MoS_2 has demonstrated excellent catalytic performance at a laboratory scale, but many technical and economic challenges need to be overcome in the industry [470]. Laboratory-scale studies usually focus on exploring basic properties and catalytic mechanisms of materials, while cost, stability, repeatability, and productivity need to be considered in large-scale applications. Here are the main gaps between laboratory size and large-scale applications.

- Cost-effectiveness: At a laboratory scale, researchers can prepare MoS_2 using high-purity, high-cost raw materials and equipment [14,471]. However, raw materials and production costs must be reduced on an industrial scale to ensure economic viability. Therefore, developing low-cost synthetic methods and sources of raw materials is necessary.
- Synthetic methods: Although CVD and other methods commonly used in the laboratory can prepare high-quality MoS_2, these methods are often unsuitable for mass production [472]. Therefore, developing scalable synthesis techniques such as liquid phase deposition or mechanical stripping are needed [350,353,354].
- Material consistency and repeatability: At the laboratory scale, prepared MoS_2 samples tend to have good reproducibility and reproducibility [473]. However, in mass production, maintaining the consistency of material performance is a challenge and requires precise control of various parameters in the production process.
- Long-term stability: MoS_2 The catalytic performance demonstrated in the laboratory must be maintained in long-term operation and industrial environments [474]. This requires MoS_2 with good chemical and structural stability, resisting the influence of prolonged electrochemical cycles and environmental factors [14].
- Scale expansion: Small batch preparation in laboratories is often difficult to enlarge directly. Large-scale applications require optimizing the production process to achieve continuous production with high efficiency and low cost.
- Environmental impact: Large-scale production of MoS_2 may pose environmental problems, such as waste disposal and energy consumption [475]. Therefore, environmentally friendly production processes must be developed to reduce environmental impacts. The challenges of poor intrinsic conductivity and long-term stability are particularly critical for commercialization. Low conductivity (e.g., in semiconducting 2H–MoS_2) leads to high overpotentials and energy losses during electrolysis, directly increasing the levelized cost of hydrogen (LCOH) in industrial-scale systems. Similarly, instability issues such as edge oxidation or phase transition (e.g., 1T to 2H) cause rapid catalyst degradation, necessitating frequent replacement and raising maintenance costs [476]. These factors undermine the economic viability and reliability of MoS_2-based electrolyzers, which must operate continuously for thousands of hours under harsh conditions [477]. Addressing these challenges is essential to achieve cost-competitive hydrogen production and enable widespread adoption of MoS_2 in the energy market. To address these gaps, interdisciplinary research collaborations with industry are needed to ensure successful translation from laboratory to industry [478]. In addition, policymakers and investor support are also key factors in achieving the large-scale application of MoS_2. Through these efforts, the application prospect of MoS_2 in the electrocatalytic hydrogen evolution reaction will be even broader.

7. Strategies to improve electrocatalytic performance of MoS_2

To fully realize the potential of MoS_2 in the electrocatalytic HER, the researchers have developed various strategies to improve its catalytic performance. These strategies aim to enhance their electrical conductivity, increase the number and accessibility of the active sites, and improve their stability. Here are some effective strategies to improve the electrocatalytic performance of MoS_2.

7.1. Nanostructuring of MoS_2

Nanostructuring is one of the critical strategies to improve the catalytic performance of MoS_2 [305]. By reducing the MoS_2 material to the nanoscale, its specific surface area can be significantly increased, thus providing more active sites while improving the electron transport performance [479,480].

7.1.1. Nanosheets, nanowires, and nanoflowers of MoS_2

When studying the nanostructures of MoS_2, various morphologies such as nanosheets, nanowires, and nanoflowers have been explored due to their unique structural and catalytic properties. MoS_2 nanosheets, prepared via exfoliation techniques, exhibit a high specific surface area and abundant edge sites, which serve as active centers for the HER [290,481]. The nanosheet structure exposes more active sites and shortens charge transfer pathways, enhancing catalytic efficiency, as shown in Fig. 11a–c [481]. For instance, the cyclic voltammetry (CV) curve (Fig. 11b) demonstrates the current response of α-MoS_2 NDs and c-MoS_2 during the first and second scans [481], with α-MoS_2 NDs exhibiting a higher current density, indicating superior electrochemical activity. Furthermore, the Tafel plot in Fig. 11c shows that α-MoS_2 NDs have a lower Tafel slope (73.2 mV per decade) than c-MoS_2 (145.8 mV per decade) [481], signifying faster electrochemical reaction kinetics.

In addition to nanosheets, MoS_2 nanowires provide one-dimensional electron transport channels, facilitating rapid charge transfer, as shown in Fig. 11d [474]. The nanowire structure also forms active sites on its surfaces and edges, further enhancing catalytic activity, as illustrated in Fig. 12e–f. For example, Fig. 11e shows the current response of MoS_2 NPs/CoS_2 NTs, CoS_2 NTs, Co MOF NWs, and pure CC at different scan rates [474], with MoS_2 NPs/CoS_2 NTs exhibiting the highest current density, indicating optimal electrochemical activity. The electrochemical impedance spectroscopy (EIS) in Fig. 11f reveals that MoS_2 NPs/CoS_2 NTs have the lowest charge transfer resistance [474], demonstrating their superior charge transfer capability. MoS_2 nanoflowers, composed of multiple layers of nanosheets, offer a unique three-dimensional structure that increases the number of active sites and facilitates electrolyte penetration and gas product release, making them highly efficient for catalytic applications [43]. As shown in Fig. 11d [474], Co MOF nanowires (NWs) supported on carbon cloth (CC) can be transformed into MoS_2 nanosheets/CoS_2 nanotubes (NTs) composite materials through chemical deposition and heat treatment processes. This structural design significantly enhances the performance of MoS_2-based electrocatalysts, making them promising candidates for energy conversion and storage applications. Collectively, the diverse nanostructures of MoS_2, including nanosheets, nanowires, and nanoflowers, provide versatile platforms for optimizing catalytic activity and advancing renewable energy technologies [43,290,474,481,482].

Furthermore, 1D MoS_2 nanostructures, such as nanorods and

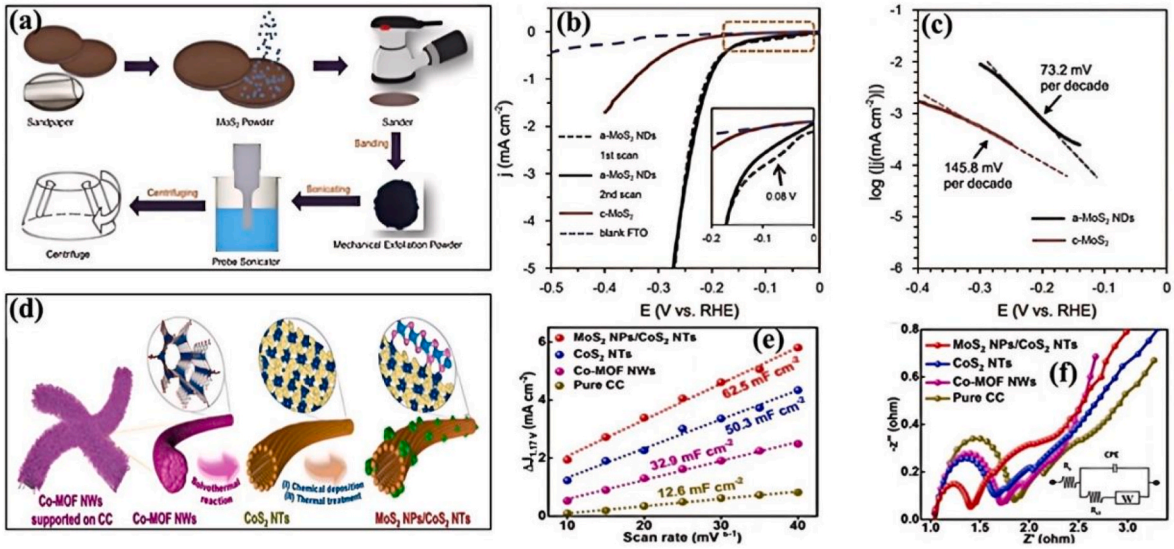


Fig. 11. (a) Exfoliation process of single- and few-layered MoS_2 nanosheets by mechanical force [481]. (b) Polarization curve of various MoS_2 electrodes [481]. (c) Tafel plots for the data presented in (b) [481]. (d) Schematic of the synthetic protocol of the MoS_2 NPs/CoS_2 NTs [474]. (e) Cdl of the pure CC, Co-MOF NWs, CoS_2 NTs, and MoS_2 NPs/CoS_2 NTs derived from the current density versus scan rate [474]. (f) Nyquist plots of the pure CC, Co-MOF NWs, CoS_2 NTs, MoS_2 NPs/CoS_2 NTs, and RuO_2 [474].

nanotubes, exhibit unique geometric properties that further enhance edge site density and catalytic performance in the HER [483]. For instance, as discussed in Section 4.1.2, MoS_2 nanotubes with high curvature edges can induce local electronic state reorganization and strain effects, which optimize the hydrogen adsorption free energy (ΔG_H) and improve HER activity. The cyclic voltammetry curves (Fig. 4c) and Tafel slopes (Fig. 4d) of template-synthesized MoS_2 nanotubes demonstrate superior HER performance compared to planar films, attributed to their enhanced edge site exposure and efficient mass transport pathways [229]. Additionally, 1D MoS_2 nanorods or nanowire-based composites (e.g., MoS_2 nanowires/CoS_2 nanotubes in Fig. 12d) provide directional electron transport channels, reducing charge transfer resistance (Fig. 12f) and increasing current density at high loads [474]. These 1D structures not only maximize the accessibility of active edge sites but also maintain structural stability under dynamic operating conditions, highlighting their potential for practical electrocatalytic applications.

7.1.2. Increasing the number of active edge sites and accessibility

The electrocatalytic performance of MoS_2 can be significantly enhanced through nanostructured strategies that increase the number of active edge sites and improve their accessibility, providing strong support for its application in the HER [273,484–489]. One practical approach is the exposure of edge sites, which can be increased through chemical or electrochemical exfoliation, as shown in Fig. 12a [484]. By carefully controlling the degree of exfoliation, these methods maximize the number of exposed edge sites without disrupting the crystal structure, thereby enhancing catalytic activity [273,484]. Another strategy is defect engineering, where controlled defects, such as sulfur vacancies or doping with other elements, are introduced on the edges or basal planes of MoS_2. These defects act as new electron acceptors or donors, modulating the electronic properties of MoS_2 and creating additional active sites [485]. For example, sulfur vacancies and doping with group VB metals have synergistically optimized the HER performance of MoS_2 nanosheets by enhancing electron transfer and catalytic activity [485].

In parallel, strain engineering has emerged as a powerful strategy to intrinsically activate the edge sites by modulating their electronic structure [23]. The introduction of controlled strain, either tensile or compressive, can significantly alter the Mo–S bond lengths and angles at the edge sites, leading to a shift in the d-band center of Mo atoms [490]. This electronic structure optimization effectively fine-tunes the hydrogen adsorption free energy (ΔG_{H^*}) towards the ideal thermoneutral value (~0 eV), thereby dramatically enhancing the intrinsic activity of each exposed edge site [491]. For instance, as illustrated in Fig. 5e and f of the manuscript, applying a modest strain of 1.5-2% on Ag-doped MoS_2 can optimize ΔG_{H^*}. Nanostructuring itself often inherently introduces beneficial strain fields. The curvature in nanocoils or the lattice mismatch at heterointerfaces within composite structures (e.g., MoS_2/-graphene) can generate localized strain, which works synergistically with increased edge site exposure and improved electrical connectivity provided by the nanostructured design [492]. This combination of geometric (increased number and accessibility) and electronic (strain-enhanced intrinsic activity) optimization represents a comprehensive approach to maximizing the electrocatalytic performance of MoS_2 [493].

Surface modification is another powerful method to improve the conductivity and accessibility of MoS_2 active sites. By forming composites with materials such as graphene and conductive polymers, the electron transport efficiency of MoS_2 can be enhanced, while synergistic effects between the components further boost catalytic activity, as shown in Fig. 12b [488]. For instance, the combination of MoS_2 with graphene oxide (GO) and polya + -niline (PANI) through hydrothermal and CVD methods has been demonstrated to improve conductivity and catalytic performance [14]. These composite materials facilitate charge transfer and stabilize the active sites, making them more accessible for catalytic reactions.

Through these nanostructured strategies, including edge site exposure, defect engineering, and surface modification, the electrocatalytic performance of MoS_2 has been significantly improved, as evidenced by enhanced HER activity and faster reaction kinetics [489]. However, to achieve industrial applications of these strategies, further research is required to optimize the synthesis processes and ensure the materials' stability, scalability, and cost-effectiveness. For example, Fig. 12a shows the deformation of MoS_2 under 0% and 20% strain conditions, where the material returns to its original state after strain release, demonstrating its mechanical robustness [484]. Fig. 12b illustrates the synthesis process of SnS_2/NRGO/PANI composite material, showcasing how advanced material design can improve the catalytic properties of MoS_2-based systems [488].

Although these methods have achieved remarkable improvements in the catalytic performance of MoS_2, further studies are needed to refine

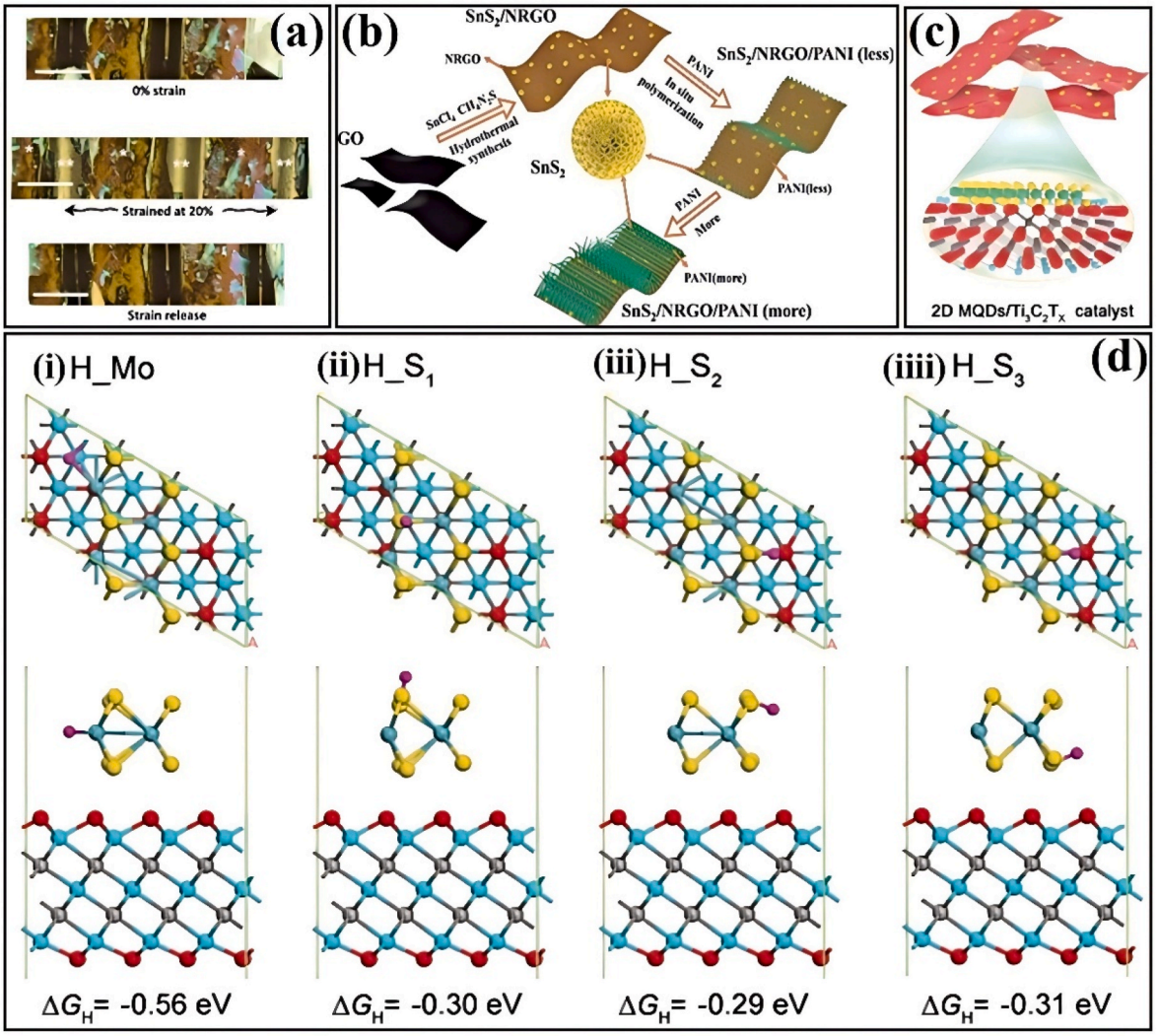


Fig. 12. (a) LSCM images obtained for thinned MoS_2 (0% strain), after stretching the electrode at approximately 20% (strained at 20%) and after releasing the electrode from the stretching condition (strain release) [484]. (b) Synthesis of SnS_2/NRGO/PANI by oxidative polymerization of aniline monomers on SnS_2/N-RGO [488]. (c) The overall graphical representation of HER with MoS_2 QDs with MXene composite [503]. (d) Electrocatalytic mechanisms of the $MoS_2/Ti_3C_2O_2$ nano-architec ture towards the HER process. The hydrogen atom adsorbed on the (a)Mo site, (b) S1 site, (c) S 2 site, and (d) S 3 site on the hybrid $MoS_2/Ti_3C_2O_2$ system. The pink ball represents the H atom [503]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

these strategies and address challenges related to long-term stability and economic feasibility. This will ensure the material can transition from laboratory research to practical industrial applications in renewable energy technologies [273,484–489].

7.1.3. Edge exposure strategy for vertically oriented nanosheet arrays

Vertically oriented nanosheet arrays are a structural design strategy that aligns the nanosheets perpendicular to the substrate by controlling the growth direction of MoS_2 crystals. This structure maximizes the exposure density of edge sites while avoiding shielding of edge activity by interlayer stacking, thereby significantly improving HER performance. The advantages of vertically oriented nanosheet arrays are mainly reflected in the following aspects: i) Maximized exposure of edge sites: The vertically oriented arrangement of nanosheets makes the edge sites of each layer directly exposed to the electrolyte, which significantly improves the utilization rate of edge active sites. Compared to traditional horizontally stacked structures, vertically oriented structures provide a higher edge/volume ratio. ii) Optimization of electron transport path: The vertically oriented structure shortens the electron transport path from the substrate to the edge site, thereby reducing the charge transfer impedance and improving the kinetic performance of the catalytic reaction. iii) Enhanced permeability of electrolyte: The vertically oriented array structure forms an open three-dimensional network, which is conducive to the penetration of electrolytes and the diffusion of reactants, thereby further improving the catalytic efficiency. Experimental studies have shown that vertically oriented growth of MoS_2 nanosheets can be achieved by manipulating synthesis conditions such as temperature, precursor concentration, and substrate type in CVD or hydrothermal methods. For example, vertically oriented MoS_2 nanosheet arrays fabricated on conductive substrates such as carbon cloth or metal foil exhibit lower HER overpotentials and higher current densities. In addition, the vertically oriented structure can further optimize the electronic structure of the edge by introducing doping (e.g., transition metals such as Ni and Co), thereby improving the catalytic performance.

7.1.4. Porous structure enhances edge accessibility

The porous structure design is a nanoengineering strategy to increase the accessibility of MoS_2 edge sites and the efficiency of reactant diffusion by introducing pores. The porous structure not only significantly increases the exposure density of edge sites, but also further improves the overall performance of the catalyst by optimizing the size and distribution of pores. The enhancement of HER performance by porous

structure is mainly reflected in the following aspects: i) High-density exposure of edge sites: The porous structure significantly increases the specific surface area of MoS_2 by introducing a large number of pores, thus providing more edge active sites. ii) Rapid transport of reactants and products: The pores in the porous structure provide a fast channel for the diffusion of reactants (e.g., H^+) and the release of products (e.g., H_2), effectively reducing mass transfer resistance. iii) Stress-induced electronic state control: Local curvature and stress effects in the porous structure can modulate the electronic structure of the MoS_2 edge site, bringing it closer to the ideal state of HER. The construction of porous structures is usually achieved by the template method, etching method, or self-assembly method. For example, porous MoS_2 films synthesized with the assistance of a hard template, such as silica spheres or polystyrene microspheres, exhibit excellent HER properties. In addition, nanopores can be introduced into the MoS_2 surface by plasma etching or chemical etching, further increasing the exposure density and accessibility of edge sites. It is important to note that the design of porous structures requires a balance between pore size and structural stability. Pores that are too large may cause structural collapse, while pores that are too small may limit the diffusion of reactants. Therefore, the rational optimization of pore size and distribution is the key to the design of porous structures.

Furthermore, the pore size distribution (PSD) plays a critical role in modulating the hydrogen adsorption free energy (ΔG_H) and HER activity by influencing both mass transport efficiency and strain-induced electronic effects [212]. An optimized PSD ensures efficient diffusion of reactants (H^+) to edge sites and desorption of products (H_2), reducing kinetic limitations that indirectly affect ΔG_H measurements under operational conditions. More importantly, the local curvature and strain generated by a well-defined pore architecture can tailor the electronic structure of MoS_2 edge sites, such as shifting the d-band center position, which directly optimizes ΔG_{H^*} toward thermoneutral values ($\approx$0 eV). For instance, controlled porosity introduces tensile strain that adjusts Mo–S bond lengths, enhancing the metallicity of edge sites and facilitating hydrogen adsorption/desorption processes [494]. Thus, precise control over PSD enables synergistic improvement in both thermodynamic (ΔG_H) and kinetic aspects of HER on MoS_2 catalysts.

7.2. Doping and heterostructures

To further improve the performance of MoS_2 in electrocatalytic HER, doping and construction of heterostructure are two effective strategies [190]. These methods can alter the electronic structure of MoS_2, provide more active sites, and improve the electron transport properties.

7.2.1. Elemental doping (N, P, Co, etc.)

- Nitrogen (N) doping: Nitrogen atoms can provide additional electrons in the MoS_2 lattice, thus regulating the material's electronic structure and chemical properties [312,495]. Nitrogen doping can improve the conductivity of MoS_2 and increase the density of the active site, thus improving its HER performance [146,190].
- Phosphorus (P) doping: Phosphorus doping can introduce p-type doping in MoS_2, which facilitates the formation of new active sites and can improve the charge distribution of the material, thus enhancing its catalytic activity against HER [496].
- Cobalt (Co) doping: Adding cobalt atoms can introduce local magnetism, thus affecting the electronic structure of MoS_2. The Co-doped MoS_2 exhibited excellent HER activity, probably due to the introduction of cobalt atoms facilitating charge transfer and distribution [307,497]. The doping strategy can enhance the catalytic activity of MoS_2 but also enhance its stability, making it more suitable for long-term electrocatalytic applications.

7.2.2. Heterostructures with other 2D materials

- Graphene/MoS_2 heterostructure: Combining MoS_2 with high-conductance graphene can form a heterostructure, which takes advantage of the high electron mobility of graphene and the high catalytic activity of MoS_2 [498]. The introduction of graphene can significantly improve the electron transmission rate and overall HER performance.
- WS_2/MoS_2 heterostructure: Construction of a heterostructure with another transition metal sulfide, WS_2, which can form a new catalytic active site at the interface [499,500]. This heterostructure can utilize different materials' synergistic effects, thus improving catalytic efficiency and stability.
- G-C_3N_4/MoS_2 heterostructure: combined with graphite phase carbon nitride (g-C_3N_4) can form a heterostructure with broadband gap [501,502]. The introduction of g-C_3N_4 helps to improve the light absorption capacity and promote charge separation and migration through the interfacial effects of heterostructures, further improving HER performance. Building heterostructures is an effective strategy to modulate electronic properties to improve catalytic activity, and charge transport paths can be optimized by interface engineering (Fig. 12c and d) [503]. Implementing these strategies provides new possibilities for the application of MoS_2 in electrocatalytic hydrogen evolution and lays a foundation for further improving its performance. However, to achieve practical applications of these structures, further studies are needed to optimize the preparation method and ensure material stability and feasibility of large-scale production.

7.3. Phase-change control

The primary focus of this review on the 2H and 1T phases of MoS_2 is driven by their predominant role and established relevance in electrocatalytic HER research. While other polymorphs such as 3R, T_1, and T_2 do exist, their discussion is limited herein due to several practical considerations [504]. The 3R phase is thermodynamically metastable compared to the 2H phase and is far less abundant in nature, resulting in a scarcity of experimental data and a lack of clear evidence demonstrating superior HER performance over the well-studied 2H/1T systems [505]. The T_1 and T_2 phases (often referring to distorted 1T derivatives like 1T') are typically metastable intermediates or distorted versions of the 1T phase. Their synthesis is challenging to control precisely, and they often suffer from poor electrochemical stability, making systematic study and application in HER less practical [106]. Therefore, the strategic emphasis on 2H and 1T phases aligns with the current understanding of the most catalytically effective and experimentally tractable materials for hydrogen evolution. The electrocatalytic performance of MoS_2 is mainly dependent on the nature of its crystalline phase [386,506]. There are two main phases of MoS_2: 2H phase and 1T. The 2H phase is the most common semiconductor phase, while the 1T phase is a metastable metallic phase showing higher conductance and catalytic activity. Therefore, controlling the phase transition of MoS_2 is one of the key strategies to improve its performance in the electrocatalytic HER.

Critically, the metastability of the 1T phase originates from its higher surface energy due to octahedral coordination and lattice distortions (e.g., shortened Mo–Mo bonds ~2.75 Å vs. 3.15 Å in 2H–MoS_2), which create a low energy barrier (~0.03 eV/atom) for phase transformation. This makes 1T-MoS_2 susceptible to environmental fluctuations (e.g., temperature changes or electrolyte interactions) [367]. Existing stabilization strategies, such as chemical doping or physical exfoliation, often introduce unintended defects (e.g., interfacial stress or reduced active site density) and face challenges in scalability and long-term durability under operational conditions [507]. For instance, lithium intercalation may lead to structural degradation, while stress-induced phase control lacks precision for industrial-scale applications.

7.3.1. Chemically stable 1T-MoS_2 phase

Chemical methods are an effective way to achieve and stabilize the 1T-MoS_2 phase. Chemical doping or interactions with other chemicals can stabilize the 1T phase of MoS_2. Insertion of lithium ions in the MoS_2 structure can enable the transition from the 2H phase to 1T phase [506,508]. The insertion of lithium ions changes the electronic structure of MoS_2 to induce a phase transition [508,509]. This method can stabilize the 1T phase to some extent but requires measures to maintain the 1T phase stability after removing lithium ions [14,506]. The 1T phase can also be stabilized by doping metal ions such as copper and silver into the structure of MoS_2 [510,511]. Adding these metal ions can contribute to the phase transition and provide additional electrons, thereby enhancing the conductance and catalytic activity of MoS_2 [512].

7.3.2. Stability of 1T-MoS_2 phase with physical methods

Physical methods provide an alternative route to stabilize the 1T-MoS_2 phase that often involves the control of external conditions, such as pressure, temperature, and stress.

- Mechanical exfoliation: through mechanical exfoliation technology, a single-layer or less-layer MoS_2 can be obtained while maintaining the 1T phase structure [513]. This method efficiently produces and maintains the 1T phase, especially when the material is transferred to other substrates.
- Applied stress: By applying external stress, MoS_2 can be induced to change from the 2H phase to the 1T phase [426]. This transition is due to the stress changing the lattice parameters and the electronic structure. Moreover, applied stress can help maintain the 1T phase.
- Control of growth conditions: In the growth process such as CVD, 1T phase MoS_2 can also be directly synthesized by accurately controlling the growth conditions (such as temperature, pressure, and atmosphere) [514]. This approach can yield a highly stable 1T phase at the source. Controlling the phase transition of MoS_2 by the above method could improve its catalytic efficiency in HER and broaden its potential in other electrocatalytic applications [213,515]. Future solutions should prioritize atomic-level precision engineering, such as developing interface strain control (e.g., core-shell structures) to suppress phase transition, integrating in-situ characterization techniques (e.g., operando TEM or XAS) to monitor real-time phase dynamics, and exploring self-healing mechanisms (e.g., electrochemical regeneration) [516]. Additionally, machine learning-assisted screening of novel stabilizers (e.g., rare-earth dopants) and standardized testing protocols (e.g., accelerated aging at >500 mA cm^{-2}) are essential to bridge the gap between laboratory research and commercial deployment [378]. These directions aim to achieve durable 1T-MoS_2 catalysts with enhanced stability under industrial conditions. However, although these strategies show excellent performance at the laboratory scale, they still face many challenges in industrial applications, such as cost-effectiveness, feasibility of large-scale production, and long-term stability. Future studies are needed to explore these strategies' utility and durability further to achieve broad applications of MoS_2 in electrocatalysis.

7.4. Surface modification

Surface modification is a vital strategy to improve the performance of MoS_2 in the electrocatalytic HER [187,347]. Introducing different functional groups on the MoS_2 surface or combined with other catalysts effectively improves the quantity and quality of the active site and optimizes the electrolyte's interaction with the catalyst. These improvements improve the catalytic activity and stability of MoS_2, thereby enhancing its performance in HER.

7.4.1. Introducing functional groups

- Sulfide treatment: By introducing additional sulfide on the surface of MoS_2, the sulfur vacancy can be repaired, which is a common defect [485,517]. This modification could enhance the structural integrity of the material and its catalytic activity because the intact S–Mo–S layer is more favorable for the transport of electrons and hydrogen adsorption.
- Oxide modification: The introduction of oxides, such as titanium oxide or zinc oxide, on the surface of MoS_2 can form an n-type semiconductor structure, which helps to improve the transmission efficiency of electrons and enhance the adsorption capacity of the surface [518,519]. Moreover, introducing oxides can enhance HER performance by providing new active sites.
- Organic functional group: The introduction of organic functional groups (such as amino, carboxyl, etc.) on the surface of MoS_2 through chemisorption or covalent bonding can change the surface charge distribution, to enhance its interaction with the electrolyte and improve the kinetic process of HER [520].

7.4.2. Composites with other catalysts

- Precious metal composite: the combination of MoS_2 with precious metals such as platinum and palladium can use the high catalytic activity of precious metals and the high stability of MoS_2 [521,522]. This composite can provide more active sites and enhance electron transport and adsorption/desorption of hydrogen through synergistic effects.
- Metal oxide composite: combined with metal oxides (such as RuO_2, IrO_2, etc.), it can form a composite material with high redox activity [523,524]. These metal oxides can act as transport channels for electrons and protons to enhance the overall electrocatalytic properties of MoS_2.
- Carbon-based composite material: combined with carbon-based materials such as graphene and carbon nanotubes, it can improve the composite material's electrical conductivity and enhance its mechanical stability and corrosion resistance [525,526]. The high specific surface area of carbon-based materials and the good electron transport properties allow this composite to exhibit excellent properties in HER.

With these surface modification strategies, the electrocatalytic performance of MoS_2 can be significantly improved, making it more suitable for use in energy conversion applications such as HER [190,347]. However, implementing these strategies requires precise control of the material synthesis and treatment conditions to ensure that the modified material has the desired properties and stability. Future studies should further explore the optimal conditions of these surface modification techniques and the stability of long-time operation to advance the commercialization of MoS_2 in practical applications.

7.4.3. Edge selective functionalization

Edge-selective functionalization is a strategy to modulate the catalytic performance of MoS_2 by introducing specific chemical groups or atoms into its edge site. Due to the coordination unsaturation and unique electronic structure of the edge sites of MoS_2 (e.g., Mo-edge and S-edge), the selective functionalization of these sites can significantly change their surface chemical environment and electronic state, thereby optimizing the hydrogen adsorption free energy (ΔG_{H^*}) and enhancing the HER activity.

(1) Mechanism of action of functionalized modification

The improvement of the catalytic performance of MoS_2 by edge-selective functionalization modification is mainly reflected in the following aspects: 1. Electronic structure regulation: The electronic

structure of the edge site can be effectively manipulated by introducing functionalized groups (such as –OH, –NH_2, –SH) or doping heterogeneous atoms (such as metal or non-metal elements) at the edge site. For example, functionalized groups can optimize hydrogen adsorption-free energy by altering the center position of the d-band at the edge site through electron supply or attraction effects. 2. Introduction of active sites: Functionalized modifications can introduce new active centers at edge sites. For example, the doping of non-metallic elements (e.g., N, P, S) can create a new coordination environment at the edge site, thereby enhancing HER activity. 3. Optimization of the surface chemical environment: Functionalized modifications can improve the hydrophilicity or hydrophobicity of the edge sites, thereby enhancing the wettability of the electrolyte and the accessibility of reactants. In addition, functionalized groups can also promote the adsorption and reduction of hydrogen ions by manipulating the local pH environment.

(2) Implementation method of functional modification

Edge-selective functionalization is typically achieved by chemical modification, plasma treatment, or electrochemical methods: Chemical modification: The introduction of functionalized groups or doped atoms into the edge site of MoS_2 by chemical reaction. For example, liquid-phase reactions can be used to enhance the catalytic performance of –OH or –NH_2 groups at the MoS_2 edge site. Plasma treatment: With plasma etching or functionalization, specific defects or functionalized groups can be introduced at the edge sites of MoS_2. For example, nitrogen plasma treatment can introduce N atoms at the edge site, thereby optimizing their electronic structure. Electrochemical methods: Metal or non-metal atoms can be selectively modified at the edge site of MoS_2 by electrochemical activation or electrodeposition. For example, Pt or Ni atoms can be introduced at the edge site by electrodeposition, which can significantly improve HER performance.

(3) Latest advances in functional modification

In recent years, important progress has been made in the study of edge-selective functionalization of MoS_2-based HER catalysts. For example: 1. Non-metal doping: Studies have shown that the introduction of N or P atoms at the edge site of MoS_2 can significantly improve its HER performance. This is because the N or P atom can optimize the electronic structure of the edge site through the electron donor effect, thereby reducing the hydrogen adsorption free energy. 2. Metal modification: The catalytic performance of transition metals (e.g., Ni, Co, Fe) or precious metals (e.g., Pt) can be significantly improved by modifying the MoS_2 edge site. For example, Pt atomic modification can form a highly active Pt–Mo–S ternary coordination structure at the edge site, thereby significantly reducing the overpotential of HER. 3. Functionalized group modification: The introduction of –OH or –NH_2 groups at the MoS_2 edge site can improve its hydrophilicity and hydrogen adsorption capacity. For example, the HER performance of the –OH group was significantly improved after the introduction of the –OH group at the MoS_2 edge site by liquid-phase chemical modification.

(4) Challenges and prospects of functional modification

Although edge-selective functionalization has great potential to improve MoS_2 catalytic performance, there are still some challenges: i) Functional precision: How to achieve atomic-level precise modification of edge sites is still a difficult problem. In the future, it is necessary to combine in situ characterization techniques and theoretical calculations to deeply understand the mechanism of functionalization. ii) Stability of modifications: The stability of functionalized groups or doped atoms may be challenged during long-term catalysis. A more stable modification strategy needs to be developed to meet the needs of practical applications. Co-design of modifications and structural optimization: Functionalized modifications need to be co-optimized with other nanostructured projects, such as vertically oriented or porous structures, to maximize catalytic performance.

7.5. Advanced synthesis technologies

Developing advanced synthesis technology is key to improving the performance of MoS_2 as a catalyst for electrocatalytic HER [527,528]. These techniques can improve the catalytic activity and stability of MoS_2 and realize the precise regulation of its structure and function. The following sections detail the development of new synthetic methods and how these methods can precisely control the phase, defects, and morphology of MoS_2.

7.5.1. Development of new synthesis methods

In recent years, various new synthetic methods have been developed to optimize the catalytic performance of MoS_2. These methods include.

- Chemical vapor deposition (CVD): CVD is an effective method for preparing high-quality, large-area MoS_2 single-layer or multilayer film [514,529]. By controlling the flow rate, temperature, and pressure of the reaction gas, the growth process and structure of MoS_2 can be precisely controlled.
- Hydrothermal/solvent thermal synthesis: this method uses water or other organic solvents to heat in closed containers to high temperature and high pressure to promote the conversion of the precursor into MoS_2 [530,531]. The method is suitable for producing nanostructures with specific morphology, such as nanosheets, nanowires, and nanofiles.
- Mechanical stripping technology: This technology removes the single or few-layer MoS_2 from the block MoS_2 by physical means, maintaining the original crystal structure of the material, which is very suitable for basic scientific research [14,532].
- Atomic layer deposition (ALD): ALD allows the control of film growth at the atomic level and is ideal for the preparation of uniform MoS_2 films with precise thickness control [533,534]. Through these new synthetic methods, MoS_2 materials with optimized properties have been produced, providing new possibilities for the design and development of HER catalysts.

7.5.2. Accurate control of phase, defects, and morphology of MoS_2

The catalytic performance of MoS_2 largely depends on its crystal phase, the type and number of defects, and the morphology of the nanostructure [14,402]. Here are some of the key control strategies.

- Phase control: multiple phases exist in MoS_2, including 2H, 1T, and 3R [91,535]. The 2H phase is the most common semiconducting phase, while the 1T phase exhibits metallic behavior. By adjusting the synthesis conditions, such as temperature, pressure, and chemical environment, phase conversion can be achieved to optimize their electrocatalytic performance [429].
- Defect engineering: the introduction of defects (such as sulfur vacancies, doping, or edge defects) in the crystal structure of MoS_2 can significantly improve its catalytic activity [387,536]. For example, sulfur vacancies can provide more active sites, while doping with other elements (such as nitrogen or phosphorus) can adjust their electronic properties.
- Morphological control: the topography of MoS_2 nanostructures (such as nanosheets, nanorods, nanowires, etc.) has an essential impact on its surface area and catalytic activity. The morphology of these nanostructures can be precisely controlled by adjusting synthesis parameters such as solvent type [97], concentration, and growth time. Through these improved synthesis technologies and precise control strategies, the catalytic efficiency and stability of MoS_2 in HER can be significantly improved, further promoting its application in the field of hydrogen energy.

7.6. MoS_2 quantum dots in electrocatalytic hydrogen production

MoS_2 quantum dots have become a research hotspot for improving HER performance due to their size-dependent quantum confinement effect and high edge proportion. Compared with traditional two-dimensional MoS_2 films or nanosheets, MoS_2 quantum dots have a higher edge/volume ratio, more abundant coordination unsaturation sites, and more flexible electronic structure manipulation capabilities. These characteristics make MoS_2 quantum dots exhibit excellent catalytic performance in electrocatalytic HER. The edge proportion of quantum dots is a key factor in determining their catalytic performance. By rationally designing and optimizing the size, morphology, and synthesis method of quantum dots, the proportion of quantum dots can be maximized, so as to significantly improve the density and utilization rate of active sites.

7.6.1. Optimization of quantum dot size

The size of quantum dots directly affects their edge proportions and electronic structure. As the size of quantum dots decreases, the proportion of edge atoms increases significantly, and the quantum confinement effect leads to a change in the structure of the electron bands, thereby optimizing the hydrogen adsorption free energy (ΔG_{H^*}). Studies have shown that when the size of MoS_2 quantum dots is in the range of 2–5 nm, the edge proportion and HER activity are optimally balanced. For instance, quantitative statistical analysis from high-resolution TEM of over 200 quantum dots synthesized via the solvothermal method revealed a Gaussian size distribution with a mean diameter of 3.2 ± 0.7 nm (mean ± standard deviation) and a polydispersity index of approximately 0.22, indicating a relatively monodisperse sample [537]. Too small size can lead to agglomeration or structural instability of the quantum dots, while too large size can reduce the edge ratio. By manipulating the synthesis conditions, such as precursor concentration, reaction time, and temperature, the size of quantum dots can be precisely controlled. For example, the size of MoS_2 quantum dots prepared by solvothermal or microwave-assisted methods can be adjusted in the nanoscale range to maximize the proportion of edges.

7.6.2. Morphology control and edge structure optimization

In addition to size, the morphology and edge structure of quantum dots also have an important impact on their catalytic performance. By manipulating the crystal growth direction of quantum dots, highly reactive edge sites (e.g., Mo-edges) can be selectively exposed. For example, MoS_2 quantum dots with triangular or hexagonal topography are able to provide a higher density of active edge sites due to their specific plane orientation. In addition, by introducing defect engineering, such as sulfur vacancies or doping, the electronic structure of the quantum dot edge can be further optimized. For example, the introduction of sulfur vacancies at the edge of MoS_2 quantum dots can enhance hydrogen adsorption capacity and thus HER activity.

7.6.3. Quantum dot assembly and dispersion control

In practical applications, the clustering of quantum dots significantly reduces their edge proportion and catalytic performance. Therefore, how to maintain the good dispersion of quantum dots is the key to maximizing the proportion of edges. By loading quantum dots on substrates with a high specific surface area (e.g., graphene, carbon nanotubes, or porous carbon), the agglomeration of quantum dots can be effectively prevented, while further improving their conductivity and stability. In addition, the self-assembly strategy of quantum dots, such as the formation of two-dimensional or three-dimensional superstructures, also provides new ideas for maximizing the proportion of edges. For example, self-assembly driven by electrostatic or van der Waals forces can be used to construct quantum dot arrays with high edge exposure densities to improve HER performance.

7.6.4. Quantitative relationship between quantum dot edge proportion and HER performance

In recent years, researchers have established a quantitative relationship between the edge proportion of quantum dots and HER performance through experiments and theoretical calculations. For example, by performing HER tests on MoS_2 quantum dots of different sizes and morphologies, it is found that the proportion of edges is positively correlated with catalytic activity. Theoretical calculations further show that the ΔG_{H^*} at the edge site tends to the ideal value (close to 0 eV) as the proportion of the edge increases, thereby significantly reducing the overpotential of HER.

7.6.5. Challenges and prospects for maximizing the quantum dots edge proportion

Although the quantum dot edge maximization strategy has shown great potential to improve HER performance, there are still some challenges: i) Precise control of size and morphology: How to achieve precise control of the size and morphology of quantum dots in large-scale preparation is still a difficult problem. ii) Stability of edge structure: The high edge proportion of quantum dots may lead to structural collapse or agglomeration during the catalytic process, affecting the long-term stability of catalytic performance. The size distribution directly influences structural integrity; a narrow distribution minimizes Ostwald ripening and aggregation, thereby preserving edge sites under operational conditions [538]. iii) Interface optimization between quantum dots and substrates: The interface interaction between quantum dots and substrates has an important impact on electron transport and catalytic performance, and more efficient loading strategies need to be developed in the future. Moreover, the width of the size distribution affects charge transfer uniformity; a monodisperse QD population facilitates consistent electron pathways, enhancing HER kinetics, while polydisperse samples suffer from localized inefficiencies [539]. By optimizing the size, morphology, edge structure, and dispersion, the strategy of maximizing the proportion of quantum dots at the edge provides an important way to improve the performance of MoS_2-based HER catalysts. In the future, the intrinsic correlation between the edge proportion of quantum dots and the performance of HER will be studied in depth by combining advanced synthesis techniques, in-situ characterization methods, and theoretical calculations, which would provide new ideas for the design of efficient and stable MoS_2 quantum dot catalysts.

7.7. MoS_2 composites in electrocatalytic hydrogen production

As a non-precious metal catalyst, MoS_2 excels in electrocatalytic HER and has excellent potential to replace expensive platinum-based catalysts. It has been shown that the activity of MoS_2 is mainly concentrated at the edge positions, which provide more catalytic active sites. Different synthesis methods and structural modifications, such as chemical stripping, edge alignment, and phase transition, can significantly improve the catalytic performance of MoS_2. For example, metal-phase 1T-MoS_2 nanosheets obtained from semiconducting 2H–MoS_2 nanostructures by chemical exfoliation demonstrated excellent HER catalytic activity with an electrocatalytic current density of 10 mA/cm^2 at low overpotentials and a slight Tafel slope [307]. In addition, the MoS_2/RGO hybrid materials formed by growing MoS_2 nanoparticles on graphene also showed excellent HER activity, which was attributed to the abundance of catalytic edge sites on the MoS_2 nanoparticles and the excellent electrical coupling with the underlying graphene network [304]. It was also found that the catalytic efficiency of MoS_2 could be further improved by tuning its morphology and structure, such as preparing it into nanorods, amorphous, bread-like, and flower-like morphologies.

In addition, the catalytic performance of MoS_2 can be further enhanced by introducing strategies such as defect engineering and phase engineering. However, despite the promising application of MoS_2 in HER, its performance is still limited by the low density of active sites and

relatively low conductivity. Therefore, researchers are exploring various strategies to overcome these limitations, such as improving charge injection and transport by forming composites with other materials, such as MoO_2, or enhancing its catalytic activity by doping with other elements, such as cobalt. The study of MoS_2 composites in electrocatalytic hydrogen production has shown that the HER performances of MoS_2 and its composites have been significantly enhanced through fine-tuning of the structure and morphology. Future studies may focus on further optimizing the structure and properties of these materials, as well as exploring new synthesis methods and strategies for more efficient and stable HER catalysts [312].

7.8. Edge site specific activation techniques

The edge site is the core source of the performance of MoS_2 electrocatalytic HER, and its activity is directly affected by the edge structure and electronic state. However, the edge sites of MoS_2 are usually in a non-optimal state after synthesis, and it is difficult to fully realize its catalytic potential. Therefore, the development of specific activation techniques for edge sites and optimization of their electronic structure and surface chemical environment is an important research direction to improve the catalytic performance of MoS_2. This section focuses on edge site-specific activation techniques such as plasma etching, electrochemical activation, and photoinducible regulation and their role in improving HER performance.

7.8.1. Plasma etching edge modification

Plasma etching is a technique that selectively removes or modifies atoms on the surface of a material by interacting with the surface of a material with a high-energy plasma. For MoS_2, plasma etching can effectively etch its basal or edge region, thus introducing more edge sites or regulating the electronic structure of the edge.

(1) Working mechanism of plasma etching

Plasma etching uses energetic particles (e.g., ions, electrons, or radicals) to interact with the MoS_2 surface to achieve the following functions: Exposure of edge sites: Plasma etching can selectively remove the basal atoms of MoS_2, exposing more edge sites, thereby significantly increasing the density of active sites. Defect introduction and electronic state manipulation: Sulfur vacancies or other defects can be introduced at the edge site during the etching process, which can manipulate the electronic structure of the edge to bring it closer to the ideal state of HER. Optimization of the chemical environment at the edge: Through selective etching, the chemical composition of the edge (e.g., Mo/S ratio) can be manipulated to further optimize the hydrogen adsorption free energy (ΔG_{H^*}).

(2) Technical realization of plasma etching

Plasma etching is usually treated with atmospheres such as argon, hydrogen, or nitrogen, which have different modification effects on the edge sites. For example: Argon plasma: Mainly used for physical etching, it can efficiently expose edge sites. Hydrogen plasma: Able to introduce sulfur vacancies and optimize the electronic structure of the edge. Nitrogen plasma: Nitrogen atoms can be doped at the edge site to further improve HER performance. Experimental studies have shown that the HER performance of the MoS_2 catalyst treated with hydrogen plasma is significantly improved, which is manifested by lower overpotential and higher current density.

7.8.2. Electrochemically activated edge reconstruction

Electrochemical activation is a technique that induces remodeling of the MoS_2 edge site by applying electrochemical conditions, such as potentials or currents. This method can dynamically manipulate the edge sites under actual working conditions to optimize their catalytic performance.

(1) Mechanism of electrochemical activation

Electrochemical activation induces the reconstitution of edge sites through electric fields or electrochemical reactions, mainly including the following processes: Dynamic generation of edge defects: During electrochemical activation, sulfur vacancies may be generated or repaired at the edge site, thereby regulating the electronic structure of the edge. Transition of edge chemical state: Electrochemical activation can change the oxidation state or chemical composition of edge sites, e.g. by partially reducing Mo^{4+} to Mo^{3+}, thereby increasing its catalytic activity. Regulation of surface adsorbents: Under electrochemical conditions, surface adsorbents at edge sites (e.g., H^+ or OH^-) can be dynamically manipulated to optimize the HER reaction pathway.

(2) Technical realization of electrochemical activation

Electrochemical activation is typically achieved by cyclic voltammetry (CV) or potentiostat treatment. For example, by performing multiple electrochemical cycles of MoS_2 in an acidic electrolyte, it is possible to induce the remodeling of edge sites, significantly improving its HER performance. In addition, electrochemical activation can be combined with other techniques, such as doping or functionalization, to further enhance catalytic performance. The results show that the electrochemically activated MoS_2 catalyst exhibits excellent HER performance with an ΔG_{H^*} at the edge site close to 0 eV.

7.8.3. Light-induced edge state regulation

Light-induced edge state manipulation is a technique that uses light to induce electronic state changes at MoS_2 edge sites. Due to the good photoresponse characteristics of MoS_2, the photoinduction technique can dynamically regulate the electronic structure and chemical reactivity of the edge site by exciting the electron-hole pair.

(1) Mechanism of light-induced regulation

Photoinducible regulation excites the electron-hole pairs of MoS_2 by illumination and mainly achieves the following functions: Dynamic manipulation of edge electronic states: Light can excite the edge sites of MoS_2 and rearrange its electronic structure, thereby optimizing hydrogen adsorption free energy. Participation of photogenerated carriers: Photogenerated electrons can directly participate in the HER reaction, accelerating the hydrogen reduction process. Promotion of edge chemical reactions: Light can promote the chemical activity of edge sites, such as accelerating the generation or repair of sulfur vacancies.

(2) Technical realization of light-induced regulation

Photoinducible manipulation is usually performed in conjunction with photoelectrochemical reactions. For example, electrochemical testing of MoS_2 under light conditions can significantly improve its HER performance. In addition, the introduction of photosensitizers (such as CdS or TiO_2) can enhance the light absorption capacity, thereby further improving the effect of photoinduced regulation. Experimental studies have shown that the activity of the edge site of the light-induced MoS_2 catalyst is significantly increased, which is manifested by higher photocurrent density and lower HER overpotential.

The edge-site-specific activation technique provides an important means to improve the performance of MoS_2-based HER catalysts. Plasma etching significantly improves the catalytic activity by introducing defects and exposing edge sites, electrochemical activation optimizes the electronic structure of edge sites by dynamically reconstructing edge sites, and photoinduced regulation uses photogenerated carriers to further enhance the activity of edge sites. In the future, the synergistic optimization of multiple activation technologies and the in-depth study

of their mechanism of action through in-situ characterization will provide new ideas for the design of efficient and stable MoS_2-based HER catalysts.

7.9. Summary and comparison of performance enhancement strategies

To provide a clear overview and facilitate comparison, the key advantages, weaknesses, challenges, and research gaps associated with the five primary strategies for enhancing MoS_2's electrocatalytic performance are summarized in Table 2.

Based on recent studies, the effectiveness of these strategies varies depends on the specific application and conditions. Doping and heterostructures have demonstrated remarkable improvements in HER performance by optimizing the electronic structure of MoS_2 and enhancing charge transfer at interfaces. For instance, MoS_2/graphene heterostructures exhibit low overpotentials (~100 mV) and high current densities due to synergistic effects [7.2.2]. Similarly, phase-transition control to stabilize the metallic 1T phase has led to exceptional catalytic activity, with overpotentials as low as 75 mV at 10 mA cm^{-2} [7.3.1]. However, the metastability of the 1T phase remains a critical limitation. Nanostructuring is highly effective for maximizing edge site exposure, with vertically oriented nanosheets showing up to 3–5 times higher edge site density and reduced Tafel slopes [7.1.3]. In contrast, surface modification and advanced synthesis technologies often serve as complementary approaches; for example, surface functionalization with Pt nanoparticles can boost activity but requires precise control to avoid degradation. Overall, combined strategies—such as doping within nanostructured frameworks or phase engineering in heterostructures—tend to yield the best results by addressing multiple limitations simultaneously (e.g., conductivity, stability, and active site density). Future work should focus on integrating these approaches to develop scalable, efficient MoS_2-based catalysts.

8. Application prospects

MoS_2 catalytic material, as a frontier, has a highly anticipated potential for application in electrocatalytic HER and other electrocatalytic fields. The following content will explore the application of MoS_2 in real HER application cases, its potential in other electrocatalytic reactions, and future research directions and trends.

8.1. Case of MoS_2 in practical HER

MoS_2 Because of its excellent catalytic performance and low cost, it has been used in several practical HER application cases.

- Industrial water electrolysis equipment: MoS_2 has been integrated into industrial-scale water electrolysis equipment to improve the yield and purity of hydrogen. Its excellent corrosion resistance and low overpotential make it ideal for improving electrolytic efficiency [540].
- Water decomposition driven by solar energy: MoS_2 is used as a cathode material, combined with the light absorption layer, to realize the water decomposition directly driven by solar energy [541, 542]. The research and development of this integrated system provide a new way for renewable energy conversion.
- Portable electrolytes: In miniaturization and portable electrolytes, MoS_2 as a catalyst is widely used because of its stability and efficiency, especially for hydrogen production in remote areas or emergency systems [543,544].

Notably, under high current densities (e.g., 100 mA cm^{-2}), MoS_2-based catalysts demonstrate practical viability when specific conditions are met: the use of metallic 1T-phase MoS_2 enhances conductivity, vertically oriented nanosheet arrays maximize edge site exposure and mass transfer, and heterostructure design (e.g., MoS_2/Mo_2C) improves interfacial charge transfer and stability, as evidenced by the HC-MoS_2/Mo_2C catalyst maintaining performance at 500 mA cm^{-2} for 24 h

Table 2
Comparison of strategies to improve the electrocatalytic performance of MoS_2 for the HER.

Strategy	Advantages	Weaknesses/Disadvantages	Key Challenges	Research Gaps/Future Directions
Nanostructuring (Section 7.1)	Increases specific surface area and exposes more active edge sites (7.1.1, 7.1.2). Vertically oriented nanosheets enhance electron transport and bubble release (7.1.3). Porous structures improve mass transfer (7.1.4).	May introduce structural defects affecting stability (5.1). Difficult to control uniformity in large-scale synthesis (6.3).	Precise control of morphology and layer number to prevent agglomeration (7.1.2). High production costs for industrial-scale application (6.3).	Develop green, scalable synthesis methods (7.1.3). Optimize the edge-to-basal-plane ratio in quantum dots (7.6.5).
Doping and Heterostructures (Section 7.2)	Modulates electronic structure, enhancing conductivity and activity (7.2.1). Heterostructures (e.g., with graphene) enable interfacial synergy, improving charge transfer (7.2.2).	Doping inhomogeneity can cause phase separation or side effects (5.5.2). Interface stability in heterostructures can be problematic (7.2.2).	Control doping type and distribution (7.2.1). Optimize interfacial charge transfer through engineering (7.2.2).	Achieve atomic-level precision in doping (5.5.2). Investigate multi-material synergistic mechanisms (8.3).
Phase-Transition Control (Section 7.3)	Metallic 1T phase offers higher intrinsic conductivity and activity than semiconducting 2H phase (7.3.1). Optimizes hydrogen adsorption free energy (ΔG_{H^*}) (2.2.2).	1T phase is thermodynamically metastable and prone to reverting to 2H phase (5.6.2). Phase transition can introduce defects (7.3.1).	Limited methods to stabilize the 1T phase effectively (7.3.1). Unclear phase transition mechanisms under dynamic conditions (5.6.2).	Develop physical/chemical stabilization strategies (7.3.2). Study correlation between phase transition and catalytic activity (8.4).
Surface Modification (Section 7.4)	Introducing functional groups (e.g., –OH, $–NH_2$) enhances hydrophilicity and activity (7.4.1). Composites with other catalysts (e.g., Pt) improve stability and performance (7.4.2).	Modified layers may detach or cause interfacial instability (7.4.2). Functional groups may degrade during long-term operation (7.4.3).	Maintaining chemical stability post-modification (7.4.3). Complex processes for large-scale functionalization (6.3).	Develop precise edge-selective functionalization techniques (7.4.3). Explore self-healing modified layers (8.3).
Advanced Synthesis Technologies (Section 7.5)	Enables precise control of phase, defects, and morphology (7.5.2). Methods like CVD and ALD allow atomic-level control (7.5.1).	High cost and strong equipment dependency (6.3). Difficult to scale up from lab to industry (6.3).	Challenges in standardization and reproducibility (7.5.2). Lack of environmentally friendly synthesis routes (6.3).	Develop green synthesis pathways (7.5.1). Advance in-situ characterization of dynamic synthesis processes (8.3).

(Fig. 7e) [244].

8.2. Potential of MoS_2 in other electrocatalytic reactions

In addition to HER, MoS_2 also shows great potential in other electrocatalytic reactions.

- Carbon dioxide reduction: Due to the unique electronic structure and active site of MoS_2, it is studied for carbon dioxide reduction reaction (CO_2RR), converting CO_2 into valuable chemicals and fuels [545–547].
- Oxygen reduction reaction: In fuel cells, MoS_2 catalyzes oxygen reduction reaction (ORR), which is expected to replace expensive platinum-based catalysts, reduce costs, and improve the commercial feasibility of fuel cells [548–550].
- Oxygen evolution reaction: It is also used for MoS_2 to catalyze the oxygen evolution reaction (OER) in the process of water decomposition, and its excellent properties make it a strong candidate for this critical reaction [550,551].

8.3. Future research direction and development trend

MoS_2 The future research and development trends in the field of electrocatalysis include.

- Interface engineering: Optimize the interaction between MoS_2 and electrolyte and substrate through interface engineering to improve the catalytic efficiency and stability [552,553].
- Development of composite materials: MoS_2 is combined with other two-dimensional materials, conductive polymers, or metal nanoparticles to form a composite catalyst to achieve better catalytic performance and stability [554,555].
- Large-scale production: develop efficient and low-cost synthesis methods to realize the large-scale production of MoS_2 to meet the needs of industrial applications [556].
- System integration and optimization: Integrate the MoS_2 catalyst with the existing energy conversion equipment and systems to optimize the overall performance and promote its commercialization process in the energy field [557,558].
- Combination of theory and experimental research: a deep understanding of the catalytic mechanism of MoS_2, combined with theoretical calculation and experimental research, to guide the design of new and efficient catalysts [191,486]. Therefore, MoS_2 has shown great potential for application in electrocatalytic hydrogen precipitation reactions and other electrocatalytic reactions, and its future research and development will have a profound impact on the field of hydrogen energy and electrocatalysis.

Future research should prioritize addressing the stability challenges of 1T-MoS_2 through atomic-level precision engineering, such as developing interface strain control (e.g., core-shell structures) to suppress phase transition, integrating in-situ characterization techniques (e.g., operando TEM or XAS) to monitor real-time phase dynamics, and exploring self-healing mechanisms (e.g., electrochemical regeneration) [559]. Additionally, machine learning-assisted screening of novel stabilizers (e.g., rare-earth dopants) and standardized testing protocols (e.g., accelerated aging at >500 mA cm^{-2}) are essential to bridge the gap between laboratory research and commercial deployment [378]. These directions aim to achieve durable 1T-MoS_2 catalysts with enhanced stability under industrial conditions.

8.4. Important parameters of MoS_2 in electrocatalytic HER in future research

8.4.1. Comparison with other materials

In the field of electrocatalytic HER, MoS_2 has become an important candidate to replace noble metal catalysts (such as Pt) due to its low cost, abundant reserves, and excellent catalytic potential. However, compared with other types of electrocatalytic materials, MoS_2 still has some gaps in terms of overpotential, catalytic efficiency, stability, etc., and also shows some unique advantages. In this section, MoS_2 will be systematically compared with other typical HER catalytic materials in terms of performance parameters, structural properties, and practical application potential, and propose future development directions.

(1) Comparison with precious metal catalysts

Noble metal catalysts, such as Pt and its base alloys, are considered to be the best catalysts for HER, with near-zero overpotential, extremely low Tafel slope, and excellent catalytic efficiency. However, its high cost and scarcity limit large-scale adoption. Performance Comparison: The overpotential of Pt-based catalysts is typically below 20 mV (at 10 mA cm^{-2}), while the overpotential of MoS_2 is typically between 150 and 200 mV, making it difficult to reach the level of precious metals even after optimization [560,561]. The Tafel slope of oPt is typically below 30 mV dec^{-1}, while the Tafel slope of MoS_2 is between 40 and 120 mV dec^{-1}, indicating a slower reaction kinetics of MoS_2. In terms of Faraday efficiency, MoS_2 is comparable to Pt, typically close to 100%, indicating its high selectivity in HER. Strengths and Weaknesses: The biggest advantage of oMoS_2 is its low cost and abundant reserves, making it an ideal candidate material for large-scale hydrogen production. However, the catalytic activity and stability of MoS_2 are still not comparable to Pt, especially under high current density and long operating conditions. Development direction: Through edge engineering, defect introduction, and phase control strategies, the performance gap between MoS_2 and precious metal catalysts is further narrowed. Develop composites with MoS_2 and a small amount of precious metals, and use synergistic effects to improve catalytic performance while reducing the amount of precious metals.

(2) Comparison with other transition metal-based catalysts

Transition metal-based catalysts (e.g., Ni, Co, Fe and their sulfides, phosphides, and nitrides) have received extensive attention in the field of HER in recent years. These materials typically have high catalytic activity and lower cost, but their stability and selectivity may be insufficient. Performance Comparison: The overpotential of transition metal phosphide (e.g., Ni_2P, CoP) and sulfide (e.g., NiS_2, CoS_2) is typically between 100 and 200 mV, which is comparable to MoS_2. The Tafel slope of these materials is typically between 40 and 80 mV dec^{-1}, which is slightly better than MoS_2, indicating faster reaction kinetics. In terms of stability, MoS_2 is generally superior to certain transition metal-based catalysts due to its chemical inertness and corrosion resistance, especially in acidic media. Strengths and Weaknesses: The advantage of MoS_2 is its relatively high chemical stability and environmental friendliness, whereas some transition metal-based catalysts may dissolve or passivate in acidic or alkaline media. However, MoS_2 has poor electronic conductivity, which limits its performance at high current densities. Development direction: The heterostructure of MoS_2 and transition metal-based catalysts was constructed, and the catalytic activity and stability were improved by using interface effects. Optimize the electronic structure and conductivity of MoS_2 to further improve its performance at high current densities [260].

(3) Comparison with carbon-based catalysts

Carbon-based catalysts (such as doped graphene, carbon nanotubes, and carbon quantum dots) have become hot spots in HER research due to their low cost, high conductivity, and tunable structural properties. However, carbon-based catalysts have low intrinsic activity and often require doping or compounding of other active materials to improve performance.

Performance Comparison: The overpotential of doped graphene and carbon nanotubes is usually higher (>200 mV), which is significantly higher than that of the optimized MoS_2. The Tafel slope of carbon-based catalysts is generally high (>100 mV dec^{-1}), indicating slower reaction kinetics. In terms of Faraday efficiency, carbon-based catalysts are generally lower than MoS_2, especially at high current densities. Strengths and Weaknesses: The advantage of carbon-based catalysts is their high conductivity and structural tunability, which can be used as a carrier to be compounded with MoS_2 to improve overall performance. However, carbon-based catalysts have low intrinsic activity, making it difficult to meet the needs of high-efficiency HER when used alone. Development direction: MoS_2 is compounded with carbon-based materials to improve electron transport performance and active site density by taking advantage of the high conductivity and large specific surface area of carbon materials. The intrinsic activity of carbon-based materials can be enhanced by doping or functionalization, and it can synergize with MoS_2 [562].

(4) Comparison with other 2D materials

In addition to MoS_2, other 2D materials (e.g., WS_2, black phosphorus, g-C_3N_4) have also been widely studied for HER. These materials have a unique layered structure and tunable electronic properties, but they have their advantages and disadvantages in terms of catalytic performance and stability. The catalytic performance of WS_2 is similar to that of MoS_2, but its edge active site density is lower, resulting in a slightly inferior overall performance than MoS_2. Black phosphorus has excellent electron transport properties, but its chemical stability is poor and it is easily degraded in air or water. g-C_3N_4 has low catalytic performance, but its photocatalytic performance is excellent and can be combined with MoS_2 for photocatalytic hydrogen production. Strengths and Weaknesses: The advantage of MoS_2 is its high chemical stability and abundant edge sites, while some 2D materials (e.g., black phosphorus) have poor stability, limiting their practical application. However, MoS_2 has poor electrical conductivity and has certain disadvantages compared to some two-dimensional materials such as black phosphorus. Development direction: Construct the heterostructure of MoS_2 and other 2D materials, and use the synergistic effect of different materials to improve the catalytic performance. Develop new two-dimensional materials and combine the advantages of MoS_2 to explore more efficient catalytic systems.

(5) Comparison with other non-precious metal catalysts: Transition metal phosphides, carbides, and nitrides

To provide a comprehensive perspective and better highlight the relative advantages and limitations of MoS_2, this section systematically compares it with other prominent non-precious metal HER catalysts, such as transition metal phosphides (e.g., Ni_2P, CoP), carbides (e.g., Mo_2C, WC), and nitrides (e.g., MoN, VN) [563]. These materials have garnered significant attention due to their high activity and unique properties [23]. The key performance parameters, advantages, and limitations are summarized in Table 3.

MoS_2's relative advantages: MoS_2 excels in edge-site engineering flexibility, allowing precise tuning of active sites through nanostructuring, doping, or defect control. Its low cost and abundance make it suitable for large-scale applications. In contrast, phosphides and carbides rely more on bulk conductivity but may suffer from stability issues (e.g., dissolution in acids for phosphides).

MoS_2's limitations: The inherent conductivity of semiconducting 2H–MoS_2 is inferior to metallic carbides or phosphides, limiting performance at high current densities. Phase instability (e.g., 1T to 2H transition) also poses challenges. Carbides and nitrides offer better stability but often at higher cost or with lower active site density.

Synergistic opportunities: Future research should focus on hybrid structures (e.g., MoS_2/CoP or MoS_2/Mo_2C composites) to combine MoS_2's edge-site activity with the conductivity of carbides/phosphides, thereby overcoming individual limitations. This comparison underscores the importance of material-specific design for optimizing HER performance.

8.4.2. *Performance at high current densities (e.g., 100 mA cm^{-2})*

The catalytic activity of MoS_2 at high current densities (≥100 mA cm^{-2}) is critical for industrial applications. Key conditions for efficient operation include: (i) Use of metallic 1T-phase MoS_2 to enhance conductivity and reduce charge transfer resistance [288]; (ii) Design of vertically oriented nanosheet arrays or porous structures to maximize edge site exposure and facilitate bubble release, mitigating mass transfer limitations [568]; (iii) Introduction of sulfur vacancies or heteroatom doping (e.g., Co, N) to optimize hydrogen adsorption free energy (ΔG_H) [569]; and (iv) Construction of heterostructures (e.g., MoS_2/graphene, MoS_2/Mo_2C) to improve interfacial charge transfer and stability. For instance, the HC-MoS_2/Mo_2C catalyst maintains stability at 500 mA cm^{-2} for 24 h (Fig. 7e), demonstrating the synergy of these strategies. Future research should focus on atomic-level edge site control and dynamic stability under industrial conditions [244].

8.4.3. *Future research directions*

Although significant progress has been made in the study of MoS_2-based electrocatalytic HER in recent years, there are still many challenges in the precise regulation and stability improvement of edge sites. In order to further promote the practical application of MoS_2-based catalysts, future research should focus on the following two key directions: atomic-level precision edge construction technology and edge stability under dynamic conditions.

(1) Atomic-level precision edge construction technology

The edge site is the main source of MoS_2 HER activity, and its structural and electronic properties directly determine the performance of the catalyst. Although traditional nanoengineering methods (such as plasma etching and chemical vapor deposition) can increase the exposure of edge sites, there are still limitations in the atomic-level precise control of edge sites. Future research needs to develop more precise edge construction techniques to achieve the directional design of edge loci and the optimization of electronic states. i) Atomic Layer Deposition

Table 3
Comparison of MoS_2 with other non-precious metal HER catalysts (typical values based on literature data).

Catalyst Type	Typical Materials	Overpotential@10 mA cm^{-2} (mV)	Tafel Slope (mV dec^{-1})	Advantages	Limitations	Reference
MoS_2	2H/1T phase	75–200	40–120	High edge-site activity, low cost, tunable defects	Poor conductivity, phase instability	[564]
Transition metal phosphides	Ni_2P, CoP	50–150	30–60	High intrinsic activity, good conductivity	Prone to dissolution in acidic media	[565]
Transition metal carbides	Mo_2C, WC	100–180	40–70	High stability, excellent conductivity	Low active site density	[566]
Transition metal nitrides	MoN, VN	120–200	50–80	Strong corrosion resistance, durability	High synthesis cost, moderate activity	[567]

(ALD) Technology: Atomic layer deposition technology can control the growth of materials with the precision of single atomic layers, and realize the precise construction of edge sites by adjusting the growth direction and crystal orientation of MoS_2. For example, by selectively exposing the Mo-edge or S-edge, the electronic structure of the edge can be manipulated to optimize the hydrogen adsorption-free energy (ΔG_{H^*}). ii) Molecular Beam Epitaxy (MBE) Technology: Molecular beam epitaxy can be used to construct MoS_2 films with specific edge structures at the atomic scale. By precisely controlling the deposition rate and growth conditions, it is possible to achieve a uniform distribution of marginal sites and a high proportion of exposure. In addition, MBE technology can also be used to construct edge structures with heterogeneous interfaces, thereby further improving catalytic performance. iii) Self-assembly and template auxiliary method: By introducing template-assisted growth techniques such as porous templates or nanowire templates, directed growth of MoS_2 and orderly arrangement of edge sites can be achieved. Combined with the self-assembly strategy, MoS_2 structures with specific geometries (e.g., nanorings, nanoribbons) can also be constructed to maximize the exposure density of edge sites. iv) Chemical modification of edge sites: While the edge site is precisely constructed, the electronic structure of the edge can be further manipulated by introducing functionalized modifications such as doped atoms or molecular ligands. For example, by introducing metal doping (e.g., Ni, Co) at the Mo-edge or non-metal doping (e.g., N, P) at the S-edge, the electronic state distribution at the edge can be effectively optimized and HER activity enhanced. In the future, breakthroughs in atomic-level precision edge construction technology will provide new design ideas for the construction of efficient and stable MoS_2-based catalysts.

(2) Research on edge stability under dynamic conditions

In practical applications, catalysts need to operate for a long time under complex dynamic conditions, and the stability of the edge site directly determines the durability and performance retention ability of the catalyst. The current research mainly focuses on the evaluation of edge activity under static conditions, while the stability of edge sites under dynamic conditions is still insufficient. In the future, in-depth research is needed from the following aspects: i) Dynamic reconstruction behavior of edge loci: During the electrochemical reaction, the edge site of MoS_2 may be reconstituted or passivated, resulting in a decrease in catalytic performance. For example, the continued production of hydrogen may cause dissolution or morphological changes at edge sites. In-situ characterization techniques (such as in-situ transmission electron microscopy and in-situ X-ray photoelectron spectroscopy) can be used to monitor the dynamic behavior of edge sites in real time and reveal their structural evolution mechanism under reaction conditions. ii) Inhibition strategy for edge passivation: Passivation of edge sites (e.g., oxidation or adsorption poisoning) is one of the main factors affecting the stability of catalysts. Future studies can inhibit the passivation of edge sites by introducing protective coatings (e.g., carbon or oxide layers) or chemical modifications (e.g., introducing antioxidant doping elements). In addition, studies have shown that the construction of edge structures with self-healing functions (such as dynamic adsorption-desorption equilibrium) is also expected to significantly improve the stability of catalysts. iii) Edge electronic state control under dynamic working conditions: Under the actual electrolysis conditions, voltage fluctuations and current density changes may cause dynamic changes in the electronic states at the edges, which may affect the catalytic performance. Through theoretical calculations (such as molecular dynamics simulations) combined with experimental verification, the variation law of edge electronic states under dynamic conditions can be studied in depth, and edge structures with dynamic adaptability can be designed. Depending on the practical requirements, long-running endurance tests (e.g., hundreds of hours of potentiostatic or galvanostatic testing) will be required in the future to evaluate the stability and fatigue resistance of edge sites. At the same time, the subsequent characterization of the deactivated catalyst can further reveal the specific mechanism of edge site inactivation and guide stability optimization. Research on the influence of environmental factors: In the actual electrolytic environment, the pH of the solution, the ion concentration, and the presence of impurities can have a significant impact on the stability of the edge site. Future research needs to systematically evaluate the mechanism of these environmental factors on edge loci and develop edge regulation strategies with environmental adaptability. Atomic-level precision edge construction technology and edge stability research under dynamic working conditions are two important directions for the development of MoS_2-based HER catalysts in the future. Through the development of advanced edge construction technology, the directional design and electronic state optimization of edge sites can be realized to maximize their catalytic activity. At the same time, through in-depth study of the stability of edge sites under dynamic conditions, can provide a scientific basis for improving the durability and practical application performance of catalysts. In the future, the synergistic development of these two directions could provide new theoretical guidance and technical routes for the design of efficient and stable MoS_2-based HER catalysts, and promote their wide application in the field of practical energy conversion.

8.5. Comparative analysis with other 2D layered materials

To provide a systematic comparison of MoS_2 with other two-dimensional (2D) layered materials—especially transition metal dichalcogenide (TMDC) catalysts—in electrocatalytic HER, a comparative table (Table 4) has been compiled based on key performance parameters, including crystal structure, bandgap, HER overpotential at 10 mA cm^{-2}, Tafel slope, advantages, and limitations. This analysis highlights the unique position of MoS_2 in the family of 2D materials and underscores the importance of multidimensional engineering (e.g., edge-site activation, phase modulation) in enhancing its catalytic performance.

MoS_2 exhibits superior HER activity among TMDCs due to its optimal hydrogen adsorption free energy ($\Delta G_{H^*} \approx 0$ eV) at edge sites (Section 3.1.1). The metallic 1T phase further enhances conductivity and kinetics, with overpotentials as low as 75 mV under optimization (Sections 5.4.2 and 7.3). In contrast, other TMDCs like WS_2 and $MoSe_2$ show higher overpotentials, primarily due to less favorable edge-site electronic structures. The comparative analysis reinforces the importance of edge-site engineering for MoS_2. While materials like graphene and g-C_3N_4 offer high conductivity or photocatalytic properties, their HER performance is limited without activation strategies (e.g., doping or compositing). MoS_2's versatility—enabled by phase control (2H to 1T transition), defect introduction, and heterostructure design (Sections 7.1–7.4)—allows it to bridge activity-stability gaps. This table aligns with the volcano plot in Fig. 3d, which relates HER activity to ΔG_{H^*}, visually emphasizing MoS_2's position near the peak compared to other materials. Future work should focus on combining MoS2's edge-site advantages with the conductivity of graphene or the light-response of g-C_3N_4 in heterostructures (Section 8.3).

9. Conclusion

This paper comprehensively summarizes the application status, research progress, and challenges of MoS_2 in electrocatalytic HER and discusses various strategies to improve its catalytic performance. With its layered structure and unique marginal active site, MoS_2 exhibits significant HER catalytic activity, making it a promising non-noble metal catalyst. Regarding catalytic properties, MoS_2 has a lower cost, abundant marginal active site, and tunable electronic structure. However, the problems of insufficient conductivity, complexity of defect control, long-term stability, and immaturity of large-scale synthesis technology have limited its application in HER.

To overcome these challenges, the researchers adopted various strategies, including nanostructuring to increase active surface area,

Table 4
Performance comparison of MoS_2 with other 2D layered materials (particularly TMDCs) in electrocatalytic HER.

Material	Crystal Structure	Bandgap (eV)	HER Overpotential (mV) at 10 mA cm^{-2}	Tafel Slope (mV dec^{-1})	Advantages	Limitations	Reference
MoS_2	2H (semiconducting), 1T (metallic)	1.2–1.8 (bulk)	100–200 (optimized down to ~75)	40–120	High edge-site activity, low cost, abundant resources; tunable electronic structure via doping/defect engineering; excellent stability in acidic/alkaline media (Sections 5.1–5.5).	Low basal-plane activity; conductivity limitations in 2H phase; stability issues in 1T phase; challenges in large-scale synthesis (Sections 5.4–5.6).	[570]
WS_2	2H dominant	~1.8 (monolayer)	150–250	50–130	Similar structure to MoS2; high chemical stability; potential for heterostructures.	Lower HER activity than MoS_2; limited edge-site density; synthetic control challenges.	[571]
$MoSe_2$	2H	~1.5	120–220	45–110	Smaller bandgap than MoS_2; improved conductivity; Se atoms modulate electronic structure.	Higher cost of Se; moderate long-term stability.	
WSe_2	2H	~1.6	130–240	50–120	High carrier mobility; potential for photocatalysis.	Moderate HER activity; complex synthesis control.	[572]
Graphene	Hexagonal lattice	Zero gap (metallic)	>300 (intrinsic)	>100	High conductivity; large surface area; mechanical stability.	Low intrinsic HER activity; requires doping/compositing with catalysts (e.g., MoS_2/graphene in Section 7.2).	[573]
g-C_3N_4	Layered polymer	~2.7	High (>400)	High	Visible-light response; suitable for photocatalytic HER; low cost.	Poor conductivity; weak HER activity; often used in composites.	[574]

doping and constructing heterostructures to adjust electronic properties, phase transition control to obtain more active phases, surface modification to enhance reactivity, and development of advanced synthetic technologies to achieve precise control of MoS_2 structure. These strategies have achieved remarkable results in improving the catalytic efficiency and stability of MoS_2.

Looking into the future, MoS_2 has a broad application prospect in the field of hydrogen energy. With advances in synthesis technology and a deeper understanding of the catalytic mechanism, it is expected that MoS_2 will be more widely used in industrial water electrolysis, solar water decomposition, and portable electrolyzers. Moreover, MoS_2 also shows its potential in other electrocatalytic reactions, such as carbon dioxide reduction, oxygen reduction reactions, and oxygen evolution reactions, and is expected to become a multifunctional electrocatalytic material. Although applying MoS_2 in the electrocatalytic hydrogen evolution reaction is still challenging, its broad application potential in hydrogen energy is apparent in the future of energy conversion and storage systems, contributing to the sustainable development of clean energy.

CRediT authorship contribution statement

Xuexue Pan: Writing – original draft, Software, Resources, Formal analysis, Conceptualization. **Yi Zhao:** Writing – original draft, Software, Methodology, Data curation. **Dinmukhambet Baimbetov:** Writing – original draft, Visualization, Validation, Project administration, Methodology, Funding acquisition. **Yevgeniy Muralev:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Samal Syrlybekkyzy:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Berik Bakhytzhanovich Akhmetov:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Qian Liu:** Writing – review & editing, Validation, Software, Resources, Formal analysis, Data curation. **Qamar Abbas:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research has been funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. BR24992964). Authors acknowledge 2023 High-level Talents Research Initiative Project (KYG2302), Topic 4 of the Second Batch of Social Public Welfare and Basic Research Projects in Zhongshan City in 2023: Basic and Applied Basic Research (No. 2023B2016), Young Innovative Talents Project for Ordinary Universities in Guangdong Province in 2024 (No. 2024KQNCX162), the 11th Batch of "Zhongshan Talent Plan" Innovation and Entrepreneurship Team Project (No. CXTD2024009) and Guangdong Province Project (No. 2023QN10ZZ01). Authors thank Yuling Fan from Zhongshan Advanced Functional Materials Engineering Technology Research Center, Zhongshan Polytechnic, for technical support.

References

[1] Elaouzy Y, El Fadar A. Water-energy-carbon-cost nexus in hydrogen production, storage, transportation and utilization. Int J Hydrogen Energy 2024;53:1190–209.
[2] Mehtab A, Ali SA, Sadiq I, Shaheen S, Khan H, Fazil M, Pandit NA, Naaz F, Ahmad T. Hydrogen energy as sustainable energy resource for carbon-neutrality realization. ACS SUstain Resour Manag 2024;1:604–20.
[3] Evro S, Oni BA, Tomomewo OS. Carbon neutrality and hydrogen energy systems. Int J Hydrogen Energy 2024;78:1449–67.
[4] Santosh M, Groves DI, Yang C-X. Habitable planet to sustainable civilization: global climate change with related clean energy transition reliant on declining critical metal resources. Gondwana Res 2024;130:220–33.
[5] Sikiru S, Oladosu TL, Amosa TI, Olutoki JO, Ansari MNM, Abioye KJ, Rehman ZU, Soleimani H. Hydrogen-powered horizons: transformative technologies in clean energy generation, distribution, and storage for sustainable innovation. Int J Hydrogen Energy 2024;56:1152–82.
[6] Zhang J. Energy access challenge and the role of fossil fuels in meeting electricity demand: promoting renewable energy capacity for sustainable development. Geosci Front 2024;15:101873.
[7] Kamran M, Turzyński M. Exploring hydrogen energy systems: a comprehensive review of technologies, applications, prevailing trends, and associated challenges. J Energy Storage 2024;96:112601.
[8] Hui Y, Wang M, Guo S, Akhtar S, Bhattacharya S, Dai B, Yu J. Comprehensive review of development and applications of hydrogen energy technologies in China for carbon neutrality: technology advances and challenges. Energy Convers Manag 2024;315:118776.

[9] Li J, Li L, Wang J, Cabot A, Zhu Y. Boosting hydrogen evolution by methanol oxidation reaction on Ni-based electrocatalysts: from fundamental electrochemistry to perspectives. ACS Energy Lett 2024;9:853–79.
[10] Yu J, Li Z, Wang C, Xu X, Liu T, Chen D, Shao Z, Ni M. Engineering advanced noble-metal-free electrocatalysts for energy-saving hydrogen production from alkaline water via urea electrolysis. J Colloid Interface Sci 2024;661:629–61.
[11] Li T, Wang B, Cao Y, Liu Z, Wang S, Zhang Q, Sun J, Zhou G. Energy-saving hydrogen production by seawater electrolysis coupling tip-enhanced electric field promoted electrocatalytic sulfion oxidation. Nat Commun 2024;15:6173.
[12] Badiger JG, Arunachalam M, Kanase RS, Sayed SA, Ahn K-S, Ha J-S, Kang SH. Highly stable MoS_2/$MnMoO_4$@Ti nanocomposite electrocatalysts for hydrogen evolution reaction. Int J Hydrogen Energy 2024;51:156–68.
[13] Cho YS, Kang J. Two-dimensional materials as catalysts, interfaces, and electrodes for an efficient hydrogen evolution reaction. Nanoscale 2024;16:3936–50.
[14] Zhang Y, Zhang R, Guo Y, Li Y, Li K. A review on MoS_2 structure, preparation, energy storage applications and challenges. J Alloys Compd 2024;998:174916.
[15] Hasimoto LH, Bettini J, Leite ER, Lima RS, Souza Junior JoB, Liu L, Santhiago M. Binary cooperative thermal treatment of cellulose and MoS_2 for the preparation of sustainable paper-based electrochemical devices for hydrogen evolution. ACS Appl Eng Mater 2022;1:708–19.
[16] Hachhach M, Akram H, Hanafi M, Achak O, Chafik T. Process design and economic assessment of large-scale production of molybdenum disulfide nanomaterials. Chem Prod Process Model 2023;18:355–68.
[17] Wei W, Hou H, Zhao Y, Fan X, Shi L, Yan Y, Wang T, Long J. A novel preparation strategy for an oil-soluble catalyst in slurry phase hydrocracking: synergistic effect and electronic regulation of Fe on MoS2. Fuel 2024;374:132465.
[18] Wang Q, Huang W, Li X, Lin S, Li Z, Ma X. Electronic regulation of MoS_2 edge sites by d electron transfer of Ni or Co to improve the activity of CO sulfur-resistant methanation. Chem Eng J 2024;480:148242.
[19] Florindo BR, Hasimoto LH, de Freitas N, Candiotto G, Lima EN, de Lourenço C, de Araujo AB, Ospina C, Bettini J, Leite ER. Patterning edge-like defects and tuning defective areas on the basal plane of ultra-large MoS_2 monolayers toward the hydrogen evolution reaction. J Mater Chem A 2023;11:19890–9.
[20] Aydinsoy EA, Aghamaliyev ZZ, Aghamaliyeva DB, Abbasov VB. A systematic review of corrosion inhibitors in marine environments: insights from the last 5 years. Proc Petrochem Oil Refin 2024;25.
[21] Xu C, Liang Y, Zhang R, Cheng J, Yu H. Ethylene carbonate-free electrolytes for high voltage lithium-ion batteries: progress and perspectives. Energy Fuels 2024;38:18208–26.
[22] Munir A, Nasir J, Ulhaq T, Iqbal J, Hussain I, Qurashi A. Current advancement in benchmarking stable water splitting electrocatalysts: a chemist perspective. Authorea Preprints 2023. https://doi.org/10.22541/au.169762730.05941206/v1.
[23] Ying Y, Fan K, Lin Z, Huang H. Facing the "cutting edge:" edge site engineering on 2D materials for electrocatalysis and photocatalysis. Adv Mater 2025;37:2418757.
[24] Zhang Z, Wang Y, Guo T, Hu P. The influence of defect engineering on the electronic structure of active centers on the catalyst surface. Catalysts 2025;15:651.
[25] Guo J, Haghshenas Y, Jiao Y, Kumar P, Yakobson BI, Roy A, Jiao Y, Regenauer-Lieb K, Nguyen D, Xia Z. Rational design of earth-abundant catalysts toward sustainability. Adv Mater 2024;36:2407102.
[26] Yadgarov L, Tenne R. Nanotubes from transition metal dichalcogenides: recent progress in the synthesis, characterization and electrooptical properties. Small 2024:2400503.
[27] Moghadasi R, Ghorbanzadeh Ahangari M, Ramzali M, Hassani Niaki M. Mechanical and electronic behaviour of TMDC nanotubes and monolayers: molecular simulations. Mol Simul 2024;50:944–53.
[28] Aditya D, Nataraj S. Structural, optical, and electronic properties of two-dimensional nanomaterials. Two Dimens Nanomater Polym Nanocompos: Proc Prop Appl 2024:167–94.
[29] Ali S, Ahmad Shah SS, Sufyan Javed M, Najam T, Parkash A, Khan S, Bajaber MA, Eldin SM, Tayeb RA, Rahman MM. Recent advances of transition metal dichalcogenides-based materials for energy storage devices, in view of monovalent to divalent ions. Chem Rec 2024;24:e202300145.
[30] Yu E, Pan Y. Enhancing the catalytic hydrogen evolution reaction (HER) of the defective borophene@ Pt/Pd/MoS_2 heterojunction. Int J Hydrogen Energy 2024;50:920–31.
[31] Mihai C, Simandan I-D, Sava F, Buruiana A-T, Bocirnea AE, Tite T, Zaki MY, Velea A. Synthesis of wrinkled MoS_2 thin films using a two-step method consisting of magnetron sputtering and sulfurization in a confined space. Sustainability 2024;16:3819.
[32] Wang Q, Luo B, Wang Z, Hu Y, Du M. Pore engineering in biomass-derived carbon materials for enhanced energy, catalysis, and environmental applications. Molecules 2024;29:5172.
[33] Mak KF, Lee C, Hone J, Shan J, Heinz TF. Atomically thin MoS_2: a new direct-gap semiconductor. Phys Rev Lett 2010;105:136805.
[34] Roy S, Joseph A, Zhang X, Bhattacharyya S, Puthirath AB, Biswas A, Tiwary CS, Vajtai R, Ajayan PM. Engineered two-dimensional transition metal dichalcogenides for energy conversion and storage. Chem Rev 2024;124:9376–456.
[35] Santosh K, Zhang C, Hong S, Wallace RM, Cho K. Phase stability of transition metal dichalcogenide by competing ligand field stabilization and charge density wave. 2D Mater 2015;2:035019.
[36] Molina-Sanchez A, Wirtz L. Phonons in single-layer and few-layer MoS_2 and WS_2. Phys Rev B Condens Matter 2011;84:155413.
[37] Strachan J, Masters AF, Maschmeyer T. 3R-MoS_2 in review: history, status, and outlook. ACS Appl Energy Mater 2021;4:7405–18.
[38] Sun C, Wang L, Zhao W, Xie L, Wang J, Li J, Li B, Liu S, Zhuang Z, Zhao Q. Atomic-level design of active site on two-dimensional MoS_2 toward efficient hydrogen evolution: experiment, theory, and artificial intelligence modelling. Adv Funct Mater 2022;32:2206163.
[39] Singh AK. Structures and defects of TMDs. In: 2D transition-metal dichalcogenides (TMDs): fundamentals and application. Springer; 2025. p. 133–98.
[40] Marinov AD, Bravo Priegue L, Shah AR, Miller TS, Howard CA, Hinds G, Shearing PR, Cullen PL, Brett DJ. Ex situ characterization of 1T/2H MoS_2 and their carbon composites for energy applications, a review. ACS Nano 2023;17:5163–86.
[41] Sharopov U. Surface defects in wide-bandgap LiF, SiO_2, and ZnO crystals: experiments and simulations. Springer Nature; 2024.
[42] Lakhani P, Bhanderi D, Modi CK. Nanocatalysis: recent progress, mechanistic insights, and diverse applications. J Nanoparticle Res 2024;26:148.
[43] Janardhanan JC, Padmanabhan NT, Jandas P, Sathyan M, Thomas RM, Mythili U, John H. Topology structure significance on the applications of morphologically diverse molybdenum disulfide. J Environ Chem Eng 2024;12:112268.
[44] Shi S, Sun Z, Hu YH. Synthesis, stabilization and applications of 2-dimensional 1T metallic MoS_2. J Mater Chem A 2018;6:23932–77.
[45] Xiao J, Long M, Li X, Zhang Q, Xu H, Chan K. Effects of van der Waals interaction and electric field on the electronic structure of bilayer MoS_2. J Phys Condens Matter 2014;26:405302.
[46] Wang Q-B, Han Z-H, Xu Q-Q, Cheng T, Yin J-Z. Reaction dynamics simulation of MoO_2 cluster precursor with melting, deoxygenation and sulfuration for MoS_2 growth by chemical vapor deposition. Appl Surf Sci 2024;669:160435.
[47] Gao Z, Nie W, Wang H, Ren S, Du D, Du S, Li J. Enhancing mechanical performance and high-temperature lubrication enabled by MoS_2/WB_2 nanolayered films. Compos B Eng 2024;275:111350.
[48] Zhang X, Wang S, Lee C-K, Cheng C-M, Lan J-C, Li X, Qiao J, Tao X. Unravelling the effect of sulfur vacancies on the electronic structure of the MoS_2 crystal. Phys Chem Chem Phys 2020;22:21776–83.
[49] Zhang X, Wang S, Lee CK, Cheng CM, Lan JC, Li X, Qiao J, Tao X. Unravelling the effect of sulfur vacancies on the electronic structure of the MoS_2 crystal. Phys Chem Chem Phys 2020;22:21776–83.
[50] Khanam Z, Xiong T, Yang F, Su H, Luo L, Li J, Koroma M, Zhou B, Mushtaq M, Huang Y. Endogenous interfacial mo− C/N− Mo-S bonding regulates the active Mo sites for maximized Li^+ storage areal capacity. Small 2024;20:2311773.
[51] Zhao Y, Zheng X, Gao P, Li H. Recent advances in defect-engineered molybdenum sulfides for catalytic applications. Mater Horiz 2023;10:3948–99.
[52] Wu J, Qiao P, An P, Zhang M, Xiu H, Song Z, Li K, Cui Y, Wang Y, Yao W. Modulating interfacial Mo-S chemical-bond enable highly-efficient charge transfer for promoted visible-light-driven photocatalytic hydrogen evolution. Appl Catal B Environ Energy 2025:125481.
[53] Cui X, Ge L, Chen X, Lv Z, Wang S, Zhou X, Zhang G. Beyond static structures: protein dynamic conformations modeling in the post-AlphaFold era. Briefings Bioinf 2025;26:bbaf340.
[54] Van Nang L, Vu TB, Dai Nguyen T, Do QD, Nguyen T-T, Phuong NTL, Phuong VTL, Nui ND, Nguyen TB, Van Duong P. Synthesis of multi-phases MoO_3-MoS_2-Mo_2S_3 nanostructure catalyst for degradation of methylene blue, rhodamine B, and crystal violet dyes. Phys Scri 2024;99:045907.
[55] Getaneh SA, Temam AG, Nwanya AC, Ejikeme PM, Ezema FI. Progress and development on the synthesis and application of two-dimensional molybdenum disulphide. Mater Sci Technol 2024;40:185–212.
[56] Li R, Huangfu Y, He P, Wu D, Zeng D, Yin S, Fan D, Zhao B. Bridging microscopic phase and defect manipulation with macroscopic core-sheath-shell structure for polarization-dominated electromagnetic wave absorption. Nano Today 2024;56:102318.
[57] Peelaers H, Van de Walle C. First-principles study of van der Waals interactions in MoS_2 and MoO_3. J Phys Condens Matter 2014;26:305502.
[58] Zhang X, Zhang Y, Yu H, Zhao H, Cao Z, Zhang Z, Zhang Y. Van der Waals-Interface-Dominated All-2D Electronics. Adv Mater 2023;35:2207966.
[59] Byskov LS, Hammer B, Nørskov JK, Clausen BS, Topsøe H. Sulfur bonding in MoS_2 and Co-Mo-S structures. Catal Lett 1997;47:177–82.
[60] Fatma I, Assad H, Kumar A. Introduction to two-dimensional nanomaterials: discovery, types and classifications, structure, unique properties, and applications. Two Dimens Nanomater Polym Nanocompos: Proc Prop Appl 2024:1–45.
[61] Zhang K, Hu S, Zhang Y, Zhang T, Zhou X, Sun Y, Li T-X, Fan HJ, Shen G, Chen X. Self-induced uniaxial strain in MoS_2 monolayers with local van der Waals-stacked interlayer interactions. ACS Nano 2015;9:2704–10.
[62] Liu X, Liu L, Wu Y, Wang Y, Yang J, Wang Z. Rosette-like MoS_2 nanoflowers as highly active and stable electrodes for hydrogen evolution reactions and supercapacitors. RSC Adv 2019;9:13820–8.
[63] Tang D-M, Kvashnin DG, Najmaei S, Bando Y, Kimoto K, Koskinen P, Ajayan PM, Yakobson BI, Sorokin PB, Lou J. Nanomechanical cleavage of molybdenum disulphide atomic layers. Nat Commun 2014;5:3631.
[64] Zhang J, Yang A, Wu X, van de Groep J, Tang P, Li S, Liu B, Shi F, Wan J, Li Q. Reversible and selective ion intercalation through the top surface of few-layer MoS_2. Nat Commun 2018;9:5289.
[65] Lee J-U, Woo S, Park J, Park HC, Son Y-W, Cheong H. Strain-shear coupling in bilayer MoS_2. Nat Commun 2017;8:1370.

[66] Wu F-B, Zhou S-J, Ouyang J-H, Wang S-Q, Chen L. Structural superlubricity of two-dimensional materials: mechanisms, properties, influencing factors, and applications. Lubricants 2024;12:138.

[67] Parija A, Choi Y-H, Liu Z, Andrews JL, De Jesus LR, Fakra SC, Al-Hashimi M, Batteas JD, Prendergast D, Banerjee S. Mapping catalytically relevant edge electronic states of MoS_2. ACS Cent Sci 2018;4:493–503.

[68] Asadi M, Kumar B, Behranginia A, Rosen BA, Baskin A, Repnin N, Pisasale D, Phillips P, Zhu W, Haasch R. Robust carbon dioxide reduction on molybdenum disulphide edges. Nat Commun 2014;5:4470.

[69] Yu L., Yan Q., Ruzsinszky A. The key role of antibonding electron transfer in surface chemisorption and heterogeneous catalysis. arXiv preprint arXiv:1812 02228 2018. https://doi.org/10.48550/arXiv.1812.02228.

[70] Satheesh D, Baskar L, Jayavelu Y, Dekshinamoorthy A, Sakthinathan VR, Daniel PJ, Vijayaraghavan S, Krishnan K, Rajendran R, Pachaiappan R. Efficient electrochemical hydrogen evolution activity of nanostructured Ag_3PO_4/MoS_2 heterogeneous composite catalyst. Chemosphere 2024;351:141220.

[71] Li L, Yu M, Gao C, Yan X, Zhang N, Bao J, Zhang X. MoS_2/CoS_2 with heterostructure in-situ grown on the surface of electrospinning carbon nanotube for efficient hydrogen evolution reaction. J Alloys Compd 2024;1003:175530.

[72] Niu S, Cai J, Wang G. Two-dimensional MoS_2 for hydrogen evolution reaction catalysis: the electronic structure regulation. Nano Res 2021;14:1985–2002.

[73] Yadav S. First principles investigation of nanomaterials for hydrogen generation and hydrogen storage. University of Toronto (Canada); 2015.

[74] Liao T, Sun Z, Sun C, Dou SX, Searles DJ. Electronic coupling and catalytic effect on H_2 evolution of MoS_2/graphene nanocatalyst. Sci Rep 2014;4:6256.

[75] Prodhomme P-Y, Raybaud P, Toulhoat H. Free-energy profiles along reduction pathways of MoS_2 M-edge and S-edge by dihydrogen: a first-principles study. J Catal 2011;280:178–95.

[76] Dai B, Su Y, Guo Y, Wu C, Xie Y. Recent strategies for the synthesis of phase-pure ultrathin 1T/1T′ transition metal dichalcogenide nanosheets. Chem Rev 2023; 124:420–54.

[77] Kivelson SA, Chang J, Jiang JM. Statistical mechanics of phases and phase transitions. 2024.

[78] Wang Z, Gu C, Jiang S, Sun T, Wang Z. The study of phase transition of MoS_2 regulated by H^+. J Phys Condens Matter 2023;35:325401.

[79] Luo R, Gao M, Wang C, Zhu J, Guzman R, Zhou W. Probing functional structures, defects, and interfaces of 2D transition metal dichalcogenides by electron microscopy. Adv Funct Mater 2024;34:2307625.

[80] Sohn W, Kim M, Jang HW. Atomic-scale insights into the 2D materials from aberration-corrected scanning transmission electron microscopy: progress and future. Small Sci 2024;4:2300073.

[81] Chua CK, Loo AH, Pumera M. Top-down and bottom-up approaches in engineering 1 T phase molybdenum disulfide (MoS_2): towards highly catalytically active materials. Chem–Eur J 2016;22:14336–41.

[82] Wang W, Zeng X, Warner JH, Guo Z, Hu Y, Zeng Y, Lu J, Jin W, Wang S, Lu J. Photoresponse-bias modulation of a high-performance MoS_2 photodetector with a unique vertically stacked 2H-MoS_2/1T@ 2H-MoS_2 structure. ACS Appl Mater Interfaces 2020;12:33325–35.

[83] de Lourenco C, de Araújo AB, Hasimoto LH, Feitosa IA, das Neves MF, Bettini J, Perfecto TM, Rocha TC, Mori TJ, Leite ER. Size-dependent electrocatalytic hydrogen evolution activity of arrays of edge-like defects in MoS_2 crystals patterned by focused ion beam. J Mater Chem A 2025;13:951–60.

[84] Jayabal S, Saranya G, Wu J, Liu Y, Geng D, Meng X. Understanding the high-electrocatalytic performance of two-dimensional MoS_2 nanosheets and their composite materials. J Mater Chem A 2017;5:24540–63.

[85] Jadhav J, Waghadkar Y, Padwal Y, Hashem M, Fouad H, Kekade SS, Terashima C, Chauhan R, Charhate S, Gosavi SW. Enhanced dye degradation using 2H-MoS_2 and 1T@ 2H-MoS_2: a comparative study. J Solid State Electrochem 2024:1–12.

[86] Pandey A, Kumari S, Goswami RN, Sharma OP, Islavath N, Khatri OP. 1T/2H-MoS_2 heterostructure for lubrication enhancement and tribo-induced phase transformation into 2H-MoS_2. ACS Appl Eng Mater 2024;2:1348–59.

[87] Naumov N, Korlyukov A, Piryazev D, Virovets A, Fedorov V. High-precision X-ray diffraction data, experimental and theoretical study of 2 H-MoS_2. Russ Chem Bull 2013;62:1852–7.

[88] Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett 1996;77:3865.

[89] Yao Y, Li S, Zha J, Lai Z, He Q, Tan C, Zhang H. Applications of polymorphic two-dimensional transition metal dichalcogenides in electronics and optoelectronics. Two-dimensional transition-metal dichalcogenides: phase engineering and applications in electronics and optoelectronics. 2024. p. 267–91.

[90] Yao Y, Li S, Zha J, Lai Z, He Q, Tan C, Zhang H. Applications of polymorphic two-dimensional transition metal dichalcogenides in electronics and optoelectronics. 2024. p. 267–91.

[91] Kiran PS, Kumar KV, Pandit N, Indupuri S, Kumar R, Wagh VV, Islam A, Keshri AK. Scaling up simultaneous exfoliation and 2H to 1T phase transformation of MoS_2. Adv Funct Mater 2024;34:2316266.

[92] Fang M, Peng Y, Wu P, Wang H, Xing L, Wang N, Tang C, Meng L, Zhou Y, Du L. Advanced 2D molybdenum disulfide for green hydrogen production: recent progress and future perspectives. Front Energy 2024;18:308–29.

[93] Karuppasamy P, Rajapanian V. Transition metal dichalcogenide (TMD)-Based 2D nanomaterials for various kinds of rechargeable batteries. 2D Nanomater: Aynth Prop Appl 2024:435–74.

[94] Hasimoto LH, das Neves MF, Perfecto TM, Bettini J, Leite ER, Capaz RB, Santhiago M. Unraveling the defects introduced on the basal plane of MoS_2 monolayers by H_2O_2 for the hydrogen evolution reaction. ACS Appl Energy Mater 2025;8:16532–40.

[95] Charapale MR, Dongale TD, Patil OA, Teli AM, Beknalkar SA, Mullani SB, Mane SM, Lee J, Masti SA. Hierarchical 3D flowers of 1T@ 2H-MoS_2 assembled with an array of ultrathin nano-petals for high-performance supercapacitor electrodes. J Solid State Electrochem 2024;28:181–95.

[96] Byrley P, Liu M, Yan R. Photochemically induced phase change in monolayer molybdenum disulfide. Front Chem 2019;7:442.

[97] Zhang Y, Kuwahara Y, Mori K, Louis C, Yamashita H. Hybrid phase 1T/2H-MoS_2 with controllable 1T concentration and its promoted hydrogen evolution reaction. Nanoscale 2020;12:11908–15.

[98] Shi X, Lin D, Xiao Z, Weng Y, Zhou H, Long X, Ding Z, Liang F, Huang Y, Chen G. Exfoliation of bulk 2H-MoS_2 into bilayer 1T-phase nanosheets via ether-induced superlattices. Nano Res 2024;17:5705–11.

[99] Song I, Park C, Choi HC. Synthesis and properties of molybdenum disulphide: from bulk to atomic layers. RSC Adv 2015;5:7495–514.

[100] Sim Y, Chae Y, Kwon S-Y. Recent advances in metallic transition metal dichalcogenides as electrocatalysts for hydrogen evolution reaction. iScience 2022;25.

[101] Zhu J, Wang Z-C, Dai H, Wang Q, Yang R, Yu H, Liao M, Zhang J, Chen W, Wei Z. Boundary activated hydrogen evolution reaction on monolayer MoS_2. Nat Commun 2019;10:1348.

[102] Hanslin SØ, Jónsson H, Akola J. Sulfur-deficient edges as active sites for hydrogen evolution on MoS_2. Phys Chem Chem Phys 2023;25:32541–8.

[103] Uddin N, Zhang H, Du Y, Jia G, Wang S, Yin Z. Structural-phase catalytic redox reactions in energy and environmental applications. Adv Mater 2020;32: 1905739.

[104] Bazghale FS, Gilak MR, Pedram MZ, Torabi F, Naikoo GA. 2D nanocomposite materials for HER electrocatalysts-a review. Heliyon 2024;10:e23450.

[105] Huang Q, Shen J, Lu Y, Ye R, Gong S. Insights into the structural evolution of MoS_2 from the semiconductive 2H to metallic 1T phase. J Phys Chem C 2023;127: 17406–14.

[106] Hossain MN, Zhang L, Neagu R, Sun S. Exploring the properties, types, and performance of atomic site catalysts in electrochemical hydrogen evolution reactions. Chem Soc Rev 2025;54:3323-3386.

[107] Sharma U, Karazhanov S, Jose R, Das S. Plasmonic hot-electron assisted phase transformation in 2D-MoS_2 for the hydrogen evolution reaction: current status and future prospects. J Mater Chem A 2022;10:8626–55.

[108] Gupta S, Robinson T, Dimakis N. Electrochemically desulfurized molybdenum disulfide (MoS_2) and reduced graphene oxide aerogel composites as efficient electrocatalysts for hydrogen evolution. J Nanosci Nanotechnol 2020;20: 6191–214.

[109] Grønborg SS, Salazar N, Bruix A, Rodríguez-Fernández J, Thomsen SD, Hammer B, Lauritsen JV. Visualizing hydrogen-induced reshaping and edge activation in MoS_2 and Co-promoted MoS_2 catalyst clusters. Nat Commun 2018;9: 2211.

[110] Wang S, Han C, Ye L, Zhang G, Hu Y, Li W, Jiang Y. Electronic properties of triangle molybdenum disulfide (MoS_2) clusters with different sizes and edges. Molecules 2021;26:1157.

[111] Helveg S, Lauritsen JV, Lægsgaard E, Stensgaard I, Nørskov JK, Clausen B, Topsøe H, Besenbacher F. Atomic-scale structure of single-layer MoS_2 nanoclusters. Phys Rev Lett 2000;84:951.

[112] Eidsvag Hk, Vajeeston P, Velauthapillai D. Doped MoS_2 polymorph for an improved hydrogen evolution reaction. ACS Omega 2023;8:26263–75.

[113] Wang Y, Qiu W, Song E, Gu F, Zheng Z, Zhao X, Zhao Y, Liu J, Zhang W. Adsorption-energy-based activity descriptors for electrocatalysts in energy storage applications. Natl Sci Rev 2018;5:327–41.

[114] Wang J, Gan X, Zhu T, Ao Y, Wang P. Recent advances of single-atom metal supported at two-dimensional MoS_2 for electrochemical CO_2 reduction and water splitting. Atmosphere 2023;14:1486.

[115] Masan SE, Rusydi F, Prabowo WA, Elisandro D, Mark-Lee WF, Karim NA, Saputro AG. Impact of hydrogen coverage trend on methyl formate adsorption on MoS_2 surface: a first principles study. ACS Omega 2023;8:6523–9.

[116] Guo S-D. Phonon transport in Janus monolayer MoSSe: a first-principles study. Phys Chem Chem Phys 2018;20:7236–42.

[117] Gul S, Syed A, Bahkali AH, Ali R, Ling Y, Sardar B, Khan M. Investigating the structural, morphological, optical, and electrical properties of MoS_2 nanostructures with PANI integration. Mater Sci Eng, B 2024;307:117542.

[118] Ekka J, Upadhyay SN, Keil FJ, Pakhira S. Unveiling the role of 2D monolayer Mn-doped MoS_2 material: toward an efficient electrocatalyst for H_2 evolution reaction. Phys Chem Chem Phys 2022;24:265–80.

[119] Lei Y, Wang J, Jiang B, Liu H, Lan H, Zhang Y, Gao G. Enhanced photo-Fenton degradation of contaminants in a wide pH range via synergistic interaction between 1T and 2H MoS_2 and copolymer tea polyphenols/polypyrrole. J Colloid Interface Sci 2024;658:74–89.

[120] Li H, Yuan X, Wei Z, Shi J, Jia Q, Ma D, Li Y, Zhang Y, Zhu X. Phase engineering of high-purity 1T-MoS_2 synthesis with organic chemical groups for enhanced supercapacitors. Mater Today Chem 2024;37:102002.

[121] Cao J, Teng F, Zhang Y, Huang J, Liu X, Zhou Q, Zhang C, Guan J. Defect-rich 1T-MoS_2 nanosheets towards efficient electrochemical hydrogen evolution by simultaneous phase and defect engineering. Int J Hydrogen Energy 2024;51: 529–35.

[122] Strachan J, Masters AF, Maschmeyer T. Critical review: hydrothermal synthesis of 1T-MoS_2–an important route to a promising material. J Mater Chem A 2021;9: 9451–61.

[123] Zhang W, Xia W, Chen Z, Zhang G, Qian S, Lin Z. Comparison of the cathodic protection of epoxy resin coating/zinc-rich coatings on defective areas under

atmospheric and immersion conditions: the secondary activation of zinc particles. Coatings 2024;14:336.
[124] Thirumalraj B, Sudhakaran M, Ji D, Li X, AlHammadi AA, Choe H, Zheng L. Engineering 1T-MoS_2 core-shells unified with nitrogen-rich amorphous carbon nanotube for ratiometric low-level detection of nitroquinoline. Sensor Actuator B Chem 2024;417:136089.
[125] Xu H, Zhu J, Ma Q, Ma J, Bai H, Chen L, Mu S. Two-dimensional MoS_2: structural properties, synthesis methods, and regulation strategies toward oxygen reduction. Micromachines 2021;12(3):240. Edited by: s Note: MDPI stays neu-tral with regard to jurisdictional claims in …; 2017:7093-7096. vol 56.
[126] Geng X, Sun W, Wu W, Chen B, Al-Hilo A, Benamara M, Zhu H, Watanabe F, Cui J, Chen T-p. Pure and stable metallic phase molybdenum disulfide nanosheets for hydrogen evolution reaction. Nat Commun 2016;7:10672.
[127] Zhou H, Yu F, Huang Y, Sun J, Zhu Z, Nielsen RJ, He R, Bao J, Goddard IIIWA, Chen S. Efficient hydrogen evolution by ternary molybdenum sulfoselenide particles on self-standing porous nickel diselenide foam. Nat Commun 2016;7:12765.
[128] Yang L, Liu P, Li J, Xiang B. Two-dimensional material molybdenum disulfides as electrocatalysts for hydrogen evolution. Catalysts 2017;7:285.
[129] Muthu J, Khurshid F, Hofmann M, Hsieh YP. Review of extrinsic factors that limit the catalytic performance of transition metal dichalcogenides (TMDs) in hydrogen evolution reactions (HER). Chemelectrochem 2024;11:e202400259.
[130] Khandaker T, Anik MAAM, Nandi A, Islam T, Islam MM, Hasan MK, Dhar PK, Latif MA, Hossain MS. Recent progress in gel catalysts: boosting efficiency for sustainable energy applications. Catal Sci Technol 2025;15:1357–89.
[131] Dong Y, Li J. Oxide cathodes: functions, instabilities, self healing, and degradation mitigations. Chem Rev 2022;123:811–33.
[132] Zhang J, Xie Z, Xi W, Zhang Y, Wang R, Gong Y, He B, Wang H, Jin J. 3D printing of tungstate anion modulated 1T-MoS_2 composite cathodes for high-performance lithium–sulfur batteries. Adv Energy Mater 2024;14:2401792.
[133] Escalera-López D, Iffelsberger C, Zlatar M, Novčić K, Maselj N, Van Pham C, Jovanovič P, Hodnik N, Thiele S, Pumera M. Allotrope-dependent activity-stability relationships of molybdenum sulfide hydrogen evolution electrocatalysts. Nat Commun 2024;15:3601.
[134] Martincová J, Otyepka M, Lazar P. Is single layer MoS_2 stable in the air? Chem–Eur J 2017;23:13233–9.
[135] Bandaru N, Kumar RS, Sneed D, Tschauner O, Baker J, Antonio D, Luo S-N, Hartmann T, Zhao Y, Venkat R. Effect of pressure and temperature on structural stability of MoS_2. J Phys Chem C 2014;118:3230–5.
[136] Sethurajaperumal A, Srivastava S, Ganesh G, Sundara R, Varrla E. Natural surfactant stabilized aqueous MoS_2 nano-lubricants for reducing friction and wear. Chem Eng J 2024;496:154080.
[137] Yang Z, Zhang X, Gao K, Zhang B, Sen FG, Bhowmick S, Zhang J, Alpas AT. Temperature-dependent frictional behavior of MoS_2 in humid environments: insights from water molecule adsorption and DFT analyses. ACS Appl Mater Interfaces 2024;16:13267–81.
[138] Du J, Han Q, Liu C, Wu H, Yang Z. In-situ transformation into MoP/MoS_2 heterogeneous structure with rich S-vacancy enhanced hydrogen evolution reaction. Appl Surf Sci 2024;649:159098.
[139] Tripathi P, Singh D, Pathak A, Verma AK, Sinha A, Singh S. Engineering MoS_2-based electrocatalysts for water splitting: a comprehensive review of doping, heterostructures, and support integration strategies. J Mater Chem A 2025;13:39603–59.
[140] Zhao W. Hydrogen production: supported Mo-based catalysts for water gas shift reaction. In: Normandie université; 2022.
[141] Sharma K, Kumar A, Ahamad T, Van Le Q, Raizada P, Singh A, Nguyen LH, Thakur S, Nguyen V-H, Singh P. Sulphur vacancy defects engineered metal sulfides for amended photo (electro) catalytic water splitting: a review. J Mater Sci Technol 2023;152:50–64.
[142] Long LN, Bich TTN. Hydrothermal phase engineering of 1T/2H MoS_2/Graphene nanocomposites for enhanced electronic, catalytic, and electrochemical performance. Adv Mater Technol 2025;10:e00454.
[143] Kumar N, Najimu MO, Cho YJ, Gilliard-AbdulAziz KL, Nikolla E, Wu Z, Wachs IE. Probing surface/bulk structural chemistry of key components of solid oxide electrochemical cells with in situ/operando raman spectroscopy. Chem Rev 2025;125:8921–55.
[144] Khatun S, Pal S, Sinha N, Das C, Ahmed T, Roy P. New age chloride shielding strategies for corrosion resistant direct seawater splitting. Chem Commun 2023;59:4578–99.
[145] Chen K, Dong W, Huang Y, Wang F, Zhou JL, Li W. Photocatalysis for sustainable energy and environmental protection in construction: a review on surface engineering and emerging synthesis. J Environ Chem Eng 2025;13:117529.
[146] Sun C, Wang C, Han G, Zhang Y, Zhao H. Pt atomic clusters/MoS_2 nanosheets/Co-doped hollow carbon nanofibers for high-current–density alkaline hydrogen production. Chem Eng J 2024;496:153665.
[147] Dang VD, Putikam R, Lin MC, Wei KH. MoS_2 nanoflowers grown on plasma-induced w-anchored graphene for efficient and stable H2 production through seawater electrolysis. Small 2024;20:2305220.
[148] Ahmad A, e Noor A, Anwar A, Majeed S, Khan S, Nisa ZU, Ali S, Gnanasekaran L, Rajendran S, Li H. Support based metal incorporated layered nanomaterials for photocatalytic degradation of organic pollutants. Environ Res 2024:119481.
[149] Pezeshk-Fallah H, Haeri SZ, Ramezanzadeh M, Ramezanzadeh B. Two-dimensional nanomaterials-based polymer nanocomposites for protective anticorrosive coatings. Two Dimens Nanomater Polym Nanocompos: Proc Prop Appl 2024:743–96.
[150] Tian H, Cui K, Sun S, Li H, Chen X. Construction of acidic microenvironments to overcome the pH dependence of iron-based catalysts and application to the degradation of micropollutants by AOPs. Chem Eng J 2024;488:150934.
[151] Cho J, Ryu S, Gong YJ, Pyo S, Yun H, Kim H, Lee J, Yoo J, Kim YS. Nitrogen-doped MoS_2 as a catalytic sulfur host for lithium-sulfur batteries. Chem Eng J 2022;439:135568.
[152] Pham PV, Bodepudi SC, Shehzad K, Liu Y, Xu Y, Yu B, Duan X. 2D heterostructures for ubiquitous electronics and optoelectronics: principles, opportunities, and challenges. Chem Rev 2022;122:6514–613.
[153] Hu B, Wu Y, Wang K, Guo H, Lei Z, Liu Z, Wang L. Gram-scale mechanochemical synthesis of atom-layer MoS_2 semiconductor electrocatalyst via functionalized graphene quantum dots for efficient hydrogen evolution. Small 2024;20:2305344.
[154] Dharman RK, Im H, Kabiraz MK, Kim J, Shejale KP, Choi SI, Han JW, Kim SY. Stable 1T-MoS_2 by facile phase transition synthesis for efficient electrocatalytic oxygen evolution reaction. Small Methods 2024;8:2301251.
[155] Chen D, Zhang Y, Feng Y, Zhang J, Zhang C, Hu J. Investigation into the stability of monometallic metal oxide electrocatalysts for hydrogen peroxide synthesis through the oxygen reduction reaction. J Mater Chem A 2025;13:19105–31.
[156] Pomerantseva E, Resini C, Kovnir K, Kolen'ko YV. Emerging nanostructured electrode materials for water electrolysis and rechargeable beyond Li-ion batteries. Adv Phys X 2017;2:211–53.
[157] Abdollahifar M, Paolella A. Anode-free batteries: the energy density prize and the stability paradox. ACS Energy Lett 2026;11:1323–1348.
[158] Priya, Srivastava S, Khatri R. Recent advances on catalysts based on MoS_2: a review on diverse applications. ChemistrySelect 2025;10:e202405247.
[159] Pan J, Liu X, Ji H, Zhu Y, Zhuang Y, Chen K, Sun N, Liu Y, Lei Y, Wang K. The strategies to improve TMDs represented by MoS_2 electrocatalytic oxygen evolution reaction. Chin Chem Lett 2024;35:109515.
[160] Wang S, Lu A, Zhong C-J. Hydrogen production from water electrolysis: role of catalysts. Nano Converg 2021;8:4.
[161] Hu J, Zhang C, Yang P, Xiao J, Deng T, Liu Z, Huang B, Leung MK, Yang S. Kinetic-oriented construction of MoS_2 synergistic interface to boost ph-universal hydrogen evolution. Adv Funct Mater 2020;30:1908520.
[162] Meng C, Chen X, Gao Y, Zhao Q, Kong D, Lin M, Chen X, Li Y, Zhou Y. Recent modification strategies of MoS_2 for enhanced electrocatalytic hydrogen evolution. Molecules 2020;25:1136.
[163] Seo B, Joo SH. Recent advances in unveiling active sites in molybdenum sulfide-based electrocatalysts for the hydrogen evolution reaction. Nano Converg 2017;4:1–11.
[164] Chen C-A, Lee C-L, Yang P-K, Tsai D-S, Lee C-P. Active site engineering on two-dimensional-layered transition metal dichalcogenides for electrochemical energy applications: a mini-review. Catalysts 2021;11:151.
[165] Ni B, Wang X. Face the edges: catalytic active sites of nanomaterials. Adv Sci 2015;2:1500085.
[166] Wang F, Xie L, Sun N, Zhi T, Zhang M, Liu Y, Luo Z, Yi L, Zhao Q, Wang L. Deformable catalytic material derived from mechanical flexibility for hydrogen evolution reaction. Nano-Micro Lett 2024;16:32.
[167] Zhang X, Hua S, Lai L, Wang Z, Liao T, He L, Tang H, Wan X. Strategies to improve electrocatalytic performance of MoS_2-based catalysts for hydrogen evolution reactions. RSC Adv 2022;12:17959–83.
[168] Zhang D-q, Chai J-x, Jia Y-x, Wang L-j, Zhao Z-l, Cao M-s. Facile preparation of few-layer MoS_2-NS by liquid-phase ultrasonic exfoliation. In: 2017 international conference on manufacturing engineering and intelligent materials (ICMEIM 2017). Atlantis Press; 2017. p. 437–42.
[169] Dong H, Chen D, Wang K, Zhang R. High-yield preparation and electrochemical properties of few-layer MoS_2 nanosheets by exfoliating natural molybdenite powders directly via a coupled ultrasonication-milling process. Nanoscale Res Lett 2016;11:1–14.
[170] Tan X, Kang W, Liu J, Zhang C. Synergistic exfoliation of MoS_2 by ultrasound sonication in a supercritical fluid based complex solvent. Nanoscale Res Lett 2019;14:1–7.
[171] Saliba M, Atanas JP, Howayek TM, Habchi R. Molybdenum disulfide, exfoliation methods and applications to photocatalysis: a review. Nanoscale Adv 2023;5:6787–803.
[172] Zhang G, Liu H, Qu J, Li J. Two-dimensional layered MoS_2: rational design, properties and electrochemical applications. Energy Environ Sci 2016;9:1190–209.
[173] Liu N, Kim P, Kim JH, Ye JH, Kim S, Lee CJ. Large-area atomically thin MoS_2 nanosheets prepared using electrochemical exfoliation. ACS Nano 2014;8:6902–10.
[174] Lu X, Utama MIB, Zhang J, Zhao Y, Xiong Q. Layer-by-layer thinning of MoS_2 by thermal annealing. Nanoscale 2013;5:8904–8.
[175] Dickinson M. Dynamic modelling of compression ring conformability in high performance engines. University of central lancashire. 2016.
[176] Karim SS, Sudais A, Shah MS, Farrukh S, Ali S, Ahmed M, Salahuddin Z, Fan X. A contemplating review on different synthesis methods of 2D-Molybdenum disulfide (MoS_2) nanosheets. Fuel 2023;351:128923.
[177] Rodríguez Á, Cakıroglu O, Li H, Carrascoso F, Mompean F, Garcia-Hernandez M, Munuera C, Castellanos-Gomez A. Improved strain transfer efficiency in large-area two-dimensional MoS_2 obtained by gold-assisted exfoliation. J Phys Chem Lett 2024;15:6355–62.
[178] Krishnamoorthy V, Bangolla HK, Chen C-Y, Huang Y-T, Cheng C-M, Ulaganathan RK, Sankar R, Lee K-Y, Du H-Y, Chen L-C. Efficient hydrogen evolution reaction in 2H-MoS_2 basal planes enhanced by surface electron accumulation. Catalysts 2024;14:50.

[179] You B, Tang MT, Tsai C, Abild-Pedersen F, Zheng X, Li H. Enhancing electrocatalytic water splitting by strain engineering. Adv Mater 2019;31:1807001.
[180] Guoping G, Qiao S, Aijun D. Activating catalytic inert basal plane of molybdenum disulfide to optimize hydrogen evolution activity via defect doping and. Strain Eng 2016;120:16761–6.
[181] Chou SS, Sai N, Lu P, Coker EN, Liu S, Artyushkova K, Luk TS, Kaehr B, Brinker CJ. Understanding catalysis in a multiphasic two-dimensional transition metal dichalcogenide. Nat Commun 2015;6:8311.
[182] Tang T, Wang Z, Guan J. A review of defect engineering in two-dimensional materials for electrocatalytic hydrogen evolution reaction. Chin J Catal 2022;43:636–78.
[183] Gao X, Zhou G, Wang H, Yin J, Zhang L, Xiao F, Siddharth K, Zhu S, Shao M. Defect engineering of molybdenum-based materials for electrocatalysis. Catalysts 2020;10:1301.
[184] Tang Z, Zhou S, Huang Y, Wang H, Zhang R, Wang Q, Sun D, Tang Y, Wang H. Improving the initial coulombic efficiency of carbonaceous materials for Li/Na-ion batteries: origins, solutions, and perspectives. Electrochem Energy Rev 2023;6:8.
[185] Zhou W, Dong L, Tan L, Tang Q. First-principles study of sulfur vacancy concentration effect on the electronic structures and hydrogen evolution reaction of MoS_2. Nanotechnology 2021;32:145718.
[186] Wang X, Zhang Y, Si H, Zhang Q, Wu J, Gao L, Wei X, Sun Y, Liao Q, Zhang Z. Single-atom vacancy defect to trigger high-efficiency hydrogen evolution of MoS_2. J Am Chem Soc 2020;142:4298–308.
[187] Liu L, Liu N, Chen B, Dai C, Wang N. Recent modification strategies of MoS_2 towards electrocatalytic hydrogen evolution. Catalysts 2024;14:126.
[188] García-Dalí S, Paredes J, Villar-Rodil S, Martínez-Jodar A, Martínez-Alonso A, Tascón J. Molecular functionalization of 2H-Phase MoS_2 nanosheets via an electrolytic route for enhanced catalytic performance. ACS Appl Mater Interfaces 2021;13:33157–71.
[189] Lau TH, Foord JS, Tsang SE. 2D molybdenum disulphide nanosheets incorporated with single heteroatoms for the electrochemical hydrogen evolution reaction. Nanoscale 2020;12:10447–55.
[190] Jia Y, Zhang Y, Xu H, Li J, Gao M, Yang X. Recent advances in doping strategies to improve electrocatalytic hydrogen evolution performance of molybdenum disulfide. ACS Catal 2024;14:4601–37.
[191] Hu W, Xie L, Gu C, Zheng W, Tu Y, Yu H, Huang B, Wang L. The nature of active sites of molybdenum sulfide-based catalysts for hydrogen evolution reaction. Coord Chem Rev 2024;506:215715.
[192] Cao Y. Roadmap and direction toward high-performance MoS_2 hydrogen evolution catalysts. ACS Nano 2021;15:11014–39.
[193] Attanayake NH, Abeyweera SC, Thenuwara AC, Anasori B, Gogotsi Y, Sun Y, Strongin DR. Vertically aligned MoS_2 on Ti_3C_2 (MXene) as an improved HER catalyst. J Mater Chem A 2018;6:16882–9.
[194] Abbas A, Luo Y, Ahmad W, Mustaqeem M, Kong L, Chen J, Zhou G, Tabish TA, Zhang Q, Liang Q. Recent progress, challenges, and opportunities in 2D materials for flexible displays. Nano Today 2024;56:102256.
[195] Liu J, Wang J, Wei B, Xue Y, Ma L, Jiang R. Unveiling the effect of organic sulfur sources on synthesized MoS_2 phases and electrocatalytic hydrogen evolution performances. Inorg Chem 2023;62:9749–57.
[196] Hu X, Yan L, Ding L, Zheng N, Li D, Ji T, Chen N, Hu J. Structural regulation and application of transition metal dichalcogenide monolayers: progress and challenges. Coord Chem Rev 2024;499:215504.
[197] Liu S, Zhou L, Zhang W, Jin J, Mu X, Zhang S, Chen C, Mu S. Stabilizing sulfur vacancy defects by performing "click" chemistry of ultrafine palladium to trigger a high-efficiency hydrogen evolution of MoS_2. Nanoscale 2020;12:9943–9.
[198] Gao Y, Liang H, Xu H, Cui D, Wu C, Chen J, Liu Y, Dou S-x, Huang W, Lin L. Emerging amorphized metastable structures to break limitations of 2D materials for more promising electrocatalysis. ACS Energy Lett 2024;9:3982–4002.
[199] Dong C, Lu L-S, Lin Y-C, Robinson JA. Air-stable, large-area 2D metals and semiconductors. ACS Nanosci Au 2024;4:115–27.
[200] Li J, Wrzesinska-Lashkova A, Deconinck M, Gobel M, Vaynzof Y, Lesnyak V, Eychmuller A. Facile and scalable colloidal synthesis of transition metal dichalcogenide nanoparticles with high-performance hydrogen production. ACS Appl Mater Interfaces 2024;16:36315–21.
[201] Chia X, Ambrosi A, Sedmidubský D, Sofer Z, Pumera M. Precise tuning of the charge transfer kinetics and catalytic properties of MoS_2 materials via electrochemical methods. Chem–Eur J 2014;20:17426–32.
[202] Liu M, Zou W, Qiu S, Su N, Cong J, Hou L. Active site tailoring of ni-based coordination polymers for high-efficiency dual-functional HER and UOR catalysis. Adv Funct Mater 2024;34:2310155.
[203] Han D, Gao N, Chu Y, Shi Z, Wang Y, Ge J, Xiao M, Liu C, Xing W. Key role of electron accessibility at the noble metal-free catalytic interface in hydrogen evolution reaction. Nano Res 2024;17:2538–45.
[204] Li G, Zhang D, Qiao Q, Yu Y, Peterson D, Zafar A, Kumar R, Curtarolo S, Hunte F, Shannon S. All the catalytic active sites of MoS2 for hydrogen evolution. J Am Chem Soc 2016;138:16632–8.
[205] Voiry D, Yang J, Chhowalla M. Recent strategies for improving the catalytic activity of 2D TMD nanosheets toward the hydrogen evolution reaction. Adv Mater 2016;28:6197–206.
[206] Dong S, Wang Z. Grain boundaries trigger basal plane catalytic activity for the hydrogen evolution reaction in monolayer MoS 2. Electrocatalysis 2018;9:744–51.
[207] Li L, Qin Z, Ries L, Hong S, Michel T, Yang J, Salameh C, Bechelany M, Miele P, Kaplan D. Role of sulfur vacancies and undercoordinated Mo regions in MoS_2 nanosheets toward the evolution of hydrogen. ACS Nano 2019;13:6824–34.
[208] Li G, Fu C, Wu J, Rao J, Liou S-C, Xu X, Shao B, Liu K, Liu E, Kumar N. Synergistically creating sulfur vacancies in semimetal-supported amorphous MoS_2 for efficient hydrogen evolution. Appl Catal B Environ 2019;254:1–6.
[209] Lim JH, Kim K, Kang JH, Kwon KC, Jang HW. Tailored two-dimensional transition metal dichalcogenides for water electrolysis: doping, defect, phase, and heterostructure. Chemelectrochem 2024;11:e202300614.
[210] Zhou Y, Yang B, Li B, Liu X. Enhancing electrocatalytic hydrogen evolution efficiency: tuning catalyst support pore size to optimize hydrogen adsorption–desorption kinetics. Inorg Chem Front 2025;12:5100-5114.
[211] Zhang H, Jin X, Lee J-M, Wang X. Tailoring of active sites from single to dual atom sites for highly efficient electrocatalysis. ACS Nano 2022;16:17572–92.
[212] Mao X, Qin Z, Ge S, Rong C, Zhang B, Xuan F. Strain engineering of electrocatalysts for hydrogen evolution reaction. Mater Horiz 2023;10:340–60.
[213] Wang X, Wu J, Zhang Y, Sun Y, Ma K, Xie Y, Zheng W, Tian Z, Kang Z, Zhang Y. Vacancy defects in 2D transition metal dichalcogenide electrocatalysts: from aggregated to atomic configuration. Adv Mater 2023;35:2206576.
[214] Qiao Z, Jiang R, Yun J, Cao D. Why the abnormal phenomena of D-band center theory exist? A new BASED theory for surface catalysis and chemistry. Chin J Catal 2024;64:44–53.
[215] Yang F, Pan Y, Jain I. Defect engineering of MoS_2/borophene/WS_2 sandwich heterostructures enhanced the HER catalytic activity and improved water splitting efficiency. J Mater Chem A 2025;13:37508–19.
[216] Cheng HW, Wang S, Chen G, Liu Z, Caracciolo D, Madiou M, Shan S, Zhang J, He H, Che R. Insights into heterogeneous catalysts under reaction conditions by in situ/operando electron microscopy. Adv Energy Mater 2022;12:2202097.
[217] Houssa M, Meng R, Afanas' ev V, Stesmans A. First-principles study of the contact resistance at 2D metal/2D semiconductor heterojunctions. Appl Sci 2020;10:2731.
[218] Li Y, Wang H, Xie L, Liang Y, Hong G, Dai H. MoS_2 nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. J Am Chem Soc 2011;133:7296–9.
[219] Huang S-Y, Sodano D, Leonard T, Luiso S, Fedkiw PS. Cobalt-doped iron sulfide as an electrocatalyst for hydrogen evolution. J Electrochem Soc 2017;164:F276.
[220] Ma Z, Niu L, Jiang W, Dong C, Liu G, Qu D, An L, Sun Z. Recent advances of single-atom electrocatalysts for hydrogen evolution reaction. J Phys: Materials 2021;4:042002.
[221] Prats H, Chan K. The determination of the HOR/HER reaction mechanism from experimental kinetic data. Phys Chem Chem Phys 2021;23:27150–8.
[222] Liao L, Zhu J, Bian X, Zhu L, Scanlon MD, Girault HH, Liu B. MoS_2 formed on mesoporous graphene as a highly active catalyst for hydrogen evolution. Adv Funct Mater 2013;23:5326–33.
[223] Keivanimehr F, Habibzadeh S, Baghban A, Esmaeili A, Mohaddespour A, Mashhadzadeh AH, Ganjali MR, Saeb MR, Fierro V, Celzard A. Electrocatalytic hydrogen evolution on the noble metal-free MoS_2/carbon nanotube heterostructure: a theoretical study. Sci Rep 2021;11:3958.
[224] He M, Kong F, Yin G, Lv Z, Sun X, Shi H, Gao B. Enhanced hydrogen evolution reaction activity of hydrogen-annealed vertical MoS_2 nanosheets. RSC Adv 2018;8:14369–76.
[225] Yang L, Yuan X, Liu R, Song R, Wang Q, Liang W. Rational design of MoS_2 nanosheet/MoS_2 nanowire homostructures and their enhanced hydrogen evolution reaction. Chalcogenide Lett 2023;20:639–48.
[226] Kong X, Xi Z, Wang L, Zhou Y, Liu Y, Wang L, Li S, Chen X, Wan Z. Recent progress in silicon− based materials for performance− enhanced lithium− ion batteries. Molecules 2023;28:2079.
[227] Zhou Y, Guo Y. Engineering defects, strain, and janus structures in transition metal dichalcogenides for enhanced hydrogen evolution reaction electrocatalysis. ACS Appl Mater Interfaces 2025;24:68869–81.
[228] He H, Guan L, Le Ferrand H. Controlled local orientation of 2D nanomaterials in 3D devices: methods and prospects for multifunctional designs and enhanced performance. J Mater Chem A 2022;10:19129–68.
[229] Seo B, Joo SH. Recent advances in unveiling active sites in molybdenum sulfide-based electrocatalysts for the hydrogen evolution reaction. Nano Converg 2017;4:19.
[230] Vo TS, Nguyen VPT, Hoang VH, Baik S, Kim K. Stoichiometric engineering of MoS_2/rGO nanocomposites for intrinsic 1T–2H phase control and enhanced photoluminescence. J Inorg Organomet Polym Mater 2025:1–16.
[231] Miao Y, Zhao Y, Zhang S, Shi R, Zhang T. Strain engineering: a boosting strategy for photocatalysis. Adv Mater 2022;34:2200868.
[232] Albaridy R, Periyanagounder D, Naphade D, Lee C-J, Hedhili M, Wan Y, Chang W-H, Anthopoulos TD, Tung V, Aljarb A. Strain-induced sulfur vacancies in monolayer MoS_2. ACS Mater Lett 2023;5:2584–93.
[233] Yu H, Zhu S, Hao Y, Chang YM, Li L, Ma J, Chen HY, Shao M, Peng S. Modulating local interfacial bonding environment of heterostructures for energy-saving hydrogen production at high current densities. Adv Funct Mater 2023;33:2212811.
[234] Zhao H, Zhu Y, Ye H, He Y, Li H, Sun Y, Yang F, Wang R. Atomic-scale structure dynamics of nanocrystals revealed by in situ and environmental transmission electron microscopy. Adv Mater 2023;35:2206911.
[235] Zhao C, Fan J, Yang Y, Munawar T, Li Q, Wang Z, Bao Q, Tu Z, Yan C. Synergistic edge–interface engineering activates stable 2H-MoS_2 in hierarchical CoS_2/MoS_2 heterostructures for efficient alkaline water electrolysis. J Power Sources 2026;667:239260.

[236] Saniya M, Raza S, Ahmad T. Demystifying hydrogen evolution: the role of advanced functional materials in powering breakthroughs. Chem Commun 2026. https://doi.org/10.1039/D5CC06180F.

[237] Singha Roy S, Madhu R, Karmakar A, Kundu S. From theory to practice: a critical and comparative assessment of tafel slope analysis techniques in electrocatalytic water splitting. ACS Mater Lett 2024;6:3112–23.

[238] Zhang L, Li B, Xu H-Y, Dong L, Shan L. Modulation strategies of d-band center for HER and AOPs applications: a comprehensive review. Inorg Chem Front 2026. https://doi.org/10.1039/D5QI02181B.

[239] Afolabi SO, Akinsooto O. Theoretical framework for dynamic mechanical analysis in material selection for high-performance engineering applications. Noûs 2021;3:15–24.

[240] Zhao Y, Tang M, He L. Transition metal (Mn, Fe, Co, Ni) and nitrogen co-doping for improving the photocatalytic activity of monolayer MoS_2. Mol Catal 2024;553:113785.

[241] Zhang X, Jia F, Song S. Recent advances in structural engineering of molybdenum disulfide for electrocatalytic hydrogen evolution reaction. Chem Eng J 2021;405:127013.

[242] Muhyuddin M, Tseberlidis G, Acciarri M, Lori O, D'Arienzo M, Cavallini M, Atanassov P, Elbaz L, Lavacchi A, Santoro C. Molybdenum disulfide as hydrogen evolution catalyst: from atomistic to materials structure and electrocatalytic performance. J Energy Chem 2023;87:256–85.

[243] Borchers A, Pieler T. Programming pluripotent precursor cells derived from Xenopus embryos to generate specific tissues and organs. Genes 2010;1:413–26.

[244] Zhang C, Luo Y, Tan J, Yu Q, Yang F, Zhang Z, Yang L, Cheng H-M, Liu B. High-throughput production of cheap mineral-based two-dimensional electrocatalysts for high-current-density hydrogen evolution. Nat Commun 2020;11:3724.

[245] Wang F, Shifa TA, Zhan X, Huang Y, Liu K, Cheng Z, Jiang C, He J. Recent advances in transition-metal dichalcogenide based nanomaterials for water splitting. Nanoscale 2015;7:19764–88.

[246] Nayana K, Sunitha A. Investigation of hydrogen evolution kinetics of metal-doped MoS_2 electrocatalysts by exploring the charge transfer coefficients. J Electroanal Chem 2025;986:119095.

[247] Sun F, Zhu S, Liu Z, Liu C, Jiang K, Zhang Y, Chen B, Zheng S. Data-driven design of metal oxide electrocatalysts with low tafel slope in oxygen evolution reaction. J Alloys Compd 2025:180964.

[248] Wang Y, Kong B, Zhao D, Wang H, Selomulya C. Strategies for developing transition metal phosphides as heterogeneous electrocatalysts for water splitting. Nano Today 2017;15:26–55.

[249] Qiang L, Bai M, Liu Z, Zhao P, He S, Zhao M, Yan Q, Wen W, Guo Q, Zhang Y. Carbon dot-driven spatial and electronic modulation of Ru on graphene for pH-universal hydrogen evolution reaction electrocatalysts. Green Chem 2025;27:12364–77.

[250] Wu Q, Xiong W, Yang G. H_2 activation and adsorbed H species on pt-based heterogeneous catalysts: fundamentals and advances. ChemCatChem 2025;17:e00902.

[251] Ungerer MJ, de Leeuw NH. Thermodynamics of hydrogen adsorption on ruthenium fcc surfaces: a density functional theory study. Phys Chem Chem Phys 2025;27:5759–72.

[252] van der Heijden O, Vos RE, Koper MT. Temperature-dependent kinetic parameters for the alkaline oxygen evolution reaction on NiFeOOH. ACS Energy Lett 2025;10:3040–9.

[253] Hiege F, Sicking LM, Kanokkanchana K, Cignoni P, Dudarev V, Ludwig A, Tschulik K. The crucial role of rotation speed on the determination of tafel slopes of electrocatalysts in rotating disk electrode experiments. ACS Electrochem 2025;1:2149–55.

[254] Sen S, Chatterjee A, Maji PK. Hydrogen evolution reaction: mechanistic insights and emerging design strategies for efficient catalysis. Adv Sustain Syst 2025:e00959.

[255] Briega-Martos V, Guzman-Soriano R, Jiang J, Yang Y. The (mis) uses of Tafel slope: kinetic analysis. Nat Catal 2025;8:863–6.

[256] Li Y. Proton exchange membrane fuel cells: electrocatalysts. In: Fuel cell fundamentals and applications. Springer; 2025. p. 195–257.

[257] Hanslin SØ, Jónsson H, Akola J. Is the doped MoS_2 basal plane an efficient hydrogen evolution catalyst? Calculations of voltage-dependent activation energy. Phys Chem Chem Phys 2023;25:15162–72.

[258] Kumar M, Ramulu B, Yu JS. Nanoarchitectonic Ni-doped edge dislocation defect-rich MoS_2 boosting catalytic activity in electrochemical hydrogen production. J Clean Prod 2023;414:137589.

[259] Han D, Gao N, Ge J, Liu C, Xing W. Activating MoS_2 via electronic structure modulation and phase engineering for hydrogen evolution reaction. Catal Commun 2022;164:106427.

[260] Dubouis N, Yang C, Beer R, Ries L, Voiry D, Grimaud A. Interfacial interactions as an electrochemical tool to understand Mo-based catalysts for the hydrogen evolution reaction. ACS Catal 2018;8:828–36.

[261] Muthu J, Khurshid F, Chin H-T, Yao Y-C, Hsieh Y-P, Hofmann M. The HER performance of 2D materials is underestimated without morphology correction. Chem Eng J 2023;465:142852.

[262] Bhardwaj A, Ismail A, Saurav KV, Elgendy A, Keerthi A, Radha B. All-edge MoS_2 by ultramicrotomy for hydrogen evolution. ACS Nano 2025;19:40516–26.

[263] Du H-G, Zhang X-F, Ding L-W, Liu J-L, Yu L-H, Zhang X-H, Dou Y, Cao L-M, Zhang J, He C-T. Engineering pore-size distribution of metal-loaded carbon catalysts by in situ cavitation for boosting electrochemical mass transfer. Appl Catal B Environ 2024;342:123396.

[264] Du J, Cai T, Han Q, Wu H, Zhao Q, Zheng L, Liu S, Yang Z. Defect-driven hydrogen evolution: enhanced hydrogen spillover on Pt-MoS_2 interface via sulfur vacancies. J Colloid Interface Sci 2025;692:137470.

[265] Ni S, Qu H, Xing H, Xu Z, Zhu X, Yuan M, Rong M, Wang L, Yu J, Li Y. Interfacial engineering of transition-metal sulfides heterostructures with built-in electric-field effects for enhanced oxygen evolution reaction. Chin J Chem Eng 2022;41:320–8.

[266] Zhou Q, Wang Z, Yuan H, Wang J, Hu H. Rapid hydrogen adsorption-desorption at sulfur sites via an interstitial carbon strategy for efficient HER on MoS_2. Appl Catal B Environ 2023;332:122750.

[267] Wang Y, Sun X, Liu Y, Zhang S, Liu F, Li Y, Xue Y, Tang C, Zhang J. Al-doping-induced electronic structure modulation of $CoSe_2$ for efficient hydrogen evolution reaction. Fuel 2024;357:129825.

[268] Xie C, Chen W, Wang Y, Yang Y, Wang S. Dynamic evolution processes in electrocatalysis: structure evolution, characterization and regulation. Chem Soc Rev 2024;53:10852–77.

[269] Nazari M, Ghaemmaghami M. Approach to evaluation of electrocatalytic water splitting parameters, reflecting intrinsic activity: toward the right pathway. ChemSusChem 2023;16:e202202126.

[270] Jin M, Zhang X, Niu S, Wang Q, Huang R, Ling R, Huang J, Shi R, Amini A, Cheng C. Strategies for designing high-performance hydrogen evolution reaction electrocatalysts at large current densities above 1000 mA cm^{-2}. ACS Nano 2022;16:11577–97.

[271] Chen B, Hu P, Yang F, Hua X, Yang FF, Zhu F, Sun R, Hao K, Wang K, Yin Z. In situ porousized MoS_2 nano islands enhance HER/OER bifunctional electrocatalysis. Small 2023;19:2207177.

[272] Wang P, Liu D, An X, Ma X, Du X, Hao X, Abudula A, Guan G. Effect of V^{2+} and V^{4+}-doping on the performance of MoS_2 catalysts for H_2 generation in microbial electrolytic cells. J Electroanal Chem 2025:119480.

[273] Wang H, Chen D-R, Lin Y-C, Lin P-H, Chang J-T, Muthu J, Hofmann M, Hsieh Y-P. Enhancing the electrochemical activity of 2D materials edges through oriented electric fields. ACS Nano 2024;18:19828–35.

[274] Liu J, Gong N, Peng W, Li Y, Zhang F, Fan X. Vertically aligned 1 T phase MoS_2 nanosheet array for high-performance rechargeable aqueous Zn-ion batteries. Chem Eng J 2022;428:130981.

[275] Han M, Yu J. Vertically oriented MoS_2 nanosheets with vast exposed edges for enhanced electrocatalytic hydrogen evolution. In: E3S web of conferences. EDP Sciences; 2021, 03019.

[276] Kong W, Li C, Wu W. A supercritical growth strategy for 1T/2H mixed-phase MoS_2 nanosheets of high activity and stability. Int J Hydrogen Energy 2023;48:31582–9.

[277] Fei H, Liu R, Wang J, Guo T, Wu Z, Wang D, Liu F. Targeted modulation of competitive active sites toward nitrogen fixation via sulfur vacancy engineering over MoS2. Adv Funct Mater 2023;33:2302501.

[278] Zhang Y, Nie K, Yi L, Li B, Yuan Y, Liu Z, Huang W. Recent advances in engineering of 2D materials-based heterostructures for electrochemical energy conversion. Adv Sci 2023;10:2302301.

[279] Ghanashyam G, Kim H. Co-doped 1T-MoS_2 microspheres embedded in N-doped reduced graphene oxide for efficient electrocatalysis toward hydrogen and oxygen evolution reactions. J Power Sources 2024;596:234088.

[280] Li X, Gao T, Ma H, Liu E, Zhao B, Sun T. Highly efficient pp heterojunction Co_3S_4/NiS_2 electrocatalyst for water splitting and electrochemical oxidation of organic molecules. Appl Surf Sci 2024;678:161127.

[281] Han W, Ning J, Long Y, Qiu J, Jiang W, Wang Y, Shah LA, Yang D, Dong A, Li T. Unlocking the ultrahigh-current-density hydrogen evolution on 2H-MoS_2 via simultaneous structural control across seven orders of magnitude. Adv Energy Mater 2023;13:2300145.

[282] Hao Y, Sun T-Y, Huang L-F. Electrochemical catalysis and corrosion of defective MoS_2: microscopic behaviors and density-functional-theory calculations. Curr Opin Electrochem 2022;34:101008.

[283] Wen Q, Zhao Y, Liu Y, Li H, Zhai T. Ultrahigh-current-density and long-term-durability electrocatalysts for water splitting. Small 2022;18:2104513.

[284] Lai W, Ma Z, Zhang J, Yuan Y, Qiao Y, Huang H. Dynamic evolution of active sites in electrocatalytic CO_2 reduction reaction: fundamental understanding and recent progress. Adv Funct Mater 2022;32:2111193.

[285] Li H, Lin Y, Duan J, Wen Q, Liu Y, Zhai T. Stability of electrocatalytic OER: from principle to application. Chem Soc Rev 2024;53:10709–40.

[286] Van Nguyen T, Tekalgne M, Nguyen TP, Van Le Q, Ahn SH, Kim SY. Electrocatalysts based on MoS_2 and WS_2 for hydrogen evolution reaction: an overview. Battery Energy 2023;2:20220057.

[287] Joseph A, Vijayan AS, Shebeeb CM, Akshay K, Mathew KPJ, Sajith V. A review on tailoring the corrosion and oxidation properties of MoS_2-based coatings. J Mater Chem A 2023;11:3172–209.

[288] Liang Z, Xue Y, Guo Y, Zhang G, Cui H, Tian J. Rationalizing and controlling the phase transformation of semi-metallic 1T′-phase and semi-conductive 2H-phase MoS_2 as cocatalysts for photocatalytic hydrogen evolution. Chem Eng J 2020;396:125344.

[289] He Y, Liu S, Priest C, Shi Q, Wu G. Atomically dispersed metal–nitrogen–carbon catalysts for fuel cells: advances in catalyst design, electrode performance, and durability improvement. Chem Soc Rev 2020;49:3484–524.

[290] Chang P, Wang T, Ding P, Guan L, Zhang S, Xing D, Tao J, Aerophobic P. MoS_2 on MOF-derived Co, N-Codoped carbon nanosheets with accelerated H_2 bubble release dynamics for efficient alkaline water splitting at 1000 mA cm^{-2}. ACS Appl Mater Interfaces 2024;16:41005–17.

[291] Zhang M, Mou X, Zhou X, Wang J, Li H, Wang C. Metal compound-based heterostructures in anodes promote high capacity and fast reaction kinetic for Lithium/Sodium-Ion storage: a review. Chemelectrochem 2024;11:e202300573.

[292] Chen B, Sui S, He F, He C, Cheng H-M, Qiao S-Z, Hu W, Zhao N. Interfacial engineering of transition metal dichalcogenide/carbon heterostructures for electrochemical energy applications. Chem Soc Rev 2023;52:7802–47.

[293] Kumral B, Barri N, Demingos PG, Adabasi G, Grishko A, Wang G, Kawase J, Onodera M, Machida T, Baykara MZ. Mechanically reliable and electronically uniform monolayer MoS_2 by passivation and defect healing. Nat Commun 2025;16:7105.

[294] Wang Y, Xue Y, Zhang C. Electrochemical product engineering towards sustainable recovery and manufacturing of critical metals. Green Chem 2021;23:6301–21.

[295] An Z-W, Xue R, Ye K, Zhao H, Liu Y, Li P, Chen Z-M, Huang C-X, Hu G-H. Recent advances in self-healing polyurethane based on dynamic covalent bonds combined with other self-healing methods. Nanoscale 2023;15:6505–20.

[296] Gong S, Meng Y, Jin Z, Hsu H-Y, Du M, Liu F. Recent progress on the stability of electrocatalysts under high current densities toward industrial water splitting. ACS Catal 2024;14:14399–435.

[297] Kolle-Gorgen E, Fortunato G, Ledendecker M. Catalyst stability in aqueous electrochemistry∇. Chem Mater 2022;34:10223–36.

[298] He B, Zhang Y, Liu X, Chen L. In-situ transmission electron microscope techniques for heterogeneous catalysis. ChemCatChem 2020;12:1853–72.

[299] Xu H, He X, Li Y, Guo Q, Sun X, Xie X, Liu L, Laine RM, Zou J, Feng X. Reassessing electrolyte design for non-aqueous magnesium batteries: atomistic structures and performance optimization. Adv Mater 2025:e14224.

[300] Zhou G, Wang J, Cheng W, Nan H, Zhao X, Wei H, Xue C, Ma Y, Yang P. Surface modified molybdenum disulfide nanosheets for corrosion resistance improvement on polyurethane coatings. Corrosion Rev 2024;42:485–96.

[301] Márquez F. MXenes in solid-state batteries: multifunctional roles from electrodes to electrolytes and interfacial engineering. Batteries 2025;11:364.

[302] Huang T-X, Cong X, Wu S-S, Wu J-B, Bao Y-F, Cao M-F, Wu L, Lin M-L, Wang X, Tan P-H. Visualizing the structural evolution of individual active sites in MoS_2 during electrocatalytic hydrogen evolution reaction. Nat Catal 2024;7:646–54.

[303] Li Q, Chen C, Luo W, Yu X, Chang Z, Kong F, Zhu L, Huang Y, Tian H, Cui X. In situ active site refreshing of electro-catalytic materials for ultra-durable hydrogen evolution at elevated current density. Adv Energy Mater 2024;14:2304099.

[304] Dai X, Wu X, Yao B, Hong Z, Jiang T, Wang ZL. Triboelectric nanogenerators powered hydrogen production system using MoS_2/Ti_3C_2 as catalysts. Adv Funct Mater 2024;34:2406188.

[305] Al Momani DE, Arshad F, Taha I, Anjum DH, Zou L. Effect of different MoS_2 morphologies on the formation and performance of adsorptive-catalytic nanocomposite membranes. npj Clean Water 2024;7:64.

[306] Zheng X, Xu J, Yan K, Wang H, Wang Z, Yang S. Space-confined growth of MoS_2 nanosheets within graphite: the layered hybrid of MoS_2 and graphene as an active catalyst for hydrogen evolution reaction. Chem Mater 2014;26:2344–53.

[307] Liu HJ, Zhang S, Chai YM, Dong B. Ligand modulation of active sites to promote cobalt-doped 1T-MoS_2 electrocatalytic hydrogen evolution in alkaline media. Angew Chem 2023;135:e202313845.

[308] Zhao L, Song Y, Xie Z, Velez K, Liu Q, An Q. Atomic-level engineering of transition metal dichalcogenides for enhanced hydrogen evolution reaction. Small Methods 2025:2500223.

[309] Yu H, Yu X, Chen Y, Zhang S, Gao P, Li C. A strategy to synergistically increase the number of active edge sites and the conductivity of MoS_2 nanosheets for hydrogen evolution. Nanoscale 2015;7:8731–8.

[310] Satheesh PP, Pandurangan K, Pandit B, Ponnusamy KM, Heo K, Chandramohan S. Near-infrared photoresponse from vertically aligned MoS_2 nanosheets/silicon heterostructure with graphene edge contact. ACS Appl Nano Mater 2026;9:627–37.

[311] Alotaibi NH, Shah JH, Nisa MU, Mohammad S, Özcan HG, Abid AG, Allakhverdiev SI. Catalytic enhancement of graphene oxide by trace molybdenum oxide nanoparticles doping: optimized electrocatalyst for green hydrogen production. Int J Hydrogen Energy 2024;62:488–97.

[312] Li S, Wang H, Qiu C, Ren J, Peng Y, Liu Y, Dong F, Bian Z. Electronic structure regulation of Fe single atom coordinated nitrogen doping MoS_2 catalyst enhances the Fenton-like reaction efficient for organic pollutant control. J Hazard Mater 2024;467:133756.

[313] Pei L, Qiao H, Chen B, Zhu X, Davis RA, Zhu K, Xia L, Dong P, Ye M, Shen J. Pt edge-doped MoS_2: activating the active sites for maximized hydrogen evolution reaction performance. Small 2021;17:2104245.

[314] Bolar S, Shit S, Murmu NC, Samanta P, Kuila T. Activation strategy of MoS_2 as HER electrocatalyst through doping-induced lattice strain, band gap engineering, and active crystal plane design. ACS Appl Mater Interfaces 2021;13:765–80.

[315] Zang Y, Niu S, Wu Y, Zheng X, Cai J, Ye J, Xie Y, Liu Y, Zhou J, Zhu J. Tuning orbital orientation endows molybdenum disulfide with exceptional alkaline hydrogen evolution capability. Nat Commun 2019;10:1217.

[316] Xiao D, Liu G-B, Feng W, Xu X, Yao W. Coupled spin and valley physics in monolayers of MoS_2 and other group-VI dichalcogenides. Phys Rev Lett 2012;108:196802.

[317] Zhang J, Cui W, Ni Y, Chen W, You D. A $MoS_2/Cu_{1.8}S/NiS@MoS_X$ heterostructured electro-catalyst for high-efficiency hydrogen evolution in alkaline solution. Int J Hydrogen Energy 2024;51:1577–85.

[318] Li M-H, Li J, Zheng X-Y, Zhou Y. Local environment regulation of transition metal dichalcogenide-based single-atom catalysts. Rare Met 2024;43:4019–37.

[319] Du X, Xu Y, Shan A, Wang R. Recent progress in the synthesis and engineering of high-performance MoS_2 electrocatalysts for the hydrogen evolution reaction. Catalysts 2025;15:626.

[320] Zhou Q, Hu H, Chen Z, Ren X, Ma D. Enhancing electrocatalytic hydrogen evolution via engineering unsaturated electronic structures in MoS_2. Chem Sci 2025;16:1597–616.

[321] Huang J, Jin M, Zhang H, Wang W, Li A, Zhu Y, Zhang J, Yin H, Xu W, Zhou M. Manipulating the d-band center of Ir by metal-support interaction to optimize the adsorption for self-powered hydrazine oxidation-assisted hydrogen generation. Energy Environ Mater 2025:e70159.

[322] Han Q, Wang Q, Wu Y, Wu S, Wang Y, Ye Q, Song S, Jia F, Li Y. Promotion of Cd species on the electrocatalytic hydrogen evolution activity of two-dimensional molybdenite. Mater Res Bull 2026:113992.

[323] Duan R, Cao G, Li J, Jiang Q, Hou C, Yang H, Wang J, Li W, Wang C, Zhang K. Heterostructure-driven d-band of MoS_2 engineering catalytic polysulfide conversion in lithium–sulfur batteries. Adv Funct Mater 2026;36:e12936.

[324] Chai H, Chen W, Li Y, Zhao M, Shi J, Tang Y, Dai X. Single-atom transition metals supported on B-doped gC_3N_4 monolayers for electrochemical nitrogen reduction. Phys Chem Chem Phys 2025;27:1661–71.

[325] Yang X, Cui W, Luo L, Ke S, Xue H, Shen L, Yang M-Q. Two-dimensional transition metal dichalcogenide edges for decomposition of hydrogen sulfide: a DFT study. Appl Surf Sci 2025:163491.

[326] Liu H, Jia Y, Hua S, Weng J, Wang L, Yang C. Lorentz force-assisted growth of romanesco-like Ni–Fe nano-cone arrays for enhanced oxygen evolution reaction at high current densities. Nanoscale 2025;17:8466–75.

[327] Ma B, Zhang Y, He C. Engineering amorphous MoS_2/RGO hybrid nanoflowers with rich edge sites boost catalytic hydrogen generation. J Catal 2025:116178.

[328] Raman R, Muthu J, Yen Z-L, Qorbani M, Chen Y-X, Chen D-R, Hofmann M, Hsieh Y-P. Selective activation of MoS_2 grain boundaries for enhanced electrochemical activity. Nanoscale Horiz 2024;9:946–55.

[329] Gopalakrishnan D, Damien D, Shaijumon MM. MoS_2 quantum dot-interspersed exfoliated MoS_2 nanosheets. ACS Nano 2014;8:5297–303.

[330] Janardhanan JC, Padmanabhan NT, Jandas PJ, Sathyan M, Thomas RM, Mythili U, John H. Topology structure significance on the applications of morphologically diverse molybdenum disulfide. J Environ Chem Eng 2024;12:112268.

[331] Kang L, Liu S, Zhang Q, Zou J, Ai J, Qiao D, Zhong W, Liu Y, Jun SC, Yamauchi Y. Hierarchical spatial confinement unlocking the storage limit of MoS_2 for flexible high-energy supercapacitors. ACS Nano 2024;18:2149–61.

[332] Liao K, Chen L, Meng R, Feng Y, Meng S, Lu H, Ma J, Peng C, Zhang C, Yang J. Reconstructable carbon Monolayer-MoS_2 intercalated heterostructure enabled by atomic layers-confined topotactic transformation for ultrafast lithium storage. J Am Chem Soc 2024;146:12020–9.

[333] Sun Y, Alimohammadi F, Zhang D, Guo G. Enabling colloidal synthesis of edge-oriented MoS_2 with expanded interlayer spacing for enhanced HER catalysis. Nano Lett 2017;17:1963–9.

[334] Zhao Y, Gu Q, Sun X, Wang D, Gong X, Yang B, Xu J, Peng B, Zhang Y, Pan C. Steric-confinement Rh_2/MoS_2 dual-atom catalyst directionally modulating adsorption configuration of ester group to boost ethanol synthesis. Chem 2024;10:3342–63.

[335] Singh AP, Xu H, Ghiami A, Tang S, Wang Z, Kalisch H, Hoffmann-Eifert S, Daus A, Ingebrandt S, Vescan A. Unravelling chemical etchant influences during assisted wet-transfer to obtain high quality MoS_2 atomic layers. Appl Surf Sci 2024;669:160331.

[336] Hai X, Chang K, Pang H, Li M, Li P, Liu H, Shi L, Ye J. Engineering the edges of MoS_2 (WS_2) crystals for direct exfoliation into monolayers in polar micromolecular solvents. J Am Chem Soc 2016;138:14962–9.

[337] Homayounfard AM, Maleki M, Ghanbari H, Kahnamouei MH, Safaei B. Growth of few-layer flower-like MoS_2 on heteroatom-doped activated carbon as a hydrogen evolution reaction electrode. Int J Hydrogen Energy 2024;55:1360–70.

[338] Orgiani P, Braglia L, Polewczyk V, Nie Z, Lavini F, Chalil SP, Chaluvadi SK, Rajak P, Morabito F, Dobovičnik E. On the origin of the improved hydrogen evolution reaction in Mn-and Co-doped MoS_2. Nanoscale 2024;16:12237–47.

[339] Kumar N, Aepuru R, Lee S-Y, Park S-J. Advances in catalysts for hydrogen production: a comprehensive review of materials and mechanisms. Nanomaterials 2025;15:256.

[340] Sun R, Hu P, Wang J, Yang F, Zhu F, Xing H, Luo J, Gao L, Wang K, Yin Z. Refractory metal-based MXenes: cutting-edge preparation and applications. Small 2025;21:2408331.

[341] Ajmal S, Huang J, Guo J, Tabish M, Mushtaq MA, Alam MM, Yasin G. Substrate engineering of single atom catalysts enabled next-generation electrocatalysis to power a more sustainable future. Catalysts 2025;15:137.

[342] Campbell E, Brown A, Nguyen HTM, He K, Batmunkh M, Zhong YL. Recent advances in selective chemical etching of nanomaterials for high-performance electrodes in electrocatalysis and energy storage. Small 2025;21:2409552.

[343] Li C, Song Z, Liu H. Octahedral copper metal-organic framework grafted with MoS_2 nanoflowers for high-performance oxygen reduction reaction. J Environ Chem Eng 2025;13:115856.

[344] Yan D, Ding B, Wang L, Li L, Ren X, Li J, Fang Q, Cao D, Zhang G, Xia C. Preparation and properties of bilayer MoS_2 with different stacking structures. Appl Surf Sci 2025;695:162875.

[345] Mao P, Bi W, Lv J, Zhang Z, Wang B, Zhong Y. Decoding buried interfaces in perovskite solar cells: core issues, strategic engineering, and prospects for high-efficiency stable devices. Adv Sci 2025;12:e12523.

[346] Jiang H, Li Y, Zhao B, Yu M, Li X, Jiang X, He G. Systematic design of Li_2S deposition modes via synergistic microporous defect engineering and transmitted orbital overlap. Adv Funct Mater 2025:e17286.

[347] Lin T, Xu R, Bo T, Hu Y, Liu Y, Zhou W. Improved HER activity of Ru nanoparticles decorated MoS_2 with S defect. Appl Surf Sci 2024;671:160704.

[348] Qian Y, Yu J, Lyu Z, Zhang Q, Lee TH, Pang H, Kang DJ. Durable hierarchical phosphorus-doped biphase MoS_2 electrocatalysts with enhanced H* adsorption. Carbon Energy 2024;6:e376.

[349] Zhang Y, Dong Y, Yan X, Peng H, Xu S, Zhu M, Jin Z, Han L, Zhang J. Heteroatom surface engineering with distinct doping ways and valence state regulation: boosting electrocatalysis performance of Ni-doped MoS_2/rGO host for excellent lithium sulfur batteries. J Energy Storage 2024;84:111023.

[350] Guo Y, Sun D, Ouyang B, Raja A, Song J, Heinz TF, Brus LE. Probing the dynamics of the metallic-to-semiconducting structural phase transformation in MoS_2 crystals. Nano Lett 2015;15:5081–8.

[351] Obando-Guevara J, González-García Á, Rosmus M, Olszowska N, González C, Morón-Navarrete G, Fujii J, Tejeda A, González-Barrio MÁ, Mascaraque A. Hydrogen absorption boosting in mildly annealed bulk MoS_2. J Mater Chem A 2024;12:24694–701.

[352] Wang C. Observation of hot-carrier photocurrent in Ruddlesden-Popper (RP) perovskite/MoS_2 heterostructure. 2024.

[353] Tomar RS. Study on sulfur vacancies in CVD grown monolayer MoS_2. Strain effects on interlayer coupling of MoS_2/WSe_2. Chicago: University of Illinois; 2024.

[354] Pisoni A, Jacimovic J, Barisic OS, Walter A, Náfrádi Bl, Bugnon P, Magrez A, Berger H, Revay Z, Forró Ls. The role of transport agents in MoS_2 single crystals. J Phys Chem C 2015;119:3918–22.

[355] Li W, Liu Y, Azam A, Liu Y, Yang J, Wang D, Sorrell CC, Zhao C, Li S. Unlocking efficiency: minimizing energy loss in electrocatalysts for water splitting. Adv Mater 2024;36:2404658.

[356] Loh JY, Yap FM, Ong W-J. 2D/2D heterojunction interface: engineering of 1T/2H MoS_2 coupled with $Ti_3C_2T_x$ heterostructured electrocatalysts for pH-universal hydrogen evolution. J Mater Sci Technol 2024;179:86–97.

[357] Zhang Y, Wang L, Chen Q, Cao J, Zhang C. Recent progress of electrochemical hydrogen evolution over 1T-MoS2 catalysts. Front Chem 2022;10:1000406.

[358] Qiao C, Wu H, Xu X, Guan Z, Ou-Yang W. Electrical conductivity enhancement and electronic applications of 2D $Ti_3C_2T_x$ MXene materials. Adv Mater Interfac 2021;8:2100903.

[359] Riaz MA, Trogadas P, Aymé-Perrot D, Sachs C, Dubouis N, Girault H, Coppens M-O. Water electrolysis technologies: the importance of new cell designs and fundamental modelling to guide industrial-scale development. Energy Environ Sci 2025;18:5190-5214.

[360] Du X, Yang X, Ding Z, Gao S, Zhang M, Su K, Li Z. Oriented self-assembly of 2D-on-3D nanoflower hierarchical structures on self-supported electrodes for enhanced electrocatalytic biomass upgrading coupled with hydrogen production reaction. J Environ Chem Eng 2025:119408.

[361] Branzi L, Fitzsimmons L, Gun'ko YK. Bottom-up synthesis of highly chiral 1T molybdenum disulfide nanosheets. Angew Chem Int Ed 2024;63:e202409313.

[362] Khanlary MR, Parhizkari M, Heydari N. Structural and optical properties of 1T-MoS_2/MoO_3 thin films prepared by spray pyrolysis method. Phys B Condens Matter 2024;680:415837.

[363] Jiang Q, Xu L, Tang Z, Xie C, Lu J, Han Z, Zhang D, Zuo C. A competitive strategy toward 1T/2H MoS_2 to balance impedance for optimizing electromagnetic wave absorption. Chem Eng J 2024;491:151854.

[364] Zhu W, Zhang B, Shi C, Cui Y. 1T-MoS_2/C composite as an efficient electrocatalyst for hydrogen evolution reaction under alkaline condition. J Phys Chem Solid 2024;185:111796.

[365] Cheng P, Sun K, Hu YH. Mechanically-induced reverse phase transformation of MoS_2 from stable 2H to metastable 1T and its memristive behavior. RSC Adv 2016;6:65691–7.

[366] Du Y, Zhao C, Li S, Dai T, Yang X, Zhu Y, Shao Q. Unlocking the potential of metastable-phase catalysts: advantages, stabilization, and applications. Chem Soc Rev 2025;54:7706–39.

[367] Ren Y, Liang M, Zhou Z, Zhang X, Yu F, Li XG, Ma J. Molecular intercalation and electron modulation stabilized 1T-MoS_2 superlattice nanoflowers with desolvation regulation for energy-efficient water production. Adv Funct Mater 2025:2502601.

[368] Ahmed W, Wang F, Fatima K, Zhang C-X, Deng H-X. TMDCs and related vdW-heterostructures: a gap analysis of hybrid synthesis and the realization of optimal properties for practical applications, current challenges, and future prospects. Adv Phys X 2025;10:2580625.

[369] Xia H, Zan L, Yuan P, Qu G, Dong H, Wei Y, Yu Y, Wei Z, Yan W, Hu JS. Evolution of stabilized 1T-MoS_2 by atomic-interface engineering of 2H-MoS_2/Fe−N_x towards enhanced sodium ion storage. Angew Chem 2023;135:e202218282.

[370] Xu C, Yu H, Huang H, Huang W, Li S, Cao Y, Lu H, Li G, Li Y, Li X. Boosting electrocatalytic activity of Ru for hydrogen evolution through engineering Ru on multiple interfaces of 1T-MoS_2 and carbon. Chem Eng J 2024;489:151295.

[371] He H, Li X, Huang D, Luan J, Liu S, Pang WK, Sun D, Tang Y, Zhou W, He L. Electron-injection-engineering induced phase transition toward stabilized 1T-MoS_2 with extraordinary sodium storage performance. ACS Nano 2021;15:8896–906.

[372] Sun J, Zhang Z, Lian G, Li Y, Jing L, Zhao M, Cui D, Wang Q, Yu H, Wong C-P. Electron-injection and atomic-interface engineering toward stabilized defected 1T-rich MoS_2 as high rate anode for sodium storage. ACS Nano 2022;16:12425–36.

[373] Das S, Swain G, Parida K. One step towards the 1T/2H-MoS_2 mixed phase: a journey from synthesis to application. Mater Chem Front 2021;5:2143–72.

[374] Zhang X, Lu Y, Liu YX, Tian G, Yang XY. 1T-MoS_2 enriched hierarchical MoS_2/MoO_3 produced by phase transformation for efficient hydrogen evolution reaction. Chem–Asian J 2023;18:e202201258.

[375] Tang J, Huang J, Ding D, Zhang S, Deng X. Research progress of 1T-MoS_2 in electrocatalytic hydrogen evolution. Int J Hydrogen Energy 2022;47:39771–95.

[376] Huang Y, Sun Y, Zheng X, Aoki T, Pattengale B, Huang J, He X, Bian W, Younan S, Williams N. Atomically engineering activation sites onto metallic 1T-MoS_2 catalysts for enhanced electrochemical hydrogen evolution. Nat Commun 2019;10:982.

[377] Li N, Li X, Wang T, Wen B, Yin Z, Feng J, Yang S, Yang Y, Yang G, Ding S. In situ transmission electron microscopy characterization and manipulation of the morphology, composition and phase evolution of nanomaterials under microenvironmental conditions. Chem Sci 2025;16:9604–37.

[378] Nematov D, Hojamberdiev M. Machine learning-driven materials discovery: unlocking next-generation functional materials–a minireview. 2025. Available at: SSRN 5219988.

[379] Li X, Xu J, Ye Y, Chen B, Xiao X. Advances in triple-phase catalysis for energy and environmental applications. Chem Soc Rev 2025;54:11545–82.

[380] Sun H, Wang Z, Meng Q, White S. Advancements in hydrogen storage technologies: enhancing efficiency, safety, and economic viability for sustainable energy transition. Int J Hydrogen Energy 2025;105:10–22.

[381] Ali H, Ajmal Z, Alzahrani AYA, Al Mughram MH, Abu-Dief AM, Al-Faze R, Hassan HM, Al-Mhyawi SR, Al-Hadeethi Y, Orooji Y. Defect-driven innovations in photocatalysts: pathways to enhanced photocatalytic applications. InfoMat 2025;7:e70040.

[382] Man P, Jiang S, Leung KH, Lai KH, Guang Z, Chen H, Huang L, Chen T, Gao S, Peng YK. Salt-induced high-density vacancy-rich 2D MoS_2 for efficient hydrogen evolution. Adv Mater 2024;36:2304808.

[383] Lian T, Li X, Wang Y, Zhu S, Yang X, Liu Z, Ye C, Liu J, Li Y, Su B. Boosting highly active exposed Mo atoms by fine-tuning S-vacancies of MoS_2-based materials for efficient hydrogen evolution. ACS Appl Mater Interfaces 2022;14:30746–59.

[384] Wang Z, Zhang X, Gao Y, Wang H. Transition metal (Fe, Co, Ni) doping enhanced monolith catalysts of 1T− MoS_2/Mo for the large-current hydrogen evolution reaction. Int J Hydrogen Energy 2024;56:75–83.

[385] Ding Y, Zeng M, Zheng Q, Zhang J, Xu D, Chen W, Wang C, Chen S, Xie Y, Ding Y. Bidirectional and reversible tuning of the interlayer spacing of two-dimensional materials. Nat Commun 2021;12:5886.

[386] Shaikh N, Annadata HV, Mishra AK, Urkude RR, Mukhopadhyay I, Ray A. Doping induced mixed polytypic interfaces of MoS_2 for superior electrocatalytic hydrogen evolution. Appl Surf Sci 2024;649:159195.

[387] Muhammad P, Zada A, Rashid J, Hanif S, Gao Y, Li C, Li Y, Fan K, Wang Y. Defect engineering in nanocatalysts: from design and synthesis to applications. Adv Funct Mater 2024;34:2314686.

[388] Zhao G-Y, Deng H, Tyree N, Guy M, Lisfi A, Peng Q, Yan J-A, Wang C, Lan Y. Recent progress on irradiation-induced defect engineering of two-dimensional 2H-MoS_2 few layers. Appl Sci 2019;9:678.

[389] Gusmão C, Palharim PH, Ramos B, Gouvêa D, Júnior OR, Teixeira ACSC. Innovative defect engineering: a novel synthesis approach for an efficient Ti^{3+}-TiO_2/SiO_2 gas-phase-photocatalyst under UV–VIS radiation. Ceram Int 2025;51:24903–15.

[390] Béjar J, Aguilar-Elguezabal A. Advanced characterization techniques for defect and interface engineering. Surface and interfacial defects in nanomaterials for sustainable energy production and storage. 2026. p. 75–88.

[391] Hsu YW, Huang SY, Hsiao CY, Hsu SY, Yeh CH, Lin J, Le PA, Chen HYT, Chen JM, Wei KH. Selectively dispersed ruthenium nanoparticles on WS_2 nanosheets fabricated with plasma exfoliation and in situ polyol-reduction as electrocatalysts for enhanced hydrogen evolution reaction. Small Methods 2026:e02108.

[392] Barah OO, David M, Joseph M. Atomic-scale characterization: a review of advances in microscopy, spectroscopy, and machine learning. J Mater Sci: Composites 2025;6:6.

[393] Kim MK, Lamichhane B, Song B, Kwon S, Wang B, Kattel S, Lee JH, Jeong HM. Enhancing electrocatalytic hydrogen evolution of MoS_2 enabled by electrochemical cation implantation for simultaneous surface-defect and phase engineering. Appl Catal B Environ Energy 2024;352:124037.

[394] Voiry D, Salehi M, Silva R, Fujita T, Chen M, Asefa T, Shenoy VB, Eda G, Chhowalla M. Conducting MoS_2 nanosheets as catalysts for hydrogen evolution reaction. Nano Lett 2013;13:6222–7.

[395] Liu L, Liu N, Dai C, Xu R, Yu G, Wang N, Chen B. MoS_2 supported Ruthenium nanoparticles with abundant sulfur vacancies significantly improved hydrogen evolution reaction. Catal Today 2024;436:114751.

[396] Fang J, Lu J, He B, Xu Z, Luo M, Song T, Wang H, Qin C, Chen Z, Luo Y. Identification of the potassium-related species as the key active sites for C–S bond couplings over K-MoS_2 materials. ACS Catal 2024;14:11604–16.

[397] Li X-Y, Zhu S-J, Wang Y-L, Lian T, Yang X-y, Ye C-F, Li Y, Su B-L, Chen L-H. Synergistic regulation of S-vacancy of MoS_2-based materials for highly efficient electrocatalytic hydrogen evolution. Front Chem 2022;10:915468.

[398] Sun L, Yue C, Zhao J, Chen P, Liu H, Wang X, Liu W. CoS_2-MoS_2-CNT composite modified separator with enhanced LiPS adsorption capacity for lithium-sulfur battery. J Alloys Compd 2024;972:172733.

[399] Fan C, Zang Z, Zhang X. Non-metal doping regulation in transition metal and their compounds for electrocatalytic water splitting. Int J Hydrogen Energy 2024;56:1273–83.

[400] Chen W, Wei W, Wang K, Cui J, Zhu X, Ostrikov KK. Partial sulfur vacancies created by carbon–nitrogen deposition of MoS_2 for high-performance overall electrocatalytic water splitting. Nanoscale 2021;13:14506–17.

[401] Voiry D, Fullon R, Yang J, de Carvalho Castro e Silva C, Kappera R, Bozkurt I, Kaplan D, Lagos MJ, Batson PE, Gupta G. The role of electronic coupling between substrate and 2D MoS_2 nanosheets in electrocatalytic production of hydrogen. Nat Mater 2016;15:1003–9.

[402] Yubiao L, Rui C, Yu L, Langlang W, Ping N, Xueqian W, Yixing M. Controlled dispersion and morphology in MoS_2/SBA-15 catalysts for enhanced COS hydrodesulfurization. Fuel 2024;373:132390.

[403] Bai H, Yang Y, Dong M, Yuan H, Huang Y, Liu X, Ni C. Structure and defect engineering synergistically boost Mo^{6+}/Mo^{4+} circulation of S_v-MoS_2 based photo-fenton-like system for efficient levofloxacin degradation. Appl Catal B Environ Energy 2024;358:124430.

[404] Telkhozhayeva M, Girshevitz O. Roadmap toward controlled ion beam-induced defects in 2D materials. Adv Funct Mater 2024;34:2404615.

[405] Seravalli L, Bosi M. A review on chemical vapour deposition of two-dimensional MoS_2 flakes. Materials 2021;14:7590.

[406] Su S, Zhao J, Ly TH. Scanning probe microscopies for characterizations of 2D materials. Small Methods 2024;8:2400211.

[407] Chen Y, Huang S, Ji X, Adepalli K, Yin K, Ling X, Wang X, Xue J, Dresselhaus M, Kong J. Tuning electronic structure of single layer MoS_2 through defect and interface engineering. ACS Nano 2018;12:2569–79.

[408] He Z, Zhao R, Chen X, Chen H, Zhu Y, Su H, Huang S, Xue J, Dai J, Cheng S. Defect engineering in single-layer MoS_2 using heavy ion irradiation. ACS Appl Mater Interfaces 2018;10:42524–33.

[409] Lin W, Wang F, Wang H, Li H, Fan Y, Chan D, Chen S, Tang Y, Zhang Y. Thermal-stable separators: design principles and strategies towards safe lithium-ion battery operations. ChemSusChem 2022;15:e202201464.

[410] Li R, Liang J, Li T, Yue L, Liu Q, Luo Y, Hamdy MS, Sun Y, Sun X. Recent advances in MoS_2-based materials for electrocatalysis. Chem Commun 2022;58:2259–78.

[411] Zi S, Zhu J, Zhai Y, Hu Y, Zhang N, Li S, Liu L, An L, Xi P, Yan CH. Surface cladding engineering via oxygen sulfur distribution for stable electrocatalytic oxygen production. Angew Chem Int Ed 2025;64:e202413348.

[412] Yuan Y, Ma Y, Li S, Cheng S, Zhang C, Zhou T, Shi J, Xia X. Alkali metal ion-induced construction of $Ti_3C_2T_x/V_2CT_x$ superlattice heterostructures for proton storage. Chem Eng J 2025;506:160291.

[413] Fang Z, Xia Y, Zhang L, Liu J, Li J, Hu B, Li K, Lu Q, Wang L. Building the confined CoS_2/MoS_2 nanoreactor via interface electronic reconfiguration to synchronously enhance activity and stability of heterogeneous Fenton-like reactions. Appl Catal B Environ Energy 2024;346:123769.

[414] Sun J, Luo B, Li H. A review on the conventional capacitors, supercapacitors, and emerging hybrid ion capacitors: past, present, and future. Adv Energy Sustain Res 2022;3:2100191.

[415] Yu Z, Gao Y, Hong X, Ji M, Chang K. Atomic vacancy defect-induced dual active sites synergistic catalysis for oxygen evolution reaction. Phys Chem Chem Phys 2025;27:15256–71.

[416] Shen W, Ye Y, Xia Q, Xi P. Progress in in situ characterization of electrocatalysis. EES Catal 2025;3:10–31.

[417] Luo L, Lan Y, Zhang Q, Deng J, Luo L, Zeng Q, Gao H, Zhao W. A review on biomass-derived activated carbon as electrode materials for energy storage supercapacitors. J Energy Storage 2022;55:105839.

[418] Lu M, Chen Z, Sun J, Xiang R. Opportunities of one-dimensional van der Waals materials and heterostructures as fuel cell catalyst layers. Carbon 2025;2:9200041.

[419] Curcio E. Techno-economic analysis of hydrogen production: costs, policies, and scalability in the transition to net-zero. Int J Hydrogen Energy 2025;128:473–87.

[420] Li D, Fan S, Li J, Li W, Zhuang Y, Li Y, Shan L, Dong L, Yao J. Preparation and characterization of bifunctional 1T-2H MoS_2-S_v/CuS catalyst for electrocatalytic hydrogen and oxygen evolution reaction. Separ Purif Technol 2025;352:128176.

[421] Xie S, Dong H, Iwuoha EI, Peng X. Phase transition of catalysts for advanced electrocatalysis. Coord Chem Rev 2024;514:215920.

[422] Wang D, Zhang X, Bao S, Zhang Z, Fei H, Wu Z. Phase engineering of a multiphasic 1T/2H MoS_2 catalyst for highly efficient hydrogen evolution. J Mater Chem A 2017;5:2681–8.

[423] Liu Z, Gao Z, Liu Y, Xia M, Wang R, Li N. Heterogeneous nanostructure based on 1T-phase MoS_2 for enhanced electrocatalytic hydrogen evolution. ACS Appl Mater Interfaces 2017;9:25291–7.

[424] Rekhila G, Boukhemikhem Z, Lahmar H, Benamira M, Trari M. Photo-electrochemical and physical properties of the spinels $NiFe_{2-x}Mn_xO_4$ for Eosin photo-oxidation. Chem Afr 2025:1–8.

[425] Zhai W, Li Z, Wang Y, Zhai L, Yao Y, Li S, Wang L, Yang H, Chi B, Liang J. Phase engineering of nanomaterials: transition metal dichalcogenides. Chem Rev 2024;124:4479–539.

[426] Sabbaghi S, Hosseinian E, Bazargan V. Strain-assisted phase transformation in two-dimensional transition-metal dichalcogenides. ACS Appl Mater Interfaces 2024;16:22676–88.

[427] Kumar K, Kundu R. Doping engineering in electrode material for boosting the performance of sodium ion batteries. ACS Appl Mater Interfaces 2024;16:37346–62.

[428] Wang X, Xu Y, Xi Y, Yang X, Wang J, Huang X, Li W, Xu K, Zhang K, Duan R. Doping engineering of phosphorus-based polyanion-type cathodes for sodium storage: a review. J Mater Chem A 2024;12:9268–95.

[429] Soni HR, Fyta M. Two-dimensional metallic/semiconducting MoS_2 under biaxial strain. ACS Appl Nano Mater 2018;1:5562–70.

[430] Pandey M, Pandey C, Ahuja R, Kumar R. Straining techniques for strain engineering of 2D materials towards flexible straintronic applications. Nano Energy 2023;109:108278.

[431] Wang Y, Ma H, Liu J, Zhang Z, Yu Y, Zuo S. Broad-spectrum hybrid-driven triple-interface Z-S cheme 1T/2H phase sailboat-like molybdenum disulfide (MoS_2)/protonated N-defect nanoporous graphitic carbon nitride (g-C_3N_4) nanosheets piezo-photocatalyst: superior degradation and hydrogen evolution. J Colloid Interface Sci 2024;665:655–80.

[432] Thayil R, Parne SR, Ramana C. 2D MoS_2 for next-generation electronics and optoelectronics: from material properties to manufacturing challenges and future prospects. Small 2025;21:2412467.

[433] Liu Y, Qin Y, Yu D, Zhuo H, Ma C, Chen K. Enhance water electrolysis for green hydrogen production with material engineering: a review. Chem Rec 2025:e202400258.

[434] Jin X, Li J, Zhu S, Tan W, Tang J, Gong X, Liu X, Zhang Y, Zhou C, Tang Z. pH-Independent lead sequestration and light management enable sustainable and efficient perovskite photovoltaics. Energy Environ Sci 2025;18:1901–10.

[435] Wang B, Tao W, Song B, Kwon S, Kim MK, Zhao R, Han B, Lee JH, Jeong HM. Sulfur-vacancy anchoring suppresses dynamic surface reconstruction in ni-doped ZnS nanospheres to trigger the lattice oxygen mechanism. Small 2026:e14661.

[436] Pasindu V, Yapa P, Dabare S, Munaweera I. Multifunctional transition metal oxide/graphene oxide nanocomposites for catalytic dye degradation, renewable energy, and energy storage applications. RSC Adv 2025;15:33162–86.

[437] Yang Y, Qiu Y, Hua B, Cai J, Zhang Y, Cao K, Shen X, Ji Q. Large-domain monolayer MoS_2 synthesis via local-feeding metalorganic chemical vapor deposition. ACS Mater Lett 2024;6:2802–8.

[438] Kim Y, Bark H, Ryu GH, Lee Z, Lee C. Wafer-scale monolayer MoS_2 grown by chemical vapor deposition using a reaction of MoO_3 and H_2S. J Phys Condens Matter 2016;28:184002.

[439] Aggarwal R, Saini D, Mitra R, Sonkar SK, Sonker AK, Westman G. From bulk molybdenum disulfide (MoS_2) to suspensions of exfoliated MoS_2 in an aqueous medium and their applications. Langmuir 2024;40:9855–72.

[440] Sahu G, Chakraborty C, Roy S, Banerjee S. Dependence of reaction time in hydrothermal synthesis of MoS_2 quantum dots: an investigation using optical tools and fractal analysis. J Cryst Growth 2024;627:127487.

[441] Bansal S. Morphological and optical characterization of hydrothermally-synthesized two-dimensional MoS_2 nanosheets. ECS J Solid State Sci Technol 2024;13:027005.

[442] Mekonnin AS, Wacławiak K, Humayun M, Zhang S, Ullah H. Hydrogen storage technology, and its challenges: a review. Catalysts 2025;15:260.

[443] Raj K, Jhala R, Pattanayak B, Singh J, Kumar P, Kaladhar M, Singh R, Bisht YS, Gautam A. A comprehensive review on the MXene-based catalysts for hydrogen generation via water splitting processes. J Mol Struct 2025:143534.

[444] Qi X, Zhu Y, Xu Y, Chen W, Hu Z, Xi L, Xie Y, Hou H, Zou G, Ji X. Phase engineering enables ultrahigh-capacity 1T/2H-MoS_2 for advanced ammonium-ion storage. Energy Storage Mater 2025;75:104063.

[445] Zhao L, Wang Y, Wen G, Zhang X, Huang X. Ammonium-driven modulation of 1T-MoS_2 structure and composite with graphene: a pathway to high-performance lithium-ion battery anodes. J Colloid Interface Sci 2025;680:151–61.

[446] Kim S-J, Maligal-Ganesh RV, Mahmood J, Babar P, Yavuz CT. Structural control over single-crystalline oxides for heterogeneous catalysis. Nat Rev Chem 2025:1–18.

[447] Zheng L, Huang H, Zhu X, Li W, Xu M, Gao J, Cao Y, Li W, He T, Wang X. Aqueous-isopropanol-based green ink formulation of single-crystalline transition metal chalcogenides for fully-printed strain-insensitive flexible sensing electronics. Sci China Mater 2025:1–11.

[448] Heydari Gharahcheshmeh M. Fabrication of conjugated conducting polymers by chemical vapor deposition (CVD) method. Nanomaterials 2025;15:452.

[449] Liang Q-M, Ma T, Lin L. Recent advances and future perspectives on metal doping strategies for regulating the electrocatalytic performance of MoS_2. J Mater Chem C 2026;14:1360-1376.

[450] Liu X, Bao Y, Yuan L, Zhao H, Tian W, Ji J. From activity to stability: dissolution-mediated surface reconstruction and redeposition in transition metal-based electrocatalysts. J Mater Chem A 2025;13:35024–53.

[451] Xu X, Chu C, Hou Z, Peng Z, Wang J, Li X, Han X, Xu H, Cheng D. Identification nonmetal doping induced S vacancy to active MoS_2 for hydrogen evolution reaction via structural descriptor. Int J Hydrogen Energy 2025;158:150348.

[452] Pradeep K, Jeffery AA, Sundaresan AP, Gunaseelan R, Rajendran S, Karthik PE, Ahn Y-H, Selvam NCS. Impact of catalyst engineering on the durability performance of self-supported catalysts in anion exchange membrane water electrolyzers: recent advances and perspectives. J Mater Chem A 2025;13:14510–39.

[453] Deng J, Hu X, Klaver AJ, Liu J, Liu B, Bai L, Xie M, Zhang D. Catalyst deactivation in the abatement of atmospheric pollutants: origin, resistance, and regeneration. Chem Rev 2025;125:11260–357.

[454] Hachhach M, Bayou S, El Kasmi A, Saidi MZ, Akram H, Hanafi M, Achak O, El Moujahid C, Chafik T. Towards sustainable Scaling-Up of nanomaterials fabrication: current situation, challenges, and future perspectives. Engineering 2025;6:149.

[455] Xiong L, Wang P, Guo P, Zhao M, Yi Z, Wei X, Huang G, Zhang L, Wang S. Freestanding oxide thin films for next-generation electronics: advances in preparation, van der Waals integration and devices. Nano Res 2025;18:94907760.

[456] Huang Z, Ren L. Large scale synthesis of carbon dots and their applications: a review. Molecules 2025;30:774.

[457] Cheng B, Wang H, Xiang S, Lu S, Ren B. MoS_2-Based composites for electrochemical detection of heavy metal ions: a review. Nanomaterials 2025;15:1639.

[458] Misia G, Prato M, Silvestri A. The impact of the crystalline phase and morphology of MoS_2 on the electrocatalytic reduction of H_2O_2. npj 2D Mater Appl 2025;10:1.

[459] Lu P, Liao P, Wang C, Xing Y, Zhang C, Xu Q, Tu R, Zhang S. Thermodynamic analysis of phase and composition during the co-deposition of SiC-HfC films by chemical vapor deposition method. J Cryst Growth 2025;652:128051.

[460] Huo J, Dou Y, Wu C, Liu H, Dou S, Yuan D. Defect engineering of metal-based atomically thin materials for catalyzing small-molecule conversion reactions. Adv Mater 2025;37:2416483.

[461] Xu X, Xu J, Lu N, Zhang M. Self-templating synthesis of Mn-Doped MoS_2 nanosheets grown on tubular N-Doped carbon with enhanced peroxidase-like performance. Langmuir 2025;41:27537–46.

[462] Xie X, Hou X, Wang C, Zhao D, Li D, Zhu P, Ye X, Suo G, Liu H, Sun D. Sandwich-like interlayer-structured TM/$Ti_3C_2T^x$ (TM= Co, Fe, Ni) synergistic catalysts for accelerating hydrogen storage kinetics of MgH_2. Int J Hydrogen Energy 2025;153:150238.

[463] Wei J, Wang X, Ma T, Mu S, Liu Y. Rational design of MoS_2-supported single-atom catalysts for enhancing phenol deoxygenation: unveiling synergistic electronic-geometric effects and a universal structure-activity descriptor. Appl Catal Gen 2025:120447.

[464] Meng Z, Zhang R, Wei W, Yi C: Advancing chemical vapor deposition through mass transfer dynamics for controlled growth of 2d materials Available at: SSRN 5320458.

[465] Abraham J, Shepherd ND, Littler C, Syllaios A, Philipose U. Engineering the morphology and properties of MoS_2 films through gaseous precursor-induced vacancy defect control. Nanomaterials 2025;15:1723.

[466] You CW, Fu T, Wang ZL, Wang YZ, Song F. 3D coral-like $Ti_3C_2T_x$ MXene heterostructures for ultrasensitive gas sensing in wildfire monitoring. Small 2025;21:e06807.

[467] Pinto FM, Wypych F, Taft CA, de Almeida La Porta F. A comprehensive look at MoS_2 nanostructures: from synthesis to tailored functionality. In: Innovative materials for energy and sustainability. Springer; 2026. p. 1–30.

[468] Panchu SJ, Raju K, Swart HC. Emerging two–dimensional intercalation pseudocapacitive electrodes for supercapacitors. Chemelectrochem 2024;11:e202300810.

[469] Teli AM, Mishra RK, Shin JC, Jeon W. Exploring the capability of Cu-MoS_2 catalysts for use in electrocatalytic overall water splitting. Micromachines 2024;15:876.

[470] Wang W-W, Chen C, Liu Z-X, Zhu Q-X, Xu Y-X, Lu Z-Q, Zhang B, Yu Z-P, Xu G-Y. From laboratory to industrial scale: nickel-based catalysts for hydrogen evolution under highcurrent–density alkaline electrolysis: WW Wang et al. Rare Met 2025:1–36.

[471] Zhu Q, Yang J, Nan T, Liu J, Tang S, Zeng W, Tang C. Antimony extraction from sulfide concentrates by direct electrolytic desulfurization in molten salt. ACS Sustainable Chem Eng 2024;12:7844–57.

[472] Shen D, Jin Y, Zhang Z, Song R, Liu M, Li W, Li X, Wu R, Li B, Li J. Recent advances in spin-coating precursor mediated chemical vapor deposition of two-dimensional transition metal dichalcogenides. Precis Chem 2024;2:282–99.

[473] Kubetschek N, Backes C, Goldie S. Algorithm for reproducible analysis of semiconducting 2D nanomaterials based on UV-VIS spectroscopy. Adv Mater Interfac 2024;11:2400311.

[474] Doan TLL, Nguyen DC, Kang K, Ponnusamy A, Eya HI, Dzade NY, Kim CS, Park CH. Advanced Mott-Schottky heterojunction of semi-conductive MoS_2 nanoparticles/metallic CoS_2 nanotubes as an efficient multifunctional catalyst for urea-water electrolysis. Appl Catal B Environ 2024;342:123295.

[475] Liang Z, Yan Q, Ou H, Li D, Zhang Y, Zhang J, Zeng L, Xing M. Effective green treatment of sewage sludge from fenton reactions: utilizing MoS2 for sustainable resource recovery, 121. Proceedings of the National Academy of Sciences; 2024, e2317394121.

[476] Tsanaktsis M. Recent developments in water electrolysis for hydrogen production. In: University of Thessaly; 2025.

[477] Li H. Vacancy engineering and heterojunction interface construction on LDH-based catalysts toward efficient alkaline water electrolysis. Waseda University; 2025.

[478] Judijanto L. Interdisciplinary synergy in translational medicine: overcoming collaboration barriers between basic researchers, Clinicians, and industry stakeholders. Eur J Appl Sci Eng Technol 2025;3:149–60.

[479] Kumar S, Chakrabortty P, Singh RV, Pai MR, Khan A, Siddiqui NA, Islam SM. Pyrene-based 2D covalent organic framework engineered with 3D-MoS_2-nanoflowers tuned with high surface area assisted in visible-light-driven photocatalytic H_2 evolution and CO_2 reduction. ACS Appl Energy Mater 2024;7:4429–44.

[480] Mou Z, Meng T, Li J, Wang Y, Wang X, Guo H, Meng W, Zhang K. Significantly enhanced photocatalytic hydrogen production performance of MoS_2/CNTs/CdS with carbon nanotubes as the charge mediators. Int J Hydrogen Energy 2024;51:748–57.

[481] Liu G, Ding L, Meng Y, Ali A, Zuo G, Meng X, Chang K, Li OL, Ye J. A review on ultra-small undoped MoS_2 as advanced catalysts for renewable fuel production. Carbon Energy 2024;6:e521.

[482] Jiang C-H, Yao C-B, Wang Z-M, Wang X, Wang LY. Heterostructure MoS_2@ ZnO nanowires: preparation, ultrafast nonlinear optical behavior and photoelectric functional application. Appl Surf Sci 2022;599:153920.

[483] Peng Z, Yilu S, En-Naji I, Khojastehnezhad A, Siaj M. Low-dimensional transition metal dichalcogenides heterostructure photoanodes for photoelectrochemical hydrogen evolution application: recent progress and prospects. Chem Commun 2026. https://doi.org/10.1039/D5CC05030H.

[484] Hasimoto LH, de Araujo AB, de Lourenço C, Merces L, Candioto G, Leite ER, Capaz RB, Santhiago M. Strain and defect-engineering on the basal plane of ultra-large MoS 2 monolayers attached onto stretchable gold electrodes. J Mater Chem A 2024;12:17338–49.

[485] Song Y, Zhou X, Wei K, Hu H, Wu M, Li M, Xie R, Wang Y, Gao F. Sulfur vacancies and group VB metal atoms doping to synergistically optimize hydrogen evolution of MoS_2 nanosheets. Colloids Surf A Physicochem Eng Asp 2024;690:133795.

[486] Huang W, Zhong T, Wang C, Fang Z, Du J, Zhao H, Tian S, Shu D, He C. Enhanced paracetamol degradation via strong covalent coupling of MoOC bonds in C/MoS_2 nanocomposites for piezoelectric activation of peroxymonosulfate: Electron bridge and enrichment. Separ Purif Technol 2025;354:128801.

[487] Lin H, Xin X, Xu L, Li P, Chen D, Turkevych V, Li Y, Wang H, Xu J, Wang L. Defect-mediated Fermi level modulation boosting photo-activity of spatially-ordered S-scheme heterojunction. J Colloid Interface Sci 2024;676:310–22.

[488] Saeed A, Khalid S, Naeem Anjum M. Challenges and opportunities: conducting polymer-graphene based nanocomposites of metal oxides and metal sulfides for supercapacitors. ChemistrySelect 2024;9:e202303527.

[489] Fan Y, Yu Y, Sun D, Qu Y, Huang L, Wei X, Su Q, Du G, Xu B, Wang K. Three-dimensional self-supporting micro-nanostructured MoS_2/CoS_2/CC heterojunction derived from ZIF-67 for high efficiency electrocatalytic hydrogen evolution in both acid and alkali electrolytes. J Alloys Compd 2024;976:173354.

[490] Xu W, Feng Y-W, Li S-J, Ma H, Zhang C-L, He J, Gadow SI, Tang X. Molybdenum and sulfur doping to create active sites and regulate d-Band centers of Ni–Mo–S electrocatalysts for the hydrogen evolution reaction. Inorg Chem 2025;64:2030–9.

[491] Zhao S, Li ZX, Guo HT, Li J, Liu ZL, Wang PF, Wang LL, Yi TF. Critical role of carbon substrates in optimizing ru-based HER catalysts: from dimensional insights to metal-support interactions engineering. Adv Funct Mater 2025:e09799.

[492] Wu N, Shi W, Wang W, Lei Y. Well-defined nanostructures: concept, impact and perspective. Small 2025:2412780.

[493] Luo J, Tong J, Zhao H, Zeng X, Liu F, Wu H, Cui H, Tan P, Pan J. The role of lattice strain in advancing electrocatalytic performance: from mechanisms to practical applications. Nanoscale 2026. https://doi.org/10.1039/D5NR04443J.

[494] Gao Y, Wang B, Jiang Z, Wang Y, Fang T. Uncovering the photoelectronic/catalytic property modulation and applications of 2D MoS_2: from the perspective of constructing heterogeneous interfaces. J Mater Chem A 2023;11:19736–63.

[495] Liu J, Di Z, Wan Y, Wang K, Sun W, Dai J, Zhang W, Ran F. Sub-micron porous Si-C/graphite anode with interpenetrated 3D conductive networks towards high-performance lithium-ion batteries. J Alloys Compd 2024:173930.

[496] Singh R, Agrohiya S, Rawal I, Ohlan A, Dahiya S, Punia R, Maan A. Porous polyaniline/flower-like hybrid phase MoS_2/phosphorus-doped graphene ternary nanocomposite for efficient room temperature ammonia sensors. Synth Met 2024;307:117676.

[497] Pan M, Zhang X, Pan C, Wang J, Pan B. Identification of Co–O–Mo active centers on Co-doped MoS_2 electrocatalyst. ACS Appl Mater Interfaces 2023;15:19695–704.

[498] Xie Q, Wang X, Chen W, Lei C, Huang B. Engineering active heterojunction architecture with oxygenated-Co, Mo bimetallic sulfide heteronanosheet and graphene oxide for peroxymonosulfate activation. J Hazard Mater 2023;448:130852.

[499] Yu X, Li Y, Fang T, Gao J, Ma Y. Interfacial and electronic modulation of W bridging heterostructure between WS_2 and cobalt-based compounds for efficient overall water splitting. Small 2024;20:2304512.

[500] Yu H, Zhang M, Cai Y, Zhuang Y, Wang L. The advanced progress of MoS_2 and WS_2 for multi-catalytic hydrogen evolution reaction systems. Catalysts 2023;13:1148.

[501] Moghimifar Z, Yazdani F, Tabar-Heydar K, Sadeghi M. Photocatalytic hydrogen evolution under visible light using MoS_2/g-C_3N_4 nano-photocatalysts. Catal Lett 2024;154:1255–69.

[502] Liu K, Chen J, Sun F, Yu J, Zhang X, Xu Y, Liu Y, Tang M, Yang Y. Enhanced degradation of azo dyes wastewater by S-scheme heterojunctions photocatalyst g-C_3N_4/MoS_2 intimately coupled Rhodopseudomonas palustris with chitosan modified polyurethane sponge carrier. Int J Hydrogen Energy 2023;48:22319–33.

[503] Huang H, Xue Y, Xie Y, Yang Y, Yang L, He H, Jiang Q, Ying G. MoS_2 quantum dot-decorated MXene nanosheets as efficient hydrogen evolution electrocatalysts. Inorg Chem Front 2022;9:1171–8.

[504] Almeida LS, Carneiro J, Colnago LA. Time domain NMR for polymorphism characterization: current status and future perspectives. Int J Pharm 2025;669:125027.

[505] Pujar MS, Padasalagi A. Advances in interface engineering of MoS_2-based heterostructures as bifunctional electrodes for efficient water splitting. ACS Appl Mater Interfaces 2025;17:44053–72.

[506] Shi Z, Zhang X, Lin X, Liu G, Ling C, Xi S, Chen B, Ge Y, Tan C, Lai Z. Phase-dependent growth of Pt on MoS_2 for highly efficient H_2 evolution. Nature 2023;621:300–5.

[507] Huang G, Chen R, Chen M, Chen X, Jiang M, Xing Y, Wang J, Liang B, Liu Q, Li X. Transfer and beyond: emerging strategies and trends in two-dimensional material device fabrication. Chem Soc Rev 2026. https://doi.org/10.1039/D5CS00531K.

[508] Xie M, Lv Z, Zhao W, Fang Y, Huang J, Huang F. Intercalated hydrates stabilize bulky MoS_2 anode for lithium-Ion battery. Chem Eng J 2023;470:144282.

[509] Yao Y, Cumberbatch H, Robertson DD, Chin MA, Lamkin R, Tolbert SH. On the interplay between size and disorder in suppressing intercalation-induced phase transitions in pseudocapacitive nanostructured MoS_2. Adv Funct Mater 2024;34:2304896.

[510] Cai L, Yang J, Shao X, Zhu X, Liu Y, Wan C, Wang F, Chen J. Copper-doped nanostructured MoS_2 with distinct nanoscale morphology for efficient bacteria inactivation and catalytic degradation of antibiotics. J Environ Chem Eng 2024;12:111537.

[511] Sharma P, Thakur D, Kumar D, Yadav O. Unveiling xanthine presence in rohu fish using Ag^{+}-doped MoS_2 nanosheets through electrochemical analysis. Appl Biochem Biotechnol 2024;196:5219–34.
[512] Mohan M, Shetti NP, Aminabhavi TM. Phase dependent performance of MoS_2 for supercapacitor applications. J Energy Storage 2023;58:106321.
[513] Yang Q, Wang K, Zhang M, Du F, Li J, Zheng C, Li J. Advancements in synthetic and electrocatalytic exploitation of guest-host intercalated 2D materials. Prog Nat Sci Mater Int 2024;34:454-469.
[514] Lyu Z, Qian Y, Zhang Q, Fang Z, Kang DJ. Liquid-phase catalyst pre-seeding for controlled growth of layered MoS_2 films over a large area via chemical vapor deposition. Nanoscale 2024;16:1906–14.
[515] Tang J, Huang J, Zhang S, Liu Z, Deng X. Synergistic low-Pt modification and Ni doping facilitate the MoS_2 phase transition for accelerating the hydrogen evolution reaction. Energy Fuels 2023;37:14914–21.
[516] Rauret DL, Manjón AG, Arbiol J. Advances in in situ and operando TEM: from basic catalysis to industry-relevant reactions and future directions. Matter 2025;8.
[517] Guan L, Chen Z, Liu Y, Wang R, Yan K, Xu Z, Li J, Liu Z, Li J, Liu H. Engineering sulfur-rich MoS_2 adsorbent with abundant unsaturated coordination sulfur sites for gaseous mercury capture from high-concentration SO_2 smelting flue gas. Chem Eng J 2024;483:149122.
[518] Liu J, Wang H, Wu H, Yang Y, Wang C, Wang Q, Jia B, Zheng J. Research progress of zinc oxide-based heterojunction photocatalysts. J Mater Chem A 2024;12:20838–67.
[519] Etafo NO, Bamidele MO, Bamisaye A, Alli YA. Revolutionizing photocatalysis: unveiling efficient alternatives to titanium (IV) oxide and zinc oxide for comprehensive environmental remediation. J Water Proc Eng 2024;62:105369.
[520] Deshwal N, Singh MB, Bahadur I, Kaushik N, Kaushik NK, Singh P, Kumari K. A review on recent advancements on removal of harmful metal/metal ions using graphene oxide: experimental and theoretical approaches. Sci Total Environ 2023;858:159672.
[521] Niu H, Wang Q, Huang C, Zhang M, Yan Y, Liu T, Zhou W. Noble metal-based heterogeneous catalysts for electrochemical hydrogen evolution reaction. Appl Sci 2023;13:2177.
[522] Gautam S, Chugh S, Gates BD. Electrodeposition of PdPt nanoparticles on edges and s-vacancies in exfoliated MoS_2 nanosheets for enhanced hydrogen evolution activity. ChemSusChem 2024;17:e202301922.
[523] Minadakis MP, Tagmatarchis N. Exfoliated transition metal dichalcogenide-based electrocatalysts for oxygen evolution reaction. Adv Sustain Syst 2023;7:2300193.
[524] Zheng S-L, Xu H-M, Zhu H-R, Shuai T-Y, Zhan Q-N, Huang C-J, Li G-R. Heterostructured electrocatalysts for the oxygen evolution reaction. J Mater Chem A 2024;12:18832–65.
[525] Venturi F. Carbon-based films: a review on mechanical and tribology properties. Mater Chem Phys 2024:129716.
[526] Tundwal A, Kumar H, Binoj BJ, Sharma R, Kumar G, Kumari R, Dhayal A, Yadav A, Singh D, Kumar P. Developments in conducting polymer-, metal oxide-, and carbon nanotube-based composite electrode materials for supercapacitors: a review. RSC Adv 2024;14:9406–39.
[527] Abimana C, Bello A, Machunda R, Chande Jande YA. Understanding the factors influencing the properties of biomass-derived porous carbon and their impacts on electrical double-layer capacitor electrodes: a comprehensive review. J Renew Energy 2024;2024:1343256.
[528] Wu X, Yan Q, Wang H, Wu D, Zhou H, Li H, Yang S, Ma T, Zhang H. Heterostructured catalytic materials as advanced electrocatalysts: classification, synthesis, characterization, and application. Adv Funct Mater 2024;34:2404535.
[529] Devendar L, Yadav V, Pothal B, Ganapathi KL, Jaiswal M. CVD growth of large-area, continuous, and defect-free MoS_2 multilayer films from solution-cast seed nanoflakes. Surf Interfaces 2024;50:104470.
[530] Liu W, Fan D, Wang W, Yang S, Lu Y, Fu L, Zhang J, Wu Y. One-pot hydrothermal synthesis and electrochemical performance of subspheroidal core–shell structure MoS_2/C composite as anode material for lithium-ion batteries. Energies 2024;17:1678.
[531] Choi J, Moon H, Fleischmann S. Simultaneous control of crystallite size and interlayer spacing of MoS_2 to achieve pseudocapacitive lithium intercalation. Electrochim Acta 2024;476:143774.
[532] Cai M, Yang J, Lu X, Lu X. Layer-by-layer self-assembly strategies of atomically thin two-dimensional nanomaterials: principles, methods, and functional applications. ACS Appl Nano Mater 2024;7:27940–59.
[533] Li Z, Zhao X, Wu S, Lu M, Xie X, Yan J. Atomic layer deposition of transition-metal dichalcogenides. Cryst Growth Des 2024;24:1865–79.
[534] Jagosz J, Willeke L, Gerke N, Becher MJ, Plate P, Kostka A, Rogalla D, Ostendorf A, Bock C. Wafer-scale demonstration of polycrystalline MoS. 2024.
[535] Wu F, Ling M, Zhang L, Zhang Q, Zhang B. Phase-incorporation-induced electromagnetic coupling of NFS@ 1T/2H–MoS_2 for enhanced microwave absorption. Compos B Eng 2024;270:111136.
[536] Wang Q, Wang Y, Li Z, Ma X. DFT study on doping effect of different transition metals on MoS_2 for enhancing the formation of S vacancies. Int J Hydrogen Energy 2024;82:416–27.
[537] Eckardt M. Spinel ferrite nanoparticles: solvent restructuring and crystal structure depending on elemental. Composition and synthesis route. 2025.
[538] Aggarwal P, Umar F, Paul A. Review of ordered pores in nanomaterials for energy applications ranging from energy storage to catalysis. ACS Appl Nano Mater 2025;8:17780–818.
[539] Sead FF, Jadeja Y, Kumar A, Mm R, Kundlas M, Saini S, Joshi KK, Noorizadeh H. Carbon quantum dots for sustainable energy: enhancing electrocatalytic reactions through structural innovation. Nanoscale Adv 2025;7:3961–98.
[540] He L, Yu G, Cheng Y, Wang N, Hu W. Non-precious metal-based catalysts for water electrolysis to produce H_2 under industrial conditions. Mater Chem Front 2023;7:5661–92.
[541] Alfa I, Hafeez HY, Mohammed J, Abdu S, Suleiman AB, Ndikilar CE. A recent progress and advancement on MoS_2-based photocatalysts for efficient solar fuel (hydrogen) generation via photocatalytic water splitting. Int J Hydrogen Energy 2024;71:1006–25.
[542] Yann R, Ngok S, Mustafa E, Liu X, Willander M, Chey CO, Nur O. Growth of Ag2S-sensitizer on MoS_2/ZnO nanocable arrays for improved solar driven photoelectrochemical water splitting. Solid State Sci 2024;147:107379.
[543] Zheng L, Cao M, Du Y, Liu Q, Emran MY, Kotb A, Sun M, Ma C-B, Zhou M. Artificial enzyme innovations in electrochemical devices: advancing wearable and portable sensing technologies. Nanoscale 2024;16:44–60.
[544] Liu K, Duan T, Zhang F, Tian X, Li H, Feng M, Wang R, Jiang B, Zhang K. Flexible electrode materials for emerging electronics: materials, fabrication and applications. J Mater Chem A 2024;12:20606–37.
[545] Dang H, Guan B, Chen J, Ma Z, Chen Y, Zhang J, Guo Z, Chen L, Hu J, Yi C. Research status, challenges, and future prospects of carbon dioxide reduction technology. Energy Fuels 2024;38:4836–80.
[546] Vadivel D, Dondi D, Capodaglio AG. Present achievements and future directions of advanced carbon dioxide reduction strategies. Curr Opin Chem Eng 2024;45:101029.
[547] Dai L, Zong J, Liang L, Li P. Two-dimensional crystalline electrocatalysts for efficient reduction of carbon dioxide. Chemelectrochem 2024;11:e202400009.
[548] Wang W, Tang L, Chen C, Wang X, Wang Y, Sun W. Engineering Pt–S–Mo and Pd–S–Mo sites in hierarchical porous MoS_2 for boosted oxygen reduction activity in microbial fuel cell. J Power Sources 2024;598:234143.
[549] He T, Wei L, Wang Y, Huang H, Jiang Q, Tang J. A review of research progress and prospects of modified two-dimensional catalysts based on black phosphorus in the oxygen reduction reaction. Catal Sci Technol 2024;14:1105–21.
[550] Sun G, Liu X, Mao H, Wu S, Liu Y, Wang T, Chi J, Wang L. Highly efficient tungsten/molybdenum-based electrocatalysts for the oxygen reduction reaction: a review. Inorg Chem Front 2024;11:682–712.
[551] Ma W, Dong Y, Li J, Wang Y, Wang T, Zheng X, Deng Y. Recent strategies for improving the catalytic activity of ultrathin transition metal sulfide nanosheets toward the oxygen evolution reaction. Mater Today Energy 2024;40:101492.
[552] Guo Y, Niu Q, Pei F, Wang Q, Zhang Y, Du L, Zhang Y, Zhang Y, Zhang Y, Fan L. Interface engineering toward stable lithium–sulfur batteries. Energy Environ Sci 2024;17:1330–67.
[553] Yao Y, He J, Zhu X, Mu L, Li J, Li K, Qu M. Wettability and heterojunction synergistic interface optimization guided Co doped MoS_2/Ni_3S_2-GO/NF catalytic electrode to boost overall water splitting. Int J Hydrogen Energy 2024;51:207–21.
[554] Kar DK, Mishra S, Mohanty PS, Si S. Two-dimensional nanomaterials-based polymer nanocomposites for catalytic and photocatalytic applications. Two Dimens Nanomater Polym Nanocompos: Proc Prop Appl 2024:541–78.
[555] Hosseini SM, Safarifard V. MoS_2@ MOF composites: design strategies and photocatalytic applications. Mater Sci Semicond Process 2024;169:107892.
[556] Li J, Pang Z, Gao C, Zhang G, Dai J, Chen T, Su X, Zhou W. Scalable production of transition metal chalcogenides/ultrathin 2D carbon nanosheets composites with a universal "All-in-One" blowing strategy. Adv Funct Mater 2024;34:2306997.
[557] Liu S, Wu D, Zhao Y, Liang Y, Zhang L, Sun J, Lin J, Wang S, Yao Y, Wan S. Recent advances and perspectives in catalyst design for converting syngas to higher alcohols. Energy Fuels 2024;38:14769–96.
[558] Ullah S, Ullah N, Shah SS, Guziejewski D, Khan F, Khan I, Ahmad A, Saeed M, Khan S, Mabood F. Theoretical and experimental progress in photothermal catalysis for sustainable energy and environmental protection: key problems and strategies towards commercialization. Renew Sustain Energy Rev 2024;201:114615.
[559] Xiang S. Characterization of atomic scale structures and functionality relationship by advanced transmission electron microscopy. Hong Kong: Hong Kong University of Science and Technology; 2025.
[560] Yu F, Zhou H, Huang Y, Sun J, Qin F, Bao J, Goddard IIIWA, Chen S, Ren Z. High-performance bifunctional porous non-noble metal phosphide catalyst for overall water splitting. Nat Commun 2018;9:2551.
[561] Zhu Y, Klingenhof M, Gao C, Koketsu T, Weiser G, Pi Y, Liu S, Sui L, Hou J, Li J. Facilitating alkaline hydrogen evolution reaction on the hetero-interfaced Ru/RuO_2 through Pt single atoms doping. Nat Commun 2024;15:1447.
[562] Yu F, Liu M, Ma C, Di L, Dai B, Zhang L. A review on the promising plasma-assisted preparation of electrocatalysts. Nanomaterials 2019;9:1436.
[563] Attarzadeh N. Design and development of transition metal-based electrocatalysts for environmentally friendly and efficient hydrogen evolution reactions (her). The University of Texas at El Paso; 2023.
[564] Wang K, Jing Y, Gao S, Liu X, Liu B, Li Y, Zhang P, Xu B. Activating and optimizing the In-Plane interface of 1 T/2H MoS_2 for efficient hydrogen evolution reaction. J Colloid Interface Sci 2023;648:709–18.
[565] An W, Liu Z, Shen T, Du Y, Huang C, Duan B, Wang C, Huang G, Yan Y, Xu S. Regulating d–p hybridization in Mo-Doped CoP nanoflowers with superwetting surfaces for water splitting at 3000 mA cm^{-2}. ACS Catal 2025;15:10358–71.
[566] Wang S, Wang L, He W, Liu D, Wang H, Yu W, Yin D, Dong X. Pt and Mo_2C nanoparticles embedded in hollow carbon nanofibers as an effective electrocatalyst for hydrogen evolution reaction in acidic and alkaline electrolytes. J Alloys Compd 2024;1005:176019.
[567] Fu C, Feng L, Yin H, Li Y, Li G, Feng Y, Cao L, Huang J, Liu Y. Synergistic coupling of hierarchical heterostructured Ni_3P/Ni/VN microflower electrocatalyst for enhanced hydrogen evolution reaction. ChemCatChem 2023;15:e202201399.

[568] Zhu Z, Yang F, Wu D, Guo Z. Directional manipulation of bubble behavior on wettability gradient surfaces: mechanisms, strategies, and applications. Mater Horiz 2026;13:589-618.
[569] Guo P, Zhang H, Dong S, An L. Density functional theory study of b-and Si-doped carbons and their adsorption interactions with sulfur compounds. Carbon Energy 2024;6:e489.
[570] Coogan Á, Gun'ko YK. Solution-based "bottom-up" synthesis of group VI transition metal dichalcogenides and their applications. Mater Adv 2021;2:146–64.
[571] Chen I-WP, Tseng Y-L, Huang JHR, Chen K-L, Liu TY, Lee J-C. Enhancing hydrogen evolution catalysis through potential-induced structural phase transition in transition-metal dichalcogenide thin sheets. J Phys Chem Lett 2024;15:2287–92.
[572] Kim JH, Sung H, Lee G-H. Phase engineering of two-dimensional transition metal dichalcogenides. Small Sci 2024;4:2300093.
[573] Zhao Y, Adiyeri Saseendran DP, Huang C, Triana CA, Marks WR, Chen H, Zhao H, Patzke GR. Oxygen evolution/reduction reaction catalysts: from in situ monitoring and reaction mechanisms to rational design. Chem Rev 2023;123:6257–358.
[574] Tang S, Wang W, Lei L, Dong P, Yang Z, Li K, Dong W, Hu N, Zhong Q, Fan H. In situ photo-deposition of amorphous nickel boride nanocluster onto graphitic carbon nitride for significantly promoting light-driven hydrogen evolution. Int J Hydrogen Energy 2025;148:150076.