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Progress in Compositional Regulation of Molybdenum Sulfide for Electrocatalytic Hydrogen Evolution

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Abstract. Against the backdrop of the accelerating global energy transition and the continued pursuit of carbon-peaking and carbon-neutrality targets, hydrogen is regarded as an important secondary energy carrier for building a low-carbon energy system because of its high gravimetric energy density, suitability for storage and transport across temporal and spatial scales, and strong compatibility with renewable energy. Water electrolysis is a key technological route for large-scale green hydrogen production; however, interfacial charge transfer and intermediate adsorption/desorption kinetics of the cathodic hydrogen evolution reaction (HER) still introduce additional energy losses. Pt-based catalysts exhibit outstanding intrinsic HER activity, but their scarcity and high cost constrain large-scale deployment. Molybdenum disulfide (MoS_2), featuring favorable hydrogen adsorption thermodynamics, abundant resources, good chemical stability, and low cost, is among the most representative non-noble-metal candidates for HER catalysis. This review discusses the crystal structure, electronic properties, and HER mechanism of MoS_2, with emphasis on the key limitations of 2H-MoS_2, including the low activity of basal planes, limited electrical conductivity, and low density of accessible active sites. The effects of phase engineering, defect and elemental doping, heterostructure construction, and morphology regulation on active-site exposure, electronic-structure optimization, and interfacial charge transport are systematically analyzed. On this basis, the major challenges facing MoS_2-based catalysts under high current densities, long-term operation, and scalable synthesis are summarized, and their prospects for industrial water electrolysis are discussed.

Keywords: molybdenum disulfide, electrocatalytic hydrogen evolution, non-noble-metal catalyst, compositional regulation, water electrolysis

1. Research background

According to the International Energy Agency report Global Energy Review 2025, global energy demand increased by 2.2% year-on-year in 2024, exceeding the average annual growth rate of 1.3% during 2013–2023; meanwhile, global energy-related CO_2 emissions rose further to a record high of 37.8 Gt [1]. At the same time, oil accounted for less than 30% of global energy demand for the first time, indicating a continued transition of the energy supply structure toward lower carbon intensity.

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As shown in Fig. 1 ,a renewable energy accounted for 38% of the increase in global energy supply in 2024, exceeding the contributions from conventional energy sources such as natural gas, coal, and oil. The rapid deployment of clean-energy technologies is reshaping the composition of incremental energy demand. Therefore, the development of efficient, low-cost, and scalable technologies for renewable-energy conversion and storage has become a major direction of the global energy transition.

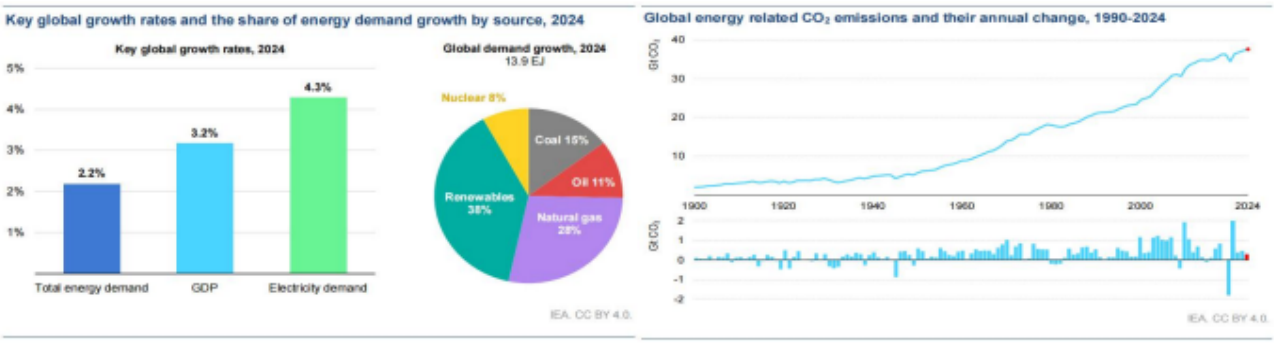

Figure 1. Global energy review 2025 [1]

China is currently at a critical stage of deep energy-structure adjustment and the development of a new energy system. Reducing dependence on conventional fossil fuels, improving the utilization of renewable energy, and promoting end-use decarbonization are important pathways for jointly achieving energy security and the carbon-peaking and carbon-neutrality targets. Hydrogen simultaneously serves as an energy carrier, an energy-storage medium, and an industrial feedstock, enabling cross-sector coupling among electricity, transportation, chemicals, and metallurgy.

Hydrogen is characterized by clean utilization, high gravimetric energy density, and broad applicability across multiple scenarios. Its industrial development is therefore important for optimizing the energy structure, enhancing energy security, and enabling deep decarbonization in hard-to-abate sectors.

From the perspective of energy-system applications, the major advantages of hydrogen can be summarized in three aspects [2]:

(1) Low-carbon characteristics and coupling potential with renewable energy

The principal electrochemical product of hydrogen utilization in fuel cells is water, and nearly no CO_2 is emitted at the point of use. When water electrolysis is powered by renewable electricity such as wind and solar energy, the life-cycle carbon emissions associated with hydrogen production can be substantially reduced, thereby establishing a low-carbon energy chain of "renewable electricity–hydrogen production–storage and transport–end use" [3]. Accordingly, green hydrogen is particularly valuable in sectors that are difficult to electrify directly, such as steelmaking, chemicals, and long-distance transportation.

(2) High gravimetric energy density and broad scenario adaptability

The lower/higher heating value of hydrogen is approximately 120–142 $MJ \cdot kg^{-1}$, substantially higher than that of conventional fuels such as gasoline. However, its volumetric energy density at ambient temperature and pressure is low; therefore, practical use requires storage and transport approaches such as compression, liquefaction, or chemical hydrogen carriers. Owing to its high gravimetric energy density, hydrogen is particularly suitable for long-distance and high-power applications with stringent requirements for range, payload, and refueling speed, while also enabling flexible conversion among electricity, hydrogen, and heat [4].

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(3) Cross-timescale energy storage and system-regulation capability

Hydrogen can serve as an important energy-storage medium linking power systems with fuel and chemical systems. Through water electrolysis, intermittent renewable electricity can be converted into chemical energy suitable for long-term storage and subsequently reused through fuel cells, gas turbines, or industrial processes. This "power–hydrogen–power/heat/chemicals" coupling pathway can enhance peak shaving, renewable-energy accommodation, and supply security in energy systems with high shares of renewable generation.

Current hydrogen-production routes mainly include fossil-fuel-based hydrogen production, industrial by-product hydrogen, and water electrolysis. As shown in Table 1, these routes differ markedly in cost, carbon emissions, resource constraints, and scale-up conditions. Compared with the first two routes, water electrolysis powered by low-carbon electricity is more consistent with deep-decarbonization requirements and has therefore become a major focus of green-hydrogen research, development, and industrialization [5]. Further scale-up depends primarily on reducing electricity consumption, electrolyzer-system cost, and the cost of key catalytic materials.

Table 1. Comparison of major hydrogen-production technologies [5]

Technology	Fossil-fuel-based H_2 production	Industrial by-product H_2	Water electrolysis
Advantages	Mature technology, large production capacity, relatively low cost	Utilizes industrial by-product gas streams; low marginal cost	Can be coupled with renewable electricity; no direct carbon emissions during operation
Limitations	High carbon emissions; requires carbon-reduction/capture measures	Constrained by upstream industrial layout and the scale of by-product gas streams	High electricity consumption and equipment cost
Cost/(CNY·kg^{-1})	6–15	8–20	15–40

2. Overview of water-electrolysis technologies

Representative water-electrolysis technologies currently include alkaline water electrolysis (ALK), proton exchange membrane water electrolysis (PEM), solid oxide electrolysis cells (SOEC), and anion exchange membrane water electrolysis (AEM). These technologies differ in operating temperature, electrolyte system, dynamic response, materials cost, and durability; their main advantages and disadvantages are summarized in Table 2 [6].

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Table 2. Comparison of water-electrolysis technologies [6]

Process	Alkaline water electrolysis	Proton exchange membrane water electrolysis	Solid oxide electrolysis	Anion exchange membrane water electrolysis
Advantages	Mature technology and relatively low equipment cost	High current density, rapid dynamic response, and high gas purity	High electrical efficiency at elevated temperature; compatible with industrial waste heat	Can employ non-noble-metal catalysts, offering low-cost potential
Disadvantages	Relatively low current density and slow dynamic response	High cost of membranes, electrodes, and noble-metal catalysts	High operating temperature and stringent requirements for start-up/shut-down and durability	Chemical stability of membranes/ionomers still requires improvement

Water electrolysis consists of two half-reactions: the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). Under an applied potential, H^+ or H_2O accepts electrons at the cathode to form H_2, whereas H_2O or OH^- loses electrons at the anode to generate O_2. Together, the two electrode reactions determine the theoretical decomposition voltage and actual energy consumption of the electrolyzer. The hydrogen produced by HER can be used as a fuel or chemical feedstock, whereas OER generally involves a more complex multielectron-transfer process and slower kinetics .

Table 3. Electrode reactions under different pH conditions

Electrode reaction	Acidic electrolyte	Neutral or alkaline electrolyte
Cathode (HER)	$4H^+ + 4e^- \rightarrow 2H_2$	$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
Anode (OER)	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

As the electrolyte pH changes, both the reactant forms and interfacial reaction pathways of HER and OER vary accordingly; the corresponding electrode reactions are listed in Table 3.

In current water-electrolysis systems, electricity cost and electrochemical polarization losses remain key factors governing the economics of hydrogen production. Alkaline electrolyzers are technologically mature, relatively inexpensive, and compatible with non-noble-metal catalysts based on Ni, Fe, Co, and Mo; nevertheless, further improvements are still required in high-current-density operation, dynamic response, and long-term stability. Therefore, reducing HER kinetic losses through regulation of catalyst composition and interfacial structure is an important research direction for improving the efficiency of alkaline water electrolysis.

2.1. Hydrogen evolution reaction

The hydrogen evolution reaction (HER) is essentially a two-electron reduction process in which protons or water molecules accept electrons at the cathode interface and ultimately form H_2. Because the proton source and interfacial solvation structure vary substantially with electrolyte pH, HER kinetics differ markedly in acidic, neutral, and alkaline media.

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As shown in Table 4, HER is generally described by three elementary steps—the Volmer, Heyrovsky, and Tafel steps—with adsorbed hydrogen (H* or Hads) as the common key intermediate. The overall reaction activity is jointly governed by the adsorption strength of H*, the ability of interfacial water molecules to dissociate, and the charge-transfer rate.

Table 4. HER mechanism

Elementary step	Acidic electrolyte	Neutral or alkaline electrolyte	Process
Volmer reaction	$M + H_3O^+ + e^- \rightarrow M–H^* + H_2O$	$M + H_2O + e^- \rightarrow M–H^* + OH^-$	Hydrogen adsorption
Heyrovsky reaction	$M–H^* + H_3O^+ + e^- \rightarrow M + H_2 + H_2O$	$M–H^* + H_2O + e^- \rightarrow M + H_2 + OH^-$	Electrochemical desorption
Tafel reaction	$2M–H^* \rightarrow 2M + H_2$	$2M–H^* \rightarrow 2M + H_2$	Chemical desorption

The typical elementary steps of HER proceed as follows. Adsorbed hydrogen is first formed through the Volmer step. H* can then generate H_2 either through the Heyrovsky electrochemical-desorption step by reacting with protons/water or through the Tafel chemical-recombination step involving two adjacent H* species. The dominant pathway and rate-determining step are not universal across catalysts and electrolytes, but depend on H* coverage, interfacial water structure, and the electronic state of the active sites.

In acidic media, the high proton activity allows HER to proceed without an additional water-dissociation step for hydrogen supply, generally resulting in rapid interfacial kinetics. According to the Sabatier principle, an ideal HER catalyst should bind H* neither too strongly nor too weakly, and its hydrogen adsorption free energy (ΔG_{H^*}) should be close to 0 eV. Pt-group metals occupy the highly active region of the HER volcano relationship and exhibit large exchange current densities; therefore, they have long served as benchmark materials for evaluating HER performance .

In alkaline media, the concentration of free H^+ is very low, and HER generally requires H_2O dissociation through the Volmer step to generate H*. The additional O–H bond cleavage and interfacial-water rearrangement therefore introduce substantial kinetic resistance. For most non-noble-metal catalysts, improving alkaline HER performance requires not only optimization of ΔGH^* but also enhanced adsorption and activation of H_2O and appropriate regulation of the adsorption/desorption of oxygen-containing intermediates such as OH* . Accordingly, constructing bifunctional active sites or heterointerfaces, or tuning the local electronic structure through doping, represents a common strategy for accelerating alkaline HER kinetics.

Overall, the electrolyte not only provides ion transport but also directly affects interfacial solvation and reactant supply. Acidic systems generally exhibit faster proton-reduction kinetics; alkaline systems are more strongly influenced by the water-dissociation step; and neutral systems are often simultaneously limited by lower ionic activity and mass transport. Catalyst design should therefore comprehensively consider H* adsorption, water activation, and interfacial charge transport under the target pH conditions.

In addition to the intrinsic properties of the catalyst, operating parameters such as temperature, current density, electrolyte concentration, and bubble mass transport also significantly affect HER. Moderate temperature increases can enhance ion migration and interfacial reaction rates, whereas excessive temperatures may accelerate electrolyte loss and material degradation. Increasing the current density raises the hydrogen-production rate per unit area but simultaneously magnifies

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ohmic polarization, concentration polarization, and bubble-coverage effects. Laboratory evaluation of catalytic activity should therefore be progressively extended to high current densities and testing conditions that more closely resemble practical electrolyzer operation .

2.2. Oxygen evolution reaction

The oxygen evolution reaction (OER) is a four-electron oxidation process in which water/hydroxyl species lose electrons and ultimately form O_2. Compared with HER, OER involves multiple adsorbed intermediates, including OH*, O*, and OOH*, as well as O–O bond formation; consequently, its reaction pathway is more complex and its kinetics are generally slower, resulting in a higher anodic overpotential.

As shown in Table 5, under the classical adsorbate evolution mechanism (AEM), OER in both acidic and alkaline media can proceed through key intermediates such as OH*, O*, and OOH*, although the modes of participation of reactants and protons/hydroxide ions differ.

Table 5. OER mechanism

Acidic electrolyte	Neutral or alkaline electrolyte
$H_2O + * \rightarrow OH^* + H^+ + e^-$	$OH^- + * \rightarrow OH^* + e^-$
$OH^* \rightarrow O^* + H^+ + e^-$	$OH^* + OH^- \rightarrow O^* + H_2O + e^-$
$O^* + H_2O \rightarrow OOH^* + H^+ + e^-$	$OH^- + O^* \rightarrow OOH^* + e^-$
$OOH^* \rightarrow O_2 + H^+ + * + e^-$	$OH^- + OOH^* \rightarrow * + H_2O + O_2 + e^-$
Overall reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	Overall reaction: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

OER performance is affected by multiple factors, including the catalyst electronic structure, surface adsorption energies, electrolyte composition, and operating conditions. Optimization primarily relies on rationally tuning the adsorption energies of intermediates such as OH*, O*, and OOH* and lowering the energy barriers for O–O bond formation and multielectron transfer. In addition to reducing the overpotential and Tafel slope, practical applications require attention to structural stability, corrosion resistance, and bubble detachment at high current densities. Increasing the temperature and optimizing the electrolyte composition can improve mass transport and reaction kinetics, whereas excessively high temperatures or strongly alkaline conditions may accelerate the degradation of membranes, electrodes, and catalyst layers [7].

In summary, HER and OER together determine the energy efficiency and operational stability of water-electrolysis systems. The following sections focus primarily on cathodic HER under alkaline/neutral conditions, using MoS_2 as a representative system to discuss recent progress in improving the activity and stability of non-noble-metal HER catalysts through phase engineering, elemental doping, defect construction, heterostructure design, and support coupling.

3. Water-electrolysis catalysts

Both HER and OER exhibit kinetic polarization during water electrolysis, and OER generally has a higher reaction barrier because it involves four-electron transfer and O–O bond formation. Appropriate catalyst selection can lower the activation energy of interfacial reactions, optimize intermediate adsorption, and accelerate electron/ion transport, thereby reducing the operating voltage of the electrolyzer and improving energy efficiency .

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3.1. Noble-metal catalysts

Noble-metal catalysts (PMCs) mainly include Pt-group metals such as Pt, Ru, and Ir, together with their alloys and compounds. Pt and Pt-based materials are representative high-performance HER catalysts, whereas Ir/Ru-based materials are more commonly used for acidic OER. Owing to their outstanding intrinsic activity and favorable interfacial reaction kinetics, noble-metal catalysts remain important in high-performance systems such as PEM water electrolysis.

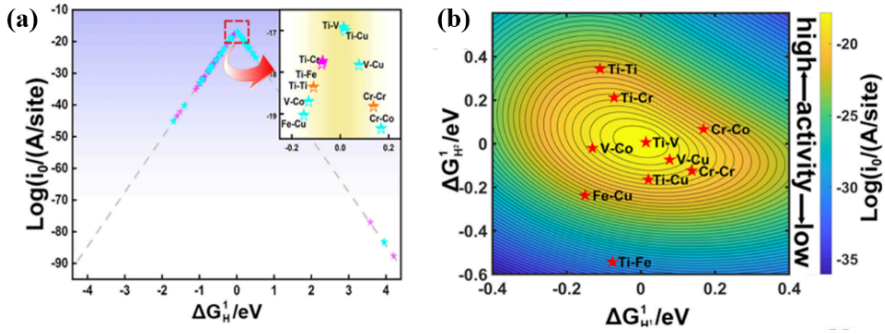

Figure 2. (a) HER is based on exchange current density（i0）Two-dimensional volcano plot of hydrogen adsorption free energy；(b) 10 Types of 3D Volcano Charts [8]

As shown in Fig. 2, the HER exchange current density typically exhibits a volcano-type relationship with the hydrogen adsorption free energy. Pt has a near-optimal H* binding strength and therefore shows a low overpotential, high exchange current density, and favorable reaction kinetics, making it a benchmark catalyst for HER evaluation. In contrast, excessively strong or weak H* adsorption on some transition metals can limit either subsequent desorption or the initial adsorption step; therefore, alloying, construction of nonmetallic compounds, or electronic-structure regulation is required to optimize adsorption energetics.

Despite their clear activity advantages, noble-metal catalysts suffer from low crustal abundance, high cost, and concentrated supply chains, which makes them unsuitable for supporting the low-cost electrocatalyst demand associated with ultra-large-scale green-hydrogen deployment. Therefore, developing non-noble-metal catalysts based on earth-abundant elements such as Ni, Co, Fe, and Mo that simultaneously provide high-current-density activity, stability, and manufacturability is an important direction for scaling up water-electrolysis-based hydrogen production.

3.2. Single-atom catalysts

Single-atom catalysts (SACs) are catalytic systems in which metal active centers are atomically dispersed and anchored on support surfaces, defect sites, or lattice coordination environments. Their key advantage is the maximization of metal-atom utilization, while well-defined metal–support coordination structures enable regulation of local electronic states and adsorption behavior. Compared with conventional nanoparticles, the performance of SACs depends more strongly on the single-atom coordination environment, support defects, and interfacial charge transfer .

As shown in Fig. 3, research on SACs generally revolves around "controllable synthesis–atomic-scale characterization–catalytic application." Strategies such as defect anchoring, coordination confinement, and spatial isolation can stabilize isolated metal centers on a variety of supports for applications in electrocatalysis, thermocatalysis, and energy conversion [9].

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Figure 3. Synthesis strategies and applications of single-atom catalysts [9]

Support selection and coordination environment are key factors determining the stability and activity of SACs. Carbon materials, metal oxides, sulfides, and related supports can stabilize single atoms through defect sites, heteroatoms, or lattice sites and regulate the electronic structure via metal–support interactions. However, under high loading or strong electrochemical driving forces, single atoms may still migrate, agglomerate, or undergo coordination reconstruction. In situ/operando characterization is therefore required to clarify the genuine active centers and their dynamic evolution mechanisms.

3.3. Non-noble-metal catalysts

Non-noble-metal catalysts (NPMCs) mainly include sulfides, phosphides, nitrides, carbides, and borides of transition metals such as Ni, Co, Fe, and Mo, as well as heteroatom-doped carbon materials. Their constituent elements are abundant and relatively inexpensive, making them important alternatives to noble metals in alkaline water electrolysis (ALK and AEM). After suitable regulation of their electronic structure and interfaces, some of these catalysts can also exhibit high HER activity in neutral and even acidic media.

Transition-metal sulfides (TMSs) constitute an important class of non-noble-metal HER catalysts. Taking MoS_2 as an example, its layered structure facilitates regulation of electronic properties through phase transformation, defects, doping, and interface engineering. In particular, metallic 1T/1T′ phases, edge sites, and specific defect sites can markedly improve electron transport and H* adsorption behavior, resulting in HER activity substantially higher than that of the unmodified basal plane of the 2H phase.

Transition-metal phosphides (TMPs) generally possess high electrical conductivity and tunable metal–phosphorus bonding and perform well in alkaline HER and some bifunctional electrocatalytic systems [10]. Transition-metal nitrides (TMNs) and carbides (TMCs) can modulate the d-band electronic structure of transition metals through interstitial N/C atoms, thereby producing certain noble-metal-like surface electronic characteristics. Transition-metal borides (TMBs) and related materials have also attracted attention for HER. The ultimate performance of each material system nevertheless depends on the actual active phase, surface reconstruction, and electrolyte environment.

As shown in Table 6, noble-metal, single-atom, and non-noble-metal catalysts each offer distinct advantages and limitations in terms of activity, cost, atomic utilization, and stability. Considering

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resource abundance, tunability, and scale-up potential, the following discussion focuses on compositional and structural regulation of MoS_2-based materials and their HER performance.

Table 6. Comparison of three classes of hydrogen-evolution catalysts

Type	Catalyst	Advantages	Disadvantages
PMC	Pt/C and composite catalysts	High HER activity	Scarce resources and high cost; poisoning/dissolution risks under some operating conditions
SACs	Pt, Co, and other single-atom catalysts	High atomic utilization	Prone to migration and agglomeration at high loading; complex control of coordination structure and stability
NPMC	Transition-metal compounds	Abundant resources, broad applicability, and good stability	Intrinsic activity is generally lower than that of Pt; conductivity and active sites require further optimization

4. Non-noble-metal MoS_2 catalysts

Transition-metal dichalcogenides (TMDs), such as MoS_2, WS_2, and NbS_2, possess typical layered structures in which strong covalent bonds connect atoms within each layer, whereas adjacent layers are stacked primarily through van der Waals interactions. MoS_2 is one of the most representative TMDs and can adopt multiple polymorphs, including semiconducting 2H and metallic 1T/1T′ phases. Its HER performance is closely related to phase structure, edge/basal-plane exposure, defect type, electron transport, and interfacial wettability, providing considerable scope for multiscale compositional and structural regulation .

4.1. Advantages of MoS_2 catalysts

MoS_2-based catalysts feature favorable hydrogen-adsorption thermodynamics, abundant resources, and excellent structural tunability, making them important candidate alternatives to Pt-based HER catalysts. Their advantages can be summarized in three main aspects:

(1) Optimizable H* adsorption thermodynamics. Theoretical and experimental studies have demonstrated that MoS_2 edge sites exhibit high HER activity, with hydrogen adsorption free energies approaching the thermoneutral region. Increasing the density of edge sites, introducing defects, or regulating the local coordination environment can further optimize the balance between H* adsorption and desorption.

(2) Rich compositional space and a broad structural-regulation window. MoS_2 can be modified through phase engineering, heteroatom doping, sulfur-vacancy construction, strain regulation, and heterointerface coupling to alter its band structure and local electronic states. Meanwhile, hydrothermal/solvothermal synthesis, chemical vapor deposition, sulfurization conversion, and intercalation exfoliation can produce materials with different dimensions and morphologies, providing multiple technological routes for active-site engineering and construction of conductive networks.

(3) Favorable resource and cost advantages. Mo and S are more abundant than Pt-group metals, and MoS_2 exhibits good chemical stability within appropriate potential windows. With rational modification, its HER activity can be extended across acidic, neutral, and alkaline media, offering

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potential material options for multiple electrolysis systems, including PEM, ALK, and AEM. It should be emphasized that true compatibility with industrial electrolyzers also depends on stability at high current densities, mechanical integrity of the catalyst layer, and consistency of scalable fabrication.

4.2. Phase engineering

The most common 2H phase of MoS_2 is semiconducting, and its relatively low in-plane/interfacial charge-transfer efficiency limits HER kinetics. Phase engineering can substantially modify the electronic structure by regulating the proportions of 2H, 1T, and 1T′ polymorphs without changing the overall chemical composition. Lukowski et al. obtained metallic-phase-rich 1T-MoS_2 nanosheets through lithium intercalation and exfoliation, demonstrating that the metallic phase can markedly reduce charge-transfer resistance and improve utilization of effective active sites [10]. Therefore, the goal of phase engineering is not simply to maximize the 1T-phase fraction, but rather to balance the high electrical conductivity provided by metallic phases with thermodynamic stability. Constructing 2H/1T (1T′) coexistence structures through local phase transformation, phase-boundary engineering, or stabilizer regulation is generally more favorable for simultaneously maintaining rapid electron transport and long-term stability.

4.3. Defect and elemental-doping regulation

Defect engineering can convert the intrinsically less-active MoS_2 basal plane into a reaction region capable of participating in HER. Xie et al. prepared defect-rich ultrathin MoS_2 nanosheets and substantially enhanced HER activity by increasing the number of coordinatively unsaturated sites . Li et al. further demonstrated that sulfur vacancies can introduce new electronic states into the basal plane of 2H-MoS_2 and, in synergy with strain, regulate the H* adsorption free energy, thereby transforming basal-plane sites from inert to active . In addition to intrinsic defects, heteroatom doping is an important approach for regulating the local electronic structure. Deng et al. reported that single-atom metal doping can alter hydrogen adsorption at neighboring S sites and demonstrated that non-noble-metal dopants such as Co and Ni have the potential to activate the MoS_2 basal plane . Importantly, increasing defect or dopant concentrations is not invariably beneficial: excessive defect concentrations may compromise lattice integrity, increase scattering, or accelerate sulfur loss. Stable active sites should therefore be achieved through coordinated design of "defect type–concentration–local strain–electronic structure."

4.4. Heterostructure and morphology regulation

Constructing conductive heterostructures can simultaneously address the limited electron transport of MoS_2 and the tendency of nanosheets to restack. Li et al. grew MoS_2 nanoparticles in situ on graphene supports, establishing rapid electron-transport pathways through intimate interfacial contact while improving MoS_2 dispersion and HER activity . Morphology regulation can also directly alter the ratio of edge to basal-plane sites. Early work by Jaramillo et al. confirmed a strong correlation between the HER activity of MoS_2 and the number of edge sites. Kong et al. subsequently constructed vertically aligned MoS_2 films that maximized exposure of the layered edges and observed that the exchange current density increased with the density of exposed edges. These findings indicate that an ideal MoS_2 electrode should simultaneously possess a high density of

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accessible active sites, a continuous conductive network, sufficient electrolyte wettability, and a stable catalyst-layer/current-collector interface.

4.5. Challenges facing MoS_2 catalysts

Although MoS_2 has substantial research value as a non-noble-metal HER catalyst, several challenges must still be overcome to translate its laboratory-scale performance into large-scale application:

(1) Intrinsic conductivity and the density of effective active sites remain limited. Conventional 2H-MoS_2 is semiconducting, and its unmodified basal plane generally exhibits low HER activity, while highly active edge sites account for only a small fraction of bulk or laterally grown structures. Although phase engineering, defect engineering, and coupling with conductive supports can improve charge transport and site utilization, a balance between high activity and structural stability is still required.

(2) Structural stability and the true active phase under operating conditions remain insufficiently understood. Under high current densities, prolonged polarization, and complex electrolyte environments, MoS_2 may undergo sulfur loss, phase transformation, surface oxidation/reconstruction, or interfacial delamination, leading to dynamic changes in the active centers. Consequently, characterization performed only before and after reaction is insufficient to fully elucidate deactivation mechanisms. In situ/operando spectroscopy and microscopy are urgently needed to track catalyst evolution under realistic operating conditions.

(3) A gap remains between scalable synthesis and device-level evaluation. Highly active MoS_2 materials prepared in the laboratory often rely on precise control of precursor ratios, temperature, atmosphere, defect concentration, or nanoscale morphology, whereas fluctuations in these parameters during scale-up can readily cause batch-to-batch variation. In addition, some high-performance strategies depend on noble-metal doping, complex supports, or multistep post-treatment, thereby diminishing cost and process advantages. Future studies should establish controllable synthesis methods for large-area electrodes and conduct long-term durability and energy-efficiency evaluations at current densities of ≥100–500 $mA \cdot cm^{-2}$ or higher.

5. Conclusions and outlook

This review systematically summarizes compositional and structural regulation strategies for MoS_2-based electrocatalysts for hydrogen evolution. MoS_2 offers advantages including abundant resources, structural designability, and tunable H* adsorption thermodynamics; however, conventional 2H-MoS_2 remains constrained by insufficient basal-plane activity, limited electron transport, and a low density of effective active sites. Existing studies demonstrate that phase engineering can improve conductivity and interfacial charge transfer by introducing metallic 1T/1T′ components; defects and elemental doping can modify local coordination environments and activate otherwise inert basal-plane sites; heterostructure construction and coupling with conductive supports can improve electron transport and create synergistic active interfaces; and morphology control, including vertical growth and ultrathinning, can enhance edge-site exposure . Future research should move beyond optimization of a single activity metric toward integrated evaluation of "high-current-density activity–long-term stability–fabrication cost–device compatibility," while strengthening the integration of in situ/operando characterization with theoretical calculations to identify the true active phases, interfacial water structures, and deactivation pathways under realistic operating conditions. Only through coordinated advances in mechanism-guided high-performance design,

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scalable synthesis, and electrolyzer-level validation can MoS_2-based non-noble-metal catalysts progress from laboratory research toward low-cost green-hydrogen production.

References

[1] Hinnemann, B., Moses, P. G., Bonde, J., et al. (2005). Biomimetic hydrogen evolution: MoS_2 nanoparticles as catalyst for hydrogen evolution. *Journal of the American Chemical Society, 127*(15), 5308–5309.

[2] Jaramillo, T. F., Jørgensen, K. P., Bonde, J., et al. (2007). Identification of active edge sites for electrochemical H_2 evolution from MoS_2 nanocatalysts. *Science, 317*(5834), 100–102.

[3] Li, Y., Wang, H., Xie, L., et al. (2011). MoS_2 nanoparticles grown on graphene: An advanced catalyst for the hydrogen evolution reaction. *Journal of the American Chemical Society, 133*(19), 7296–7299.

[4] Kong, D., Wang, H., Cha, J. J., et al. (2013). Synthesis of MoS_2 and $MoSe_2$ films with vertically aligned layers. *Nano Letters, 13*(3), 1341–1347.

[5] Lukowski, M. A., Daniel, A. S., Meng, F., et al. (2013). Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS_2 nanosheets. *Journal of the American Chemical Society, 135*(28), 10274–10277.

[6] Xie, J., Zhang, H., Li, S., et al. (2013). Defect-rich MoS_2 ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. *Advanced Materials, 25*(40), 5807–5813.

[7] Deng, J., Li, H., Xiao, J., et al. (2015). Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS_2 surface via single-atom metal doping. *Energy & Environmental Science, 8*(5), 1594–1601.

[8] Li, H., Tsai, C., Koh, A. L., et al. (2016). Activating and optimizing MoS_2 basal planes for hydrogen evolution through the formation of strained sulphur vacancies. *Nature Materials, 15*(1), 48–53.

[9] El-Shafie, M. (2023). Hydrogen production by water electrolysis technologies: A review. *Results in Engineering, 20*, 101426.

[10] Sun, H. A., Xu, X. M., Kim, H., et al. (2023). Electrochemical water splitting: Bridging the gaps between fundamental research and industrial applications. *Energy & Environmental Materials, 6*(5), 12441.