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Topical Review

Extending MoS₂-based materials into the catalysis of non-acidic hydrogen evolution: challenges, progress, and perspectives

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Abstract

Water splitting is regarded as among the most prospective methods of generating green hydrogen. Switching electrolytes of water electrolysis from acidic to non-acidic ones will enable the use of noble-metal-free electrocatalysts and mitigate material corrosion, thus lowering the capital cost of water electrolyzers and improving their operational stability. However, increasing electrolyte pH will degrade the hydrogen evolution reaction (HER) activity because of the reduced concentration of H_3O^+ as reactants, making non-acidic HER sluggish. To accelerate HER, MoS₂-based materials with the advantages of unique atomistic structure, low cost, and high abundance have been considered prospective electrocatalysts to substitute for Pt in acid. Great efforts are being spent on extending MoS₂-based materials into the catalysis of non-acidic HER, and their further development requires clarification of the existing challenges and current progress. However, it has not yet been discussed for non-acidic HER on MoS₂-based electrocatalysts. To mitigate the disparity, we systematically overview MoS₂-based electrocatalysts for non-acidic HER, covering catalytic mechanisms, modulation strategies,

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Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. materials development, current challenges, research progress, and perspectives. This review will contribute to the rational design of MoS₂-based materials for high-performance HER in non-acidic conditions.

Keywords: MoS₂, hydrogen evolution reaction, non-acidic, electrocatalyst

1. Introduction

Developing viable and renewable energy storage and transition technologies is critical, given the massive consumption of conventional fossil fuels and escalating environmental issues [1-3]. Possessing high gravimetric energy density as well as zero-carbon emission, H₂ emerges as the most prospective energy carrier that can substitute diminishing natural resources [4-6]. Recently, H₂ generation by water electrolysis, which can be driven using renewable electricity, has attracted broad interest due to the abundant sources, high product purity, mild reaction conditions, as well as little pollution [7, 8]. However, large overpotentials of electrocatalytic water splitting are inevitably desired due to the slow electrode reaction kinetics, thus leading to low energy efficiency [9].

The overall performance of electrocatalytic water splitting is significantly influenced by electrolytes. Due to the high concentration of protons as a stable provider of reactants, acidic solutions are regarded as the ideal electrolytes for electrocatalytic hydrogen evolution reaction (HER) [10, 11]. So far, most studies on HER have been focused on acidic conditions. Nonetheless, electrolytic cells operated in acidic solutions inevitably generate corrosive vapor at high temperatures, which not only contaminates the produced H₂ but also corrodes the device [12, 13]. Moreover, the lack of corrosion-resistant noble-metal-free anode materials in acid necessitates the use of high-cost Ir or Ru oxides, contributing to the prohibitive capital cost of water electrolyzers. Adopting non-acidic electrolytes helps address the aforementioned issues by enabling the utilization of noble-metal-free electrocatalysts and mitigating the material corrosions, thus making non-acidic water electrolysis appealing.

More than the nature of electrolytes, electrocatalysts directly interact with water electrolysis reactants and products, and their activity and stability determine the electrode kinetics and further the reaction overpotential. Various materials have been measured for HER. Among them, noble metals containing Pt, Ir, and Ru possess outstanding HER activities under wide pH conditions, but the scarcity and high cost heavily limit their wide-scale usage [14–16]. In addition, they possess poor stability, especially under large current densities [17, 18]. As a result, it is urgently desirable to decrease the utilization of noble metals and explore non-precious metal-based catalysts with outstanding performance comparable to Pt as well as superior stability.

 MoS_2 , which belongs to transition metal dichalcogenides (TMDs), has attracted substantial interest and is considered a prospective substitute to the Pt-based HER electrocatalysts under acidic conditions due to its unique atomistic

structure, promising performance, low cost, and high abundance [19-21]. Unfortunately, low densities of the active sites (limited to only unsaturated edges) and poor electronic conductivities as the 2D semiconductor make it much inferior to Pt-based catalysts [22-24]. Worse still, MoS₂-based catalysts only demonstrated promising HER activity under acidic conditions but poorer HER performance under non-acidic conditions [25]. The catalytic mechanisms of MoS₂-based catalysts for non-acidic HER remain unclear, which further hinders their rational design and large-scale applications for industrial production. To optimize the properties of MoS2based electrocatalysts and extend their applications into nonacidic HER, multiple attempts have been made and significant progress was achieved (figure 1). Their further development requires distinguishing the distinct HER mechanisms in different pH electrolytes, proposing innovative strategies to overcome the challenges and establishing the explicit structureactivity-pH relationships. In this regard, a systematic review is still lacking.

To mitigate the above gaps, we carefully overview MoS₂based electrocatalysts for non-acidic HER, covering catalytic mechanisms, modulation strategies, materials development, current challenges, research progress, and perspectives. Specifically, we start by discussing MoS2-based materials with various atomistic structures and the corresponding physicochemical characteristics with the goal of uncovering the relationships between their structures and HER performance in pH-universal solutions. Subsequently, we moved to comment the current understanding of the HER mechanisms in pHuniversal ranges by comparing the HER behavior in acidic and non-acidic media. Following that, we discussed the specific strategies of engineering MoS₂ to improve the non-acidic HER performance and carefully assessed their recent progress. Finally, we summarized the current challenges of utilizing MoS2-based materials for non-acidic HER and gave some potential research directions.

2. HER mechanisms under alkaline/neutral conditions

2.1. Structures and properties of molybdenum dichalcogenides

As a representative TMD, MoS_2 exhibits a graphite-like structure, whose monolayer comprises one layer of Mo atoms sandwiched in the middle of two layers of S atoms [26–29], and multiple monolayers are stacked together by van der Waals (vdW) forces with a sheet spacing of 6.5 Å [30, 31]. In particular, MoS_2 contains three distinct crystal structures

Future perspectives

MoS₂-based materials with the advantages of unique atomistic structure, low cost, and high abundance have been considered prospective electrocatalysts in highly efficient hydrogen evolution reaction (HER) electrolysis. To further enhance the practical properties of MoS₂-based materials for non-acidic HER, the conditiondependent electrocatalyst reconstruction (e.g. redox and phase change) should be clarified. Innovative strategies can be combined to simultaneously enhance the intrinsic HER activity, boost the electronic conductivity, and increase the number of active sites. In the future, the following directions can be considered to advance their scalable applications: (a) precisely fabricate MoS₂based materials with well-defined and novel structural/electronic properties; regarding this, high-entropy compositions and introducing single atoms may be promising strategies to further modulate MoS₂ and improve the performance. (b) Subtly design a series of pH gradients toward research of the interplay among the structure, activity, and pH, and establish the rigorous structure-activity-pH relationships over MoS₂-based materials and beyond. (c) Monitor, understand, and control the evolution of MoS2-based electrocatalysts and electrolytes during long-term and practical water electrolysis conditions. (d) Examine and optimize practical performance with water electrolysis devices. With the continuous efforts from researchers, MoS2-based materials will play increasing roles in low-cost and high-performance water electrolysis for green H₂ generation.

involving 1T, 2H, and 3R phases, as displayed in figures 2(a) and (b) [32, 33]. Among them, 2H-MoS₂ is a hexagonal symmetry structure with the Mo atom in octahedral coordination. Except for the stacked state, the structure of the rhombohedral symmetric 3R phase is remarkably identical to the 2H phase. Different from the 2H phase, the tetragonal structure of 1T-MoS₂ contains a pair of S atoms and a single Mo atom at each of the interval locations, forming octahedral coordination. The three types of MoS₂ exhibit various electronic structures because of the different geometric configurations, as shown in figures 2(c)-(e). As the sole metallic phase, 1T MoS₂ shows a continuous band structure with no gap, leading to great conductivity, while the other two phases as semiconductors possess large band gaps [30]. In general, the catalytic activity and stability depend on the electronic structures of catalysts, and the different environment of Mo atoms in three phases leads to distinct orbital level states [34]. As revealed in figures 2(f) and (g), the d_{xy} and d_{x-y}^2 orbitals of Mo in the 2H phase are incompletely occupied, while the d_z^2 orbital is fully occupied, thus making the 2H phase a semiconductor. As for the 1T phase, the incomplete filling of the degenerated d_{xy} , d_{xz} , and d_{yz} orbitals gives it a metallic ground state [35]. As for stability, the 2H phase is known as a thermodynamically stable phase dominant in nature in contrast to the other two, and the three phases can transform into each other under certain conditions. For example, the transformation from 1T or 3R to 2H phase can be facilely achieved through simple calcination at different temperatures [36, 37]. By intercalating small guest molecules, extra electrons from guest molecules will transfer to the MoS_2 layer and further occupy the d_{xy} and d_{x-y}^2 orbitals of Mo, thus inducing the transformation from the 2H to 1T phase [38, 39]. Furthermore, doping or exerting strains enable to cause the phase transformation because of the structural distortion and distinct occupied state of the Mo-d band [40-42].

As mentioned, the complex MoS₂ nanostructures and their various properties strongly rely on synthetic techniques. Current preparation methods could be broadly divided into two major classes, including the top-down approach and the bottom-up approach [45]. Exfoliation, which contains mechanical exfoliation and liquid-phase exfoliation, is one of the top-down approaches to prepare the monolayer or fewlayer MoS₂ [46, 47]. Mechanical exfoliation can be operated by rubbing out the MoS₂ flakes coated on a substrate using a sticky tape, which is only suitable for lab-scale synthesis due to the low yield. Liquid-phase exfoliation can be facilely conducted by chemical (molecule or ion intercalation) or physical treatment (stirring, bubbling, or grinding) with low-cost but low-quality products. Bottom-up methods, on the other hand, possess better controllability than top-down approaches [48]. Physical layer deposition (physical vapor deposition (PVD)) is one of the bottom-up techniques, which can be applied only to prepared thin layers of MoS₂ with non-uniform sizes of crystalline grain [49]. In comparison, chemical vapor deposition (CVD) is applicable to both thin and thick layers. In the deposition process, a sulfur vapor is passed over a substrate coated with Mo, and the resultant has good quality but low yield. Analogously, the atomic layer deposition (ALD) technique is also suitable for thin and thick films with high efficiency and purity. Moreover, the in situ growth of MoS₂ with controllable size and morphology can be conducted with the help of solutions by hydrothermal or solvothermal methods, which are considered cheap and scalable [50]. The methods are tabulated in table 1 in detail.

2.2. Reaction pathway under a pH-universal range

The HER process involves the transfer of two electrons, occurring through hydronium (H_3O^+) ions or water (H_2O) molecules as reactants, which depends on the pH of the electrolytes [59, 60]. In the first Volmer step, H* can be generated by H_3O^+ ions or H_2O molecules adsorption from the electrolytes to the cathodic surface to form the reaction intermediate (figure 3).

Volmer step in step 1:

In acidic conditions:

$$H_3O^+ + e^- + * \leftrightarrow H^* + H_2O.$$
 (1)

In alkaline conditions:

$$H_2O + e^- + * \leftrightarrow H^* + OH^-$$
(2)

where * means the active site on the catalyst.

In the second step, H_2 molecules are generated by two distinct mechanisms. One is the Heyrovsky step, which occurs at the low H^* coverage on the surface of catalysts, as described as follows.



Figure 1. Timeline of recent developments of MoS₂-based electrocatalysts in pH-universal range.



Figure 2. Different phase structures for MoS_2 [43, 44]. (a) Reproduced from [43]. CC BY 3.0. and (b) [44] John Wiley & Sons. [© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim]. The corresponding band structure for (c) 1T, (d) 2H, and (e) 3R phase. Simplified orbital energy level for (f) 1T and (g) 2H and 3R phase [30]. Reproduced from [30], with permission from Springer Nature.

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Method	Precursors	Conditions	Properties	References
Exfoliation	Bulk MoS ₂ , Nitto tape, Au/PS substrates	Repeatedly stuck and moved using Nitto tape for more than 100 times to form the uniform distribution, then the carrier tape was pressed on the top of Au/PS substrates with a cotton swab	A tunable level of tensile strain, local phase transition, and abundant edges	[51]
Liquid-phase exfoliation	As-prepared MoS ₂ , n-butyl lithium	Glove box, mixed for 6–48 h, and heating at 60 $^{\circ}$ C	Metallic phase, monolayer, and proliferated density of catalytic active sites	[52]
Liquid-phase exfoliation	Bulk MoS ₂ powder	Ultrasonication for 5 min; laser-induced exfoliation (a nanosecond pulsed Nd:YAG laser machine)	Ultrastable, few-layer, rich in S vacancies, metallic 1T phase	[53]
PVD	MoS ₂ target, carbon cloth	The deposition time was kept at 1000 s; the sputtering power was adjusted from 70 to 150 W	Vertically grown on the carbon cloth; abundant exposed edge sites	[54]
CVD	MoO ₃ powder, sulfur powder, SiO ₂ /Si substrate	Annealing at 750 °C for 40 min under Ar protection	Monolayer; average size of tens of micrometers	[55]
CVD	Silicon substrates, MoO ₃ , sulfur powder, n-butyl lithium	Annealing at 750 $^\circ\text{C},$ 5% H_2/Ar for 48 h	High quality, uniform, monolayer, 1T/2H phase	[56]
ALD	MoCl ₅ , H ₂ S, AAO/Ti ₃ C ₂ film as a substrate	Passing time of the precursors was 5 and 2 s; cleaning time of N_2 was 60 s; number of ALD cycles was set as two to ten cycles	Uniformly distributed; nanoporous; controllable size and thickness	[57]
Hydrothermal method	Ammonium heptamolybdate, thiourea, and deionized water	In autoclave at 200 $^{\circ}\mathrm{C}$ for 22 h	Porous MoS ₂ nano islands; controllable Mo- or S-rich environment	[58]

Table 1. Different synthesis methods of MoS_2

Heyrovsky pathway in step 2: In acidic conditions:

$$\mathbf{H}^* + \mathbf{H}_3 \mathbf{O}^+ + \mathbf{e}^- \leftrightarrow \mathbf{H}_2 + * . \tag{3}$$

In alkaline conditions:

$$H^* + H_2O + e^- \leftrightarrow H_2 + OH^- + *.$$
(4)

On the other hand, H_2 formation can also take place through the Tafel step at high coverage of H^* , in which two nearby H^* can unite by chemical desorption to generate an H_2 molecule, as exhibited as follows.

Tafel pathway in step 2:

In both acidic and alkaline conditions:

$$2H^* \leftrightarrow H_2 + 2^* . \tag{5}$$

The H_3O^+ ion is a well-known reactant of HER due to the high concentration as a proton provider in strong acidic electrolytes, while in alkaline solutions with high concentration, H_2O molecules are inevitably the primary reactant due to the low-concentrated H_3O^+ ions [61, 62]. Unlike the single H_3O^+ or H_2O reduction occurring in concentrated acidic or alkaline solutions, respectively, the HER mechanism is more complicated in the neutral environment because it involves the reduction of both H_3O^+ ions and H_2O molecules, which are the dominant reactions at low and high overpotentials, respectively [63–66]. Because industrial H_2 production requires operating at high current density, H_2O reduction is expected to be the main HER pathway under neutral conditions, which is similar to the alkaline cases [67]. Aiming at the utterly different HER behavior in these three conditions, we summarized possible scenarios of the reason for the sluggish HER kinetics under non-acidic environments. However, it is still challenging to determine which scenario can truly reflect the real HER process in non-acidic environments so far.

2.3. Reason for the sluggish HER kinetics in non-acidic environments

Non-acidic electrolytes have been demonstrated to seriously slow down the HER kinetics. Remarkably, as displayed in figures 4(a)–(c), the HER activities of Au(111), Pt(111), and polycrystalline Ir fall off with the rising pH of solutions [63]. The HER activity for the aforementioned catalysts in non-acidic conditions is much lower than that in acid media, especially two to three orders of magnitude lower in alkaline



Figure 3. Electrocatalytic HER process on the catalysts under acid and alkaline environments [59]. John Wiley & Sons [59]. [© 2022 Wiley-VCH GmbH].

electrolytes than in acidic environments [68]. The typical HER polarization profile changes when increasing the pH value, leading to a current-plateau region and pure diffusion-limiting currents at higher overpotentials, which can also be reflected in the parameters of kinetics and thermodynamics, containing exchange current density (j_0) , hydrogen adsorption free energy ($\Delta G_{\rm H}$), onset potential, as well as Tafel slope, respectively [69]. In this part, we first summarized the possible scenarios according to the current reports of HER in alkaline electrolytes, including water dissociation theory, hydrogen binding energy (HBE) theory, and interface transfer theory, focusing on the critical factors governing the overall reaction. Then, we further talked about HER in neutral environments by highlighting its complicated kinetics controlled by the diffusion of H₃O⁺ ions and H₂O molecules, thus revealing the possible reason for the sluggish HER kinetics in non-acidic solutions.

2.3.1. Water dissociation theory. Under acidic conditions, the solutions with sufficient H⁺ can serve as a stable H^{*} donor when applied an overpotential, while in non-acidic media, H₂O molecules are the unique proton provider. Therefore, the HER kinetics in alkaline media is usually limited by the energy barrier due to the sluggish water dissociation. In this case, Markovic et al created a precedent for revealing how water dissociation affects the alkaline HER kinetics [61, 70, 71]. Because the adsorbed hydroxyl (OH*) can compete against hydrogen adsorption on a single active site and suppress the subsequent H_2 generation, they concluded that it has a dominant role in HER, and the alkaline HER activity is hindered by H₂O dissociation. Thus, optimizing the tradeoff between the H* adsorption rate and the OH* desorption rate is an effective strategy to enhance the HER performance under alkaline conditions. Introducing dual active sites is a promising method by which one site is responsible for



Figure 4. Linear sweep voltammetry (LSV) curve when the rotation rate was set at 1600 r.p.m. for (a) Au(111), (b) Pt(111), and (c) Ir-poly [63]. Reproduced from [63], with permission from Springer Nature. (d) The evolution of overpotential at 5 mA cm⁻² on Pt(111) with different 3d transition metal hydroxide sites [61]. Reproduced from [61], with permission from Springer Nature. (e) Structure of the X (Fe, Co, and Ni) and O co-doped 1T-MoS₂. (f) Free-energy diagrams and the corresponding structures of the HER process on the surface of catalysts [74].Reproduced from [74]. CC BY 4.0. (g) Peak splitting ΔE_p as a function of the peak CD for OH adsorption on Pt(110) [77]. Reprinted with permission from [77]. Copyright (2017) American Chemical Society. (h) Illustration of OH transfer process under alkaline conditions [79].Reprinted with permission from [79]. Copyright (2019) American Chemical Society.

H^{*} adsorption, while the separated other oxyphilic sites can powerfully capture OH* for water dissociation [72]. Benefitting from the active site separation, the competition between H* and OH* can be effectively weakened, thereby improving the kinetics of the Volmer step (equation (2)). Based on this principle, Markovic et al specifically designed a well-defined Pt(111) catalyst for optimizing hydrogen adsorption combined with Ni(OH)₂ clusters as extra sites for the strengthened hydroxide interaction (figure 4(d)), effectively boosting the H₂O dissociation. In addition, other oxyphilic candidates, such as metals (Ru), were also capable of enhancing the overall HER performance [63, 73]. Markovic et al also discussed the alkaline HER mechanism on MoS₂ [61, 70]. They attributed the sluggish alkaline HER kinetics to not only the initial water dissociation process but also the strong adsorption of OH⁻ on the surfaces of MoS₂, indicating that the H adsorption on the edge sites of MoS₂ suffers from the interference caused by the OH⁻ species in alkaline conditions. Inspired by the 'dual active site' strategy, Zhang et al atomically engineered metal doping sites onto metallic 1T-MoS₂ [74] and revealed that co-doping nickel and oxygen into 1T-MoS₂ could serve as the new active sites for H^{*} absorption and then optimize the OH* binding energy on the adjacent S sites, thereby assisting the process of water dissociation and hydrogen generation from their intermediate states (figures 4(e) and (f)).

However, it is still doubted whether the dual active sites indeed have a driving role in the alkaline HER activity. It is likely that the boosted HER kinetics can be caused by the changed electronic structure after introducing the dualsite rather than the promoted water dissociation due to the functional separation of active sites [75, 76]. The improved HER performance can also derive from the optimized HBE caused by the change of electronic structure on active sites when a second species is introduced. For instance, Intikhab et al and Rebollar et al argued that OH* adsorption does not influence the HER activity because the OH-modulated process is not workable on Pt(110) after studying the roles of OH* and the alleged 'dual active site' mechanism in the alkaline HER [77, 78]. The evolution of HER kinetics with different OH adsorption strengths, which is further determined by the cation ion species of the solutions, can only be explained by a direct Volmer step. Conversely, OH species take no part in reducing accessible active sites and slowing HER kinetics. The findings revealed that the origin of kinetic barriers is the interfacial water state rather than adsorption energy, which



Figure 5. (a) The LSV curves and (b) CV plots of platinum in the buffered solutions saturated with H_2 - and Ar, respectively [62]. (c) HBEs on Pt(110) and (100) surfaces vs. the solution pH [62]. Reproduced from [62], with permission from Springer Nature. (d) CVs for Pt(111) in electrolytes with different pH [10]. (e) CVs of Pt(111) at the buffered solution with pH 10 [10]. (f) The relationship between temperature coefficient of the double layer potential and the applied voltage on Pt(111)/Ni(OH)₂ and Pt(111) [10]. Reproduced from [10], with permission from Springer Nature.

can well explain the evolution of HER kinetics under different pH (figure 4(g)). These uncertainties have promoted more thorough interactions between active sites and intermediates under alkaline conditions.

Although there are still many doubts about the dual active site strategy, it is believed that OH⁻ is still one of the key factors in the origin of slow HER kinetics under alkaline conditions. By in situ x-ray absorption near edge structure spectra, Jia et al further explored the relationship between the hydroxyl transport and the alkali metal cation (AM^+) under strongly alkaline conditions [79]. They proposed that the formation of adsorbed OH^* - $(H_2O)_x$ - AM^+ in the HER process facilitated the OH* transfer from the catalyst surface to the electrolytes to form the $OH^{-}(H_2O)_x$ -AM⁺, thereby selectively promoting the transfer of OH^* (figure 4(h)). Note that they highlighted the key of transport process of OH* rather than adsorption of OH* in the alkaline HER process, which was differentiated from the water dissociation theory. They showed that the hydroxyl transfer kinetics could be changed by adjusting the cation species (e.g. Li⁺, Na⁺, K⁺) and their concentrations, thus enhancing the overall HER activity. Up to now, atomic- or molecular-level insights into whether the aforementioned theories are feasible in the alkaline HER process have remained unclear, and the specific role of the hydroxyl is also unclarified.

2.3.2. HBE theory: is HBE still a valid descriptor under non-acidic conditions?. Viewing that the HER processes under both alkaline and acidic conditions involve the interactions between hydrogen intermediates and catalysts, many reports argued that the HER activity still depends on HBE in alkaline environments [62, 75, 76]. Conway *et al* examined the absorbed hydrogen on Pt, which may be related to the mechanism of HER and reverse hydrogen oxidation reaction (HOR) [80, 81]. They suggested that the overpotential-deposited H species (H_{OPD}) with weak binding strength kinetically took part in the HER process, while the strongly bonded underpotential-deposited H (H_{UPD}) is involved during HOR, following dissociative H₂ adsorption. H_{OPD} coverage was scarcer under alkaline conditions compared with that in acidic environments, leading to sluggish kinetics in the former reaction. Yan et al are the pioneers in verifying this inference on polycrystal Pt that the HBE was considered the unique derivation for monotonically decreasing HER activity in the solutions with different pHs ranging from 0 to 13 (figures 5(a)) and (b)) [62, 82, 83]. As exhibited in figure 4(b), the peaks at lower potential and higher potential in the H_{UPD} region can correspond to the hydrogen adsorption/desorption at the (110) and (100) planes of Pt, which are attributed to the weakly and strongly bonded H, respectively [84, 85]. Significantly, one can see that both peaks shift positively with the increased pH values of the electrolytes. HBE, which can be further related to the peak potential (E_{peak}) of the H_{UPD} desorption, exhibits a great linear correlation with the solution pH (figure 5(c)). As a result, the stronger HBE means a higher *H activation barrier, thus giving rise to the sluggish HER kinetics under strong alkaline conditions, which can also be observed in MoS_2 . Li et al pre-activated MoS₂ by electrochemically polarizing MoS₂ at negative potentials in acidic solutions or immersing MoS₂ into certain acid solutions, like trifluoromethane sulfonamidate [86]. They found that protons can be intercalated into the interlayer space of MoS₂ during the activating process, which was equal to increasing H_{OPD} coverage under alkaline conditions. Benefiting from the intercalate protons, the electrical conductance and the adsorption energy of hydrogen atoms can be optimized, thereby dramatically improving the HER activity and even possessing excellent stability in alkaline solutions compared with that of non-activated MoS₂.

Furthermore, the same trends can also be observed in other metal catalysts, including Ir, Pd, and Rh (figure 5(d)) [49]. It shows a great linear correlation between the E_{peak} and the pHuniversal HER activity (i_0) , revealing that HBE can be changed at different hydroxyl conditions and thus determine the HER performance. Nonetheless, HBE might be the inherent limitation nature of a specific material and not be determined by changing the pH value [87]. Zheng et al explained this contradiction by assuming that the changed HBE can be caused by different water dipole orientations under different OHenvironments [82], which was further confirmed by the theoretical calculation on Pt surface by Cheng et al [88]. Specifically, precisely taking into account solvent and applied potential, they adopted quantum mechanics molecular dynamics to in situ model the $H_2O/Pt(100)$ interface under the condition of H_{UPD}. The electrode tended to be more hydrophobic with rising negative applied potential, which can be observed that the orientation distribution of H2O became consistent with the surface, increasing the hydrogen binding in turn (figures 5(e)) and (f)). Thus, they concluded that the alters in H₂O orientation were the main origin of pH-dependent HBE on Pt.

However, the HBE descriptor cannot explain the opposite phenomenon on the surfaces of Pt(111), as revealed in figure 5(g) [10]. The cyclic voltammetry (CV) curves in the hydrogen adsorption region (0.1-0.35 V vs. reversible hydrogen electrode (RHE)), which was considered the H_{UPD} region, remained hardly altered with the changes of pH values, while the onset potential in the H_{OPD} region (-0.1 to 0.05 V vs. RHE) exhibited a negative shift with the increased pH values. As a result, it is hard to account for the remarkable relationship between pH and the HER overpotential of Pt(111) by the H_{UPD} adsorption energy. Because the HER/HOR kinetics is strongly determined by the pH, although the H_{UPD} hardly shifts with the changes of pH, many studies suggested that the H_{UPD} is not just dependent on hydrogen adsorption [10, 79, 89]. It stands to reason that the atomic-level electrochemical interface structure, such as the electric double layer, should be taken into account. Ledezma-Yanez et al presented a model to predict the H* adsorption rate, which was according to the idea that the barrier for HER in alkaline conditions relied on how closely the electrode potential was correlated with the potential of zero free charge (pzfc) [10]. The hydrogen adsorption occurs by the electron transfer across the electric double layer (H₃O⁺ and OH⁻ under acidic and alkaline conditions, respectively), and the electronic transfer rate relies on the easy or hard interfacial water reorganization, which is further determined by the interfacial electric field, in other words, the position of the pzfc. The result shows that under acidic conditions, the H_{UPD} region approaches the pzfc of Pt(111) (figure 5(g)), whereas it is distant from the pzfc under alkaline conditions, implying that the interfacial water with a strong electric field under alkaline conditions is hard to reconstruct in the electron transfer process, leading to sluggish hydrogen adsorption. When Ni(OH)2 was further combined with Pt(111), as displayed in figure 4(d), the thermal coefficient decreased due to the weakened electric field because the pzfc shifted to the negative potential (figures 5(h) and (i)) [90]. As a result, the barrier for hydrogen adsorption can be reduced, thus improving the overall activity. This model revealed that the HBE might not be the unique evaluation metric of the HER activity, which can also be determined by the rate of hydrogen adsorption further depending on the strength of the interfacial electric field.

2.3.3. HER mechanisms in neutral environments. As mentioned, the H₃O⁺ ion serves as the dominant reactant due to the high concentration as a proton provider in strong acidic electrolytes, while in strong alkaline solutions, H₂O inevitably becomes the primary reactant ascribed to the low concentration of H_3O^+ ions. Compared with them, the neutral HER process seems to be more complex, involving both the H_2O and H_3O^+ reduction in the overall reaction [91]. As illustrated in figure 6(a), under low cathodic overpotentials approaching the equilibrium potential, H_3O^+ reduction is the dominant process, and the current rises steadily in this stage with the sufficient H_3O^+ supplement despite its low concentration. When the cathodic overpotential continues to increase, the rapid reaction rate generates the pH difference between the surface of the catalyst and the bulk solution due to the rapid H_3O^+ consumption and delayed supply. As a result, the reaction occurs under the control of mass diffusion, showing a plateau in the polarization curve. Note that the H₂O molecule is a bystander in the aforementioned two stages because it requires a higher overpotential for further dissociation [92]. Switching from H_3O^+ ions to H_2O molecules as the primary reactant occurs at high potentials, resulting in the increase of the current. As a result, the HER process in neutral electrolytes is complicated because its behavior approaches under acidic and alkaline conditions at low and high overpotentials, respectively, as well as a characteristic current plateau under medium overpotentials.

Accordingly, many reports divided several potential regions for HER according to the different HER behavior in the pHuniversal range. Conway and Tilak first reported that the H2O molecule could supersede H_3O^+ as the reactant in an alkaline solution or for pH > approximately 5 [80]. Then, Carmo *et al* proposed the influence of the diffusion on pH values at the interface between catalysts and solutions [67]. They suggested that the interfacial pH values might be significantly distinct from the bulk in unbuffered electrolytes, although the HER occurs at medium reaction rates, especially under near-neutral conditions (pH = 4-10), as shown in figure 5(a). Takanabe's group proposed that the HER mechanisms are determined by reactants, electrolytes, and their concentrations (figure 6(b)) [92–95]. In 0.5 M Na₂SO₄ with different pH, the main reactant of HER altered from H_3O^+ to H_2O at pH = 4, leading to the extra overpotential change in the pH range of 4-11, while it shows no difference between the required overpotential and the oblique line in the region of acidic (1-3) and alkaline pH (11-13) (figure 6(c)). Therefore, based on the HER kinetic behaviors, the universal pH can be divided into three regions: acidic (1-5), neutral (5-9), and alkaline (9-13) (figure 6(d)).



Figure 6. (a) The relationship between CV curves and pH of electrolyte in H₂-saturated, unbuffered electrolytes [93]. Reprinted from [96], Copyright (2011), with permission from Elsevier. (b) The η_{10} in various solutions on Pt electrode with bubbling hydrogen [94]. Reprinted with permission from [94]. Copyright (2016) American Chemical Society. (c) The relationship between the HER activity of electrodes and 0.5 M Na₂SO₄ solutions with different pH [95]. John Wiley & Sons [95]. [Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (d) The current density limited by the diffusion of H₃O⁺ and OH⁻ at different pH electrolytes [92]. Reproduced from [92] with permission from the Royal Society of Chemistry. (e) The relationship between the artificial LSV curves and different limited factors in 1.0 mol 1⁻¹ NaH₂PO₄ electrolyte. (f) Evolution of the relative fraction of simulated kinetic, concentration, and solution resistance overpotentials at -10 mA cm^{-2} and NaH₂PO₄ concentration [93]. Reprinted with permission from [93]. Copyright (2015) American Chemical Society.

Because HER is diffusion controlled due to the low concentration of H_3O^+ , some reports suggested that using buffered electrolytes could, to some extent, solve the undersupply of H_3O^+ at the interface [96, 97]. Takanabe's group explored the HER properties in near-neutral buffered solutions and concluded that the HER kinetics was still limited by the slow mass transport of PO_4^{3-} . When the electrocatalytic HER was operated in 2 M sodium phosphate at pH 5, the applied overpotential (kinetics overpotential, concentration overpotential, and ohmic potential drop) is mainly contributed by the concentration overpotential, as shown in figures 6(e) and (f). Therefore, the overpotential derived from mass transport needs to be reduced by taking into account the electrolyte engineering when using neutral buffered electrolytes.

Considering the inevitable additional overpotentials due to the water dissociation under neutral conditions, promoting direct water dissociation is regarded as an effective thought to boost the HER performance. Unfortunately, it is still elusive for the water dissociation in neutral electrolytes because most assumptions at present were made by extrapolating the findings from acidic and alkaline HER, where the alkaline HER mechanism also remains controversial, and even the HER behaviors are not exactly the same in neutral and alkaline electrolytes. Despite the fact that water dissociation was widely accepted as one rate-determining step for the neutral HER, the observed performance trend was inconsistent: some reports proposed that the HER performance in alkaline electrolytes outperformed that in neutral electrolytes, while others found the opposite [62, 82, 88, 98-100]. In summary, the neutral and alkaline HER processes remain unclear, and their mechanisms are also debatable, which requires further investigation in deep.

3. Modulation strategies of MoS₂-based HER catalysts

The tremendous potential significantly encouraged many researchers to make great efforts to the development of MoS_2 based electrocatalysts toward HER. However, the small proportion of edge sites on the MoS_2 nanosheet and the poor conductivity as a semiconductor seriously limited its activity. In this section, we will introduce some common strategies to modulate MoS_2 for better HER performance.

3.1. Increasing the number of active sites

Multiple strategies have been reported to increase the number of active sites for MoS_2 , such as nanostructuring, creating defects, and engineering phases. The MoS_2 edge with poor inversion symmetry leads to rich structures, in which the unsaturated atoms on the edges with high reactant affinity serve as one of the most crucial active sites [101–103]. The first strategy is nanostructuring MoS_2 with various morphologies. Kibsgaard *et al* successfully prepared porous MoS_2 by adopting a double-gyroid-like silica template (figure 7(a)) [104]. The developed catalyst exposed a significant portion of edge sites, thanks to its wide surface area benefitting from the mesoporous structure, which improved the HER performance with a low Tafel slope of 50 mV dec⁻¹ (figure 7(b)). Defect engineering, as another effective strategy, was successfully



Figure 7. (a) Preparation of mesoporous MoS_2 . (b) Tafel slope of DG MoS_2 [104]. Reproduced from [104], with permission from Springer Nature. (c) Illustrations of additional active edge sites on MoS_2 . (d) LSV curves and (e) Tafel slope of various catalysts [105]. John Wiley & Sons [105]. [© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (f) Schematic illustrations of the phase transition by chemically exfoliated MoS_2 nanosheets. (g) Polarization curves of chemically exfoliated MoS_2 nanosheets. (g) Polarization curves of chemically exfoliated MoS_2 nanosheets. (i) LSV curves of various MoS_2 samples after iR correction [107]. Reprinted with permission from [107]. Copyright (2016) American Chemical Society.

introduced by Xie et al by forming abundant cracks on the basal plane of MoS2 caused by the partially limited oriented crystal growth with excess thiourea (figure 7(c)), thus exposing more active sites to improve the HER activity with a η_{10} of lower than 200 mV and a Tafel slope of 50 mV dec⁻¹ (figures 7(d) and (e)) [105]. In addition, another popular strategy for producing more active MoS2 sites during the transition process is phase engineering [25]. In 2013, Lukowski et al prepared 1T-MoS₂ nanosheets using chemical exfoliation with n-butyllithium as intercalators, significantly enhancing the HER activity ($\eta_{10} = 187$ mV and Tafel slope of 43 mV dec⁻¹), as shown in figures 7(f) and (g) [52]. The higher density of active sites by ten times (activated inert basal plane) and fast electron transport were primarily responsible for the improved HER performance. Later, Voiry et al further confirmed that the basal plane had dramatic impact on catalytic activity, while the edge sites of the 1T-MoS₂ were not the primary activity contributor, which was told apart from the 2H phase [106]. Further combined phase and defect engineering, the significance of phase, edges, and sulfur vacancy, as well as their synergistic effect on HER activity, were thoroughly explored by Yin *et al* [107]. The obtained 1T-MoS₂ nanosheets with abundant mesoporous achieved an outstanding HER performance with η_{10} of 153 mV and a Tafel slope of 43 mV dec⁻¹ (figures 7(h) and (i)).

3.2. Enhancing the intrinsic catalytic activity

The electronic states of MoS₂ can be optimized through doping [108–111], vacancy engineering [112–114], strain engineering [115], heterostructure engineering [116–119], etc, to improve the intrinsic catalytic activity of the active sites. For example, P-doped MoS₂ with different doping concentrations was successfully synthesized by Xue's group (figure 8(a)) [119]. The introduction of P not only adjusted the electronic states of MoS₂ aiming at facilitating H^{*} adsorption, but it also created new HER active sites, exhibiting a promising HER property ($\eta_{10} = 43$ mV and Tafel slope of



Figure 8. (a) Left: stability test of P-doped MoS₂ nanosheets; upper right: calculated HBE for P-doped MoS₂; bottom right: structures of P-doped MoS₂ with hydrogen absorbed on the P site [119]. Reprinted with permission from [119]. Copyright (2017) American Chemical Society. (b) Illustration of MoS₂ doped by transition metals [108]. (c) LSV curves for different samples doped by various transition metals [108]. (d) Energy level for all samples [108]. Reprinted with permission from [108]. Copyright (2017) American Chemical Society. (e) The etching step to create S-vacancy [112]. (f) STEM image of the etching monolayer MoS₂ [112]. (g) The LSV curves and (h) corresponding Tafel plots of different etching monolayer MoS₂ [112]. (i) The projected electronic density of states of the d-band for the Mo atoms of MoS₂-EGMO with 12.5% concentration [112]. Reprinted with permission from [112]. Copyright (2020) American Chemical Society. (j) Illustration of MoS₂ with strain-induced S-vacancy on the basal plane [115]. (k) Relationship between the band structure of MoS₂ and applied strain [115]. (l) Relationship between $\Delta G_{\rm H}$ and applied strain for MoS₂ with various S-vacancy [112]. (n) Free-energy diagrams in acidic media [122]. John Wiley & Sons [122]. [© 2021 Wiley-VCH GmbH].

34 mV dec $^{-1}$), which was close in comparison to Pt. As displayed in figure 8(b), Chen's group proposed an idea to enhance the HER property of MoS₂ by directly doping transition metals (Fe, Co, Ni, Cu, and Zn) to further modulate the energy level [118], where Zn doping made the best HER performance ($\eta_{10} \approx 140 \text{ mV}$ and Tafel slope of 51 mV dec⁻¹) due to the most suitable position in the energy level (figures 8(c)) and (d)) that can enable electron transfer that required more reduced energy consumption. Creating S-vacancy and further adjusting its concentrations and types not only can activate the inert basal plane but also regulate the surrounding electron state [120]. The effects of vacancy states with different concentrations and distributions were studied currently by adopting the H₂O₂ etching method to create a well-proportioned single S-vacancy on the basal plane (figure 8(e)) [112]. The optimal HER performance on MoS2 with 12.5% dispersive S-vacancy (figure 8(f)) reached a Tafel slope of 48 mV dec⁻¹ and η_{10} of 131 mV (figures 8(g) and (h)), which was caused by the more sufficient exposed active sites with further optimized electronic states and the accelerated electrical transfer efficiency (figure 8(i)). Based on the S-vacancy engineering, Li et al attempted to put strains on the S-vacancy-rich MoS_2 [115]. When a tensile strain was applied (figure 8(j)), emerging bands shifted nearer to the Fermi level, and the amount of band states rose compared with those of V-MoS₂ without strain (figure 8(k)), which can further optimize the HBE (figure 8(1)), enhancing the HER activity. Moreover, constructing heterostructures could accelerate charge transfer and adjust the interfacial electrical configuration [3, 121]. Gong et al designed the monodispersed sandwich-structured $MoO_2/MoS_2/C$ hollow nanoreactors (figure 8(m)) with the 'conductor/catalyst/protector' configuration to improve the



Figure 9. (a) Structure of the MoS₂/rGO hybrid. (b) LSV plots and (c) corresponding Tafel slope of the catalysts [124]. Reprinted with permission from [124]. Copyright (2011) American Chemical Society. (d) The preparation process of the MoS₂/g-C₃N₄. (e) The LSV plots and (f) Tafel slope for the catalysts. (g) The interfacial electron transfer between MoS₂ and g-C₃N₄. The charge accumulation and depletion are labeled in red and orange, respectively. (h) The calculated free-energy diagram for different samples. (i) Free-energy diagram on MoS₂/g-C₃N₄ under various hydrogen coverage [125]. Reprinted from [125], Copyright (2016), with permission from Elsevier.

HER activity [122]. As the conductor configuration, metallic MoO₂ substrates with high intrinsic conductivity could facilitate the charge transfer to the catalytic MoS₂, while C shells as the protector can prevent the interior catalysts from corrosion under acidic conditions, thus optimizing the H adsorption kinetics (figure 8(n)) and exhibiting a superb HER activity ($\eta_{10} \approx 77$ mV and Tafel slope of 41 mV dec⁻¹) and long durability.

3.3. Improving the electrical conductivity

Besides limited numbers of active sites and unsatisfactory intrinsic activity, another reason that hinders the performance of MoS₂ is electrical conductivity [123]. Growing MoS₂ on some conductive substrates is one of the effective ways to accelerate electron transport. Li *et al* initially adopted a method for targeted hydrothermal fabrication of MoS₂ nanoparticles on reduced graphene oxide sheets (figure 9(a)) [124]. Benefiting from the great electrical coupling to the graphene substrate as well as the sufficiently exposed edge sites on MoS₂, the MoS₂/rGO displayed superior electrocatalytic properties with $\eta_{10} \approx 100$ mV and Tafel slope of 41 mV dec⁻¹ (figures 9(b) and (c)). Similarly, Fu *et al* reported the synthesis of ultrathin $MoS_2/g-C_3N_4$ vdW layers (figure 9(d)) [125]. Such heterostructure showed superior HER performance approaching commercial Pt (figures 9(e) and (f)), which was attributed to the strong interfacial coupling between MoS_2 and $g-C_3N_4$ by Mo-N bonding (figure 9(g)), thus enhancing HER kinetics (figures 9(h) and (i)). Besides, other strategies, including doping, phase engineering, defects engineering, heterostructure engineering, etc, can also, to some extent, accelerate the electron transport of MoS_2 [52, 108, 112, 119, 122].

Shortly, the presented three strategies have been demonstrated to effectively boost the catalytic properties of MoS_2 based materials for HER, which is highly desired to be combined to generate potential synergistic enhancement.

4. Recent progress of MoS₂-based HER catalysts in the pH-universal range

More than common strategies, specific methods were developed in different electrolytes to modulate MoS_2 and optimize their HER performance. In this section, we will give detailed discussions on the specific methods



Figure 10. (a) Free-energy profiles for HER [128]. Copyright Elsevier Publication, 2015. (b) The structure of the nitrogenase FeMo cofactor, hydrogenase, and MoS₂ slab exposed the Mo edge [128, 130]. Relationship between exchange current density vs. (c) MoS₂ area coverage and (d) MoS₂ edge length. (e) Evolution of the exchange current density with the calculated Gibbs free H adsorption energy for molybdenum disulfide and the pure metals [128]. Reprinted with permission from [128]. Copyright (2005) American Chemical Society. The HER performance of (f) MoS₂/CoSe₂ [22], Reproduced from [22]. CC BY 4.0. (g) 1T-MoS₂/CoS₂ [116], John Wiley & Sons [116]. [© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim] and (h) SA-Pt/MoS₂ [131]. John Wiley & Sons [131]. [© 2021 Wiley-VCH GmbH].

and current progress of boosting MoS₂-based catalysts in pH-universal electrolytes.

4.1. In acidic electrolytes

As a representative 2D layered material, MoS₂ is very stable in most acids, which is an essential criterion for an HER catalyst; thus, it has been widely investigated as the HER electrocatalyst [126]. However, bulk MoS_2 was found to be somehow inert toward HER, which was reported by Tributsch and Bennett [127]. MoS_2 was never regarded as a prospective candidate before the 21st century. As seen in figure 1, until 2005, inspired by nitrogenase and hydrogenase, Hinnemann et al first demonstrated via density functional theory calculations that MoS₂ was indeed active toward HER in acidic conditions just at some specific regions over the MoS₂ nanosheets, such as the unsaturated edge sites of the MoS_2 plane (figures 10(a) and (b)) [128]. Later, in 2007, Jaramillo et al confirmed the active site of MoS₂ experimentally by quantitatively adjusting the content of edge sites and basal sites on MoS₂ [129]. The measured HER activity of MoS₂ catalysts displayed great linear correlation with the number of their edge sites (figures 10(c)and (d)), and MoS₂ was further identified with a nearoptimal binding strength with HER intermediates from the volcano-type plots for HER catalysts (figure 10(e)). Therefore, MoS_2 was verified to be active toward HER theoretically and experimentally.

Aiming at optimizing the hydrogen bonding energy and enhancing the acidic HER activity, multiple methods have been reported, such as phase engineering [106, 107], doping [108–111], defect engineering [112–114], heterostructure engineering [116–119], as well as their synergetic modulation. Benefitting from the abundant specific strategies and increasingly clarified understanding of the acidic HER mechanism, a great breakthrough has been achieved for MoS2-based electrocatalysts in acidic HER. In 2015, Gao et al prepared the MoS₂/CoSe₂ heterostructure and first got the overpotential at 10 mA cm⁻² lower than 100 mV (figure 10(f)) [22]. In 2020, combining phase and heterostructure engineering, Song's group reported a novel interface-induced strategy on 1T-MoS₂/CoS₂ hetero-nanostructure, which exhibited promising HER performance and approached to Pt (figure 10(g)) [116]. Up to now, some MoS₂-based electrocatalysts outperforming Pt have been designed and reported. For instance, Zhang's group controllably synthesized hybrid SA-Pt/MoS₂ nanosheets by a solar-irradiation strategy and achieved an excellent HER activity with η_{10} of 44 mV, which was even lower than commercial Pt (52 mV) [131].



Figure 11. Designable approaches for alkaline HER according to the possible reaction theories [60, 74]. Reprinted from [60], Copyright (2020), with permission from Elsevier.

4.2. In alkaline electrolytes

Unlike acidic HER, the development of MoS₂-based catalysts for alkaline HER appeared later and began to spring up recently. As discussed in section 2, the actual HER process in alkaline electrolytes and the key factors influencing the alkaline HER kinetics remain uncertain, making it desperately necessary to address the ambiguous reaction mechanisms [105]. Generally, the previously discussed common strategies can also be applied to boost the alkaline HER kinetics of MoS₂-based electrocatalysts, and some promising performance has been reported in alkaline media [74, 131]. Nevertheless, different from acidic HER, where the H adsorption/desorption dominate the reaction rates, alkaline HER involves complex water disassociation, making the modulation strategies insufficient. Recent efforts of developing MoS₂based electrocatalysts for alkaline HER target to achieve either or both of the following goals: (a) promoting the water dissociation and (b) optimizing the hydrogen adsorption/desorption kinetics (figure 11). The specific strategies and progress are elaborated as follows.

4.2.1. Creating dual active sites. Although the function of hydroxyl species in alkaline HER is still puzzling, it is still believable that OH^- is one of the critical attributes in the HER activity. Nonetheless, as mentioned earlier, the adsorbed OH^* can compete with hydrogen adsorption on a single active site. Thus, the competition between OH^* and H^* adsorption

needs to be overcome, which is extremely challenging. Therefore, creating dual active sites with separated functions is one of the effective ways to address this issue. Under this concept, metal oxides/hydroxides with favorable H2O dissociation can be constructed with MoS₂ to achieve efficient HER catalysis [137]. In 2017, Zhang et al synthesized a novel 3D Ni(OH)₂/MoS₂ hybrid catalyst, where OH⁻ adsorption was administered by Ni(OH)2, and MoS2 accelerated the H adsorption and subsequent H_2 formation (figure 12(a)) [132]. The interfacial cooperation resulted in beneficial binding energetics of H* and OH* species and reduced the energy barrier of the H₂O dissociation process in the Volmer step (figure 12(b)). Owing to numerous active interfaces, this electrocatalyst showed great HER activities in 1 M KOH aqueous solution with η_{10} of 80 mV and a Tafel slope of 60 mV dec⁻¹ (figure 12(c)). On the heels of Zhang *et al*, Yang's group significantly boosted the HER kinetics in alkaline solution by precisely hybridizing vertical MoS₂ nanosheets with layered double hydroxide (LDH) [133]. As shown in figure 12(d), following the same classification by functionalization, the MoS₂/NiCo-LDH hybrid exhibited a much low overpotential of 78 mV at 10 mA cm⁻² and a low Tafel slope of 76.6 mV dec⁻¹ in 1 M KOH electrolyte. Similarly, NiVFe, $Co(OH)_2$, and Co_3S_4 were also reported to assist the OH⁻ capture and enhance the alkaline HER property (figures 12(e) and (f)) [134–136]. Although the functions of the so-called dual active sites are not conclusive yet, as discussed earlier, the influences of OH⁻ cannot be denied, and this strategy indeed



Figure 12. (a) Schematic illustration of the fabrication and (b) the corresponding free-energy diagram for Ni(OH)₂/MoS₂ hybrid catalyst. (c) LSV curves of the catalysts [132]. Reprinted from [132], Copyright (2017), with permission from Elsevier. (d) The polarization curves, free-energy diagram, and schematic illustration of the MoS₂/NiCo–LDH [133]. Reprinted from [133], Copyright (2017), with permission from Elsevier. Schematic illustration of (e) MoS₂/NiVFe and (f) Co₃S₄–MoS₂ heterostructure [134, 136]. Reprinted from [134, 136], Copyright (2023), with permission from Elsevier.

dramatically enhanced the alkaline HER performance. Future efforts can be made to precisely tune the coupling between MoS_2 with the OH^- adsorbent material by controlling the lattice plane for formed heterointerfaces, manipulating the hybridization extent, and optimizing the electronic configurations. Moreover, the dual-site strategy complicates the identification and clarification of active species. Advanced characterization tools may be needed to clarify them further.

4.2.2. Controlling the electronic structure of the catalysts.

The adsorption abilities of H* and OH* can be determined by regulating the electronic structure of the electrocatalysts [138, 139]. The occupied molecular orbitals of H₂O mainly consist of p orbitals [105]. Because the water dissociation process on MoS₂ mainly involves the coupling between the O p orbital of water and the Mo d orbital, regulating the orientation of the Mo d orbital to be perpendicular can optimize the orbital coupling extent with water molecules, thus accelerating the H₂O dissociation process, which is different from that in acidic conditions involved in the orbital coupling between Mo d_z^2 orbital and H⁺ s orbital [140]. In acidic conditions, for example, although the d_z^2 orbitals of Mo atoms in the 1T-MoS₂ are perpendicular to the basal plane (figures 13(a) and (b)), it exhibits an unfavorable orbital coupling with H⁺ due to its location in the central sublayer (figure 13(e)). Therefore, introducing Co on the surface of the basal plane can directly construct a vertical orbital near the Fermi energy level (figures 13(c)) and (d)), thus optimizing the HBE (figures 13(e) and (f)). In alkaline conditions, for comparison, Zang et al successfully endowed MoS₂ with outstanding alkaline HER performance via orbital modulation caused by C doping [141], which displayed a preeminent η_{10} of 45 mV, obviously outperforming that of undoped MoS₂. Further characterization suggested that the electronic state and coordination environment of MoS₂ have been substantially altered after C doping. As shown in figures 13(g) and (h), C atoms with empty $2p_z$ orbital can partially substitute S atoms on the basal plane of MoS₂, generating sp^2 hybrid in the outermost sublayers of MoS_2 , and therefore remaining pz orbital perpendicular to the basal plane for H₂O adsorption. The vertical p_z orbital then showed an apparent orbital bonding and electron transfer with absorbed H₂O (figure 13(i)), in contrast to pure MoS₂ (figure 13(i)), thus exhibiting enhanced H2O adsorption and optimized H2O dissociation energy barrier compared with those of pure MoS₂ (figure 13(k)). In addition, the electronic structure of S atoms near the C atom was changed and activated after the C doping, which could serve as the H adsorption site with optimized HBE for further H₂ generation. However, defect engineering, which is the effective idea to adjust the electronic state and enhance the acidic HER performance, as mentioned earlier, seems to be less effective for alkaline HER due to the interference of the H₂O dissociation process. This is because the Mo sites exposed at edge and S-vacancies show stronger OH⁻ adsorption ability in alkaline environments [142], which competes with H adsorption. Thus, this strategy may not work well in alkaline environments.

From the above, several reported MoS₂-based electrocatalysts demonstrated superior HER performance under alkaline



Figure 13. (a) Projected DOS and (b) partial electron density distributions of $1T-MoS_2$. (c) Projected DOS and (d) partial electron density distributions of Co-1T-MoS₂. (e) Calculated Gibbs free-energy diagram of HER for Co-1T-MoS₂, $1T-MoS_2$, and $2H-MoS_2$. (f) Illustration of HER process on Co-1T-MoS₂ [141]. Reprinted with permission from [141]. Copyright (2019) American Chemical Society. (g) The top-view and side-view sp² hybrid orbitals (labeled as red circle). (h) The empty 2p orbitals (labeled as red circle) vertical to the basal plane. The electrostatic potential of H₂O adsorbed on the basal plane of (i) C-MoS₂ and (j) MoS₂. (k) The relative energy diagram along the reaction coordinates on the basal plane of MoS₂ and C-MoS₂, respectively [142]. Reproduced from [142]. CC BY 4.0.

conditions than that under acidic conditions, which were even comparable to that of Pt [134, 143, 144]. Nonetheless, the mechanism underlying the high performance was not very unclear, which requires theoretical calculations and advanced characterizations to get deeper understandings to clarify them. In addition to the activity, the stability at a large current should be further improved to match the application requirement.

4.3. In neutral electrolytes

Because acidic and alkaline HER potentially involves corrosive electrolytes [12, 13, 59], water splitting in neutral conditions has attracted interest because of its mild condition close to the freshwater, expanding a choice of suitable electrocatalysts with good stability, eco-friendliness, and low cost for potentially directly split seawater [64, 145]. Recently, some MoS₂-based catalysts in neutral conditions have been reported, which were mainly designed following similar strategies for acidic or alkaline conditions. For example, Li *et al* designed a core–shell configuration with carbon-supported MoCS_x heterostructure as the core and the defect-rich MoS₂ nanosheet as the shell [146], and the obtained C-MoCS_x@MoS₂ displayed a superior HER activity in 1.0 M PBS ($\eta_{10} \approx 163$ mV and Tafel slope of 70 mV dec⁻¹). Liu's group synthesized an Fe-doped MoS₂ nanosheet array supported by 3D carbon fibers with $\eta_{10} \approx 119 \text{ mV}$ and a Tafel slope of 90 mV dec⁻¹ in buffered seawater [147]. However, most neutral HER properties of MoS₂-based electrocatalyst understanding is not that competitive, and the same material usually demonstrated much better HER performance in acidic or alkaline electrolytes [23, 86, 148–150]. Compared with the breakthroughs of MoS_2 based catalysts made for acidic and alkaline HER, catalyzing HER in neutral conditions by MoS₂-based materials is still in the developing stage (figure 14 and table 2 in detail). In particular, MoS₂-based materials are still inferior to benchmarking Pt catalysts to catalyze HER in neutral electrolytes, and their stability was also not competitive compared with the counterparts in alkaline and acidic electrolytes. Along with further boosting the neutral HER performance, deeply understanding the neutral HER process and clarifying the mechanisms of MoS₂-catalyzed neutral HER are urgently needed.

As discussed in section 2, water is the sole provider of protons in neutral and alkaline electrolytes. The overall HER process should consider not only the H₂O dissociation on the catalyst surface but also the mass transport of the associated intermediates (H₂O or OH⁻) at the electrode/electrolyte interface [91]. Recent reports have demonstrated that the flexibility of the interfacial H-bonded water layer strongly



Figure 14. Comparison of the overall HER performance on currently reported typical MoS₂-based catalysts in the pH-universal range.

		Overpotential	Tafel slope	Stability	
Catalyst	Electrolyte	at 10 mA cm^{-2}	$(mV dec^{-1})$	(cycles)	References
1T-MoS ₂ /CoS ₂	0.5 M H ₂ SO ₄	26	43	1000	[116]
P-MoS ₂	0.5 M H ₂ SO ₄	43	34	5000	[119]
1T@2H-MoS ₂ /C	0.5 M H ₂ SO ₄	64	49	1000	[151]
MoS ₂ nanowall	0.5 M H ₂ SO ₄	95	78	3000	[152]
N-MoS ₂	0.5 M H ₂ SO ₄	70	41	5000	[153]
Rh-MoS ₂	0.5 M H ₂ SO ₄	67	54	5000	[154]
Pd, Ru-MoS _{2$-x$} OH _y	0.5 M H ₂ SO ₄	45	82	1000	[155]
MoO ₂ /MoS ₂ /C	0.5 M H ₂ SO ₄	77	41	1000	[122]
$(N, PO_4^{3-})-MoS_2/VG$	0.5 M H ₂ SO ₄	85	42	1000	[156]
Co-MoS ₂ -1.4	0.5 M H ₂ SO ₄	56	32	1000	[157]
W-MoS ₂ /MoO ₂ /CNT	0.5 M H ₂ SO ₄	62	44	5000	[158]
Co-Pd-MoS ₂	0.5 M H ₂ SO ₄	49.3	43.2	10 000	[159]
$Pt@MoS_2(1T)$	0.5 M H ₂ SO ₄	88.43	55.69	1000	[160]
MoSSe(1T)	0.5 M H ₂ SO ₄	49	140	10 000	[161]
NiO@1T-MoS ₂	1.0 M KOH	46	52	2000	[74]
1T-MoS ₂ /CoS ₂	1.0 M KOH	71	60	1000	[116]
Ni(OH) ₂ /MoS ₂	1.0 M KOH	80	60	500	[132]
MoS ₂ /NiCo-LDH	1.0 M KOH	78	76.6	3000	[133]
Co-1T-MoS ₂	1.0 M KOH	84	47	2000	[140]
C-MoS ₂	1.0 M KOH	45	46	1000	[141]
Ru-MoS ₂ /CNT	1.0 M KOH	50	62	3000	[162]
Co-MoS ₂ /Ni ₃ S ₂	1.0 M KOH	89	62	1000	[163]
R-MoS2@NF	1.0 M KOH	71	100	5000	[164]
MoS ₂ /NiVFe	1.0 M PBS	141	95.44	2000	[134]
N, Mn co-doped MoS ₂	1.0 M PBS	70	65	5000	[165]
MoS ₂ @Ni/CC	1.0 M PBS	140	154	3000	[166]
MoS ₂ /CC-3	1.0 M PBS	230	84	2000	[167]
$C-MoCS_x@MoS_2$	Seawater	312	128	8 h	[146]
Fe-MoS ₂	Seawater	119	90	30 h	[147]

Table 2. HER performance of various catalysts in acidic, alkaline, and neutral electrolytes.

relies on the pH of the electrolyte with a negative correlation [10, 168, 169]. The decreased flexibility can prevent intermediates from diffusing into the bulk electrolyte through the interfacial layer, thus inhibiting the regeneration of active sites. However, the presence of the nonspecifically adsorbed OH^- species at high pH values in alkaline electrolytes can accelerate the transport of the intermediates across the flexible interfacial layer [79], thereby making the neutral electrolytes, unfortunately, possess the lowest transport capacity due to the most rigid interfacial water layer, which may be the probable reason of the low performance for most electrocatalysts in neutral electrolytes. Based on the aforementioned findings, some works have reported that the reorientation of the interfacial water can be induced by the negatively charged surfaces, such as the chalcogen species on the surface of the transition metals as an electron acceptor to regulate the orientation of the interfacial water [170, 171]. Such transition metal-chalcogen structure makes MoS_2 a promising electrocatalyst, and reorienting the interfacial water can serve as the potential strategy to boost HER the kinetics in neutral electrolytes by decorating the state of the surface chalcogen species of MoS_2 .

5. Future Perspectives

Electrocatalytic HER displays prospective potentials for largescale hydrogen generation. Non-acidic HER has attracted sustained rising attention recently due to its superiority, including low corrosion, eco-friendliness, and safety, especially neutral HER for its promising economic viability for direct seawater electrolysis. However, there existed significant room to design high-performance HER catalysts under non-acidic conditions. In this review, based on a typical noble-metal-free HER electrocatalyst, i.e. MoS₂, we synthetically overviewed its progress of catalyzing HER in non-acidic conditions. Starting by discussing the current understanding of the non-acidic HER process and its reason for the slow kinetics, we highlighted three possible mechanisms in the HER process under alkaline conditions, such as water dissociation theory, HBE theory, and interface transfer theory, to evaluate the roles of OH^- , H^+ , and H_2O . We then demonstrated the two reduction steps involving the switching of the two reactants (H_3O^+ and OH⁻) in neutral HER. Next, we introduced phase- and electronic structure-dependent catalytic properties for MoS₂based materials. Following that, we carefully summarized the modulation strategies and recent progress of MoS₂-based electrocatalysts in the pH-universal range, and we clarified the correlation between structure, physicochemical property, and the HER activity.

By comparing the status in acidic, alkaline, and neutral conditions, we conclude that MoS_2 -based materials for non-acidic (particularly neutral) HER are still in the developing stage, and there is still a great room to further optimize them. To provide comprehensive insights and precise modulation of non-acidic HER, we highlight several challenges that require to be addressed as follows.

(a) Inconclusive mechanism of HER in

non-acidic electrolytes

Compared with the thorough insights into the acidic HER mechanism on MoS₂-based electrocatalysts, it is still puzzling for the non-acidic HER mechanisms. The studies focusing on the HER mechanisms under neutral and alkaline conditions are still relatively low in numbers, and controversies remain existing. It is unclear whether the current theories for alkaline HER can be valid to reflect the actual HER process of neutral HER and further inspire the development of MoS₂-based electrocatalysts. According to the interface transfer theory, the behavior of the ions in the electric double layer in alkaline conditions is far different from that in acidic conditions, thus leading to the different HER kinetics. So, what is the actual behavior at the interface in neutral HER? Because the catalytic reaction involves the surface of catalysts strongly consistent

with the electric double layer, it is vital to deeply understand the role of the electric double layer in different electrolytes accelerating mass transport.

The current understanding of the HER mechanism in nonacidic conditions is mainly derived based on Pt catalysts. Note that the HER mechanism on MoS₂-based electrocatalysts with more complicated surface structures may be different from that of Pt. In addition to the electrolyte pH, the specific anions and cations of the electrolyte may also influence the specific catalytic process, complicating the clarification of the corresponding mechanisms.

To address the presented challenges, advanced microscopy and spectroscopy techniques can be used to track the dynamic catalyst states and the reaction intermediates (e.g. OH^- , H^+ , and H_2O) to get more thorough insights into the reaction process [172, 173]. In this aspect, *in situ* and operando characterizations are powerful for monitoring the transient catalytic states. In addition, atomic-scale calculations can supplement the experimental tools to get insight into the reaction pathways.

(b) Unsatisfactory non-acidic HER performance

As shown in figure 14, MoS_2 -based electrocatalysts are still inferior to Pt in catalyzing HER in neutral electrolytes. In addition, most activity and stability of MoS_2 -based electrocatalysts are mainly measured by a conventional three-electrode cell in mild conditions. A large room still exists for boosting the HER performance of MoS_2 -based materials to drive practical water electrolysis. The harsh water electrolysis condition may induce changes in both electrocatalysts and electrolytes, which are critical to the catalytic performance by influencing the active species and electrode–electrolyte interface [25], in particular for seawater electrolysis, where catalysts may suffer from the corrosion of Cl^- ions and surface dissolution/redeposition of metal cations [174].

To further enhance the practical properties of MoS_2 based materials for non-acidic HER, the condition-dependent electrocatalyst reconstruction (e.g. redox and phase change) should be clarified. And innovative strategies can be combined to simultaneously enhance the intrinsic HER activity, boost the electronic conductivity, and increase the number of active sites [175, 176]. Fabricating high-entropy compositions and introducing single atoms may be promising strategies to further modulate MoS_2 and improve the performance. Well-designed configurations, such as the core–shell structure, may be helpful to protect MoS_2 from the influences of impure ions from the electrolytes. With continuous efforts from researchers, MoS_2 based materials will play increasing roles in low-cost and highperformance water electrolysis for green H₂ generation.

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