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Multi-interface engineering of nickel-based electrocatalysts for alkaline hydrogen evolution reaction

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Abstract

High gravimetric energy density and zero carbon emission of hydrogen have motivated hydrogen energy to be an attractive alternative to fossil fuels. Electrochemical water splitting in alkaline medium, driven by green electricity from renewable sources, has been mentioned as a potential solution for sustainable hydrogen production. Hydrogen evolution reaction (HER), as a cathodic half-reaction of water splitting, requires additional overpotential to obtain protons via water adsorption/dissociation, suffering from slow kinetics in alkaline solution. Robust and active nickel (Ni)-based electrocatalyst is a promising candidate for achieving precious-metal comparable performance owing to its platinum-like electronic structures with more efficient electrical power consumption. Various modification strategies have been explored on Ni-based catalysts, among which multi-interface engineering is one of the most effective routines to optimize both the intrinsic activity of Ni-based electrocatalysts and the extrinsic stacked component limitations. Herein, we systematically summarize the recent progress of multi-interface engineering of Ni-based electrocatalysts to improve their alkaline HER catalytic activity. The origin of sluggish alkaline HER kinetics is first discussed. Subsequently, three kinds of interfaces, geometrically and reactively, conductive substrate/electrocatalyst interface, electrocatalyst internal heterointerface, and electrocatalyst/electrolyte interface, were cataloged and discussed on their contribution mechanisms toward alkaline HER. Particular focuses lie on the microstructural and electronic modulation of key intermediates with energetically favorable adsorption/desorption behaviors via rationally designed interfaces. Finally, challenges and

perspectives for multi-interface engineering are discussed. We hope that this review will be inspiring and beneficial for the exploration of efficient Ni-based electrocatalysts for alkaline water electrolysis.

Keywords: Interface, electrocatalyst, alkaline, hydrogen evolution reaction

INTRODUCTION

The scalable and sustainable production of hydrogen is essential to alleviating the environmental and energy crises[1-5]. In addition to holding a significantly higher energy density than conventional fossil fuels, hydrogen emits no greenhouse gases, endowing it as a cleaner energy source[6]. In light of these characteristics, it offers a vast range of applications in smart grids, residential heating systems, hydrogen vehicles, and fuel cell systems. Currently, coal gasification and steam reforming account for more than 96% of the world's annual hydrogen output, during which excessive energy would be consumed and vast amounts of greenhouse gases would be inevitably released into the atmosphere[7,8]. Therefore, it is attractive and desirable to upgrade the hydrogen production method from conventional techniques to the innovative technology, e.g., ion exchange membrane-based water electrolysis, to further fulfill the ambitious carbon neutral goals and facilitate the transition toward low-carbon power systems[9]. Specifically, the proton exchange membrane (PEM) can be assembled into membrane electrode assemblies (MEAs) as a water electrolyzer to directly produce high-purity hydrogen from water. More significantly, PEM could be further coupled with renewable and intermittent energy (solar, wind, tidal, *etc.*) to store the energy/electricity into chemical forms and integrated within the power grid (acting as load) to relieve network bottlenecks with improved system flexibility[10]. Despite these unique benefits, the practical applications of these devices face obstacles due to the expensive electrolyte-tolerant parts and catalysts. Typically, precious metal (oxides)-based catalysts and titanium alloy/stainless-steel components are essential for the stable operation of PEM electrolyzers in acidic medium. Comparatively, an anion exchange membrane (AEM) electrolyzer, in which alkaline electrolyte is employed as the ion diffusion and reactive media, can introduce earth-abundant metals (Ni/Co/Fe, *etc.*) as catalyst materials, enabling promising application perspectives with great advantages than PEM electrolyzers[11]. Nevertheless, the unsatisfactory performance of these non-precious metal catalysts generally results in high energy barriers and low energy efficiency. Consequently, the pursuit of cost-effective, reliable, and high-performing catalysts has emerged as a significant research frontier for alkaline water splitting technology[12,13].

Principally, electrocatalytic water splitting includes hydrogen evolution reaction (HER) for the cathode and oxygen evolution reaction (OER) for the anode, respectively[14]. Unlike the abundant protons supplied in acidic electrolyte, the HER undergoes a sequential two-step process in alkaline conditions, during which the protons are generated via the water dissociation firstly and transformed into hydrogen molecular subsequently[15,16]. This additional water adsorption/dissociation step in alkaline electrolyte accounts for more than 2-3 orders of magnitude slower kinetics than that of acidic conditions[17,18]. Moreover, the inclusion of extra steps would also result in extra energy consumption, defined as the overpotentials beyond the thermodynamic energy. Therefore, the advancement of electrocatalysts is crucial in order to diminish these excessive overpotentials and accelerate the reaction kinetics[19]. It is widely acknowledged that platinum (Pt)-based materials have the best HER electrocatalytic performance[20,21]. However, their application is hindered by the high cost and scarce storage[22]. In order to address these issues, earth-abundant non-precious metal materials have triggered extensive attention, among which nickel (Ni)-based materials have exhibited great potentials owing to their earth abundance, cost-effectiveness, and, most importantly, holding similar electronic properties to Pt[23]. Unfortunately, Ni-based electrocatalysts currently still cannot completely replace Pt due to their relatively strong H adsorption, insufficient active sites, and high energy barriers for water adsorption/dissociation in alkaline conditions, which hampered their

practical application. Therefore, the dilemma of conventional Ni-based catalysts lies in that the sole Ni content cannot simultaneously promote the water dissociation and the desorption of adsorbed hydrogen intermediate (H_{ad}) in alkaline medium, not to mention the potential modulation of hydroxy groups. Therefore, rationally designing and fabricating Ni-based electrocatalysts with excellent intrinsic activity is still a grand challenge at present[24].

During the last decade, growing interests have been attracted in the construction of multi-component composite systems to intentionally overcome the limitations of sole Ni catalyst via different strategies, e.g., (Ni) metal alloying/dealloying[25-27], heteroatom doping[28-30], strain engineering[31-33], multi-interface engineering[34-38], *etc*. Among them, the multi-interface engineering has exhibited substantial potential to synergistically optimize the entire HER systems from different perspectives: geometrically and chronologically, three interfaces, including (1) conductive substrate/electrocatalyst interface; (2) internal interface of electrocatalyst; and (3) electrocatalyst/electrolyte interface, could be optimized to fundamentally facilitate the alkaline HER performance. Specifically, close and flawless contact between the conductive substrate and electrocatalyst could effectively minimize the charge transfer resistance and benefit the HER kinetics with smaller overpotential. Secondly, multi-component Ni-based catalysts with wisely heterointerface engineering (e.g., ensemble effect and electronic modulation) enable the optimization of both the thermodynamics and kinetics of HER processes. Thirdly, a robust electrocatalyst/electrolyte interface is significant for achieving a stable HER performance, particularly for high current density conditions. The generated gas bubbles could induce great inner pressure at the interface and lead to severe catalyst damage or structure failure. During high current density and prolonged operation, the accumulation of bubbles and generation of joule heat can cause the electrocatalyst to easily detach from the conductive substrate. By optimizing the substrate/electrocatalyst interface, the binding strength between the electrocatalyst and the substrate can be enhanced, resulting in improved stability of the electrocatalyst. By introducing defect sites or constructing heterostructures to optimize the internal interface of electrocatalyst, the intrinsic catalytic activity of the electrocatalyst can be enhanced, leading to higher conversion efficiency of reactant species and promoting long-term stable operation of the electrocatalyst. Additionally, by adjusting the wettability of electrocatalyst/electrolyte interface, the wetting properties of the electrolyte and the bubble detachment rate can be improved, allowing the electrocatalyst to exhibit superior performance during prolonged catalytic processes. Therefore, reasonable multi-interface design can significantly break the activity limitation of electrocatalysts.

Recent advances of interface engineering for alkaline HER electrocatalysts have been summarized in several reviews. Xu *et al.* thoroughly summarized the atomic heterointerface engineering for improving the catalytic performance of electrocatalysts[39]. Wei *et al*. focused on the advances in building heterostructured catalysts for accelerating the Volmer step in alkaline conditions[40]. Huang *et al.* discussed a series of representative heteroatom-modified electrocatalysts with properly designed multi-component interfaces and highlighted the optimized HER reaction pathway[41]. These reviews mostly focus on the interface engineering of the electrocatalyst itself, whereas the other two types of interface with both conductive substrate and electrolyte still lack detailed discussion, especially based on the electrocatalytic HER mechanism. Herein, the multi-component functions, design protocols and synthesis approaches of multi-interface engineering are summarized and discussed for exploring efficient Ni-based alkaline HER electrocatalysts [Figure 1]. We first summed up the alkaline HER mechanism, the origin of the sluggish kinetics for elementary steps, and the critical electrochemical parameters to evaluate the HER performance. Afterward, detailed discussions on the aforementioned three types of interfaces are organized, focusing on the internal interface of electrocatalyst to modulate the HER elementary process thermodynamically and kinetically. Finally, the challenges and prospects of multi-interface engineering for the design of alkaline HER electrocatalysts are discussed.

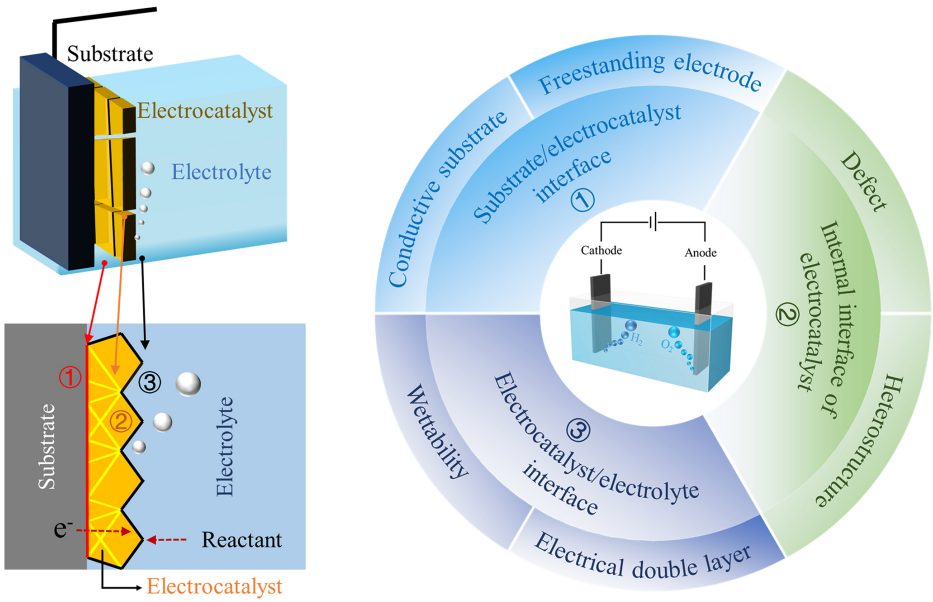

Figure 1. Schematic illustration of multi-interface structure and engineering strategies.

FUNDAMENTAL MECHANISMS OF ALKALINE HER

A typical water electrolyzer consists of three stacked components: a cathode, an anode, and an electrolyte. Two half reactions, HER and OER, occur at the cathode and anode, respectively. Although the reaction of splitting water into hydrogen and oxygen was discovered in acidic electrolyte, the water splitting in alkaline electrolyte has been commercialized on a large scale for a century owing to its more economic efficiency with robust electrocatalysts. The cathodic HER is recognized as a relatively basic catalytic reaction involving a two-electron transfer process, which could be divided into two elementary steps regardless of whether it occurs in acidic or alkaline electrolyte: (i) hydrogen adsorption step (Volmer step), during which a proton (H^+) combines an electron on the active sites to generate an adsorbed hydrogen intermediate; (ii) hydrogen desorption step (Heyrovsky/Tafel step), during which the obtained H_{ad} would form hydrogen molecule and desorb from the catalyst surface via either Heyrovsky or Tafel step. The detailed HER process is illustrated as the following elementary steps [Figure 2].

For acidic HER, the generation of hydrogen molecules is associated with the hydrogen adsorption free energy (ΔG_H) on the active sites. The well-established Sabatier principle indicates that the interaction between an optimal catalyst and the reactive intermediates should not be too strong or weak. Therefore, ΔG_H has been widely accepted as a descriptor for the acidic HER. However, unlike acidic electrolyte containing a large number of available protons, alkaline HER needs to first adsorb water molecules and then overcome additional energy barriers to dissociate the water to produce protons. Therefore, the Volmer step in alkaline medium is controlled not only by ΔG_H but also determined by the adsorption and dissociation energy barriers of H_2O molecules. Moreover, the adsorption/desorption behavior of accompanied hydroxyl groups (OH_{ad} and OH^-) would also bring complexity for the overall reaction efficiencies. A delicate balance between these determinants needs to be optimized to achieve an efficient alkaline HER performance. Too weak water molecule adsorption strength could not generate sufficient reactants, while too strong H_{ad}/OH_{ad} adsorption strength would result in a poisoning effect as the surface-active sites would be overly occupied.

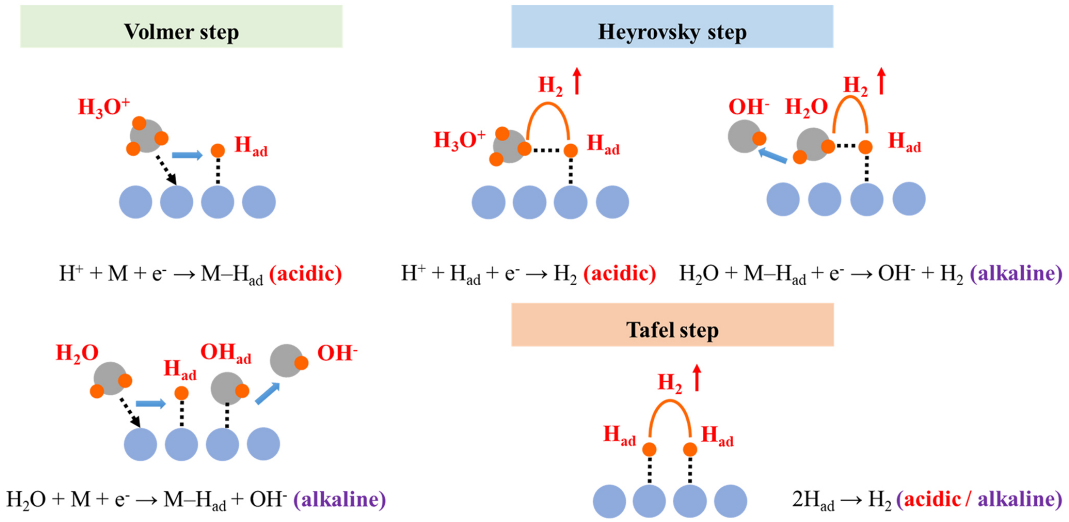

Figure 2. Schematicillustrationforthe elementaryHERstep: Volmer step and Heyrovsky step/Tafel step. balls in blue: active sites; grey: O atom; orange: H atom, respectively.

ELECTROCHEMICAL PARAMETERS OF HER

The performance of a given HER electrocatalyst is commonly assessed using a few key electrochemical parameters, including overpotential (η), Tafel plot, electrochemical impedance spectroscopy (EIS), turnover frequency (TOF), stability, *etc*. Through these parameters, the detailed reaction thermodynamics and kinetics information could be extracted. In this section, a concise overview of these parameters will be provided.

Overpotential

The representative polarization curves are obtained by graphing the geometric current density against the applied potential. The η is described as the potential gap between the actual applied potential for triggering the reaction and the thermodynamic equilibrium potential. A larger η indicates an increased electricity consumption, thereby resulting in a limited energy conversion efficiency. A satisfactory electrocatalyst should exhibit a higher current density at a low overpotential. Nernst equation elucidates the relationship between the HER equilibrium potential (E_{HER}) and the standard hydrogen electrode potential (E_{SHE}) which is defined as 0 V at any temperature.

$$E_{HER} = E_{SHE} + \frac{RT}{zF} \times \ln \frac{\alpha_{H^+}^2}{p_{H_2}} \quad (1)$$

$$E_{HER} = 0.059 \times \mathrm{pH} \quad (2)$$

$$E = E_{HER} + \eta \quad (3)$$

where R is the gas constant, T represents the temperature in kelvins, z denotes the number of electrons transferred (z = 2 for HER), F is the Faraday constant (96,485 C mol^{-1}), α_{H^+} depicts the activity of H^+ in aqueous solution, and p_{H_2} is the partial pressure of H_2 (Eq. 1). In the certain condition (T = 298 K, unit H_2 partial pressure), E_{HER} can be considered as reversible hydrogen electrode (RHE) which also depends on pH values (Eq. 2). Therefore, the actual applied potential (E) equals to E_{HER} plus η (Eq. 3).

The origins of η include the activation barriers of electrochemical reactions, ion migration, and internal resistance of the measurement system (R_S). An excellent catalyst can reduce the activation energy barriers required for initiating the reaction. Ion migration and series resistances are mostly dependent on external testing system configurations. The ohmic potential drop caused by R_S can be corrected by iR compensation. Therefore, the terminal E can be given by

$$E = E_{HER} + \eta - iR_s \tag{4}$$

Generally, the overpotential needed to achieve a current density of 10 mA cm^{-2} (geometric current density) (η_{10}) has been widely accepted as a criterion for evaluating the catalytic activities of different HER electrocatalysts. This current density corresponds to a 12.3% solar-to-fuel efficiency in solar water splitting. Essentially, owing to the different loading masses and accessible active areas for catalysts prepared via various methods, η_{10} based on geometric area is not suitable to evaluate the intrinsic activity of HER electrocatalysts. Therefore, the specific activity (based on real surface area) is proposed to measure the catalyst activity, which can be calculated by normalizing the current to the Brunauer-Emmett-Teller (BET) surface area or the electrochemical surface area (ECSA).

Tafel plot

Tafel plot can be well employed to investigate the inherent kinetics information of the electrocatalyst, which is derived from the experimentally measured polarization curves. When the solution concentration at the electrode surface is comparable to that of the bulk solution, the overpotential connected with the electrode kinetics can be significantly correlated with the current density by the Butler-Volmer equation, denoted as

$$i = i_0\left[e^{\alpha f\eta} - e^{-(1-\alpha)f\eta}\right] \tag{5}$$

where i represents the current density, i_0 is the exchange current density under reversible conditions, α is the charge transfer coefficient, and f equals to F/RT. In the region of high overpotential, Eq. 5 can be simplified to

$$\eta = -\left(\frac{2.303RT}{\alpha F}\right)\log i_0 + \left(\frac{2.303RT}{\alpha F}\right)\log i \tag{6}$$

According to Eq. 6, the relationship between overpotential and Tafel slope (b) can be expressed as

$$\eta = b\log(|i/i_0|) \tag{7}$$

where i_0 is the rate of charges entering or leaving the electrocatalyst surface under reversible conditions in an electrolyte, which can be extracted at the overpotential of zero. A high i_0 indicates the easier polarization of the electrocatalyst, and a lower activation overpotential to trigger the electrode reaction. The possible reaction mechanisms can be inferred from the value of the Tafel slope. For example, the Tafel slope of $b > 120$, $40 \leq b \leq 120$ or $b < 40$ mV dec^{-1} indicates that the Volmer, Heyrovsky, or Tafel step could be the HER rate-determining step (RDS), respectively. An electrocatalyst with a high i_0 and a low Tafel slope has always been an attractive proposition.

Charge transfer resistance

For an electrochemical reaction, the charge transfer characteristics are an important descriptor of an electrocatalyst activity, which can be evaluated from the EIS measurement technique within a reasonable frequency band. Generally, EIS measurements are conducted at the amplitude of perturbation voltage of 5-10 mV and over an applied potential beyond onset potential (at this potential, the catalysts should exhibit appreciable activity). The charge transfer resistance can provide information about the charge transfer process, which significantly depends on the analyzed frequency range. Specifically, (i) the resistance at the high-frequency region is independent of the applied potential owing to the non-faradic process, which can be employed to evaluate the resistances between electrode and catalyst; (ii) the resistance at the medium-frequency region is usually employed to reflect the charge transport within the catalyst; and (iii) the resistance at the low-frequency region is used to study the charge transfer resistance (R_{ct}) of interfacial charge transfer between the electrocatalyst and the solution. When the reaction current is not controlled by the mass-transfer resistance and at low overpotentials, R_{ct} can be expressed as

$$R_{ct} = \frac{RT}{nFi_0} \tag{8}$$

where n is the number of transferred electrons. Smaller values of R_{ct} indicate faster reaction kinetics and potentially better catalytic performance.

Turnover frequency

TOF is defined as the number of the desired product per active site in unit time (second, Eq. 9) at a predefined applied potential, which is an important parameter for measuring the intrinsic activity of an electrocatalyst. Nevertheless, the exact value of TOF is difficult to measure because the actual population of active sites cannot be accurately determined for heterogeneous catalysis. In some instances, the TOF can be obtained by calculating the total catalyst loadings, no matter whether they are truly involved in the catalytic process. In other cases, many researchers reported that the sole surface atoms or the easily accessible surface catalytic sites of the electrocatalysts participate in the catalytic process and generated the TOFs accordingly. Nonetheless, such results are meaningful when similar electrocatalysts are compared.

$$\mathrm{TOF} = \frac{n_{product}}{n_{active\ sites} \times t} \tag{9}$$

For HER, assuming that Faradaic efficiency is 100%, and the number of H_2 can be can be expressed as

$$n_{H_2} = \frac{It}{zF} \tag{10}$$

Consequently, Eq. 10 can be simplified to

$$\mathrm{TOF} = \frac{I \times N_A}{z \times n_{active\ sites} \times F} \tag{11}$$

where I is current (A), z represents the quantity of electron transferred per molecule (z = 2, for HER), and N_A denotes the Avogadro number (6.022×10^{23}).

Stability

Besides the intrinsic activity, the time-dependent stability is also a very important parameter for potential applications, especially under high current conditions. Two approaches exist for evaluating the durability of an HER electrocatalyst, including the chronopotentiometry (CP)/chronoamperometry (CA) and accelerated cyclic voltammetry (CV) tests. CP/CA test is conducted by recording the curve of potential/current over time under a fixed current/potential, respectively. For CP or CA test, most reported works are performed at a current density lower than 200 mA cm^{-2}. In fact, for practical application, durability test at higher current densities is encouraged for mimicking the real working conditions in AEM. In CV test, generally, larger than 1,000 CV cycles are repeated by recording the potential with the current response. By comparing the polarization curves before and after CV cycles, it can be seen that the less η increment, the better the stability of the electrocatalysts.

MULTI-INTERFACE ENGINEERING OF ALKALINE HER ELECTROCATALYSTS

For a complete electrocatalytic HER process, electrons from the external power source would structurally and chronologically go across three interfaces to reach the active site and participate in the reaction, including conductive substrate/electrocatalyst, electrocatalyst internal and electrocatalyst/electrolyte interfaces. Therefore, engineering these multi-interfaces is very important to optimize the overall electrocatalytic performance, which will be meticulously reviewed in this section.

Conductive substrate/electrocatalyst interface

In order to enhance electron transport efficiency with minimal charge resistance and avoid the electroheat energy waste, a geometric and electric close interfacial contact between an active electrocatalyst and a conductive substrate is essential. Most commercial and experimental electrodes are currently made by coating active catalyst materials onto a conductive substrate with the assistance of polymer binders, inevitably resulting in a vulnerable interfacial adhesion and hindrance to electron transport. In order to strengthen this interface, *in-situ* synthesizing catalytically active materials on conductive substrates or directly preparing self-supported freestanding electrode/electrocatalyst has been documented to address these interface issues.

Conductive substrate

The commonly used conductive substrates mainly include nickel (NF)/copper foam, Ni-based alloy foam, carbon cloth, carbon paper, *etc*., among which the NF has been reported as the most popular electrode substrate. On the choice of the conductive substrate, NF has enjoyed widespread application as its distinctive interlinked third-dimensional (3D) microstructure provides merits as light weight, high porosity, reliable mechanical strength, chemical stability, and promising electrical conductivity. Moreover, its employment could also act as the nickel source during the synthesis, offering further opportunities for constructing Ni-based compounds with multi-interface. For example, through a two-step synthetic procedure, specifically, the 1st step preparation of $NiMoO_4 \cdot xH_2O$ nanowire arrays followed by the 2nd step pyrolysis process, Liu *et al.* constructed MoO_2-Ni nanowire arrays supported on NF as an efficient HER catalyst [Figure 3A-J]. Benefiting from the *in-situ* grown MoO_2-Ni heterostructure with an atomically infused interface, the HER kinetics was enhanced by the upraised atomic *d* orbital[42]. The optimized MoO_2-Ni@NF electrocatalyst exhibited exceptional Pt-like HER performance in 1 M KOH[42]. Chang *et al.* electrodeposited amorphous Ni-Co-Fe ternary phosphides ($Ni_4Co_4Fe_1$-P) on NF as a self-supported catalytic electrode for alkaline HER. The integration of multimetallic phosphide on the NF surface allows sufficient exposure of surface sites[43]. Therefore, the $Ni_4Co_4Fe_1$-P electrode presented good HER catalytic performance (-61 mV at -20 mA cm^{-2})[43]. Ni-Cu-P@Ni-Cu catalyst was also prepared using electrodeposition as an efficient electrode for HER. During electrodeposition, NF provided sufficient active sites for the growth of dendrites with unique structures. Its high active electrochemical area, the convenient mass transfer channels

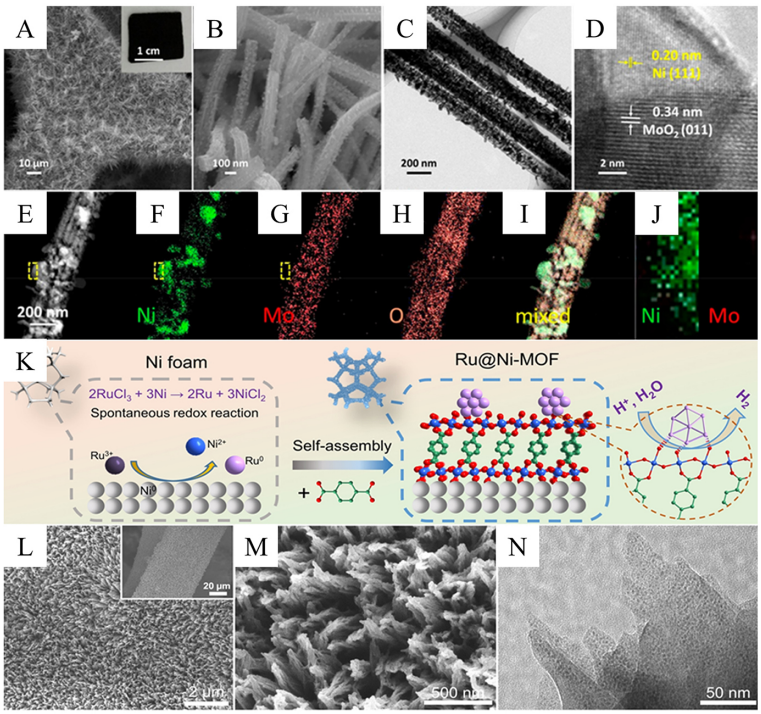

Figure 3. (A and B) SEM images of MoO_2-Ni on NF. (C) TEM, (D) HRTEM, (E-J) HAADF-STEM images and elemental analysis results of MoO_2-Ni nanowires. (K) Schematic illustration of the formation of Ru@Ni-MOF grown on NF. (L, M) SEM and (N) TEM images of Ru@Ni-MOF. This figure is quoted with permission from Liu *et al.*[42] and Deng *et al.*[45].

provided by the porous structure, and the synergistic effect between Cu and Ni led to the excellent electrocatalytic activity (-70 mV at 10 mA cm^{-2}) of the catalyst[44]. Deng *et al.* designed a definite metal-support interfacial bond to enhance the intrinsic activity of noble metals (Ru, Ir, and Pd)[45]. Through a spontaneous redox strategy, three kinds of quantum-sized metal nanoparticles propped against Ni-based metal-organic framework (Ni-MOF) nanohybrids (Ru@Ni-MOF, Ir@Ni-MOF, and Pd@Ni-MOF) were rationally prepared. As shown in Figure 3K-N, Ru^{3+} and metallic Ni on the NF surface spontaneously underwent a redox reaction, during which Ni^{2+} ions were also coordinated with 1,4-benzenedicarboxylic acid (H_2BDC) to shape Ni-MOF nanosheets. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images demonstrated the uniform distribution of Ru nanoparticles anchored (2-4 nm) on the Ni-MOF surface. The strong interfacial interaction between the nanoparticles and Ni-MOF ensured not only the structural stability but also adequate exposure of active sites. More significantly, the electronic structure of hybrid materials was successfully modulated by the charge exchange in the formed Ni-O-M (Ru, Ir, Pd) bridge bond with enhanced HER kinetics. Consequently, the Ru@Ni-MOF catalyst exhibited superior HER performance, even superior to commercial Pt/C. Theoretical calculation demonstrated that the interfacial-bond-induced electron transfer resulted in the optimized adsorption of H_2O and H leading to the excellent alkaline HER performance[45]. Electrochemical dealloying strategy was also used to prepare nickel nanotube arrays on NF and achieved a high HER kinetics[46]. Liang *et al.* synthesized MoO_2/Ni heterostructure on NF by hydrothermal followed by pyrolysis in N_2 and H_2 atmosphere[47]. Firstly, using hydrothermal methods, the $NiMoO_4 \cdot xH_2O$ nanosheet was formed on the NF surface, and then the $NiMoO_4 \cdot xH_2O$ precursor transformed into MoO_2/Ni under N_2 and H_2 atmosphere gas environments. The *in-situ* transformation of the precursor ensured the stability of the interface between the active site (MoO_2/Ni) and the substrate (NF). Eventually, the MoO_2/Ni@NF displayed robust HER performance in an alkaline electrolyte[47]. Similarly, Ni-doped tungsten oxide grown on NF catalyst

(Ni-WO_x@NF) was also prepared by first hydrothermal and then annealing to produce hydrogen from seawater. The Ni-WO_x catalyst grew vertically on the NF surface with rapid charge transfer and low η_{10} (45.69 mV)[48]. In addition, using one-step solvothermal method, the W-doped Ni-$C_3S_3N_3$-based coordination polymer (CP) catalyst was also prepared on NF (W-NT@NF). The metal-organic polymers were grown in situ on NF with low interfacial resistance and a great many of exposed active sites, which achieved excellent dual-functional HER and urea oxidation reaction performance[49]. In the traditional thermocatalysis field, such as selective oxidation, hydrogenation or water-gas shift reaction, Ni/TiO_2 systems have proven to be good catalysts. However, their poor electrical conductivity limits their application in electrocatalysis. Zhou *et al.* synthesized Ni/TiO_2 composites on conductive NF as a HER electrode[50]. The disclosed electronic interaction between Ni and TiO_2, coupled with excellent electrical conductivity of NF, endowed the composites with outstanding HER performance[50].

Ni-based alloy foams could provide more growth sites when the conductive substrate is combined with active substance by hydrothermal methods. For instance, a HER electrocatalyst ($NiFeCoS_x$@$FeNi_3$) consisting of Co_3S_4 and Ni-Fe sulfide on $FeNi_3$ foam was prepared. The synergistic interaction among multi-elements and the unique structure together gave the catalyst outstanding catalytic performance. In alkaline solution, the η_{10} of $NiFeCoS_x$@$FeNi_3$ is 88 mV[51]. In addition to Ni-based conductive substrates, copper substrates could also serve as good conductive substrates. A dynamic hydrogen bubble template (DHBT) method is a practical approach to fabricating the porous alloy electrodes. The porous Ni-Co catalyst on a copper substrate electrode was prepared using the DHBT method and exhibited outstanding stability[52]. Zhang *et al.* prepared an efficient HER electrocatalyst by coating metallic Ni onto Cu_2S nanoarrays using the commercial copper foam as a substrate and unveiled a preferable HER activity (η < 200 mV at 500 mA cm^{-2}). Finally, theoretical analyses indicated that the Ni-S interaction between metallic Ni and Cu_2S interface can optimize the adsorption energy of hydrogen and thus promote HER kinectics[53].

Moreover, carbon cloth has been widely used as a conductive substrate for HER because of its superior electric conductivity, low cost, and robust mechanical flexibility. Yang *et al.* prepared an electrocatalyst containing W_2C nanowires decorated with Ni nanoparticles on carbon cloth[54]. It only required a low overpotential of 37 mV to obtain current densities of 10 mA cm^{-2}, which was comparable to the commercial Pt/C catalyst. Moreover, the experimental results indicated that the close interaction between Ni nanoparticles and W_2C nanowires can effectively accelerate electron transport[54]. A NiO/Ni heterostructure on carbon cloth (NiO/Ni@CC) was fabricated by *in-situ* electrochemical oxidation after electrodepositing metallic Ni on the surface of carbon cloth. The existence of heterostructure and the superior electric conductivity of carbon cloth made the catalyst exhibit a low η_{10} of 40 mV for alkaline HER[55]. Theoretical calculations by Wang *et al.* predicted that coupling Ni_3C with metallic Ni can balance H and H_2O adsorption energies. Subsequently, they fabricated an integrated heterostructure catalyst consisting of Ni_3C nanosheets and Ni nanoparticles on carbon cloth, demonstrating excellent electrocatalytic HER activity (η_{10} = 98 mV)[56]. Inspired by the distinctive water dissociation ability of V-O species, a novel Ni/V_2O_3 heterostructure was prepared on carbon cloth and characterized as an alkaline HER electrocatalyst, an excellent HER activity of low overpotential (η_{10} = 44 mV) was revealed[57]. Carbon microfibers derived from skim cotton were also introduced as conductive substrates for HER catalyst. Sun *et al.* synthesized Mo_2C and metallic Ni-modified carbon microfibers. The carbon microfibers were prepared by carbonizing cotton fibers with a porous structure and a large specific surface area, which showed promising characteristics as an efficient inexpensive HER electrocatalyst[58].

Freestanding electrocatalyst/electrode

In addition to preparing binder-free electrocatalysts by off-the-shelf substrates, self-supported electrocatalysts could also be directly prepared using the bottom-up approach, namely freestanding electrocatalysts. The freestanding electrocatalyst with the absence of an interface, or denoted as the integrated catalyst electrode, enables a faster electron transfer rate through the interior of the electrodes.

The electrospinning technique is efficient in preparing freestanding electrocatalysts. For instance, Yang *et al.* fabricated novel Ni/NiO-carbon nanotubes (CNTs) composite nanofibers by electrospinning and followed thermal treatment[59]. Without extra reducing agents and carbon source, the $Ni(Ac)_2$/polyvinylpyrrolidone (PVP) precursor can decompose to reductive gaseous H_2, CO, CH_4 during the vacuum heat treatment, which could facilitate the NiO reduction and CNT growth. The optimized Ni/NiO-CNTs composite can deliver an excellent HER activity (η_{10} = 98 mV) in 1 M KOH[59]. The freestanding CNF-Ni/NiO-Pd electrode was also prepared by Barhoum *et al.* via electrospinning, pyrolysis, and atomic layer deposition, sequentially[60]. This self-supported composite was employed as a highly efficient HER electrocatalyst. The surface graphitic layers can keep the Ni/NiO from corrosion, and the synergistic effect of different substances at the interfaces attributed the catalyst to excellent performance. The optimized CNF-Ni/NiO-Pd electrocatalyst exhibited a low overpotential (η_{10} = 63 mV) and a remarkably small Tafel slope of 72 mV dec^{-1}[60]. As shown in Figure 4A, Li *et al.* prepared the Ni/CeO_2@N-CNFs catalyst consisting of Ni/CeO_2 hetero-nanoparticles and N-doped carbon nanofibers using the electrospinning-carbonization method[61]. The metal/semiconductor heterojunction consisting of Ni/CeO_2 can trigger the self-driven charge transfer and thus facilitate the charge transfer rate, leading to the suitable adsorption energies for reactive intermediate species. Therefore, the Ni/CeO_2@N-CNFs electrocatalyst showed superb HER activities with an overpotential of 100 mV at 10 mA cm^{-2}[61]. Chemical reduction is another feasible method for obtaining freestanding electrodes. Tao *et al.* first prepared 3D Ni nanofiber material as an electrode through a magnetic-field-assisted reduction method and then modified the 3D Ni electrode by $FeCl_3$ solution to obtain Fe@Ni-nanofiber electrodes[62]. The distinctive structure of 3D electrodes guaranteed full exposure of the catalytic sites and rapid mass and charge transfer. Therefore, this Fe@Ni nanofiber electrode displayed HER excellent activity, with overpotential as low as 55 mV at 10 mA cm^{-2}[62]. In our previous work, we reported a simple procedure for preparing a freestanding surface disordered NiCu solid solution (NiCuDSS) as an efficient HER electrode [Figure 4B-E]. During the hydrothermal reduction process, NH_4^+ tailored the reduction/nucleation rate of Cu^{2+}/Ni^{2+} ions, leading to its special intertwined 3D microstructure. The unique 3D framework can practically provide a fast electron conduction path and promote bubble separation from the electrode surface. The optimized catalyst displayed superior HER activity (-322 mV at 1,000 mA cm^{-2}) and outstanding durability. The theoretical calculations demonstrated that the substitution of Cu can facilitate the hydroxyl desorption from the active sites and thus enhance the kinetics of the overall Volmer reaction[63]. Additionally, Li *et al.* synthesized a composite of N/P co-doped carbon shell-coated Ni-Ni_3P nanoparticles on 3D graphene frameworks via sequential hydrothermal and thermal treatments. As a result, the obtained Ni-Ni_3P@NPC/rGO electrocatalyst exhibited superior HER electrocatalytic performance[64].

Briefly, the interfacial charge transfer resistance between electrocatalyst and conductive substrate can greatly affect the overall catalytic performance of electrocatalyst. The electron transfer between the conductive substrate and electrocatalyst can be facilitated by chemically *in-situ* growth of active species on a conductive substrate. In addition, the intrinsic conductivity of freestanding electrocatalysts without a conductive substrate needs special attention.

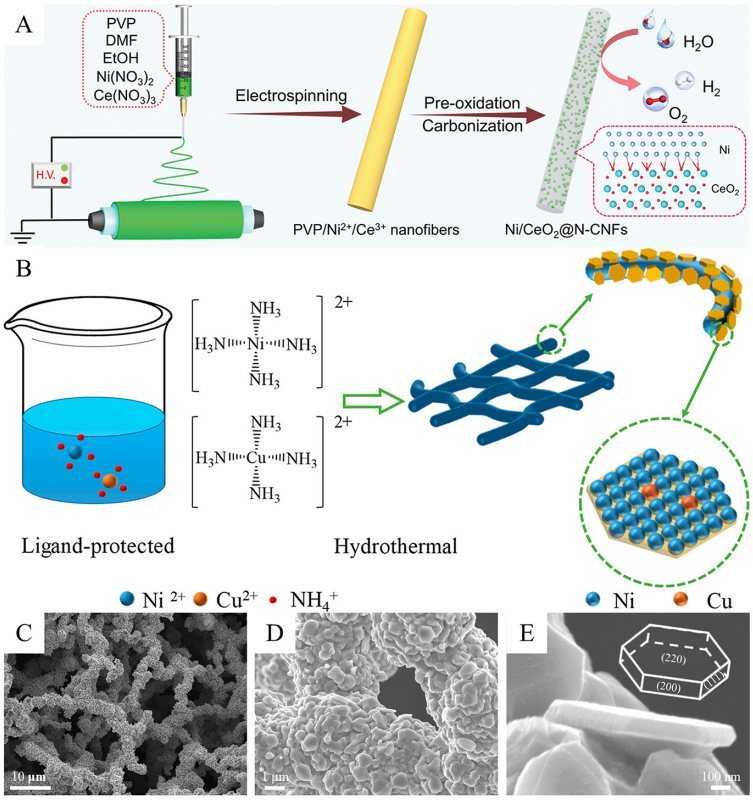

Figure 4. (A) Schematic illustration of the synthesis process of Ni/CeO_2@N-CNFs. (B) Schematic representation of the preparation of NiCuDSS electrocatalysts. (C-E) SEM images of prepared $Ni_{0.95}Cu_{0.05}$DSS at different magnifications. This figure is quoted with permission from Li *et al.*[61] and Zhang *et al.*[63].

Internal interface of electrocatalyst

For enhancing the intrinsic catalytic activity of materials, an efficient approach is to create atomic-level or phase-level heterogeneous interfaces inside the electrocatalysts. Multi-interface catalysts in the electrocatalytic field, defined as the catalysts containing interfaces between different components, have received a lot of attention. Interesting physicochemical features could be induced towards the multi-interface catalysts owing to the differences in the geometric and electronic structures of the unequal components. The preferred combination of different components thus can modulate the electrocatalytic reaction pathways and improve reactive kinetics. Although interfaces with variable atomic arrangements can lead to different electron transfer or interfacial resistances, two distinctive interfacial effects have been well identified, namely the ensemble and electron effects. The former originates from the multi-component heterointerfaces, where the interconnected active sites with different local electronic structures can regulate and facilitate the adsorption/desorption procedure of various reactive intermediate species. Therefore, the multi-interface can offer an energetically favorable pathway for a multi-step catalytic process when the individual elementary reaction occurs on its preferred component and so greatly enhances the overall reaction efficiency. Comparatively, the latter (electron effect) means that the different components have electronic interaction at the interface, which could further trigger an interfacial charge redistribution. As a consequence, the adsorption behaviors of key intermediates could be modulated by coupling their electronic structures via electron effect. It may be noted that in a composite electrocatalyst, the ensemble effect and electron effect could hardly be clearly separated; actually, they synergistically accelerate the HER process. Therefore, the rational multi-interface engineering holds great promise to maximize these effects. In order to achieve the atomic design of multi-interfaces, several innovative preparation methods have been

explored, e.g., defecting engineering, vacancy or heteroatom doping, the phase-level heterostructure engineering, *etc.*

Atomic interface via defect engineering

The defect can be defined as the nonuniform composition in a material, including vacancies, heteroatom dopants, *etc*., which could significantly affect the electron distribution around the defective sites. The electronic arrangement of the catalyst is closely related to its catalytic activity; consequently, atomic defect engineering could effectively tune the electronic configuration of catalysts, which, in turn, is used to regulate its electrocatalytic performance.

The rational design of non-metallic element vacancies has been revealed as a convenient defect engineering strategy to enhance catalytic activity. For instance, by introducing sulfur vacancies to Ni_3S_2, Jia *et al.* successfully tuned the hydrogen adsorption behaviors on Ni sites to improve HER activity (η_{10} = 88 mV) in 1 M KOH[65]. Additionally, oxygen vacancies have also attracted increasing attention. Li *et al.* prepared Ni/Fe/Mo-based electrocatalyst with oxygen vacancies on NF, which was in situ converted to amorphous NiFeMo (oxy)hydroxide during electrocatalysis, exhibiting outstanding intrinsic activity and sufficient active sites for alkaline HER[66]. The Ni/MoO_2 has been proven to be highly reactive for hydrogen production. Liang *et al.* synthesized an efficient HER catalyst (Ni/MoO_{2-x}) consisting of a Ni nanocluster loaded on the surface of oxygen-vacancy-rich MoO_2[67]. X-ray photoelectron spectroscopy (XPS) results indicated that the Ni-O-Mo bonds and oxygen vacancies promoted the migration of electrons from the oxygen to the nickel atom. Furthermore, the theoretical calculations revealed that charge transfer optimized the free energy of intermediates on Ni/MoO_{2-x}, which endowed it with excellent catalytic properties[67].

Metal ion doping has also been shown to be another effective approach to modulating the electronic configuration of catalysts. For example, based on Ni/Co-doped $MoSe_2$ catalysts, Mao *et al.* revealed that doping Ni/Co atoms could effectively modulate the electronic structure of $MoSe_2$[68]. Experimental and theoretical analyses showed that the doped Ni/Co atoms can regulate the position of the *d*-band center and optimize electrical conductivity of catalyst, which, in turn, adjusts the strength of the interactions between adsorbed hydroxyl (OH_{ad}) and active sites. The optimal hydroxyl adsorption strength would facilitate the Volmer step, thus enhancing the overall alkaline HER kinetics [Figure 5A-E][68]. As shown in Figure 5F, by controlling the reaction conditions, Zhong *et al.* synthesized Ni-doped CoSe with and without Co vacancies, respectively[69]. Theoretical and experimental results demonstrated that the Co vacancy and Ni atom located in the vicinity of Se atoms synergistically affect its electron distribution, leading to the upshift of Se 4p(z) orbital. Consequently, the ΔG_H of Se atoms was significantly optimized, resulting in an advanced HER activity[69]. Jiao *et al.* designed an effective strategy for increasing quantity of active sites by annealing Ni-MOF at different temperatures. The incorporation of trivalent Ni^{3+} resulted in a delicate atomic rearrangement and provided more catalytic active sites. Therefore, the as-prepared Ni/NiO nanoparticles displayed excellent HER performance (η_{10} = 41 mV)[70]. Tang *et al.* prepared a heterostructure catalyst consisting of V-doped NiFe layered double hydroxide (LDH) and Ni nanoparticles, possessing excellent HER catalytic performance (η_{10} = 19 mV)[71].

Introducing vacancies or heteroatom dopants into electrocatalysts has been confirmed as useful atomic interface engineering to enhance the electrocatalytic performance. However, some problems still need to be solved. For instance, there remains a need for a greater focus on the stability and *in-situ* reconstruction of defect-rich catalysts. Additionally, the precise control of the coordination environment of the doping site has yet to be available.

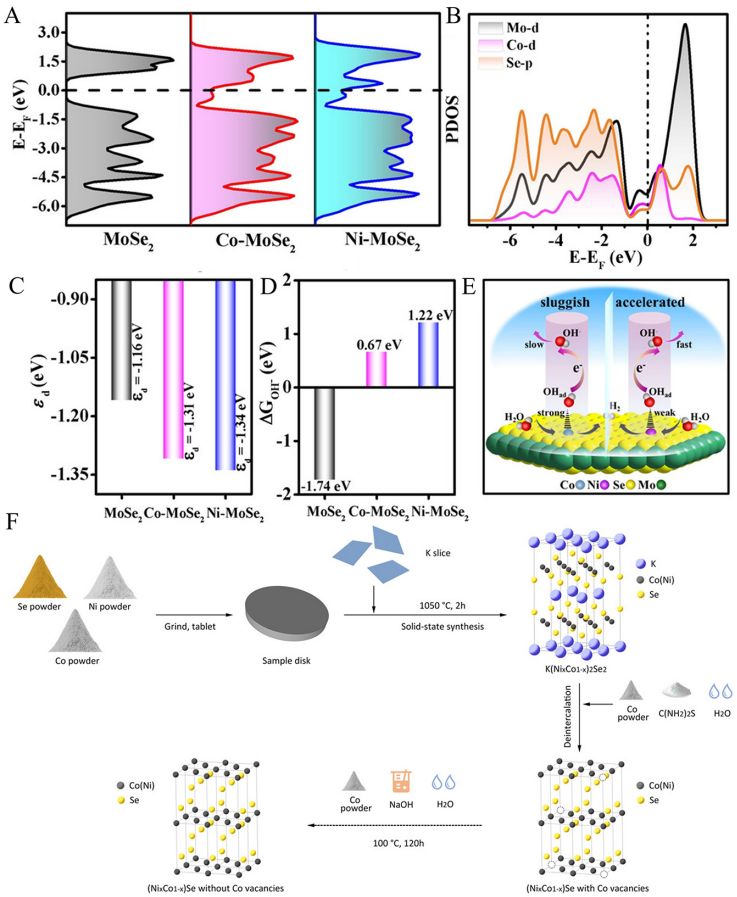

Figure 5. (A) The TDOS charts of $MoSe_2$, Co-$MoSe_2$, and Ni-$MoSe_2$. (B) The PDOS charts of Co-$MoSe_2$. (C) The comparison of d-band centers (ε_d) of $MoSe_2$, Co-$MoSe_2$, and Ni-$MoSe_2$. (D) The Gibbs free energy of OH_{ad}. (E) Schematic diagram of catalytic action of OH_{ad} transfer in alkaline HER process. (F) Schematic diagram of the synthesis method of $(Co_{1-x}Ni_x)_2Se_2$ with and without vacancies. This figure is quoted with permission from Mao *et al.*[68] and Zhong *et al.*[69].

Interface at heterostructures

The unique physicochemical properties of heterostructured electrocatalysts lead to their excellent HER performance. Heterostructured electrocatalysts composed of different components usually have higher catalytic activity than a single-component catalyst due to the aforementioned synergistic ensemble and electron effects. Therefore, developing heterostructured electrocatalysts with distinctive ensemble effect/electron effect is considered an effectual approach to obtain satisfactory HER performance.

The different multi-components usually have specific catalytic activities for different elementary steps (for distinct intermediates). When these active sites are rationally combined, the overall reaction kinetics thus can be synergistically enhanced. For example, nickel oxide could effectively expedite the water adsorption and dissociation step to generate protons, while metallic nickel can further facilitate hydrogen desorption to generate hydrogen molecules. Based on this dual active site conception, Huang *et al.* developed heterostructured efficient HER catalysts (Mo-NiO/Ni) by doping metal Mo atoms into NiO and coupled with metallic Ni[72]. Theoretical and experimental analyses have been used to comprehensively investigate its catalytic mechanisms. Doping Mo heteroatoms into NiO could not only accelerate the water dissociation and rapid transfer of H to the adjacent Ni sites to generate H_2 but also maintain the structural stability of NiO crystal [Figure 6A-C]. As a consequence, the Mo-NiO/Ni catalyst exhibited an excellent HER

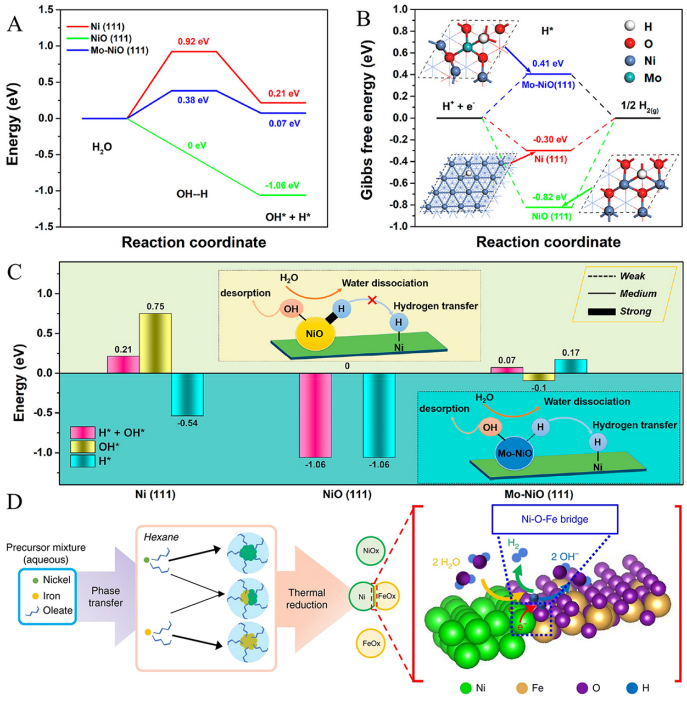

Figure 6. (A) Calculated H_2O dissociation barriers and (B) Gibbs free energies of H adsorption on different theoretical models. (C) Summary of adsorption energy of various reactive intermediates on the three surfaces. (D) Schematic diagram of the catalyst preparation and the representation of the alkaline HER process on the Ni-γ-Fe_2O_3 interface. This figure is quoted with permission from Huang *et al.*[72] and Suryanto *et al.*[76].

performance with η_{10} of 50 mV and the Tafel slope of 86 mV dec^{-1}[72]. Gu *et al.* synthesized a 3D sponge built via graphene nanocages in which Ni nanoparticles and single atoms coexisted using a facile one-pot strategy[73]. The H_2O molecule was preferentially adsorbed on the atomic Ni sites within the graphene cage, then dissociated into OH_{ad} and H_{ad}. Subsequently, Ni nanoparticles provided active sites for H adsorption to produce molecular hydrogen. The synergistic catalytic effect between Ni nanoparticles and atomic Ni sites endowed the composite catalyst with excellent HER performance (η_{10} = 27 mV)[73]. Pt electrodes have excellent catalytic HER performance under acidic conditions, while their HER performance under alkaline conditions is unsatisfactory owing to the lack of water adsorption/dissociation sites. To enhance the HER activity of Pt electrodes in alkaline conditions, Xue *et al.* modified the electrode with Ni-Fe clusters. This heterostructured catalyst exhibited an excellent HER performance, which mostly originated from the synergistic promotion of the facilitated water dissociation ability of Ni-Fe clusters and the optimized hydrogen adsorption ability of Pt[74]. Additionally, a special heterostructured HER catalyst (Ni/NiFe-LDO), comprising Ni nanoparticles and NiFe-layered double oxide (LDO) on NF, was successfully constructed, which exhibited η_{10} = 29 mV in 1.0 M KOH electrolyte. Detail characterizations indicated that the synergistic interface effect between NiFe-LDO nanosheets and Ni nanoparticles improved its HER activity. The metal oxides were beneficial for water activation because of their strong H_2O adsorption ability; subsequently, OH was adsorbed on NiO active sites; meanwhile, Ni nanoparticle active sites were responsible for the adsorption of H. In summary, it has been widely acknowledged that properly constructing a multi-component interface could significantly enhance the kinetics of Volmer-step reaction via the distinctive ensemble effect as decoupling the generation and desorption of hydrogen intermediate[75].

In heterogeneous catalysts, interfacial electron transfer could be initiated between different components due to their unequal energy band structures, leading to changes in the adsorption and desorption behavior of

intermediates, which is strongly associated with the HER activity of the electrocatalyst. Therefore, the rational design of efficient alkaline HER electrocatalysts could also be realized by modulating the electronic interactions at the interface. For instance, a nanoparticle catalyst with abundant metallic Ni/γ-Fe_2O_3 interfaces was developed as an efficient HER electrocatalyst, as shown in Figure 6D. Theoretical calculations indicated that the strong electronic interactions at the Ni/γ-Fe_2O_3 interfaces resulted in its good HER catalytic activity[76]. Sun *et al.* developed a series of hybrid electrocatalysts via implanting bixbyite-type lanthanide metal sesquioxides in metallic Ni toward HER[77]. The Yb_2O_3 could provide abundant active sites and optimize the free energies of water dissociation and hydrogen adsorption. Therefore, the screened Ni/Yb_2O_3 electrocatalyst exhibited excellent HER performance (η_{10} = 20 mV) and outstanding durability (360 h at 500 mA cm^{-2})[77]. The interphasic synergy with charge redistribution in monometallic structures was also reported to successfully tune the adsorption-desorption strength of intermediate species (H/OH) in HER processes. Electronic structure analysis showed that a lot of Ni *d* band electrons at the Fermi level could accelerate the charge transfer from $Ni(OH)_2$ to Ni-N/Ni-C. Accordingly, the prepared $Ni(OH)_2$@Ni-N/Ni-C heterostructured electrocatalyst displayed decent HER activity with an overpotential of 113 mV at 100 mA cm^{-2}[78]. Yang *et al.* obtained a hybrid electrocatalyst via anchoring metallic Ir nanoparticles on Ni-MOF nanosheets[79]. The interaction between Ir and Ni-MOF promoted the charge redistribution by the Ni-O-Ir bridge, inducing the adsorption optimization of H_2O and intermediate species, thus enhancing the electrochemical kinetics of pH-universal HER processes[79]. Analogously, it was shown that the charge transfer behaviors at different heterogeneous interfaces between metals and metal oxide-containing components, such as Co-Ni-P/MoS_2[80], Ni/$Ni(OH)_2$[81,82], Ni/W-$Ni(OH)_2$[83], Ni/MoO_2[84], Ni/MoN[85], and Ni/NiO-$Ti_3C_2T_x$ MXene[86], could confer superior catalytic performance. In addition, constructing the electrocatalysts with multiple interfaces has been shown to be a feasible scheme for HER electrocatalysts. For example, Zhou *et al.* constructed a Ni-CeF_3-VN multi-interfaces catalyst and displayed excellent HER activity (η_{10} = 33 mV)[87]. The experimental and theoretical analyses showed that electrons moved from Ni to VN/CeF_3, resulting in the acceleration of Volmer step on Ni/VN interface and recombination of H on Ni/CeF_3 interface, respectively, thus synergistically facilitating the rate of the multi-step HER in alkaline solution[87]. Liu *et al.* reported the multi-interface coil-like NiS-Ni_2P/Ni electrocatalyst prepared on NF. The NiS/Ni and Ni_2P/Ni interfaces were served as electrochemical active sites and exhibited superior HER catalytic activity with overpotentials of 115 and 53 mV at 10 mA cm^{-2} in neutral and alkaline electrolyte[88].

Moreover, metal-organic polymers, particularly conjugated variants, have become increasingly important in the field of electrocatalysis due to their customizable composition, varying metal oxidation states, abundant active sites, and impressive conductivity. These polymers can be prepared under relatively mild conditions. By fine-tuning metal active sites and strategically using functionalized ligands, it is possible to precisely design active sites and foster strong interactions between ligands and metal sites. Therefore, polymers can also be utilized to modify the internal interface of electrocatalyst. For example, Liu *et al.* prepared a self-supported bimetallic Mo-Ni-$C_3N_3S_3$ CP (Mo-NT@NF), featured by robust metal-ligand interactions and varying H_2O adsorption energy[89]. A range of Mo-NT@NF samples were prepared using a simple solvothermal method, and their multivalent metal states and performance towards HER were systematically assessed. The theoretical calculations and experiments revealed that the strong adsorption of the Mo^{5+} site of water molecules weakens the O-H bond, in conjunction with efficient proton transfer by the proton relay N and S, leading to a highly effective HER catalysis on the site[89]. Zhang *et al.* presented a simple and cost-effective approach to fabricate ultrasmall Ni/NiO_x heterostructures coated with carbon nano-onions (CNOs) through a single-step thermal decomposition of ultra-thin 2D Ni-based CPs (CPs)[90]. The rapid low-temperature graphitization of CPs is crucial for enhancing the performance and scalability of the catalysts prepared. By confining the process within low-temperature graphitization conditions, the ultrasmall size of the Ni/NiOx heterojunction (< 5 nm) is guaranteed, leading to a significant increase in interfacial areas and a concurrent rise in active site density. Given the favorable electronic configuration of

Ni^{3+} for OH_{ad} adsorption, the ultrasmall NiO_x phase enhances the intrinsic catalytic activity for water decomposition. The low-temperature graphitization process also allows CNOs to maintain abundant hydrophilic functional groups, facilitating efficient mass transfer[90].

For multi-component heterostructured electrocatalysts, decoupling the different elementary steps on various active components has been shown to improve the overall reaction kinetics. Moreover, regulating the charge transfer behavior between diverse components can also reduce the reaction energy barrier or tune intermediate adsorption behaviors, which is an effective strategy to enhance the catalytic performance.

Electrocatalyst/electrolyte interface

In addition to the intrinsic activity of the electrocatalyst, the mass transport between the electrocatalyst and electrolyte interface is also very important for the overall reaction performance. Especially in the high current density condition, a great many of bubbles would be generated on the electrode surface, which will hinder the contact between the electrolyte and electrode, bringing about a decline in catalytic performance. Through the interfacial wettability engineering of the electrode surface and the rational design of electrical double layer (EDL) structure, the mass/electron transfer between reactive species and active sites can be well promoted to improve the HER performances.

Wettability

The wettability of electrocatalysts can significantly affect the catalytic activity under high current density conditions. The most distinctive difference between low (< 100 mA/cm^2) and high current HER processes is the population of generated gas bubbles during the reaction. If gas bubbles cannot timely detach from the electrode surface, the small air bubbles would coalesce into larger ones as they minimize their surface energy. The large air bubble coverage on electrodes would create an insulator barrier between electrolyte and catalysts, resulting in shrunken effective surface area and high cross-interface ionic resistance with deteriorated HER catalytic performance. Moreover, the attached gas bubbles will continue to grow until the increased buoyancy overcomes the adhesion force between the bubble and catalyst, leading to the induced inner stress at the bubble/catalyst interface which could potentially trigger severe structural damage with compromised catalytic activity. Therefore, engineering the (electrocatalyst/electrolyte) interfacial hydrophilicity and aerophobicity can provide a fast mass and charge transfer pathway to improve the electrocatalytic activity.

Kim *et al.* fabricated a series of morphology-controlled metallic Ni electrocatalysts to systematically investigate the effect of wettability on hydrogen bubble release behaviors [Figure 7A][91]. The wettability (hydrophilicity or aerophobicity) of the catalyst surface is closely related to its porousness. The optimal superaerophobic Ni electrocatalyst exhibited the best HER performance with the highest porosity of approximately 52% among the Ni catalysts. It is observed that the unique superaerophobic surface structure of the metallic Ni electrocatalyst combined with the effective mass transport can accelerate the detachment of H_2 bubbles, substantially improving catalytic performance[91]. As shown in Figure 7B-M, Xu *et al.* first prepared 3D-printed Ni electrodes, modified with active materials of $MoNi_4$ and NiFe LDH, which exhibited superior electrocatalytic HER performance[92]. The special porous structure of 3D Ni electrodes allows fast bubble generation and release, providing generous active sites. The $MoNi_4$@3D Ni electrode only required an overpotential of 104 mV at 500 mA cm^{-2}[92]. Fujimura *et al.* employed Ni microarray electrodes prepared by photolithography and electrodeposition; the correlation between HER efficiency and surface wettability was explored[93]. Furthermore, *in-situ* video surveillance of the electrode surface during the HER process clearly demonstrated that the size of generated air bubbles increased as the wettability of the electrode surface decreased. The larger bubbles will increase the ohmic loss and block the active sites on the

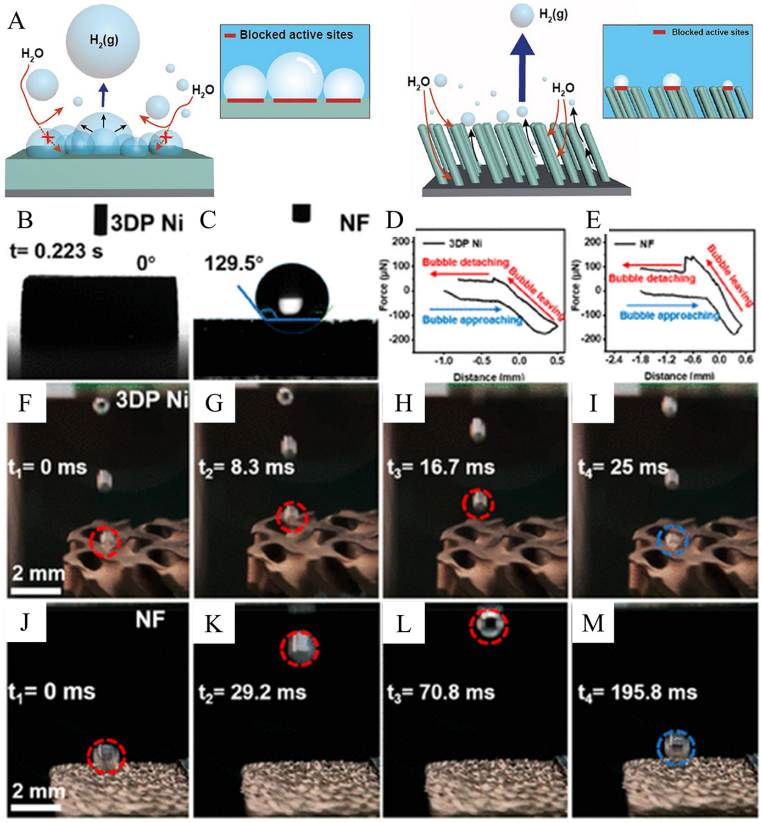

Figure 7. (A) Schematic illustrations of the H_2 bubble-release behavior of different Ni catalysts. (B) Contact angles on 3DP Ni and (C) NF. (D) Bubble adhesive force measurements of 3DP Ni and (E) NF. (F-I) Digital images of bubble release from 3DP Ni and (J-M) NF structures. This figure is quoted with permission from Kim *et al.*[91] and Xu *et al.*[92].

electrode surface[93]. Shang *et al.* fabricated a HER electrocatalyst (Ni/NiMoN) constructed by NiMoN nanowire arrays modified by metallic Ni nanoparticles on a copper foam[94]. Theoretical analysis indicated that the Ni nanoparticles can accelerate H_2O dissociation rate, boosting the feed of protons in the neutral media. Simultaneously, hydrogen bubbles can quickly leave the electrocatalytic surface to refresh the catalytic active sites because the dense nanowire arrays endow the electrode surface with superaerophobic properties. Therefore, the Ni/NiMoN electrode demonstrated excellent HER activity (η_{10} = 33 mV) in a neutral media[94]. Li *et al.* designed superhydrophilic Ni-based multi-component array (Ni NCNA) catalyst on NF, which only needed -47 mV to achieve 10 mA cm^{-2}. The water contact angle analysis displayed that it took only 0.2 s for the water droplet to completely spread on the electrode surface. Owing to its superhydrophilic properties, the Ni NCNA catalyst can operate stably under high current conditions[95]. A typical graphite electrode surface can be transformed into a superhydrophilic structure after Ni-Sb alloy modification using a one-step electrodeposition method. Benefiting from its superhydrophilic surface property, the optimized Ni-Sb alloy electrode achieved superior HER electrocatalytic performance[96]. Moreover, Yu *et al.* prepared a Ni-Mo-based catalyst with superhydrophilic and aerophilic surfaces. Owing to its high intrinsic activity and porous structure, the Ni-Mo-based catalyst presented remarkable HER activity in all-pH media[97]. Therefore, the appropriate modulation of surface wettability, specifically, minimizing the size of gas bubbles at detachment, would be beneficial to alleviate the inner stress and facilitate the rapid release of the generated air bubbles from the electrode surface, enabling enhanced high current density HER performance.

Electrical double layer

The EDL is where the electrochemical reaction takes place. The inner/outer Helmholtz plane (IHP/OHP) and the diffuse layer together form the EDL [Figure 8][98]. IHP is crucial for an electrochemical reaction, which contains various reaction-involving molecules and ions. For alkaline HER, the main species are H_2O, adsorbed H_{ad} and OH_{ad}/OH^- from water dissociation, and H_2 and specific cations from the electrolyte solution. The transfer impedance of reactive species in EDL can increase the overall reaction overpotential and energy loss. Unfortunately, it is very hard to directly monitor the interfacial effect of EDL during alkaline HER due to the lack of effective methods for detecting interfacial species. This is because the structural or compositional changes of EDL could only be studied via *in situ/operando* technology due to its instantaneous property changes with the applied electric field, and the thickness of EDL is only around 1-10 nm. Despite the difficulties in studying EDL, researchers have been working to reveal the *in-situ* changes in EDL during the HER process to direct the rational design of excellent HER electrocatalysts.

For example, Zhang *et al.* employed interfacial chemistry engineering to tune the adsorption free energy of H_2O dissociation and H simultaneously[99]. The hybrid $Ni_{0.2}Mo_{0.8}N$ microrod arrays supported on NF were decorated with Ni nanoparticles. Theoretical analysis suggested that the $Ni_{0.2}Mo_{0.8}N$ and Ni acted as adsorption active sites for hydrogen and hydroxyl, respectively, synergistically promoting alkaline HER. The resulting $Ni_{0.2}Mo_{0.8}N$/Ni electrocatalyst exhibited excellent HER electrocatalytic activity (-70 mV at 300 mA cm^{-2}). Moreover, further finite-element-based simulations indicated that an enhanced local electric field around Ni particles was formed, which led to an increased hydrated K^+ concentration in IHP and thus accelerated the subsequent water dissociation elementary step [Figure 9A][99]. Similarly, Gao *et al.* reported a nanocone-assembled Ru_3Ni electrocatalyst, which displayed a superior HER electrocatalytic performance with an overpotential of 168 mV at 1,000 mA cm^{-2} and a high mass activity with a low loading of only 0.08 mg cm^{-2} of Ru_3Ni[100]. The density functional theory (DFT), finite-element-based simulations and experimental results comprehensively revealed that the enrichment of hydrated K^+ at the sharp tip led to the intensive polarization of interfacial H_2O and reduced the energy barrier for water dissociation [Figure 9B][100]. Tuning the local reaction environment in alkaline electrolyte has been shown to be a potential method to improve the HER catalytic performance. Tan *et al.* successfully developed a local H_3O^+-rich microenvironment, namely a local acid-like environment, in 1 M KOH solution and achieved superior HER performance[101]. Comprehensive analyses indicated that the formation of localized acid environments was mainly due to the following reasons: oxygen vacancy-rich MgO nanosheets can promote the production of H_3O^+; the redistribution of electrons between Pt and MgO results in the formation of electron-rich Pt species; owing to the electrostatic attraction, H_3O^+ accumulates around negatively charged Pt species. Consequently, as shown in Figure 9C-E, the Pt/MgO electrocatalyst displayed superb intrinsic HER activity (η_{10} = 39 mV) in 1 M KOH, which is even comparable to Pt/C under acidic conditions[101].

The additive in electrolyte can also regulate the structure of EDL to improve HER reaction kinetics. For instance, Amaral *et al.* investigated the impact of incorporating three homemade salicylate ([Sal])-based ionic liquids (ILs) in KOH electrolyte solutions on HER[102]. Electrochemical analysis indicated increased currents and a slight impact on activation energy in the IL-containing electrolytes. Tafel analysis and EIS demonstrate that the Volmer reaction is the rate-limiting step of HER, with a significant reduction in overall impedance observed in the IL-enhanced electrolytes, promoting stable operation. The charge transfer and polarization resistances are notably lowered in the IL-containing solutions, particularly following the addition of [Bmim][Sal], with the influence of the additives diminishing as temperature rises. This research suggested that incorporating small quantities of specific ILs into KOH electrolytes could enhance HER performance in alkaline environments[102]. Then, Amaral *et al.* also synthesized two bromide-based ILs and studied their impact as additives in alkaline electrolytes for HER[103]. Electrochemical analysis was conducted

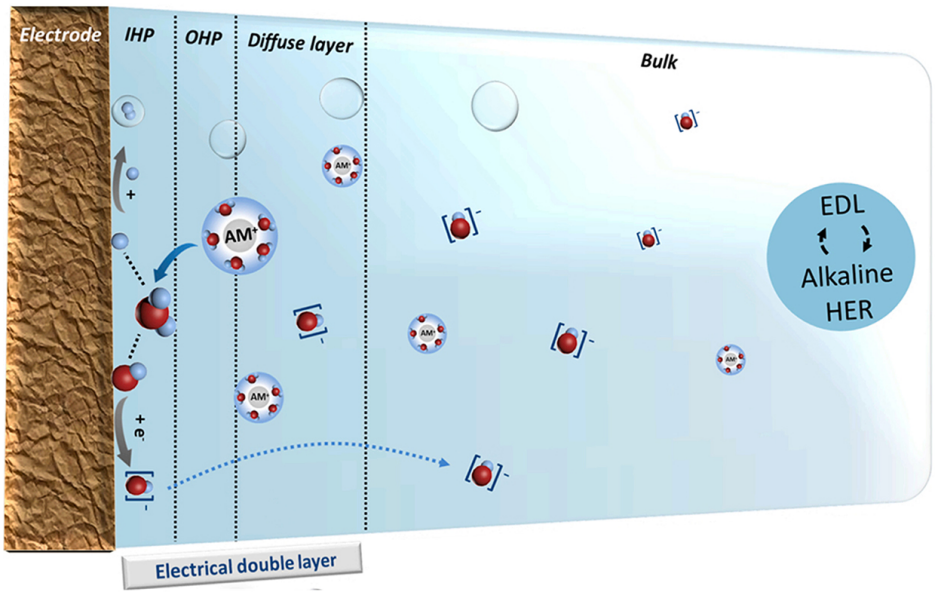

Figure 8. Simplistic view of EDL for alkaline HER. Red: O; Blue: H. This figure is quoted with permission from Jiang *et al.*[98].

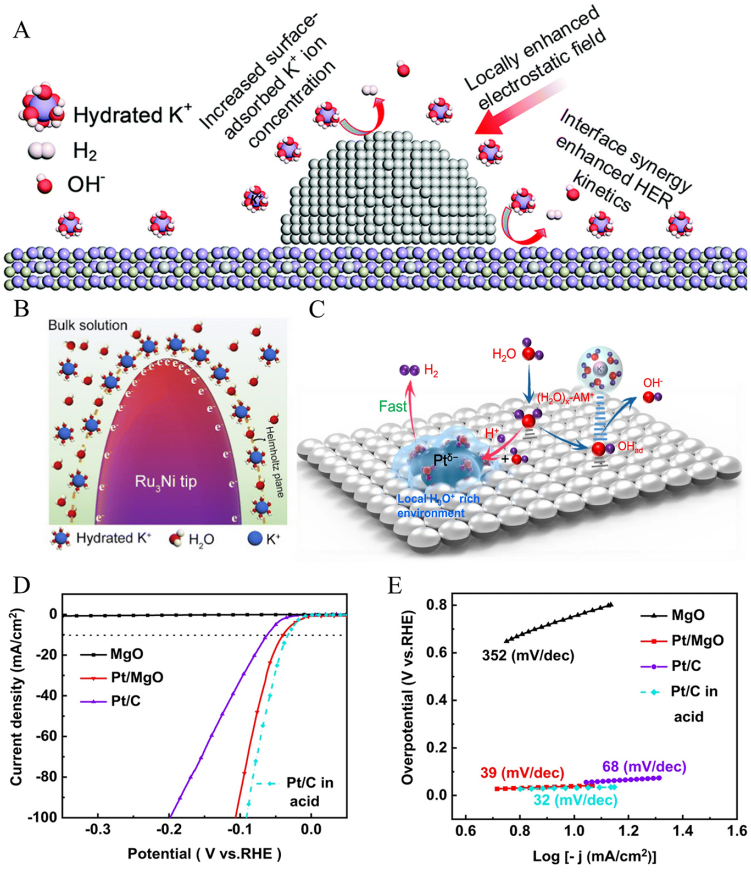

Figure 9. (A) Schematic diagram of the excellent activity of $Ni_{0.2}Mo_{0.8}N$/Ni. (B) Schematic representation of the interfacial model for Ru_3Ni. (C) Schematic representation of reaction mechanism. (D) Linear sweep voltammetry (LSV) curves of MgO, Pt/MgO, and Pt/C. (E) The corresponding Tafel plots were calculated from the LSV curves of MgO, Pt/MgO, and Pt/C. This figure is quoted with permission from Zhang *et al.*[99], Gao *et al.*[100] and Tan *et al.*[101].

using Pt electrodes in an 8 M KOH electrolyte without ILs and with the addition of 1 or 2 vol.% of each IL. The inclusion of 2 vol.% of [Beim][Br] resulted in higher current densities. These homemade bromide-based additives influenced the HER kinetics, resulting in slightly elevated Tafel slopes and minor changes in the charge transfer coefficient and exchange current density. Impedance measurements revealed a significant reduction in overall impedance in the presence of the bromide-based ILs in the alkaline electrolytes, with Nyquist plots showing a predominant intermediate frequency relaxation associated with adsorbed hydrogen. The bromide-based ILs demonstrate an improvement in electrolyte properties and enhance the efficiency of alkaline electrolysis[103].

SUMMARY AND OUTLOOK

In conclusion, as HER is an electrochemical process involving a ternary gas-liquid-solid interface, the rational design of multi-interface in electrodes is extremely significant for enhancing alkaline HER performance. Herein, we summarized the recent progress in interface engineering for Ni-based HER electrocatalysts, including substrate/electrocatalyst interface, internal heterointerface of electrocatalyst, and electrocatalyst/electrolyte interface. The latest advancements of interface engineering on Ni-based catalysts discussed in the review have been summarized in Table 1. The polymer binders can retard the electron transfer across the substrate/electrocatalytic interface (from the conductive substrate to the active site), so the method of in situ grown catalytic active materials on conductive substrates or directly preparing freestanding electrodes has been proposed to solve this problem. The intrinsic catalytic activity of electrocatalyst is closely related to its electronic structure, which can be rationally tuned by engineering its internal heterointerface. For example, the electron distribution at the interface can be well regulated by introducing defects or heterostructures, thus optimizing the adsorption and desorption behavior of key intermediate species to improve the catalytic performance. Moreover, the mass transfer at an electrocatalyst/electrolyte interface is particularly important under high current conditions in HER process. By adjusting the wettability of the catalyst surface and the EDL structure, the mass transport efficiency can be greatly improved. Although great progress and achievements have been made in advanced HER electrocatalysts by multi-interface engineering, several key issues remain to be addressed.

(1) The interfacial compatibility between the conductive substrate and catalytic materials can largely determine their binding strength, thus proving crucial for the overall stability of the electrode, especially for the high current density working conditions in alkaline medium. The generation, coalescence, and detachment of large amounts of gas bubbles could induce great stretch pressure at the interface, which would not only result in decreased effective surface area and high ionic diffusion resistance but also bring fatal damage to the electrode structures. Therefore, delicate interface construction aiming to minimize the bubble size while maximizing their transport/release should be given more attention, which has not been fully investigated.

(2) It is well established that defects or heterogeneous interfaces can lead to charge redistribution at the interface, which can achieve rational regulation of the adsorption/desorption characteristics of key reaction intermediates. As an important intrinsic determinant, the intrinsic electronic structure and interactions with intermediates can also determine the electrocatalyst by influencing the intrinsic conductivity and reaction energy barrier. For alkaline water splitting, OH_{ad} has an important role in both cathodic (HER) and anodic (OER) reactions. It had been pointed out that the adsorption behavior of OH_{ad} is deeply intertwined with OER activity, which is associated with the bonding strength of the active site and oxygen. The crystal field theory provides theoretical guidance for the design of OER electrocatalyst. In octahedral symmetry, the *d*-orbital and ligand electrons repel each other, causing the *d*-orbital energy levels to split into high-energy orbitals e_g and low-energy orbitals t_{2g}. The occupancy of e_g orbitals in the design of OER catalysts has been

Table 1. Summary of Ni-based catalysts for alkaline hydrogen evolution reaction

Catalysts	Substrate	Electrolyte	Current density (mA cm^{-2})	Overpotential (mV)	Ref.
MoO_2-Ni NWs	Ni foam	1 M KOH	10	58.4	[42]
$Ni_4Co_1Fe_4$-P	Ni foam	1 M KOH	20	61	[43]
Ni-Cu-P@Ni-Cu	Ni foam	1 M KOH	10	70	[44]
Ru@Ni-MOF	Ni foam	1 M KOH	10	22	[45]
Ni NTAs/NF	Ni foam	1 M KOH	10	101	[46]
MoO_2/Ni@NF	Ni foam	1 M KOH	10	50.5	[47]
Ni-WOx@NF	Ni foam	1 M KOH	10	45.7	[48]
W-NT@NF	Ni foam	1 M KOH	10	88	[49]
Ni/TiO_2	Ni foam	1 M KOH	10	46	[50]
NiFeCoS_x@$FeNi_3$	$FeNi_3$ foam	1 M KOH	10	88	[51]
Ni-Co alloy		1 M KOH	10	54	[52]
Cu_2S@Ni	Cu foam	1M NaOH	500	200	[53]
W_2C-Ni/CC	Carbon cloth	1 M KOH	10	37	[54]
NiO/Ni@CC	Carbon cloth	1 M KOH	10	40	[55]
Ni-Ni_3C/CC	Carbon cloth	1 M KOH	10	98	[56]
Ni/V_2O_3	Carbon cloth	1 M KOH	10	44	[57]
Ni/NiO-CNTs		1 M KOH	10	98	[59]
C-20Ni-Pd		1 M KOH	10	590	[60]
Ni/CeO_2@N-CNFs		1 M KOH	10	100	[61]
Fe@Ni NFs		1 M KOH	10	55	[62]
$Ni_{0.95}Cu_{0.05}$DSS		1 M KOH	100	179	[63]
Ni-Ni_3P@NPC/rGO		1 M KOH	20	200	[64]
Vs-Ni_3S_2/NF	Ni foam	1 M KOH	10	88	[65]
Ni/NiFeMoOx/NF	Ni foam	1 M KOH	10	22	[66]
Ni/MoO_{2-x}/NF	Ni foam	1 M KOH	10	27	[67]
Ni-$MoSe_2$	Carbon cloth	0.1 M KOH	10	98	[68]
$Co_{0.9}Ni_{0.1}Se$		1 M KOH	10	185.7	[69]
Ni/NiO-400	Carbon cloth	1 M KOH	10	41	[70]
P-V-NiFe LDH NSA	Ni foam	1 M KOH	10	19	[71]
Mo-NiO/Ni		1 M KOH	10	50	[72]
SGNCs		1 M KOH	10	27	[73]
NiFe@Pt		0.1 M KOH	10	70	[74]
Ni/NiFe-LDO	Ni foam	1 M KOH	10	29	[75]
Ni-Fe NP	Carbon fiber paper	1 M KOH	10	46	[76]
Ni/Yb_2O_3		1 M KOH	10	81	[77]
$Ni(OH)_2$@Ni-N/Ni-C	Ni foam	1 M KOH	10	60	[78]
Ir@Ni-NDC		1 M KOH	10	19	[79]
Co-Ni-P/MoS_2		1 M KOH	10	116	[80]
Ni/$Ni(OH)_2$		1 M KOH	10	77	[81]
Ni-$Ni(OH)_2$/NF	Ni foam	1 M KOH	10	72	[82]
Cu_2O@NWNH	Cu foam	1M PBS	10	39	[83]
Ni/MoO_2@NF-E	Ni foam	1 M KOH	10	19	[84]
Ni-MoN	Cu foam	1 M KOH	100	61	[85]
Ni-NiO/$Ti_3C_2T_x$		1 M KOH	10	72	[86]
Ni-CeF_3-VN	Ni foam	1 M KOH	10	33	[87]
NiS-Ni_2P/Ni/NF	Ni foam	1 M KOH	10	53	[88]
Ni-80	Ni film	1 M KOH	10	135	[91]
$MoNi_4$-MoO_2	3DP Ni	1 M KOH	500	104	[92]

Ni microdots	Cu film	1 M KOH	50	476	[93]
Ni NCNAs	Ni foam	1 M KOH	10	47	[95]
Ni-Sb alloy	Graphite	1 M KOH	10	158	[96]
Pt/Ni-Mo-N-O	Ni foam	1 M KOH	100	40.6	[97]
$Ni_{0.2}Mo_{0.8}N$/Ni	Ni foam	1 M KOH	100	40	[99]
NA-Ru_3Ni/C		1 M KOH	1000	168	[100]

widely used as a descriptor of bonding strength between the active site and oxygen. Transition metal ions with e_g orbital occupancy approaching 1 generally have better OER intrinsic activity. Active atoms with high occupancy ($e_g > 1$) will be too weakly bonded to oxygen, while low occupancy ($e_g < 1$) will be too strongly bonded to oxygen. Based on the above understanding, for the design of internal heterointerface of electrocatalyst towards alkaline HER, the adsorption strength of OH_{ad} can also be tuned by adjusting the e_g orbital occupancy of the active site so as to promote water dissociation or alleviate the poison effect of OH_{ad}. Moreover, understanding its intrinsic mechanism is mostly based on the oversimplified theoretical calculations and lack of effective *in-situ* characterization. Therefore, the effect of the internal heterointerface of electrocatalyst is worthy of further study.

(3) At present, few researches focus on mass transfer at gas-liquid-solid interface, namely, electrocatalyst/electrolyte interface. In fact, for the industrial water electrolyzer, the mass transfer capacity of the electrocatalyst under high current conditions is particularly important, which can be improved by engineering wettability and EDL of the electrocatalyst. Nevertheless, the reaction mechanism and its physical structure at the electrocatalyst/electrolyte interface need more in-depth study, which depends on more accurate in situ characterization techniques.

In fact, when optimizing the substrate/electrocatalyst interface, constraints imposed by the substrate characteristics often limit the use of milder methods for in situ growth of active species on the conductive surface. To enhance the intrinsic activity of electrocatalysts, commonly employed methods, such as high-temperature treatments or mechanical ball milling, are utilized to introduce defect sites at the internal interface of electrocatalysts. However, this approach is in conflict with the mild reaction conditions required for optimizing the catalyst-substrate interface, posing challenges to achieving both objectives simultaneously. Furthermore, optimizing the electrocatalyst/electrolyte interface through control of wettability or EDL is predominantly achieved by modulating the surface morphology of the electrocatalyst. However, this process necessitates changes in reaction conditions, making it challenging to simultaneously meet the growth requirements of active species and precisely introduce defect sites, thereby imposing higher demands on material synthesis methods.

Although optimizing three interfaces simultaneously poses certain challenges through conventional experimental methods, the integration of advanced material synthesis techniques can partially mitigate this issue. For example, after growing active species on a conductive substrate using conventional hydrothermal synthesis, plasma etching can introduce vacancy-like defect sites on the electrocatalyst surface. Additionally, techniques such as magnetron sputtering or atomic layer deposition can be combined to precisely fabricate heterostructures on the electrocatalyst surface to enhance the intrinsic catalytic activity. These methods differ from conventional approaches in their ability to circumvent the need for harsh reaction conditions and stringent substrate requirements, thereby enabling simultaneous optimization of all three interfaces alongside traditional preparation techniques.

In summary, the multi-interface design for the electrocatalyst is crucial to the HER electrocatalyst performance, including activity and stability. When designing efficient HER electrocatalysts, it is imperative to consider the synergistical modulation of these three key interfaces simultaneously.

DECLARATIONS

Authors' contributions

Proposed the topic of this review: Wang C
Wrote the manuscript: Zhang X, Guo Y, Wang C
Reviewed the manuscript: Wang C

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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