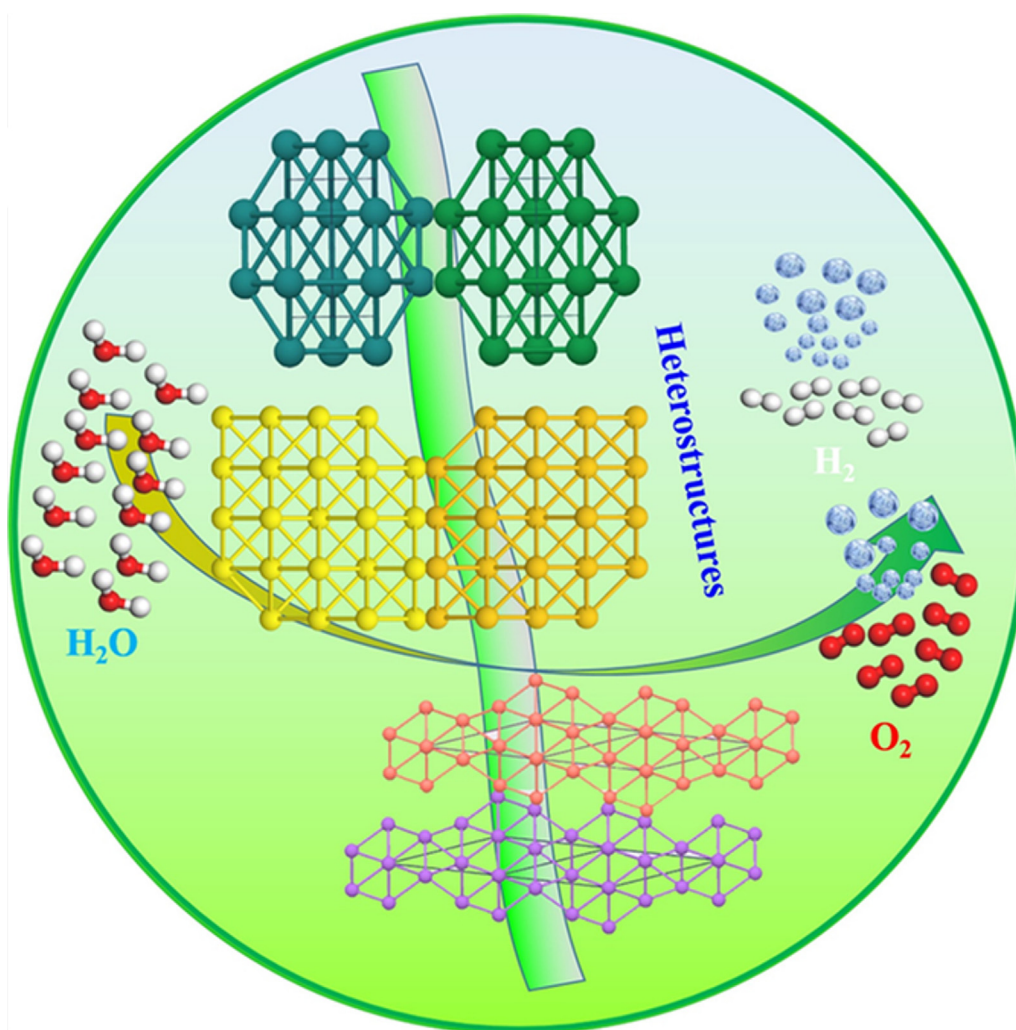


REVIEW

Rational Design of Heterostructured Nanomaterials for Accelerating Electrocatalytic Hydrogen Evolution Reaction Kinetics in Alkaline Media

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Abstract

Owing to the merits of high energy density, as well as clean and sustainable properties, hydrogen has been deemed to be a prominent alternative energy to traditional fossil fuels. Electrocatalytic hydrogen evolution reaction (HER) has been considered to be mostly promising for achieving green hydrogen production, and has been widely studied in acidic and alkaline solutions. In particular, HER in alkaline media has high potential to achieve large-scale hydrogen production because of the increased durability of electrode materials. However, for the currently most prominent catalyst Pt, its HER kinetics in an alkaline solution is generally 2–3 orders lower than that occurring in an acidic solution because of the low H^+ concentration in alkaline electrolytes. Fortunately, construction of heterostructured electrocatalysts has proved to be an efficient strategy for boosting alkaline HER kinetics because of their various structural merits. The synergistic effect is a unique characteristic of heterostructures, which means that one functional active site serves as a promoter for water dissociation and another one takes a charge of moderate hydrogen adsorption, thus synergistically improving HER performance. In addition, each building block of the heterostructures is tunable, providing more flexibility and chances to construct optimal catalysts. Furthermore, due to the presence of Fermi energy difference between the two components at the interface, the electronic structure of each component could possibly be rationally modulated, thus much enhanced HER performance in alkaline electrolyte can be achieved. With a deeper understanding of on nanoscience and rapid development of nanotechnology, more sophisticated alternative designing strategies have been explored for constructing high-performance heterostructured electrocatalysts. This review presents an outline of the latest development of heterostructured catalysts toward alkaline HER and the rational design principles for constructing interfacial heterostructures to accelerate alkaline HER kinetics. The basic reaction pathways of HER in alkaline media are first described, and then emerging efficient strategies to promote alkaline HER kinetics, including synergistic effect, strain effect, electronic interaction, phase engineering, and architecture engineering. Finally, current existing challenges and research opportunities that deserve further investigation are proposed for the consideration of novel heterostructures towards practical applications.

Keywords: Interfacial heterostructure; Hydrogen production; Water dissociation; Hydrogen adsorption; Synergistic effect

1. Introduction

Traditional fossil fuels are unsustainable energy sources with high carbon contents, hence large consumption of fossil fuels has led to energy crisis and severe environmental problems inevitably, which prompts the exploration on sustainable and effective alternatives to traditional fossil fuels. Hydrogen has carbon-free feature and high mass energy density (ca. $120 \text{ MJ} \cdot \text{kg}^{-1}$), thus it has been considered as the most promising candidate for solving the above increasing issues [1,2]. To make hydrogen competitive with fossil fuels, producing hydrogen in an energy-efficient, cost-effective, and environmental-friendly manner is crucially important.

Electrochemical water splitting, which consists of cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER), has long been regarded as a highly promising and efficient route to the sustainable production of hydrogen [3,4]. Generally speaking, the performance of both cathodic HER and anodic OER electrocatalysts is the key factor that determines the overall efficiency of electrochemical water splitting [5,6]. Specifically, the cathodic HER kinetics in an alkaline condition is much slower as compared to that in an acidic condition, as the H^+ concentration in alkaline electrolytes is much lower. Furthermore, different from the acidic HER process, the alkaline HER process

involves water molecule dissociation step (the Volmer step) to produce hydrogen atoms, which is relatively difficult to occur [7–9]. Hence, it remains challenging to rationally design and prepare high-performance HER electrocatalysts toward large-scale hydrogen production in alkaline conditions.

Generally, in alkaline media, HER process proceeds in two steps: (1) a water molecule is cleaved on the catalyst surface, generating a OH^- ion and a hydrogen adatom (H_{ads} , the Volmer step); (2) the formed hydrogen adatom interacts with another water molecule (the Heyrovsky step) or combines with another hydrogen atom (the Tafel step) to form the product of a hydrogen molecule. As each of these steps requires different adsorption intermediates, it is remarkably complex to obtain efficient catalysts that can accelerate the reaction rates of both steps [8]. Even for the most distinguished catalyst, Pt, it is unable to efficiently catalyze the water molecule cleavage in alkaline media, hence the Volmer step is the rate-determining step (RDS) of Pt and its catalytic activity is generally considered to be lower than that in acidic media by 2–3 orders [8,10,11]. Though many efforts have been devoted into this research area, the HER performance of most currently reported catalysts cannot fulfill the requirement for industrial application.

Recently, the rational design of interfacial heterostructures has exhibited great potential to break the bottleneck in this area and attracted significant

research attention. Typically, heterostructured materials have two or more categories of active sites at the interface, which is very beneficial for promoting the alkaline HER process. For instance, in the previously reported Pt/Ni(OH)₂ heterostructure catalyst, Ni(OH)₂ species take charge of water molecule dissociation, while Pt species are highly responsible for the hydrogen atom adsorption and the final product hydrogen molecule formation. Since Ni(OH)₂ has strong water molecule cleavage capability, and Pt has moderate hydrogen adsorption energy approaching the ideal adsorption state, much enhanced HER activity in alkaline media is achieved on Pt/Ni(OH)₂ heterostructure owing to the interfacial synergistic effect [12]. This type of bicomponent materials exhibits much promoted HER activity compared with the corresponding mono-component catalysts. In addition, each component of the heterogeneous materials is adjustable, providing more flexibility and chances to construct optimal catalysts. Furthermore, due to the presence of Fermi energy difference between the two components at the interface, the electronic structure of each component could possibly be rationally modulated, thus much improved HER performance in alkaline media can be achieved.

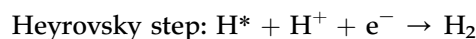
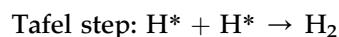
Although many of the reported heterostructured catalysts have been shown to exhibit much improved catalytic activity, some drawbacks from the heterostructure combination need to be settled. For instance, many types of electrocatalysts still show very limited catalytic activity and stability because their active sites are only located at the interface area of heterostructure, making the utilization rate of active sites in the whole heterostructure incredibly low [10,13–18]. Moreover, because of the relatively high cost and low reserve of noble metal Pt, the rational devise and fabrication of heterostructured catalysts with high performance and free of platinum group metal (PGM) toward large-scale hydrogen production in alkaline media are urgently desired [19–23], but it remains significantly challenging to make the electrocatalytic performance of PGM-free materials competitive to Pt-based catalysts [24–33]. To break the above bottlenecks, several efficient strategies for rational design of heterostructures on the nanoscale have been developed [34–46]. Therefore, it is important to summarize the latest progresses in the rational devise and synthesis of advanced heterostructured electrocatalysts for alkaline HER.

Herein, first, the fundamentals and principles of HER are briefly introduced, with emphasis on the reaction processes in alkaline conditions. Based on the alkaline HER mechanisms, efficient strategies for accelerating the catalytic performance of

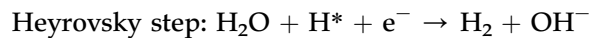
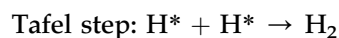
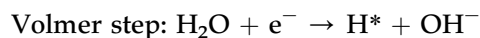
heterostructures, including synergistic effect, strain effect, electronic interaction, phase engineering, and architecture engineering, are then detailedly discussed. Lastly, the challenges and perspectives in designing efficient heterostructured electrocatalysts are provided. This review article is intended to outline the major challenges and key reaction mechanisms underlying the promotion of catalytic activity for interfacial heterostructures, which are expected to inspire more innovative designs of novel heterostructures for catalytic applications in the near future.

2. Basics and rational design principles of heterostructures for alkaline HER

In general, the HER process occurring in different media is a two-charge transfer reaction, which requires efficient electrocatalysts to overcome the Gibbs free energy barrier of every intermediate step, especially the energy barrier of the RDS. Under acidic conditions, the generally accepted HER pathways are related to the adsorption/desorption of a hydrogen intermediate (H*) via the Volmer-Tafel or the Volmer-Heyrovsky mechanism [8–10]. The detailed reaction pathways occurring in an acidic HER process are listed as following:



Different from the pathways of acidic HER, the intermediate H* under alkaline conditions is considered to be produced from H₂O molecule dissociation rather than proton ion reduction. The reaction pathways of HER in alkaline electrolytes can be expressed as following:



The reaction pathways for both acidic and alkaline HER are depicted in Fig. 1. Generally, the energy needed to actuate the entire reaction is dependent upon the involved reaction routes. Electrocatalysts in alkaline conditions usually show lower activity in acidic solutions [47,48]. The

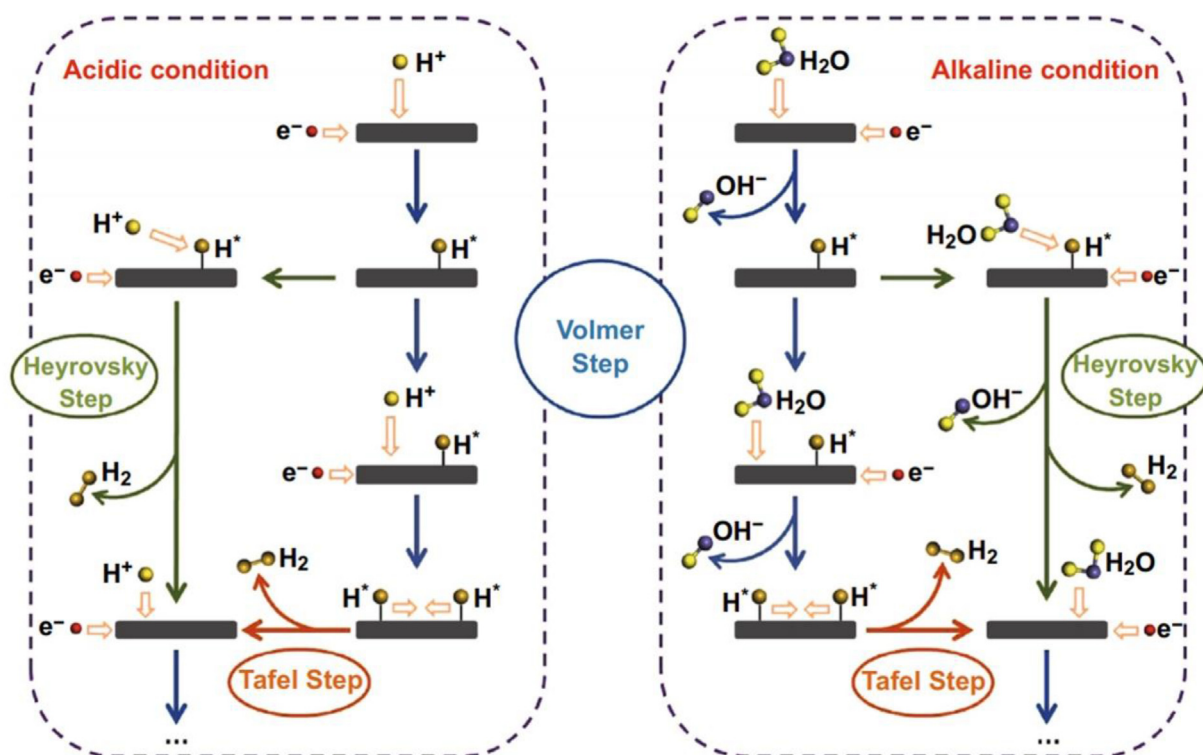


Fig. 1. Schematics showing the reaction pathways of HER under acidic and alkaline conditions. (Reprinted with permission from reference [64]. Copyright 2018, Springer).

significantly lower H^* coverage ratio in an alkaline condition than that in an acidic condition makes the Volmer step the RDS in an alkaline HER process. Recent studies have shown that the intrinsic HER activity in an alkaline condition is mainly determined by hydrogen-binding energy (HBE) and hydroxyl-binding energy (OHBE) on electrocatalysts surface, as well as water dissociation energy [49–51]. Active sites with moderate HBE are desired to achieve efficient hydrogen species adsorption and hydrogen molecule desorption simultaneously. Whereas active sites with higher OHBE in heterostructured catalysts are favorable for water molecule dissociation [52,53]. Quantitative analysis of these factors that contribute to the alkaline HER kinetics needs further investigation.

Many practical strategies have proven to be effective in promoting alkaline HER performance. For example, alloying of transition metals is demonstrated to be a significantly efficient approach to improve HER performance in alkaline electrolytes. Thanks to the optimized electronic states, Ni_4Mo nanoparticles have demonstrated excellent catalytic activity, comparable to benchmark Pt/C [54,55]. However, the unsatisfactory stability of transition metal alloys under alkaline conditions limits their large-scale industrial application [56–58]. Encouragingly, many research works have reported that building interfacial heterogeneous structures is a

highly effective strategy to achieve excellent alkaline HER activity and stability simultaneously. Since Markovic's group originally demonstrated that the HER electrocatalytic activity in $1.0 \text{ mol} \cdot \text{L}^{-1}$ KOH electrolyte could be increased by seven times via depositing homogeneously dispersed $Ni(OH)_2$ nanoclusters on Pt electrode [12], great progresses on fabricating high-performance interfacial heterostructures with minimal utilization of or even free of noble metals have been achieved.

On the consideration of the above basics and fundamental principles for alkaline HER, the rational design principles of interfacial heterostructures for accelerating alkaline HER kinetics can be summarized as follows: 1) the electron conductivity of heterostructured catalysts should be as high as possible to fulfill the requirement of electrocatalysis; 2) one component of the heterostructures should have strong capacity to dissociate water molecules, which is always considered to be the RDS for the alkaline HER; 3) the component taking charge of water molecule dissociation usually should possess strong hydroxyl adsorption capacity, which is favorable to enrich water molecules around the active sites for accelerating alkaline HER kinetics; 4) another composition responsible for the Heyrovsky/Tafel steps should have suitable H^* intermediate adsorption energy, usually considered to be as

close to zero as possible, which is believed to be beneficial for both hydrogen molecule formation and desorption; 5) The combination of two components in interfacial heterostructures should be better favorable for efficiently modulating the electronic structure of multifunctional active sites, accelerating the Volmer and Heyrovsky/Tafel steps, or even the OER kinetics simultaneously.

3. The emerging efficient strategies for promoting alkaline HER kinetics

Theoretically, improvements in the reaction rates of either Volmer step or Heyrovsky/Tafel step can lead to alkaline HER improvement. Specifically, most of the reported results illustrate that the H₂O dissociation process is the RDS in alkaline electrolytes [59–62], which is mainly ascribed to the very stable H–OH bonds of water molecules. However, the electrocatalytic performances of interfacial heterostructures are actually barely satisfactory if the active sites adsorb hydrogen atoms too strongly or too weakly [11]. Therefore, to design high-efficiency electrocatalysts toward alkaline HER, careful consideration needs to be taken on both the Volmer and Heyrovsky/Tafel steps. After exploring numerous heterostructured electrocatalysts applied in alkaline HER, the five most important strategies for improving catalytic performances are summarized, which can provide a guideline for further design of advanced novel interfacial heterostructures.

3.1. Synergistic effect

The synergistic effect is utilized to describe an interesting phenomenon, which is widely existed in nature: two factors corporately function much better than a mere combination of the two parts [63,64]. Most importantly, if one component has strong water molecule cleavage capacity, and another component has moderate hydrogen atom adsorption capacity, the whole HER rate can be significantly improved after the effective combination of the two functional active sites by constructing heterostructure interfaces, which is the core meaning of synergistic effect.

As discussed above, the alkaline HER process involves H₂O cleavage step that yields adsorbed H* intermediate at first and the Heyrovsky or Tafel step to generate H₂ molecule subsequently. It has been widely reported that the benchmark Pt electrocatalyst is highly active for the Heyrovsky or Tafel step. The combination of Pt with another component, which has strong hydrolysis capacity, can be an efficient route to accelerate HER kinetics.

As shown in Fig. 2a, H₂O molecules preferred to be cleaved at the margin of Pt cluster and near the Ni(OH)₂ surface, proving significantly boosted H₂O molecule cleavage capacity on Ni(OH)₂ [65].

Apart from Pt, precious-metal Ru has also been demonstrated to be efficient for upgrading alkaline HER kinetics. For instance, Wang et al. fabricated hollow (Ru-Co)O_x nanosheet arrays (Fig. 2b) derived from hollow Ru-Co metal-organic framework via the nano-Kirkendall effect. The atomic and electronic structures of the as-prepared (Ru-Co)O_x nanosheet arrays were carefully investigated in detail. The atomic structure was revealed by selected area electron diffraction (SAED) pattern (Fig. 2c) and high-resolution transmission electron microscopic (HRTEM) image (Fig. 2d), which showed randomly arranged nano-crystallites with clear lattice fringes that were assigned to the (101) and (400) planes of Co-doped RuO₂ and Ru-doped Co₃O₄, respectively, substantiating that the inter-doped (Ru-Co)O_x heterostructured nanosheets were formed. As for the electronic structure (Ru-Co)O_x, it is modulated by the presences of heteroatom doping and heterogeneous nano-interface, thus optimizing active Ru sites to achieve the goal of weakening intermediate H* adsorption. In addition, owing to the wide existence of well-acknowledged interfacial synergistic effect in heterostructured materials, the Co sites in Ru-doped Co₃O₄ may accelerate water molecule dissociation step for enhanced alkaline HER performance [66]. Similar to noble-metal-based materials, PGM-free heterostructured electrocatalysts have also exhibited much enhanced catalytic performance because of the existing interfacial synergistic effect. Zhou's group synthesized MoC/FeO/CoO/CC electrocatalyst via the conversion from metal precursors by rapid Joule-heating method. The corresponding HRTEM images demonstrate the formation of heterostructures. Because multi-component heterostructures consist of multi-metallic carbides and oxides, which provide ample active sites coupled with the complex synergistic effect between different components for boosting electrocatalysis, the overpotential for the as-prepared MoC/FeO/CoO/CC catalyst to reach the current density of 10 mA·cm⁻² toward alkaline HER was only 121 mV [67].

Although synergistic effect can efficiently promote alkaline HER kinetics, the synergistic effect in heterostructure engineering has its own drawbacks. For example, the heterostructured catalysts for alkaline HER might experience potential surface reconstruction in the electrochemical reaction process [68], which gains more difficulty in

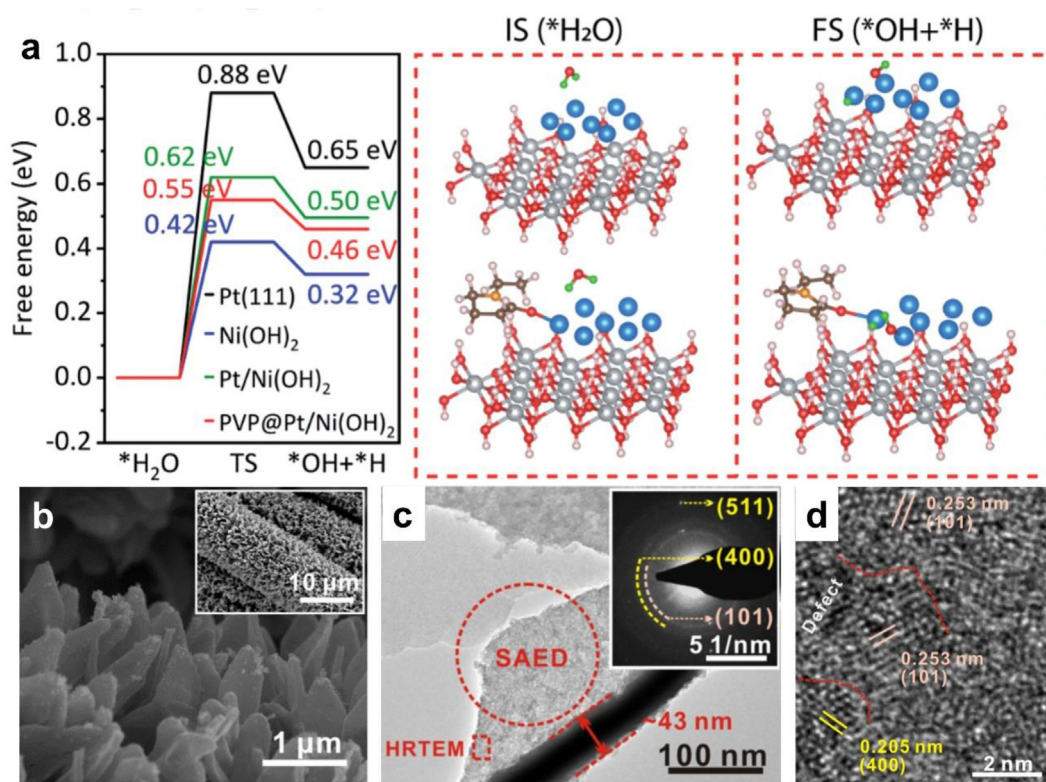


Fig. 2. (a) The energy profiles for H_2O dissociation on different substrate surfaces. The initial (IS) and final (FS) optimized configurations of H_2O adsorption and dissociation on the $\text{Pt}/\text{Ni}(\text{OH})_2$ (top) and $\text{PVP}@/\text{Pt}/\text{Ni}(\text{OH})_2$ (bottom) surfaces are presented on the right. [Reprinted with permission from reference [65]. Copyright 2021, Royal Society of Chemistry]. (b) SEM, (c) TEM and (d) HRTEM images of $(\text{Ru-Co})\text{O}_x$ nanoarrays. Inset in (b) is a low-magnification SEM image of $(\text{Ru-Co})\text{O}_x$ nanosheet arrays, and the inset in (c) shows the related SAED pattern of $(\text{Ru-Co})\text{O}_x$ nanoarrays. [Reprinted with permission from reference [66]. Copyright 2020, Wiley-VCH].

detecting the real active sites responsible for intrinsic HER. Therefore, a concrete analysis of each specific catalytic system is required to explore the influence of surface reconstruction on the interface environment. And the balanced factors contributing to the enhanced activity, including ensemble effect and electronic effect, should be carefully weighted to explain the catalytic mechanism [68].

3.2. Strain effect

The differences in crystal structures and chemical compositions of two or multiple components can lead to lattice mismatch. Generally speaking, the lattice mismatch in heterostructures can manifest as lattice strain, which originates from the comprehensive interaction of tension and compression. In the past decades, lattice strain engineering is a promising strategy to promote electrocatalytic activity and is commonly employed in electrochemical reactions [69,70], such as water splitting, nitrogen fixation, oxygen reduction, carbon dioxide reduction, nitrite reduction, and methanol oxidation. In general, the role of lattice strain engineering is limited and the catalytic

enhancement is remarkable in most situations when the intrinsic catalytic activity is approaching the volcanic vent. The relevant volcanic plots corresponding to water molecule dissociation and H^* intermediate adsorption in alkaline HER processes are shown in Fig. 3 [71,72]. Considering these factors, the strain effect functions better in noble-metal-based heterostructures. For instance, strain engineering is able to significantly improve the intrinsic HER activity of Pt/Ir/Rh-based heterostructured materials in an alkaline condition since the intrinsic catalytic activity of these novel metals for alkaline HER locates near the peak of the volcano plot [73,74].

As for the functional mechanism of improving catalytic activity by introducing lattice strain, it is usually perceived that introducing lattice strain into electrocatalysts can effectively modulate the adsorption/desorption strength of various reactants and intermediates, thus the calculated Gibbs free energy differences of proposed reaction pathways and energy barrier of the RDS can be probably regulated, therefore the intrinsic activity of nanoscale catalysts can be increased accordingly. Furthermore, based on the classical d-band center theory, it is generally accepted that once a

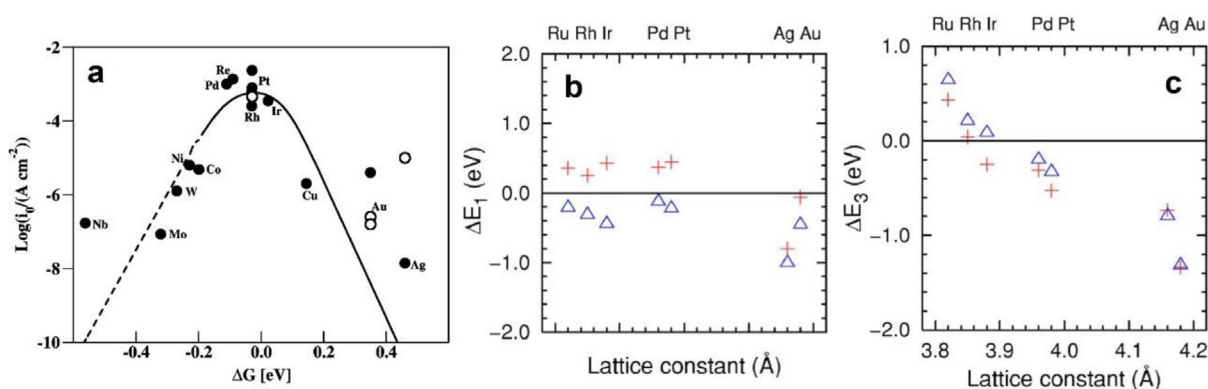


Fig. 3. (a) Calculated energies of H^* adsorption on some pure transition metals. [Reprinted with permission from Reference [72]. Copyright 2010, American Chemical Society. (b) Water molecule dissociation barrier on several oxygen-covered pure Pt-group metals. (c) Water molecule dissociation barrier on clean surfaces of several pure Pt-group metals. Reprinted with permission from Reference [71]. Copyright 2006, American Physical Society.

shift occurs in the d-band center of active metals, the binding energy of adsorbates on catalysts surface could be efficiently modulated [75,76], thus the intrinsic HER catalytic activity under an alkaline condition can be substantially promoted. Studies have shown that by introducing 1% lattice strain, the calculated d-band center can be shifted by ca. 0.1 eV relative to the Fermi level [77]. For instance, Kim et al. prepared Pt-based core-shell nanocrystals applied in alkaline HER (Fig. 4).

The Pt-based core-shell nanocrystals consist of metallic Pd polyhedron serving as the core and outer layer Pt acting as the thin shell, and the lattice mismatch between the two crystal phases leads to the typical strain effect. Experimental and theoretical calculations indicate that both compressed and tensile strain effects can be obtained by changing the crystal structure of the inner core species. For instance, using PdH with larger lattice parameters as the inner core, tensile strain effect of outer Pt shell can be achieved; while choosing Pd with smaller lattice parameters as the inner core, compressed strain effect of outer Pt shell can be observed. Further investigation found that the strength of strain effect decreases as the thickness of outer Pt shell increases. The high-angle annular dark-field scanning transmission electron microscopic (HAADF-STEM) image clearly confirms that the Pt (111) lattice spacing of PdH@Pt is expanded to 2.28 Å (Fig. 4b), causing the formation of a small tensile strain on Pt surface, which induced a decreased average work function value and shifted d-band center of Pt sites, thus optimizing H^* and OH^* adsorption energies, leading to a weaker H^* intermediate binding strength and stronger water molecule dissociation capacity, boosting alkaline HER performance correspondingly. Theoretical investigation results indicate that compared with the estimation of the ideal periodic model, the

lattice strain effect is reduced with the relaxation of uppermost Pt layer, and the corresponding hydrogen intermediate adsorption strength diminishes and water molecule dissociation ability strengthens as the Pt layer number increases [78]. In addition, constructing typical core-shell nanostructures can also efficiently improve the reaction kinetics of Heyrovsky/Tafel step due to the effective regulation of surface electronic structures of active metal sites. For example, Tian's group designed and fabricated Au@Pd constituted core-shell nanostructure as a significantly efficient catalyst for alkaline HER [79]. Detailed experimental analysis results demonstrate that the significant improvement of alkaline HER activity results from the lattice strain effect induced by constructing the extraordinary core-shell nanostructure. Specifically, lattice mismatch exists in Au@Pd_{1,0} due to the different lattice parameters between the core Au nanoparticle and surrounded Pd shell. Such mismatch induces lattice strain over a few atomic layers around the interface, resulting in the shift of d-band center. The altered d-band center could affect the adsorption of reactant species and thus alter catalytic activity. For the Au@Pd_{1,0} sample, the optimal lattice strain led to the optimized H^* adsorption energies, thus the best catalytic activity toward alkaline HER was achieved. Aiming to reduce the fabrication cost of catalysts, many efforts about the application of strain effect in non-precious metal-based catalysts have been devoted, unfortunately, the relevant progress is not satisfying. As a representative example in this field reported by Cai's group, a nickel catalyst with compressive strain was fabricated via one-step electrochemical deposition. The as-prepared nickel catalyst exhibited enhanced HER activity in 1.0 mol·L⁻¹ KOH electrolyte, which shows an overpotential of 85.9 mV at the

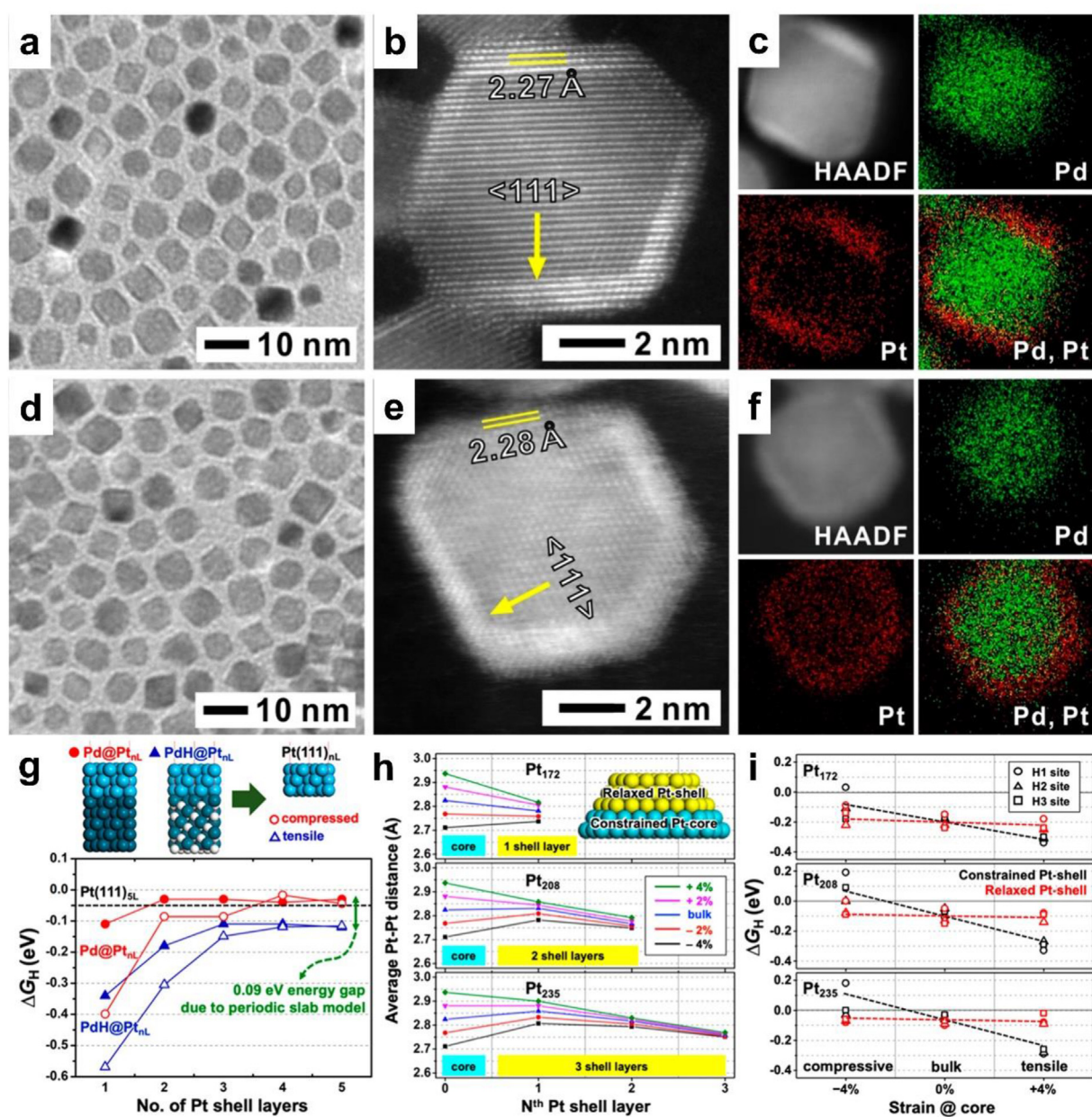


Fig. 4. Low-magnification TEM images of (a) Pd@Pt and (d) PdH@Pt core-shell octahedra. HAADF-STEM images of (b) a Pd@Pt and (e) a PdH@Pt octahedron. EDS elemental mappings of (c) a Pd@Pt and (f) a PdH@Pt octahedron. (g) Calculated Gibbs free energy of H adsorption (ΔG_H) for the Pd@Pt_{nL} (filled circles) and PdH@Pt_{nL} (filled triangles) core-shell models with different number of Pt layers. The ΔG_H values for bare, tensile and compressed Pt(111)_{nL} are represented by the dashed line, empty triangles and empty circles, respectively. (h) Average in-plane Pt-Pt distance in the nonperiodic nanocluster models that consist of 1–3 layers of relaxed Pt shells and two-layer constrained Pt cores. (i) Calculated ΔG_H for the nonperiodic nanocluster models without (black) and with (red) geometrical relaxation. Reprinted with permission from reference [78]. Copyright 2019, American Chemical Society.

current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ associated with a Tafel slope of $91.4 \text{ mV} \cdot \text{dec}^{-1}$ [80].

Even though the strain effect in heterostructure engineering can efficiently improve alkaline HER kinetics, some important challenges need to be addressed to promote the application of strain effect in practical alkaline water electrolysis. For example, how to finely control the strength of strain effect to achieve the goal of significantly boosting electrocatalytic activity remains to be a

major obstacle [81]. Another limitation of strain engineering is its application scope. The performance enhancement induced by strain effect is limited, which usually works well in materials with H* adsorption strength approaching the volcanic maximum. Most of these candidates are noble-metal-based materials, which will inevitably increase the fabrication cost of advanced catalysts toward green hydrogen production. The final concern about strain effect in electrolysis is the

issue of catalytic stability after introducing tensile or compressed strains on the surface or subsurface of nanomaterials [82].

3.3. Electronic interaction

Electronic interaction abundantly exists in interfacial heterostructures. The interaction of different components in heterostructures can efficiently accelerate electron transport at the interface. To be specific, the differences in the Fermi energy and band alignment of the two or multiple components in heterostructures can result in electron transfer at the interfaces, which is favorable for modulating electronic structure of heterostructured catalysts [83–85]. Based on the above design principle, multi-metallic catalysts have been developed to achieve optimum H^* binding strength through efficient modification of surface electronic structures. The HER performance on Pd overlayer supported on a series of metallic surfaces follows a volcano relation, and Pd/PtRu catalyst exhibits the highest HER catalytic activity owing to its near zero adsorbed H^* binding energy [86]. Apart from noble-metal-based heterostructures for accelerating alkaline HER kinetics, non-noble-metal-based heterostructures are growing rapidly in the exploration of advanced alkaline HER catalysts. For example, Zhang et al. fabricated an interfacial $CePO_4/MoP$ heterostructure catalyst loaded on carbon cloth (CC) by precisely anchoring a rare earth metal compound $CePO_4$ onto MoP for electrochemical alkaline water splitting. Experimental test results show that $CePO_4/MoP/CC$ exhibited higher alkaline HER catalytic activity than MoP/CC and bare CC. Theoretical investigation results suggest that the Mo d-band centers in all the counterpart samples, such as the as-prepared CeO_2/MoP (-1.08 eV), $CePO_4/MoP$ (-1.25 eV), $CePO_4/CeO_2/MoP$ (-1.28 eV), and $CePO_4/CeO_2(O_v)/MoP$ (O_v denotes oxygen vacancy) (-1.34 eV) are farther away from the Fermi energy level than that in the sample of MoP (-0.57 eV), and the negative shift of d-band center weakens H–Mo binding strength. The hetero-interface in $CePO_4/CeO_2(O_v)/MoP$ promotes effective charge transfer and shifts the d-band center of Mo downwards, therefore it is beneficial for H^* adsorption on active Mo sites [87]. Besides, the combination of transition metal-based composites as novel interfacial heterostructures can also exhibit enhanced HER performance in alkaline electrolytes. For example, Ji et al. fabricated a novel framework nanostructured catalyst derived from Ni-Co Prussian blue analog nanocubes, namely $(Ni,Co)_2P$ nanoframe (NF), which is

composed of hetero-phase Ni_2P-Co_2P nanoparticles embedded in the N-doped carbon substrates (Fig. 5a–d). The as-synthesized $(Ni,Co)_2P$ NFs exhibited significantly higher intrinsic HER catalytic activity than the counterpart samples including $(Ni,Co)_2P$ nanocubes (NCs), Ni_2P nanosheets (NSs), and Co_2P nanoboxes (NBs) in alkaline electrolytes (Fig. 5e). The $(Ni,Co)_2P$ NFs delivered a small Tafel slope of 62.3 $mV \cdot dec^{-1}$ (Fig. 5f) and displayed negligible current density degradation after 3000 voltammetric cycles and 30 h durability test (Fig. 5g) in 1.0 $mol \cdot L^{-1}$ KOH electrolyte [88]. As suggested by the density functional theory (DFT) calculations, the electronic interaction between Ni_2P-Co_2P heterostructure interface can efficiently boost H_2O molecule dissociation capacity and achieve moderate H^* intermediate adsorption energy, thus significantly promoting alkaline HER performance.

Moreover, the combination of metals with semiconductors often produces Mott-Schottky heterojunctions. The Schottky barrier is formed at the interface, which allows the irreversible transport of electrons through the interface and thus results in charge accumulation or depletion near the interface. Consequently, the electronic properties of the metal-semiconductor interface would be adjusted, thereby affecting the catalytic performance [89]. As a typical example, the heterostructures consisting of Ru and RuO_2 loaded onto the N, P-doped carbon material are also found to be effective for improving alkaline HER activity. Theoretical calculation results suggest that the extraordinary Ru– RuO_2 Mott-Schottky heterojunction facilitates the adsorption/desorption of H^* species, thus the intrinsic catalytic activity of alkaline HER is promoted [90]. Specifically, the d-band center of the Mott-Schottky heterojunction ($E_d = -3.28$ eV) falls in-between RuO_2 ($E_d = -3.33$ eV) and metallic Ru ($E_d = -3.10$ eV). As the metallic Ru is considered as the HER active sites, this indicates that the formation of Ru– RuO_2 Mott-Schottky heterojunction leads to the weakened adsorption of important reaction intermediates (such as H^* , OH^*) and may effectively improve the catalytic activity, as compared to metallic Ru alone. Furthermore, some recent studies have demonstrated that the charge depletion site has stronger H–OH bond cleavage capacity, whereas the charge accumulation site has moderate hydrogen atom adsorption capacity, thus the HER kinetics can be accelerated through optimizing the Volmer and Heyrovsky/Tafel steps synergistically in alkaline media. For instance, Li and coworkers constructed Cu nanodot-decorated Ni_3S_2 nanotubes (Fig. 6a and b), which can efficiently catalyze the HER process in an alkaline

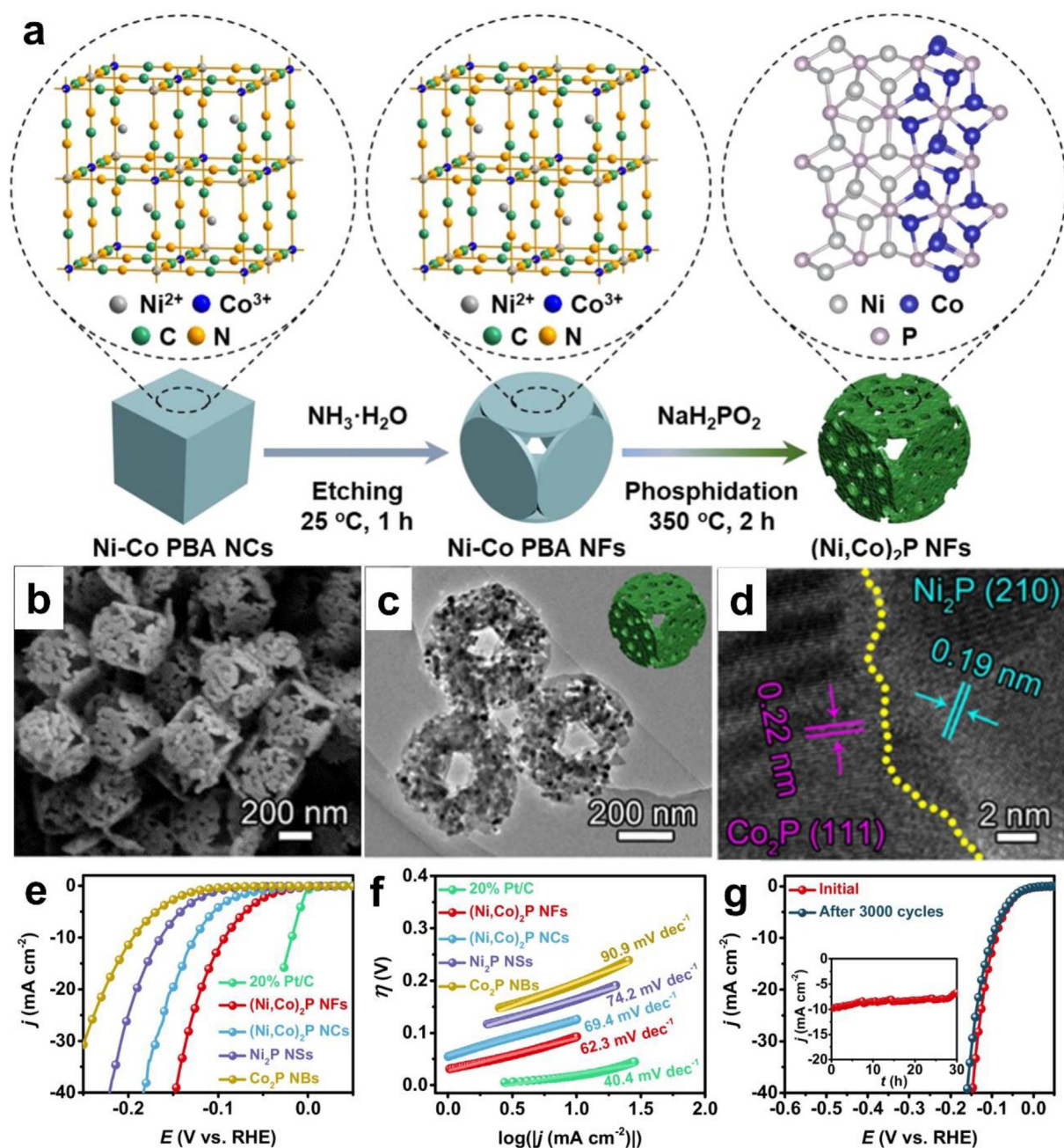


Fig. 5. (a) Schematic synthesis route for $(\text{Ni,Co})_2\text{P}$ nanoframes. (b) SEM, (c) TEM, and (d) HRTEM images of $(\text{Ni,Co})_2\text{P}$ nanoframes. (e) LSV curves, (f) Tafel plots, and (g) stability test of $(\text{Ni,Co})_2\text{P}$ nanoframes in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte. Inset in (g): chronoamperometric test at overpotential of 100 mV. [Reprinted with permission from Reference [88]. Copyright 2021, American Chemical Society].

solution [91]. The electronic interaction between Ni_3S_2 and Cu can induce moderate electron transfer from Cu to Ni_3S_2 . The charge-depleted Cu species adsorb and activate H_2O molecules effectively, thus promoting the cleavage of H–OH bonds; whereas the charge-accumulated Ni_3S_2 species have weakened S–H bonds and led to moderate H atom adsorption capacity, which is very beneficial to H_2 molecule formation. Consequently, this Cu/ Ni_3S_2 hybrid exhibited significantly enhanced alkaline hydrogen evolution

activity and stability. These results demonstrate that it is possible to achieve the optimization of the Volmer and Heyrovsky/Tafel steps synergistically through one stone. These studies propose new design guidelines for the optimization of the adsorption/desorption strength of related HER intermediates on the heterostructured catalyst interface under alkaline conditions.

When compared with their bulk counterparts, ultrathin nanosheets with thickness of just one or several atomic layers have extraordinary surface-

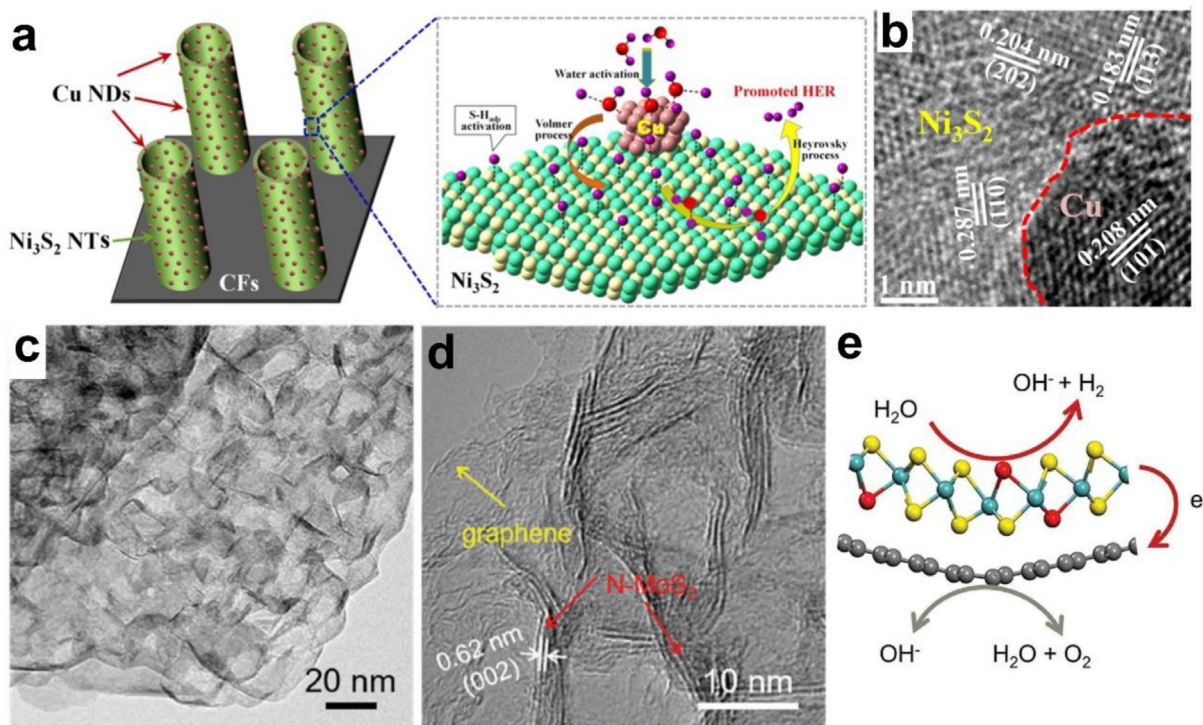


Fig. 6. (a) Schematic illustration for the mechanism of promoting alkaline HER performance by constructing Cu/Ni₃S₂ heterostructure. (b) HRTEM image of Cu/Ni₃S₂ heterostructure. [Reprinted with permission from Reference [91]. Copyright 2018, American Chemical Society. (c–d) HRTEM images of G@N-MoS₂. (e) Schematic representation of promoted electrocatalytic activities in G@N-MoS₂ heterostructures toward alkaline OER, HER and ORR, due to the electron transfer effects. Reprinted with permission from Reference [101]. Copyright 2017, Wiley-VCH.

to-volume ratios, resulting in remarkable physical, chemical and electrical properties [92–95]. So far, the large group of 2D nanomaterials includes diverse compounds that encompass nearly every element in the periodic table [96–98]. The previously proposed chemical vapor deposition (CVD) growth, self-assembly pathways, and liquid/mechanical exfoliation strategies are the most popular methods for accurate fabrication of 2D nanomaterials [99,100]. The isolated atomic planes in 2D nanomaterials can be recombined and stacked layer by layer in a precisely chosen sequence to obtain interfacial heterostructures, which are often described as van der Waals heterostructures, which have exceptional electrical transmissions, providing a new structural platform in electrocatalysis. As illustrated in Fig. 6c–e, Tang and co-workers [101] constructed an extraordinary van der Waals heterostructure, namely graphene/N-doped MoS₂ (denoted as G@N-MoS₂), via the classical CVD method. The N-MoS₂ nanosheets with an ultrathin thickness were locally bent to an extent and tightly binded with previously deposited graphene substrate to form vertical van der Waals heterostructures and 3D mesoporous frameworks. These heterostructured 3D frameworks were considered to afford multifunctional modifications of 2D nanomaterials: the interfacial charge

reallocation in the van der Waals heterostructure facilitates charge transfer, and the strong coupling interaction with graphene and doping of nitrogen atoms efficiently promotes electronic conductivity as well as intrinsic catalytic activity of 2H N-MoS₂ basal planes toward HER under an alkaline electrolyte. Consequently, the onset potential of this novel catalyst was reduced by nearly 100 mV compared to its counterparts. Such outstanding electrochemical properties arose from improved electron transfer and efficient charge redistribution induced by the intensely coupled interactions between locally bent N-MoS₂ basal planes and graphene, resulting from their different Fermi energy levels and different work function values.

In summary, we have discussed three strategies for effectively modifying the electronic structure of heterostructured electrocatalysts: (1) the combination of functional ordinary phases, including metals, alloys, metallic oxides, metallic phosphides, metallic phosphates, etc.; (2) the construction of Mott-Schottky heterojunctions constituting of metals and semiconductors; (3) the heteroatom doping in van der Waals heterostructures, especially doping in extraordinary phases.

Noteworthy, the intensity of electronic structure modulation should be moderate, since tiny changes in the electronic structure have a high

probability to significantly affecting the adsorption strength of reactants and transient intermediates, which might cause catalytic performance degradation. Therefore, the choice of different components in heterostructures deserves more consideration, and only suitable combinations can efficiently improve alkaline HER kinetics. As for the electronic interaction for improving catalytic activity, the great challenge lies in that: how to achieve moderate, usually meaning neither too strong nor too weak, electronic interaction? Do other factors, including the exposed facet of crystals and the size of usually believed inert support, can influence the electronic structure of active sites [89,102]? If so, how to realize the fine modulation and final optimization of electronic structure engineering on the consideration of all the above factors?

3.4. Phase engineering

Crystal phase has been considered to be an important structural parameter that determines the physical/chemical properties and relevant functionalities of nanomaterials in general. Particularly, unconventional phases in nanomaterials, which are thermodynamically unstable in the bulk state, have the potential to endow nanomaterials with intriguing properties, which might be very beneficial for promoting alkaline HER kinetics. Because 3d-M hydroxides display favorable water dissociation capacity [103–105], many efforts have been devoted into the further improvement of their water dissociation kinetics and the relevant progress is inspiring. For example, Shi's group accurately prepared α - and β -Ni(OH)₂/Pt heterostructure hybrids, and found that the intrinsic catalytic activity of β -Ni(OH)₂/Pt heterostructure toward alkaline HER was much higher than that of α -Ni(OH)₂/Pt heterostructure counterpart [106]. The experimental results and theoretical calculations both suggest that the superior intrinsic activity of β -Ni(OH)₂/Pt heterostructure catalyst originated from the larger inter-lamellar spacing of β -Ni(OH)₂ phase compared with that of α -Ni(OH)₂ phase, which enables much easier access to active metal sites for H₂O molecule adsorption and OH⁻ ion desorption. Similar phenomena of promoting alkaline water splitting performance by phase engineering were also observed by Qiao's group [107]. They synthesized the homogeneously dispersed face-centered-cubic (fcc) Ru nanoparticles with ultrasmall average diameter loading on the well-acknowledged g-C₃N₄/C support (denoted as Ru/g-C₃N₄/C). The electrochemical HER turnover frequency of Ru/g-C₃N₄/C

heterostructure catalyst in alkaline electrolytes showed approximately 2.8 and 2.5 times higher than those of benchmark Ru/C and Pt/C catalysts, respectively. DFT calculation results clearly reveal that the fcc Ru possessed a relatively weaker H* intermediate adsorption free energy (ΔG_{H^*}) value (-0.48 eV) than that of hexagonal close-packed (hcp) Ru (-0.83 eV). Considering the hydrolysis kinetics of water molecule dissociation step, the fcc Ru phase displays much lower energy barrier than hcp one. The achieved proper H* intermediate adsorption energy and much promoted kinetics for water molecule dissociation make a major contribution to the enhanced HER activity of the fcc Ru.

The different components in the aforementioned heterostructures usually are in crystal phase. Recently, heterostructures with co-existence of amorphous and crystal phases have drawn increasing interest, which contain the innovative amorphous/crystalline heterointerface (Fig. 7). The amorphous component in this kind of novel hetero-phase configuration is considered to provide an abundance of active sites due to a large amount of unsaturated coordination sites and structural defects, while the crystalline composition with relatively higher electronic conductivity can ensure facile electron transfer at the interfaces of heterostructure [108]. As a typical example, Liu's group proposed a novel heterostructure electrocatalyst consisting of amorphous Ni(OH)₂ and crystalline CuS for HER catalysis in an alkaline electrolyte [109]. The crystalline CuS part is intended to accelerate charge transfer, while the amorphous Ni(OH)₂ component with the feature of possessing short-range order but lack of long-range order provides a large number of active sites, resulting in the significantly enhanced alkaline HER kinetics. A similar phenomenon was also observed by Zhang's group, who prepared the three-dimensional (3D) Ni(OH)₂/MoS₂ heterostructured nanomaterials with abundant interfacial active sites toward electrocatalytic HER in an alkaline electrolyte by a facile two-step method. This heterostructure comprised of crystalline MoS₂ and amorphous Ni(OH)₂ (Fig. 8) [48]. It is rationally argued that the amorphous Ni(OH)₂ part could to a large extent provide abundant interfacial active sites for OH⁻ ions adsorption and H–OH bonds breaking. The moderate electron transfer from amorphous Ni(OH)₂ part to crystalline MoS₂ component can efficiently optimize binding energy for the H* intermediate. In summary, the amorphous structure has a higher density of active sites, higher concentration of unsaturated coordination bonds, and wider modulation ranges of composites and

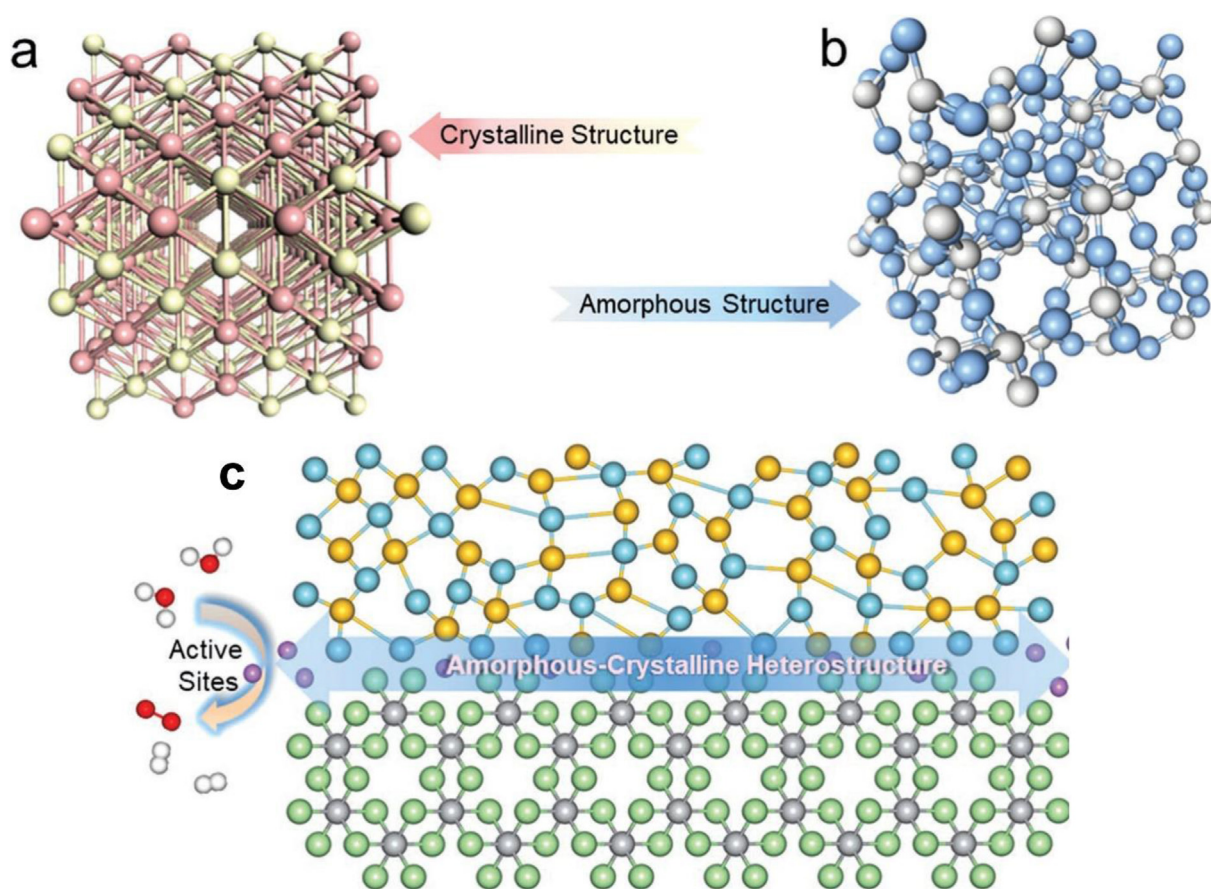


Fig. 7. The atomic illustrations for (a) crystalline, (b) amorphous, and (c) amorphous-crystalline nanomaterials. Reprinted with permission from Reference [108]. Copyright 2022, Wiley-VCH.

electronic structures compared with a crystalline structure. Therefore, amorphization engineering of 3d-M hydroxides can effectively modulate their affinity for OH^- ion and promote water molecule dissociation capacity.

Similar phenomena are also observed on 3d-M oxides. For instance, Yang et al. synthesized a novel amorphous/crystalline $\text{CrO}_x\text{-Ni}_3\text{N}$ heterostructure (Fig. 9a) consisting of amorphous CrO_x and crystalline Ni_3N for electrocatalytic water splitting in an alkaline electrolyte. The amorphous CrO_x could provide abundant unsaturated coordination active sites for catalysis, while the crystalline Ni_3N might be beneficial for charge transfer on the interface. Amorphous CrO_x is an excellent facilitator of water molecule dissociation due to its chaotic structure and abundant oxygen vacancies. Electrochemical tests (Fig. 9b and c) show that the amorphous/crystalline $\text{CrO}_x\text{-Ni}_3\text{N}$ heterostructure exhibited the significantly promoted alkaline HER catalytic activity compared with the mono-component counterpart CrO_x and Ni_3N . According to the calculation results of charge density (Fig. 9f), electrons are transferred from Ni and Cr atoms to neighboring N and O atoms, causing strong charge

accumulation around O and N atoms, which indicates an intimate electronic interaction between CrO_x and Ni_3N , and is very favorable for the adsorption/desorption of H^* and OH^* species on this extraordinary amorphous/crystalline $\text{CrO}_x\text{-Ni}_3\text{N}$ heterostructure interface. The $\text{CrO}_x\text{-Ni}_3\text{N}$ heterostructure, in which the amorphous CrO_x part functions as a promoter for H_2O molecule adsorption (Fig. 9g), exhibits greatly improved H_2O molecule adsorption strength (with adsorption energy of -1.02 eV), which is superior to that of Ni_3N (with adsorption energy of -0.61 eV). The $\text{CrO}_x\text{-Ni}_3\text{N}$ heterostructure also shows a relatively smaller $\Delta G_{\text{OH-H}}$ value of -0.12 eV compared with those of homo-component including amorphous CrO_x and crystalline Ni_3N (Fig. 9h), suggesting that the cleavage of H-OH bonds could increase the adsorbed H^* intermediate concentration at the $\text{CrO}_x\text{-Ni}_3\text{N}$ interface, thereby accelerating the HER kinetics under alkaline conditions. Besides, the as-fabricated $\text{CrO}_x\text{-Ni}_3\text{N}$ heterostructure shows a higher ΔG_{H^*} value on the Ni-N hollow site (-0.08 eV) compared with those on the constituting homo-part including amorphous CrO_x (-1.09 eV) and crystalline Ni_3N (-0.30 eV). The absolute value

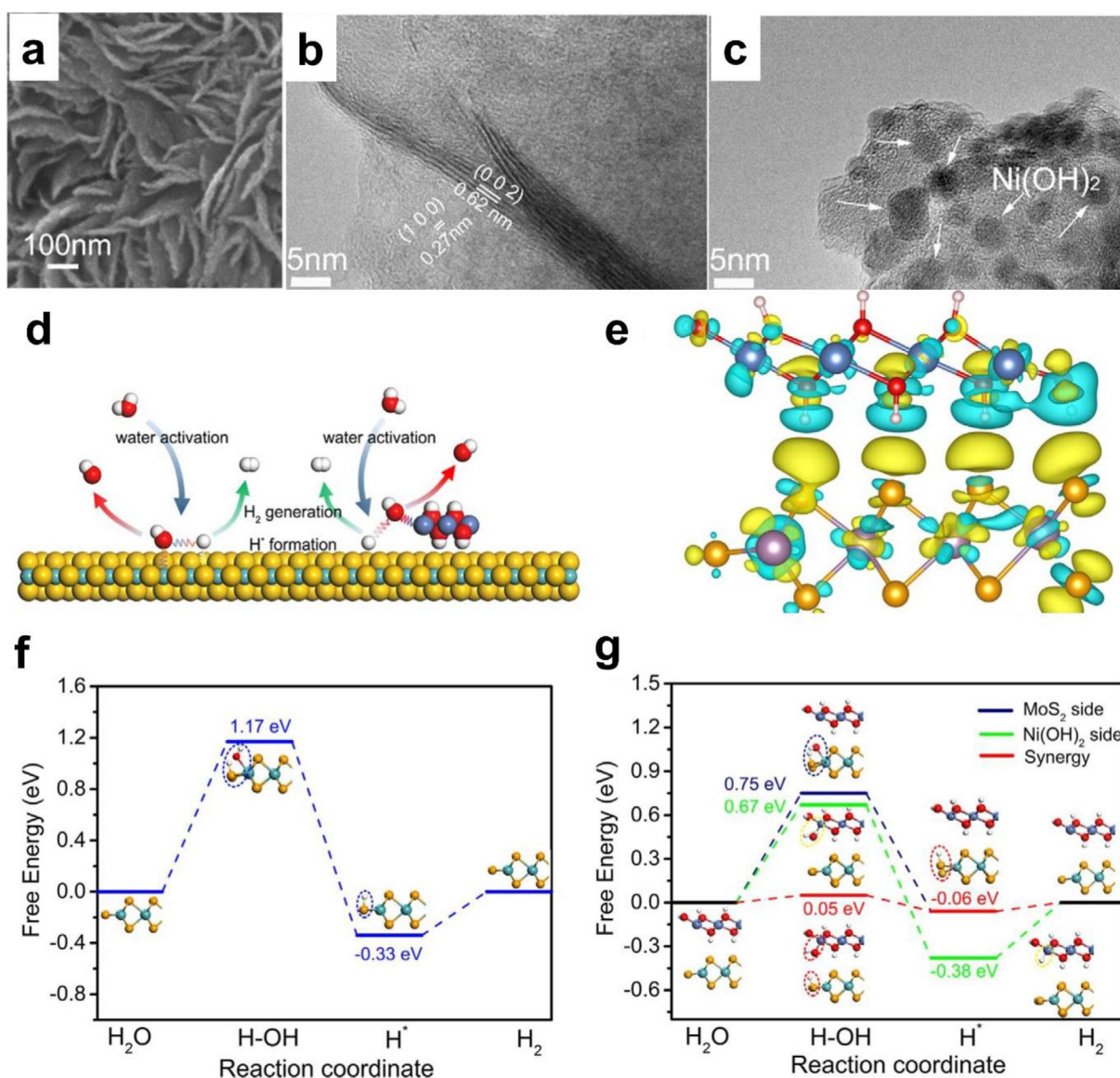


Fig. 8. (a) SEM image of Ni(OH)₂/MoS₂@CC. TEM images of (b) MoS₂@CC, and (c) Ni(OH)₂/MoS₂@CC. (d) Schematic illustration of key intermediate steps of HER processes on MoS₂ catalyst and Ni(OH)₂/MoS₂ heterostructured catalyst. (e) Isosurfaces of local charge density difference at the Ni(OH)₂/MoS₂ interface (cyan and yellow are 0.001 eÅ⁻³ isosurfaces). The free energy diagram for HER on the (f) MoS₂ edge and (g) Ni(OH)₂/MoS₂ interface. The insets show the surface structures of catalysts at different stages. The H, O, S, Ni and Mo atoms are represented by white, red, orange, blue and gray spheres, respectively. Reprinted with permission from Reference [48]. Copyright 2017, Elsevier.

of ΔG_{H^*} for the CrO_x-Ni₃N heterostructure is much closer to zero, suggesting that the optimization of H* intermediate adsorption strength at the proposed CrO_x-Ni₃N interface and the significantly enhanced intrinsic catalytic activity for HER in alkaline media can be achieved [110].

Nevertheless, the interfacial CrO_x-Ni₃N heterostructure shows a higher overpotential than the benchmark Pt plate catalyst at the current density of 10 mA·cm⁻². To further increase the intrinsic alkaline HER activity, Dong et al. fabricated a novel crystalline/amorphous Ni(OH)₂/NiMoO_x heterostructure electrocatalyst (Fig. 10a and b), which exhibits Pt-like performance for HER catalysis

(Fig. 10c) in 1.0 mol·L⁻¹ KOH electrolyte. The integrated electrode structure delivers the enhanced charge transfer capability and superior electronic conductivity. Meantime, the constructed electrocatalysts have mixed crystalline and amorphous phases, comprising crystalline Ni(OH)₂ and amorphous NiMoO_x, indicating the generation of sufficient interfaces, which is beneficial for electrocatalysis. Experimental results indicate that H₂O molecule dissociation mainly occurs on the crystalline Ni(OH)₂ component (the relevant reaction equation can be described as: H₂O + e⁻ → H* + OH⁻), then the following chemical desorption of hydrogen intermediate (generally revealed as:

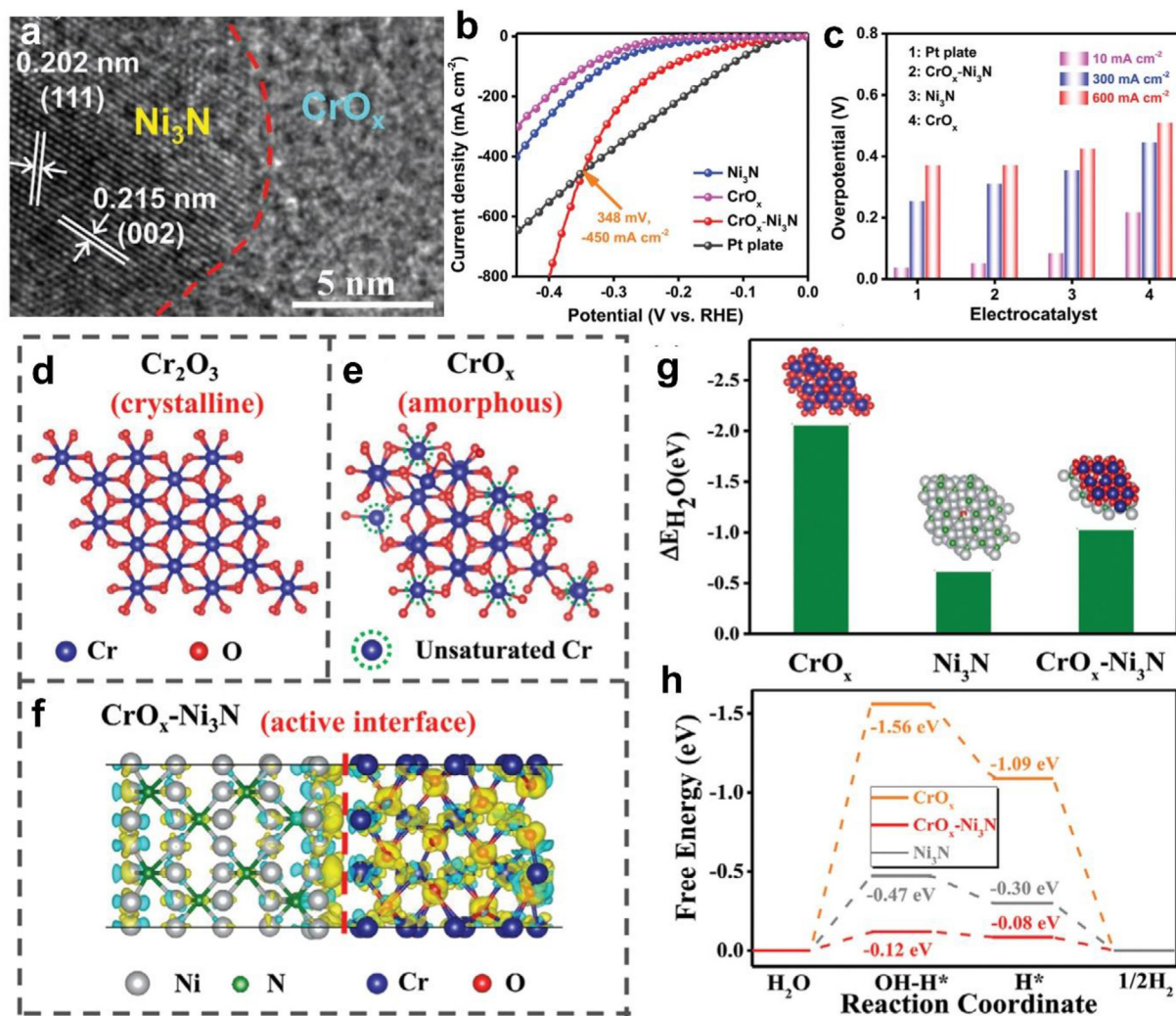


Fig. 9. (a) HRTEM image of $\text{CrO}_x\text{-Ni}_3\text{N}$. (b) HER polarization curves, and the corresponding (c) overpotential plots of the CrO_x , Ni_3N , $\text{CrO}_x\text{-Ni}_3\text{N}$, and Pt plate at -10 , -300 , $-600 \text{ mA}\cdot\text{cm}^{-2}$. Atomic models of (d) crystalline Cr_2O_3 and (e) amorphous CrO_x . (f) The 3D charge density difference of $\text{CrO}_x\text{-Ni}_3\text{N}$ interfaces with an isosurface value of $0.9 \times 10^{-3} \text{ e}\text{\AA}^{-3}$ on the left. (g) Adsorption energies of water on Ni_3N , CrO_x , and $\text{CrO}_x\text{-Ni}_3\text{N}$. Insets: the corresponding adsorption structures. (h) The calculated Gibbs free energy plots of H^* and OH-H^* adsorption for the Ni_3N , CrO_x , and $\text{CrO}_x\text{-Ni}_3\text{N}$. [Reprinted with permission from Reference [110]. Copyright 2022, Wiley-VCH].

$2\text{H}^* \rightarrow \text{H}_2$) and electrocatalytic desorption of H_2 molecule (rationally described as: $\text{H}^* + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \text{H}_2$) steps can effortlessly occur on the amorphous NiMoO_x component [111]. Aiming to further promoting the intrinsic charge-transfer property of transition metal oxides, Huang et al. fabricated amorphous NiWO_4 nanoparticles decorated on crystalline Ni_3S_2 nanosheets as an efficient electrocatalyst toward an alkaline HER process (Fig. 10d). The heterostructure catalyst required very low overpotential of 274 mV at the current density of $-100 \text{ mA}\cdot\text{cm}^{-2}$ and exhibited remarkable stability during 75 h durability test in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte, which was much superior to the original single-component crystalline Ni_3S_2 . Theoretical calculation results reveal that the adsorption capacity of H_2O molecule is changed

from endothermic on pristine Ni_3S_2 ($\Delta G_{\text{H}_2\text{O}} = 0.21 \text{ eV}$) to exothermic at the proposed $\text{NiWO}_4/\text{Ni}_3\text{S}_2$ interface ($\Delta G_{\text{H}_2\text{O}} = -0.86 \text{ eV}$), which indicates that the Volmer step was strongly reinforced at this extraordinary heterostructure interface of $\text{NiWO}_4/\text{Ni}_3\text{S}_2$. Moreover, when the HER intermediate H^* was adsorbed onto $\text{Ni}_3\text{S}_2/\text{NF}$, the S-H bond had a very short length of 1.37 \AA and the corresponding ΔG_{H^*} is calculated as 0.64 eV , showing that adsorbed H^* intermediate had a strong affinity with the S site. In contrast, after the growth of amorphous NiWO_4 nanoparticles on crystalline Ni_3S_2 nanosheets, the corresponding S-H bond was extended to 1.44 \AA when H^* intermediate was adsorbed on the Ni_3S_2 phase located on the heterostructure interface region and the ΔG_{H^*} became more positive (-0.15 eV). Thanks to the construction of

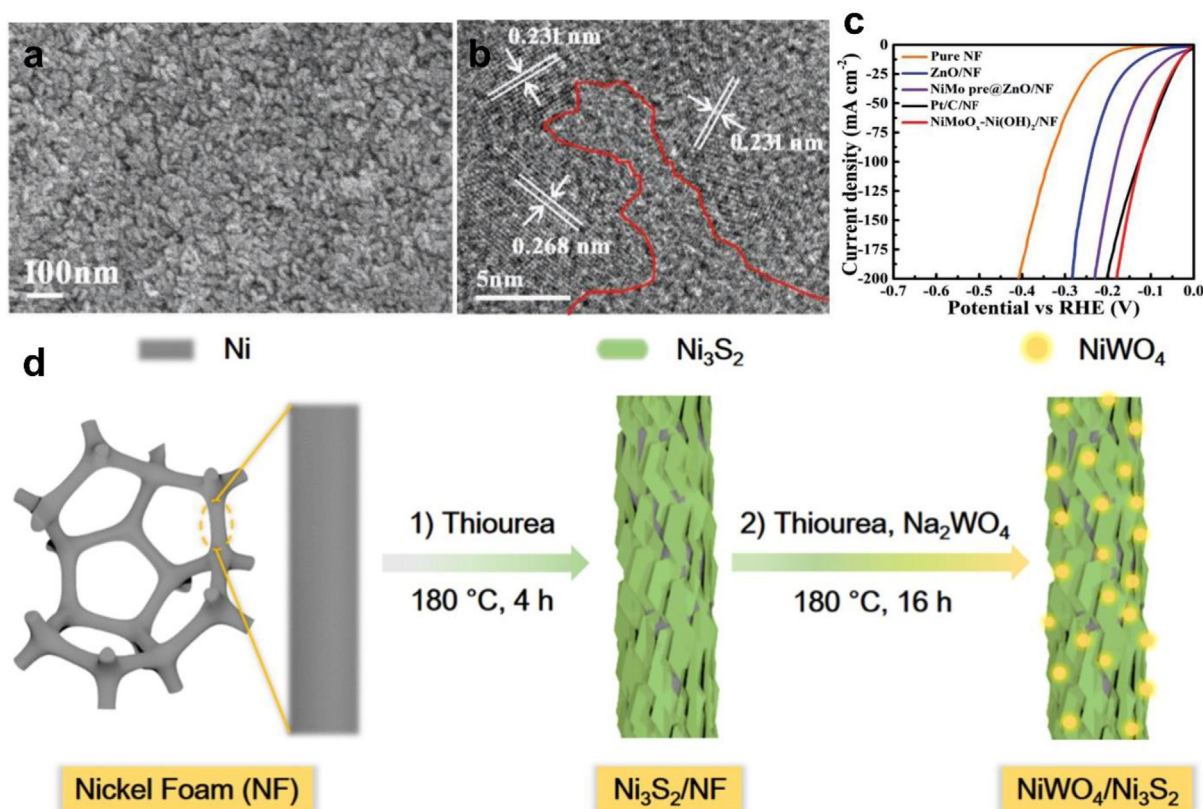


Fig. 10. (a) SEM image of electrodeposited NiMo pre@ZnO/NF. (b) HRTEM image of catalyst after soaking. (c) LSV curves tested in 1.0 mol·L⁻¹ KOH at scanning rate of 5 mV·s⁻¹. Reprinted with permission from Reference [111]. Copyright 2019, Wiley-VCH. (d) Schematic illustration for preparing NiWO₄/Ni₃S₂ heterostructures. Reprinted with permission from Reference [112]. Copyright 2020, Elsevier.

amorphous/crystalline heterostructure that forms abundant interfacial active sites and the stronger electronic interactions between amorphous NiWO₄ phase and crystalline Ni₃S₂ phase, the Volmer and Heyrovsky steps of HER can be accelerated, thereby much improved HER properties under alkaline conditions were obtained [112].

Compared with metal compounds, it is more challenging to prepare amorphous noble metals, hence relatively less noble-metal-based amorphous-crystalline heterostructures have been reported. As a typical example, Cao et al. fabricated an extraordinary heterostructure consisting of amorphous RuCu nanosheets loading on the substrate of crystalline Cu nanotubes toward an HER process under an alkaline solution. Theoretical calculation results indicate that H₂O molecules can be activated on the active Ru sites. Moreover, the calculated d-band center of Ru (-1.46 eV) is much closer to the Fermi level compared with that of state-of-art catalyst Pt (-2.31 eV), confirming that metallic Ru can form stronger bonds with O atoms, thus leading to the exothermal H₂O adsorption process. Simultaneously, the constructed heterostructure interface between the crystalline Cu

nanotubes and amorphous RuCu nanosheets is crucially important to significantly improve the electrocatalytic HER performance in an alkaline electrolyte since the amorphous RuCu phase has abundant unsaturated coordinating bonds, which can greatly promote the adsorptions of water molecules and transient intermediates, while the crystalline Cu nanotubes with excellent electronic conductivity property can substantially facilitate the transfer of electrons. Therefore, the 3D amorphous RuCu nanosheets displayed an apparent catalytic activity towards alkaline HER that is comparable with benchmark Pt/C catalyst [113].

Although the above reports demonstrate the efficiency of phase engineering for accelerating alkaline HER kinetics, some issues and challenges of this strategy still need to be resolved in practical electrocatalysis. For instance, the electric conductivity of amorphous materials is an inevitable concern, and how to balance the higher intrinsic activity and poorer electric conductivity of amorphous phases compared with the crystalline remains an open question [114]. Another issue is the stability of the as-prepared unconventional phase during the electrocatalysis, which may experience

phase transformation during long-term stability test. As for the phase transformation in the electrochemical alkaline HER process, relevant research works suggest that the as-formed unconventional phases with relatively higher electrocatalytic activity may be transformed to the stable phase, thus exhibiting catalytic activity deactivation. For example, transition metal chalcogenides with 1T' phases usually exhibit higher catalytic activity than the corresponding 1H phase toward alkaline HER. Since the 1T'-to-1H phase transform requires a very low energy barrier (eg., 0.7 V for MoS₂ to achieve 1T'-to-1H transformation), upon the electrochemical reaction process, the phase change could probably occur and the catalytic performance would be degraded [115]. If the currently considered “active” phase is transformed to another phase and this transformation process is irreversible, then what is the real active phase on earth?

3.5. Architecture engineering

Construction of nanoscale materials with significantly higher specific surface area, such as fabricating hollow nanostructures with abundant pores, can contribute to the exposure of more interfacial active sites and significant facilitation of mass transfer, such as the diffusion of aqueous reactants to the surface of catalysts on the heterogeneous liquid-solid interface. For instance, Zhang's group synthesized 3D hollow porous CeO_x/CoP heterostructure using a MOF as the sacrificing template [116] (Fig. 11). The 2D Co-MOF-derived structure made up of hollow triangle plate arrays has much larger exposed surface areas, abundant interfacial active sites, as well as much shorter diffusion pathways to enhance

electrochemical performances. The forming of enriched heterogeneous interfaces in this CeO_x/CoP heterostructure can effectively modify the surface electronic structure of active metal sites and generate a large amount of structural defect sites, leading to much enhanced intrinsic activity of HER toward the Volmer step under alkaline media. Notably, the above-mentioned synthesis strategy with the assistance of templates is commonly used for the construction of hollow nanostructures, including hard, soft and self-sacrificed templates. In a typical work reported by Guo's group [117], ZIF-67 served as a morphologic hard template using Co salt species as the metallic precursor. Then, a novel Co₃S₄@MoS₂ heterostructure with hollow architecture consisting of abundant inter-connected nanopores forming on the surface of uniform polyhedrons was obtained by a two-step hydrothermal procedure in sequence. Owing to the formation of hollow heterostructure with abundant interfacial active sites and the presence of synergistic effect between Co₃S₄ and MoS₂, the Co₃S₄@MoS₂ heterostructure showed the enhanced catalytic performance toward alkaline HER. The electrocatalytically active surface areas can be significantly increased by formation of extraordinary mesoporous structures. For example, Deng et al. fabricated crystalline/amorphous PtPd/NiB heterostructure with the typical core-shell architecture derived from PtPd mesoporous truncated octahedral nanocages with crystalline phase (Fig. 12) (denoted as c-PtPd-MTONs) for alkaline water splitting. The synergistic hybridization of c-PtPd MTONs with amorphous phase NiB (a-NiB) nanosheets on this extraordinary heterostructure interface resulted in abundant intrinsic active sites and efficiently modulated electronic state on the interface. All the

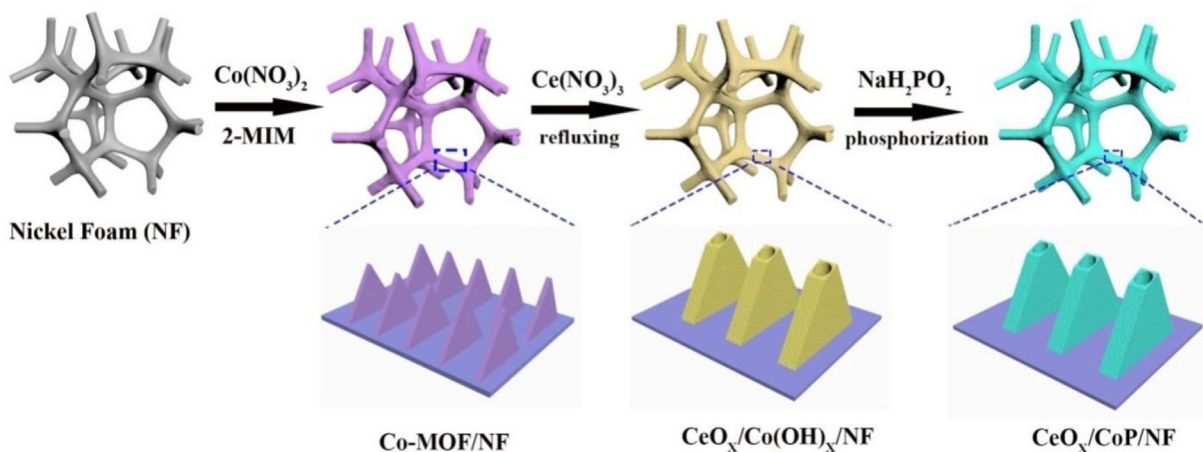


Fig. 11. Schemes showing the fabrication process of CeO_x/CoP/NF. [Reprinted with permission from Reference [116]. Copyright 2020, Wiley-VCH].

above-mentioned factors can contribute to much boosted HER activity. As expected, the proposed crystalline-PtPd@amorphous-NiB heterostructure with typical core-shell architecture showed significantly enhanced intrinsic activity toward HER in alkaline media, which greatly outperformed the benchmark Pt/C catalyst [118].

Although architecture engineering can indeed promote alkaline HER kinetics, some important issues about architecture engineering need to be taken into account. For example, abundant narrow or closed pores including micropores and mesopores are often difficult for reactants to diffuse into and thus not available for catalysis. Another issue lies in the challenge of constructing heterostructures with abundant and easily accessible interfaces. Current reports in this field mainly focus on improving specific surface areas of individual components, while the interfaces between different architected materials may not be effectively increased.

4. Challenges and Perspectives

This mini review aims to present a comprehensive overview of the latest progress in the emerging efficient strategies for promoting HER kinetics in alkaline media via construction of various heterostructure interfaces. In particular, enhanced HER performance in alkaline media has been achieved because of the intriguing synergistic effect, strain effect, electronic interaction, phase engineering, and architecture engineering. As for the emerging amorphous/crystalline heterostructures, the structural merits of amorphous/crystalline materials endow them with magic catalytic performance due to the significantly increased number of interfacial active sites and unsaturated coordination sites. The distinctive atomic arrangement in the heterogeneous surface is believed to be the major factor that contributes to the acknowledged interfacial synergistic effect between the crystalline and amorphous

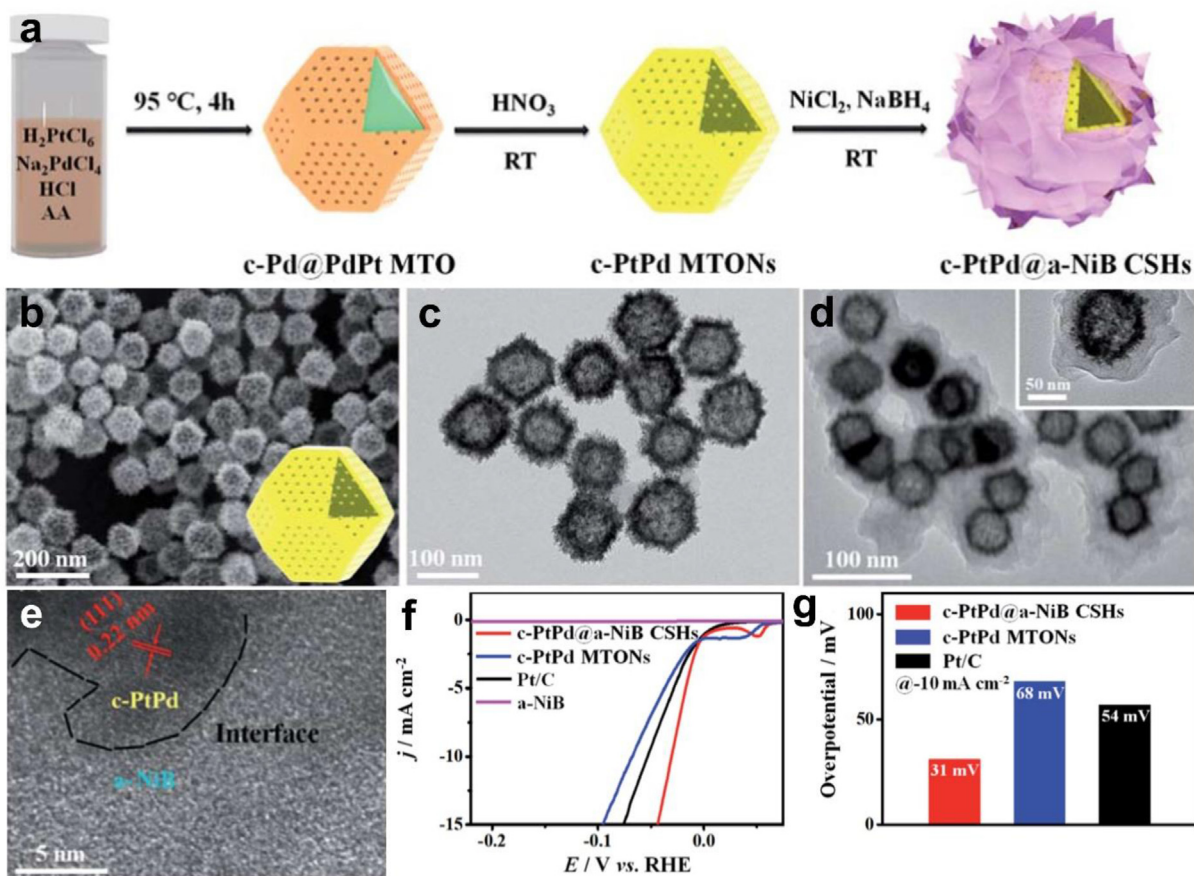


Fig. 12. (a) Scheme showing the formation process of *c*-PtPd@*a*-NiB core-shell heterostructures. (b) SEM and (c) TEM images of the *c*-PtPd mesoporous truncated octahedral nanocages. (d) TEM and (e) HRTEM images of the *c*-PtPd@*a*-NiB core-shell heterostructures. (f) HER polarization curves for various catalysts. (g) Comparison of the overpotentials at -10 mA cm^{-2} . Reprinted with permission from Reference [118]. Copyright 2020, Royal Society of Chemistry.

components. As the most promising next-generation candidate, interfacial heterostructures offer more opportunities in the field of energy-related catalysis. However, these newly emerged catalysts are still facing some hurdles and challenges.

1) Despite the concrete amorphous/crystalline heterostructures have shown attractive merits in promoting catalytic activity, it is challenging to regulate the two different crystal phases in single-metal based materials, particularly for noble metals, because of the difficulties of balancing crystallization levels through conventional manufacturing strategies. Therefore, to fully understand the physical and chemical function mechanisms of these extraordinary amorphous/crystalline heterostructures, novel fabrication techniques should be developed for the accurate manipulation of crystal structures.

2) Because of the atomic disorder of the amorphous phase, the in-depth explorations of atomic coordinating environments on the amorphous/crystalline interfaces are significantly exhausting. Few studies are experimentally focusing on the characterization of these complicated heterostructures so far, thus significant challenges in the field of identifying real active sites that are responsible for HER under alkaline conditions still remain to be settled. To make matters worse, the atomic structure of amorphous/crystalline heterostructures proposed by DFT simulation only could represent the local atomic structure, and the relevant theoretical investigation results could be debatable due to the discrepancy of geometric structures viewed from the global perspective. Therefore, tremendous efforts should be devoted to investigate the atomic coordination settings at amorphous/crystalline heterostructure interfaces.

3) The structural integrality of interfacial heterostructures throughout the electrochemical reaction process is critical to have remarkable stability. Although some advanced *in-situ* characterization techniques have been conducted for investigating the structural changes of interfacial heterostructures during the long-term stability evaluation process, in-depth assessments of this specific structural shifts are still inadequate. Therefore, the structural stability of interfacial heterostructures should be monitored to deeply understand the real catalytically active sites associated with the correlation between the atomic structure merits of heterointerfaces and their electrochemical properties.

4) Despite significant development in the utilization of interfacial heterostructures in catalysis, the intensive and clear understanding of the functional mechanisms for promoting catalytic

kinetics needs further exploration, to give much further insights into the basis and design principles of advanced heterostructured catalysts. More advanced operando characterization techniques should be developed and applied to probe transient intermediates at the catalyst-electrolyte interfaces during the electrochemical reaction process, providing more opportunities for the large-scale application of interfacial heterostructures in sustainable energy-related catalyses, such as photo/electrochemical oxygen-related process, carbon dioxide reduction, nitrate reduction, methanol oxidation reactions, etc.

Apart from the above issues and challenges, abundant new opportunities are emerging as the rapid development of other disciplines, including condensed matter physics and artificial intelligence. The blooming of inter-connected disciplines provides highly promising perspectives for the application of heterostructure engineering in catalysis. It is expected that more advanced heterostructured catalysts with novel and finely controlled crystal structure toward targeted reactions, designed by the inspiration of inter-disciplinary including materials science, condensed matter physics, and artificial intelligence, will come out in the near future. In addition, the introduction of machine learning technology will screen off many unnecessary or unmeaningful combinations automatically, which largely promotes the experimental efficiency in the synthesis of novel heterostructures. Furthermore, with the assistance of high-performance computing, many complex problems in quantum chemistry will be neatly solved, and precise computing of huge systems with a large number of atoms will become possible, which will provide new insights into the catalytic reaction mechanisms. Finally, with the development of technical physics, it is possible to detect more information about the atomic, electronic or even magnetic properties of heterostructured catalysts during the reaction process, which will shed new light on the construction of “structure-performance” relationship in heterostructured catalysis. All the above opportunities will feedback and continuously optimize the design principles of hetero-interfaces, which is desired to concurrently promote the development of materials chemistry and relevant inter-disciplinary subject.

Author contributions

Hai-Bin Ma is responsible for preparation of original manuscript by surveying different literatures. Xiao-Yan Zhou and Jia-Yi Li collected relevant data and statics from recently reported

results. Hong-Fei Cheng and Ji-Wei Ma conducted the refinement of this manuscript. Hong-Fei Cheng and Ji-Wei Ma are responsible for the conceptualization, supervision and finalization of the manuscript. All the listed authors have carefully read and agreed with the published version of this manuscript.

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Conflicts of interest

These authors declare no financially competing interest.

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用于促进碱性介质中析氢反应动力学的异质结构电催化剂的合理设计

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摘要

在碱性介质中, 由于电极材料的较高的稳定性, 电催化析氢反应 (HER) 具有实现大规模制氢的巨大潜力。然而, 即使对于最突出的铂催化剂, HER 在碱性介质中的反应动力学也比在酸性介质中慢 2-3 个数量级, 这是由于碱性环境下质子的浓度较低。异质结构催化剂具有多种结构优势, 研究表明, 构建异质结构电催化剂是促进碱性 HER 动力学的有效策略。协同效应是异质结构的一个独特特征, 这意味着一个功能活性位点作为水解离的促进剂, 另一个活性位点则负责适度的氢吸附, 从而协同提高 HER 催化性能。此外, 异质结构中的每个构建模块都是可调节的, 为构建最佳催化剂提供了更多的灵活性和可能性。同时, 由于界面处两个组分之间存在费米能级差, 可以合理地调控每个组分的电子结构, 从而大幅度提高碱性介质中的 HER 催化性能。随着对纳米结构的深入理解, 人们开发了更先进的设计策略来构建高性能异质结构电催化剂。本文综述了异质结构催化剂在碱性 HER 方面的最新发展, 以及构建界面异质结构以促进碱性 HER 动力学性能的合理设计原则。我们首先介绍了 HER 在碱性介质中的基本反应途径, 然后详细讨论了促进碱性 HER 动力学的新兴有效策略, 包括协同效应、应变效应、电子相互作用、相工程和结构工程, 最后提出了未来面向实际应用的新型异质结构催化剂设计所面临的挑战和研究机遇。

关键字: 界面异质结构; 制氢; 水离解; 氢吸附; 协同效应。