Applications of Nickel-Based Electrocatalysts for Hydrogen Evolution Reaction

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The desire to exploit clean and sustainable energy sources with high gravimetric energy density has greatly inspired the exploration of hydrogen energy as an affordable alternative to fossil energy. Electrocatalytic water splitting is an efficient method for the low-cost production of pure H₂, but the use of platinum (Pt)-like active electocatalysts for the hydrogen evolution reaction (HER) remains necessary. In attempts to replace high-value, scarce Pt catalysts, nickel-based materials are being developed, as earth-abundant HER electrocatalysts. Recently, a number of advanced nickel (Ni)-based catalysts have been developed by rational synthesis strategies, including morphology control, structure tailoring, and interface engineering, significantly improving the HER performance. This review summarizes recent achievements in the application of Ni-based HER electrocatalysts and demonstrates the advantages of each category in enhancing the HER performance. The current progress in the theory of water evolution and various modern techniques for characterizing catalysts are also reviewed, along with the rational design of Ni-based nanostructure catalysts. Finally, the challenges in the practical applications of Ni-based HER catalysts are highlighted.

1. Introduction

Converting renewable energy resources such as wind and solar energy into chemical fuels has been proposed as an efficient and carbon-neutral strategy. Hydrogen, as the most promising candidate fuel, possesses a high energy density and generates zero emission during consumption. Thus far, hydrogen is still mainly prepared in the industry via methane reforming promoted by steam. This process not only influences the energy efficiency, but also reduces the purity of the hydrogen products due to the existence of carbon-containing residues. Among the many sustainable approaches to H₂ generation, electrolytic water splitting is a clean and secure method owing to the abundance of water resources and high-purity products.

The water-splitting reaction comprises two half-reactions, namely, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The HER can be expressed in different ways depending on the reaction conditions, including acidic, alkaline, and neutral solutions. The rate-determining step of the reaction depends on the intrinsic property of catalysts. In acidic media, the reaction involves hydrogen adsorption (Volmer step), followed by electrochemical (Heyrovsky step) or chemical hydrogen desorption (Tafel step).

\[ \text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} \text{Volmer} \]  
\[ \text{H}^+ + \text{e}^- + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \text{Heyrovsky} \]  
\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \text{Tafel} \]

In alkaline media, the Volmer step is the process where a water molecule is reduced into an adsorbed hydrogen atom and hydroxide anion. After that, two adsorbed hydrogen atoms are combined to generate a hydrogen molecule (Tafel step) or bonded with a water molecule to generate a hydrogen molecule and a hydroxide anion (Heyrovsky step).

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^- \text{Volmer} \]  
\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \text{Tafel} \]
\[ \text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^- \text{Heyrovsky} \]

The Volmer step in acidic condition exhibits the reduction of a hydrion into an adsorbed hydrogen atom, indicating that the
catalytic activity is related to the ability of hydrogen adsorption for electrocatalysts. Different from the acidic condition, the Volmer step in the alkaline condition involves the adsorption of water and the desorption of the hydride anion, revealing that different reaction mechanisms can greatly influence the thermodynamic and kinetic properties for electrocatalysts. For example, platinum (Pt) has proven that the catalytic activity in alkaline solution is lower than that in the acidic solution because of the low water adsorption energy and high hydride anion adsorption energy. Hence, an optimal HER catalyst in alkaline media can effectively accelerate the Volmer step. Although the HER involves only two electrons per hydrogen molecule, additional energy is required to overcome the barriers in the reaction process. This results in sluggish kinetics and low energy-conversion efficiency.\[12–16\]

To reduce the energy barriers and electrical energy, at present, noble metals (such as Pt, Pd, and Ir) are regarded as the most efficient and durable electrocatalysts for the conversion of \( \text{H}_2\text{O}^- \) (acid) and \( \text{H}_2\text{O} \) (alkaline) to \( \text{H}_2 \).\[17–22\]

Unfortunately, their scarcity and high cost impede the large-scale utilization of these noble metal electrocatalysts, thus prompting the development of cheap catalysts.

In the past few years, extensive efforts have been made to develop cost-effective non-noble metal catalysts.\[23–30\] As nickel was recognized as a prospectively effective catalyst, researchers have devoted energy to exploring the fundamental mechanism and enhancing the activity of Ni-based catalysts via rational design.\[31\] Ni-based materials, including Ni metal oxides, sulfides, selenides, tellurides, and phosphides, with remarkable catalytic HER performance and outstanding conductivity have attracted particular attention.\[32–36\] Numerous reports on enhancing the catalytic performance by means of morphology control and optimization of the chemical structures, along with external excitation using strain, magnetism, and an electric field, have been documented.\[4,37–39\] The main solution is to manufacture advanced Ni-based catalysts with a designed structure and morphology to directly obtain a low overpotential. Nowadays, with the help of progressive techniques including synchrotron-radiation X-ray absorption fine structure (XAFS) and spherical aberration electron transmission microscopy (STEM), the atomic arrangement and the local environment of catalysts can be clearly observed, especially for single-atom catalysts.\[40\] Moreover, in situ testing technologies such as in situ XAFS, in situ synchrotron X-ray powder diffraction (SXRD), and in situ scanning electrochemical microscopy (SECM) are indispensable tools for further tracking catalyst evolution during the HER process.\[41,42\]

Theoretical modeling methods, especially d-band theory and density functional theory (DFT), can provide an atomistic understanding of the HER, as well as provide the directives needed to develop advanced catalysts. Under the guidance of DFT, the search for promising catalyst candidates has been significantly accelerated, and the fundamental catalytic mechanism can also be clearly elucidated. According to the Sabatier principle, for the perfect HER catalyst, the Gibbs free energy for hydrogen adsorption (\( \Delta G_{\text{H}_2} \)) should be close to zero. This means that the binding energy when the active sites are coupled with hydrogen atoms should be neither too weak nor too strong, thus facilitating the hydrogen adsorption and desorption processes.\[43–45\] With this new insight, the researchers have focused on tuning the electronic structure of catalysts to reduce the reaction barrier and lower the hydrogen adsorption energy.\[46–49\] This can help achieve ideal catalysts for the HER. In this review, we summarize the recent progress of Ni-based catalysts, revealing their distinctive electronic properties, surface engineering, and modulation of the metal support interactions. The type, characterization, and electrocatalytic mechanism of Ni-based catalysts are discussed, along with detailed strategies for the rational design and optimization of Ni-based catalysts. Exploring the associations between the catalytic activity and electronic structure enables us to provide some insights into the past and future directions of Ni-based HER catalysts, which may be helpful for the design and widespread implementation of these catalysts.

2. Recent Progress

2.1. Metallic Nickel and Nickel-Based Alloys

In the study of electrocatalytic water splitting, metallic Ni is utilized as an electrocatalyst for the HER because of its high catalytic activity, cost-effectiveness, and excellent stability.\[17,50\] Theoretical progress has allowed the identification of details of the HER mechanism over the past few years. By describing linear correlations between the binding energies of intermediates, Nørskov et al. used DFT calculations to construct a volcano plot, which revealed the \( \Delta G_{\text{H}_2} \) for different metals.\[51\] The volcano plot (Figure 1) shows that among the non-noble transition metals, the \( \Delta G_{\text{H}_2} \) of Ni is closest to zero, which proves that Ni certainly holds great promise for the HER. Indeed, French chemist Paul Sabatier first discovered the catalytic effect of metallic Ni powder when studying the hydrogenation of acetylene under the thermally induced action of nickel oxide as early as 19th century and successfully applied this catalyst to other hydrogenation reactions.\[52\]

Generally, the maximum of the volcano plot corresponds to the highest reaction rate for hydrogen evolution. Thus, it is feasible for the binding energy of intermediates to be located close to zero, which is just the case for metallic Ni. Therefore, metallic Ni is regarded as the perfect HER catalyst, the Gibbs free energy for hydrogen adsorption (\( \Delta G_{\text{H}_2} \)) should be close to zero. This means that the binding energy when the active sites are coupled with hydrogen atoms should be neither too weak nor too strong, thus facilitating the hydrogen adsorption and desorption processes.\[43–45\] With this new insight, the researchers have focused on tuning the electronic structure of catalysts to reduce the reaction barrier and lower the hydrogen adsorption energy.\[46–49\] This can help achieve ideal catalysts for the HER. In this review, we summarize the recent progress of Ni-based catalysts, revealing their distinctive electronic properties, surface engineering, and modulation of the metal support interactions. The type, characterization, and electrocatalytic mechanism of Ni-based catalysts are discussed, along with detailed strategies for the rational design and optimization of Ni-based catalysts. Exploring the associations between the catalytic activity and electronic structure enables us to provide some insights into the past and future directions of Ni-based HER catalysts, which may be helpful for the design and widespread implementation of these catalysts.

![Volcano plot for the HER catalyzed by various pure metals and metal overlayers. Reproduced with permission.\[51\] Copyright 2006, Springer Nature.](image-url)
to the peak of the volcano through the rational design of HER catalysts by optimizing hydrogen adsorption. Ni is considered one of the most effective materials for optimizing the interaction with the active sites, promoted by the structural features and synergistic effects. At present, various strategies such as the template method of nickel salt reduction and electrochemical deposition on different substrates are used to manufacture nanoscale metallic Ni with an ultra-high surface area, abundant active sites, and good conductivity, thus improving the catalytic performance. For example, loading Ni nanoparticles on porous carbon can improve the conversion and desorption of hydrogen on the surface of the catalyst, which not only prevents particle agglomeration, but also exerts a synergistic effect on the electrocatalytic activity. Thus, Ding et al. synthesized Ni nanoparticles encapsulated in 3D nitrogen-enriched porous carbon, which required an overpotential of only 94 mV to reach a current density of 10 mA cm\(^{-2}\) and could maintain a low potential after 3000 cycles of cyclic voltammetry (CV) under alkaline conditions.\(^{[53]}\)

Notably, the Ni nanostructure provided excellent HER activity. However, the unsatisfactory stability of Ni catalysts due to the generation of nickel hydride in the HER process hinders the rapid progress of the reaction.\(^{[54,55]}\) Alloying is a valid strategy for altering the properties of the catalyst surface. For instance, Zhang et al. prepared a NiMo alloy from NiMo nanosheet arrays on nickel foam using a coprecipitation thermal reduction method at 180 °C. The as-prepared material exhibited Pt-like activity and only required an overpotential of 35 mV to approximate the current density of 10 mA cm\(^{-2}\) in alkaline conditions.\(^{[56]}\) Another facile method of fabricating NiMo alloys was explored by Nairan et al. They creatively applied an aqueous solution-based preparation method with the assistance of a magnetic field to produce NiMo alloy nanowire arrays, where the catalytic HER current density reached 10 mA cm\(^{-2}\) at 17 mV in 1 M KOH. This excellent catalytic ability, which is significantly better than that of commercial Pt/C, is mainly attributed to optimization of H adsorption energy by the synergistic effect between Ni and Mo, as well as the existence of numerous active sites and surface defects.\(^{[57]}\) By coupling different metal atoms in the alloy, the strong metal interaction would affect the adsorption energy, ultimately determining the catalytic activity. The scaling relationships of alloys can be avoided by inducing peculiar geometric and electronic structures as the isolated metal-site bonding. Therefore, rational design of bimetallic catalysts on the atomic level is a novel strategy for synthesizing alloy catalysts with extraordinary properties. Ding et al. prepared the anisotropic superstructures of the single Pt atom-anchored hexagonal closed-packed Ni (Pt/Ni ASs) nanosheets by a facial solvothermal method.\(^{[58]}\) The Pt/Ni ASs as HER catalyst show an overpotential of 28 mV to reach 10 mA cm\(^{-2}\) and the mass activity is 1060% higher than that of Pt/C in alkaline media. Based on first-principles calculations, the pristine Ni was more favorable for water dissociation, while the single Pt atom was responsible for hydrogen formation. This synergistic interaction of the bimetallic Ni-based catalyst provides a new strategy for designing HER catalysts.

Multicomponent alloys, such as CuAlNi and NiMoFe, can also afford a similar catalytic effect with rational design, thus making them an optimal platform material for catalyst exploration and performance screening.\(^{[59–62]}\) Yao et al. developed a high-entropy CuNiMoFe alloy, the HER performance of which exceeded that of the majority of non-noble catalysts (Figure 2a).\(^{[63]}\) The CuNiMoFe alloy was tightly attached to the layered Cu skeleton in the body-centered cubic (BCC)-precipitated CuAlNiMoFe. Therefore, the Cu skeleton acts as an electron/mass transfer channel, and the surface of the high-entropy alloy CuNiMoFe provides active sites for catalysis. These advantages of the CuNiMoFe alloy afforded overpotentials lower than 183 and 240 mV to attain current densities of 100 and 1840 mA cm\(^{-2}\) in 1 M KOH and pH 7 buffer electrolytes, respectively (Figure 2b,c). Moreover, the structure and catalytic efficiency of CuNiMoFe alloy was stable after long-term HER at 50 mV (Figure 2d,e). Simultaneously, DFT suggests that the fabricated electrode could cause the water decomposition barrier to decrease to 0.52 eV, which promotes the conversion of water to H\(_2\) (Figure 2f). Gupta et al. synthesized Co–Ni–B nanoparticles through a facile reduction method in NaBH\(_4\) solution, which are highly effective for HER in wide pH range.\(^{[64]}\) Based on experiments and DFT results, the presence of Ni leads to B enrichment on the surface and can also provide extra electrons to Co sites, which are beneficial to improve the HER activity for the catalyst. Co–Ni–B as the HER electrocatalyst shows the overpotentials of 209, 170, 83, 60, and 45 mV to reach 2 mA cm\(^{-2}\) for pH 1, 4.4, 7, 9.2, and 14 respectively, indicating the capable HER performance in different pH conditions (Figure 2g,h).

These nickel-based alloys are promising for accelerating HER kinetics in a wide pH range. However, the uncontrollable thickness for the nickel-based alloy does not maximally expose active sites, which restricts the application for HER. Therefore, preparing an ultrathin nickel-based alloy with a lower water decomposition barrier and optimum hydrogen adsorption is of vital importance.

### 2.2. Nickel-Based Oxide and Hydroxide

Usually, nickel of metallic phase is most stable during the HER process, while the overpotential needed for metallic nickel nucleation provides the chance of nickel-based oxide and hydroxide as HER catalysts.\(^{[32,65–68]}\)

#### 2.2.1. Nickel-Based Oxide

The size, surface morphology, and microstructure are important factors that can be adjusted to improve the thermal stability and HER performance of the material. Ito et al. prepared porous nickel oxide nanoparticles with adjustable pore sizes by annealing NiO nanoparticles in hydrogen atmosphere. The NiO skeleton in the nanoporous structure inhibits the rapid growth of pores, and the small pore size beneficially impacts the catalytic activity of the electrode in water electrolysis.\(^{[69]}\) This fusion method is simple and easily executed, but the nanomaterials are partially agglomerated due to annealing in the synthesis process, which greatly affects the specific surface area and compromises the catalytic activity. To avoid this problem, Wang et al. loaded NiO\(_x\) on the surface of bamboo-like carbon nanotube substrates. This method broadens the catalyst surface area and takes full advantage of the active sites of NiO\(_x\), thereby improving the catalytic performance for electrocatalytic hydrogen evolution. Just 79 mV was required achieve a benchmark current density.
of 10 mA cm$^{-2}$ in alkaline solution. However, there is still a gap in the electrochemical performance of NiO compared with that of Pt/C owing to the lack of H adsorption sites in the former. As such, Kou and co-workers presented carbon doping as a strategy for activating NiO. The carbon dopant substitutes the third layer of six-coordinated Ni in NiO, as shown by structural analysis, generating undercoordinated nickel sites that are active for H adsorption. DFT calculations show that the water decomposition barrier of carbon-doped NiO is 0.81 eV, which is lower than that (1.17 eV) of the surface without carbon doping. This indicates that carbon dopants can act as active sites to stimulate the dissociation of water molecules because of their unique electronic structure. Moreover, by plotting the projected density of states (PDOS) of the C surface structure, the authors discovered that C doping can effectively decrease the bandgap from $\approx 1.5$ eV to $\approx 0.6$ eV. This suggests that C doping could afford increased conductivity of Ni$_{3+}$O$_x$, which is conducive to electron transport in the HER. The high electron density around the top Ni layer on the surface was also determined by comprehensively analyzing the charge density diagram and atomic charge difference. This further confirms that C doping provided additional H-binding sites on the NiO surface. The overpotential of the sample at a current density of 10 mA cm$^{-2}$ was as low as 27 mV in alkaline aqueous solution, outperforming all reported NiO catalysts. This is attributed to the excellent chemical composition and electronic structure of the carbon-doped sample. That study provides a novel idea for the synthesis of water-alkali HER catalysts.

Figure 2. a) Typical cross-sectional SEM image of nanoporous CuAlNiMoFe electrode. b) Polarization curves for different electrodes in 1 M PBS electrolyte. c) Polarization curves for different electrodes in 1 M KOH electrolyte. d) Long-term stability measurement of nanoporous CuAlNiMoFe alloy electrode at overpotential of 50 mV for 200 h. e) Polarization curves of nanoporous CuAlNiMoFe electrode before and after the stability test. f) Reaction energy diagram of water dissociation on the surface of different catalysts at different stages of the reaction. a–f) Reproduced with permission. Copyright 2020, Wiley-VCH GmbH. g) Linear polarization curves in pH 7 (0.5 M KPi solution) of Co–Ni–B with different Ni concentrations from 10 to 50%. Inset shows the plot of overpotential at 10 mA cm$^{-2}$ versus Ni concentration in Co–Ni–B catalyst. h) Linear polarization curves for Pt electrode, Co-30Ni–B, Co–B, and Ni–B electrocatalysts. g–h) Reproduced with permission. Copyright 2016, Elsevier.
2.2.2. Nickel-Based Hydroxide

Nickel-based hydroxides are important HER catalysts. Generally speaking, reports on single-phase Ni(OH)$_2$ are very limited, but composite Ni(OH)$_2$ nanomaterials are in the rapid development stage. Rao and co-workers reported hydrotalcite Ni(OH)$_2$ nanosheets, obtained by in situ growth on nickel foam, for electrocatalytic hydrogen evolution. This synthesis is effective and simple and can exclude the effect of electrode adhesion. More importantly, Ni(OH)$_2$ nanosheets fabricated by this method can be evenly distributed on the nickel foam.$^{[74]}$ In view of the extensive room for improvement in the catalytic performance of Ni(OH)$_2$ (250 mV), Yong proved that Ni(OH)$_2$ can reduce the energy barrier of the water decomposition step using a hybrid comprising Ni(OH)$_2$ and WP nanorods (in alkaline media).$^{[75]}$ Subsequently, Liu et al. designed a Ni/Ni(OH)$_2$ dual-composition electrocatalyst on nickel foam, considering the weak H adsorption on Ni. Coral-like Ni/Ni(OH)$_2$ with a 3D layered structure was prepared by a two-step electrodeposition process. This special structure is conducive for transfer of the generated H to the Ni site in Ni(OH)$_2$, encouraging rapid evolution of H and H$_2$. Thus, Ni/Ni(OH)$_2$ displayed an overpotential of only 53 mV when the cathodic current density was 10 mA cm$^{-2}$ in alkaline condition.$^{[76]}$

Another appealing strategy is the logical design of Ni nanolayered double hydroxides (LDHs). Ni-based LDHs have the advantages of simple processing, low synthesis cost, and favorable stability. Moreover, mixed-valence transition metal ions can be added to the LDH structure to improve the HER performance.$^{[77–78]}$ However, there are still some problems such as the low charge transfer rate and relatively high overpotential. Thus, further modification is required to accelerate the large-scale application of Ni nano-LDHs. Optimization methods include accurately controlling the architecture of LDHs, increasing the number of active sites in the LDH structure, and improving the conductance of the LDH scaffolds. Cai et al. designed 3D porous NiFe LDH nanosheets electrodeposited on Ni nanochains in a meticulous manner. The core–shell nanostructure, observed by scanning electron microscopy (SEM), is beneficial for enlarging the surface area of the catalyst and exposing more active sites. The low charge transfer resistance ($R_C$) also reflects the high conductivity of the Ni@NiFe LDH.$^{[79]}$ Accordingly, in the HER, the Ni@NiFe LDH electrode could achieve 92 mV at 10 mA cm$^{-2}$ in 1 M KOH aqueous solution. Nevertheless, the authors are still working on improving the HER performance of the material by producing thinner nanosheets. Despite this, 2D LDHs assembled with defects are excellent carriers for anchoring single atoms, which would lead to the exposure of numerous active sites while augmenting their intrinsic activity.$^{[80–83]}$

Inspired by this, Zhai et al. synthesized active HER catalysts named Ru1/D-NiFe LDH in a straightforward manner via electrochemical deposition and wet-etching processes.$^{[84]}$ Single atoms of Ru were uniformly immobilized on ultrathin defect NiFe LDH nanosheets ($\approx$4.2 nm) (Figure 3a). The bright Ru single atoms detected by spherical aberration-corrected high-angle annular dark-field (HAADF)–STEM (Figure 3b) and the absence of the characteristic Ru peak confirmed by extended X-ray absorption fine structure (EXAFS) (Figure 3c) could assist in determining the location of single-atom Ru in LDHs. Furthermore, the authors demonstrated the mechanism underlying the HER activity by combined analyses using the DFT model, in which they found that Ru1/D-NiFe LDH effectively improved the H adsorption energy (Figure 3d). Thus, Ru1/D-NiFe LDH as a kind of water-alkali electrocatalyst exhibits an overpotential of 18 mV at 10 mA cm$^{-2}$ and persistent cyclic stability over 100 h in alkali environment (Figure 3e,f). As expected, its unique chemical composition and structural design offer further guidelines for the development of scalable and low-cost HER catalysts. Furthermore, the strong interaction between metallic clusters and NiFe LDHs also plays an important role in HER. Zhang et al. prepared Rh nanocluster-integrated NiFe LDHs (Rh/NiFePh-LDH) via the facial hydrothermal method.$^{[85]}$ By coupling with Rh, the NiFe-LDH only needed an overpotential of 58 mV at 10 mA cm$^{-2}$ in alkaline media, which drastically reduces about 280 mV compared with NiFe-LDH (Figure 3g). Experiments and DFT results collectively confirmed that the significantly enhanced HER activity is related to the strong interaction between the Rh clusters and NiFe-LDH (Figure 3h,i).

Due to the controllable thickness and abundant active sites, nickel-based oxide and hydroxide are promising candidates for HER catalysts in alkaline condition. However, the instability in acidic media and low ionic conductivity for nickel-based oxide and hydroxide limit their application as highly active HER catalysts in a wide pH range. Even so, the nickel-based oxide and hydroxide are efficient HER catalysts, which are expected to further development with technological advances.

2.3. Ni-Based Dichalcogenides (Sulfide, Selenide, and Telluride)

Ni-based dichalcogenides with remarkable electrocatalytic HER performance have attracted particular attention. Compared with the hard basic O$^{2–}$ ions of Ni-based oxide/hydroxide, Ni-based sulfides possess soft basic S$^{2–}$/S$^{2–}_2$ ions, which have more covalent properties.$^{[86]}$ Moreover, coupling Ni atoms with S$^{2–}$/S$^{2–}_2$ ions endows the Ni atoms with more valence electrons. Ni-based dichalcogenides with these properties exhibit relatively good conductivity, which can accelerate electron transport and improve the HER performance.

2.3.1. Ni-Based Sulfide

Jiang et al. used a novel microwave-assisted method to synthesize NiS, NiS$_2$, and Ni$_3$S$_2$ with comparable crystal sizes and specific surface areas.$^{[87]}$ Under alkaline conditions, the Ni$_3$S$_2$ electrocatalysts with a large electrochemically active surface area, good conductivity, and unique surface chemistry, which are beneficial for water splitting, exhibited the highest HER activity (Figure 4a). Although Ni$_3$S$_2$ showed the highest HER activity, the overpotential of 335 mV to reach a current density of 10 mA cm$^{-2}$ was still inadequate for use and an HER electrocatalyst. Ion engineering emerged as an effective means of tuning the electronic structure and increasing the number of active sites, resulting in an appropriate energy for the adsorption of reaction intermediates on the catalyst surface. Chen et al. introduced N doping to improve the alkaline HER catalytic activity of Ni$_3$S$_2$.$^{[88]}$ The N–Ni$_3$S$_2$ electrode required 110 mV to reach a current density of 10 mA cm$^{-2}$ (Figure 4b), which is less than that of Ni$_3$S$_2$ (210 mV).
Theoretical results indicated that N doping could significantly adjust the electronic structure of the catalyst surface and thus facilitate electron transfer, as well as lower the adsorption energy of the intermediate (Figure 4c–f). Introducing N, which is more electronegative than S, into the Ni$_3$S$_2$ lattice is beneficial for improving the HER activity. Hence, doping with a more electronegative anion, such as F, could possibly result in a more optimized electronic structure for the Ni$_3$S$_2$ catalyst. This is conducive to improving the HER performance. He et al. prepared F-doped Ni$_3$S$_2$ via the facile vapor-phase fluorination of Ni(OH)$_2$ nanosheets and subsequent hydrothermal sulfuration of F-Ni(OH)$_2$. As an electrocatalyst, the F-Ni$_3$S$_2$ nanosheets exhibited superior HER reaction kinetics and a very small overpotential (38 mV at 10 mA cm$^{-2}$) in 1 M KOH. However, both of the earlier reports displayed unsatisfactory Ni$_3$S$_2$ thickness. To improve the HER performance, the fabrication of cation (e.g., Fe, Sn, Mo, Zn, and V)-doped Ni$_3$S$_2$ with superior activity compared with that of pure Ni$_3$S$_2$ has also been considered an effective strategy for optimizing the adsorption/desorption energetics of intermediates. Zhang et al. synthesized Fe–Ni$_3$S$_2$ nanosheets to achieve improved HER performance in alkaline media. Fe doping could increase the electrochemical active surface area (ESCA), thereby accelerating water splitting and optimizing the hydrogen adsorption energy of Ni$_3$S$_2$, which collectively improved the HER activity. Moreover, doping with Fe significantly decreased the hydrogen adsorption energy ($\Delta G_{\text{H}}$) from 0.6 to 0.31 eV, which is beneficial for increasing the HER activity of Ni$_3$S$_2$ (Figure 4g–h). Moreover, the energy for adsorption...
of water on Fe–Ni$_3$S$_2$ is lower than that on Ni$_3$S$_2$ ($-0.73$ vs. $-0.29$ eV), indicating a low energy barrier for water activation on the surface of Fe–Ni$_3$S$_2$ (Figure 4j,k). 2D ultrathin nanosheets with a high specific surface area, numerous active sites, and superior conductivity have been widely reported as HER catalysts.[91] Unlike layered materials,
2D nonlayered materials exhibit a unique catalytic mechanism as their edges are occupied by dangling bonds. These unconventional dimensions of dangling bonds at the edges enable greater chemical activity than facial bonding, thus reinforcing the catalytic performance. In general, 2D-layered materials undergo strong lateral chemical bonding in the planes, while weak van der Waals interactions are operative between planes, impelling atoms to form 2D structures during the nucleation and growth process. However, as a nonlayered material, the formation of Ni-based dichalcogenide ultrathin nanosheets is not spontaneous, owing to the lack of an intrinsic driving force for anisotropic growth. Changing the composition through postsulfuration of the precursor, such as Ni(OH)$_2$, is an effective and promising method for obtaining nanostructured Ni$_3$S$_2$. Unfortunately, structural stability is often destroyed by the collective lattice expansion involving individual layers and crystal-phase transformation during the sulfuration process, which leads to the formation of thick sheets or nanoparticles.

To explore an efficient and general strategy for preparing nonlayered Co–Ni$_3$S$_2$ ultrathin nanosheets, our previous work reported the topochemical conversion of ultrathin layered Ni(OH)$_2$. Co–Ni(OH)$_2$ was used as a template to fabricate the Co–Ni$_3$S$_2$ ultrathin nanosheets through a facile vapor-phase sulfuration method, avoiding the morphological change induced by recrystallization (Figure 5a). SEM images showed that the microsized Co–Ni$_3$S$_2$ nanosheets were densely coated on the surface of the Ni foam (Figure 5b–d). The ultrathin 2D Ni(OH)$_2$ nanosheets provide a well-retained template for topochemical conversion. This restricts epitaxial lattice expansion and swelling of the few monolayer-thick structures. Atomic force microscopy

Figure 5. a) Scheme illustration of the synthetic procedure of Co–Ni$_3$S$_2$. b) SEM images of Ni foam. c) SEM images of Co–Ni(OH)$_2$. d) SEM images of Co–Ni$_3$S$_2$. e) AFM image of Co–Ni$_3$S$_2$. f) DOS of d-band of Ni$_3$S$_2$ and Co–Ni$_3$S$_2$. g) Calculated free-energy diagram of HER for Ni$_3$S$_2$ and Co–Ni$_3$S$_2$. a–g) Reproduced with permission.[93] Copyright 2021, Wiley-VCH GmbH.
(AFM) characterization indicated that the thickness of the Co–Ni$_3$S$_2$ ultrathin nanosheets could be controlled to less than 4 nm (Figure 5e). Notably, nonlayered Ni, NiO, and NiP ultrathin nanosheets could also be obtained through the template-assisted method, implying the universality of this strategy. The Co–Ni$_3$S$_2$ ultrathin nanosheets with a small lateral size and rich exposed edges exhibit highly enhanced catalytic activity. In comparison with Ni(OH)$_2$ and pure Ni$_3$S$_2$, Co–Ni$_3$S$_2$ shows Pt-like HER performance, requiring an overpotential of only 158 mV to reach a current density of 100 mA cm$^{-2}$. Density of states (DOS) calculations suggested that the d-band center ($\epsilon_d$) of the Co–Ni$_3$S$_2$ (110) surface was much closer to the Fermi level than that of Ni$_3$S$_2$ (−1.59 vs. −1.8 eV). It was established that Co doping improved the conductivity and increased hydrogen adsorption on the catalyst (Figure 5f). $\Delta G_{\text{H}_2}$ was used as a parameter to further quantify the enhanced HER performance of Co–Ni$_3$S$_2$. For Ni$_3$S$_2$, $\Delta G_{\text{H}_2}$ was 0.43 eV from DFT calculations, while $\Delta G_{\text{H}_2}$ could be effectively decreased to 0.13 eV due to Co doping (Figure 5g). This indicates that the superior HER activity of Co–Ni$_3$S$_2$ is attributed to enhanced hydrogen adsorption due to the doping effect.

2.3.2. Ni-Based Selenide

Nickel selenides (NiSe and NiSe$_2$), which are nonlayered Ni-based chalcogenides, have emerged as promising HER catalysts, owing to their good conductivity and electrochemical reactivity. Compared with Ni-based sulfide, nickel selenides can easily interact with the heteroatom-doped carbon matrix, which effectively induces the charge redistribution and regulates the interfacial structure. Huang et al. prepared Ni$_x$Se$_y@$NC core–shell nanohybrids by the Ni–MOF template to improve pH-universal HER catalytic performance.$^{[94]}$ Ni$_{0.85}$Se@NC exhibits the overpotentials of 131 135, and 183 mV at 10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$, 1 M KOH, and 1 M PBS solutions, respectively. DFT analysis confirmed that the C atom bridging to the N dopant is the active site for HER, and Ni$_{0.85}$Se$_2$ played an important role for regulating the charge distribution via van der Waals forces. Therefore, Ni$_{0.85}$Se$_2@$NC showed superior hydrogen adsorption and metallic behavior with increased electron density near the Fermi level (Figure 6a–d).

Like nonlayered Ni$_3$S$_2$, engineering ultrathin NiSe nanosheets is also considerably difficult because of the innate deficiency in the driving force for anisotropic growth of the nonlayered structure. Cai et al. introduced a solid-state reaction to achieve interface-confined epitaxial growth of NiSe films on Ni foils.$^{[95]}$ Nevertheless, the strict preparation requirements, uncontrollable thickness, and limited surface area are undoubtedly obstacles to the large-scale application of these of NiSe films as HER catalysts. Wu et al. proposed an acid-etching method for synthesizing ultrathin Ni(OH)$_2$ nanosheets, followed by topotactic phase engineering to obtain nonlayered NiSe nanosheets (Figure 6e,f).$^{[96]}$ Intact transformation from layered Ni(OH)$_2$ to nonlayered NiSe was achieved because of the template effect of the ultrathin structure. The $R_x$ and $R_z$ values of the NiSe electrode are lower than those of Ni(OH)$_2$, indicating rapid charge transfer in NiSe. As an HER catalyst, NiSe displays a very low overpotential of 177 mV at 10 mA cm$^{-2}$ in basic media, which is lower than that of Ni(OH)$_2$ (278 mV).

2.3.3. Ni-Based Telluride

Te, which is less electronegative and displays stronger metallic properties than S and Se, is more suitable for optimizing the electronic structure and improving the conductivity of Ni-based catalysts. Xiang et al. reported a one-step hydrothermal method of preparing NiTe$_x$ (NiTe, Ni$_2$Te$_2$, and Ni$_2$Se$_6$Te$_2$) nanosheets.$^{[97]}$ The theoretical results indicated that the d-band center of nonstoichiometric Ni$_2$Se$_6$Te$_2$ approaches the Fermi level, which promotes the adsorption of hydrogen intermediates on the catalyst...
surface. Moreover, the electronic states close to the Fermi level were obviously increased, revealing higher charge carrier density, along with favorable charge transfer and conductivity of Ni$_{2.86}$Te$_2$ for HER. In addition, $\Delta G^{\text{st}}$ of Ni$_{2.86}$Te$_2$ (0.6 eV) is smaller than that of NiTe (0.8 eV), which demonstrates that Ni$_{2.86}$Te$_2$ can significantly enhance the HER activity. When used as a HER catalyst, Ni$_{2.86}$Te$_2$ exhibits superior behavior, with overpotentials of 166 and 253 mV to reach current densities of 10 and 100 mA cm$^{-2}$ in the presence of H$_2$SO$_4$; these values are smaller than that of NiTe (297 mV).

According to the discussion above, the ultrathin Ni-based dichalcogenides not only have good electrical conductivity, but also can maximize expose active sites by facial synthesis, making Ni-based dichalcogenides promising electrocatalysts to accelerate HER kinetics. Nevertheless, this strategy has not been realized in commercial applications because of the unsatisfying stability during HER. How to simplify the synthesized process of 2D ultrathin Ni-based dichalcogenides to be applied in practical HER catalysts is of vital importance.

### 2.4. Single-Atom Ni

Taylor proposed that the metal atoms with one coordination on the surface of the catalyst show the different catalytic activity compared with the metals atoms in saturated coordination.\cite{98}

After that, Crawford et al. found the “single-atom state” of Ni in nickel carbonyl, which exhibited specific catalytic activity compared with pure Ni metal.\cite{99} Due to the electronic interaction between single atoms and support, the chemical and catalytic properties can be affected by the electronic perturbations such as shifts in the energy of the d-band center. Normally, when the transition metal bonds are with adsorbates (e.g., H atoms and oxygen-containing intermediates), more electrons will fill and occupy the antibonding orbits. Therefore, the energy level of the d-band center is related to the binding of hydrogen adsorption to the catalysts’ surface, which makes it possible to improve hydrogen adsorption by regulating the energy level of the d-band center (e.g., heteroatom doping).\cite{100} In addition, reducing the size of nanoparticles to the atomic scale can theoretically enable maximum atom utilization efficiency, as well as afford high activity and selectivity in the catalytic reaction.\cite{101} Therefore, single-atom catalysts with high atom utilization and unique electronic structures have attracted considerable attention. Since then, many Ni single-atom catalysts with high catalytic efficiency have been developed to apply to HER.

Zhang et al. enhanced the hydrogen evolution activity, achieving a current density of 10 mA cm$^{-2}$ at an overpotential of 53 mV in 0.5 M H$_2$SO$_4$ (Figure 7d), by decorating isolated Ni atoms on the base plane of layered MoS$_2$ nanosheets supported on multichannel carbon nanofibers (Figure 7a,b).\cite{102} XAFS analysis was used to prove the formation of a shortened Ni—S bond and distorted structure due to modification of the basal plane of MoS$_2$ by the Ni atoms (Figure 7c). This achievement indicates that surface modulation on the atomic-scale desirably adjusts the surface chemistry and improves the catalytic performance (Figure 7d). The catalyst showed excellent performance in long-term stability tests (Figure 7e). DFT calculations (Figure 7f) showed that decoration with isolated Ni atoms could construct new electronic states and consequently tune the adsorption behavior of H atoms to enable complexation with S atoms, thereby optimizing the hydrogen evolution activity and catalyst durability. Recently, Pattengale et al. investigated the active site of single-atom Ni-anchored 1T-MoS$_2$ by in situ X-ray absorption spectroscopy (XAS) measurement in both acidic and alkaline media.\cite{103} In acidic condition, single-atom Ni(II) was reduced without intrinsic structure change during HER, while the structural reconstruction to form Ni$_2$S$_3$O was observed in alkaline conditions (Figure 7g–j). These results directly revealed that the active sites of single-atom Ni in Ni@1T-MoS$_2$ changed in different catalytic media, which provided insights into the dynamic evolution of HER catalysts.

Ni single-atom catalysts have been proposed to accelerate HER kinetics and some progress has been achieved. With the development of the technique, researchers can discover the structural information during the HER process by ex situ and in situ tests. Combined with experimental characterization and theoretical calculations, the active sites and catalytic mechanism can be clearly demonstrated. However, the research of electronic interaction between single-atom and support is same and important but is relatively difficult because of the great barrier to detect the electronic state accurately, especially during the HER process. Therefore, the more accurate probe and faster detection are needed to monitor this transient state under reaction condition.

### 2.5. Other Nickel Compounds (Phosphide, Nitride, Carbide, and Heterostructures)

#### 2.5.1. Nickel-Based Phosphides

In addition to nickel oxides, hydroxides, and dichalcogenides, other types of robust and inexpensive Ni-based HER electrocatalysts have also been developed. Nickel-based phosphides have attracted enormous interest due to the high electronic conductivity and high activity. During the HER process, phosphorus in nickel-based phosphide can moderate bonding to the intermediates (hydron or hydroxyl ion) and form interfacial for accepting proton and hydride. Various Ni–P catalysts with different stoichiometric ratios and different structural forms, including nanoparticles, nanorods, and nanosheets, have been synthesized by solvothermal reaction or by the conversion of transition metal oxides/hydroxides to phosphides, which requires intricate steps. To this end, Wang et al. devised a simple approach for manufacturing 3D self-supported biphasic Ni$_3$P$_4$–Ni$_3$P nanosheet arrays through one-step phosphorylation of nickel foam. This catalyst, when used in the cathode, exhibits an overpotential of 120 mV at 10 mA cm$^{-2}$ and provides good stability in acidic solutions. These results are attributed to the microporous skeleton and the synergistic effect between the Ni$_3$P$_4$ and Ni$_3$P phases.\cite{104} Given that the interfacial electron transfer in poly morphs leads to electrochemical activity of electrocatalysts, Liu and co-workers synthesized Ni$_2$P–Ni$_3$P$_2$ poly morphs (Figure 8a) by phosphorylation, taking Ni$_3$S$_2$ single-crystal octahedron as a template.\cite{105} This polytype displays superior HER properties in alkaline solution, with an overpotential of 59.7 mV to reach...
10 mA cm\(^{-2}\) (Figure 8b). DFT calculations verified the decrease in $|\Delta G_{\text{H*}}|$ (Figure 8b). DFT calculations verified the decrease in $|\Delta G_{\text{H*}}|$, indicating that two-phase coupling enhanced the electrocatalytic activity, from the aspect of theoretical calculation (Figure 8c). In reality, this method of controlling the interfacial charge by developing metallic–metalloid compounds as highly efficient electrocatalysts is worthy of further exploration as a
feasible strategy. Furthermore, Wang et al. reported 3D honeycomb Ni$_2$P. The obvious advantage of this structure is that it has a larger number of exposed catalytic active sites and has a large specific surface area, which are more conducive to reducing the overvoltage for the acidic HER. The honeycomb skeleton is also more conducive to electron transmission and electron exchange. It was found that the electrocatalytic hydrogen evolution performance of this honeycomb Ni$_2$P is close to that of the precious metal Pt/C, which confirms the relationship between the structure and properties.\cite{106} Despite morphological control, the electrocatalytic performance can be further improved by heteroatom doping. Metal dopants in Ni$_2$P have been experimentally demonstrated to enhance the HER activity. For instance, Li et al. reported the remarkable catalytic activity of Ni$_2$P with a combination of Fe dopants.\cite{107} Moreover, using DFT theory, Partanen et al. corroborated that the most promising dopants were iron and cobalt, while doping with copper was unlikely to be efficient.\cite{108}

### 2.5.2. Nickel-Based Nitrides

Because Ni$_3$N is a good promoter of water dissociation, this compound is a prospective candidate for use in HER electrocatalysis.\cite{109} However, the strong adsorption of H on Ni$_3$N hinders the rapid desorption of hydrogen and the subsequent production of H$_2$. To this end, Zhang et al. verified that the higher-valence Mo dopant in Ni$_3$N has the lowest surface reaction activity and excellent hydrogen adsorption/desorption thermodynamics compared with Ni$_3$N doped with W and V, from the perspective of the
energetics of the adsorption of hydrogen and hydroxyl substances.[116] It was revealed that Mo, W, and V doping can afford a low initial overpotential owing to the favorable hydrogen adsorption energy. Among these dopants, only Mo can effectively promote the kinetics of the alkaline HER as it induces favorable energetics for hydroxyl adsorption. Thus, gas-phase nitridation was used to transfer nickel hydroxide/NiMo–LDH to Mo–Ni3N nanosheets. The synthesized sample with a flaky morphology had a larger number of exposed sites for H adsorption, with an ultralow overpotential of 12 mV at 10 mA cm−2 and a small Tafel slope of 64 mV dec−1 in alkaline media. In another report, Niu et al. designed Ni3N/MoO2, which had a significant effect as a HER catalyst. First, Mo-doped nickel oxide (Mo–NiO) was obtained by annealing the Mo–Ni(OH)2 nanosheet arrays. The prepared Mo–NiO was then transformed into Ni3N/MoO2 in situ by phase separation in ammonia atmosphere. Based on DFT computation, the authors explicitly revealed that the combination of MoO2 and Ni3N could not only reduce the energy barrier for water dissociation, but also accelerate hydrogen desorption (Figure 8f). Ni3N/MoO2 afforded an impressive voltage of 21 mV at 10 mA cm−2 for the alkaline HER (Figure 8d), making it one of the best transition metal nitride-based electrocatalysts.[111] The Ni3N catalysts can provide fast charge and abundant active sites to support the HER. Nevertheless, Ni3N is impressive to corrosion and passivation in basic media, which lead to significantly attenuated activity for HER. Sun et al. synthesized Ni3N with a cobalt-doped carbon shell (Co–C)/Ni3N to enhance stability for HER in alkaline condition.[112] Due to the carbon layer, Ni3N can maintain intrinsic properties after 5000 scanning cycles, which is more stable compared with pure Ni3N in alkaline condition.

2.5.3. Nickel-Based Carbides

Ni3C has been extensively reported as HER catalyst due to the appropriate DOS near the Fermi level, good electronic conductivity, and superior chemical stability. For example, Fan et al. synthesized nanocrystalline Ni3C wrapped in a graphite shell sustained by a graphene nanoribbon, via hot filament chemical vapor deposition.[118] Unfortunately, the nanoparticles were prone to agglomeration during high-temperature reduction, thus lowering the catalytic activity. Consequently, Wang et al. proposed Ni3C nanoparticles implanted in a porous carbon network (Ni3C@PCN) via a controllable annealing process.[114a] The Ni3C nanoparticles were evenly distributed in the ultrasmall nanoporous carbon sheets. The as-obtained specimen possesses a near-zero onset potential at −65 mV and requires 203 mV to reach 20 mA cm−2 under acidic conditions. Moreover, Ni3C@PCN shows high durability, ascribed to its protection from peripheral carbon. To improve the catalytic activity of Ni3C, another team exploited a facial process to form Ni3C coupled with Ni nanoparticles, grown in situ on a flexible carbon cloth (Ni–Ni3C/CC) (Figure 8g). DFT calculations were used to analyze the efficiency of Ni–Ni3C in the HER, which proved that Ni–Ni3C could provide a ΔGads value of 0.29 eV, which is better than that of Ni (0.43 eV) or Ni3C (0.66 eV) (Figure 8i). Based on electrochemical evaluation, an overpotential of only 98 mV in 1 M KOH was required at 10 mA cm−2, outperforming Ni3C@CNT (132 mV at 10 mA cm−2) and Ni/Ni3C-NCNT (184 mV at 10 mA cm−2),[114b,c] among others. Therefore, Ni–Ni3C can be regarded as a superior Ni3C-based catalyst for alkaline HER (Figure 8i).[114d] There are comparatively fewer strategies for the efficient synthesis of nanoscale Ni-based carbides relative to other Ni-based compounds, still leaving room for exploration.

2.5.4. Nickel-Based Metal Organic Frameworks

Metal organic frameworks (MOFs), also known as porous coordination polymers, have attracted increasing attention in the field of electrocatalysis. Owing to their unique porous configuration, highly dispersed metal components, and ultrahigh specific surface area, MOFs generally exhibit excellent HER activity.[115,116] In addition to the abundant open channels, active Ni centers with good redox properties can be uniformly exposed in the frame. In particular, the unique shape and morphology of Ni–MOFs remained unchanged after postprocessing. Different metal components, especially iron group elements (Fe and Co), could be introduced into Ni–MOFs to generate a synergistic effect and improve the catalytic performance.[117–119] For example, Zhang and co-workers fabricated FePc@Ni–MOF and used it as a working electrode, achieving excellent HER performance and enhanced stability due to the strong coupling between FePc and 2D Ni–MOF.[120] Do et al. combined amorphous molybdenum sulfide (MoS2) and Ni-MOF-74 to fabricate MoS2/Ni-MOF-74. The as-fabricated catalyst afforded a desirable Tafel slope of 53.1 mV dec−1 and a low onset potential of −114 mV in acidic media, attributed to the ability of the newly formed NiMoS phase to cooperatively reduce the hydrogen adsorption energy of the electrocatalyst.[121] In addition, Ni-MOFs can form a carbon-based framework through high-temperature reduction. The presence of metals can also promote graphitization of the carbon matrix. Therefore, the conductivity can be improved, and aggregation and corrosion of the transition metal can be prevented. In accordance with this, Shao et al. successfully developed NiO/graphite carbon nanocomposites by annealing Ni–MOF at 300 °C. SEM was used to confirm that the microstructure was successfully maintained.[122] Wang et al. also prepared MoOx@Ni-MOF by fitting polyol and anions into the pores of Ni-MOF through a one-step hydrothermal reaction. This sample was converted to NiMo–C by heating in NH3 atmosphere, resulting in excellent catalytic performance.[123] Ni–MOFs as precursors can be oxidized, phosphorylated, or sulfided to obtain Ni–MOF derivatives with various compositions.[124,125] Motivated by this, Lin et al. developed a simple strategy to completely phosphorylate MOFs deposited on Ni foam and generate cotedoped (Fe0.1Ni0.9)2P(O)/NF (Figure 9a).[126] This catalyst only demands 87 mV to drive 10 mA cm−2 and can maintain ≈20 mA cm−2 for 40 h without distinct fluctuations in 1 M KOH (Figure 9b,c).

2.5.5. Nickel-Based Heterostructures

Heterogeneous catalysts have been widely used in electrocatalysis and have attracted the attention of researchers. Considering that the hydrogen evolution process in alkaline medium involves the adsorption/desorption of a variety of particles (such
as \( \text{H}_2\text{O}, \text{H}_2, \text{OH}^-, \text{and H}^+ \), catalysts with dual or multiple types of active sites on the surface may predominantly promote the HER. Moreover, different material components can be concurrently incorporated to facilitate the adsorption/desorption of these different particles. In addition, electronic interactions between multiple components at the interface of the heterostructure may play an important role in changing the electronic structure. Subbaraman et al. proved that the heterojunction of \( \text{Ni(OH)}_2 \) nanoclusters on the surface of a platinum electrode afforded eightfold higher activity for catalytic hydrogen evolution, driving an upsurge in research on the principle of interfacial synergy in the field of electrocatalysis. It is rational to assume that the mutual matching of various compounds of metallic Ni with known catalytic activity can optimize the energy for adsorption of water molecules and hydrogen ions.\(^{[127]}\) Lately, a number of related materials have been reported. For example, \( \text{Ni}_3\text{S}_2 \) with a continuous Ni—Ni bond network exhibits inherent metal behavior, which is instrumental in influencing the charge transfer and catalytic activity, and \( \text{Ni(OH)}_2 \) has superior ability to chemically adsorb \( \text{OH}^- \) and oxygenated water oxidation intermediates. Based on this, Li et al. prepared an interface comprising \( \text{Ni}_3\text{S}_2/\text{Ni(OH)}_2 \) flakes on Ni foam as an efficient hydrogen evolution electrode.\(^{[128]}\) Similarly, Lai et al. synthesized a Ni/\( \text{Ni(OH)}_2 \) heterostructure (Figure 9d) on a Ni foam substrate by simple electrodeposition and aging treatment.\(^{[129]}\) DFT simulations were performed to further evaluate the mechanism underlying the HER activity. The value of \( \Delta G_{\text{H*}} \) changed from 1.46 eV on \( \text{Ni(OH)}_2 \) and \( \text{Ni}/\text{Ni(OH)}_2 \) to 0.58 eV on the Ni/\( \text{Ni(OH)}_2 \) heterostructured catalyst, reflecting that the H adsorption energy was maximized at the heterojunction interface (Figure 9e,f). Thus, this electrocatalyst requires only 30 mV to achieve a current density of 10 mA cm\(^{-2} \) in alkaline condition (Figure 9g).

Figure 9. a) Synthesis sketch of \((\text{Fe}_{0.1}\text{Ni}_{0.9})_2\text{P(O)}/\text{NF}\). b) HER polarization curves of \((\text{Fe}_{0.1}\text{Ni}_{0.9})_2\text{P(O)}/\text{NF}\) and other catalysts in 1.0 M KOH obtained at 5 mV s\(^{-1} \). c) Chronoamperometric curve of \((\text{Fe}_{0.1}\text{Ni}_{0.9})_2\text{P(O)}/\text{NF}\) obtained at a potential of \(-0.126 \text{ V vs RHE}\) in 1.0 M KOH without IR correction. a–c) Reproduced with permission.\(^{[126]}\) Copyright 2020, Royal Society of Chemistry. d) High-resolution transmission electron microscopy (HRTEM) images of the AC–Ni/NF sample. e) Calculated free energy for atomic hydrogen adsorption on Ni, \( \text{Ni(OH)}_2 \), and \( \text{Ni}/\text{Ni(OH)}_2 \). f) Mechanism for the enhanced HER on \( \text{Ni}/\text{Ni(OH)}_2 \) heterostructure. g) Polarization curves of AC–Ni/NF and contrast samples at a scan rate of 2 mV s\(^{-1} \) in 1 M KOH. d–g) Reproduced with permission.\(^{[129]}\) Copyright 2021, Elsevier.
Table 1. Summary of the HER catalytic activity of Ni-based catalysts.

| Catalysts                  | Overpotential at 10 mA cm⁻² [mV] | Catalytic conditions | Ref  |
|----------------------------|----------------------------------|----------------------|------|
| N-doped 3D porous Ni/C     | 94                               | alkaline             | [53] |
| Ni/Mo nanosheets           | 35                               | alkaline             | [56] |
| NiMo alloy                 | 17                               | alkaline             | [57] |
| Pt/Ni ASs                  | 28                               | alkaline             | [58] |
| CuNiMoFe alloy             | 9.7                              | acidic               | [63] |
| Co–Ni–B                    | 333                              | acidic               | [64] |
| NiO₂                        | 170                              | neutral              |      |
| NiO₂                        | 120                              | alkaline             | [70] |
| C-doped NiO                | 27                               | alkaline             | [71] |
| Ni(OH)₂–WP                 | 77                               | alkaline             | [73] |
| Ni/Ni(OH)₂                 | 53                               | alkaline             | [74] |
| 3D porous NiFe LDH         | 92                               | alkaline             | [79] |
| Ru₁/D-NiFe LDH             | 18                               | alkaline             | [84] |
| Rh/NiFePh-LDH              | 58                               | alkaline             | [85] |
| Ni₅S₂                      | 335                              | alkaline             | [87] |
| N-doped Ni₅S₃              | 110                              | alkaline             | [88] |
| F-doped Ni₅S₃              | 38                               | alkaline             | [89] |
| Fe–Ni₅S₂                   | 47                               | alkaline             | [90] |
| Co–Ni₅S₂                   | 80                               | alkaline             | [93] |
| Ni₅Se₆@NC                  | 131                              | acidic               | [94] |
| Ni₅Se₆@NC                  | 135                              | alkaline             |      |
| Ni₅Se₆@NC                  | 183                              | neutral              |      |
| Ni₅Se₆@NC                  | 177                              | alkaline             | [96] |
| Ni₂S₃Te₂                   | 166                              | acidic               | [97] |
| MCM@MoS₂–Ni                | 53                               | acidic               | [102]|
| Ni@Ti–MoS₂                 | 80                               | alkaline             | [103]|
| Ni₉P–Ni₉P                  | 120                              | acidic               | [104]|
| Ni₅P–Ni₅P                  | 59.7                             | alkaline             | [105]|
| Ni₅P–Ni₅P                  | 67                               | acidic               | [106]|
| Fe-doped Ni₅P              | 106                              | alkaline             | [107]|
| Mo dopant in Ni₅N          | 12                               | alkaline             | [110]|
| Ni₅N/MoO₂                  | 21                               | alkaline             | [111]|
| (Co–C)/Ni₅N                | 50                               | alkaline             | [112]|
| Ni₅C@PCN                   | 98                               | alkaline             | [114a]|
| Ni₅C@CNT                   | 132                              | alkaline             | [114b]|
| Ni₅Ni₅C–CNT                | 184                              | alkaline             | [114c]|
| Ni–Ni₅C                    | 98                               | alkaline             | [114d]|
| Fe₈P@Ni–MOF                | 334                              | alkaline             | [120]|
| MoS₂Ni–MOF–74              | 167                              | acidic               | [121]|
| Fe₈S₃Ni–MOF–74             | 87                               | alkaline             | [126]|
| Ni₅S₃Ni(OH)₂               | 48                               | alkaline             | [128]|
| Ni/Ni(OH)₂                 | 30                               | alkaline             | [129]|

3. Conclusion

In conclusion, this article reviews some of the Ni-based materials in HER catalysts in recent years (Table 1). We also briefly introduce the practical application of HER in energy conversion under the background of being carbon neutral. Many efforts have focused on increasing the specific surface area to expose more active sites of the catalyst, and these catalysts hold the satisfactory potential in catalyzing HER with comparable activity with Pt catalyst. Nevertheless, it remains controversial of the HER mechanism on Ni-based catalysts surfaces. Under the guidance of DFT, the HER kinetics on Ni-based catalysts can be understood at the atomistic level, which is available to guide the design of Ni-based catalysts and then optimize the catalytic performance. A range of strategies for designing Ni-based HER catalysts have been guided by DFT, including heteroatomic doping, alloying, epitaxial growth, and tuning surface electronic property.

Despite the achievements accomplished thus far in relation to Ni-based catalysts, several challenges are worth further study to better understand the reaction mechanisms involved in these catalytic processes, to develop HER catalysts that are low cost, efficient, and stable, and to integrate these catalysts into practical systems for energy conversion: 1) The valence of Ni atom may change under the HER, which affects the catalytic activity. In situ monitoring of the dynamic change of Ni valence during the reaction process is beneficial to deeply understand the mechanism of Ni-based catalysts. Although existing characterization methods (e.g., X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), XAS, SEM, and transmission electron microscopy (TEM)) can analyze changes in the catalyst morphology and structure before and after HER, it is difficult to monitor the electrochemical reactions that occur at the surface of catalysts during the HER process. In addition, a terrific amount of bubbles on the catalyst surface during the HER process and the scattering effect of the electrolyte are great barriers for accurate detection, which needs to be modulated according to the actual situation. Operating characterization including in situ Raman combined surface-enhanced Raman spectroscopy (SERS), in situ XRD, and in situ XAS may be suitable candidates for studying the states of surface metal species and structural transition during the catalytic process. PeakForce SECM analysis may be a suitable method to obtain the correlation between the surface morphology and the catalytic activity. However, the complicated experiment and lower resolution of SECM hinder its practical application in current research. With the development of operando tests, the interaction between the structure reconstruction and catalytic activity on Ni-based catalysts can be further studied under the reaction. 2) Theoretical simulations can explore the interaction between intermediates adsorption and catalysts. However, the intermediates adsorbed on the surface of Ni-based and other catalysts are still difficult to be directly detected. The advanced technique is needed for probing the transient state on the catalyst surface. In addition, the active sites of Ni-based catalysts are usually considered as only the nearest atoms around the Ni center, while the atoms on the second or even third shell may also affect the catalyst activity. 3) It has been proved that the
magnetic field can positively affect the Lorentzian movement of diffusion of electrolyte and gas bubbles, which can accelerate mass transport especially for the highly magnetic nickel oxides. Therefore, external conditions including magnetic field, strain, temperature, and pH may contribute to enhancing the kinetics for some Ni-based catalysts, opening interesting possibilities for improving catalytic efficiency. Moreover, Ni-based catalysts are not stable enough for industrial hydrogen production, which impedes scale-up production. The large-scale and economic synthesis of stable Ni-based HER catalysts is expected to enable the utilization of clean and renewable energy sources.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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