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Self-supported electrocatalysts for the hydrogen evolution reaction

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Electrocatalytic water splitting is a promising technology for producing clean hydrogen fuel. The development of cost-effective, highly efficient, and excellent durable electrocatalysts for the hydrogen evolution reaction (HER) plays an important role in industrial electrolytic water splitting. Using self-supported electrodes is regarded as an impactful strategy for designing electrocatalysts with exceptional activity and high stability, compared with conventional powder electrocatalysts. Herein, recent progress in different substrates including nickel foam (NF), carbon cloth (CC), titanium foil (TF), stainless steel (SS), iron foam (IF), cobalt foam (CF), copper foam (CFM), molybdenum foil (MF), and so on for self-supported electrocatalysts is systematically overviewed, with a special focus on the vacancy engineering, morphological control, heterostructure construction, alloying design, and doping regulation, as well as the design and fabrication route. This review may promote future research and provide a guideline for selecting suitable materials and substrates for fabricating self-supported electrodes with outstanding HER performances, thereby further enhancing the large-scale application of electrolyzing water.

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1 Introduction

Currently, it is an undeniable fact that the depletion of traditional primary energy sources (natural gas, crude oil, and coal) is becoming an increasingly serious problem,^{1–5} which needs to be solved immediately. Therefore, high gravimetric energy density hydrogen (H₂) has attracted broad interest in this regard by virtue of its clean, sustainable, zero carbon footprint, and environmentally friendly features.^{6–11} H₂ is a perfect medium for energy storage. Hydrogen does not naturally form on Earth, and must be produced by the decomposition of other molecules.

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Approximately 95% of the hydrogen yield around $50 \times 10^6 \text{ t a}^{-1}$ (around 50 million tonnes per annum) is generated through steam reforming of natural gas and subsequent water–gas shift reactions with electrolysis.¹² The formation of H_2 from natural gas will lead to harmful or polluting side-products. Considering the limited supplies of natural gas and the greenhouse effect of CO_2 , producing H_2 from this method does not solve the needs of renewable energy storage. It should be mentioned that on a weight-by-weight basis H_2 produces almost four times more energy than the equivalent weight of gasoline. Fortunately, the production of H_2 from water through electrolysis is a clean and environmentally benign process, resulting in only oxygen being generated as a byproduct. In addition, when H_2 is burned, H_2 as a renewable fuel only generates water without by-products including sulfide, nitric oxide, and carbon dioxide. Furthermore, with the ongoing

development of the economy and the global industrialization process, human beings have to deal with the universal threat of global warming and air pollution.^{13–19} Thereinto, H_2 , a promising energy carrier, is capable of solving the environmental problems caused by the consumption of fossil fuels. However, the strategies of producing H_2 in industry derived from steam methane reforming, biomass conversion, and coal gasification are not energy-efficient and economical.²⁰ Since water electrolysis was first studied by Troostwijk and Diemann in 1789, it has been extensively investigated by researchers around the world.^{21–23} Alternatively, electrolyzing water is a desirable method to yield H_2 with high purity and efficiency.^{24–26} Accordingly, efficient and stable electrocatalysts are urgently developed and used for the HER.

Recently, several electrocatalysts have been synthesized for the HER, and most of the electrocatalysts are in the form of powder.



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In this review, we summarize recent developments in the area of self-supported electrodes for the HER (Fig. 1). We comprehensively review many important kinds of self-supported substrates. In the discussion, particular attention is paid to the defect and morphology engineering, interface regulation, doping, and catalytic performance of these HER electrocatalysts. Finally, we briefly point out the critical challenges in HER electrode design and performance.

2. Electrochemical hydrogen evolution reaction

2.1 Mechanisms of electrochemical HER

The electrocatalytic HER involves a two-electron transfer reaction occurring at the electrode/electrolyte interface.³⁶

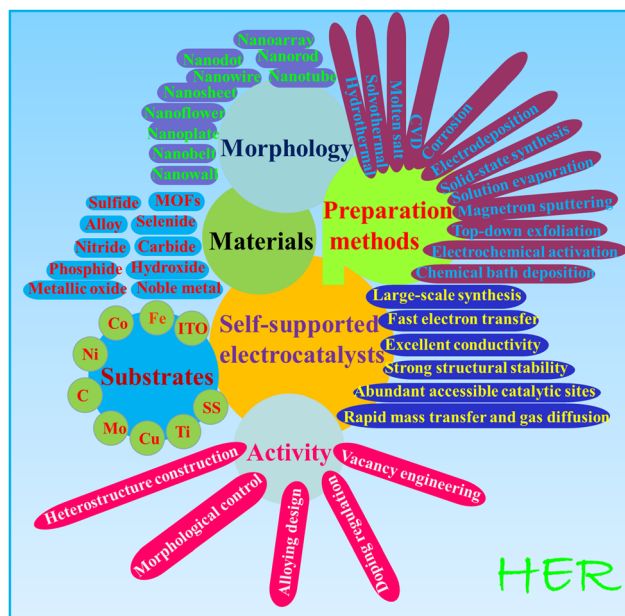


Fig. 1 Overview of the topic covered in this article.

Thereinto, H_2 is produced at the cathode through the reduction of either a proton (H^+) in acidic media or H_2O in alkaline media, both of which contain multiple steps (Fig. 2). It should be noted that the HER process in a neutral solution is similar to that in an alkaline solution. Moreover, electrocatalysts are required to lower the energy barriers in each step.

2.1.1 HER in acidic media. In an acidic solution, first, hydronium ions coupled with electrons form reactive hydrogen intermediates H^* at active sites (where $*$ represents an active site on the electrode surface, and H^* is the hydrogen atom adsorbed on the active site) *via* the electrochemical adsorption process (Volmer step, eqn (1)). Subsequently, there are two possible reaction pathways: one is the electrochemical desorption process (Heyrovsky step, eqn (2)), where the generated H^* combines a new pair of H^+ and electron (e^-) in the solution to produce H_2 molecules, and then desorbed; the second is the chemical desorption process (Tafel step, eqn (3)), in this case, two nearby H^* obtained by the Volmer step are recombined directly to yield H_2 molecules. In acidic

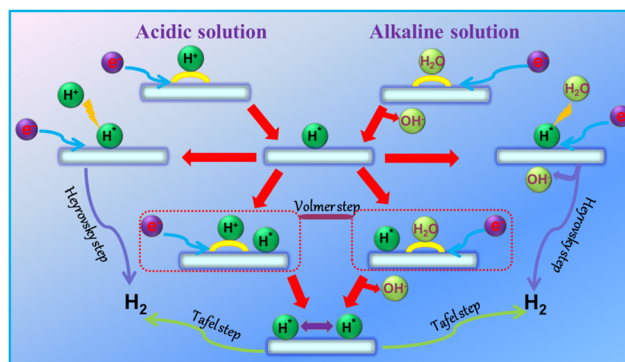
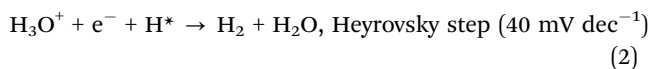
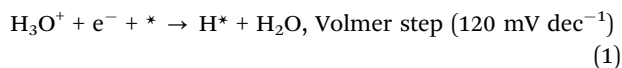
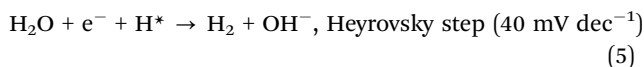
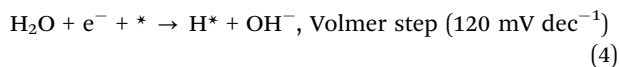


Fig. 2 Schematic process for the HER under acidic and alkaline solutions.

media, the HER pathway with different Tafel slopes is as follows:



2.1.2 HER in alkaline media. Compared with the HER in acidic media, the HER in alkaline solution shows a slower kinetic rate, because extra energy is required to dissociate H_2O molecules to obtain enough H^+ .³⁷ Therefore, the alkaline HER is first initiated by water adsorption and dissociation process to produce H^* on active sites (Volmer step, eqn (4)), which is the rate-determining step (RDS). Then, at low coverage of H^* on the catalyst surface, H^* will preferably combine with an electron and H_2O molecule to generate an H_2 molecule (Heyrovsky step, eqn (5)); When the H^* coverage is high, the H_2 molecule will be formed through binding two adjacent H^* atoms (Tafel step, eqn (6)). Additionally, it should be mentioned that the low water adsorption energy and water dissociation are conducive to the effective alkaline HER.^{38–41} In an alkaline solution, the reaction formula and Tafel slope for the HER are described as follows:



2.2 Parameters for evaluating electrocatalysts

As shown in Fig. 3, several significant parameters are usually utilized to evaluate the performance of an electrocatalyst, such as overpotential (η), Tafel slope, exchange current density (j_0), stability, electrochemically active surface area (ECSA), specific and mass activity, turnover frequency (TOF), electrochemical impedance spectroscopy (EIS), and faradaic efficiency (FE). These parameters can furnish penetrative information about the thermodynamics and kinetics of the HER. These parameters are introduced briefly in this section.

2.2.1 Overpotential. Theoretically, the driving thermodynamic potential of the HER is 0 V *versus* the reversible hydrogen electrode (RHE), while the extra potential is routinely required to drive the reaction in a practical reaction system. The extra potential is called overpotential, which is a critical parameter to assess the performance of catalysts. The overpotential value can be determined by linear sweep voltammetry (LSV) with a function between the current density and overpotential. The overpotential mainly comprises the activation overpotential, resistance potential, and concentration overpotential in the electrochemical systems.⁴² The activation



Fig. 3 The parameters for evaluating the HER performance.

overpotential, an intrinsic property of the catalyst, can be reduced by using an efficient catalyst. The concentration overpotential derives from a sudden change in the concentration near the electrode/electrolyte interface owing to the sluggish diffusion rate.⁴³ This can be decreased by distributing the electrolyte *via* stirring the solution. The resistance overpotential can be depressed by employing ohmic drop compensation, which can be realized in many modern electrochemical workstations equipped with automatic compensation for IR loss. For ease of quantifying the overpotential, three η values at the current densities of 1 (η_1), 10 (η_{10}), and 100 (η_{100}) mA cm^{-2} are frequently utilized to compare the activities between different catalysts. η_1 is called an “onset overpotential”, which suggests that the current density starts to tremendously increase.³⁰ η_{10} , an important criterion, corresponds to the solar water-splitting efficiency of 12.3%, which is generally chosen as the comparison standard for different catalysts.⁴⁴ A smaller η_{10} implies a better electrocatalytic activity to some extent. However, it cannot directly discriminate the activity of a catalyst by just comparing the η_{10} value, because the loading content of the catalyst on the electrode with the same geometrical area is totally different. Therefore, for evaluating and comparing the real HER activity of catalysts, researchers should load the same amount of a catalyst on a standard glassy carbon electrode with low roughness to achieve the activity per unit mass. η_{100} is another key criterion for catalyst evaluation in practical applications. Furthermore, potentials are frequently measured and quoted regarding reference electrodes other than the RHE,

which is greatly inconvenient from an experimental standpoint. The common references are the saturated calomel electrode (Hg/Hg₂Cl₂) in acidic media or the mercuric oxide electrode (Hg/HgO) in alkaline media. Meanwhile, the counter electrode should be a convenient one, which cannot affect the performance of the working electrode. Over the past few decades, the Pt electrode is prevalently used as the counter electrode due to its outstanding stability and excellent electrical conductivity, which, however, can be dissolved into Pt²⁺ for a long-term test. Then, the produced Pt²⁺ transfers to the working electrode surface, resulting in enhancing the activity of the working electrode.⁴⁵ To ensure the authenticity of the test data, some stability electrodes including graphite rod, conductive glass, carbon cloth, and titanium mesh should be served as the counter electrodes. To unify the standard of evaluation, the potentials should be calibrated to the RHE according to the following equations:

$$E(\text{RHE}) = E(\text{Hg}/\text{Hg}_2\text{Cl}_2) + E^\circ(\text{Hg}/\text{Hg}_2\text{Cl}_2) + 0.0592 \times \text{pH} \quad (7)$$

$$E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + E^\circ(\text{Ag}/\text{AgCl}) + 0.592 \times \text{pH} \quad (8)$$

$$E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + E^\circ(\text{Hg}/\text{HgO}) + 0.0592 \times \text{pH} \quad (9)$$

2.2.2 Tafel plot and exchange current density. The Tafel plot is often applied to exhibit the relationship between current density and overpotential in the HER.⁴⁶ From eqn (10), the Tafel slope and exchange current density can be derived. The Tafel slope is plotted by η as a function of $\log|j|$, and b can be extrapolated from the linear portion of the Tafel plot. The Tafel slope shows the intrinsic property of a catalyst and discerns the charge transfer kinetics and probable reaction pathways, as well as the rate-determining step of the hydrogen evolution process,⁴⁷ which generally can be used for explaining the catalyst mechanism of the HER. It has been elaborated that the HER kinetics contains three main steps: Volmer, Heyrovsky, and Tafel as the rate-determining steps with corresponding Tafel slopes of 120, 40, and 30 mV dec⁻¹ observed at the low overpotential values/current densities.⁴⁸ Note that the above Tafel slope values are not absolute, because the Tafel slope is determined by the coverage of the absorbed hydrogen.⁴⁹ The smaller b indicates that less η is required to achieve the same current density increment, signifying faster electron-transfer kinetics. On the other hand, j_0 , relying on the reaction activation energy at the surface of the electrocatalyst, is a critical kinetic parameter for revealing the inherent catalytic activity of an electrocatalyst under reversible conditions, which can be valued by assuming η of being zero.⁵⁰ In addition, electrolyte composition and temperature also affect the value of j_0 .⁵¹ A superior electrocatalyst should possess a high j_0 and a small b simultaneously.

$$\eta = a + b \log j \quad (10)$$

2.2.3 Electrochemical impedance spectroscopy. EIS can provide information about the electrode/electrolyte interface in the catalytic system.⁵² The charge transfer resistance (R_{ct}),

which exhibits the interface charge transfer process of an electrode, can be gained by fitting the diameter of the semi-circle in the high-frequency region.⁵³ For the HER, a smaller R_{ct} value indicates a faster reaction rate and high charge transfer efficiency, rendering a smaller overpotential. Additionally, the uncompensated ionic and ohmic resistances of the electrochemical measurement process are also obtained based on the EIS Nyquist plots.

2.2.4 Electrochemically active surface area. In electrochemical reactions, the geometric surface area is generally employed to calculate the current density. However, it is difficult to guarantee the standard flat of a catalyst.⁵⁴ To reveal the intrinsic activity, ECSA can be used to assess the performance of a catalyst, which reflects the effective catalytic areas of a catalyst.⁵⁵ One of the most regularly used ECSA calculation methods is measuring cyclic voltammetry (CV) in the non-faradaic regions at different scanning rates.⁵⁶ When conducting the CV test, the variation of non-Faraday current density (j) should be linearly related to the scan rate (ν); thus, it provides the electric double-layer capacitance (C_{dl}) derived from the slope (eqn (11)),⁵⁷ where the slope is twice C_{dl} . The large C_{dl} expounds more active sites exposing and current density enhancing. The ECSA is proportional to C_{dl} , thus the ECSA of the catalyst is calculated according to eqn (12). In addition, ECSA can also be measured by underpotential deposition or advanced electron microscopy.^{58–60} It should be mentioned that the chemical nature and construction of the electrodes may overestimate ECSA and thus underestimate the catalytic activity.⁶¹ Moreover, although ECSA manifests some information on the number of active sites of the electrocatalyst, it does not mean that all active sites play a catalytic role in the HER. Even so, ECSA can still act as a key reference for the comparison of similar component materials.

$$C_{\text{dl}} = \frac{j}{\nu} \quad (11)$$

$$\text{ECSA} = \frac{C_{\text{dl}}}{C_s} \quad (12)$$

where C_s is the specific capacitance of a flat standard electrode (1 cm²), it is usually between 20 and 60 $\mu\text{F cm}^{-2}$. The average value of 40 $\mu\text{F cm}^{-2}$ is frequently used for flat electrodes.^{54,62,63}

2.2.5 Turnover frequency. TOF is an important parameter for evaluating the intrinsic activity of each catalytic site on catalysts, which is defined by the number of H₂ moles per catalytic site per unit of time at a given potential. A high TOF value implies prominent catalytic activity. However, it is a great challenge to obtain a precise number of active sites per unit area for voluminous HER catalysts, because catalysts generally have readily accessible surface atoms/catalytic groups and some unattainable internal atoms/catalytic species. Therefore, various approximate strategies are carried out. For instance, researchers endeavor to measure the TOF value with a reasonable approach that only considers the surface atoms or the easily accessible catalytic sites on the catalysts. In other cases, the TOF is calculated by using the total catalytic species in the

catalysts, which comprise all the accessible catalytic sites and some inaccessible catalytic sites originating from the surface and interior of catalysts. Although the two kinds of methods cannot provide an accurate value compared with the real TOF value of the active sites, they may still furnish a useful way to compare the catalytic activity or efficiency of similar catalysts. A common method to estimate TOF value is according to eqn (13) and (14). Based on eqn (13), the number of active sites (n) is obtained by the CV test from -0.2 V to $+0.6$ V vs. RHE at a scan rate of 20 or 50 mV s⁻¹ in 1.0 M phosphate buffer solution (PBS, pH = 7). In addition, other methods for quantifying the number of active sites are also applied, such as the copper underpotential deposition method and estimating the number of molecules on the active surface.^{64–67} When the number of active sites is determined, the TOF (s⁻¹) can be calculated with eqn (14).

$$n = \frac{Q}{2F} \quad (13)$$

$$\text{TOF} = \frac{IN_A}{2Fn} \quad (14)$$

where Q is the voltammetric charge calculated by the integral curve of CV, I is the current (A) during the linear sweep measurement, N_A denotes the Avogadro constant (6.023×10^{23} mol⁻¹), F is the Faraday constant (96 485 C mol⁻¹), and n is the number of active sites (mol). The factor 1/2 in the equation means that two electrons are consumed to generate one H₂ molecule.

2.2.6 Specific and mass activities. The specific and mass activities are key quantitative parameters to evaluate the catalytic activity of electrocatalysts at a defined overpotential. The specific activity is the current density per unit real surface area of the catalyst, which can be measured by normalizing the current to the ECSA. The ECSA normalized activity is relatively accurate, because ECSA can reveal the intrinsic surface area of the catalyst.^{68,69} The current normalized by the loading mass is the mass activity, which is normally valid for the comparison of a similar material system.⁷⁰ The mass activity is positively correlated with the active surface area of catalysts, namely, catalysts with larger surface area usually present a higher mass activity.⁷¹

2.2.7 Faradaic efficiency. Faradaic efficiency is another crucial parameter to evaluate the performance of an electrocatalyst, which illustrates the proportion of electrons partaking in the HER *versus* total electrons provided by an external circuit in the HER.⁷² FE is defined as the ratio of the experimental to the theoretical amount of H₂ production. The theoretical H₂ production can be calculated from the chronoamperometry or chronopotentiometry test, and the experimental H₂ generation can be collected by the gas chromatography or drainage method. The FE of electrons is usually less than 100% due to the by-products forming on the electrode surface during the HER.

2.2.8 Stability. Long-term stability, which shows the long-term ability to retain the initial catalytic activity of the electrocatalysts, is a crucial indicator to evaluate the practical

applications of an HER catalyst.⁷³ Generally speaking, two assessment approaches are performed, such as continuous CV and chronoamperometry (potential-time curve) or chronopotentiometry test (current-time curve). In the case of the CV test, potential cycles usually are consistent with that of the LSV range. The stability is evaluated by comparing the LSV curve change before and after the repetitive CV cycles (normally 1000–10 000 cycles). While the LSV curves remain negligible variation as the initial one or the overpotential marginally increases less than 10% with respect to the initial value, suggesting great durability. With regard to the chronopotentiometry (CP) or chronoamperometric (CA) measurements, which are usually conducted at a constant current density of 10 mA cm⁻² or applied overpotential for at least ten hours. The longer duration without potential (or current) change presents excellent endurance. Even so, ten hours are not enough for HER. We recommend using a longer time test, such as 100 hours. Additionally, along with the accumulating and releasing of H₂ bubbles on electrodes, the measured current-time curve displays a unique serrate shape.⁷⁴ Unfortunately, the produced H₂ bubbles can cover the catalytic sites, leading to slow HER kinetics.⁷¹ Meanwhile, the release of H₂ bubbles may peel the active materials from the electrode surface, resulting in lowering HER performance. To a certain extent, the negative effect of H₂ bubbles can be weakened through stirring or using self-supported electrodes.

2.3 Density functional theory (DFT)

As a vital computational tool, DFT, which is based on quantum mechanics, can not only illuminate the correlations between the electrocatalytic performances and physical/chemical properties of catalysts at an atomic level but also calculate the electronic structure of the whole catalytic system.⁷⁵ With the exuberant development of computer technology, DFT calculations have been widely used to explore the electrocatalytic mechanisms, identify the active sites, and predict potential catalysts.^{76–78} In particular, it is very hard to probe the intermediate states of electrocatalytic reactions and electron transfer because of their short lifetimes and complex reaction conditions, leading to ambiguous active sites indefinite and inconclusive electrocatalytic mechanisms.⁷⁹ Therefore, coupling experiment with DFT calculations is an effective method to identify the active sites, deeply discern the catalytic mechanisms of the HER, as well as rationally design new advanced electrocatalysts.

2.3.1 The Gibbs free energy of hydrogen adsorption (ΔG_{H^*}). The Gibbs free energy of hydrogen adsorption has been extensively regarded as a crucial descriptor for theoretically predicting and evaluating the catalytic activity of the HER catalysts,⁸⁰ which can reflect the electronic state of the catalyst surface. As guided by the volcano plot (Fig. 4), an optimal HER catalyst should have a nearly zero ΔG_{H^*} , which not only promotes the charge/mass transfer with fast kinetics but also facilitates adsorbed H (H_{ads}) bond breaking and rapidly release of H₂ molecules under this condition.^{81,82} When ΔG_{H^*} is too negative, the intermediate H_{ads} will bind strongly with the electrocatalyst surface, thereby promoting the initial Volmer step, but retarding the subsequent

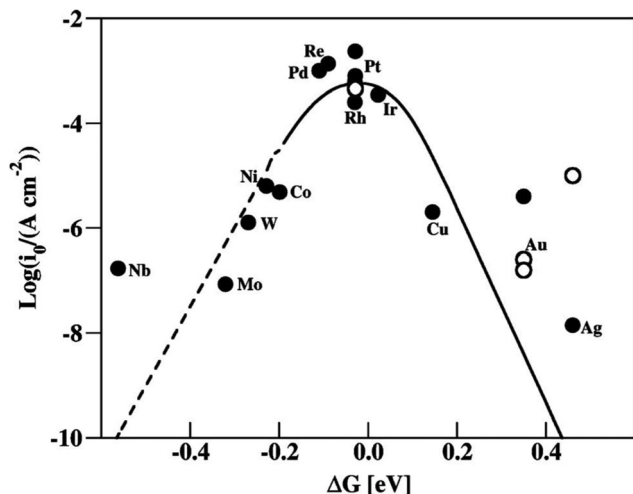


Fig. 4 A volcano plot.⁸²

Heyrovsky or Tafel steps. When ΔG_{H^*} is too positive, H_{ads} shows insufficient interaction with the electrocatalyst surface, resulting in a slow Volmer step.^{83–85} Therefore, appropriate ΔG_{H^*} is very important for enhancing H_2 evolution. By modeling the possibly produced intermediates of hydrogen adsorption, reduction, and desorption processes, ΔG_{H^*} can be calculated from eqn (15).⁸⁶

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S \quad (15)$$

where ΔE_{H^*} is the hydrogen chemisorption energy, ΔE_{ZPE} is the zero-point energy difference between the adsorbed and gas phases, T is the room temperature (298.15 K), and ΔS is the entropy change.

2.3.2 The d-band center theory. The d-band center theory was first established by Nørskov and Hammer, which has been successfully used to describe the tendency in the activity of transition metal-based electrocatalysts.^{87–90} Particularly, the d-band center theory manifests that the hydrogen or oxygen adsorption strength depends on the d states of metals.^{91–93} For instance, when H^* adsorbs on the surface of the metal catalysts, the metal–hydrogen (M–H) bond will be formed through hybridizing the H^* orbital with the metal d orbital. Basically, the interplay between H^* orbital and the metal d orbital can generate a fully filled bonding orbital with low energy and a partially filled anti-bonding orbital with high energy, where the occupancy of the anti-bonding orbital determines the M–H bond strength.⁹⁴ Generally speaking, the low anti-bonding orbital occupancy will result in a high M–H bond strength. Therefore, the inherent surface adsorption ability of H^* can be qualitatively construed and forecasted through computing the local d-band states of a metal surface.⁹⁵ Moreover, the position of the d-band center (ϵ_d) relative to the metal's Fermi level also has a great impact on the M–H bond strength. When the metal's Fermi level gets close to the d-band center, the anti-bonding orbital becomes higher due to the decreased occupancy, leading to a stronger H^* adsorption.⁹⁶ Apart from the d-band filling, the bandwidth of the d-band also influences the adsorption strength on the catalyst surface. When fixing the

filling level of the d-band, a diminished bandwidth will elevate the level of the d-band center, thereby resulting in a strong adsorption interaction.^{97–99} For calculating the effect of ϵ_d on the adsorption interactions, the corresponding ϵ_d is defined as the local average of the d electron energies (eqn (16)).

$$\epsilon_d = \frac{\int_{-\infty}^{+\infty} x\rho(x)dx}{\int_{-\infty}^{+\infty} \rho(x)dx} \quad (16)$$

where x is the energy level and $\rho(x)$ is the density of states of the corresponding d-orbital.

3. Design and fabrication of self-supported electrocatalysts

3.1 Carbon-based substrates

Carbon-based substrates mainly contain carbon fiber paper (CFP), graphite plate (GP), and CC, which exhibit augmented conductivity, strong flexibility, and high resistance to strong acidic and alkaline electrolytes.^{100–103} To improve the solvent-accessible hydrophilic surface, carbon-based substrates should be treated before use. Several methods of treating carbon-based substrates have already been reported, for instance, CC was cleaned using acetone and ethanol under ultrasonication to remove impurities, respectively, and then dried at 60–80 °C for many hours. Whereafter, CC was treated with concentrated nitric acid with the hydrothermal method or reflux method.^{104–107}

In addition, chemical oxidation with potassium permanganate, electrochemical oxidation, air calcination treatment, and plasma methods were also utilized.^{108–111} Therefore, the carbon-based substrates were widely used to construct the self-supported electrodes for the HER by virtue of their advantages. For example, the Mo–Fe–Ni phosphides nanowires were prepared on carbon cloth, which shows superefficient alkaline HER performance with an overpotential of 75 mV at the current density of 10 mA cm^{−2} and superior long-term electrochemical stability for 20 h electrolysis.¹¹² The improved HER performance could be attributed to the synergistic effects between multiple catalytic centers (Mo, Fe, and Ni), as well as the facilitated evolved-gas escape. In similar research, Wen *et al.* provided a general strategy for fabricating self-supported nanoporous Cu-doped CoP nanorod arrays on CC (Cu–CoP NRAs/CC) *via* a hydrothermal method followed by a low-temperature phosphatization route, showing enhanced HER performance in a wide pH range.¹¹³ The resultant Cu–CoP NRAs/CC electrode exhibited wonderful HER performance with 44 mV overpotential to reach a current density of 10 mA cm^{−2} in 0.5 M H₂SO₄ solution. Simultaneously, it needed overpotentials of 81 mV in 1.0 M KOH and 137 mV in 1.0 M PBS at the same current density, respectively. It also presented prominent stability under different pH conditions for 40 h. The exceptional HER performance could be ascribed to the strong heteroatomic interactions induced by many lattice distortions and defects. Zheng *et al.* successfully synthesized bimetallic carbide Ni₆Mo₆C nanodots embedded on NiMoO_x nanosheets arrays anchored on an activated carbon cloth (Ni₆Mo₆C/NiMoO_x/ACC)

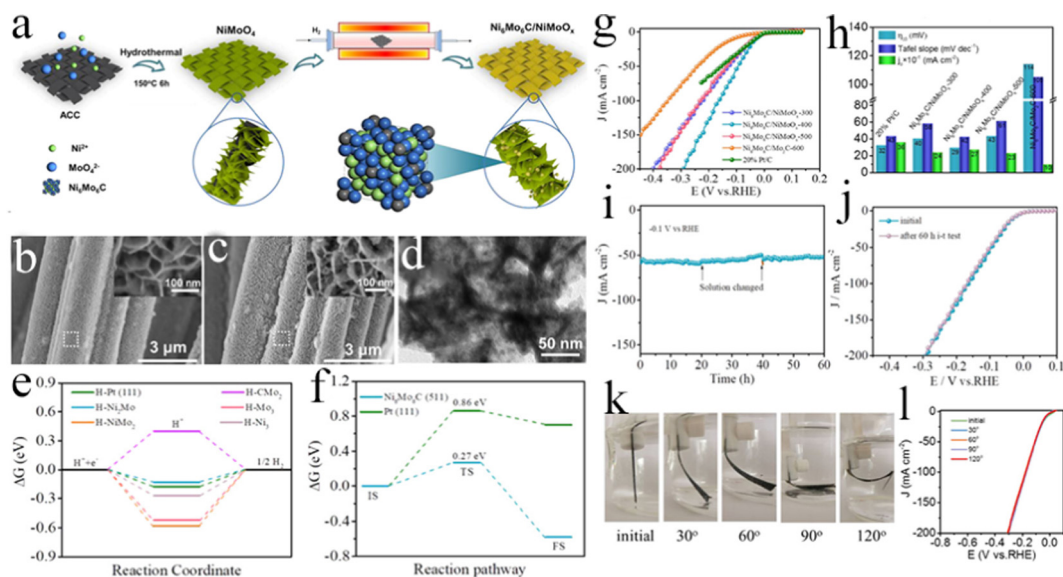


Fig. 5 (a) Schematic illustration of the preparation of $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x\text{-T}$. (b) Field emission scanning electron microscope (FESEM) images of NiMoO_4 nanosheets grown on ACC at different resolutions. (c) FESEM images of $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x\text{-400}$ at different resolutions. (d) Transmission electron microscope (TEM) images of $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x\text{-400}$. (e) Calculated ΔG_{H^+} values for H adsorption on different sites of $\text{Ni}_6\text{Mo}_6\text{C}$ (511) and Pt (111). (f) Gibbs free energy diagram of the water dissociation path on $\text{Ni}_6\text{Mo}_6\text{C}$ (511) and Pt (111). (g) HER polarization curves of different electrocatalysts without iR compensation in 1 M KOH solution at 2 mV s^{-1} . (h) Comparison of η_{10} , Tafel slope, and j_0 of various electrocatalysts. (i) i - t curve of $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x\text{-400}$ at 100 mV overpotential in 1 M KOH solution, and (j) corresponding LSV curves after constant electrolysis for 60 h. (k) Digital images of the distorted $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x\text{-400}$ electrode under the HER test, and (l) corresponding LSV curves.¹¹⁴

via controlling the diffusion of carbon atoms into precursor NiMoO_4 nanosheets with carbothermal hydrogen reduction (Fig. 5a).¹¹⁴ The as-formed NiMoO_x nanosheet arrays grown on ACC with unique hierarchical structures (Fig. 5b–d) could greatly enhance both the mass transport and electric conductivity. In virtue of the moderated hydrogen adsorption ability ($\Delta G_{\text{H}^+} = -0.13 \text{ eV}$) and low water dissociation energy barrier ($\Delta G_{\text{b}} = 0.27 \text{ eV}$) on $\text{Ni}_6\text{Mo}_6\text{C}$ (Fig. 5e and f), the open microstructure of the $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x$ hybrid, and the high conductive ACC support, the $\text{Ni}_6\text{Mo}_6\text{C}/\text{NiMoO}_x/\text{ACC}$ flexible electrode displayed a small overpotential of 29 mV to achieve 10 mA cm^{-2} with long-term stability for 60 h of constant electrolysis, even superior to the benchmark Pt/C and most of the reported nonprecious metal catalysts (Fig. 5g–j). Exclusively, as exhibited in Fig. 5k and l, it showcased excellent flexibility, which could remain unchanged for the HER performance under different bending angles. Therefore, this work provided a good idea to fabricate HER electrocatalysts with highly efficient, inexpensive, and flexible merits for practical application and commercialization. Liu *et al.* synthesized a three-dimensional (3D) self-supported binder-free integrated electrode constructing a few layered N, P dual-doped carbon-encapsulated ultrafine MoP nanocrystal/MoP cluster hybrids on CC (FLNPC@MoP-NC/MoP-C/CC) for attractive HER performance.¹¹⁵ The FLNPC@MoP-NC/MoP-C/CC electrode was fabricated through an electrodeposition process and an *in situ* phosphatization. The preparation of the FLNPC@MoP-NC/MoP-C/CC electrode with several steps is depicted in Fig. 6a. First, a layer of the polyaniline (PANI) film on CC (PANI/CC) was generated by an electrodeposited method. Second, the MoO_3

microrods ($\text{MoO}_3\text{-MRs}$) were *in situ* arrayed on PANI/CC to form $\text{MoO}_3\text{-MRs}/\text{PANI}/\text{CC}$ by a hydrothermal route with the predecessors of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and tartaric acid. Subsequently, another PANI film layer was further electrodeposited on the $\text{MoO}_3\text{-MRs}/\text{PANI}/\text{CC}$ electrode to obtain PANI/ $\text{MoO}_3\text{-MRs}/\text{PANI}/\text{CC}$. Finally, the as-formed PANI/ $\text{MoO}_3\text{-MRs}/\text{PANI}/\text{CC}$ was annealed in a PH_3 atmosphere, achieving a 3D self-supported integrated FLNPC@MoP-NC/MoP-C/CC electrode by means of converting $\text{MoO}_3\text{-MRs}$ into MoP-NC/MoP-C hybrids and carbonizing PANI films into few layered N, P dual-doped carbon. From Fig. 6b–d, the FLNPC@MoP-NC/MoP-C/CC electrode showed remarkable HER performance with extremely low overpotentials over the entire pH range ($j = 10 \text{ mA cm}^{-2}$ at $\eta = 74, 69, \text{ and } 106 \text{ mV}$ in $0.5 \text{ M H}_2\text{SO}_4, 1.0 \text{ M KOH}, \text{ and } 1.0 \text{ M PBS}$ solutions, respectively). Besides, owing to the protection of few layered N, P dual-doped carbon, FLNPC@MoP-NC/MoP-C/CC presented long-term durability for 50 h testing in acidic, neutral, and alkaline media (Fig. 6e–g), indicating the great potential for electrolyzing water application. The excellent electrocatalytic performance could be ascribed to the following virtues: (1) 3D porous structure of the electrode with large specific surface area could furnish more active sites and facilitate electrolyte diffusion, as well as forcefully lower the charge transport resistance;¹¹⁶ (2) the well-dispersed MoP-NCs embedded in few-layered N, P dual-doped carbon could increase the specific surface area, resulting in exposing more active sites; (3) the N, P dual-doped carbon layer could not only boost the porousness and electroconductivity of the entire electrode, enhancing the contact between the active sites and the electrolyte, and shortening the charge transfer pathway, but

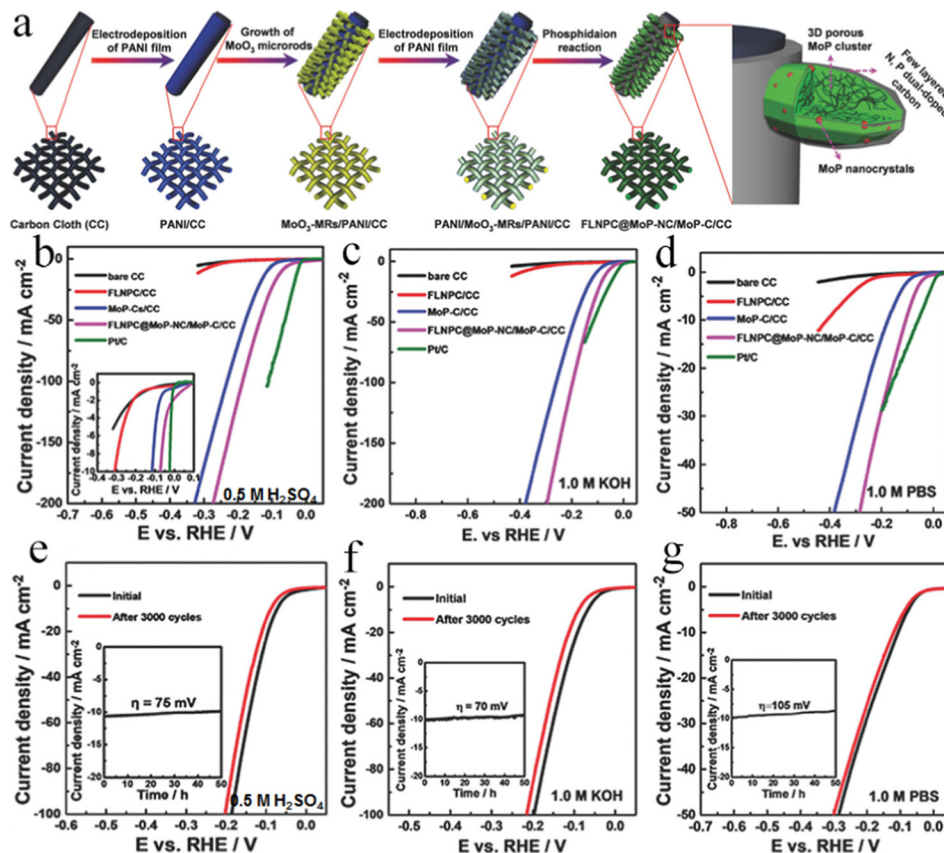


Fig. 6 (a) Fabrication process of few layered N, P dual-doped carbon-encapsulated MoP nanocrystal/MoP cluster hybrids on CC. (b–d) LSV curves of bare CC, FLNPC/CC, MoP-C/CC, FLNPC@MoP-NC/MoP-C/CC, and Pt/C in 0.5 M H₂SO₄, 1.0 M KOH, and 1.0 M PBS electrolytes at 2 mV s⁻¹. (e–g) LSV curves of FLNPC@MoP-NC/MoP-C/CC initially and after 3000 cycles in 0.5 M H₂SO₄, 1.0 M KOH, and 1.0 M PBS medium. Insets of (e–g) are time-dependent current density curves of FLNPC@MoP-NC/MoP-C/CC under a static overpotential for 50 h.¹¹⁵

can also prevent MoP-NCs from corrosion and aggregating;¹¹⁷ (4) N doping of carbon layers could provide extra active sites by changing the electron density in graphitic carbon;¹¹⁸ (5) the synergistic effect between MoP components and few layered N, P dual-doped carbon could optimize the ΔG_{H^*} values to improve the H^{*} adsorption, resulting in promoting the HER performance. This work put forward a broad strategy for guiding the fabrication of various self-supported electrodes for the HER. Lately, numerous works have been devoted to exploring the economical and efficient alternatives based on transition metal dichalcogenides, which showed potential electrocatalytic HER activities owing to their optimal ΔG_{H^*} .^{62,119–122} Among them, molybdenum disulfide (MoS₂) is a well-known electrocatalyst due to its natural abundance, distinct catalytic mechanism, low price, tunable electronic structure, and good chemical stability.^{123–128} A 3D self-supported cross-linked (3DSC) Co-doped MoS₂ (Co-MoS₂) nanostructured HER electrocatalyst on CC was designed and synthesized by creative nanostructure engineering.¹²⁹ Benefiting from the special structure, MoS₂ nanosheets exposed more copious active sites on the edges, making ion transfer and bubble release easy and smooth. Moreover, the unique structure also enhanced the stability and advanced electron transfer *via* direct bonding with CC. On the other hand, the Co element in MoS₂ could raise the

overall conductivity, resulting in optimizing the electron transfer path and activating the adjacent S sites. As a consequence, the 3DSC Co-MoS₂ electrode integrated on CC could reach the current density of 10 and 100 mA cm⁻² with merely 40 and 119 mV overpotentials, respectively, surpassing other MoS₂-based HER electrocatalysts reported recently. This research exhibited a facile integration strategy and a new method for boosting inexpensive and high-activity electrocatalysts. Pang and co-workers reported a versatile and effective method to synthesize Re/ReS₂ self-supporting array electrodes with abundant S defects on CC (Re/ReS₂/CC).¹³⁰ The optimized S-defect-rich Re/ReS₂/CC exhibited outstanding electrocatalytic HER performance, providing ultralow overpotentials of 42 and 44 mV at 10 mA cm⁻² in acidic and alkaline solutions, respectively, and corresponding small Tafel slopes of 36 and 53 mV dec⁻¹, which were comparable to many promising HER catalysts. Experiments and DFT results demonstrated that the S defects in Re/ReS₂/CC could afford sufficient active sites, boost charge transfer kinetics, and optimize ΔG_{H^*} at the active sites, resulting in high-caliber electrocatalytic HER performance. Sun *et al.* used a simple two-step method of dip-coating and electrochemical reduction to synthesize self-supported molybdenum oxide stabilized ultrafine palladium electrocatalysts on CC (MoO_x-Pd/CC), which showed a small Tafel slope of 45.75 mV dec⁻¹,

an ultralow overpotential of 25 mV at 10 mA cm⁻², and outstanding durability for at least 7 days in 0.5 M H₂SO₄ solution, surpassing the bare Pd/CC and MoO_x/CC and also comparable to the commercial Pt mesh electrode.¹³¹ The experimental results and DFT calculations presented that MoO_x could not only effectively downsize and disperse Pd nanoparticles by exposing more active sites, but also tune the electronic structure of the Pd surface, boosting their intrinsic catalytic activity. Hu *et al.* fabricated a self-supported economical Ni-doped Mo₂C electrocatalyst with nanoflower morphology on CFP through a molten salt method.¹³² Compared to the conventional solid-phase approach, the molten salt method can prepare products with a uniform chemical composition, great crystal morphology, and pure phase by using a low melting point salt as a reaction medium at low temperatures for a short time.^{133–137} Based on this method, the as-obtained fluffy and porous nanoflower-like structure showed a large specific surface area, resulting in exposing more active sites and promoting charge transfer. The optimal Ni-doped Mo₂C electrocatalyst exhibited high-efficient HER performance with a low overpotential of 56 mV at 10 mA cm⁻², a small Tafel slope of 27.4 mV dec⁻¹, and long-term stability for 35 h electrolysis in 0.5 M H₂SO₄ solution, which is superior to most of the noble-metal-free electrocatalysts. DFT calculations indicated that the Ni doping could cause a down shift of ϵ_d , which enabled H_{ads} to desorb from the catalyst surface easily, thus enhancing the intrinsic catalytic activity. Recently, metal-organic frameworks (MOFs) have received great attention in the electrocatalytic field due to their intrinsically porous structures, large specific surface areas, and well-dispersed metal sites.^{138–144} Unfortunately, the catalytic performance of most MOFs was markedly hampered by their improper adsorption/desorption energy of intermediates generated in electrocatalysis and quite poor electrical conductivity. In view of these issues, Geng *et al.* developed a simple method to directly fabricate novel high conductive Co-doped Cu-catecholate nanorod arrays on CC (CuCo-CAT/CC) as binder-free electrodes for the HER in alkaline and neutral media.²⁷ Electrochemical results demonstrated that CuCo-CAT/CC showed evidently improved HER performance with low overpotentials of 52 and 143 mV at 10 mA cm⁻² in alkaline and neutral solutions, respectively, exceeding that of the reported non-noble metal-based electrocatalysts or comparable to the commercial Pt/C electrocatalysts. DFT calculations proved that Co doping could not only optimize ΔG_{H^+} and adsorption energy of water (ΔE_{H_2O}) of Cu-CAT, thereby facilitating the Volmer and Heyrovsky steps, but also boost the electrical conductivity of Cu-CAT. Furthermore, the CuCo-CAT nanorod arrays on CC presented an open porous interconnected structure, resulting in decent stability for the HER in alkaline and neutral solutions. This study elaborated a new strategy to design conductive MOF-based electrocatalysts for highly efficient HER. Besides CC and CFP, graphite plate (GP) was also a distinguished substrate. For example, a superhydrophilic NiCo–CeO₂ nanoparticle array was integrally deposited on GP (NiCo–CeO₂/GP) by simple anion intercalation heightened electrodeposition method and subsequent high-temperature selective reduction.¹⁴⁵ The superhydrophilic self-supported

NiCo–CeO₂/GP electrode had many traits, such as boosting electron conduction, accelerating bubble release, and preventing catalyst shedding. Owing to the superhydrophilic self-supported electrode and the synergistic interaction between NiCo and CeO₂, it displayed outstanding HER performance with low overpotentials of 34 mV (140 mV) at 10 mA cm⁻² (500 mA cm⁻²) and striking stability in alkaline electrolytes. Notably, the coupled CeO₂ could favor dissociating water and facilitate hydrogen adsorption, drastically enhancing the HER performance of the NiCo alloy. More importantly, CeO₂ was also applied to boost the electrocatalytic activities of NiFe and NiCu alloys, indicating its versatility. Meanwhile, an alkaline electrolyzer with NiCo–CeO₂/GP as the cathode and NiCo(OH)_x–CeO₂/GP as the anode exhibited a low voltage of 1.45 V at 10 mA cm⁻² and a prominent stability at 500 mA cm⁻², outperforming that of the Pt/C||RuO₂ electrolyzer. This work presented a simple method to synthesize the low-priced NiCo–CeO₂ electrocatalyst and proved its potential for producing H₂ at large current densities.

3.2 Titanium-based substrates

Titanium materials have been deemed as the optimum substrate candidates due to their natural abundance, excellent corrosion resistance to acidic and alkaline media, processability, and good chemical stability.^{146–150} Inspired by the merits, Li *et al.* fabricated Co-doped anatase TiO₂ nanorod arrays on a Ti plate (Co-TiO₂@Ti(H₂)) with 1D structure, abundant oxygen vacancies (OVs), and good hydrophilic feature by ion exchange process and calcination treatment (Fig. 7a–c).¹⁵¹ As displayed in Fig. 7d–f, the as-formed Co-TiO₂@Ti(H₂) provided a much low overpotential of 78 mV at 10 mA cm⁻², a small Tafel plot of 67.8 mV dec⁻¹, and outstanding long-term durability at a large current density of 480 mA cm⁻² for the alkaline HER. DFT calculations demonstrated that the excellent hydrophilic surface could facilitate water adsorption, the Co atoms could lower the free energy of water adsorption/dissociation and H intermediate, as well as ample OVs could grab OH⁻ to efficiently promote water dissociation and H intermediate desorption. The work provided a promising electrode for cost-effective and energy-efficient HER. To enhance the HER performance of the Pt catalyst along with minimizing the Pt loading, an effective electrode was designed, which was constructed by using 3D Ti mesh (3D-Ti) as a substrate to yield TiO₂ nanotubes (TiO₂ NTs), followed by implanting a Pt nanocluster *via* an atomic layer deposition method.¹⁵² The as-formed Pt_x/TiO₂ NTs@3D-Ti catalysts showed a low overpotential of 53 mV at 10 mA cm⁻² in 0.5 M H₂SO₄ solution, which was superior to that of the commercial 20 wt% Pt/C catalysts. The experiments and DFT results implied that the Pt–O–Ti bond between the Pt nanocluster and TiO₂ nanotube could not only boost the durability of the Pt nanocluster anchored on TiO₂ nanotubes but also greatly enhance the HER performance. The improved HER activity may be attributed to the following reasons: (1) the 3D pore structure from Ti mesh could facilitate gas diffusion easily and furnish more surface contact between the electrode and the electrolyte; (2) the regular TiO₂ nanotubes possessed a

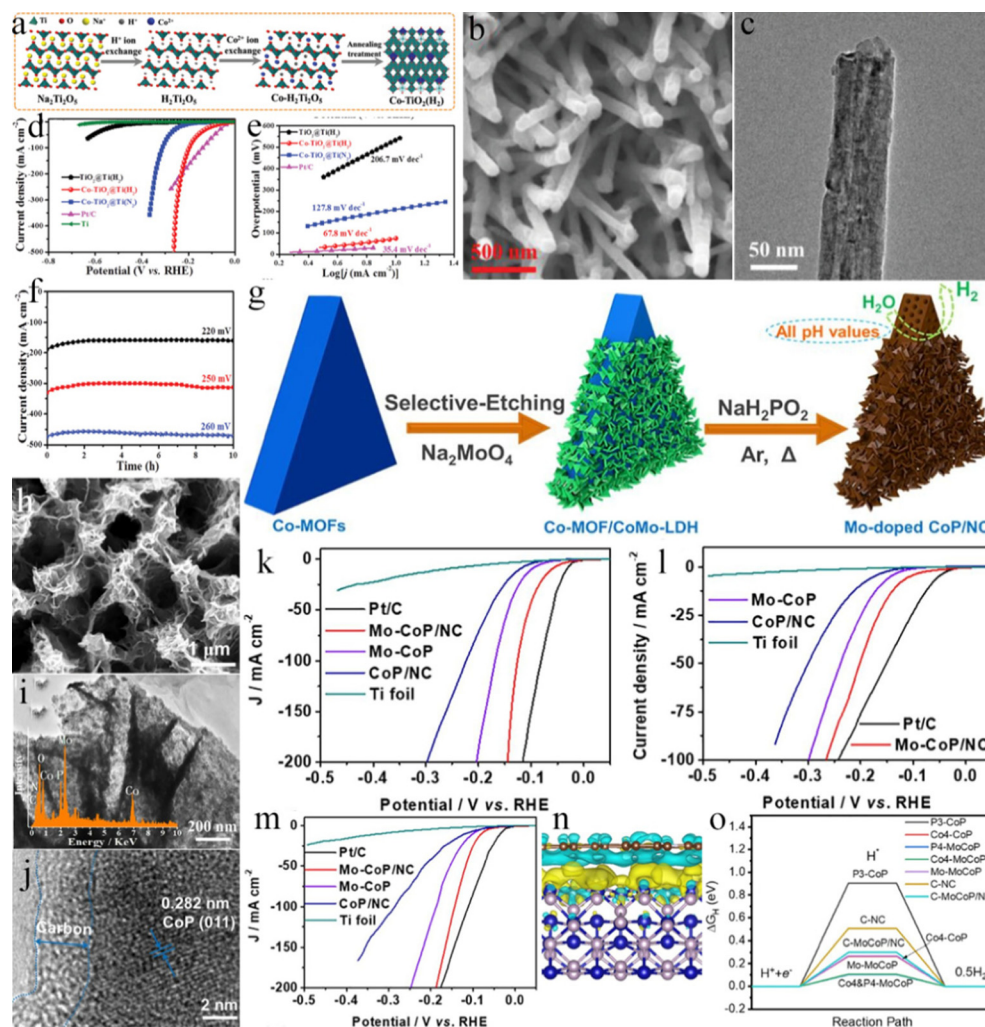


Fig. 7 (a) Schematic illustration of the ion exchange process for Co-TiO₂@Ti(H₂). (b) FESEM, and (c) TEM images of Co-TiO₂@Ti(H₂). (d) LSV curves in 1.0 M KOH solution. (e) Tafel plots derived from (d). (f) *i*-*t* Curves with different potentials in 1.0 M KOH solution.¹⁵¹ (g) The synthesis process of hierarchical porous Mo-CoP/NC arrays on TF. (h) FESEM, (i) TEM, and (j) high-resolution transmission electron microscopy (HRTEM) images of Mo-CoP/NC/TF. (k-m) LSV curves in 0.5 M H₂SO₄, 1.0 M PBS, and 1.0 M KOH electrolytes. (n) The local charge density difference isosurfaces (± 0.0005 e Bohr⁻³ isosurfaces, cyan: -, yellow: +). (o) HER free energy diagrams for various sites.¹⁸⁷

high specific surface area for scattering Pt nanocluster and offered 1D channel for transferring electron. Besides, Ru species, which are much cheaper than Pt species, have favorable dissociation kinetics of the absorbed water, exhibiting excellent HER performance.¹⁵³⁻¹⁵⁶ Consequently, Wang *et al.* provided a strategy to synthesize a hybrid catalyst by decorating TiO₂ nanotube arrays (TNAs) with crystalline Ru_{0.33}Se nanoparticles.¹⁵⁷ Due to the large-specific surface area of TNAs, Ru_{0.33}Se nanoparticles could be evenly distributed without aggregation, exposing more active sites. As a result, the fabricated Ru_{0.33}Se@TNA showed an improved HER activity with an overpotential of 57 mV at 10 mA cm⁻², a small Tafel slope of 50 mV dec⁻¹, and outstanding catalytic stability. The enhanced HER performance of Ru_{0.33}Se@TNA catalysts stemmed from the following aspects: (1) the increased active sites by the good dispersion of Ru_{0.33}Se nanoparticles on the TNAs with large-specific surface area; (2) the boosted charge transfer efficiency

because of the contracted electron transport pathway distributed by TNAs; and (3) the strong synergistic effect between Ru_{0.33}Se and TiO₂. Additionally, Li *et al.* forecasted that the defect-rich RuO₂/TiO₂ hybrids could dramatically modulate the electron structure of RuO₂, resulting in boosting the water splitting.¹⁵⁸ More importantly, ϵ_d of Ru in defective RuO₂/TiO₂ shifted to a low-energy level owing to the strong synergistic effect, and reduced the interaction between the adsorbed oxygen species and Ru sites, benefiting the HER performance. Consequently, defective RuO₂/TiO₂ hybrids on Ti mesh (D-RuO₂/TiO₂/TM) were reasonably developed by impregnating Ru precursor over TM followed by a thermal-oxidative method at high temperatures. As expected, the as-obtained D-RuO₂/TiO₂/TM catalyst presented excellent activity with a low overpotential of 71 mV at 50 mA cm⁻² for the HER in an alkaline solution. Moreover, because of the partial metallic nature of Se species, MoSe₂ shows high electrical conductivity.¹⁵⁹ In addition,

its edge site surface energy is larger than that of the terrace sites, making Mo and Se edges in the MoSe₂ atomic layers more active for the HER.^{160–163} Zhang's group successfully fabricated few-layered MoSe₂ nanosheets with a mixed 1T/2H phase on Ti substrates (1T@2H-MoSe₂/Ti) *via* a simple one-step solvothermal method.¹⁶⁴ The 1T@2H-MoSe₂/Ti electrode showed great HER catalytic activity with an overpotential of 133 mV at 20 mA cm⁻² and excellent stability for long-term electrolysis. The good electrocatalytic performance was owing to the synergistic effects of the special few-layered nanosheet morphology, conductive 1T metallic phase, and 1T@2H-MoSe₂ directly grown on the Ti substrate. Furthermore, alloy catalysts could result in superior electrocatalytic performance owing to the synergistic effect between different metal atoms.^{165–169} In this regard, a 3D NiMo alloy nanowire array on a titanium substrate was successfully constructed by a simple and effective magnetic field-assisted strategy with a short reaction time and low temperature.¹⁷⁰ The 3D NiMo alloy displayed significantly enhanced alkaline HER catalytic activity with ultra-low overpotentials of 17 and 98 mV at 10 and 400 mA cm⁻², a small Tafel slope of 28 mV dec⁻¹, and prominent long-term stability, which were better than most non-noble metal-based electrocatalysts and even comparable to the Pt-based electrocatalysts. More importantly, the small Tafel slope suggested that the NiMo electrode could reduce the kinetic energy barrier for the Volmer step, thereby enhancing the alkaline HER activity. The enhanced catalytic activity may come from the lattice distortions induced by Mo incorporation, low contact resistance, more active sites at nanowires surface, as well as superior charge/mass transport and H₂ bubbles abilities. Interestingly, Zhao *et al.* synthesized FeP nanosheets on the Ti foil.¹⁷¹ After etching in concentrated acid, the native oxide layer on the surface of the FeP nanosheet was removed. The as-treated FeP nanosheet showed significantly enhanced HER performance with the overpotentials 79 (95) and 95 (102) mV at 10 and 20 mA cm⁻² in 0.5 M H₂SO₄ (1 M KOH) electrolyte, respectively. Oxygen vacancy in transition metal oxides (TMOs) plays a key role in catalytic fields, which have been used to regulate the electron structure for improving the HER activity.^{172–176} Liu *et al.* successfully established simple calcination and electrochemical activation strategy to remarkably increase the OV content and get theoretical insight into how the concentration of OVs influences the activity of spinel TMOs for the alkaline HER.¹⁷⁷ The self-supported spinel NiCo₂O₄ nanowire arrays with tunable concentrations of OVs on TMs exhibited extremely great HER performance. Impressively, it only required a low overpotential of 317 mV to achieve a current density of 360 mA cm⁻². In addition, the effective route could efficiently produce OVs in CoFe₂O₄ and NiFe₂O₄ for boosted HER activity. Furthermore, the DFT calculations indicated that the increasing concentration of OVs on the surface of NiCo₂O₄ could not only lower the adsorption energy of water molecules but also reduce their dissociation energy barrier on the surface of the catalyst, thus resulting in excellent HER performance. As a typical HER electrocatalyst, the application of pyrite-type cobalt disulfide (CoS₂) is limited by its deficient activity and weak durability because of the slow water dissociation kinetics and oxygen-related corrosion.^{178–180} In view of this, an effective electrocatalyst

containing a CeO₂-decorated CoS₂ nanowire array on a Ti plate was fabricated through constructing Lewis acid–base Ce···S pairs.¹⁸¹ Correspondingly, the optimized electrocatalyst showed an enormous HER performance with a low overpotential of 36 mV at 10 mA cm⁻² and unchanged activity over 1000 h electrolysis in an alkaline solution. Experimental and theoretical results indicated that the improved alkaline HER performance of CoS₂ is induced by the interfacial Lewis acid–base Ce···S pairs with neither too strong nor too weak acidity–basicity. Besides, the interfacial Lewis acid–base Ce···S pairs kinetically promoted interfacial water dissociation, sped the subsequent HER steps, as well as established a special interfacial electronic and geometric configuration for weakening O₂ adsorption on the catalyst surface and thus inhibiting corrosion during the alkaline HER. These above findings could provide guidance to design CeO₂-based electrocatalysts for water splitting. In addition to CoS₂, the CoP electrocatalyst has also received great attention for the HER.^{182–186} Likewise, Wang's group utilized a synergistic electronic and geometric tailoring strategy to rationally fabricate hierarchically porous N-doped carbon incorporated Mo-doped CoP nanosheet arrays on the titanium foil (Mo-CoP/NC/TF) *via* etching Co-based MOFs (Fig. 7g–j).¹⁸⁷ From Fig. 7k–m, the synthesized Mo-CoP/NC/TF electrocatalysts exhibited outstanding performance and superior stability for the pH-universal HER, requiring overpotentials of 59, 130, and 78 mV at 10 mA cm⁻² in acidic, neutral, and alkaline solutions, respectively. DFT calculations (Fig. 7n and o) and experimental results suggested that the excellent catalytic activity of Mo-CoP/NC/TF could be attributed to the following points: (1) a strong synergistic effect between the Mo doping and N-doped carbon could effectively tailor the electronic structures of CoP, resulting in thermo-neutral adsorption of hydrogen-containing intermediates and fast interfacial charge transfer kinetics for Mo-CoP/NC; (2) the hierarchical porous self-supported electrode could not only furnish more accessible active sites, but also facilitate electrolyte diffusion and the gas release.

3.3 Nickel-based substrates

Nickel foam has been widely employed as a substrate for HER electrodes owing to its excellent electrical conductivity, low price, hierarchical porous structure, commercial availability, as well as 3D cross-linked network.^{188–193} For example, Chen *et al.* reported a facile and simple one-pot aqueous strategy to synthesize ultrathin rhodium-iridium nanosheets on NF (RhIr NSs/NF) at room temperature.¹⁹⁴ The catalyst exhibited high HER performance in both 1.0 M KOH and 0.5 M H₂SO₄ solutions with the overpotentials of 15 and 14 mV at 10 mA cm⁻² and long-term durability. The excellent HER performance was mainly attributed to the high conductivity, large ECSA, and strong synergistic effect between the bimetals. Recently, metal nitrides have received widespread attention due to their excellent conductivity, superior chemical stability, excellent mechanical robustness, and special electronic structure.^{195–199} Scalp Ni₃N nanosheets were fabricated on 3D NF (Ni₃N NSs/NF) with the high-efficient electrocatalytic property through ammonification engineering.²⁰⁰ The self-supported

electrodes had many advantages including (1) the Ni_3N NSs *in situ* were formed on NF without using a binder and conducting agent, thus simplifying the electrode preparation process, preventing catalyst shedding, and reducing the cost; (2) high contents of active Ni_3N NSs catalysts could be realized on NF, leading to abundant catalytic active sites; (3) the seamless contact of Ni_3N NSs and NF guaranteed the rapid charge transfer and conductivity of the integrated electrode. As expected, Ni_3N NSs/NF exhibited an ultralow overpotential of 34 mV at 10 mA cm^{-2} , a small Tafel slope of 54 mV dec^{-1} , and long-term durability in 1 M KOH solution. DFT results showed that the synergistic effect between Ni_3N and NF, as well as more effective facets for H_{ads} could accelerate reaction kinetics. Our group successfully fabricated a PVP gel encapsulated Pt/Ni(OH)_2 heterojunction on NF ($\text{PVP@Pt/Ni(OH)}_2\text{/NF}$) by a facile solution evaporation method (Fig. 8a–g).²⁰¹ The obtained self-supported $\text{PVP@Pt/Ni(OH)}_2\text{/NF}$ only required overpotentials of 12, 37, and 60 mV to reach current densities of 10, 50, and 100 mA cm^{-2} in 1.0 M KOH electrolyte, respectively, rivaling the Pt/C catalyst (Fig. 8h). Furthermore, the catalysts displayed an extremely low Tafel slope of 21.5 mV dec^{-1} (Fig. 8i) and outstanding long-term durability for 50 h without obvious decay (Fig. 8j). Additionally,

the loading of Pt contents in $\text{PVP@Pt/Ni(OH)}_2\text{/NF}$ was very low (0.35 wt%), improving the utilization efficiency of Pt-based catalysts. DFT calculations were applied to investigate the effect of PVP on the alkaline HER. The results indicated that PVP molecules at the interface could lower the water dissociation energy and optimize ΔG_{H^*} on the Pt/Ni(OH)_2 heterostructure (Fig. 8k and l), resulting in great activity for the alkaline HER. Furthermore, compared with the Tafel slopes and the electron state of Pt/Ni(OH)_2 with and without the PVP gel involved, the PVP gel could not only boost water dissociation to generate enough protons, but also improve the desorption of H_{ad} to enhance the HER kinetics by redistributing the charges of Pt/Ni(OH)_2 . Our work exhibited a convenient strategy for designing a Pt/Ni(OH)_2 heterostructure and enhancing the utilization efficiency of Pt-based catalysts. Analogously, Kong *et al.* reported a facile and simple approach to fabricating Pt-decorated $\text{TiO}_2/\beta\text{-Ni(OH)}_2$ nanosheet arrays based on two-dimensional (2D) Ti_3C_2 through anodic electrodeposition coupling with the hydrothermal method (Fig. 9a–h).²⁰² Initially, few-layered Ti_3C_2 nanoplates were evenly riveted on NF in the anodic electrodeposition process. Ni^{2+} ions were easily yielded from NF in acidic conditions, which could act as the nucleation sites for $\beta\text{-Ni(OH)}_2$ nanosheets on the surface of

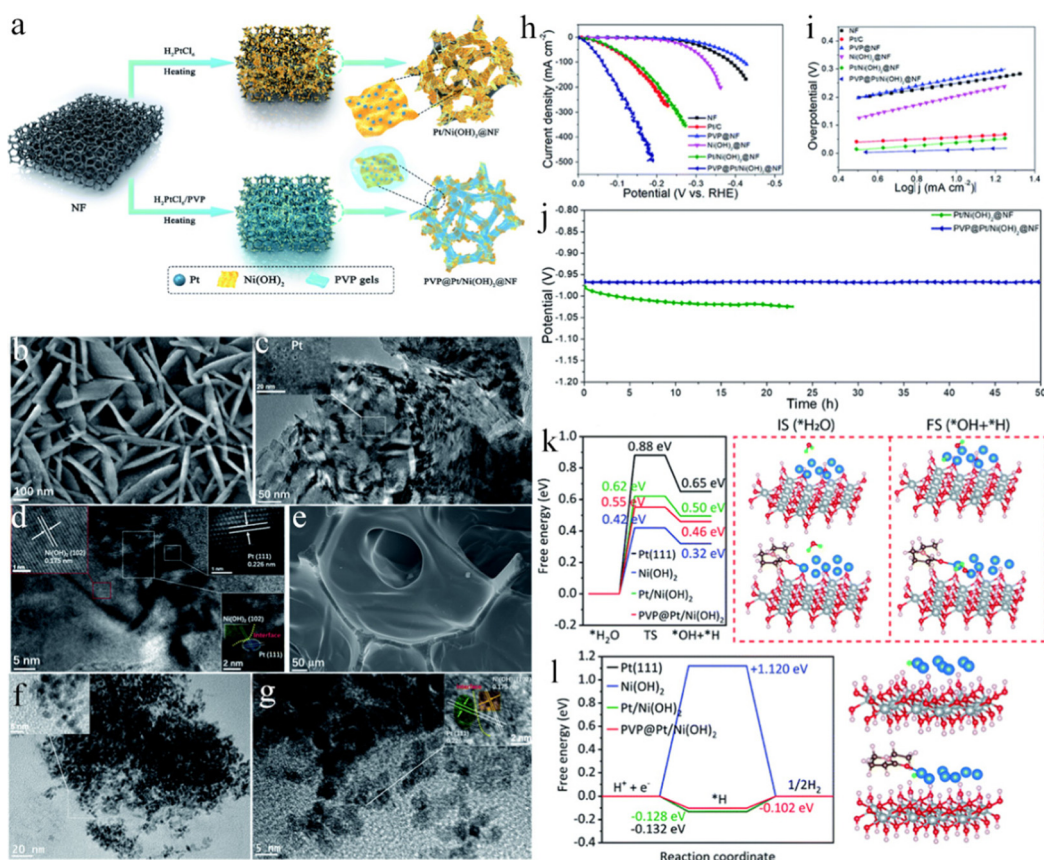


Fig. 8 (a) The preparation procedures of $\text{Pt/Ni(OH)}_2\text{/NF}$ and $\text{PVP@Pt/Ni(OH)}_2\text{/NF}$. (b) The FESEM, (c) TEM, and (d) HRTEM images of the $\text{Pt/Ni(OH)}_2\text{/NF}$ sample. (e) The FESEM, (f) TEM, and (g) HRTEM images of the $\text{PVP@Pt/Ni(OH)}_2\text{/NF}$ sample. (h) LSV curves. (i) Tafel plots. (j) CP test of $\text{Pt/Ni(OH)}_2\text{/NF}$ and $\text{PVP@Pt/Ni(OH)}_2\text{/NF}$ at 10 mA cm^{-2} for 50 h without IR compensation. (k) H_2O dissociation energy profile for different substrate surfaces. The initial and final optimized configurations of H_2O adsorption and dissociation on the Pt/Ni(OH)_2 and PVP@Pt/Ni(OH)_2 surfaces are given on the right side. The silver, red, pink, blue, brown, and orange balls display Ni, O, H, Pt, C, and N atoms, respectively. (l) ΔG_{H^*} profile for different substrate surfaces.²⁰¹

2D Ti_3C_2 . During the facile hydrothermal reaction, Ti_3C_2 could accelerate dissociating H_2O into hydroxyl anions, subsequently reacting with adsorbed Ni^{2+} to produce $\text{Ni}(\text{OH})_2$ species. Meanwhile, Pt^0 and TiO_2 species were generated *via* the reduction of $\text{Pt}(\text{IV})$ and the partial oxidation of Ti_3C_2 . The prepared $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2/\text{NF}$ presented a superior performance for alkaline water electrolysis under large industrial current densities. For the HER (Fig. 9i), the $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2/\text{NF}$ delivered low overpotentials of 107, 145, and 184 mV at the industrial current densities of 500, 1000, and 1500 mA cm^{-2} , respectively, and excellent electrochemical stability at 500, 700, and 1400 mA cm^{-2} for at least 12 h (Fig. 9j), which far outperformed most reported HER electrocatalysts. In particular, the $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2/\text{NF}$ electrodes could reach 10, 500, and 1000 mA cm^{-2} at the voltages of 1.37, 1.83, and 1.95 V, respectively, attaining extraordinary overall water splitting performances, which also preserved good long-term durability for at least 25 h. The outstanding electrocatalytic activity was the collaboration of the hydrophilic surface for facilitating the electrolyte wetting, rapid kinetics of water dissociation and H^* recombination, a strong synergistic effect of Pt and $\text{TiO}_2/\text{Ni}(\text{OH})_2$, and unique array architecture for promoting gas bubble releasing. This work developed effective nanoarray support for alkaline water electrolysis under large current densities. Song's group fabricated a MOF-derived Ru doped cobalt-nickel oxide heterostructure nanosheet arrays grown *in situ* on NF ($\text{Ru-Co}_3\text{O}_4\text{-NiO-NF}$).²⁰³ The synthesized $\text{Ru-Co}_3\text{O}_4\text{-NiO-NF}$ could efficiently

preserve the merits of 2D Co-MOF precursors with leaf-shaped nanosheet morphology and simultaneously possess the mechanical strength and skeleton integrity of the 3D NF network, resulting in exposing more active sites and quickening the charge or mass transfer.²⁰⁴ As a result, the optimized $\text{Ru-Co}_3\text{O}_4\text{-NiO-NF}$ showed a superior HER performance achieving a current density of 10 mA cm^{-2} and 100 mA cm^{-2} at overpotentials of 44 mV and 115 mV in 1 M KOH solution, respectively, superior to that of the commercial 20 wt% Pt/C catalysts. Furthermore, the self-supported electrode maintained electrocatalytic activity over 60 h at 100 mA cm^{-2} without apparent decrease. Experiments and DFT calculation results indicated that Ru-doping and $\text{Co}_3\text{O}_4\text{-NiO}$ heterointerface could cooperatively adjust the electronic state of Ni and Co sites, thereby optimizing the H_2O adsorption/desorption and hydrogen adsorption in the alkaline HER. This work not only afforded an effective and scalable synthesis method to design a MOF-derived self-supported electrode, but also raised a new strategy to synthesize the excellent alkaline HER electrocatalysts through engineering morphology and regulating electronic structure. Nickel phosphide catalysts have attracted considerable attention owing to their great catalytic activities for the HER.^{205–210} Yan *et al.* constructed 3D self-supported, hierarchical, and edge-rich Ni_2P nanosheet arrays on NF ($\text{Ni}_2\text{P NSs-NF}$) for the HER.²¹¹ Several in-plane nanopores were produced on the $\text{Ni}_2\text{P NSs}$ in the phosphatization step, benefiting from the electrolyte soakage and H_2 molecules release. Meanwhile, abundant

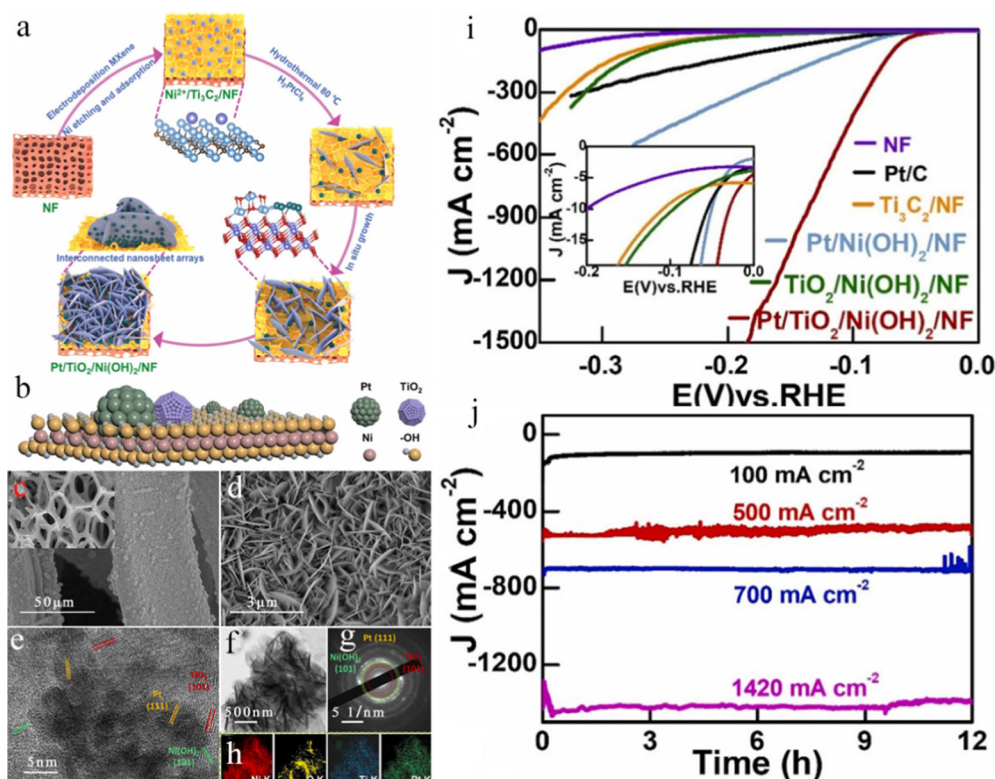


Fig. 9 (a) Fabrication process of $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2/\text{NF}$ nanosheet arrays. (b) Schematic illustration of $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2$ nanosheets. (c) FESEM image of $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2/\text{NF}$. (d) Corresponding magnified FESEM image. (e) TEM image of $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2$ arrays, and corresponding (f) HRTEM image, (g) selected area electron diffraction (SAED) pattern, (h) elemental mapping. (i) LSV curves. (j) CP test of $\text{Pt}/\text{TiO}_2/\text{Ni}(\text{OH})_2/\text{NF}$ in 1.0 M KOH solution at different overpotentials.²⁰²

active edges on the Ni₂P NSs could expose more active sites. Owing to the 3D open nanostructure with abundant edges in the Ni₂P NSs, the Ni₂P NSs-NF electrode displayed superior HER performance both in alkaline and acidic solutions, which needed low overpotentials of 89 mV in 1 M KOH solution and 67 mV in 0.5 M H₂SO₄ solution to reach 10 mA cm⁻² with low Tafel slopes of 82 and 57 mV dec⁻¹, respectively. Additionally, the self-supported Ni₂P NSs-NF electrode exhibited good cycling stability for the HER both in alkaline and acidic solutions even after 10 000 runs. Similarly, Wang *et al.* developed a new method for fabricating tripod-like Ni_xP nanowires on NF (Ni_xP/NF).²¹² The method contained the processes of removing Mo cations in nickel molybdate nanowires *via* electrochemical oxidation and the following phosphorization. The optimized self-supported Ni_xP/NF presented a small 71 mV overpotential at 10 mA cm⁻². More significantly, the overpotential of Ni_xP/NF was only increased by about 4 mV at 200 mA cm⁻² after 2000 CV runs, and the activity above 360 mA cm⁻² showed little loss after 40 h electrolysis, outshining the benchmark Pt/C catalyst. Therefore, this self-supported electrode could be used practically for H₂ production *via* water electrolysis. The HER performance of transition-metal phosphides was affected greatly by the phosphorus content.^{213–217} Zhou *et al.* provided a facile strategy to integrate P-rich NiP₂ and P-poor Ni₅P₄ into self-supported in-plane heterostructures *via* anion substitution of S in NiS/NiS₂ by P, in which P atoms at the in-plane interfaces served as active sites to adsorb H*, thereby favoring the HER by tuning the electron distribution between NiP₂ and Ni₅P₄.²¹⁸ The self-supported NiP₂/Ni₅P₄ heterostructures were synthesized through gas-phase sulfurization and phosphorization processes using the precursors of commercial NF, sulfur, and red phosphorous. Initially, the NF reacted with sulfur to produce high-crystalline NiS/NiS₂ nanoparticles on NF at an optimal annealing temperature. Subsequently, the NiS/NiS₂ nanoparticle acted as a sacrificial template for *in situ* forming in-plane NiP₂/Ni₅P₄ heterostructures on conductive NF by thermal phosphorization with red phosphorus powder. The resultant NiP₂/Ni₅P₄ heterostructure only required ultralow overpotentials of 30 and 76 mV to reach 10 and 100 mA cm⁻² with a Tafel slope of 30.2 mV dec⁻¹ in acidic solution, which outperformed most of the earth-abundant electrocatalysts and was comparable to Pt catalysts (30/72 mV at 10/100 mA cm⁻²). Specifically, it could be used at a large current density and only needed 247 mV to achieve 2 A cm⁻², showing great potential for the commercialization of water electrolysis. DFT calculations elucidated that the interfacial hybridization between P 2p and H 1s orbitals at the interface of the NiP₂/Ni₅P₄ catalyst led to an optimal H-adsorption strength and a fast kinetic process. This work furnished a new design principle for fabricating excellent electrocatalysts for industrial water electrolysis.

3.4 Copper-based substrates

Compared with NF, CFM possesses a lower cost and higher electrical conductivity and therefore acts as a highly favourable substrate for the HER.²¹⁹ However, the corrosion resistance and electrocatalytic activity of CFM are generally lower than those of NF. As reported, platinum-based catalysts showed the

benchmark activity;^{220–222} however, there were fewer studies on their HER performance under high current densities in neutral electrolytes. Tan *et al.* proposed a simple synthetic strategy to directly *in situ* deposit blackberry-shaped Pt nanocrystals with low contents on CFM for the HER in a neutral solution.²²³ Compared with the commercial 20 wt% Pt/C electrocatalysts pasted on CFM, the self-standing Pt@Cu foam exhibited low overpotentials of 35 and 438 mV at 10 and 1000 mA cm⁻², respectively. Meantime, due to the strong interaction between Cu and Pt, it showed outstanding durability in CA measurement at high current densities (100 to 400 mA cm⁻²) and 1000 cycles LSV tests achieving 1000 mA cm⁻². DFT calculations revealed that the optimized ΔG_{H*} on the Pt@Cu interface could facilitate efficient proton adsorption and rapid release of produced H₂. Moreover, Pt@Cu displayed effective water dissociation owing to the existence of a small amount of Cu(OH)₂ on CFM, which could easily adsorb OH⁻ in a neutral solution, thus further facilitating dissociating water.^{224–226} This work provides a new strategy for designing self-supported electrocatalysts by establishing strong metal-metal interactions between active materials and substrates. Furthermore, Ru-doped Cu₂₊₁O vertically arranged nanotube arrays *in situ* prepared on CFM (Ru/Cu₂₊₁O NT/CFM) were reported by Cao's group, which presented a small overpotential of 32 mV at 10 mA cm⁻² in the alkaline HER.²²⁷ Dramatically, the alkaline electrolyzer employing Ru/Cu₂₊₁O NT/CFM as a bifunctional electrocatalyst only required 1.53 V voltage to reach a current density of 10 mA cm⁻², superior to the benchmark of IrO₂(+)/Pt(−) counterpart (1.64 V at 10 mA cm⁻²). The remarkable performance of the Ru/Cu₂₊₁O NT/CFM catalyst originated from its high conductive substrate and special Ru-doped nanotube structure, which offered a high electrochemically active surface area and 3D gas diffusion channel. Song *et al.* reported a simple one-pot solution method to fabricate a self-standing 3D CFM electrode integrated with *in situ* grown Ag nanodots decorated Cu₂O porous nanobelts at room-temperature, which exhibited an overpotential of 108 mV at 10 mA cm⁻², a low Tafel slope of 58 mV dec⁻¹, and high durability for at least 20 h at 200 mV.²²⁸ The good performance could be ascribed to the porous nanobelts with abundant active sites and the fast electron transfer between Ag@Cu₂O and conductive CFM support. Moreover, the low-cost, high-efficient, and long-durable electrocatalysts that operated well at high current densities are strongly demanded by industry H₂ production.^{229–234} Therefore, the high-throughput scalable preparation method should be developed. Based on this, Zhang *et al.* synthesized high-performance and low-cost 2D MoS₂-based HER electrocatalysts on CFM through a scalable top-down exfoliation method followed by a thermal treatment.²³⁵ The catalysts possessed a great acidic HER activity with an overpotential of 412 mV at a high current density of 1000 mA cm⁻², a small Tafel slope of 60 mV dec⁻¹, and good durability for 24 h. In addition, an inexpensive mineral-based catalyst with outstanding performance for the high-current-density HER was also fabricated using the same approach. Noteworthy, except for the cost of the CFM, the price of MoS₂ mineral-based catalyst was only 10 US\$ m⁻², which is almost 30 times lower than the commercial Pt/C catalysts, highlighting a magnificent potential for large-scale industry

H₂ production. Li *et al.* utilized a simple electrochemical method to successfully synthesize a grass-like Ni/Cu nanosheet array on CFM (Ni/Cu/CFM).²³⁶ First, a grass-like Cu nanosheet array was produced *via* partially electrochemical oxidizing CFM in 3 M NaOH solution and then an electrochemical reduction in 1 M Na₂SO₄ solution at room temperature. Finally, the grass-like Ni/Cu/CFM was fabricated by electrochemically reducing NiSO₄ solution on the surface of the Cu nanosheet array at room temperature. The resultant grass-like Ni/Cu/CFM electrode showed excellent HER performance with a Tafel slope of 42.7 mV dec⁻¹ and an overpotential of 38 mV at 10 mA cm⁻², which was far lower than 156 mV of Ni/CFM and 246 mV of Cu nanosheet array/CFM electrode. Meanwhile, the as-prepared Ni/Cu/CFM electrode also exhibited superior catalytic durability because of its solid structure, which displayed 50 h stability at the current density of 30 mA cm⁻², indicating outstanding durability. The excellent electrocatalytic activity should be ascribed to the unique grass-like structure, which could expose more effective active sites and facilitate electrolyte penetration and gas diffusion. Yao *et al.* fabricated mesoporous Cu nanowires shelled with ultrathin WC layer self-supported on CFM through the chemical oxidation and *in situ* electro-reduction route followed by a simple and rapid magnetron sputtering (Fig. 10a-e).²³⁷ The as-obtained

Cu@WC/CFM catalyst exhibited low overpotentials of 92, 119, and 173 mV at 10 mA cm⁻² in acidic, alkaline, and neutral solutions with high stability over 12 h (Fig. 10f and g). The enhanced HER performance could be attributed to the following reasons: (1) the large surface area of the mesoporous structure with exposed active sites boosted the H⁺ transfer and the bubbles release; (2) the small work function between Cu (core) and WC (shell) reduced the contact potential; (3) the lattice mismatch of WC and Cu optimized both the atomic and electronic structures of WC. Tong *et al.* successfully synthesized a bamboo leaves-like amorphous FeO_x coated Cu₃P on CFM, and the bamboo leaves-like morphology facilitated the mass transfer and more active site exposing.²³⁸ As a result, the binder-free FeO_x coated Cu₃P@Cu exhibited a low overpotential of 48 mV at 10 mA cm⁻² for the alkaline HER, even exceeding the Pt/C catalyst at a large current density. Benefiting from the special hierarchical hollow nanowire array nanostructure with large surface area, good conductivity, abundant active sites, as well as fast mass/transport ability, a two-step synthetic route to synthesize hierarchical Cu₂S hollow nanowire arrays grown on CFM (Cu₂S HNAs-CFM) was proposed (Fig. 10h).²³⁹ The obtained hierarchical Cu₂S HNAs-CFM electrode showed admirable alkaline HER activity with a low overpotential of 125 mV at 100 mA cm⁻² (Fig. 10i), which was comparable to the performance of Pt/C-CFM

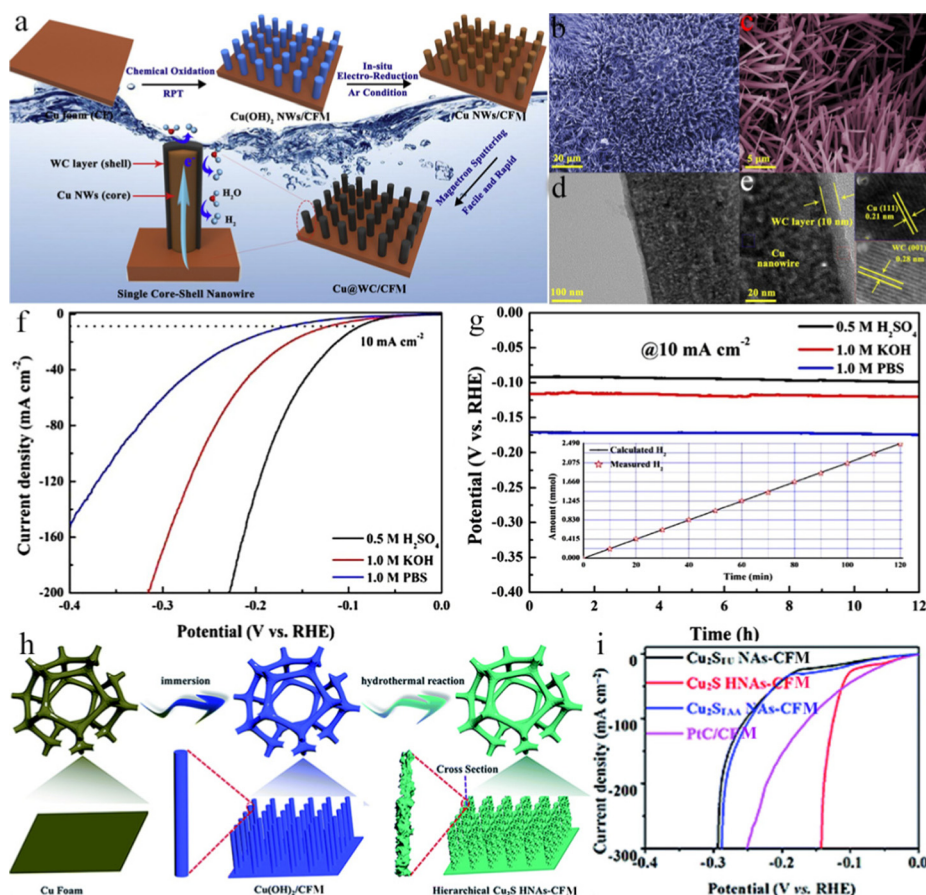


Fig. 10 (a) Schematic illustration for the formation mechanism of Cu@WC/CFM. (b and c) FESEM, (d) TEM, and (e) HRTEM images of Cu@WC/CFM. (f) LSV curves for Cu@WC/CFM in 0.5 M H₂SO₄, 1.0 M KOH, and 1.0 M PBS solutions. (g) CP tests of Cu@WC/CFM. The inset is the line of the amount of H₂ gas.²³⁷ (h) Preparation of a hierarchical Cu₂S HNAs-CFM electrode. (i) LSV plots.²³⁹

and most reported electrocatalysts. Altogether, these meaningful works demonstrated the practicability of synthesizing high-performance HER electrode based on CFM.

3.5 Stainless steel substrates

Stainless steel is not only more resistant to corrosion in acid and alkaline solutions, but also cheaper than CC, NF, titanium-based substrates, and CFM, which have been more emphasized heavily.^{240–246} Recently, Zhu *et al.* fabricated an efficient bifunctional electrocatalytic electrode of nanoporous nickel-iron hydroxides ($\text{NiFe}(\text{OH})_x$) nanosheet arrays combined metal Ni/Fe *in situ* grown on stainless steel fiber felt (SSF) by a facile electrodeposition method at room temperature.²⁴⁷ The constructed electrode showed distinguished electrocatalytic activity for water splitting, requiring overpotentials of 100 and 210 mV at 10 mA cm^{-2} in 1 M KOH media for the HER and oxygen evolution reaction (OER), respectively. Served as both anode and cathode for overall water splitting, the synthesized electrode also displayed extraordinary performance, achieving an overall cell voltage of 1.80 V to gain a current density of 100 mA cm^{-2} . Moreover, no obvious potential drop was observed after a long-term stability test. The improved water splitting performance was attributed to the special vertically ultrathin nanosheets with abundant active sites, more dangling bonds, and a synergistic effect between the $\text{NiFe}(\text{OH})_x$ nanosheets and SSF substrate. The exceptional dual-functional catalyst could not only effectively lower the total cost but also simplify the electrolytic device. The strong metal-support interaction has been used to design and fabricate metal-support catalysts, which is a simple and effective approach to forming unique electronic structures and modifying the interface on the surface of the catalyst for enhancing HER performance.^{248–253} Ascertaining that, our group directly fabricated Na_xWO_3 nanotube bundle support on a stainless mesh (SM) substrate *via* a facile hydrothermal method, followed by anchoring Pt nanoparticles with a low load-level (1.44%) on the as-prepared Na_xWO_3 nanotube bundles ($\text{Pt/R-Na}_x\text{WO}_3\text{@SM}$) *via* the *in situ* chemical reduction, successfully establishing Pt-sodium tungsten bronze hybrid electrocatalysts.²⁵⁴ Specially, the Na_xWO_3 nanotube bundles were synthesized without using additives and surfactants, and $\text{Na}_2\text{S}_2\text{O}_8$ reagent was employed as an acid source instead of the strong corrosive including HCl, HNO_3 , as well as H_2SO_4 . As expected, owing to the nanotube bundle morphology with 3D structure and the strong metal-support interaction between Pt and Na_xWO_3 , the optimized $\text{Pt/R-Na}_x\text{WO}_3\text{@SM-170}$ catalyst exhibited excellent HER performance with low overpotentials of 20 and 46 mV at 10 and 100 mA cm^{-2} , a small Tafel slope of 18.6 mV dec^{-1} , as well as good stability over 3000 CV runs and CA test for 25 h in 0.5 M H_2SO_4 media. Additionally, its activity even exceeded the benchmark 20 wt% Pt/C catalysts at a high current density (69 mV at 100 mA cm^{-2}). Impressively, it showed 10.8-fold higher mass activity than the Pt/C catalyst at 20 mV overpotential. DFT calculations manifested that the charge transfer between the R- Na_xWO_3 nanotube bundle and Pt nanoparticles could increase the electrons on the surface of the Pt nanoparticle, and thus negatively shift ε_d , leading to fast desorbing hydrogen intermediate and re-exposing the active sites on the Pt surface,

eventually achieving outstanding the HER activity. This work provided a reliable route to synthesize sodium tungsten bronze for feasible support. Edison *et al.* electrochemically synthesized ruthenium nanoparticles on cathodically treated stainless-steel mesh. The experimental results showed that its acidic HER performance is very close to that of the bare Pt.²⁵⁵ Moreover, Balogun's group developed a simple method to improve the HER performance of Co-based heterojunction catalysts with dual nanostructures on 3D stainless steel mesh (SSM) *via* non-oxygen anionic modifying CoO.²⁵⁶ The compounds including CoO-CoP (SSM/CoOP), CoO-Co_xN (SSM/CoON), and CoO-CoS_x (SSM/CoOS) could be produced after phosphorizing, nitriding, and sulfuring CoO, respectively, where SSM/CoOP exhibited the best HER performance with a small overpotential of 21 mV at a current density of 10 mA cm^{-2} , comparable to the benchmark Pt/C catalysts (19 mV) and superior to that of SSM/CoON (44 mV) and SSM/CoOS (142 mV), evincing the non-oxygen treatment route benefitting for enhancing the HER activity. The excellent activity of SSM/CoOP could arrive from the following merits: (1) the strong electronic interaction between CoO and CoP and (2) the 1D nanowires and 2D nanosheets dual nanostructures, which could forcefully increase active surface, expose more active sites, and boost the ion/electron transfer, and thus significantly optimizing ΔG_{H^+} , resulting in improving catalytic activity. Hu *et al.* incorporated iron oxyhydroxide (FeOOH) on Co_4N nanowires supported on 3D SSM ($\text{FeOOH@Co}_4\text{N/SSM}$) by a facile hydrothermal and chemical bath deposition process.²⁵⁷ The as-synthesized $\text{FeOOH@Co}_4\text{N/SSM}$ hybrid electrocatalyst showed a low overpotential of 92 mV at 10 mA cm^{-2} , a small Tafel slope of 34 mV dec^{-1} , and excellent stability for the alkaline HER. DFT analyses indicated that the enhanced HER performance of $\text{FeOOH@Co}_4\text{N}$ was owing to the suitable ε_d of Co_4N adjusted by the strong electronic interaction between Co_4N and FeOOH. Yao *et al.* synthesized self-supported $(\text{Ni},\text{Co})_3\text{C}$ mesoporous nanosheets/N-doped carbon $(\text{Ni},\text{Co})_3\text{CNs@NC}$ on a conductive SSM with controllable sizes from $1 \text{ cm} \times 1 \text{ cm}$ to $25 \text{ cm} \times 25 \text{ cm}$ through a simple and fast electrodeposition method followed by carbonization (Fig. 11a–e).²⁵⁸ The as-fabricated catalyst exhibited small overpotentials of 58, 118, and 71 mV at 10 mA cm^{-2} in acidic, neutral, and basic solutions, respectively, with high stability (Fig. 11f–i), which outperformed that of most non-noble metal carbide-based catalysts in a pH-universal solution. The eminent activity could be attributed to the special ultrathin nanosheet-like morphology, large specific surface area, and strong synergetic effect of Ni and Co. As shown in Fig. 11j–l, DFT calculations revealed that the bimetallic NiCo carbide was favorable for the HER due to its good metallic conductivity, appropriate ΔG_{H^+} , and downshifted ε_d . This work provided a facile and viable strategy to prepare large-scale excellent catalysts for the HER in a wide pH electrolyte.

3.6 Molybdenum-based substrates

Compared to the common conductive substrates including CFP, CC, and GP, the monolithic Mo foil or plate can be directly utilized as a molybdenum source and self-supported substrate.^{259–266} In addition, due to the chemically inert Mo substrate, the

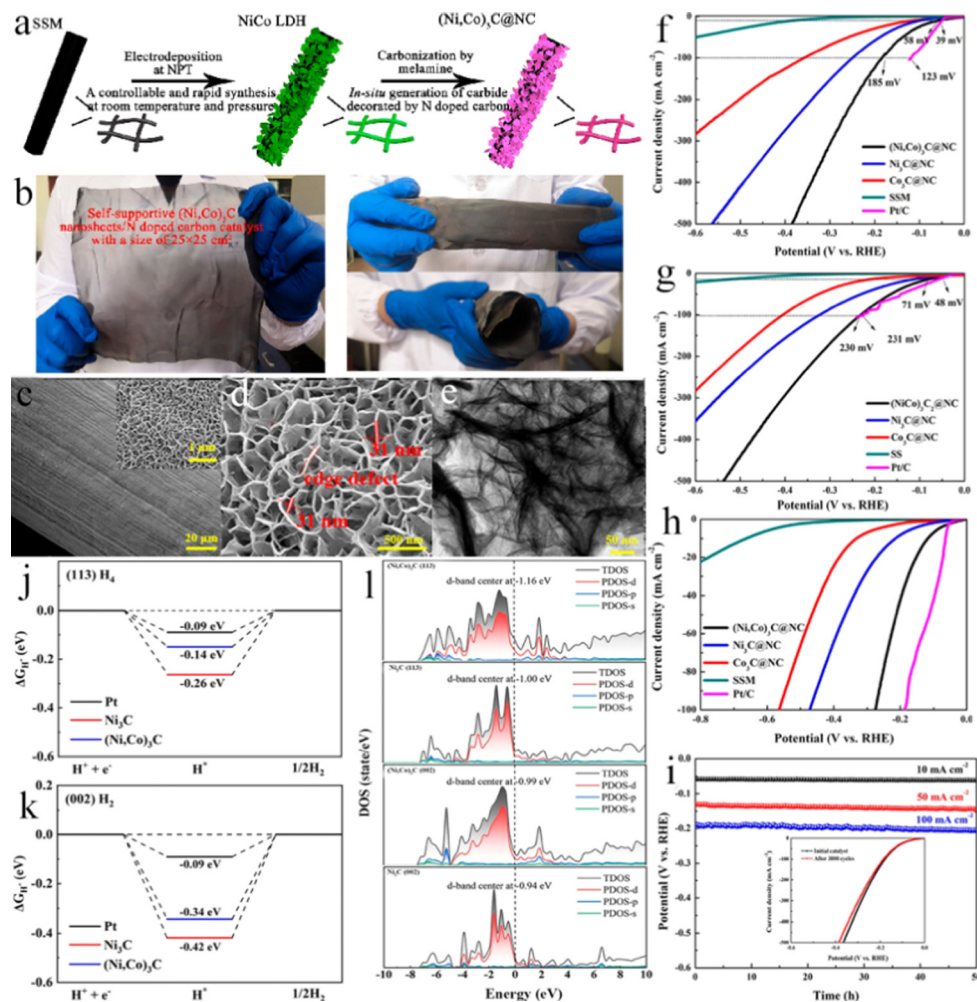


Fig. 11 (a) Schematic illustration of the formation mechanism. (b) Digital images of the catalyst with flexible property (size of 25 cm × 25 cm). (c and d) FESEM, and (e) TEM images of (Ni,Co)₃C NSs@NC. (f–h) LSV curves for (Ni,Co)₃C NSs@NC in 0.5 M H₂SO₄, 1.0 M KOH, and 1.0 M PBS solutions. (i) CP test at different current densities in 0.5 M H₂SO₄ solution; (i inset) LSV curves before and after the stability test. Schematic energy profiles for the HER (j) (113) and (k) (002). (l) Total and partial electronic density of states (TDOS and PDOS) calculated for (Ni,Co)₃C (113), Ni₃C (113), (Ni,Co)₃C (002), and Ni₃C (002).²⁵⁸

Mo-based electrode can be applied directly in both acidic and alkaline solutions.²⁶⁷ Recently, Guo *et al.* reported the large-scale fabrication of vertically standing MoP nanosheet arrays (NSAs) on the Mo substrate through topotactically phosphorizing MoS₂ by a facile two-step chemical vapor deposition (CVD) method.²⁶⁸ Initially, MoS₂ NSAs on the Mo substrate (MoS₂ NSAs/Mo) were synthesized by the CVD process using MoO₃ and S powders as the evaporation precursors. Subsequently, the formed MoS₂ NSAs/Mo precursor was topotactically switched to MoP NSAs/Mo. The as-synthesized MoP NSAs/Mo possessed excellent structural robustness, completely exposed active sites, and much adjoining space, benefiting for boosting the electrochemical kinetics and releasing the H₂ bubbles during the HER. As a result, the self-supported MoP NSAs/Mo electrode exhibited outstanding acidic and alkaline HER performance with overpotentials of 95 and 106 mV at 10 mA cm⁻², respectively, and small Tafel slopes of 50 and 56 mV dec⁻¹. Moreover, its activity remained unchanged even after 5000 cycles

of repeating the CV test at 100 mV s⁻¹, as well as 36 h electrolysis at a high current density in both acidic and alkaline solutions. Zhao *et al.* provided a simple bottom-up approach to synthesizing heterostructured CoP nanoarray/MoO₂ films on the Mo foil (CoP–MoO₂/MF) employing pre-oxidized MF supported cobalt hydroxide-carbonate nanoneedles as the precursor.²⁶⁹ The CoP–MoO₂/MF heterostructure exhibited superior HER activity with low overpotentials of 65 and 42 mV at 10 mA cm⁻² in acidic and alkaline electrolytes, prosperous long-term stability, large exchange current density, and high turnover frequency. The experiments and DFT results indicated that MoO₂ was in favor of adsorbing water, cleaving H–O bonds, and facilitating hydrogen transfer. Moreover, heterointerfacial charge redistribution could optimize the ΔG_{H^+} on the heterointerface of CoP–MoO₂, which could be reduced from 0.08 eV on CoP (011) and 0.78 eV on MoO₂ (011) to 0.02 eV on CoP–MoO₂, significantly enhancing the HER performance and accelerating the catalytic kinetics. The large-scale synthesis of cheap, efficient, and stable electrocatalysts used

at high current densities in HER is very important and indispensable for industrial H_2 generation.^{270–272} Liu's group developed a large-scale strategy to efficiently and economically fabricate $MoSe_2$ - Mo_2N Schottky heterojunction flakes on inexpensive industrial-grade molybdenum substrates through a simple solid-state synthesis method.²⁷³ The preparation process was as follows, first, MoO_3 prisms were seamlessly synthesized on Mo substrates *via* a controlled calcination process, and then the $MoSe_2$ - Mo_2N Schottky heterojunction catalyst was achieved by a facile thermal treatment under the H_2/NH_3 mixture atmosphere. As a result, the as-formed $MoSe_2$ - Mo_2N /Mo electrode showed a low overpotential of 76 mV at the current density of 10 mA cm^{-2} for the alkaline HER. Besides, it delivered a high current density of 1000 mA cm^{-2} at the overpotential of 462 mV, superior to that of a commercial Pt/C catalyst. DFT results demonstrated that the formed Schottky heterojunction between $MoSe_2$ and Mo_2N could prompt self-driven electron transfer that not only optimized the electronic structure at heterointerfaces but also adjusted the free energy of hydrogen adsorption and dissociation. Subsequently, they also successfully constructed a molybdenum oxide-phosphide (MoO_2 -MoP) seamless electrode on Mo substrate using the same method.²⁷⁴ The MoO_2 -MoP mesh electrode achieved an industrial current density of 800 mA cm^{-2} at a low overpotential of 362 mV and showed excellent stability at high current densities for 200 h in an alkaline electrolyte. Additionally, it yielded a current density of 1000 mA cm^{-2} at 293 mV in 1.0 M KOH solution, but required an overpotential of only 215 mV to reach the same current density in 5.0 M KOH solution, which was practical for industrial alkaline HER. Similarly, a self-standing MoC- Mo_2C heterojunction was also constructed on a Mo sheet utilizing CO_2 as the carbon resource and electrons as the reducer in molten carbonate *via* a one-step electrodeposition method (Fig. 12a–d).²⁷⁵ The as-prepared MoC- Mo_2C heterojunction exhibited outstanding HER performances (Fig. 12e–j) with low overpotentials of 256 and 292 at a high current density of 500 mA cm^{-2} in acidic and alkaline solutions, respectively, with long-term stability for at least 1000 h, a large TOF, and a high industrial operating temperature of about 70°C , indicating a cost-effective catalyst for the HER operating at industry-level conditions. Experiments and DFT calculations (Fig. 12k–m) verified that the decent HER activity of the MoC- Mo_2C heterojunction self-supported electrode in acidic and alkaline electrolytes was due to the profitable ΔG_{H^+} , low water dissociation energy, hydrophilic surface, and special 3D porous structure. This work proposed a facile strategy to fabricate large-scale electrodes ($3\text{ cm} \times 11.5\text{ cm}$), which could be expanded to the preparation of diverse carbide electrodes with sensibly designed microstructures, adjustable compositions, and excellent performances for practical applications.

3.7 Cobalt-based substrates

The strategy of nitrogen doping into metal phosphides has been extensively utilized to tune electronic structure, hydrogen adsorption free energy and water dissociation free energy, *etc.*, thereby enhancing their HER performance.^{2,276–280} By virtue of

this phenomenon, a nitrogen-doped CoP nanoarray grown on 3D porous CF was prepared for the HER and OER in water electrolysis.²⁸¹ The as-obtained CoP-N/CF required overpotentials of 100 and 260 mV for the HER and OER to reach a current density of 50 mA cm^{-2} , respectively, in alkaline conditions. Furthermore, as a bifunctional catalyst for the electrolyzing water reaction in a two-electrode system, it needed a cell voltage of 1.61 V to achieve a current density of 50 mA cm^{-2} , even exceeding the benchmark catalyst system of $RuO_2/CF@Pt/C/CF$ (1.78 V). Additionally, the electrolyzer showed outstanding stability after 25 h of continuous operation at 50 mA cm^{-2} . The results revealed that doping of non-metallic nitrogen into CoP could greatly boost its catalytic activity, durability, kinetics, and catalytic efficiency for the HER and the OER. Similarly, the interface-strengthened CoP nanosheet array with Co_2P nanoparticles on CF as a self-supported electrocatalyst exhibited low overpotentials of 68 and 256 mV at 10 mA cm^{-2} for the HER and the OER, respectively.²⁸² Meanwhile, the CoP/ Co_2P /CF as both anode and cathode for overall splitting water delivered a low voltage of 1.57 V to achieve 10 mA cm^{-2} with stability for over 58 h. Zhang's group elaborately fabricated flower-like Fe-Ni bimetallic layered double hydroxide on ultrahigh porosity CF (FeNi LDH/CF), and then flower-like FeNiP-LDH/CF was obtained through a phosphorization process in a tube furnace.²⁸³ The hierarchical FeNiP-LDH/CF catalyst offered a current density of 10 mA cm^{-2} at a low overpotential of 39 mV for the alkaline HER, which was superior to that of the Pt catalyst (53 mV). In addition, the electrode could keep steady HER performance over 16 h during CA measurement at an industrial-level current density of $500\text{--}600\text{ mA cm}^{-2}$. This decent HER performance could be assigned to several advantages, including the special porous nature of CF, the strong synergistic effect of bimetallic electrocatalysis, unique nanoflower-like morphology constructed by LDHs, as well as coupling interaction of transition metals and phosphorus. Subsequently, they also fabricated NiCoP/CF electrocatalysts, which only required overpotentials of 47 and 126 mV to reach 10 and 100 mA cm^{-2} , and retained excellent stability at a current density higher than 500 mA cm^{-2} for over 16 h.²⁸⁴ Additionally, other bimetallic phosphides also exhibited highly efficient overall water splitting under a large current density in industries. A seamless integrated Fe_2P - Co_2P /CF electrode was successfully fabricated (Fig. 13a), which only required 145(243), 208(291), and 254(317) mV for alkaline HER(OER) to reach current densities of 100, 500, and 1000 mA cm^{-2} , respectively (Fig. 13b and c).²⁸⁵ Remarkably, using Fe_2P - Co_2P /CF for overall water splitting at room (25°C) and quasi-industrial (65°C) temperatures, the operating voltages were 1.87 and 1.71 V to deliver 500 mA cm^{-2} , respectively, along with long-term stability for at least 300 h (Fig. 13d and e). The outstanding performance was owing to the *in situ* grown seamless integrated electrode with excellent conductivity and good stability, as well as the strong coupling effect between Fe_2P and Co_2P , indicating it met the application of industrial water splitting for large-scale renewable H_2 production. Interface engineering is an effective strategy for enhancing the water adsorption and

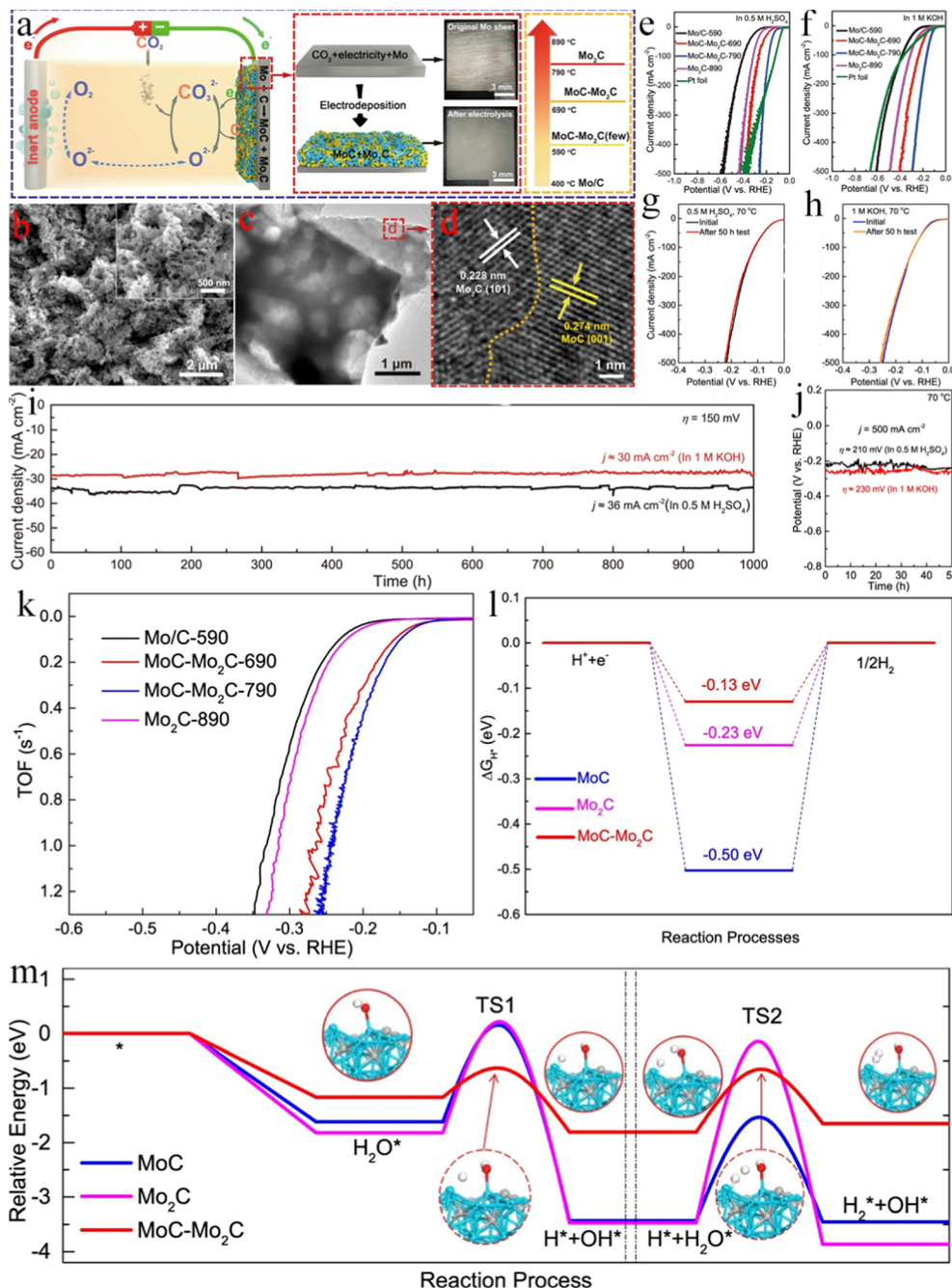


Fig. 12 (a) Schematic of synthesizing MoC–Mo₂C in molten carbonate and digital pictures of the Mo electrode before and after electrolysis. (b) FESEM, (c) TEM, and (d) HRTEM images of the synthesized MoC–Mo₂C. (e and f) LSV curves for MoC–Mo₂C in 0.5 M H₂SO₄ and 1 M KOH solutions. (g and h) LSV curves before and after stability tests in 0.5 M H₂SO₄ and 1 M KOH solutions at 70 °C. (i) The long-term electrolysis stability test of MoC–Mo₂C at 150 mV overpotential in 0.5 M H₂SO₄ and 1 M KOH solutions. (j) Stability test in both 0.5 M H₂SO₄ and 1 M KOH medium at 500 mA cm⁻² and 70 °C. (k) TOF curves of different electrodes. (l) Calculated ΔG_{H^+} diagram of the HER in an acidic solution. (m) Relative energy diagram of water dissociation on MoC, Mo₂C, and MoC–Mo₂C, including the two steps of water dissociation, in alkaline solution, TS: transition state.²⁷⁵

dissociation and optimizing the ΔG_{H^+} , thereby improving the heterostructured catalyst's HER performance in acidic and alkaline solutions.^{286–290} The low-cost interfacial Co₂N/Co grown on CF was reported, which displayed superior HER activity with overpotentials of only 12 and 64 mV to produce 10 and 100 mA cm⁻², respectively, substantially lower than those of Pt/CF (20 and 98 mV).²⁹¹ In addition, it showed

exceedingly robust stability after the 10 000 CV and CP test at 10 and 100 mA cm⁻² for at least 100 h. The ΔG_{H^+} values at two interfacial sites of Co₂N/Co were computed to be only –0.02 and –0.04 eV. In the contrast, both Co₂N and Co presented strong hydrogen affinity (–0.27 to –0.40 eV). The DFT computational results indicated that the interfacial sites of Co₂N/Co could improve the HER activity. Correspondingly, a

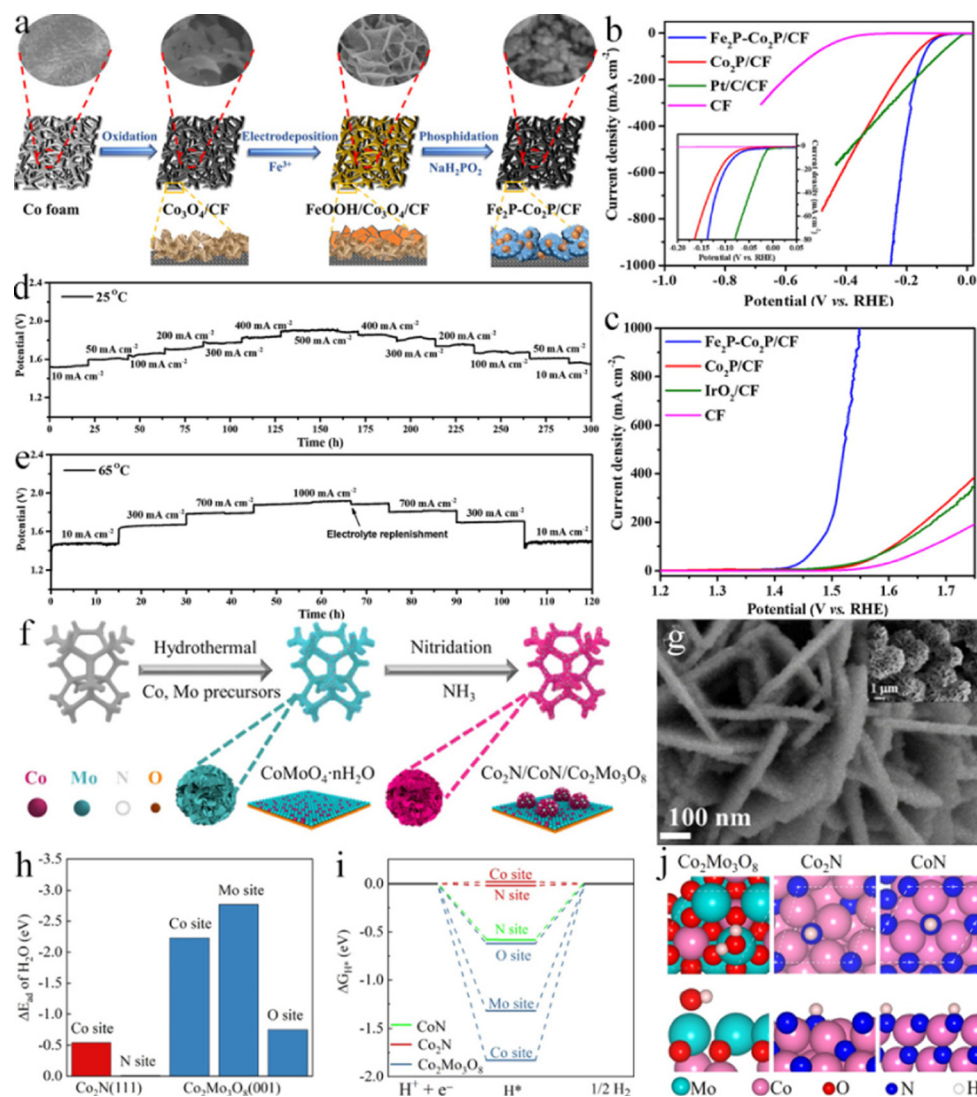


Fig. 13 (a) Schematic illustration of preparing a seamlessly integrated electrode of $\text{Fe}_2\text{P}-\text{Co}_2\text{P}/\text{CF}$. (b and c) LSV curves of different catalysts for the alkaline HER and OER. (d) Multistep CP curves of $\text{Fe}_2\text{P}-\text{Co}_2\text{P}/\text{CF}$ under different current densities for overall water splitting at 25°C . (e) Multistep CP curves of $\text{Fe}_2\text{P}-\text{Co}_2\text{P}/\text{CF}$ under different current densities for overall water splitting at 65°C .²⁸⁵ (f) Schematic illustration to fabricate the $\text{Co}_2\text{N}/\text{CoN}/\text{Co}_2\text{Mo}_3\text{O}_8/\text{CF}$ catalyst. (g) FESEM images of $\text{Co}_2\text{N}/\text{CoN}/\text{Co}_2\text{Mo}_3\text{O}_8/\text{CF}$ catalyst. (h) Adsorption energies (ΔE_{ad}) of H_2O and (i) ΔG_{H^+} for the HER on different sites of the Co_2N (111), CoN (111), and $\text{Co}_2\text{Mo}_3\text{O}_8$ (001) surfaces. (j) Top and side views of the optimal adsorption structures of H_2O and H on Co_2N (111), CoN (111), and $\text{Co}_2\text{Mo}_3\text{O}_8$ (001) surfaces, respectively.²⁹²

CF-supported $\text{Co}_2\text{N}/\text{CoN}/\text{Co}_2\text{Mo}_3\text{O}_8$ heterostructure with hierarchical and nanoporous architecture was fabricated by a hydrothermal route followed by nitridation treatment (Fig. 13f and g), which exhibited high activity and excellent durability for the alkaline HER, exceeding most reported non-precious catalysts.²⁹² DFT calculations (Fig. 13h–j) indicated that the $\text{Co}_2\text{Mo}_3\text{O}_8$ component facilitated H_2O dissociation and Co_2N promoted the hydrogen adsorption and recombination. Wang *et al.* built super-hybrid metal sulfide nanoarrays on CF (super- $\text{Co}_3\text{S}_4/\text{P-WS}_2/\text{Co}_9\text{S}_8/\text{CF}$) by a simple one-step method.²⁹³ The as-synthesized super- $\text{Co}_3\text{S}_4/\text{P-WS}_2/\text{Co}_9\text{S}_8/\text{CF}$ consisted of a metallic Co_3S_4 nanosheet, a P doped WS_2 nanosheet and Co_9S_8 nanoparticles, which just required 58, 70, and 129 mV in alkaline, acidic, and neutral solutions, respectively, to achieve

10 mA cm^{-2} , and showed rapid kinetics and good long-term durability. The experimental and theoretical results demonstrated that the robust activity in super- $\text{Co}_3\text{S}_4/\text{P-WS}_2/\text{Co}_9\text{S}_8/\text{CF}$ mainly originated from the unique electronic structure, special nanoarray morphology, and multiple heterointerfaces, which not only boosted the electric conductivity for electron transfer but also maximized the active heterointerfaces exposing for mass transport, resulting in Pt-like ΔG_{H^+} and favorable H_2O adsorption and dissociation energy for all-pH HER. For instance, the interface between $\text{Co}_3\text{S}_4/\text{WS}_2$ could enhance the HER activity *via* optimizing ΔG_{H^+} , and the $\text{Co}_3\text{S}_4/\text{WS}_2$ and $\text{Co}_9\text{S}_8/\text{WS}_2$ heterostructures were in favor of H_2O adsorption and dissociation, thereby enabling the outstanding HER performance in a wide pH range. The strategy in this work could

inspire the future synthesis of high-performance metal sulfide-based heterostructures for the HER. Like WS_2 , the CeO_2 nanorod array was also employed to decorate Co_3S_4 nanosheets, forming a heterogeneous hierarchical $\text{Co}_3\text{S}_4/\text{CeO}_2$ nanorod array on CF ($\text{Co}_3\text{S}_4/\text{CeO}_2\text{-CF}$) through a simple ionic liquid-assisted one-step hydrothermal approach.²⁹⁴ The as-synthesized $\text{Co}_3\text{S}_4/\text{CeO}_2\text{-CF}$ with the favorable heterointerfaces and hierarchical core-shell structures demonstrated high-performance HER and OER activity, which only required overpotentials of 74.9 mV and 213 mV to reach the current density of 10 mA cm^{-2} in 1.0 M KOH electrolyte. To attain the current density of 10 mA cm^{-2} , the $\text{Co}_3\text{S}_4/\text{CeO}_2$ -based electrolytic water device merely needed 1.64 V in an alkaline solution, lower than that of the Pt/C and RuO_2 -assembled electrolysis device (1.70 V).

3.8 Iron-based substrates

The corrosion method has been widely used to synthesize self-supported electrodes on metal surfaces without electricity

input, intricate synthetic process, and high temperature, and the metals served as substrates and precursors.^{295–298} Consequently, a simple and industrially-compatible one-pot corrosion route for the fast preparation of amorphous RuO_2 -decorated FeOOH nanosheets on iron foam (FF-Na-Ru) within 60 min was developed.²⁹⁹ The as-fabricated electrode could rapidly release the generated gas bubbles owing to its super-hydrophilic and aerophobic feature, ensuring fast HER kinetics. Therefore, the FF-Na-Ru electrocatalyst presented a superior performance for the HER (30 mV at 10 mA cm^{-2}) and electrolyzer (1.46 V at 10 mA cm^{-2}) with high operational stability in 1 M KOH solution. DFT calculations confirmed that the strong electronic interactions between RuO_2 and FeOOH could enhance the electrocatalytic HER activity. The metastable FeS with ultrathin nano fan-like morphology on the 3D porous IF was prepared by the *in situ* sulfurization method (Fig. 14a–c), which showed efficient and long-term HER performance in alkaline simulated seawater and neutral electrolyte with low

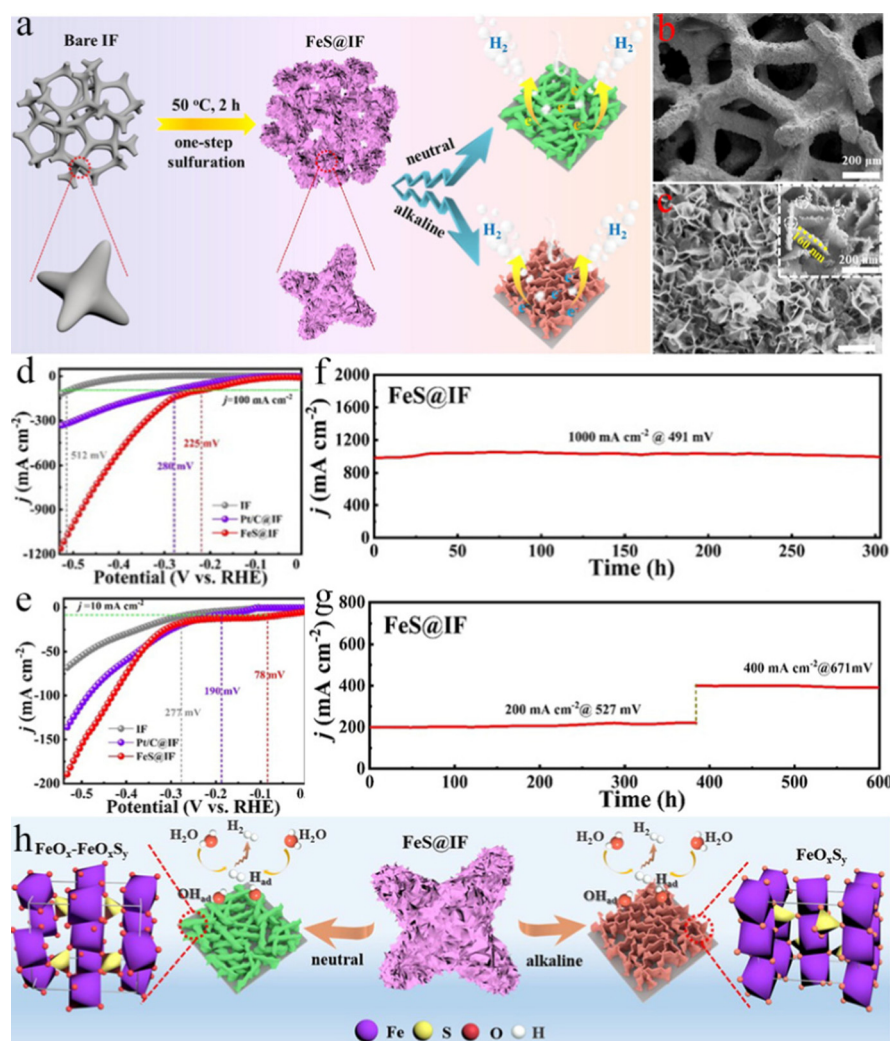


Fig. 14 (a) The synthesis of the FeS@IF electrode, and tested the electrochemical performance in both neutral and alkaline solutions. (b and c) FESEM images of the FeS@IF electrode. (d and e) LSV curves of the FeS@IF electrode in alkaline simulated seawater solution and 1.0 M PBS solution. (f and g) CP tests for the FeS@IF electrode in alkaline simulated seawater and 1.0 M PBS medium. (h) Schematic mechanism of the FeS@IF electrode in the HER process.³⁰⁰

overpotentials of 63 and 78 mV at 10 mA cm⁻², respectively (Fig. 14d and e).³⁰⁰ Strikingly, it also exhibited outstanding stability for at least 300 h in alkaline simulated seawater solution at 1 A cm⁻² with neglect deterioration (Fig. 14f). Surprisingly, the FeS@IF electrode was continuously electrolyzed for over 600 h at an industrial-grade current density in a neutral solution (Fig. 14g). The decent activity and robustness were attributed to the fast gas release and mass transfer induced by the highly-dispersed fan-like structure and the strong interaction between corrosion-resistant FeO_xS_y protection layers and 3D porous IF (Fig. 14h). Based on the doping effect, Ru, Ni dual-doped Fe₂O₃ catalyst with a lily-shaped morphology was constructed on IF (RuNi-Fe₂O₃/IF) through a simple one-step hydrothermal method for alkaline water electrolysis.³⁰¹ The RuNi-Fe₂O₃/IF electrode produced a large current density of 100 mA cm⁻² at overpotentials of 75 and 329 mV for the HER and the OER, respectively. Besides, the overall water splitting needed cell voltages of 1.66 and 1.73 V to achieve 100 mA cm⁻² in 1.0 M KOH and 1.0 M KOH seawater solutions, respectively. Moreover, the electrode displayed excellent long-term stability, retaining 100 mA cm⁻² for over 100 h, which was superior to the two-electrode cell assembled by noble catalysts. The excellent activity and durability of RuNi-Fe₂O₃/IF could be ascribed to the intact lily-shaped morphology and the strong electronic coupling between the Ru/Ni doping and Fe₂O₃ host. Chai's group fabricated phosphorus doped inverse spinel Fe₃O₄ on IF (P-Fe₃O₄/IF) for the alkaline HER, which exhibited an ultralow overpotential of 138 mV at 100 mA cm⁻².³⁰² More inspiringly, coupling NiFe LDH/IF with P-Fe₃O₄/IF for splitting water showed excellent durability for over 1000 h at 1 A cm⁻², and even for 25 000 s at 10 A cm⁻² in 6.0 M KOH at 60 °C, exhibiting great potential for the industrial H₂ production. DFT calculations suggested that the octahedral Fe site with excellent conductivity facilitated the water dissociation through a biomolecule Volmer reaction mechanism, greatly boosting the proton supply.³⁰³ Meanwhile, Δ*G*_{H*} of the P atom in inverse spinel Fe–O–P as an active site was theoretically calculated to be 0.01 eV, benefitting the alkaline HER. They also investigated the effect of F doping on bimetallic phosphide, and the results showed that F doping could affect the valence state and electronic structure of Co and Fe ions, thereby enhancing HER performance.³⁰⁴ As a result, the as-synthesized F-Co₂P/Fe₂P/IF exhibited outstanding HER catalytic activity, which required low overpotentials of 229.8, 260.5, 292.2, and 304.4 mV to deliver 500, 1000, 2000, and 3000 mA cm⁻², respectively. Meantime, it could retain a long-term durability in 1.0 and 6.0 M KOH electrolytes at different high current densities for industrial water splitting. For further improving the HER performance of the bimetallic phosphide, they fabricated a self-supported CoFeOH/CoFeP on the IF substrate (CoFeOH/CoFeP/IF) with superior alkaline HER performance, requiring overpotentials of 114.9, 194.9, 221.8, 249.7, and 266.1 mV in 1.0 M KOH (25 °C) to reach 100, 500, 1000, 2000, and 3000 mA cm⁻², together with over 100 h durability (at 500 and 1000 mA cm⁻²).³⁰⁵ When integrating with NiFe-LDH/IF in a two-electrode cell, the voltage of NiFe-LDH/IF (+)||CoFeOH/CoFeP/IF (–) is only 1.57 V (7.6 M KOH 70 °C) at

2500 mA cm⁻². Even in 1.0 M KOH (25 °C) media, it merely demanded 1.88 V. The outstanding HER performance of CoFeOH/CoFeP/IF showed great potential for large-scale H₂ production.

3.9 Other substrates

Besides the substrates discussed above, other substrates including W foils, indium tin oxide (ITO) glass, SiO₂/Si, Au/Si, and MoNi foam have also been used as HER electrode substrates. For instance, Li *et al.* developed a WS₂ nanosheet electrocatalyst fabricated on the W foil (WS₂/W) by a mild bottom-up method (Fig. 15a).³⁰⁶ The vertically arranged WS₂ ultra-thin nanosheets formed on the W substrate could reduce the effect of the contact resistance and improve the conductivity of WS₂ (Fig. 15b–d). Moreover, the W and S vacancies in the WS₂/W heterostructure could offer more active sites for the HER. DFT calculations demonstrated that the chemical bonds could be formed between the W foil and WS₂, leading to fast electron transport. This electrocatalyst exhibited HER activity with an overpotential of 108 mV for 10 mA cm⁻², a low Tafel slope of 45.5 mV dec⁻¹, and good stability. Xie *et al.* fabricated a vertically aligned defect-rich MoS₂ (DR-MoS₂) nanowall (NW) on the highly conductive ITO glass with a facile hydrothermal reaction (Fig. 15e and f).³⁰⁷ Benefiting from the more exposed active edge sites, the coarse surface, as well as the potent nanowall structure, the DR-MoS₂ NW catalyst with an optimized thickness displayed a low overpotential of 95 mV to reach 10 mA cm⁻² in an acidic solution. Furthermore, the HER stability of DR-MoS₂ NW could be maintained due to the close contact between the NW structure and the conductive ITO substrate. Vikraman *et al.* synthesized the metal-doped MoSe₂ layers on SiO₂/Si and Au/Si substrates using the solution bath technique (Fig. 15g), which exhibited improved acidic HER activity due to the more edge facets and enhanced electrical conductivity, requiring overpotentials of 86, 87, and 88 mV at 10 mA cm⁻² for Cu-, Mn-, and Fe-doped MoSe₂, respectively.³⁰⁸ Considering the advantages of nickel and molybdenum substrates, Zhou *et al.* fabricated a self-supported NiO/MoO₂ heterostructure with large crystal-amorphous interfaces utilizing MoNi foam as the metal source and substrate by a mild and practical anodizing-assisted molten-salt strategy (Fig. 15h).³⁰⁹ The prepared diamond-like NiO/MoO₂-100-2 catalyst exhibited excellent alkaline HER activity with a low overpotential of 48 mV at 10 mA cm⁻², a small Tafel slope of 51.5 mV dec⁻¹, and good stability, which could be derived from three main factors: (1) the activated substrate by a pre-anodizing process facilitated the etching of subsequent molten salt, exposing more available active sites; (2) the NiO crystal/amorphous MoO₂ heterojunction with high-density distribution modified the electron density and d-band structure near the Fermi level, resulting in optimizing hydrogen adsorption/desorption energy and boosting charge transfer. In detail, the NiO crystals promoted the alkaline water dissociation to fast produce active hydrogen (Volmer step), thereby benefitting for the subsequent Heyrovsky and Tafel steps on the amorphous MoO₂ region; (3) the modulated electron state of NiO and MoO₂ was also

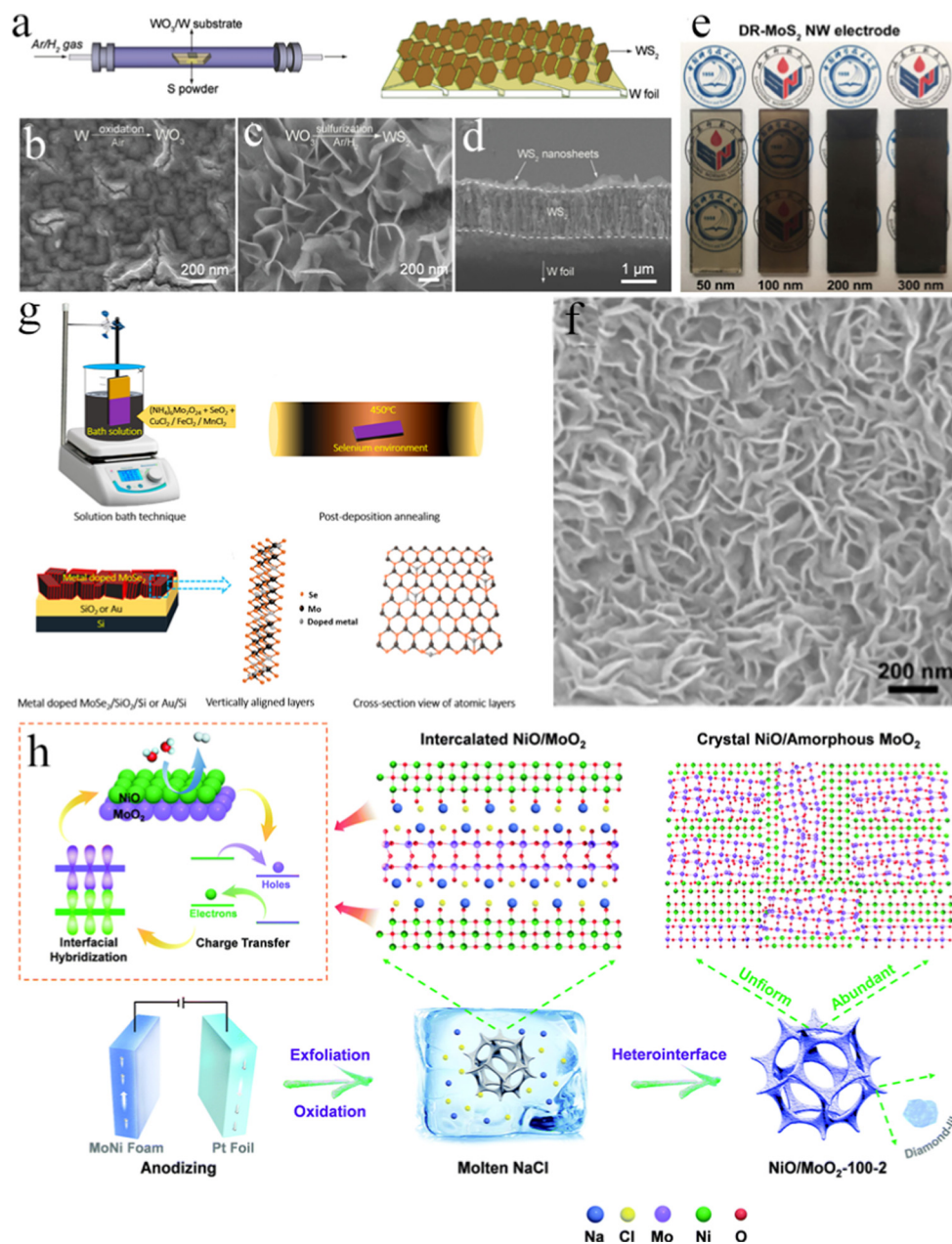


Fig. 15 (a) Fabrication of WS_2 process. (b and c) FESEM images of WO_3 and WS_2 nanosheets on the W foil. (d) Side-view FESEM.³⁰⁶ (e) Digital photograph of the DR- MoS_2 NW catalysts with different thicknesses and variable transparency.³⁰⁷ (f) FESEM image of the DR- MoS_2 NW.³⁰⁷ (g) Illustrations of metal-doped MoSe_2 deposition.³⁰⁸ (h) Illustration of preparation of the NiO/MoO_2 sample.³⁰⁹

propitious to improve conductivity and optimize hydrogen adsorption.

4. Future perspectives

In this review, we comprehensively summarized the latest advances in various substrates for supporting electrocatalysts. Compared to the published reviews on the design or modification of electrocatalyst materials, this article focuses on substrates and their impacts on electrolytic water, which can provide an innovative strategy or guidance to develop

high-efficient electrocatalytic electrodes. The investigations on self-supported electrodes have received great attention and have achieved a series of progress in the field of electrocatalytic water splitting. Notwithstanding, how to keep the advantages of the self-supported electrodes for large-scale fabrication and application is still a great challenge. To boost electrocatalytic activity and achieve wide applications in the industry, there are some suggestions for developing self-supported electrodes as exhibited in Fig. 16. For instance, (1) It is important to develop advanced substrates, which is the base on the self-supported electrodes; (2) large-scale synthetic methods are explored to serve for electrocatalytic water splitting; (3) the fundamental



Fig. 16 Challenges and future perspectives of self-supported electrodes.

reaction mechanisms of HER need more experimental data and theory analysis; (4) *in situ* spectroscopic technologies are used to evaluate the electrocatalytic performance and investigate interface effects and stability of self-supported electrodes; and (5) appropriate evaluation methods need to be established for evaluating the performance of electrocatalysts.

Currently, 3D macroporous metal foams (especially NF, CF, CFM, IF, and so on) are widely used to support electrocatalysts. Although these substrates exhibit relatively excellent conductivity, their mechanical strength cannot meet the practical long-term test at a large current density and high temperature.³³ In addition, these metal foams may become extremely fragile and broken during the pyrolysis of precursors under a high temperature. Accordingly, the synthesis method for self-supported electrocatalysts will be limited. Furthermore, CC is a preferential alternative to metal foam, which possesses not only good mechanical flexibility and elasticity, but also high-temperature stability. Nevertheless, its conductivity is weaker than that of metal foam, adversely affecting the catalytic performance of self-supported electrodes.³¹⁰ Whereas, most of the present attention is mainly paid to designing and tailoring electrocatalysts, the study on substrates is rarely reported. Therefore, more studies should be conducted to develop efficient and advanced substrates, which can not only enhance the catalytic activity of the self-supported electrodes but firmly operate for a long time in practical applications. Moreover, the chemical and physical properties of substrates essentially determine their performances and applications. Thus, the effect of substrate properties on the electrocatalytic performance needs

to be further clarified. For instance, the interface between the active materials and the conductive substrates has a crucial impact on the electron transfer and durability properties, which are merely studied. Therefore, their relationship should be intensively investigated to get more information about the adhesive force between active materials and substrates, which may include the electrostatic attraction, van der Waals interaction, and covalent bonding.³¹¹ For enhancing the HER performance, effective strategies should be used to tailor the interface. Besides, tedious procedures and low yield usually appear in the process of constructing self-supported electrocatalysts. Therefore, it is essential to exploit facile and easily scalable synthetic methods. In addition, the mass of the catalyst loaded on substrates shows dramatic effects on the HER performance. When the catalyst loading is high with a large thickness, the catalysts will easily dissolve in the electrolyte during testing due to their delamination from the substrate. On the other hand, when the loading is small with thin active layers, low catalytic activity will be observed.³¹ Therefore, it is necessary to ensure the optimal amount of catalysts for efficient water splitting.

For developing advanced HER electrocatalysts, it is necessary to investigate the fundamental reaction mechanism. Theoretical calculations and *in situ* spectroscopic investigations are effective and powerful tools to reveal the catalysis mechanism and structural transformation of electrodes. *In situ operando* analytic techniques such as Raman, X-ray photoelectron spectroscopy, X-ray diffraction, and Fourier-transform infrared spectroscopy have been successfully employed to probe the surface species in the HER, facilitating simultaneously

determining the real catalytic active sites and mechanisms.^{312–315} Meanwhile, transmission electron microscopy can give insight into the morphology, microstructure, and chemical properties of catalysts at the nanoscale. With *in situ* transmission electron microscopy, dynamic processes of catalytic reactions in both gas and liquid environments can be deeply investigated in real time.^{316–318} Additionally, more refined characterization should be utilized at an atomic level. For instance, *ex situ* and *in situ* synchrotron radiation-based characterizations can study the electronic structure, oxidation states, and coordination environment.^{319–321} Besides, more high-resolution techniques should be rapidly and timely developed to investigate the reaction processes and the evolution of surface/interface/bulk. For instance, near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and synchrotron radiation-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) are useful tools to analyze the surface information under working conditions, as well as detect the active intermediates and radicals in the combustion field, respectively.^{322–324} However, these techniques are rarely utilized in the field of electrocatalysis to probe the active intermediates during the HER. Therefore, multi-techniques should be exhaustively developed to probe simultaneously the structural information and reaction intermediates in the catalysis field, visualizing the HER pathways. Furthermore, the self-supported electrode with well-aligned nanostructures can remarkably influence the efficiency of mass transport during the HER.^{325–327} In particular, the property of the nanostructure surface plays a key role in the microscale mass transport for the multi-phase system. For example, the 1D/2D nanostructured electrode can quickly remove the produced gas bubble, promoting the HER.^{328–330} However, it is difficult to systematically investigate the mass transport effects and mechanisms for different surface nanostructures and active materials. The coupling of computational modeling with experiments will help to comprehend the mass transport mechanisms. Therefore, developing effective computational modeling should be taken into account in detail.

For stability performance, most of the reported self-supported electrodes work well under a current density below 10 mA cm⁻² for dozens of hours, but cannot satisfy the requirement of industrial water electrolysis, which needs overpotentials of less than 300 mV at 500 mA cm⁻² with stability for thousands of hours.³³¹ To obtain a tough self-supported electrode, the catalysts with an optimal adsorption energy of intermediates and porous structure are feasibly designed and fabricated, which can promote releasing H₂ bubbles from the surface and boost mass transfer.³³² Meanwhile, the stability-affecting factors should be focused on and investigated in-depth, such as substrate material, catalyst structure/phase, electrode/electrolyte hydrophilic performance, catalyst/substrate interface property, mechanical behavior, and so on. The intrinsic stability of most electrocatalysts in acid/alkaline solutions is not yet completely comprehended. Thus, the chemical and structural durability upon long-term testing and polarizing in strong acidic/alkaline electrolytes should be paid more attention. Furthermore, the decline mechanisms of electrocatalysts deserve to be further investigated, which can be understood in the following respect

especially, such as the electrocatalysts dissolving, active materials converting, substrate corroding, active materials peeling, catalyst surface covering, and catalyst size increasing. In addition, the decline mechanism in different testing conditions ought to be studied separately. For a better understanding of the decline mechanisms, effective mitigation strategies should be proposed, and *in situ* characterization technique and chemical modeling also need to be developed. Furthermore, a reliable evaluation of the catalytic performance should be urgently addressed for different electrocatalysts. To compare the electrocatalyst performance, the presently used current density based on geometric electrode area may not reflect some dominant factors including substrate effect, catalyst dimension and size, mass loading, morphology, specific surface area, and testing condition. Therefore, comprehensive evaluation standards comprising η , Tafel slope, j_0 , TOF value, specific activity based on mass and ECSA, and FE should be formulated for convincing comparison.

5. Conclusions

Exploring low-cost, highly efficient and extremely robust HER electrocatalysts is greatly crucial for industrial electrolytic water splitting for sustainable H₂ production. Compared to the conventional coated electrodes in the powder form, the self-supported electrodes with *in situ* integrated catalytically active phase on appropriate substrates are propitious for simplifying the fabrication of electrodes, decreasing interface resistance, exposing more abundant active sites and improving stability, and they have promising potential for practical applications in water splitting. In this review, we systematically summarized the state-of-the-art development of self-supported electrodes using different substrates for effective HER. The efficient strategies for enhancing electrocatalyst performance, such as heteroatomic doping, improving conductivity, building heterostructures, tuning wettability, surface/defect engineering, and so on, are emphasized. Meanwhile, the synthesis routes, including hydrothermal/solvothermal, electrodeposition, molten salt, calcination, CVD, thermal-oxidative, magnetic field assisted, electrochemical activation, solution evaporation, top-down exfoliation, bottom-up, magnetron sputtering, chemical bath deposition, solid-state synthesis, corrosion, and anodizing-assisted molten-salt methods, are also discussed. Furthermore, various electrocatalysts containing Fe₂O₃, Fe₃O₄, Co₃O₄, Co₂Mo₃O₈, CoO, NiO, NiCo₂O₄, Cu₂₊₁O, Cu₂O, TiO₂, RuO₂, CeO₂, MoO₂, Na_xWO₃, FeS, CoS₂, Co₃S₄, Co₉S₈, Cu₂S, MoS₂, WS₂, ReS₂, MoSe₂, Ru_{0.33}Se, NiMo alloy, NiCo alloy, RhIr alloy, Co, Ag, Ru, Pd, Pt, Ni(OH)₂, NiFe(OH)_x, FeOOH, Ti₃C₂, Ni₆Mo₆C, (Ni,Co)₃C, MoC, Mo₂C, WC, Co₂N, CoN, Co₄N, Ni₃N, Mo₂N, Fe₂P, CoP, Co₂P, Ni₂P, Ni₅P₄, Cu₃P, MoP, and MOFs with nanowire, nanorod, nanodot, nanosheet, nanoflower, nanotube, nanoplate, porous nanobelt, nanoarray, and nanowall morphologies are also introduced. Although significant progress towards materials design/synthesis and property investigation has been made, great challenges remain in the further development of self-supported electrodes.

In summary, we hope that the strategies discussed in this work can provide a background and a better insight into self-supported electrodes utilized in catalytically electrolyzing water. We believe that constructing a self-supported electrocatalyst is a promising and challenging strategy to develop a hydrogen economy.

Author contributions

Jin Li: conceptualization; writing-original draft; visualization. Jian Zhang: data curation; visualization. Jinke Shen: data curation; visualization. Haipeng Chen: data curation; visualization. Honghui Wu: words and sentence editing. Guilong Liu: data curation; visualization. Donglei Guo: data curation; visualization. Changzhou Yuan: funding acquisition; supervision; writing-review & editing. Naiteng Wu: funding acquisition; supervision; writing-review & editing. Xianming Liu: funding acquisition; supervision; writing-review & editing.

Conflicts of interest

There are no conflicts to declare.

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