Journal of Electroanalytical Chemistry 921 (2022) 116679

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Review

Application of heteroatom doping strategy in electrolyzed water catalytic materials

Rui Zhang, Xiangheng Du, Shanshan Li, Jibiao Guan, Yini Fang, Xiao Li, Yinchen Dai, Ming Zhang *

School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, China

ARTICLE INFO

Keywords:
Heteroatom doping
HER/OER catalyst
Crystal structure
Catalytic activity
Potential mechanism

ABSTRACT

The development of clean and renewable new energy to solve the shortage of fossil energy and environmental pollution is an important research direction in the future. Hydrogen energy has been regarded as a kind of future energy because of its excellent characteristics of pollution-free and high calorific value. In addition, the electrolyzed water technology can also be combined with renewable energy sources such as solar energy to achieve complete recycling of hydrogen energy. In actual production, the realization of efficient water splitting relies to a large extent on the low-cost, high-activity and durable hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) reaction catalysts. Recently, heteroatom-doped transition metal-based water electrolysis catalyst materials have shown excellent electrocatalytic performance and durability for HER and OER, showing great potential for replacing precious metal-based catalysts. This article reviews the application of heteroatom doping strategies in transition metal-based catalytic materials and their latest research progress. First, summarize the internal relationship of heteroatom doping strategy to the morphology and catalytic activity of electrolyzed water catalytic materials. Then, the preparation process of heteroatom-doped transition metal-based catalytic materials for water electrolysis and the reasons for the improved performance and related mechanisms are discussed. Finally, the opportunities and challenges for the future development of heteroatom-doped transition metal-based catalytic materials are emphasized from the perspectives of catalytic mechanism and improvement measures.

Contents

---

* Corresponding author at: School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, China.
E-mail address: zhangming@zstu.edu.cn (M. Zhang).

https://doi.org/10.1016/j.jelechem.2022.116679
Received 6 May 2022; Received in revised form 10 July 2022; Accepted 3 August 2022

1. Introduction

With the increasingly prominent environmental problems and the global energy shortage, more and more researchers strive to find new renewable energy to replace fossil fuels [1–4]. According to a report by the International Energy Agency, by 2040, global energy demand will increase substantially, and carbon dioxide emissions will reach 35.7 gigatons/year [5,6]. Therefore, accelerating the establishment of a low-polluting and sustainable energy system on a global scale is a huge challenge facing humanity [7,8]. Hydrogen (H_2), due to its high energy density and clean, environmentally friendly, and pollution-free, is the best new energy to replace non-renewable fossil fuels [9–11]. So far, methane reforming and coal gasification technology is the primary way to produce hydrogen energy, but it mainly relies on fossil energy and does not fundamentally solve the problem [7,12]. Hydrogen production by electrolysis water is another essential hydrogen production technology with high energy conversion efficiency, high purity of hydrogen products, and simple equipment [13,14]. From the perspective of environmental protection and energy-saving, available resources, such as solar or wind power generation and water splitting technologies, provide an attractive method for producing hydrogen in a sustainable manner [15,16]. In Fig. 1, the development and application of renewable energy such as solar energy and wind energy have problems such as spatial and temporal discontinuity, low energy transmission efficiency, etc. One promising solution is to combine the electricity generated by these renewable energy sources to drive the decomposition and preparation of water, which can truly achieve sustainable hydrogen production, reduce air pollution and energy consumption, and build green cities. Due to the high overpotential of the electrolytic water hydrogen production technology, an effective and robust electrocatalyst is required to accelerate the reaction kinetics of the cathode hydrogen evolution reaction and the anode oxygen evolution reaction [17–19]. The theoretical voltage of electrolyzed water is 1.23 V, but there is a specific resistance in the decomposition process, and the actual voltage required is higher than the theoretical voltage [20,21]. In the 1890 s, water electrolysis had its first commercial demonstration [22–24]. After more than 100 years of development, electrochemically splitting water only accounts for 4 % of the global H_2 supply, mainly due to the high cost and low efficiency, which are insufficient for commercial production [25]. In fact, the energy conversion efficiency of commercial electrolyzed water systems is above average, about 65–73 %, and hydrogen production through electrolysis of water is feasible for commercial use [5]. Therefore, it is necessary to find a suitable electrocatalyst to reduce the overpotential of water splitting, improve the decomposition efficiency, and achieve the purpose of saving energy and reducing consumption [26–28]. At present, the best catalytic performance is the platinum-based noble metal catalyst for hydrogen evolution catalytic reaction and Ir-Ru oxide for oxygen evolution reaction [29]. Their advantage is that they have very low initial overpotentials of HER and OER, but their disadvantage is high price. The scarcity of precious metal catalysts has made researchers devote themselves to developing electrolyzed water catalytic materials without precious metal catalysts, the most common of which are transition metal-based compounds [30].

The outermost layer of transition metal atoms has more uncoordinated electrons, which is conducive to the adsorption and desorption of hydrogen, thereby accelerating the efficiency of water decomposition [31–33]. Transition metal-based compounds mainly include transition metal phosphides [34–37], sulphides [38–40], carbides [41–43], nitrides [44–46], oxides [47–49], hydroxides [50–53], etc. OER water electrolysis catalysts are mainly transitioned metal-based oxides and hydroxides. Although a single transition metal-based compound has a greater price advantage, its catalytic activity is still far from the precious metal-based electrolyzed water catalytic materials and commercial applications [54,55]. As shown in Fig. 2, heteroatom-doped water electrolysis catalysts may have various advantages, exhibiting higher catalytic activity and lower power consumption than a single corresponding counterpart. Heteroatom doping technology is an effective method to improve catalytic activity and catalytic performance of catalysts [56–58]. The substitution effect of heteroatoms on intrinsic atoms can destroy the crystal structure of catalytic materials and cause changes in the electronic environment and performance [59]. Heteroatom doping is divided into single-atom doping and polyatomic doping. From the point of view of hydrogen evolution reaction, heteroatom doping improves the electronic environment on the surface of catalytic materials, increases conductivity, and reduces the free energy of hydrogen adsorption [21,60,61]. Secondly, heteroatom doping is an effective method to increase the number of active sites. Changes in the crystal structure will cause defects and provide more adsorption sites and activity centers for HER intermediates [62]. Finally, it showed higher catalytic activity of electrolyzed water than the original compound [63–65].

In this review, the research progress of electrocatalysts synthesized by heteroatom doping strategies in hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and overall water splitting

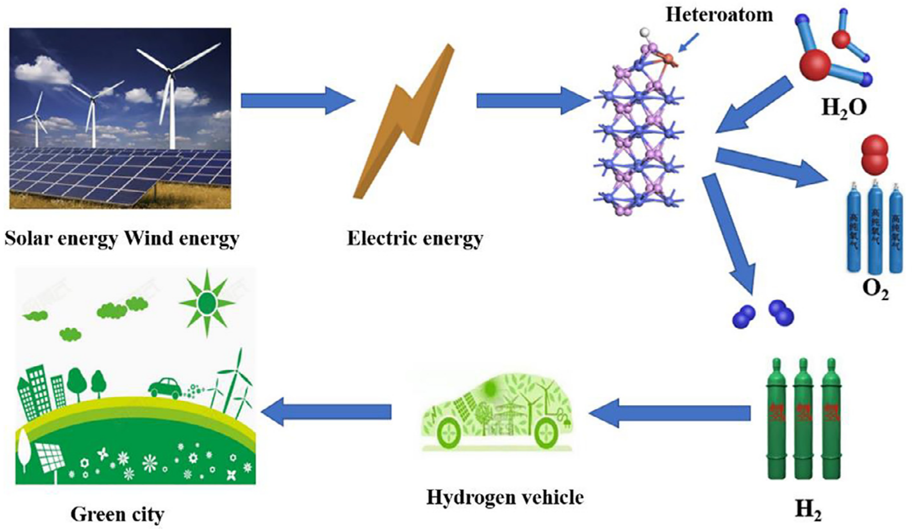

Fig. 1. Combination of renewable solar energy, wind energy and water electrolysis for hydrogen production.

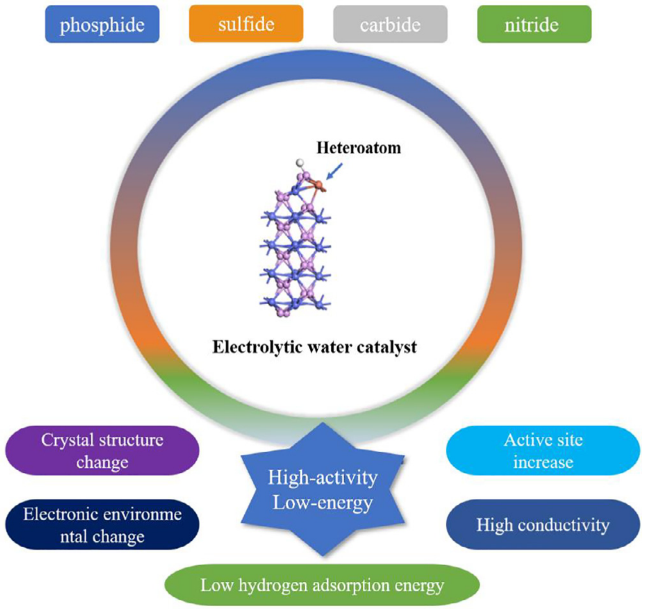

Fig. 2. Heteroatom-doped water electrolysis catalysts and their performance advantages.

(OWS) is reviewed, with emphasis on the design and synthesis strategies and the mechanism for improving catalytic activity. First, the HER/OER reaction mechanism and general methods for evaluating catalytic performance are briefly reviewed. Then, the research progress of heteroatom-doped electrocatalysts in recent years is introduced, and some typical works are analyzed. Finally, the challenges and difficulties faced by heteroatom-doped bifunctional electrocatalysts are discussed to provide some help for exploring more promising electrocatalysts.

2. Reaction mechanism of electrocatalytic water splitting

Hydrogen production by water electrolysis is a simple and low-cost method for producing hydrogen [66,67]. When electrolyzing water, due to its low conductivity, water is a weak electrolyte, and an electrolyte needs to be added to enhance the conductivity of the solution. In general, electrolytes are divided into three types, alkaline electrolytes, proton exchange membranes (PEM), and solid oxide electrolytes (SOE) [68–70]. Compared with other electrolytes, alkaline electrolytes are favorable for the OER reaction. Under the condition of high current density and low battery voltage, the utilization of high-efficiency bifunctional non-precious metal catalysts has excellent potential in the direction of water electrolysis industrialization.

The water-splitting reaction consists of two half-reactions, which are divided into the cathode HER reaction and the anode OER reaction [71,72]. The HER reaction requires two electrons, and the OER reaction requires 4 electrons [71,73]. However, high barriers to reaction and slow kinetics ultimately lead to low energy conversion efficiency and unnecessary energy loss.

$$\text{Totalwatersplittingreaction:}2H_2O \rightarrow 2H_2 + O_2 \tag{1}$$

Under acidic electrolyte conditions.

$$\text{Cathode:}2H^+ + 2e^- \rightarrow H_2, E_c = 0V \tag{2}$$

$$\text{Anode:}2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E_a = 1.23\ V \tag{3}$$

Under alkaline electrolyte.

$$\text{Cathode:}2H_2O + 2e^- \rightarrow H_2 + 2OH^-, E_c = -0.83\ V \tag{4}$$

$$\text{Anode:}4OH^- \rightarrow O_2 + 2H_2O + 4e^-, E_a = -0.40\ V \tag{5}$$

Although the total reaction is the same, it contains multiple steps, and different electrochemical reactions occur in different electrolytes [74]. The values of Ec and Ea refer to an ordinary hydrogen electrode (NHE) [75]. However, a higher potential is always required to drive each reaction step, and the needed additional potential is called the water split overpotential (η) [76]. In addition, there are some other reaction resistances, such as contact resistance and solution resistance [77].

$$\text{Actualoperatingpotential for total water splitting : EOP} = 1.23\,\text{V} + \eta_a + \eta_c + \eta_{other} \tag{6}$$

From the formula, we can find that the most critical factor in reducing the overall water splitting energy consumption is to reduce the overpotential of each part [78]. Therefore, it is necessary to reduce the overpotential and speed up water electrolysis by using excellent cathode and anode catalysts that do not contain precious metals and are relatively inexpensive [79,80].

2.1. Cathodic HER reaction

In acid electrolyte, HER is a two-electron transfer process, which includes the following steps [81]:

(1) A proton in H_3O^+ is captured by an electron, which produces adsorbed hydrogen ions (H*) on the surface of the catalytic material.

$$H_3O^+ + e^- + * \rightarrow H_2O + H^*, \text{(Volmerreaction)} \tag{7}$$

(2) H_3O^+ combines with an H* and an e^- to produce an H_2 molecule.

$$H_3O^+ + H^* + e^- \rightarrow H_2 + H_2O, \text{(Heyroskyreaction)} \tag{8}$$

(3) Two adjacent adsorbed hydrogen atoms couple to form hydrogen molecules.

$$H^* + H^* \rightarrow H_2, \text{(Tafelreaction)} \tag{9}$$

The alkaline electrolyte is similar to the acid, and the details are as follows:

(1) A water molecule and an electron combine on the surface of the catalyst to form H*.

$$H_2O + e^- + * \rightarrow H^* + OH^-, \text{(Volmerreaction)} \tag{10}$$

(2) H* combines a water molecule and an electron to produce an H_2 molecule.

$$H^* + H_2O + e^- \rightarrow H_2 + OH^-, \text{(Heyroskyreaction)} \tag{11}$$

(3) As in acid, two adsorbed hydrogen ions (H*) combine to produce a hydrogen molecule.

$$H^* + H^* \rightarrow H_2, \text{(Tafel reaction)} \tag{12}$$

In these reaction steps, * represents active surface sites, H* represents adsorption of hydrogen ions, and more active sites correspond to faster hydrogen adsorption and desorption [11,82]. The first step is the Volmer reaction, followed by the Heyrovsky reaction and the Tafel reaction through two reaction pathways to generate the final hydrogen molecule [83]. The required reaction kinetics under alkaline conditions is higher than that required in acids, because the alkaline electrolyte requires water to dissociate before H* can be formed [84]. Because no matter what kind of step in the HER process requires the participation of H*, the amount of free energy of hydrogen adsorption is significant [85]. The ΔGH* of noble metal catalysts such as Pt-based catalytic materials is close to zero. If ΔGH* deviates from the reference zero too much, it will require more free energy for adsorption and desorption, slowing down the rate of hydrogen generation and increasing power consumption [86–88].

2.2. Anodic OER reaction

The OER reaction process requires 4 electrons, and the reaction mechanism is more complicated, with lower reaction kinetics, involving 3 adsorption intermediates of OH*, O*, and OOH* [89–91]. The OER reaction steps and reaction mechanism are as follows:

(1) OER step of acid electrolyte.

$$H_2O + * \rightarrow HO* + H^+ + e^- \quad (13)$$

$$HO* \rightarrow O* + H^+ + e^- \quad (14)$$

$$O* + H_2O \rightarrow HOO* + H^+ + e^- \quad (15)$$

$$HOO* \rightarrow * + O_2 + H^+ + e^- \quad (16)$$

(2) OER step in alkaline electrolyte.

$$OH^- + * \rightarrow HO* + e^- \quad (17)$$

$$HO* + OH^- \rightarrow O* + H_2O + e^- \quad (18)$$

$$O* + OH^- \rightarrow HOO* + e^- \quad (19)$$

$$HOO* \rightarrow * + O_2 + H_2O + e^- \quad (20)$$

Compared with HER, the OER reaction involving complex reaction pathways is slower; and is generally considered a process with higher thermodynamic and kinetic requirements in water electrolysis. Essentially, oxygen evolution results from the oxidation of hydroxyl groups in alkaline solutions or water molecules under acidic conditions [92]. In the OER process, due to the accompanying electron and proton transfer, *, HO*, and HOO* intermediates are sequentially produced. The bond-forming interactions in these intermediates are critical to the catalytic activity. OER mainly adsorbs reactants on the surface to form adsorbed intermediates, promoting the charge transfer between electrodes and reactants. The adsorption of intermediaries can be widely used to explore the electrocatalytic ability of OER [93,94]. In acidic solutions, ruthenium/iridium oxide is most suitable for OER, while transition metal catalysts are more suitable for OER in alkaline media [95,96].

2.3. General method of evaluating performance

Essentially, a good catalyst should have small onset potential (η_0) and overpotential (η), large exchange current density (j_0), small Tafel slope and charge transfer resistance (Rct), large electrical Chemical surface area (ECSA) and good stability [97–99]. These parameters should be comprehensively considered when evaluating the catalytic performance of nanocatalytic materials.

The overpotential, the difference between the experimentally observed potential and the thermodynamically determined potential of an electrochemical reaction, is considered to be one of the most important values for evaluating water splitting catalysts, since it is the large overpotential that causes the electrochemical water electrolysis system to fail. low energy conversion efficiency [100]. In order to compensate for the drop in ohmic voltage between the working and reference electrodes, iR compensation is necessary for the performance of the working electrode [101,102].

The Tafel slope is a very important catalytic efficiency parameter, which can be obtained by transforming the LSV curve, and is mainly used to infer possible reaction steps and corresponding reaction mechanisms. The smaller the slope of the Tafel value corresponds to the faster reaction kinetics and exchange current density, that is, a larger current density can be generated with a smaller overpotential change [103–105].

EIS is used to study the kinetics of electrocatalytic reactions at the electrolyte/electrode interface. The charge transfer resistance can be used to analyze the interfacial charge transfer process of the electrodes. The diameter of the semicircle in the high frequency region corresponds to the R_{ct} value, and the smaller the value, the faster the reaction rate, while the diameter of the semicircle in the low frequency region corresponds to the adsorption resistance (R_{ad}) [106]. The large electrochemically active surface area (ECSA) can enhance the absorption of water molecules and intermediates on the surface of the catalytic material, and provide more electrochemically active sites [107,108].

From a practical application point of view, stability is another critically important parameter that can be used to evaluate the ability of catalysts to keep their catalytic activity unchanged during long-term operation [109]. The long-term stability and application potential of electrolytic water catalytic materials can be evaluated by recording the change of overpotential at a certain current density or by recording the change of cathode current density under an applied overpotential for a period of time, or by accelerated CV cycle test.

3. Application of heteroatom doping in catalytic materials for hydrogen evolution reactions

Although a single catalyst has a certain improvement in the catalytic performance of water electrolysis, it is still insufficient for large-scale industrialization. Therefore, it is necessary to find a method to optimize the structure of a single nano-catalytic material and improve the catalytic performance. The methods for improving single transition metal catalytic materials include photoelectric deposition [110], heterostructures, alloys, composite material [111,112],salt-assisted methods [113], dielectric barrier discharge (DBD) plasma technology [114] and heteroatom doping technology, among which heteroatom doping technology is simple to operate, low cost and the advantages of good catalytic performance have attracted the attention of many researchers. Heteroatom doping technology is a strategy to improve the catalytic performance by introducing some other atoms to adjust the crystal structure of nano catalytic materials [115]. Zhou et al., [116] used $Ni(OH)_2$/NF as a substrate to prepare P-doped NiS_2-NiS nanorod arrays by hydrothermal method as excellent HER catalysts. Under alkaline conditions, when the current density is 10 mA cm^{-2}, the cathodic hydrogen evolution overpotential is 141 mV; the catalytic current is stable at 20 mA cm^{-2}, with no apparent attenuation within 30 h, with good stability and durability [117]. This is attributed to the effective reduction of the charge transfer resistance by phosphorus doping, the induction of additional active sites and the enhanced catalytic kinetics, and the large specific surface area of the nanorod arrays, exposing more active sites and accelerating the catalytic reaction [118]. Zhao et al., [119] developed appropriate Ni-doped $MoSe_2$ nanosheets, which can significantly reduce the overpotential and enhance the HER activity in alkaline electrolytes, which are promising non-noble metal electrocatalysts. In summary, Heteroatom doping technology can improve the crystal structure and electronic environment of nano catalytic materials, so that the active site and electrical conductivity increase, thereby reducing the hydrogen adsorption energy.

In order to alleviate the agglomeration of active species, many researchers grow nano catalysts on supports. The most used substrates include carbon cloth, metal foam, fiber, etc. The replacement of metal atoms in the crystal structure of transition metal-based compounds by heteroatoms will cause changes in the chemical bonds between the particles, thereby affecting the binding energy between the atoms and the surrounding electronic environment, and ultimately changing

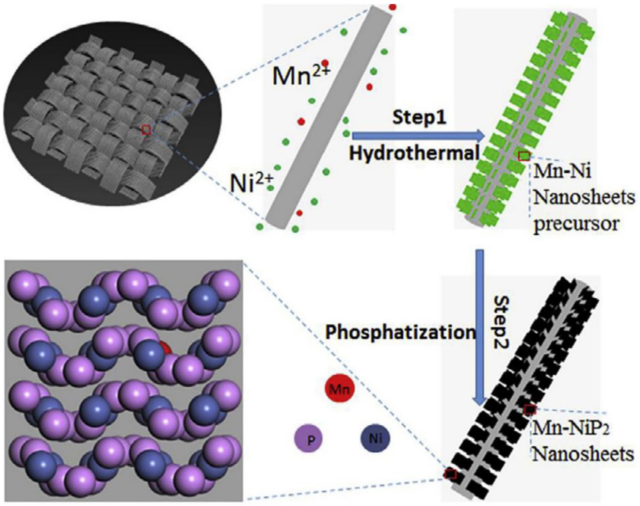

Fig. 3. Preparation process of Mn-doped NiP_2 nanosheets on carbon cloth [124].

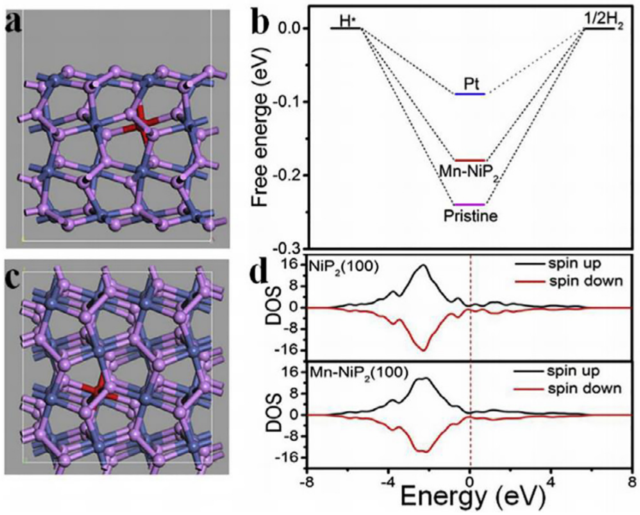

Fig. 4. (a) top view and (c) side view of Mn-NiP_2 NSs/CC(1 0 0) crystal plane; (b) hydrogen adsorption free energy ΔGH*; (d) Ni atoms on NiP_2 and Mn-NiP_2 (1 0 0) DOS, doped with 3.1% Mn on the second layer [124].

the crystal structure and catalytic activity of the catalytic material [120]. In addition, similar atom sizes can increase the success rate of heteroatom doping strategies. Guang et al., [121] prepared a self-supporting nanoporous CoBP electrocatalytic material, and the synergistic electronic effect of the addition of B and P elements on the surface optimized the desorption of H atoms, provided more active areas, and had good HER activity and stability. The most researched non-precious metal catalysts are transition metal-based catalytic materials, especially the fourth cycle of cobalt-based and nickel-based electrolytic water catalytic materials. Next, we discussed the heteroatom-doped catalyst materials of different transition metal-based compounds.

3.1. Heteroatom doped transition metal phosphide catalytic materials for water electrolysis

After a long period of research, the heteroatom doping technology has become a feasible strategy to improve the catalytic performance. Compared with pure TMP_S, the doped TMP_S exhibits better electrocatalytic HER activity [131–133]. For example, Wang et al., [125] in Fig. 3 successfully synthesized Mn-doped NiP_2 three-dimensional nanosheet electrocatalysts (Mn-NiP_2 NSs/CC) on carbon cloth, which exhibited good catalytic activity at wide pH and better stability than pure NiP_2. It can be seen from Fig. 4 that the ΔGH* of NiP_2 on the (0 0 1) surface is 0.24 eV, while the ΔGH* of Mn-NiP_2 is reduced to 0.18 eV after manganese doping, which is attributed to the change of adjacent nickel atoms from manganese atoms The acquisition of electrons leads to the weakening of the interaction between the surface and the hydrogen atoms, resulting in a decrease in the free energy of hydrogen adsorption [134,135]. This provides a powerful strategy for reducing the hydrogen adsorption energy and improving the catalytic activity [136].

There are many transition metal phosphide catalytic water electrolysis materials prepared by heteroatom doping technology. For example, Wen et al., [126] prepared a V-Ni_2P NSAs/CC nanosheet array-structured catalytic material for water electrolysis for hydrogen evolution by a simple two-step hydrothermal phosphating method to drive 10 mA cm^{-2} in 1 M KOH alkaline electrolyte. The initial overpotential required for the current density is a lower 85 mV, better than that of the single nickel phosphide catalyst. The potential mechanism for the performance improvement is that the synergistic effect between vanadium and nickel atoms produces a large number of lattice defects and distortions on the surface of the V-Ni_2P NSAs/CC catalytic material, which changes its electronic structure and increases the active surface area, thereby improving the electrolysis of water. Meanwhile, Wen et al., [122] reported a facile method to fabricate self-supporting nanoporous Cu-doped CoP nanorod arrays on carbon cloth by hydrothermal and low-temperature phosphating processes. The interaction between Cu-CoP NRAs/CC atoms induces many lattice distortions and defects, which further provides many efficient reaction sites and active centers on the nanorods, showing good catalytic performance [137]. This shows that the introduction of other atoms can destroy the original lattice structure of transition metal phosphides, form a large number of lattice distortions, provide more active sites, and further improve the hydrogen evolution performance. Combined with a suitable electrode process, heteroatom-doped phosphides are promising for industrial hydrogen production to meet our practical application needs. Table 1 summarizes the HER parameters of heteroatom-doped electrocatalysts in acidic and alkaline electrolytes [138].

3.2. Heteroatom-doped transition metal sulfide catalytic materials for water electrolysis

To date, noble metal platinum-based catalysts for water electrolysis have been regarded as the most efficient HER catalysts due to their closest-to-zero Gibbs free energy for hydrogen adsorption and desorption [139]. However, the scarcity of resources and high price limit its practical application in large-scale hydrogen production [140]. Therefore, it is necessary to find suitable electrocatalysts to replace. Liu et al., [141] prepared Au-decorated Ni_3S_2 nanosheet catalytic materials with good HER and OER performance under alkaline conditions. The strong electronic coupling at its interface can tune the electronic structure of Ni_3S_2 to optimize the free energy of adsorbed intermediates for efficient overall water splitting, thus confirming that transition metal sulfides are noble metal-free and well-performing catalysts for water electrolysis. Ni_3S_2 disulfide nanostructures have attracted widespread attention due to their low cost, high activity, and simple preparation process, and are considered as potential HER electrocatalysts.

For example, Qu et al., [142] used a simple one-step hydrothermal method to directly grow vanadium-doped Ni_3S_2 nanowire arrays on nickel foam. The doped catalytic material exhibits excellent electrocatalytic performance for the hydrogen evolution reaction, outperforming pure Ni_3S_2 and other Ni_3S_2-based compounds. The initial potential of V-Ni_3S_2 nanowires is as low as 39 mV, which is comparable to platinum-based noble metal catalysts. First-principles calculations

Table 1
Heteroatom-doped hydrogen evolution reaction catalyst.

Catalyst	Electrolyte	Morphology	η_{10} (mV)	Tafel slope (mV dec^{-1})	References
Cu-CoP	0.5 M H_2SO_4	Nanosphere	44	86	[122]
	1 M KOH		81	102	
Fe-CoP	1 M KOH	Nanowires	78	75	[123]
Mn-NiP_2	0.5 M H_2SO_4	Nanosheets	69	45	[124]
	1 M KOH		97	61	
W-CoP	0.5 M H_2SO_4	Nanoneedles	32	57	[125]
	1 M KOH		77	65	
V-Ni_2P	1 M KOH	Nanosheets	85	95	[126]
Co-VS_2	1 M KOH	Nanorods	164.5	52.2	[127]
Fe-CoP	1 M KOH	Nanoparticles	151	53.9	[128]
C-Co_2P	1 M KOH	Nanoporous	30	36.9	[129]
Pt-FeNi@C, P	0.5 M H_2SO_4	Nanoparticles	53	35.9	[130]
	1 M KOH		52	34.1	

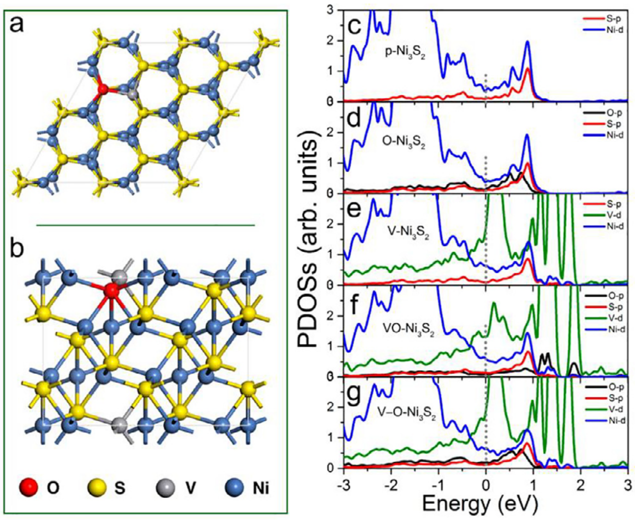

Fig. 5. Calculation of the relaxed bulk structure and partial density of states of the V-Ni_3S_2 superlattice formed by the substitution of a V-O bond by a Ni − S bond [142].

(Fig. 5) reveal the intrinsic mechanism of V atom doping to enhance the performance, and vanadium doping greatly enhances the free carrier density near the Fermi level and increases the electrical conductivity, thereby greatly enhancing the catalytic activity.

Transition metal sulfides have a graphene-like sheet-like layered structure. Many studies have shown that the hydrogen evolution performance of transition metal sulfide nanomaterials depends on the number of exposed S atoms in the edge structure [143,144]. The introduction of defects and doping can effectively improve the intrinsic activity of transition metal sulfides by creating more boundary active sites. With the in-depth research of scholars from all over the world, there are also some problems in the preparation of electrocatalysts by heteroatom doping of transition metal sulphides [145]. At present, the stability of electrocatalytic electrodes prepared is relatively poor, cannot be used on a large scale, and the electrocatalytic mechanism of transition metal sulfides is relatively shallow. Therefore, how to change the edge structure, doping technology and other technologies to design a controllable morphological structure to give high catalytic activity and good stability is a problem that still needs to be solved [146–148].

4. Application of heteroatom doping in catalytic materials for oxygen evolution reaction and overall water splitting

For OER, the reaction kinetics mainly depend on the ease of adsorption and desorption of intermediates. Therefore, adjusting the chemical composition of catalysts and changing the structure of nanocatalysts by introducing other atoms is an effective way to improve their activity and stability [149]. As shown in Fig. 6, Lu et al., [150] prepared tungsten-doped nickel–cobalt phosphide, a nano catalytic material with multiple active sites. Studies have shown that it has multiple catalytic sites for water splitting and hydrogen production. Benefiting from the moderate binding ability between tungsten and hydrogen atoms, the tungsten sites can efficiently convert the adsorbed hydrogen ions into H_2, and the synergistic effect between the nickel–cobalt sites and the tungsten sites can accelerate the HER

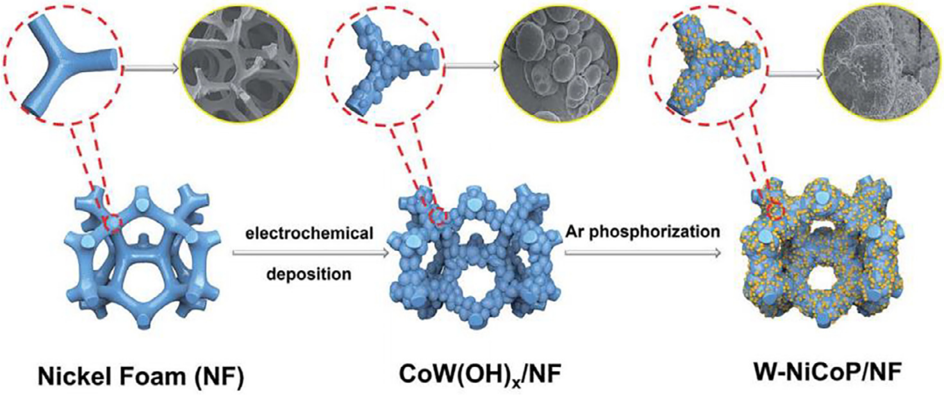

Fig. 6. Schematic diagram of synthesis of W-NiCoP/NF.

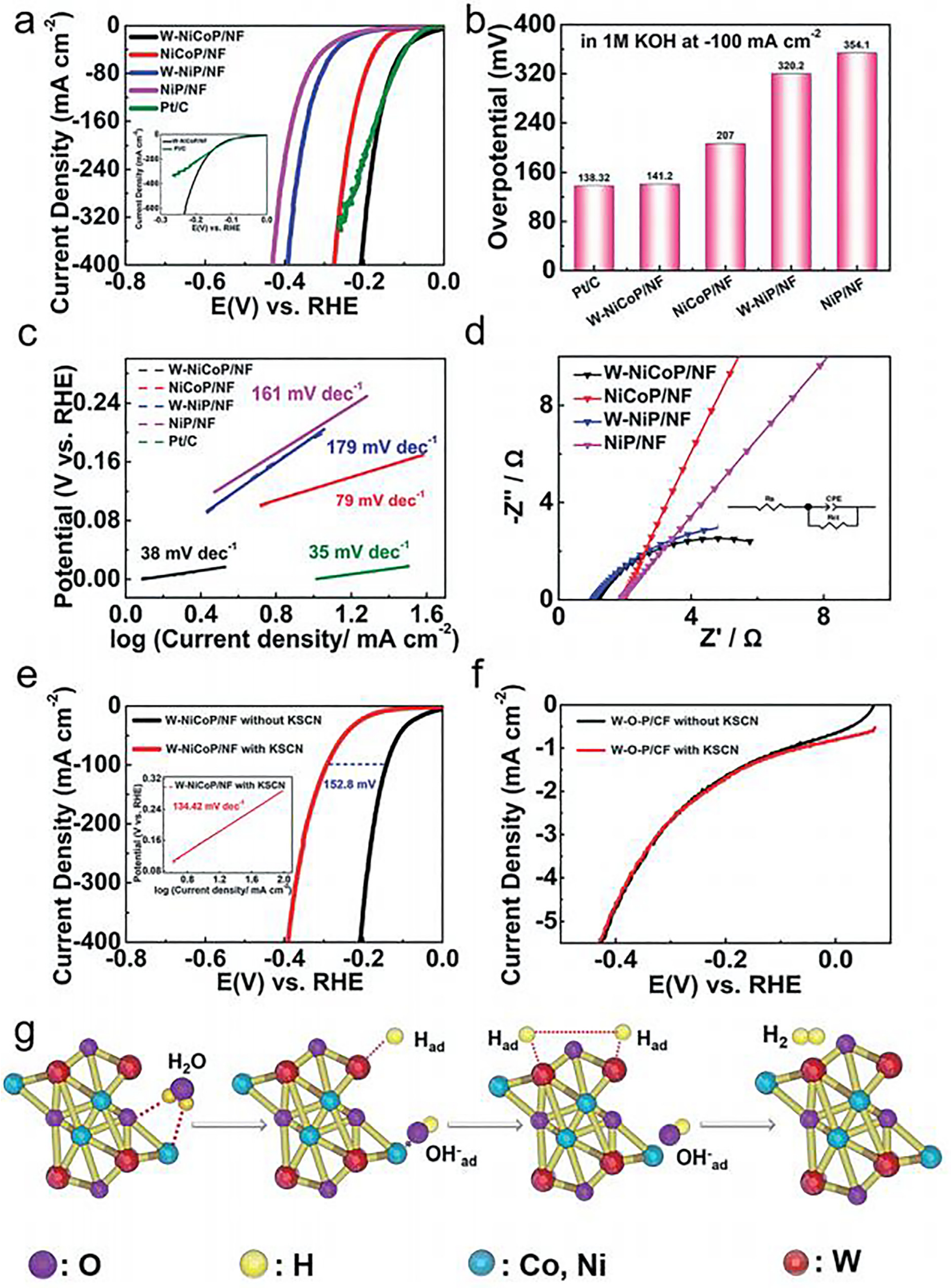

Fig. 7. Electrochemical test and HER process mechanism of W - NiCoP/NF [150].

reaction efficiency, and it is more efficient than platinum. Noble metal-based catalysts come close. W-NiCoP/NF also shows excellent oxygen evolution reaction performance and thus excels in overall water splitting. Cobalt-nickel phosphide successfully introduced W atoms, regulated the surface structure of nanomaterials, exhibited good electrocatalytic water splitting ability, provided a theoretical basis

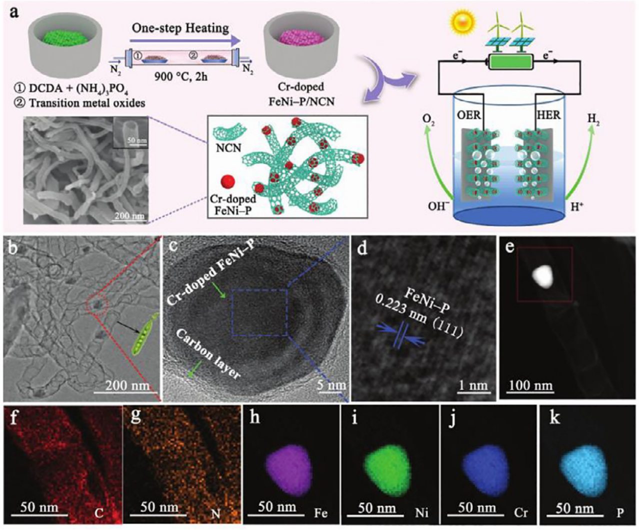

Fig. 8. Schematic diagram of preparation and crystal structure characterization of Cr-doped FeNi–P/NCN [153].

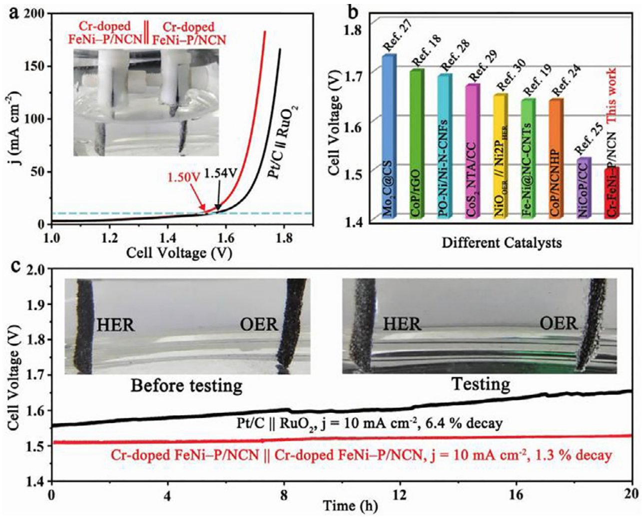

Fig. 9. Performance test of total water splitting and comparison with noble metal-based catalysts [153].

for the synthesis of electrocatalysts doped with heteroatom, and pointed out the direction for satisfying industrial hydrogen production [151,152].

In a recent report, regarding the potential performance-enhancing mechanism, it has been demonstrated that W-Ox can act as a support for hydrogen adsorption. Through density functional theory calculations in acidic media, it is proved that tungsten has free energy for hydrogen adsorption (ΔGH*) that is very close to that of noble metal platinum in the HER process. The process of water decomposition under the action of W-NiCoP/NF is summarized in Fig. 7. When water molecules are adsorbed on the surface of tungsten-nickel-phosphorus, it is stabilized and dissociated by the nickel–cobalt sites with vital hydride binding energy, and the tungsten sites can effectively accelerate the conversion of H_{ad} to H_2.

In addition to single HER catalysts, the design and synthesis of OER catalysts and bifunctional overall water splitting (OWS) catalysts also have great potential in developing of water electrolysis for hydrogen production [154,155]. As shown in Fig. 8, Wu et al., [153] developed a newly designed chromium-doped iron-nickel-phosphorus nanoparticles encapsulated in nitrogen-doped carbon nanotubes (Cr-doped carbon nanotubes) with unprecedented electrocatalytic activity through simple one-step heat treatment. In 1 M KOH solution, the synthesized chromium-doped FeNi-P/NCN showed excellent oxygen evolution and hydrogen evolution [136]. When using chromium-doped FeNi-P/NCN as a bifunctional catalyst for bulk water splitting, only 1.50 V is required to drive a current density of 10 mA cm^{-2}, which is superior to the typical benchmark total water-splitting reaction catalysts platinum/carbon and Ruthenium oxide compound. Density functional theory calculations confirmed that chromium doping into the FeNi matrix could effectively change the relative Gibbs adsorption energy and reduce the theoretical overpotential. Furthermore, the synergistic effect between Cr-doped FeNiP nanoparticles and nanocarbons effectively promotes charge transfer and enhances the electrocatalytic activity of the hybrid catalysts [153].

Durability testing and practical application potential for HER, OER and total water splitting. In Fig. 9, Wu et al., [153] further evaluated the overall water splitting activity in 1 M KOH solution using a Cr-doped FeNi-P/NCN catalyst as a two-electrode configuration of cathode and anode, and with platinum Industrial electrodes using carbon as the cathode and ruthenium oxide as the anode catalyst were compared [156]. It can be seen from Fig. 9c that the Cr-doped FeNi–P/NCN catalyst exhibits excellent overall water splitting performance, achieving a stable current density of 10 mA cm-2 with only a low cell voltage of 1.50 V, which is superior to commercial catalysts (1.54 V @ 10 mA cm-2 for platinum/carbon || ruthenium oxide) and most previously reported non-noble metal bifunctional electrocatalysts. Meanwhile, the durability of the actual water electrolysis reactor was tested at a current density of 10 mA cm-2, and the water splitting process could work stably for at least 20 h, indicating that the Cr-doped FeNi–P/NCN catalyst is suitable for Good stability of hydrolysis reaction [157].

The key step of electrocatalytic water cracking is to develop high activity and low cost electrocatalysts to accelerate HER and OER [162,163]. The nanocatalyst prepared by heteroatom doping has high activity and good stability in alkaline solution, which can maximize the electrocatalytic hydrogen production while minimizing the energy consumption. With the continuous in-depth research of researchers in various countries and fields, a new type of bifunctional OER/HER electrocatalyst will be realized in the near future and show excellent performance to meet our practical application needs [164,165]. Table 2 summarizes the electrochemical performance parameters of heteroatom-doped bifunctional electrocatalysts in overall water splitting.

Table 2
Heteroatom-doped overall water splitting catalyst.

Catalyst	Electrolyte	Morphology	η_{10} (mV)		Tafel slope(mV dec^{-1})		References
			HER	OER	HER	OER	
Ni/NiP	1 M KOH	Nanoflocs	130	270	58.5	73.2	[158]
Fe/ Ni_5P_4	1 M KOH	Nanosheets	94.5	217.3	91	45.7	[159]
P/Ni_3S_2-NiS	1 M KOH	Nanorods	141	178	75	37	[116]
Cr/Co_2P	1 M KOH	Nanowires	37	253	65	50	[160]
Mo/CoP	1 M KOH	Nanowires	64	262	57.3	49.4	[161]
V/CoP	1 M KOH	Nanorods	62	222	55.2	166.2	[21]
Au/ Ni_3S_2	1 M KOH	Nanosheets	97	230	72	51	[141]

5. Conclusion and outlook

Sustainable energy-driven electrochemical water splitting plays an integral role in realizing the hydrogen economy, and the development of cost-effective catalysts with high activity and long-term durability is critical for achieving economic hydrogen production. In this review, we summarize the research progress of heteroatom-doped transition metal-based catalysts for water electrolysis, focusing on material design and synthesis strategies, electrochemical performance, and related mechanisms for activity enhancement. According to the latest research, heteroatoms mainly include molybdenum, vanadium, tungsten, copper, manganese, vanadium, nitrogen, oxygen, etc. In general, the excellent catalytic performance of heteroatom-doped transition metal-based water electrolysis catalysts can be attributed to: (1) Heteroatom doping can change the growth mode and crystal structure of catalytic materials, generate a large number of lattice defects and lattice distortions, and increase HER adsorption sites and active centers. (2) Heteroatom doping can increase the density of reaction sites in catalytic materials and adjust the adsorption/desorption capacity of reaction intermediates. When combined with highly reactive materials, the electron transport ability is enhanced, and the catalytic material is fully contacted with the electrolyte to accelerate the release of gas. (3) The doping of heteroatoms improves the electronic environment of the catalytic material, which is beneficial to accelerate the adsorption and desorption of hydrogen ions, resulting in a decrease in the free energy of hydrogen adsorption $\Delta G\ H^*$, thereby improving the efficiency of electrolytic water splitting.

The study of heteroatom-doped water electrolysis catalysts is a very attractive research field, and great research progress has also been achieved, but its catalytic performance is insufficient for practical applications under strong acid or strong base conditions. Regarding its practical application, the scaled-up synthesis of catalysts is a great obstacle, and although many heteroatom-doped transition metal-based water electrolysis catalysts exhibit excellent activities and meet the performance requirements for practical applications, most synthesis processes are still limited to experiments At the chamber level, developing cost-effective and scalable synthesis strategies is one of the biggest challenges.

1. Understand the in-depth reaction mechanism of HER and OER catalytic water electrolysis reactions. The identification of a rational reaction mechanism will provide direction for the development of efficient electrocatalysts. In HER, the bonding between catalyst surface atoms and hydrogen atoms is the key to enhance the catalytic activity. However, there is currently a lack of theories on revealing the catalytic mechanism and microstructure. It is necessary to establish reliable multi-scale theoretical calculation models and in-situ characterization methods, combining theory with practice, to understand the dynamic process of water splitting, design reasonable electrocatalysts, and improve the overall efficiency of water splitting.
2. Using multiple technologies such as heterostructure and doping to design nanomaterials with controllable morphology, giving high catalytic activity and stability. In general, HER in acidic electrolytes and OER in alkaline conditions may suffer from low catalytic activity, poor stability or low corrosion resistance when used for overall water splitting. In order to further enhance the activity performance and high stability of electrocatalysts, various strategies, such as polyatomic doping, heterostructures, and strain engineering, can be employed to modulate the microstructure and effectively enhance the catalytic activity.

In conclusion, heteroatom doping technology is a promising and challenging strategy to design and synthesize efficient electrochemical water-splitting catalysts, and the field of electrochemical hydrogen production powered by renewable energy also has a bright future.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Y. Yan, B.Y. Xia, B. Zhao, X. Wang, A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting, J. Mater. Chem. 4 (2016) 17587–17603.

[2] J.L. Ramos, B. Pakuts, P. Godoy, A. García-Franco, E. Duque, Addressing the energy crisis: using microbes to make biofuels, Microb. Biotechnol. 15 (2022) 1026–1030.

[3] W. Dong, H. Xiao, Y. Jia, L. Chen, H. Geng, S.U.H. Bakhtiar, Q. Fu, Y. Guo, Engineering the defects and microstructures in ferroelectrics for enhanced/novel properties: an emerging way to cope with energy crisis and environmental pollution, Advanced Science, n/a (2022) 2105368.

[4] C. Yuan, S. Liu, N. Xie, The impact on chinese economic growth and energy consumption of the Global Financial Crisis: An input-output analysis, ENERGY 35 (2010) 1805–1812.

[5] G. Zhao, K. Rui, S.X. Dou, W. Sun, Heterostructures for electrochemical hydrogen evolution reaction: A review, Adv. Funct. Mater. 28 (2018) 1803291.

[6] R. Poudyal, P. Loskot, R. Nepal, R. Parajuli, S.K. Khadka, Mitigating the current energy crisis in Nepal with renewable energy sources, Renew. Sustain. Energy Rev. 116 (2019) 109388.

[7] F. Dawood, M. Anda, G. Shafiullah, Hydrogen production for energy: An overview, Int. J. Hydrogen Energy 45 (2020) 3847–3869.

[8] G.A. Naikoo, F. Arshad, I.U. Hassan, M.A. Tabook, M.Z. Pedram, M. Mustaqeem, H. Tabassum, W. Ahmed, M. Rezakazemi, Thermocatalytic hydrogen production through decomposition of methane-A review, Front. Chem. 9 (2021).

[9] Z. Abdin, A. Zafaranloo, A. Rafiee, K. Khalilpour, Hydrogen as an energy vector, Renew. Sustain. Energy Rev. 120 (2020).

[10] S.G. Simoes, J. Catarino, A. Picado, T.F. Lopes, S. di Berardino, F. Amorim, F. Gírio, C.M. Rangel, T. Ponce de Leão, Water availability and water usage solutions for electrolysis in hydrogen production, J. Cleaner Prod. 315 (2021) 128124.

[11] R. Koutavarapu, C. Venkata Reddy, B. Babu, K.R. Reddy, M. Cho, J. Shim, Carbon cloth/transition metals-based hybrids with controllable architectures for electrocatalytic hydrogen evolution - A review, Int. J. Hydrogen Energy 45 (2020) 7716–7740.

[12] F.G. de Medeiros, F.W. Lopes, B. Rego de Vasconcelos, Prospects and technical challenges in hydrogen production through dry reforming of methane, Catalysts 12 (2022).

[13] D.L. Stoji , M. Mar eta, S.P. Sovilj, e. Miljanj Hydrogen generation from water electrolysi“ possibilities of energy saving, Journal of Power Sources, 118 (2003) 315-319.

[14] J.E. Lee, I. Shafiq, M. Hussain, S.S. Lam, G.H. Rhee, Y.-K. Park, A review on integrated thermochemical hydrogen production from water, Int. J. Hydrogen Energy 47 (2022) 4346–4356.

[15] J. Andersson, S. Grönkvist, Large-scale storage of hydrogen, Int. J. Hydrogen Energy 44 (2019) 11901–11919.

[16] O. Nematollahi, P. Alamdari, M. Jahangiri, A. Sedaghat, A.A. Alemrajabi, A techno-economical assessment of solar/wind resources and hydrogen production: A case study with GIS maps, Energy 175 (2019) 914–930.

[17] Y. Zheng, Y. Jiao, Y. Zhu, L.H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S.Z. Qiao, Hydrogen evolution by a metal-free electrocatalyst, Nat. Commun. 5 (2014) 3783.

[18] J. Bellosta von Colbe, J.-R. Ares, J. Barale, M. Baricco, C. Buckley, G. Capurso, N. Gallandat, D.M. Grant, M.N. Guzik, I. Jacob, E.H. Jensen, T. Jensen, J. Jepsen, T. Klassen, M.V. Lototskyy, K. Manickam, A. Montone, J. Puszkiel, S. Sartori, D.A. Sheppard, A. Stuart, G. Walker, C.J. Webb, H. Yang, V. Yartys, A. Züttel, M. Dornheim, Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives, Int. J. Hydrogen Energy 44 (2019) 7780–7808.

[19] Y. Shi, Y. Xu, S. Zhuo, J. Zhang, B. Zhang, Ni2P nanosheets/Ni foam composite electrode for long-lived and pH-tolerable electrochemical hydrogen generation, ACS Appl. Mater. Interfaces 7 (2015) 2376–2384.

[20] B. You, Y. Sun, Innovative strategies for electrocatalytic water splitting, Acc. Chem. Res. 51 (2018) 1571–1580.

[21] X. Du, Y. Fang, J. Guan, S. Li, L. Wang, M. Zhang, Vanadium doped cobalt phosphide nanorods array as a bifunctional electrode catalyst for efficient and stable overall water splitting, Int. J. Hydrogen Energy 46 (2021) 599–608.

[22] J. Turner, G. Sverdrup, M.K. Mann, P.-C. Maness, B. Kroposki, M. Ghirardi, R.J. Evans, D. Blake, Renewable hydrogen production, Int. J. Energy Res. 32 (2008) 379–407.

[23] T.B. Ferriday, P.H. Middleton, M.L. Kolhe, Review of the hydrogen evolution reaction—A basic approach, Energies 14 (2021).

[24] Y. Zhang, Z.X. Hui, H.Y. Zhou, S.F. Zai, Z. Wen, J. Chen Li, C.C. Yang, Q. Jiang, Ga doping enables superior alkaline hydrogen evolution reaction performances of CoP, Chem. Eng. J. 429 (2022) 132012.

[25] I. Staffell, D. Scamman, A. Abad, P. Balcombe, P. Dodds, P. Ekins, N. Shah, K. Ward, The role of hydrogen and fuel cells in the global energy system, Energy Environ. Sci. 12 (2018).

[26] W. Chen, B. Yang, Q. Yu, L. Mao, Z. Fan, Q. Wang, W. Shangguan, Effect of Rh oxide as a cocatalyst over Bi0.5Y0.5VO4 on photocatalytic overall water splitting, Appl. Surf. Sci. 355 (2015) 1069–1074.

[27] S. Esiner, R.E.M. Willems, A. Furlan, W. Li, M.M. Wienk, R.A.J. Janssen, Photoelectrochemical water splitting in an organic artificial leaf, J. Mater. Chem. A 3 (2015) 23936–23945.

[28] J. Song, C. Wei, Z.-F. Huang, C. Liu, L. Zeng, X. Wang, Z.J. Xu, A review on fundamentals for designing oxygen evolution electrocatalysts, Chem. Soc. Rev. 49 (2020) 2196–2214.

[29] X. Xu, W. Zhong, S. Yan, L. Zhang, G. Liu, Y. Du, Advanced catalysts for hydrogen evolution reaction based on MoS2/NiCo2S4 heterostructures in Alkaline Media, Int. J. Hydrogen Energy 45 (2020) 1759–1768.

[30] Y. Yang, K. Zhang, H. Lin, X. Li, H.C. Chan, L. Yang, Q. Gao, MoS2–Ni3S2 heteronanorods as efficient and stable bifunctional electrocatalysts for overall water splitting, ACS Catal. 7 (2017) 2357–2366.

[31] G. Wei, Y. Yang, Y. Li, L. Zhang, Z. Li, R. Mo, Improving the catalytic activity of bentonite-based bismuth ferrites composite via mechanical activation for photo-Fenton process, Materials Chemistry and Physics 260 (2021).

[32] H. Yang, L. Dai, D. Xu, J. Fang, S. Zou, Electrooxidation of methanol and formic acid on PtCu nanoparticles, Electrochim. Acta 55 (2010) 8000–8004.

[33] S.M. El-Refaei, P.A. Russo, N. Pinna, Recent advances in multimetal and doped transition-metal phosphides for the hydrogen evolution reaction at different ph values, ACS Appl. Mater. Interfaces 13 (2021) 22077–22097.

[34] X. Yang, A.-Y. Lu, Y. Zhu, M.N. Hedhili, S. Min, K.-W. Huang, Y. Han, L.-J. Li, CoP nanosheet assembly grown on carbon cloth: A highly efficient electrocatalyst for hydrogen generation, Nano Energy 15 (2015) 634–641.

[35] J. Song, J. Xiang, C. Mu, B. Wang, F. Wen, C. Su, C. Wang, Z. Liu, Facile synthesis and excellent electrochemical performance of CoP nanowire on carbon cloth as bifunctional electrode for hydrogen evolution reaction and supercapacitor, Sci. China Mater. 60 (2017) 1179–1186.

[36] O.S. Vereshchagin, D.V. Pankin, M.B. Smirnov, N.S. Vlasenko, V.V. Shilovskikh, S. N. Britvin, Raman spectroscopy: A promising tool for the characterization of transition metal phosphides, J. Alloy. Compd. 853 (2021) 156468.

[37] C.-C. Weng, J.-T. Ren, Z.-Y. Yuan, Transition metal phosphide-based materials for efficient electrochemical hydrogen evolution: A critical review, ChemSusChem 13 (2020) 3357–3375.

[38] X. Zhou, X. Yang, H. Li, M.N. Hedhili, K.W. Huang, L.J. Li, W. Zhang, Symmetric synergy of hybrid CoS2 WS2 electrocatalysts for the hydrogen evolution reaction, J. Mater. Chem. 5 (2017) 15552–15558.

[39] X. Shang, J.-Q. Chi, S.-S. Lu, B. Dong, X. Li, Y.-R. Liu, K.-L. Yan, W.-K. Gao, Y.-M. Chai, C.-G. Liu, Novel CoxSy/WS2 nanosheets supported on carbon cloth as efficient electrocatalyst for hydrogen evolution reaction, Int. J. Hydrogen Energy 42 (2017) 4165–4173.

[40] T. Takata, M. Jung, T. Matsunaga, T. Ida, M. Morita, H. Motohashi, X. Shen, C.G. Kevil, J.M. Fukuto, T. Akaike, Methods in sulfide and persulfide research, Nitric Oxide 116 (2021) 47–64.

[41] C. Wan, B.M. Leonard, Iron-doped molybdenum carbide catalyst with high activity and stability for the hydrogen evolution reaction, Chem. Mater. 27 (2015) 4281–4288.

[42] L. Bolin, Bimetallic carbide of Co_3W_3C enhanced non-noble-metal catalysts with high activity and stability for acidic oxygen reduction reaction, RSC advances, v. 8 (2018) pp. 12292-12299-12018 v.12298 no.12222.

[43] J. Pötschke, M. Dahal, M. Herrmann, A. Vornberger, B. Matthey, A. Michaelis, Preparation of high-entropy carbides by different sintering techniques, J. Mater. Sci. 56 (2021) 11237–11247.

[44] Z. Chen, Y. Ha, Y. Liu, H. Wang, H. Yang, H. Xu, Y. Li, R. Wu, In Situ formation of cobalt nitrides/graphitic carbon composites as efficient bifunctional electrocatalysts for overall water splitting, ACS Appl. Mater. Interfaces 10 (2018) 7134–7144.

[45] S. Yu, X. Wang, H. Pang, R. Zhang, W. Song, D. Fu, T. Hayat, X. Wang, Boron nitride-based materials for the removal of pollutants from aqueous solutions: A review, Chem. Eng. J. 333 (2018) 343–360.

[46] A. Zakutayev, S.R. Bauers, S. Lany, Experimental synthesis of theoretically predicted multivalent ternary nitride materials, Chem. Mater. 34 (2022) 1418–1438.

[47] T. Niyitanga, H.K. Jeong, Thermally reduced graphite oxide/carbon nanotubes supported molybdenum disulfide as catalysts for hydrogen evolution reaction, Int. J. Hydrogen Energy 44 (2019) 977–987.

[48] A. Ganguly, O. Anjaneyulu, K. Ojha, A.K. Ganguli, Oxide-based nanostructures for photocatalytic and electrocatalytic applications, CrystEngComm 17 (2015) 8978–9001.

[49] H.R. Devi, R. Chikkegowda, D. Rangappa, A.K. Yadav, Z. Chen, K.K. Nanda, Trimetallic oxide-hydroxide porous nanosheets for efficient water oxidation, Chem. Eng. J. 435 (2022) 135019.

[50] H. Liang, F. Meng, M. Cabán-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang, S. Jin, Hydrothermal continuous flow synthesis and exfoliation of NiCo layered double hydroxide nanosheets for enhanced oxygen evolution catalysis, Nano Lett. 15 (2015) 1421–1427.

[51] M.H. Wang, Z.X. Lou, X. Wu, Y. Liu, J.Y. Zhao, K.Z. Sun, W.X. Li, J. Chen, H.Y. Yuan, M. Zhu, S. Dai, P.F. Liu, H.G. Yang, Operando High-Valence Cr-Modified NiFe Hydroxides for Water Oxidation, Small, n/a (2022) 2200303.

[52] Z. He, J. Zhang, Z. Gong, H. Lei, D. Zhou, N. Zhang, W. Mai, S. Zhao, Y. Chen, Activating lattice oxygen in NiFe-based (oxy)hydroxide for water electrolysis, Nat. Commun. 13 (2022) 2191.

[53] H.Y. Yuan, P.F. Liu, H.G. Yang, Peculiar double-layered transition metal hydroxide nanosheets, Matter 5 (2022) 1063–1065.

[54] Y. Li, R. Li, D. Wang, H. Xu, F. Meng, D. Dong, J. Jiang, J. Zhang, M. An, P. Yang, A review: Target-oriented transition metal phosphide design and synthesis for water splitting, Int. J. Hydrogen Energy 46 (2021) 5131–5149.

[55] W. He, R. Zhang, J. Zhang, F. Wang, Y. Li, J. Zhao, C. Chen, H. Liu, H.L. Xin, Promoting the water dissociation of nickel sulfide electrocatalyst through introducing cationic vacancies for accelerated hydrogen evolution kinetics in alkaline media, J. Catal. 410 (2022) 112–120.

[56] J. Duan, S. Chen, M. Jaroniec, S. Qiao, Heteroatom-doped graphene-based materials for energy-relevant electrocatalytic processes, ACS Catal. 5 (2015) 5207–5234.

[57] R. Kumar, S. Sahoo, E. Joanni, R.K. Singh, K. Maegawa, W.K. Tan, G. Kawamura, K.K. Kar, A. Matsuda, Heteroatom doped graphene engineering for energy storage and conversion, Mater. Today 39 (2020) 47–65.

[58] P. Xu, D. Wu, L. Wan, P. Hu, R. Liu, Heteroatom doped mesoporous carbon/graphene nanosheets as highly efficient electrocatalysts for oxygen reduction, Journal of Colloid and Interface Science 421 (2014) 160–164.

[59] C. Guan, W. Xiao, H. Wu, X. Liu, W. Zang, H. Zhang, J. Ding, Y.P. Feng, S.J. Pennycook, J. Wang, Hollow Mo-doped CoP nanoarrays for efficient overall water splitting, Nano Energy 48 (2018) 73–80.

[60] M. Kuang, G. Zheng, Nanostructured bifunctional redox electrocatalysts, Small 12 (2016) 5656–5675.

[61] N. Ullah, R. Ullah, S. Khan, Y. Xu, Boron nitride-based electrocatalysts for HER OER, and ORR: A mini-review, Frontiers of Materials Science 15 (2021) 543–552.

[62] Y. Wang, X. Li, M. Zhang, J. Zhang, Z. Chen, X. Zheng, Z. Tian, N.Q. Zhao, X. Han, K. Zaghib, Y. Wang, D. Yida, W. Hu, Highly active and durable single-atom tungsten-doped NiS0.5 Se0.5 nanosheet@NiS0.5 Se0.5 nanorod heterostructures for water splitting, advanced materials (deerfield beach, Fla.) 34 (2022) e2107053.

[63] W. Chen, C. Ge, J.T. Li, J.L. Beckham, Z. Yuan, K.M. Wyss, P.A. Advincula, L. Eddy, C. Kittrell, J. Chen, D.X. Luong, R.A. Carter, J.M. Tour, Heteroatom-doped flash graphene, ACS Nano (2022).

[64] Q. Zhang, D. Zhang, Y. Zhou, J. Qian, X. Wen, P. Jiang, L. Ma, C. Lu, F. Feng, X. Li, Preparation of heteroatom-doped carbon materials and applications in selective hydrogenation, ChemistrySelect 7 (2022) e202102581.

[65] P. Zhang, Z. Wang, P. Wang, X. Hui, D. Zhao, Z. Zhang, L. Yin, Heteroatom doping-induced defected Co3O4 electrode for high-performance lithium oxygen battery, ACS Applied Energy Materials 5 (2022) 3359–3368.

[66] D. Jang, J. Kim, D. Kim, W.-B. Han, S. Kang, Techno-economic analysis and Monte Carlo simulation of green hydrogen production technology through various water electrolysis technologies, Energy Convers. Manage. 258 (2022) 115499.

[67] Z. Angeles-Olvera, A. Crespo-Yapur, O. Rodríguez, J.L. Cholula-Díaz, L.M. Martínez, M. Videa, Nickel-based electrocatalysts for water electrolysis, Energies 15 (2022).

[68] M.S. Syali, D. Kumar, K. Mishra, D.K. Kanchan, Recent advances in electrolytes for room-temperature sodium-sulfur batteries: A review, Energy Storage Mater. 31 (2020) 352–372.

[69] Y.H. Li, K.S. Zhao, Dielectric analysis of nanofiltration membrane in electrolyte solutions: influences of electrolyte concentration and species on membrane permeation, J. Colloid Interface Sci. 276 (2004) 68–76.

[70] T.S. Bhat, P.S. Patil, R.B. Rakhi, Recent trends in electrolytes for supercapacitors, J. Storage Mater. 50 (2022) 104222.

[71] J.M. Buriak, C. Toro, K.-S. Choi, Chemistry of materials for water splitting reactions, Chem. Mater. 30 (2018) 7325–7327.

[72] S. Chu, E. Coccia, M. Barborini, L. Guidoni, Role of electron correlation along the water splitting reaction, J. Chem. Theory Comput. 12 (2016) 5803–5810.

[73] J. Guan, Y. Wang, Electrocatalysts for oxygen/hydrogen-involved reactions, Molecules 27 (2022).

[74] K. Liu, P. Cao, W. Chen, C.I. Ezeh, Z. Chen, Y. Luo, Q. Liu, H. Zhao, Z. Rui, S. Gao, Z. Yin, X. Sun, X. Yu, Electrocatalysis enabled transformation of earth-abundant water, nitrogen and carbon dioxide for a sustainable future, Materials, Advances 3 (2022) 1359–1400.

[75] H. Sun, Z. Yan, F. Liu, W. Xu, F. Cheng, J. Chen, Self-supported transition-metal-based electrocatalysts for hydrogen and oxygen evolution, advanced materials (deerfield beach, Fla.) 32 (2019) e1806326–e.

[76] H. Du, R.-M. Kong, X. Guo, F. Qu, J. Li, Recent progress in transition metal phosphides with enhanced electrocatalysis for hydrogen evolution, Nanoscale 10 (2018) 21617–21624.

[77] A. Chinnappan, C. Baskar, S. Baskar, G. Ratheesh, S. Ramakrishna, An overview of electrospun nanofibers and their application in energy storage, sensors and wearable/flexible electronics, J. Mater. Chem. C 5 (2017) 12657–12673.

[78] Y. Manoharan, S.E. Hosseini, B. Butler, H. Alzahrani, B. Foua, T. Ashuri, J. Krohn, Hydrogen fuel cell vehicles; current status and future prospect, Applied Sciences 9 (2019).
[79] L.-H. Qian, W.-W. Dong, H.-B. Li, X. Song, Y. Ding, Fe-doped NiCo2S4 catalyst derived from ZIF – 67 towards efficient hydrogen evolution reaction, Int. J. Hydrogen Energy 47 (2022) 8820–8828.
[80] J. Cheng, X. Yang, X. Yang, R. Xia, Y. Xu, W. Sun, J. Zhou, Hierarchical Ni3S2@2D Co MOF nanosheets as efficient hetero-electrocatalyst for hydrogen evolution reaction in alkaline solution, Fuel Process. Technol. 229 (2022) 107174.
[81] X. Li, X. Hao, A. Abudula, G. Guan, Nanostructured catalysts for electrochemical water splitting: current state and prospects, J. Mater. Chem. A 4 (2016) 11973–12000.
[82] H. Liu, X. Qian, Y. Niu, M. Chen, C. Xu, K.-Y. Wong, Hierarchical Ni-MoSex@CoSe2 core-shell nanosphere as highly active bifunctional catalyst for efficient dye-sensitized solar cell and alkaline hydrogen evolution, Chem. Eng. J. 383 (2020) 123129.
[83] S. Anantharaj, V. Aravindan, Developments and perspectives in 3d transition-metal-based electrocatalysts for neutral and near-neutral water electrolysis, Adv. Energy Mater. 10 (2020) 1902666.
[84] S. Marini, P. Salvi, P. Nelli, R. Pesenti, M. Villa, M. Berrettoni, G. Zangari, Y. Kiros, Advanced alkaline water electrolysis, Electrochim. Acta 82 (2012) 384–391.
[85] J. Greeley, J.K. Nørskov, L.A. Kibler, A.M. El-Aziz, D.M. Kolb, Hydrogen evolution over bimetallic systems: understanding the trends, ChemPhysChem 7 (2006) 1032–1035.
[86] M.D. Bhatt, J.Y. Lee, Advancement of platinum (Pt)-free (Non-Pt precious metals) and/or metal-free (non-precious-metals) electrocatalysts in energy applications: A review and perspectives, Energy Fuels 34 (2020) 6634–6695.
[87] A. Bruix, Y. Lykhach, I. Matolínová, A. Neitzel, T. Skála, N. Tsud, M. Vorokhta, V. Stetsovych, K. Ševčíková, J. Mysliveček, R. Fiala, M. Václavů, K.C. Prince, S. Bruyère, V. Potin, F. Illas, V. Matolín, J. Libuda, K.M. Neyman, Maximum noble-metal efficiency in catalytic materials: atomically dispersed surface platinum, Angew. Chem. Int. Ed. 53 (2014) 10525–10530.
[88] D. He, L. Zhong, S. Gan, J. Xie, W. Wang, Z. Liu, W. Guo, X. Yang, L. Niu, Hydrogen peroxide electrosynthesis via regulating the oxygen reduction reaction pathway on Pt noble metal with ion poisoning, Electrochim. Acta 371 (2021) 137721.
[89] Q. Liang, G. Brocks, A. Bieberle-Hütter, Oxygen evolution reaction (OER) mechanism under alkaline and acidic conditions, Journal of Physics: Energy 3 (2021) 026001.
[90] M.-I. Jamesh, M. Harb, Tuning the electronic structure of the earth-abundant electrocatalysts for oxygen evolution reaction (OER) to achieve efficient alkaline water splitting – A review, Journal of Energy, Chemistry 56 (2021) 299–342.
[91] A. Dutta, N. Pradhan, Developments of metal phosphides as efficient OER precatalysts, The Journal of Physical Chemistry Letters 8 (2017) 144–152.
[92] D. Böhm, M. Beetz, M. Schuster, K. Peters, A.G. Hufnagel, M. Döblinger, B. Böller, T. Bein, D. Fattakhova-Rohlfing, Efficient OER catalyst with low ir volume density obtained by homogeneous deposition of iridium oxide nanoparticles on macroporous antimony-doped tin oxide support, Adv. Funct. Mater. 30 (2020) 1906670.
[93] F. Zeng, C. Mebrahtu, L. Liao, A.K. Beine, R. Palkovits, Stability and deactivation of OER electrocatalysts: A review, Journal of Energy Chemistry 69 (2022) 301–329.
[94] K. Wang, Y. Wang, B. Yang, Z. Li, X. Qin, Q. Zhang, L. Lei, M. Qiu, G. Wu, Y. Hou, Highly active ruthenium site stabilized by modulating electron-feeding for sustainable acidic oxygen-evolution electrocatalysis, Energy Environ. Sci. (2022).
[95] Y. Yang, W.-J. Wang, Y.-B. Yang, P.-F. Guo, B. Zhu, K. Wang, W.-T. Wang, Z.-H. He, Z.-T. Liu, Ru-doped NiFe layered double hydroxide as a highly active electrocatalyst for oxygen evolution reaction, J. Electrochem. Soc. 169 (2022) 024503.
[96] X. Xie, L. Du, L. Yan, S. Park, Y. Qiu, J. Sokolowski, W. Wang, Y. Shao, Oxygen Evolution Reaction in Alkaline Environment: Material Challenges and Solutions, Advanced Functional Materials, n/a (2022) 2110036.
[97] J.F. Callejas, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Synthesis, characterization, and properties of metal phosphide catalysts for the hydrogen-evolution reaction, Chem. Mater. 28 (2016) 6017–6044.
[98] R. Bernasconi, M.I. Khalil, D.S. Cakmakci, Y. Bektas, L. Nobili, L. Magagnin, C. Lenardi, Electrocatalytic layers for hydrogen evolution reaction based on nickel phosphides: cost-effective fabrication and XPS characterization, J. Mater. Sci. 57 (2022) 9370–9388.
[99] J. Zhao, J. Wang, Z. Chen, J. Ju, X. Han, Y. Deng, Metal chalcogenides: An emerging material for electrocatalysis, APL Mater. 9 (2021) 050902.
[100] P.M. Bodhankar, P.B. Sarawade, P. Kumar, A. Vinu, A.P. Kulkarni, C.D. Lokhande, D.S. Dhawale, Nanostructured Metal Phosphide Based Catalysts for Electrochemical Water Splitting: A Review, Small, n/a (2022) 2107572.
[101] L. Yu, Z. Ren, Systematic study of the influence of iR compensation on water electrolysis, Materials Today Physics 14 (2020) 100253.
[102] Y. Shi, B. Zhang, Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction, Chem. Soc. Rev. 45 (2016) 1529–1541.
[103] M.R. Gennero de Chialvo, A.C. Chialvo, The Tafel-Heyrovsky route in the kinetic mechanism of the hydrogen evolution reaction, Electrochem. Commun. 1 (1999) 379–382.
[104] A. Kahyarian, A. Schumacher, S. Nesic, Mechanistic Investigation of Hydrogen Evolution Reaction from Multiple Proton Donors: The Case of Mildly Acidic Solutions Containing Weak Acids, Journal of The Electrochemical Society, 166 (2019) H320-H330.
[105] Y. Liu, J. Li, W. Huang, Y. Zhang, M. Wang, X. Gao, X. Wang, M. Jin, Z. Hou, G. Zhou, Z. Zhang, J. Liu, Surface-induced 2D/1D heterostructured growth of ReS2/CoS2 for high-performance electrocatalysts, ACS Appl. Mater. Interfaces 12 (2020) 33586–33594.
[106] N. Moradighadi, S. Nesic, B. Tribollet, Identifying the dominant electrochemical reaction in electrochemical impedance spectroscopy, Electrochim. Acta 400 (2021) 139460.
[107] R. Sharma, S. Gyergyek, S.M. Andersen, Critical thinking on baseline corrections for electrochemical surface area (ECSA) determination of Pt/C through H-adsorption/H-desorption regions of a cyclic voltammogram, Appl. Catal. B 311 (2022) 121351.
[108] J. He, L. Guan, Y. Zhou, P. Shao, Y. Yao, S. Lu, L. Kong, X. Liao, One-pot preparation of mesoporous KxPMo12O40 (x = 1, 2, 3, 4) materials for oxidative desulfurization: electrochemically-active surface area (ECSA) determines their activity, React. Chem. Eng. 5 (2020) 1776–1782.
[109] C. Hu, L. Zhang, J. Gong, Recent progress made in the mechanism comprehension and design of electrocatalysts for alkaline water splitting, Energy Environ. Sci. 12 (2019) 2620–2645.
[110] X. Hu, Y. Li, X. Wei, L. Wang, H. She, J. Huang, Q. Wang, Preparation of double-layered Co − Ci/NiFeOOH co-catalyst for highly meliorated PEC performance in water splitting, Advanced Powder Materials 1 (2022) 100024.
[111] X. Zheng, Y. Cao, X. Han, H. Liu, J. Wang, Z. Zhang, X. Wu, C. Zhong, W. Hu, Y. Deng, Pt embedded Ni3Se2@NiOOH core-shell dendrite-like nanoarrays on nickel as bifunctional electrocatalysts for overall water splitting, Sci. China Mater. 62 (2019) 1096–1104.
[112] J. Wang, X. Zheng, Y. Cao, L. Li, C. Zhong, Y. Deng, X. Han, W. Hu, Developing indium-based ternary spinel selenides for efficient solid flexible Zn-air batteries and water splitting, ACS Appl. Mater. Interfaces 12 (2020) 8115–8123.
[113] P. Li, H. Wang, W. Fan, M. Huang, J. Shi, Z. Shi, S. Liu, Salt assisted fabrication of lignin-derived Fe, N, P, S codoped porous carbon as trifunctional catalyst for Zn-air batteries and water-splitting devices, Chem. Eng. J. 421 (2021) 129704.
[114] T. Wang, X.-Z. Fu, S. Wang, Etching oxide overlayers of NiFe phosphide to facilitate surface reconstruction for oxygen evolution reaction, Green, Energy Environ. 7 (2022) 365–371.
[115] H.S. Jadhav, H.A. Bandal, S. Ramakrishna, H. Kim, Critical review, recent updates on zeolitic imidazolate framework-67 (ZIF-67) and its derivatives for electrochemical water splitting, Adv Mater 34 (2022) e2107072.
[116] B. Zhou, J. Li, X. Zhang, J. Guo, Engineering P-doped Ni3S2-NiS hybrid nanorod arrays for efficient overall water electrolysis, J. Alloy. Compd. 862 (2021) 158391.
[117] Z. Wang, H. Liu, R. Ge, X. Ren, J. Ren, D. Yang, L. Zhang, X. Sun, Phosphorus-doped Co3O4 nanowire array: A highly efficient bifunctional electrocatalyst for overall water splitting, ACS Catal. 8 (2018) 2236–2241.
[118] Y. Liu, X. Hua, C. Xiao, T. Zhou, P. Huang, Z. Guo, B. Pan, Y. Xie, Heterogeneous spin states in ultrathin nanosheets induce subtle lattice distortion to trigger efficient hydrogen evolution, J. Am. Chem. Soc. 138 (2016) 5087–5092.
[119] G. Zhao, X. Wang, S. Wang, K. Rui, Y. Chen, H. Yu, J. Ma, S.X. Dou, W. Sun, Heteroatom-doped MoSe2 nanosheets with enhanced hydrogen evolution kinetics for alkaline water splitting, Chemistry – An Asian Journal 14 (2019) 301–306.
[120] Q. Kang, M. Li, J. Shi, Q. Lu, F. Gao, A universal strategy for carbon-supported transition metal phosphides as high-performance bifunctional electrocatalysts towards efficient overall water splitting, ACS Appl. Mater. Interfaces 12 (2020) 19447–19456.
[121] H.-L. Guang, S.-L. Zhu, Y.-Q. Liang, S.-L. Wu, Z.-Y. Li, S.-Y. Luo, Z.-D. Cui, A. Inoue, Highly efficient nanoporous CoBP electrocatalyst for hydrogen evolution reaction, Rare Met. 40 (2021) 1031–1039.
[122] L. Wen, Y. Sun, C. Zhang, J. Yu, X. Li, X. Lyu, W. Cai, Y. Li, Cu-doped CoP Nanorod arrays: efficient and durable hydrogen evolution reaction electrocatalysts at all ph values, ACS Applied Energy Materials (2018).
[123] C. Tang, R. Zhang, W. Lu, L. He, X. Jiang, A.M. Asiri, X. Sun, Fe-Doped CoP nanoarray: A monolithic multifunctional catalyst for highly efficient hydrogen generation, Adv. Mater. 29 (2017) 1602441.
[124] X. Wang, H. Zhou, D. Zhang, M. Pi, J. Feng, S. Chen, Mn-doped NiP 2 nanosheets as an efficient electrocatalyst for enhanced hydrogen evolution reaction at all pH values, J. Power Sources 387 (2018) 1–8.
[125] Z. Ren, X. Ren, L. Zhang, C. Fu, X. Li, Y. Zhang, B. Gao, L. Yang, P.K. Chu, K. Huo, Tungsten-doped CoP Nanoneedle arrays grown on carbon cloth as efficient bifunctional electrocatalysts for overall water splitting, ChemElectroChem 6 (2019) 5229–5236.
[126] L. Wen, J. Yu, C. Xing, D. Liu, X. Lyu, W. Cai, X. Li, Flexible vanadium-doped Ni2P nanosheet arrays grown on carbon cloth for an efficient hydrogen evolution reaction, Nanoscale 11 (2019) 4198–4203.
[127] T. Feng, C. Ouyang, Z. Zhan, T. Lei, P. Yin, Cobalt doping VS2 on nickel foam as a high efficient electrocatalyst for hydrogen evolution reaction, Int. J. Hydrogen Energy 47 (2022) 10646–10653.
[128] X. Chen, B. Yu, Y. Dong, X. Zhu, W. Zhang, S. Ramakrishna, Z. Liu, Electrospun porous carbon nanofibers decorated with iron-doped cobalt phosphide nanoparticles for hydrogen evolution, J. Alloy. Compd. 918 (2022) 165733.
[129] W. Xu, G. Fan, S. Zhu, Y. Liang, Z. Cui, Z. Li, H. Jiang, S. Wu, F. Cheng, Electronic Structure Modulation of Nanoporous Cobalt Phosphide by Carbon Doping for Alkaline Hydrogen Evolution Reaction, Adv. Funct. Mater. 31 (2021) 2107333.
[130] Y. Wang, C. Wang, L. Jin, H. Shang, F. Ren, M. Yuan, Y. Du, Synergistically engineering ultralow Pt doped FeNi alloy/FeNi phosphide nanoparticles for advanced hydrogen evolution reaction, Colloids Surf., A 604 (2020) 125313.

[131] K. Chen, X. Huang, C. Wan, H. Liu, Efficient oxygen reduction catalysts formed of cobalt phosphide nanoparticle decorated heteroatom-doped mesoporous carbon nanotubes, Chem. Commun. 51 (2015) 7891–7894.

[132] D.K. Kim, S. Bong, X. Jin, K.-D. Seong, M. Hwang, N.D. Kim, N.-H. You, Y. Piao, Facile in Situ Synthesis of Multiple-Heteroatom-Doped Carbons Derived from Polyimide Precursors for Flexible All-Solid-State Supercapacitors, ACS Appl. Mater. Interfaces 11 (2019) 1996–2005.

[133] Y. Wang, Y. Shen, Y. Zhou, Z. Xue, Z. Xi, S. Zhu, Heteroatom-Doped Graphene for Efficient NO Decomposition by Metal-Free Catalysis, ACS Appl. Mater. Interfaces 10 (2018) 36202–36210.

[134] X. Du, J. Wang, Y. Fang, Y. Liu, Y. Wu, J. Guan, S. Li, L. Wang, S. Lei, M. Zhang, Okra-like hollow Cu0.15-CoP/Co3O4@CC nanotube arrays catalyst for overall water splitting, Int. J. Hydrogen Energy 47 (2022) 7168–7179.

[135] H. Jin, X. Liu, S. Chen, A. Vasileff, L. Li, Y. Jiao, L. Song, Y. Zheng, S.-Z. Qiao, Heteroatom-Doped Transition Metal Electrocatalysts for Hydrogen Evolution Reaction, ACS Energy Lett. 4 (2019) 805–810.

[136] V. Vij, S. Sultan, A.M. Harzandi, A. Meena, J.N. Tiwari, W.-G. Lee, T. Yoon, K.S. Kim, Nickel-Based Electrocatalysts for Energy-Related Applications: Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution Reactions, ACS Catal. 7 (2017) 7196–7225.

[137] L. Wen, Y. Sun, C. Zhang, J. Yu, X. Li, X. Lyu, W. Cai, Y. Li, Cu-Doped CoP Nanorod Arrays: Efficient and Durable Hydrogen Evolution Reaction Electrocatalysts at All pH Values, ACS Applied Energy Materials 1 (2018) 3835–3842.

[138] Q. Zhu, M. Shao, S.H. Yu, X. Wang, Z. Tang, B. Chen, H. Cheng, Z. Lu, D. Chua, H. Pan, One-Pot Synthesis of Co-Doped VSe2 Nanosheets for Enhanced Hydrogen Evolution Reaction, ACS Applied Energy Materials 2 (2019) 644–653.

[139] Y. Qu, M. Yang, J. Chai, Z. Tang, M. Shao, C.T. Kwok, M. Yang, Z. Wang, D. Chua, S. Wang, Z. Lu, H. Pan, Facile Synthesis of Vanadium-Doped Ni(3)S(2) Nanowire Arrays as Active Electrocatalyst for Hydrogen Evolution Reaction, ACS Appl Mater Interfaces 9 (2017) 5959–5967.

[140] Y. Du, H. Qu, Y. Liu, Y. Han, L. Wang, B. Dong, Bimetallic CoFeP hollow microspheres as highly efficient bifunctional electrocatalysts for overall water splitting in alkaline media, Appl. Surf. Sci. 465 (2019) 816–823.

[141] H. Liu, J. Cheng, W. He, Y. Li, J. Mao, X. Zheng, C. Chen, C. Cui, Q. Hao, Interfacial electronic modulation of Ni3S2 nanosheet arrays decorated with Au nanoparticles boosts overall water splitting, Appl. Catal. B 304 (2022) 120935.

[142] Y. Qu, M. Yang, J.W. Chai, Z. Tang, M. Shao, C.T. Kwok, M. Yang, Z. Wang, D.H. C. Chua, S. Wang, Z. Lu, H. Pan, Facile Synthesis of Vanadium-Doped Ni3S2 Nanowire Arrays as Active Electrocatalyst for Hydrogen Evolution Reaction, ACS Appl. Mater. Interfaces 9 (7) (2017) 5959–5967.

[143] Z. Zou, Q. Wang, Synergistic Effect of Bimetallic Sulfide Synthesized by a Simple Solvothermal Method for High-Efficiency Oxygen Evolution Reaction, Energy Fuels 35 (2021) 17869–17875.

[144] K. Zhang, P. Jiang, Q. Gu, Y. Leng, P. Zhang, Z. Li, Y. Li, Design of cobalt-iron complex sulfides grown on nickel foam modified by reduced graphene oxide as a highly effect bifunctional electrocatalyst for overall water splitting, Int. J. Energy Res. 46 (2022) 7320–7333.

[145] B. Zhou, R. Gao, J.-J. Zou, H. Yang, Surface Design Strategy of Catalysts for Water Electrolysis, Small 18 (2022) 2202336.

[146] T. Kajana, A. Pirashanthan, D. Velauthapillai, A. Yuvapragasam, S. Yohi, P. Ravirajan, M. Senthilnanthanan, Potential transition and post-transition metal sulfides as efficient electrodes for energy storage applications: review, RSC Adv. 12 (2022) 18041–18062.

[147] Z. Zhang, S. Tang, X. Lin, C. Liu, S. Hu, Q. Huang, N, P-doped multiphase transition metal sulfides are used for efficient electrocatalytic oxygen evolution reaction, Appl. Surf. Sci. 584 (2022) 152546.

[148] R. He, X. Huang, L. Feng, Recent Progress in Transition-Metal Sulfide Catalyst Regulation for Improved Oxygen Evolution Reaction, Energy Fuels 36 (2022) 6675–6694.

[149] F. Yu, H. Zhou, Y. Huang, J. Sun, F. Qin, J. Bao, W.A. Goddard, S. Chen, Z. Ren, High-performance bifunctional porous non-noble metal phosphide catalyst for overall water splitting, Nat. Commun. 9 (2018) 2551.

[150] L. Shan-Shan, Tungsten-doped Ni–Co phosphides with multiple catalytic sites as efficient electrocatalysts for overall water splitting, Journal of materials chemistry A, v. 7 (2019) pp. 16859-16866-12019 v.16857 no.16828.

[151] J. Kim, K. Lee, Research Trend in Electrocatalysts for Anion Exchange Membrane Water Electrolysis, JOURNAL OF THE KOREAN ELECTROCHEMICAL SOCIETY 25 (2022) 69–80.

[152] P. Purnami, N. Hamidi, M.N. Sasongko, E. Siswanto, D. Widhiyanuriyawan, I.P. Tama, W.S. Nugroho, I.N.G. Wardana, Enhancement of hydrogen production using dynamic magnetic field through water electrolysis, Int. J. Energy Res. 46 (2022) 7309–7319.

[153] Y. Wu, X. Tao, Y. Qing, H. Xu, F. Yang, S. Luo, C. Tian, M. Liu, X. Lu, Cr-Doped FeNi-P Nanoparticles Encapsulated into N-Doped Carbon Nanotube as a Robust Bifunctional Catalyst for Efficient Overall Water Splitting, Adv Mater 31 (2019) e1900178.

[154] P.M. Bodhankar, P.B. Sarawade, P. Kumar, A. Vinu, A.P. Kulkarni, C.D. Lokhande, D.S. Dhawale, Nanostructured Metal Phosphide Based Catalysts for Electrochemical Water Splitting: A Review, Small 18 (2022) 2107572.

[155] Y. Yu, Q. Chen, J. Li, P. Rao, R. Li, Y. Du, C. Jia, W. Huang, J. Luo, P. Deng, Y. Shen, X. Tian, Progress in the development of heteroatom-doped nickel phosphates for electrocatalytic water splitting, J. Colloid Interface Sci. 607 (2022) 1091–1102.

[156] F. Yu, L. Yu, I.K. Mishra, Y. Yu, Z.F. Ren, H.Q. Zhou, Recent developments in earth-abundant and non-noble electrocatalysts for water electrolysis, Materials Today, Physics 7 (2018) 121–138.

[157] L. Yan, B. Zhang, J. Zhu, Y. Li, P. Tsiakaras, P. Kang Shen, Electronic modulation of cobalt phosphide nanosheet arrays via copper doping for highly efficient neutral-pH overall water splitting, Appl. Catal. B 265 (2020) 118555.

[158] G.-F. Chen, T.Y. Ma, Z.-Q. Liu, N. Li, Y.-Z. Su, K. Davey, S.-Z. Qiao, Efficient and Stable Bifunctional Electrocatalysts Ni/NixMy (M = P, S) for Overall Water Splitting, Adv. Funct. Mater. 26 (2016) 3314–3323.

[159] J. Qi, T. Xu, J. Cao, S.Q. Guo, Z. Zhong, J.-C. Feng, Fe doped Ni5P4 nanosheet arrays with rich P vacancies via phase transformation for efficient overall water splitting, Nanoscale (2020).

[160] Y. Liu, Y. Xing, X. Zheng, S. Xu, D. Li, D. Jiang, Synergistically enhancing electrocatalytic activity of Co2P by Cr doping and P vacancies for overall water splitting, Appl. Surf. Sci. 600 (2022) 154099.

[161] Y. Zhao, J. Chen, S. Zhao, W. Zhou, R. Dai, X. Zhao, Z. Chen, T. Sun, H. Zhang, A. Chen, Mo-doped NiCoP nanowire array grown in situ on Ni foam as a high-performance bifunctional electrocatalyst for overall water splitting, J. Alloy. Compd. 918 (2022) 165802.

[162] K. Hu, J. Fang, X. Ai, D. Huang, Z. Zhong, X. Yang, L. Wang, Comparative study of alkaline water electrolysis, proton exchange membrane water electrolysis and solid oxide electrolysis through multiphysics modeling, Appl. Energy 312 (2022).

[163] W. Li, H. Tian, L. Ma, Y. Wang, X. Liu, X. Gao, Low-temperature water electrolysis: fundamentals, progress, and new strategies, MATERIALS ADVANCES.

[164] J. Chi, H. Yu, Water electrolysis based on renewable energy for hydrogen production, Chin. J. Catal. 39 (2018) 390–394.

[165] D.M.F. Santos, C.A.C. Sequeira, J.L. Figueiredo, HYDROGEN PRODUCTION BY ALKALINE WATER ELECTROLYSIS, Quim. Nova 36 (2013) 1176–1193.