

Multicomponent transition metal oxides and (oxy)hydroxides for oxygen evolution

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ABSTRACT

Oxygen evolution reaction (OER) is the core electrode reaction in energy-related technologies, such as electrolytic water, electrocatalytic carbon dioxide reduction, rechargeable metal-air batteries, and renewable fuel cells. Development of well-stocked, cost-effective, and high-performance OER electrocatalysts is the key to the improvement of energy efficiency and the large-scale commercial implementation of these technologies. Multicomponent transition metal oxides and (oxy)hydroxides are the most promising OER catalysts due to their low cost, adjustable structure, high electrocatalytic activity, and outstanding durability. In this review, a brief overview about the mechanisms of OER is first offered, accompanied with the theory and calculation criteria. Then, the latest advances in the rational design of the related OER electrocatalysts and the modulation of the electronic structure of active sites are comprehensively summarized. Specifically, various strategies (including element doping, defect engineering, and fabrication of binderless catalysts) used to improve the OER performance are detailedly discussed, emphasizing the structure–function relationships. Finally, the challenges and perspectives on this promising field are proposed.

KEYWORDS

oxyhydroxide, mixed oxide, oxygen evolution reaction, single-atom catalyst, water splitting

1 Introduction

In recent centuries, traditional fossil fuels have been consumed at an alarming rate, and the energy crisis has become the focus of global attention. Moreover, a mass of carbon dioxide greenhouse gas was released by the massive consumption of fossil fuels, which in turn causes severe environmental issue, and therefore the development of environmentally friendly energy technologies with non-hazardous emissions that can be applied on a large scale and in a sustainable manner is imperative [1]. Therefore, people are actively developing new technologies to make rational use of renewable resources such as solar and wind energy. At present, steam reforming and water electrolysis ($\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$; $\Delta G = +237,200 \text{ J}\cdot\text{mol}^{-1}$, $\Delta E = 1.23 \text{ V}$ vs. reversible hydrogen electrode (RHE)) are renewable methods to produce hydrogen, and the generated H_2 can serve as fuel for fuel cell, one of environmentally friendly energy technologies. However, the steam reforming method is not the best choice, because it will produce CO_2 and H_2 at the same time, thereby reducing the purity of H_2 and affecting the life cycle and efficiency of fuel cells. Since the combustion product of hydrogen fuel cells is water, it will be the best choice for available fuel cells. Furthermore, the electrochemical decomposition of water can massively generate high-purity hydrogen. By converting renewable clean energy sources such as solar energy and wind energy into electrical energy and further to chemical energy, electrolyzed water is an efficient and sustainable method for hydrogen production and is an environmentally friendly alternative energy production method for large-scale storage and use of renewable energy in the future. The electrolyzed water consists of two half reactions, namely the

cathode hydrogen evolution reaction (HER) and the anode oxygen evolution reaction (OER). HER is a relatively simple two-electron transfer reaction that can occur over many metals at low overpotentials. In contrast, the reaction mechanism of OER is more complicated because OER is a four-electron transfer process, and its kinetic rate is relatively slow [2]. In this process, a four-electron proton coupling reaction occurs that four protons break away from two water molecules to form an oxygen molecule, which requires a large overpotential to effectively promote the reaction. Generally, the overpotential of OER is much higher than the theoretical decomposition voltage of water (1.23 V). In the process of forming O–O double bond during the OER, the disadvantages of thermodynamics and kinetics of removing the four electrons are the main reason for the low efficiency of the water splitting system. Therefore, the overall efficiency of the electrolyzed water is greatly hindered by the excessive overpotential of the OER, which limits the application of electrocatalytic water splitting on an industrial scale [3].

The design and synthesis of highly efficient OER catalysts is the key to improving the water splitting reaction rate [4–6]. In addition, for rechargeable metal-air batteries and renewable fuel cells, OER is also an important half-reaction [7]. These environmentally friendly batteries are not only harmless to the environment, but also have higher theoretical specific energy and energy density as well as lower production costs. Additionally, because the oxygen they use comes from the air, these batteries have become the focus of recent research such as lithium-air batteries, zinc-air batteries, and so on [8]. Therefore, the improvement of the energy conversion efficiency of rechargeable

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metal-air batteries also urgently requires the development of efficient and stable OER electrocatalysts to accelerate the slow kinetics [9]. Noble metal-based iridium and ruthenium oxides (IrO_2 and RuO_2) are the most active OER electrocatalysts, because these noble metal-based catalysts have low OER overpotentials (Fig. 1) [10–13]. However, due to the scarcity of raw materials, their production costs are relatively high, and the durability is insufficient. Therefore, they cannot be used in corrosive and destructive water electrolysis processes due to the increase in the costs of production, which severely restricts the large-scale application of noble-metal-based catalysts [14–16]. Later, studies have found that the oxides and hydroxides of group VIII 3d metals (Fe, Co, and Ni) also have excellent OER catalytic performance [17–21]. When they are combined with other metals to form mixed oxides, their catalytic ability can be compared with Ir and Ru based oxides under alkaline conditions [22–27]. Therefore, people have invested a lot of energy to fabricate high-performance transition metal-based OER catalysts that can replace expensive noble metal-based materials [28].

Researchers have reported various materials with significant OER activity, such as sulfides [30], nitrides [31], metal-organic frameworks (MOFs) [28, 32, 33], perovskites [34–36], spinels [21, 37–39], layered double hydroxides (LDHs) [40–42], and hollow materials [43, 44]. These catalysts not only have low cost and high activity, but also have relative stability under oxidizing conditions, making the water splitting process feasible. Among them, transition metal compounds based on non-noble metals have become a hot spot in the research of OER catalysts due to their abundant active sites and adjustable electronic structures [45]. In alkaline media, the surface of transition metal based OER catalysts is easily oxidized to oxides and hydroxides due to the rapid surface remodeling and phase change in the electrochemical oxidation process. For example, the catalyst surface is converted into metal oxyhydroxides ($\ast\text{OOH}$), which have been proposed as the active sites [46, 47]. Therefore, transition metal oxides or hydroxides and

their derivatives are the subjects of intensive research [9, 48, 49]. Various oxides and hydroxides (e.g., $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2$ and $\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$) have been widely used for the OER [3, 50]. There are a great number of high-performance OER catalysts prepared using different strategies. Based on a large number of studies, it has been found that in multi-metal systems, the synergy effect between different metal elements can tune electronic structure and local coordination environment, thus enhancing the catalytic efficiency of OER [24, 51, 52]. By further reconstructing the surface and microstructure of high-efficiency catalysts, introducing catalytically active oxyhydroxides on the surface, and preparing different structures with highly catalytic activity, the efficiency of OER can be greatly improved [53, 54]. Therefore, an in-depth understanding of the modification of the catalyst surface and microstructure is of great significance for elucidating catalytic mechanism and rationally designing electrocatalysts [55]. For example, Wu et al. found that mesoporous $\text{Fe}_{11\%}\text{-NiO}$ supported on Ni foam (NF) achieved an ultra-low η_{10} of 206 mV at the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, which is even superior to commercial RuO_2 and most noble metal based OER catalysts. Additionally, the $\text{Fe}_{11\%}\text{-NiO}$ bimetallic catalyst exhibited long-term OER stability [56].

In this review, we introduce different reaction mechanisms of OER, discuss their possible reaction path, and compare the OER performance on various catalysts as the start. Furthermore, we present the theory and calculated parameters of characterizing the activity of OER electrocatalysts. Secondly, we summarize OER electrocatalysts in a classification of different preparation strategies, which are element doping strategy, defect engineering strategy, and synthesis of binderless catalysts. Finally, we provide possible challenges together with some suggestion of future directions as the conclusion. We hope that this review will provide some systematic insights for the development of non-noble-metal-based OER electrocatalysts and promote related technologies.

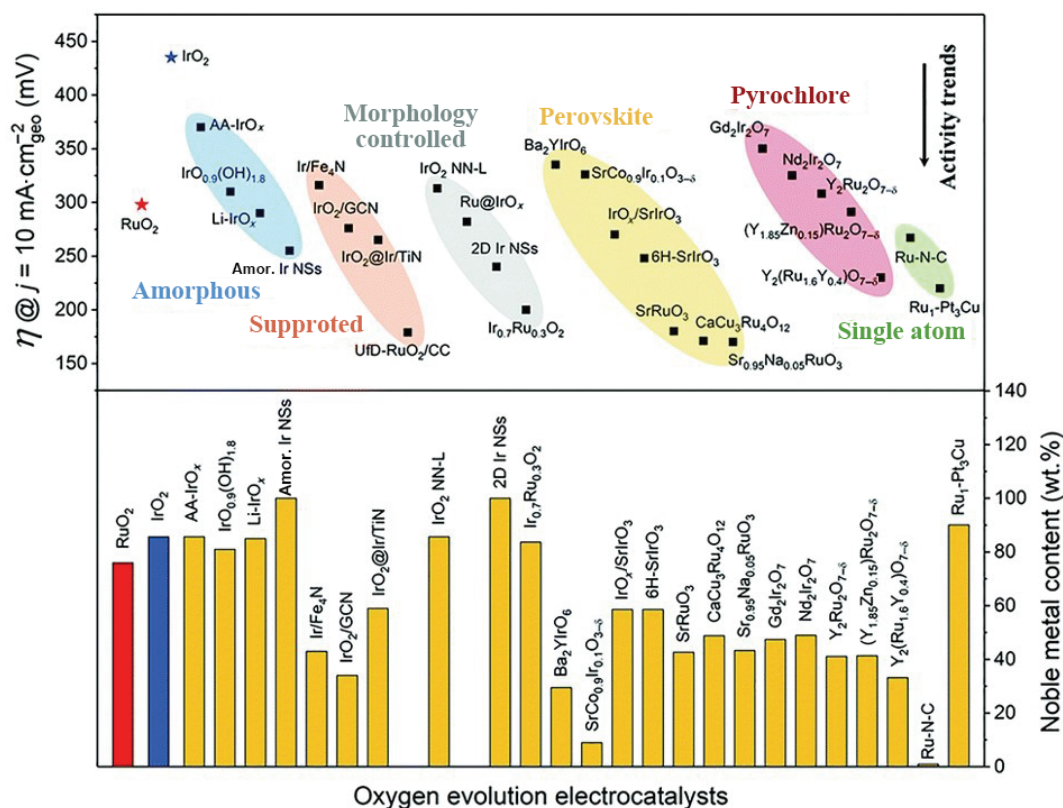


Figure 1 Electrochemical OER activities on noble metal (Ir, Ru, and Pt) based catalysts under acidic conditions. Reproduced with permission from Ref. [29], © Royal Society of Chemistry 2020.

2 Brief introduction to OER

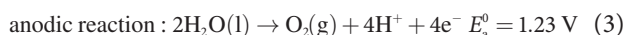
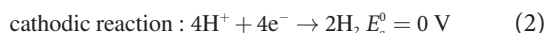
2.1 OER mechanism

OER is a four-electron-proton transfer process with slow reaction kinetics and the OER mechanism is very complicated. There have been abundant in-depth researches on the mechanism of OER according to different rate-determining steps (RDSs) [57]. Using the metal oxidation process as the RDS is the most common OER mechanism. The blue line and the red line indicate the OER mechanism under acidic and alkaline conditions, respectively (Fig. 2). The black line indicates that the evolution of O_2 involves the formation of intermediate hydrogen peroxide ($M\text{-OOH}$), and it is also possible for two adjacent O atoms ($M\text{-O}$) to react directly to produce oxygen (green).

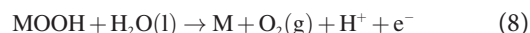
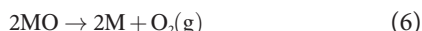
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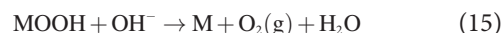
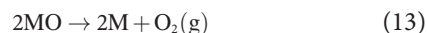
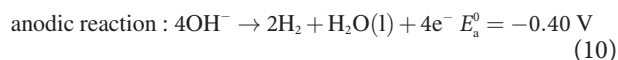
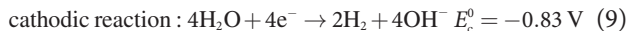
Under acidic conditions:



Reaction mechanism in acidic environment:



Under alkaline conditions:



2.2 Diverse types of OER mechanism

Among different OER mechanisms proposed by researchers, adsorbate evolution mechanism (AEM) for the OER proposed by Rossmeisl, and lattice oxygen evolution mechanism for the OER (LOER/LOM) proposed by Rong are generally accepted. These reaction mechanisms differ in many respects, such as catalytic process, energy barrier, active site, features, and so on [29]. In the last century, Reier et al. proposed many reaction mechanisms including OER, with most of them based on AEM (Eqs. (16)–(19)) [59]. In this mechanism, water molecules are firstly

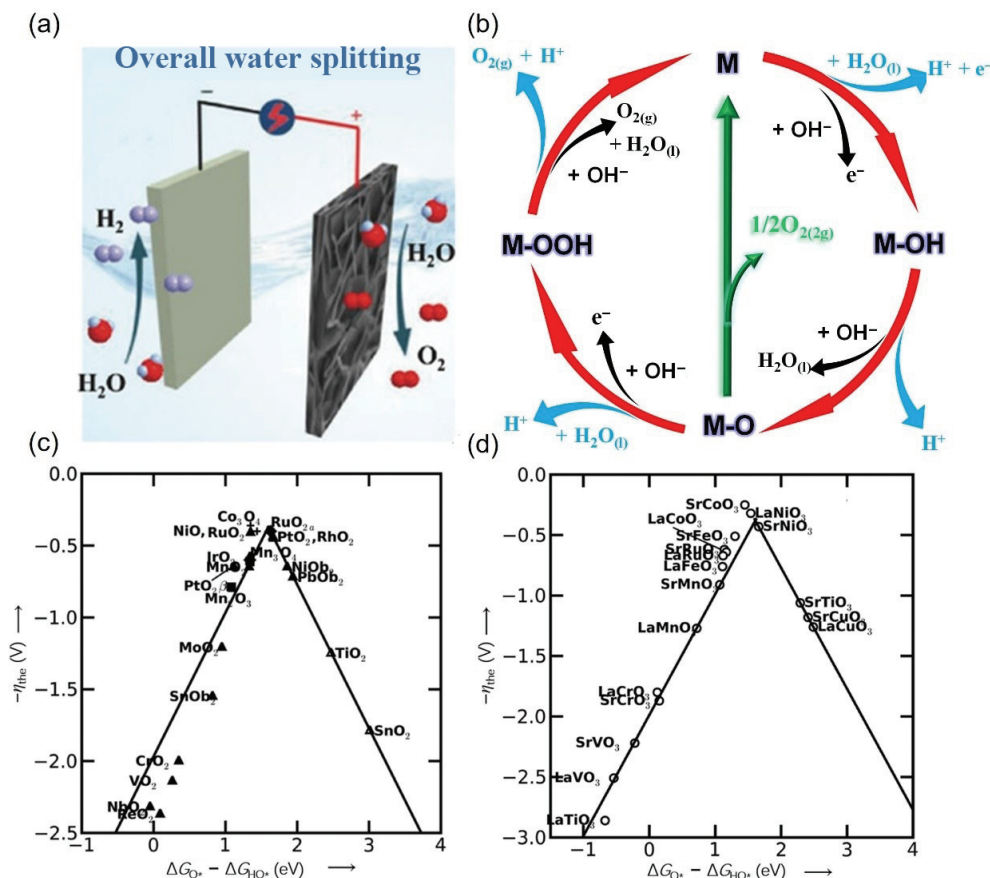
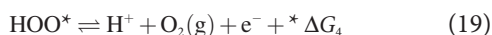
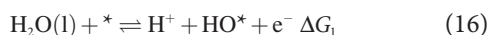
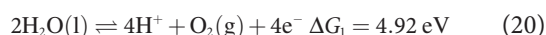


Figure 2 Schematic diagrams of (a) a water electrolysis device and (b) common electrolytic water reaction mechanism. (c) and (d) Activity trends towards OER. The negative theoretical overpotential was plotted against the standard free energy of $\Delta G_{HO^*} - \Delta G_{O^*}$ step. The volcano curve was established by using the scaling relation between $\Delta G_{HO^*} - \Delta G_{O^*}$ and $\Delta G_{O^*} - \Delta G_{HO^*}$. (c) and (d) Reproduced with permission from Ref. [58], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2011.

adsorbed on the surface of the catalyst, resulting in charge–proton transfer, chemical bond cleavage and formation, adsorption and desorption of surface oxygen intermediates, and other processes to generate molecular oxygen [60].



On this basis, Rossmeislet firstly proposed the most recognized OER path based on density functional theory (DFT), which involves four synergistic proton–electron transfer paths as shown in Fig. 3. A water molecule is firstly attached to the active site, dissociating a proton to form HO^* , and then removing the second proton to form O^* . Subsequently, another water molecule launches a nucleophilic attack on oxygen (O^*), forming HOO^* , desorbing O_2 , and releasing the active site in sequence. The overall oxygen evolution half reaction in an acid is denoted by Eq. (20) [1]



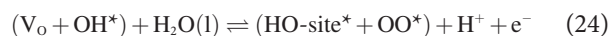
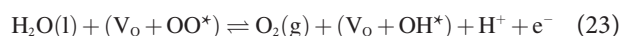
The theoretical oxygen evolution potential under standard conditions is 1.23 V, and the Gibbs free energy (ΔG) of the total reaction under equilibrium conditions is 4.92 eV. The ΔG of each proton–electron transfer step can be expressed by the Gibbs free chemical adsorption energy of two adsorbed oxygen intermediates in the form of function, but the G of each basic step can be different. From the thermodynamics, the overpotential required for the entire reaction is related to each element reaction, and the maximum change in Gibbs free energy (ΔG_{max}) is defined as the potential determination step (PDS). On this basis, theoretical overvoltage of OER (η_{OER}) can be determined by Eq. (21) under standard conditions

$$\eta_{\text{OER}} = (\Delta G_{\text{max}}/e) - 1.23 \text{ V} \quad (21)$$

In actual OER catalysis, there is usually a basic step of which ΔG is larger than 1.23 eV, which leads to a large theoretical overpotential [61]. For example, the calculated reaction path and ΔG of reference RuO_2 indicated that Eq. (3) is the PDS of OER [62]. This means that the adsorption of intermediate species O^* on the surface of RuO_2 is too strong to prevent the formation of HOO^* . Based on this understanding, the activity of Ru-based catalysts can be improved by decreasing the binding energy of RuO_2 to intermediate O^* species or promoting the formation of HOO^* [63]. For example, the combination of Cr oxide with RuO_2

could significantly improve the activity of the catalyst and promote the formation of HOO^* [64]. It can be concluded that the activity of OER catalysts depends largely on the adsorption strength of different oxygen intermediates at the active site [65].

With the development of OER catalysts, some catalytic phenomena cannot be explained by AEM mechanism. For example, it has been found that the OER catalytic activity of some materials exceeds the limits of volcanic relationships, and the activity of some catalysts can be pH-dependent on the RHE scale [66]. One explanation for this difference is that these catalysts do not actually follow the reaction mechanism mentioned above. Inspired by this, more OER mechanisms have been proposed, among which LOER mechanism is the most widely studied. Based on LOER mechanism, lattice oxygen in the OER potential region of the catalyst directly participates in the formation and evolution of oxygen [67]. However, a number of reaction processes have been proposed, and there is no consensus on the basic response pathway of LOER [68]. For example, based on the study of LaNiO_3 , Bockris and Otagawa proposed a reaction pathway involving lattice oxygen, in which metal ions adsorb intermediate species to form hydrogen peroxide and decompose to produce oxygen [69]. Rong et al. proposed a major reaction pathway (Fig. 3), in which lattice oxygen participates in the reversible formation of surface oxygen vacancies (V_O). Subsequently, this result has been further described and summarized in Eqs. (22)–(25) as follows



Because the mechanism of LOER has not been thoroughly studied, a unified understanding has not been formed. For example, the debate between AEM and LOER regarding catalytic active sites and the effect of competition and binding still exists. Herein, we summarize some characteristics of the proposed mechanisms: (1) Most LOER mechanisms involve four uncoordinated proton–electron transfer steps; (2) since the activity of the catalyst is still dependent on the binding energy between the intermediate oxygen and the active site, the OER constraint exists, but this limitation may cause the catalyst to exhibit higher activity; (3) the role of oxygen vacancy in the catalytic process leads to the hypothesis that oxygen vacancy is crucial for the occurrence of OER. Based on the above discussion, AEM and LOER can be

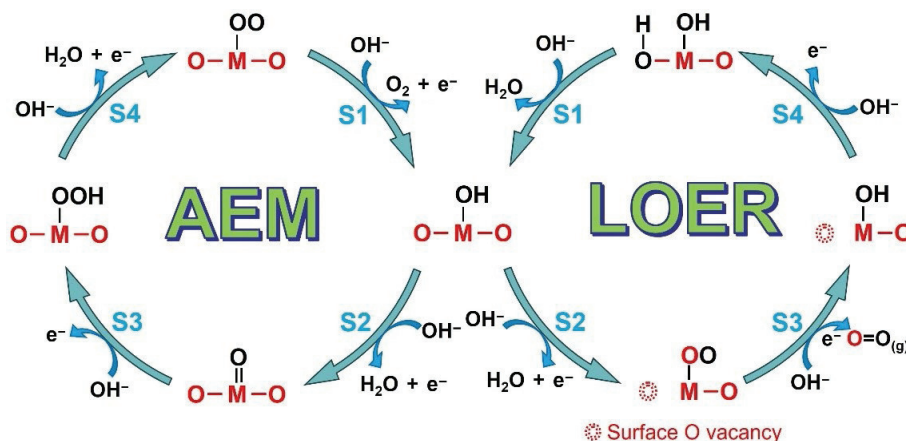


Figure 3 Schematic diagram of main pathway of AEM and LOER mechanisms.

compared from the aspects of catalytic pathway, active site, energy barrier, and characteristics (Fig. 4). The differences include the basic catalytic process (cationic redox of AEM and anionic redox of LOER), the catalytic energy barrier (relatively low LOER based on DFT calculations), and the active site (coordination unsaturated metal ions of AEM and coordination unsaturated oxygen ions of LOER). There are several ways to distinguish different mechanisms. Firstly, considering the proton and electron transfer steps, the OER activity of AEM is pH independent, whereas the OER activity of LOER is pH dependent. As described above, some of the basic reactions of LOER are uncoupled electron–proton transfer steps, which in turn exhibit pH dependence on catalytic activity. Therefore, the relationship between OER activity and electrolyte pH can be used as an important criterion to identify LOER. Secondly, since the concentration of oxygen vacancy in catalyst is closely related to LOER mechanism, some studies have reported the LOER mechanism triggered by increasing oxygen vacancy concentration. Therefore, from the perspective of material properties, the LOER mechanism may be followed when the catalyst contains many oxygen vacancies. Finally, because lattice oxygen participates in the OER under LOER mechanism, isotope labeling experiment is the most accurate method to identify LOER mechanism. LOER can be confirmed by the presence of unlabeled oxygen atoms in the reaction product after labeling oxygen element isotopes in the electrolyte.

2.3 Phenomenon of OER related to the mechanism

With the in-depth research of OER electrocatalytic mechanisms, the relationship between the performance of catalysts and OER mechanisms has attracted extensive research interest such as the activity and stability of catalysts, M–O bond covalence, and crystal

defects [71]. Furthermore, there are other confusing phenomena that can also be explained by the OER mechanisms like the activity difference between crystalline and amorphous metal oxides and so on.

2.3.1 Stability predicted by theoretical studies

Studies of OER mechanisms have shown that the stability of the catalyst is mainly dependent on its solubility in the electrolyte [72]. Therefore, some hypotheses have been proposed about the relationship between catalytic activity and stability (Figs. 5(a)–5(g)). For example, Kolpak et al. proposed a fundamental relationship between LOER and stability of perovskite catalysts based on theoretical calculations (Fig. 5(c)). The results showed that lattice oxygen participates in the OER through the reversible formation of surface oxygen vacancies as the mechanism of oxygen evolution changes from AEM to LOER, which reduces the stability of the catalyst. They also suggested that the metal cation at the B site in ABO_3 is less likely to contribute electrons and is more prone to oxygen evolution through the LOER mechanism, resulting in the poor stability. In addition, Binniger et al. proved the relationship between dissolution and LOER through theoretical calculation based on thermodynamics. They hypothesized that three interrelated processes occurred simultaneously at the electrode, namely conventional OER (Eq. (26)), chemical dissolution of metal oxides (Eq. (27)), and lattice OER (Eq. (28)).

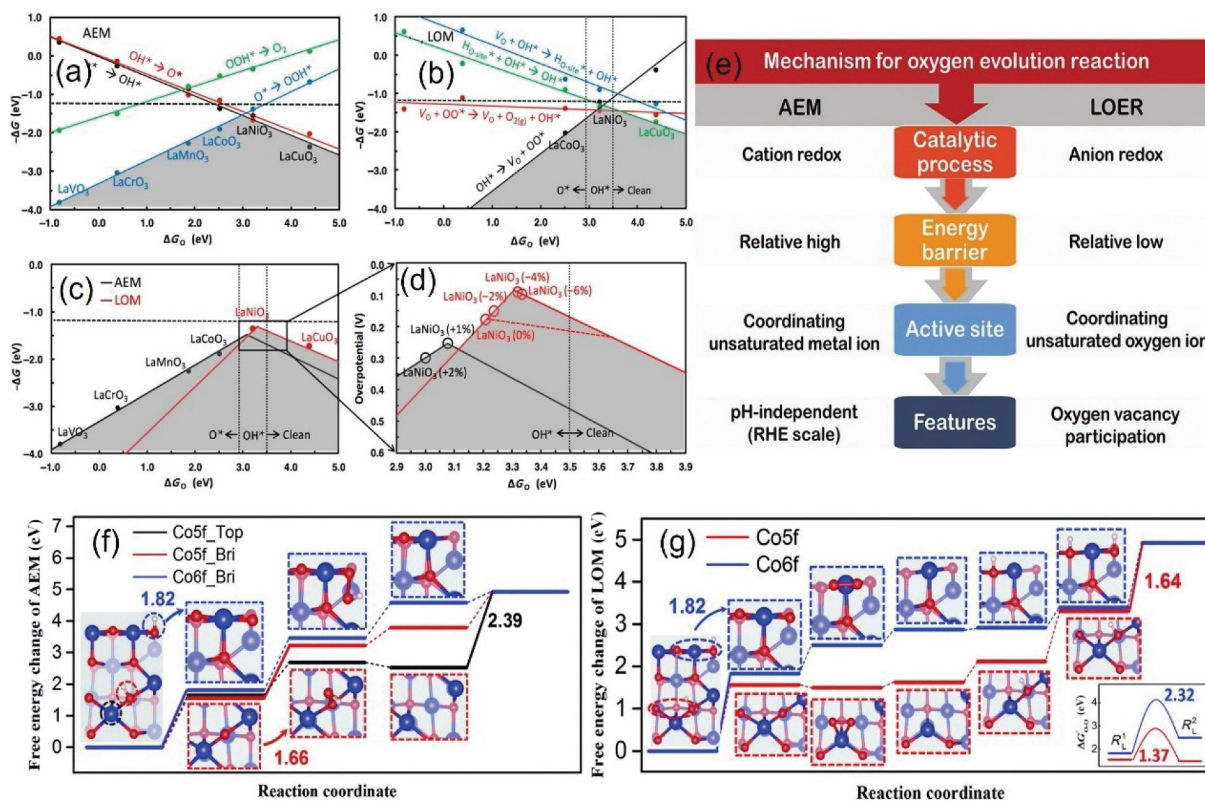
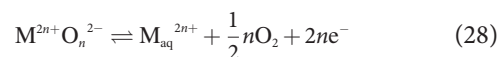
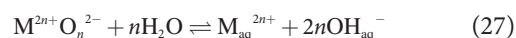
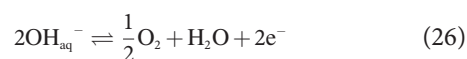


Figure 4 Negative reaction free energies vs. ΔG_{O} of each OER steps via (a) AEM and (b) LOM. The shaded region in (c) shows the overall OER active volcano with AEM (black) and LOM (red) taken into account. (d) Theoretical overpotential. (e) Comparison of AEM and LOER mechanisms. The free energy change of different active sites on the most stable surface via (f) AEM and (g) LOM. (a)–(d) Reproduced with permission from Ref. [67], © American Chemical Society 2018. (e) Reproduced with permission from Ref. [29], © Royal Society of Chemistry 2020. (f) and (g) Reproduced with permission from Ref. [70], © Royal Society of Chemistry 2020.

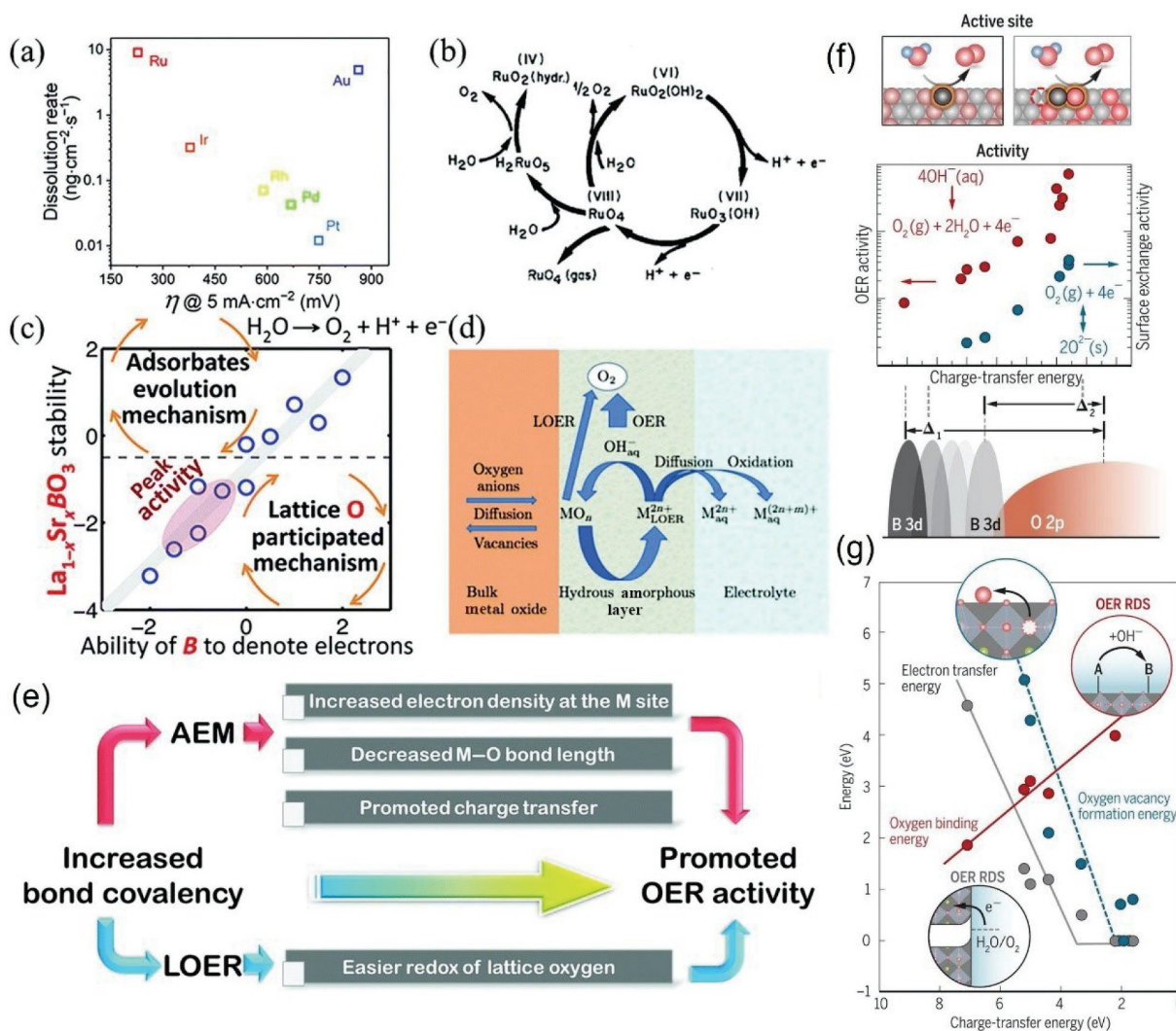


Figure 5 (a) The relationship between the overpotential and dissolution rate of metal electrodes. (b) Description of oxygen evolution and corrosion on Ru and RuO₂ electrodes. (c) The basic relationship between LOER and stability of perovskite catalysts. (d) Schematic diagram of LOER primary route and structure of catalyst surface. (e) Schematic diagram of the effect of M–O bond on the OER [63, 80, 83–86]. (f) Schematic diagrams. (g) The relationship between ΔE and RDSs. (a) and (e) Reproduced with permission from Ref. [29], © Royal Society of Chemistry 2020. (b) Reproduced with permission from Ref. [88], © The Electrochemical Society 1983. (c) Reproduced with permission from Ref. [61], © American Chemical Society 2016. (d) Reproduced with permission from Ref. [87], © Binniger, T. et al. 2015. (f) and (g) Reproduced with permission from Ref. [89], © Hwang, J. et al. 2017.

By calculating the chemical potentials of the three reactions under equilibrium conditions, it was found that these reactions are not independent. At a potential higher than the oxygen evolution equilibrium potential, metal dissolution and OER occur simultaneously, which explain the relationship between structural changes and solubility in many experiments (Fig. 5(d)). Meanwhile, with the progress of LOER, metal cations may be further oxidized to higher and more soluble valence states, which will lead to electrode instability [73]. Compared with AEM, the possible reason for the relatively low stability of the catalyst in LOER is that the reversible formation of oxygen vacancies leads to the insertion or removal of oxygen into the lattice, resulting in the collapse of the overall crystal structure. In the AEM mechanism, the intermediate only interacts with the electrode surface that avoid the occurrence of the above situation.

2.3.2 The relationship between activity and crystallinity

The difference in activity between crystalline and amorphous metal oxides has been revealed in many works, and a relatively uniform conclusion has been reached: The OER activity of amorphous metal oxides is significantly higher than that of crystalline metal oxides, which may be caused by the difference in the number of catalytic active sites between of them [73]. From

OER mechanisms and the relationship between activity and crystallinity, a conclusion can be drawn: For well-crystallized metal oxides, oxygen precipitation is mainly through the AEM; for amorphous metal oxides, oxygen precipitation is mainly through the LOER mechanism, and the reaction barrier is lower than that of AEM, thus improving the activity. Furthermore, compared with amorphous materials, the insertion and removal of oxygen in the lattice of high-crystalline materials are relatively difficult, indicating that LOER process is more likely to occur on amorphous catalysts. In addition, considering the similar nucleophilic attack steps in the AEM and LOER mechanisms, amorphous catalysts are more favorable for the presence of electrophilic oxygen species, and the difference in the local structure of the two materials leads to different adsorption strengths for regulating the intermediate species, resulting in different activities as well.

2.3.3 The relationship between OER activity and bond covalency/defects

The covalent properties of M–O bonds in metal oxides, especially multi-metallic oxides, will greatly affect their catalytic activity and stability [74–76]. According to related research, the overlap of the M d band and the O 2p band determines the strength of M–O

bond [77–79]. For example, from the perspective of OER mechanism, the increase in covalent bonds leads to an increase in the electron density of Ir site and a decrease in the electrostatic interaction with oxygen intermediates, thereby weakening the binding energy of Ir and O intermediates, which is conducive to the formation of electrophilic O intermediates [80]. In this case, the electrophilicity of oxygen intermediates will be enhanced, thereby promoting the nucleophilic attack of water molecules. On the other hand, the strong M–O bond state is the key to triggering the LOER mechanism. The enhancement of M–O covalent bond leads to the shift of Fermi level to O 2p band, thus facilitating OER activity. However, the increase of overlap between M d band and O 2p band will further strengthen the binding between M and O* and hinder the formation of OOH* according to the AEM mechanism, which is not conducive to the improvement of OER activity. In addition, the decrease of energy gap between M d band and O 2p band is conducive to the formation of oxygen vacancies under LOER mechanism. Therefore, lattice oxygen is easy to be thermally oxidized, making LOER process easy to occur. In addition to the covalent properties of M–O bonds, the crystal defects that can be divided into cation defects and anion defects also significantly affect the catalytic performance of OER, and their effects on catalytic performance can also be understood from the perspective of catalytic mechanism. It was reported that with the introduction of oxygen vacancies, the valence state of metal ions changes to form a more covalent M–O bond, and a new gap state will be introduced to improve the conductivity and activity of OER catalysts. For example, anionic defects lead to changes in the geometry of MO₆ octahedron, optimizing the electronic structure of d band that adjusts the adsorption energy. Most importantly, oxygen vacancies are highly related to the LOER mechanism and are directly involved in the original pathway. Therefore, as more oxygen vacancies exist in the lattice, the LOER mechanism will be triggered.

2.3.4 The relationship between OER activity and metal d band structure

The concepts of d-band occupancy rate and d-band center as well as the electronic structure of d band are important parameters to describe catalyst activity [81]. The charge transfer energy (ΔE) which is the energy gap between d band center and O 2p band center greatly affects catalytic activity (Fig. 5(f)). It can be observed that the binding energy of oxygen (O*) increases with the increase of ΔE , and the PDS of OER in AEM mechanism changes from Step 2 to Step 3 (Fig. 5(g)). Furthermore, high oxidation states lead to the increased M–O covalence and hybridization. Therefore, for Ru- and Ir-based perovskites that bind too strongly to O*, the reduction of overlap between M d band and O 2p band and the weakening of M–O bond are beneficial to improving OER activity [11]. In addition, increasing the overlap between d band and O 2p band results in a significant reduction in oxygen vacancy formation energy (E_{vac}) (Fig. 5(b)), which may contribute to LOER [82].

2.4 Criteria for evaluating OER catalysts

Many factors including the external reaction environment conditions and the element composition and microstructure of the catalytic material itself all affect the performance of OER. As we all know, different OER catalysts have their own appropriate environmental conditions such as temperature, pressure, pH value, and so on. Recent studies have generally focused on the effects of internal composition and structure of catalysts. Based on the research on the changes of various components and characterization diagrams of different samples, researchers concluded that the catalytic performance is very sensitive to the

microstructure and electrochemical activity specific surface area (ECSA) of the component materials since the increased ECSA leads to higher exposure of reaction active sites, which helps to improve the catalytic performance. If the catalyst itself has high conductivity to promote the electron transfer of OER, the catalytic ability can be enhanced. Although further modification can improve its performance to a certain extent, some studies reported that another decisive factor is the internal binding strength in the reactants of the OER. Furthermore, it has been reported that the performance drawbacks of various OER catalysts are mainly caused by inherent reaction activation barriers and some other resistances such as solution resistance and contact resistance. The factors affecting the electrocatalytic OER performance are far more than these points. Therefore, some important parameters need to be carefully measured and calculated to better evaluate and compare the catalytic activity of these OER catalysts including the overpotential (η), the exchange current density (j_0), Tafel slope (b) of electrocatalysts, and so on. These parameters are not only crucial evaluation criteria to evaluate the performance of OER, but also essential to provide important information about the electrochemical mechanism [9].

Total electrode activity is usually obtained by measuring cyclic voltammetry (CV) or linear sweep voltammetry (LSV). Since the illegal pull capacitance current may contribute a part of the total current, it can only obtain a preliminary evaluation from the CV and LSV results. To compare the total electrode activity, two different methods are proposed, including measuring the steady-state current under a given overpotential or the overpotential under a given steady-state current [9].

Tafel diagrams derived from the LSV curves reflect the relationship between the overpotential (η) and the current density (j). The linear region of Tafel curve can be fitted to Tafel equation $\eta = b \log(j) + a$ (b : Tafel slope). In addition, when η is assumed zero, another important parameter, the exchange current density (j_0), can be obtained from the Tafel equation. Parameter (j_0) is a measure of the intrinsic electrocatalytic activity of the material at reversible potential. Generally speaking, lower value of Tafel slope and larger exchange current density mean better electrocatalytic performance of OER [9].

Faraday efficiency reflects the utilization efficiency of electrons in electrochemical system which can be obtained by calculating the ratio of experimentally generated O₂ (n_{O_2}) to theoretically generated O₂ ($n_{\text{O}_2'}$). Specifically, under a constant oxidation current (I) for a certain time (t), a fluorescence-based oxygen sensor can be used to detect the amount of O₂ generated in the experiment. If the generation of an O₂ molecule needs to consume four electrons, the corresponding theoretical amount of O₂ can be obtained according to the following equation: $n_{\text{O}_2'} = (It)/4F$. Therefore, the Faraday efficiency can be calculated as follows: Faraday efficiency = $n_{\text{O}_2}/n_{\text{O}_2'} = 4Fn_{\text{O}_2}/(It)$ [9].

Turnover frequency (TOF) is defined as the number of reactants that is converted into the required product at each catalytic site per unit time, showing the inherent catalytic activity of each catalytic site. The value of TOF can be calculated according to the following equation: $\text{TOF} = (ja)/(4Fn)$ (j : the measured current density at a given overpotential; a : the area of the working electrode; n : the number of moles of the active material). In practice, not all atoms in the material have catalytic activity or equal accessibility. Therefore, it is impossible to obtain the accurate TOF value of catalytic materials such as OER electrocatalysts. However, it is still relevant and useful for comparing similar catalytic materials. The good structure and catalytic stability of materials are also very important for their practical applications. In general, there are two methods to evaluate their catalytic stability. One method is to measure the

change of current with time (I - t curve). For this measurement, it is best to set the current density greater than $10 \text{ mA}\cdot\text{cm}^{-2}$ and the detection time longer than 10 h. Another method is to conduct cyclic CV or LSV test. The number of cycles should exceed 5,000 to illustrate the stability of the material [9]. The first method may lead to potential errors, and the second method may lead to potential errors when the material is not completely flat, easy to damage under harsh electrochemical conditions, or there is no sheet morphology. Therefore, it is recommended to adopt a method suitable for evaluating the catalyst and its properties [23]. Herein, we introduce some of the most common and essential criteria among various parameters of performance characterization (Fig. 6) [23]. In conclusion, the lower value of the overpotential and the Tafel slope, the better electrochemical activity and long-term stability of the OER catalysts.

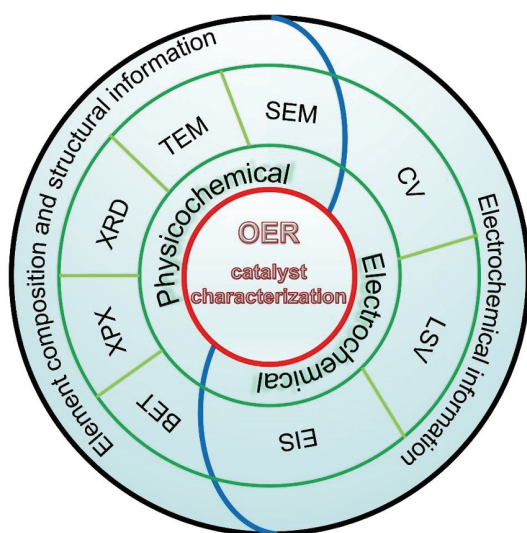


Figure 6 Characterization techniques for OER catalysts.

3 Strategies to improve the OER performance of multicomponent metal (oxy)hydroxides

As an important reaction of many renewable energy technologies, OER has become a huge obstacle to the industrial application of water electrolysis due to its slow kinetics and high overpotential [90]. Recently, transition metal elements have attracted much attention because of their high resource abundance, environmental friendliness, satisfied catalytic activity as well as low preparation cost, which often exist in the form of metal oxides or metal hydroxides (Table 1) [91–93]. Since we can no longer rely on precious metals, the first problem is the availability of catalyst material resources. The second problem involves health and environmental hazards that the materials should bring less harm to users and environment. In this point, current research showed that other compounds have potential hazards except iron, cobalt, and nickel based OER catalysts. The third problem is the conductivity of catalysts. Although heteroatom doping into metal lattice is effective in improving the catalytic activity, doping beyond a certain limit will turn the metal surface into a semiconductor or even an insulating surface, which should be avoided in electrocatalytic water decomposition, because it will greatly increase the ohmic drop and make the reaction difficult. The fourth one is the need to develop catalysts with larger active surface area, which will allow a reduction in the amount of catalyst. Another fundamental problem is the current selectivity of OER catalysts, because they often have strong redox reactions in the potential window of OER. In this case, researchers need to

know where the applied current is consumed since a high-performance OER electrocatalyst should have more current selectivity for OER rather than its own redox reaction. Finally, the corrosion resistance of the catalyst is also a point worthy of attention because the medium for water electrolysis will be highly acidic or alkaline, which requires that the materials should have extremely high corrosion resistance. For sulfides, selenides, and phosphides, the heteroatoms (S, Se, and P) are well known corrosion inhibitors [23].

Recently, to develop more practical OER catalysts, abundant related studies have been carried out. Researchers found that the size, morphology, and crystal phase will influence the catalytic OER performance of catalysts. The electronic conductivity can be improved by introducing vacancies and doping other heteroatoms [94]. Moreover, the presence of binder has a profound impact on the catalytic performance. The development of binderless catalysts can also improve the activity of catalysts to a certain extent (Table 1). Herein, we introduce high-performance catalyst materials according to different catalyst preparation strategies which are element doping strategy (including metal element doping and non-metal element doping), defect engineering strategy (including heterostructure source defects, doping source defects, and vacancy defects), and the strategy of preparing binderless catalysts.

3.1 Element doping

The element doping strategy can be used to significantly boost the catalytic activity of OER by changing the composition of the catalyst itself and taking advantage of the cooperation effect between different components [151]. The introduction of additional atoms provides an effective method to adjust the valence and electronic states. In this section, according to diverse types of doped atoms, we comprehensively classify multicomponent (oxy)hydroxides by doping strategy in terms of two representative groups: metallic element doping (including single-atom doping and multi-metal doping) and non-metallic element doping.

3.1.1 Metallic element doping

The strategy of doping metal atoms accounts for a large proportion in recent research [152]. For example, doping cobalt or nickel in molybdenum nitride greatly reduces the overpotential and improves their electrocatalytic OER activity. NiFe-based catalysts have become one of the most attractive OER electrocatalysts because of their medium adsorption affinity for reaction intermediates, brilliant coordination with reaction site, and low manufacturing cost [153]. After doping iron atoms into nickel-based materials, the electrocatalytic OER performance of NiFe-based catalyst can be greatly improved due to the increase of the conductivity, active centers, and physical or electronic properties as well as the synergistic effect between Fe and Ni atoms [99]. Herein, according to the dispersion of doped metal atoms, this strategy can be subdivided into single-atom and multi-atom doping strategies.

3.1.1.1 Single-atom doping

The single-atom doping strategy is to use different methods to dope various metal elements into the base catalyst materials in the form of atomic dispersion [104, 154, 155]. For example, Jiang et al. doped monatomic Pt with low-OER activity into porous NiO nanocubic crystalline phases using an extensible nanocubistic casting method with silica as a hard template (Fig. 7(a)) [156]. Transmission electron microscope (TEM) images and high-angle annular dark-field scanning TEM (HAADF-STEM) revealed that monatomic Pt atoms have been doped inside the NiO (Figs. 7(b)–7(d)). From X-ray photoelectron spectroscopy (XPS)

Table 1 Comparison of electrochemical parameters of various non-noble-metal-based OER electrocatalysts

Catalyst sample	Electrolyte	Current density (mA·cm ⁻²)	Overpotential (mV)	Tafel slope (mV·dec ⁻¹)	Ref.
Ni ₃ Fe _{1-x} S	1 M KOH	200	441	—	[17]
ENWs-FeNi-C ₂ O ₄	1 M KOH	10	215	54.5	[19]
(Fe,Co)OOH/MI	1 M KOH	100	290	73	[20]
meso-Mn ₁ Fe ₁ O _x	1 M KOH	10	275	52	[22]
NiCo LDH/NiCoS	1 M KOH	10	207	48	[24]
NiCo LDH	1 M KOH	10	264	62	[24]
V-NiFe ₂ O ₄ @Ni ₂ P	1 M KOH	50	230	160.8	[25]
NiFe ₂ O ₄ @Ni ₂ P	1 M KOH	50	330	188.3	[25]
Mn-NiFe ₂ O ₄	1 M KOH	50	200	47	[26]
NiMo-Fe	1 M KOH	10	217	30.05	[27]
Mn-NSG	1 M KOH	10	296	38	[30]
LaCo _{0.75} Fe _{0.25} O ₃ YSNs	1 M KOH	10	310	58	[35]
HO _{oct} -NFO NC/IF	1 M KOH	10	260	36.1	[37]
N-CDs/NiFe-LDH/NF	1 M KOH	100	260	43.4	[40]
Ru@NiV-LDH	1 M KOH	10	272	60	[41]
NiFe LDH-PMo12/NF	1 M KOH	100	249	47.5	[42]
Co _{0.15} -Fe ₂ (MoO ₄) ₃	1 M KOH	10	273	59.8	[48]
NiFeV nanofiber	1 M KOH	10	263	47	[49]
NiFeCr-LDH	1 M KOH	10	189	29.63	[50]
LiCoO _{1.8} Cl _{0.2}	1 M KOH	200	290	55.4	[53]
Ru ₁ /D-NiFe LDH/NF	1 M KOH	100	218	31	[95]
Ce@NiFe-LDH/NF	1 M KOH	10	206	40.1	[96]
Ni@NiFe LDH/NF	1 M KOH	10	218	66.3	[97]
Ru/Rh-FeOOH@Ti ₃ C ₂ T _x	1 M KOH	10	223	63.6	[98]
Fe-NiTe-Ni ₁₂ P ₅ /NF	1 M KOH	100	340	66	[99]
Ni ₂ P/Fe ₂ P/Fe ₃ O ₄	1 M KOH	10	365	59	[100]
NiFe LDH/NiTe/NF	1 M KOH	50	228	51.04	[101]
NiHCF/Ni(OH) ₂	1 M KOH	10	242	48	[102]
Fe,Ni-CoS ₂	1 M KOH	10	242	35	[103]
W-NiS _{0.5} Se _{0.5}	1 M KOH	10	171	51	[104]
NiO/Co ₃ O ₄ @NC	1 M KOH	10	240	73	[105]
CoFeWO _x	1 M KOH	10	231	32	[106]
Co-Mo-P/CoNWs	1 M KOH	20	270	60	[107]
Ni/NiFeMoO _x /NF	1 M KOH	10	255	35	[108]
BaTiO ₃ @MOF-Fe/Co	1 M KOH	10	247	38.4	[109]
MoS ₂ /rFeNiCo ₂ O ₄	1 M KOH	10	270	39	[110]
NiCo _{2-x} Fe _x O ₄ NBs	1 M KOH	10	274	42	[111]
P/MoCo ₃ O ₄ @CC	1 M KOH	10	294	59.4	[112]
P-Fe ₂ NiO ₄ /CNS	1 M KOH	10	220	52.2	[113]
S-FeOOH/IF	1 M KOH	10	244	59	[114]
γ-FeOOH NAs/NF	1 M KOH	10	286	51	[115]
β-Ni ₂ P ₂ O ₇ /GNR	1 M KOH	10	320	68	[116]
LaNi _{9.5} Fe _{0.25} Co _{0.25} O ₃	1 M KOH	10	410	65	[117]
S _{5.84%} -LaCoO ₃	1 M KOH	10	364	126.7	[118]
LaCo _{0.5} Ni _{0.5} O ₃ HoMSs	1 M KOH	10	330	59	[119]
Ce-LaCoO ₃ (5.6%)	1 M KOH	10	450	112	[120]
La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O ₃ nanofibers	1 M KOH	10	345	188	[121]
Sr ₃ FeCoO _{7-δ}	1 M KOH	10	343	63	[122]

(Continued)

Catalyst sample	Electrolyte	Current density (mA·cm ⁻²)	Overpotential (mV)	Tafel slope (mV·dec ⁻¹)	Ref.
SnCo _{0.9} Fe _{0.1} -(OH) ₆	1 M KOH	10	300	42.3	[123]
h-Co _{0.34} Fe _{0.33} Ni _{0.33} -LDH	1 M KOH	10	195	53	[124]
Ni _{0.5} Co _{0.5} -MOF-74	1 M KOH	10	270	49	[125]
NiFeCe-LDH	1 M KOH	10	242	34	[126]
NiFeV-LDH	1 M KOH	10	287	32.7	[127]
Ni(OH) ₂ -TCNQ/GP	1 M KOH	100	340	71	[128]
NiFe _{1.2} Cr _{0.8} O ₄ /nickel support	1 M KOH	100	285	60	[129]
γ-CoOOH NS	1 M KOH	10	300	38	[130]
NiFe/NiCo ₂ O ₄ /NF	1 M KOH	10	340	45.5	[131]
NiO@Ni@Carbon fiber	1 M KOH	10	300	60	[132]
Co ²⁺ intercalated NiFe LDH	1 M KOH	10	265	47	[133]
Ni-Fe (oxy)hydroxide	1 M KOH	20	~ 320	24	[134]
Ni-Fe hydroxide	1 M KOH	20	~ 295	36.2	[135]
NiFe-LDH/NF	1 M KOH	10	251	46	[136]
CoFeNiO _x /NF	1 M KOH	10	240	—	[137]
MnCoOP	1 M KOH	10	320	52	[138]
Co ₂ P-PCA-800	1 M KOH	10	470	81.1	[139]
CoMnO@CNT/CNF	1 M KOH	10	374	66	[140]
Ni-MnO/rGO	0.1 M KOH	10	370	67	[141]
CoMn ₂ O ₄ /rGO	0.1 M KOH	10	310	56	[142]
CoMn ₂ O ₄ /carbon nanofibers	0.1 M KOH	10	337	82	[143]
Fe-CoP/Ni(OH) ₂	1 M KOH	10	206	32	[144]
Co ₃ V ₂ O ₈	1 M KOH	10	359	65	[145]
S-NiCoFe LDHs	1 M KOH	10	206	46	[146]
Ni _x Co _{3-x} O ₄	1 M KOH	10	—	66	[147]
PS-CoAl LDH	1 M KOH	10	248	61	[148]
Co ₃ O ₄ /MoS ₂	1 M KOH	10	230	45	[149]
FeCoO _x -VO-S	1 M KOH	10	—	21	[150]
Ni(Fe)OOH	1 M KOH	10	285	47	[150]

profiles, compared with PtO₂ nanoparticles (NPs) dispersed or Pt atoms embedded on the surface of NiO via atomic layer deposition, internally doped Pt atoms have extremely obvious advantages in promoting the active phase transformation (Figs. 7(e)–7(h)). This difference suggests that bulk doping is the key point to break the solidly maintained Ni–O bond in the lattice, resulting in relatively low η_{10} of 358 mV. DFT calculations revealed that the phase transition barrier from NiO to NiOOH can be reduced by 0.26 eV per formula unit (f.u.) under the condition of monatomic Pt doping, which demonstrates that doped Pt atoms weaken the nearby Ni–O bond and accelerate the solid phase transition from rock NiO to active layered γ -NiOOH, leading to a significant increase in its electrochemical mass activity (MA) that the MA of 0.5 wt.% Pt/NiO is 3 orders of magnitude higher than that of NiO (Figs. 7(i)–7(k)).

Ding et al. doped a series of metals (Mo, W, Fe, Ru, Co, Rh, and Ir) into the controlled crystal phase NiOOH using hydrothermal synthesis. The prepared catalysts (Co, Rh, and Ir-doped NiOOH) exhibited proper OER thermodynamics as well as kinetic properties with relatively low overpotential and Tafel slope. CV and electric transport spectroscopy (ETS) were simultaneously measured via the on-chip strategy, indicating that the electron transport characteristics across the intermediate state are highly

related to the oxidation/reduction of Ni^{III/IV}, and the high-valence Ni^{III/IV} is the catalytic active center of OER (Figs. 8(a)–8(c)) [157]. In addition, DFT calculations revealed the *in-situ* conductivity of the key intermediate states during OER. The results revealed that the activity of OER and intermediates conductivity show positive correlation, which can be explained by the double exchange (DE) interaction effect between adjacent metal ions with different d-orbital space (Figs. 8(d)–8(i)). Moreover, the two sets of redox peaks before OER showed phase transition from insulator to semiconductor/nickel-based hydroxide, which directly verified the prediction of DFT calculations. On that basis, the OER mechanism of doped transition metal catalysts was established to explain the relationship between the electrocatalytic activity and the conductivity of intermediate materials as well as the configuration and spin state of the electrons.

Li et al. used hydrothermal synthesis method to dope Zr atoms into Co₃O₄, which was then *in situ* grown on NF (Zr-Co₃O₄/NF) as an efficient OER electrocatalyst [158]. As shown in TEM and high resolution TEM (HRTEM) images, the morphology of nanowires was transformed into braided nanoarrays composed of nanowires and ultrathin nanosheets by doping Zr, providing a larger ECSA (Figs. 9(a)–9(d)). The η_{20} of Zr-Co₃O₄/NF catalyst was 307 mV, and the Zr-Co₃O₄/NF exhibited 20-h endurance in

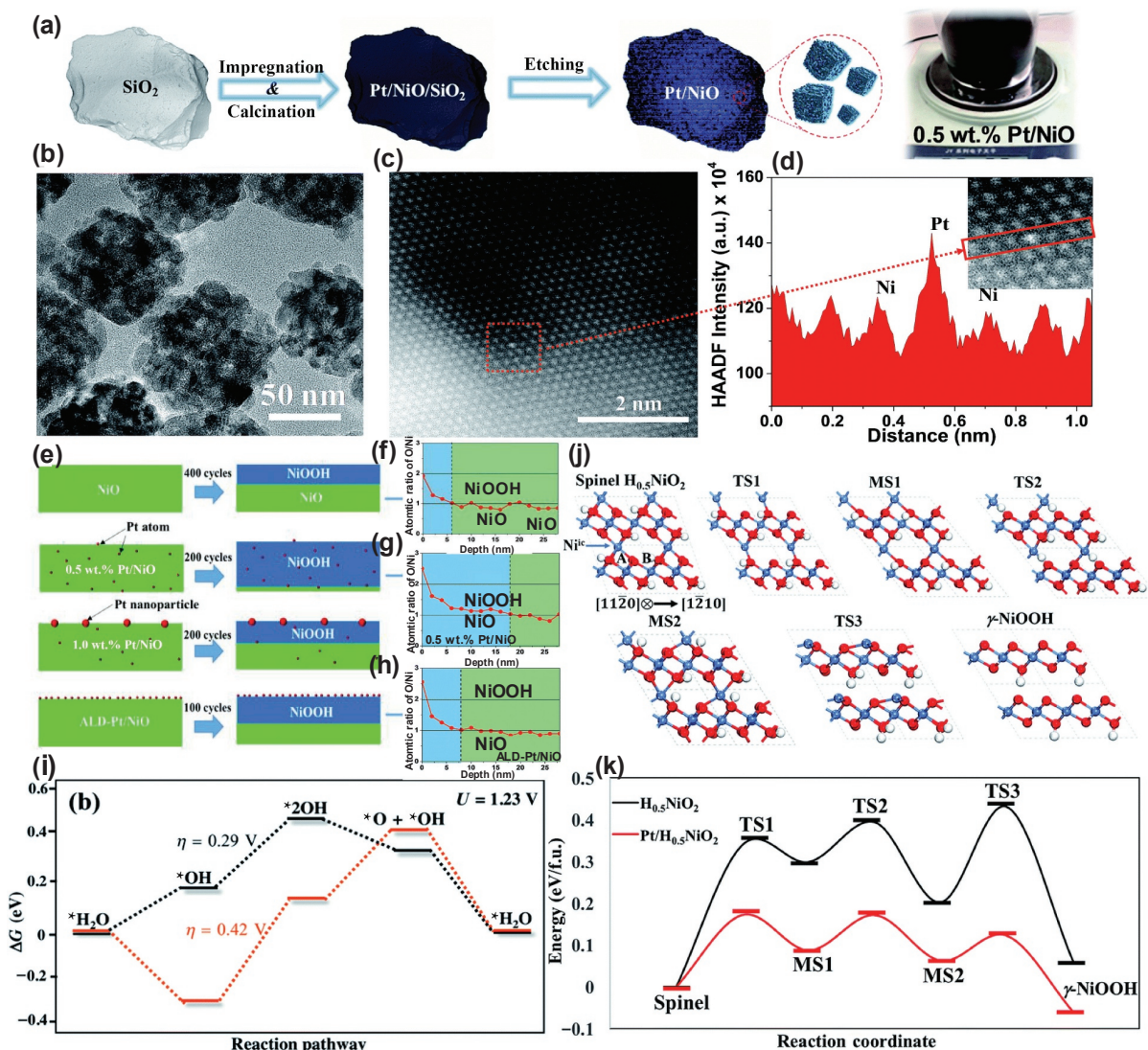


Figure 7 (a) Schematic diagram of synthesis process of bulk monatomic Pt doped NiO nanocubes. (b) TEM and (c) HAADF-STEM images and (d) HAADF signal analysis of 0.5 wt.% Pt/NiO. (e) Schematic diagrams of the phase transformation behavior. XPS profiles of (f) pure NiO, (g) 0.5 wt.% Pt/NiO, and (h) ALD-Pt/NiO. (i) Energy distribution image of OER at $U = 1.23\text{ V}$. (j) Key intermediate structures of $\text{H}_{0.5}\text{NiO}_2$. (k) Energy profiles of spinel $\text{H}_{0.5}\text{NiO}_2$ undergoing phase transition to $\gamma\text{-NiOOH}$ of pure/Pt-doped $\text{H}_{0.5}\text{NiO}_2$. (a)–(k) Reproduced with permission from Ref. [156], © Royal Society of Chemistry 2018.

1 M KOH. DFT calculations demonstrated that doped Zr atoms can regulate the electronic structure of Co_3O_4 and effectively reduce the Gibbs free energy of the RDS of OER, thus improving the electrocatalytic performance (Figs. 9(e)–9(h)). Furthermore, Gao et al. prepared a series of NiFe LDHs materials doped with different transition metals (Cr, Mn, and Co) by hydrothermal synthesis method and systematically studied the doping effect in OER by DFT calculations [159]. TEM and HRTEM images showed that the morphologies of the prepared samples were lamellar (Figs. 9(i) and 9(j)), and the Ni, Fe, and Cr atoms were uniformly distributed in the catalyst (Figs. 9(l)–9(o)). DFT calculations revealed that the doped transition metal atoms can enhance the catalytic performance by optimizing the electronic states of Ni and Fe atoms as active sites and greatly reducing the reaction energy barrier of the potential limiting step (Figs. 9(p) and 9(q)). In addition, the interfacial effect produced by monatomic doping is also beneficial to the binding of materials with intermediate species during OER. The intrinsic activity of OER is in the order of Cr-NiFe LDHs > Co-NiFe LDHs > Mn-NiFe LDHs > NiFe LDHs, and the optimal sample Cr-NiFe LDHs (0.1:3.2:0.9) exhibited outstanding stability and low η_{10} of 340 mV (Figs. 9(r) and 9(s)).

Recent studies have showed that transition metal Co oxides or

hydroxides are promising OER catalysts [160–162]. Bo et al. synthesized a Cr-doping ternary CoFeCr hydroxide composite supported on nickel foam which has a layer of monodispersed microspheres with a diameter of about 200 nm through a facile electrodeposition method [163]. Doping Cr promotes Co atoms to occupy octahedral positions and changes the electronic structure of Co. Co-based spinel phase not only has an optimized electronic structure, but also preferentially grows into clusters due to its cubic lattice structure [164–166], which has a significant impact on the transformation of the original material to the microspheres, making it an active phase for improving OER electrocatalytic activity [165, 167]. However, the spinel phase can only be obtained by Cr incorporation which proves that doping Cr is of great significance to optimize the catalyst morphology. Since doping Cr has a regulatory effect on the oxidation state of Co, the doped Cr was partially oxidized to a high valence state 6^+ after OER, and the generated electrons can be transferred to the Co valence state and significantly reduce ΔG ($\text{Co}^{3+} \rightarrow \text{Co}^{3+}$ on CoCrOOH), so that Co remains in a relatively low valence state Co^{3+} , resulting in accelerated process of $\text{M-O} + \text{OH}^- \rightarrow \text{M-OOH} + \text{e}^-$ by the evidence from Tafel slope and electrochemical impedance spectroscopy (EIS) plots. The η_0 and η_{100} of the $\text{Co}_5\text{Fe}_3\text{Cr}_2\text{-LDH}$ are as low as 200 and 270 mV, respectively (Table 2).

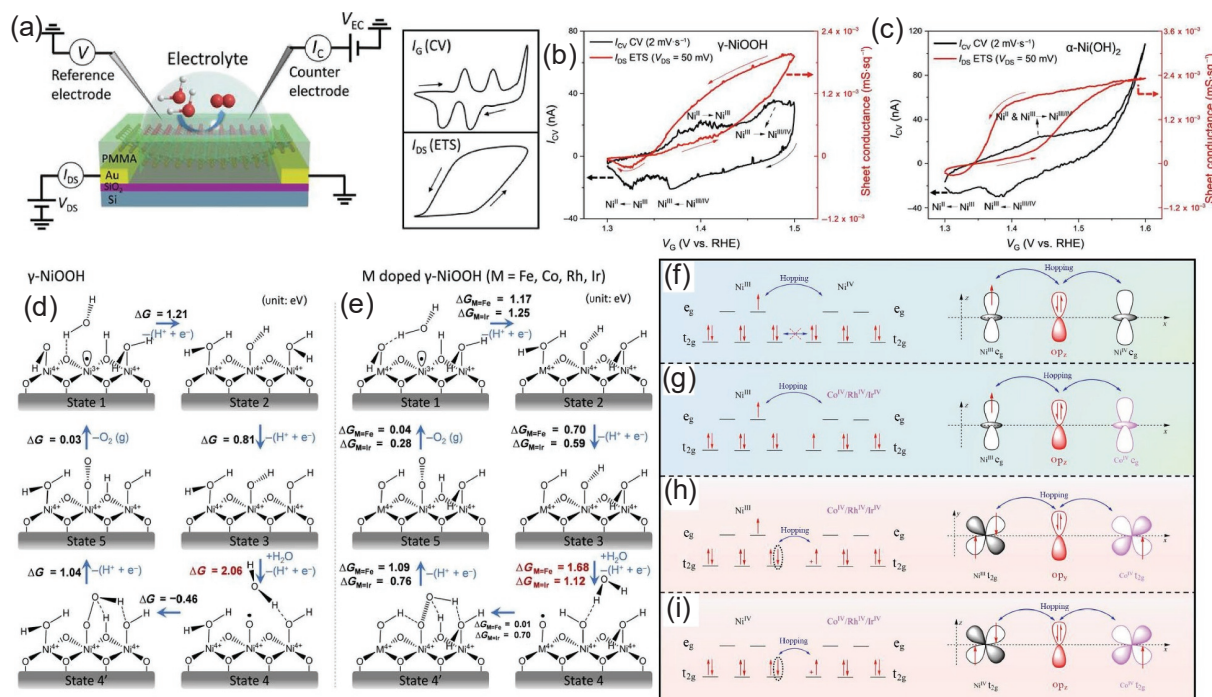


Figure 8 (a) Schematic diagram of experimental apparatus and typical test result of (b) γ -NiOOH and (c) α -Ni(OH)₂ for simultaneous measurement of on-chip CV and ETS. OER mechanism on (d) γ -NiOOH and (e) metal-doped γ -NiOOH (M: Fe, Co, Rh, Ir) samples. (f) and (g) DE interactions in γ phase lattices and their conductive pathways (left part: d orbital occupancy of two adjacent metal ions, right part: the DE interaction and the spatial orientation of the d orbital is taken into account). Schematic diagram of possible DE interaction of e_g orbitals between (f) Ni^{III} and Ni^{IV} , as well as (g) Ni^{III} and $Co^{IV}/Rh^{IV}/Ir^{IV}$. Schematic diagram of possible DE interaction or hopping pathway of t_{2g} orbitals between (h) Ni^{III} and $Co^{IV}/Rh^{IV}/Ir^{IV}$, as well as (i) Ni^{IV} and $Co^{IV}/Rh^{IV}/Ir^{IV}$. (a)–(i) Reproduced with permission from Ref. [157], © Wiley-VCH GmbH 2021.

Furthermore, the potential and microstructure can be satisfactorily maintained over 24 h. Although it has been reported that single atom catalysts (SACs) have high activity for various electrocatalytic reactions, these catalysts show limited OER performance. Recently, there is also related research on doping a variety of elements to overcome this shortcoming. Zhang et al. reported a bi-metal Ni and Fe single atom catalyst (Ni₄Fe-O-G SACs) anchored on two-dimensional (2D) graphene simultaneously through ions adsorption and graphene oxide (GO) template method [168]. Compared with Ni-N-G SAC and Ni(OH)₂/G, Ni-O-G SAC exhibited higher OER catalytic activity. Moreover, they used X-ray absorption near edge structure (XANES) and Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) spectra to check the potential bonding forms between Fe, Ni, and other elements of Ni₄Fe-O-G SACs. Strikingly, the coefficient effect between the co-existed single Ni and Fe atoms can adequately promote the charge transfer rate to notably boost the OER activity. The η_{10} of the optimal Ni₄Fe-O-G SAC (single Ni and Fe atoms with the appropriate ratio of 4) is as small as 247 mV in alkaline electrolyte, surpassing other NiFe based catalysts [167–169]. *O formation has been reported to be closely related to the oxidation of hydroxyl groups and the desorption of hydrogen protons [170], and electrons need to be transported from the hydroxide to the Ni site. Theoretical calculations revealed that compared with Ni-N-G SACs, the high oxidation state of Ni site in Ni-O-G SACs can significantly attract the electrons and improve the transport efficiency, thus reducing the barrier energy of ΔG_2 . Therefore, the OER activity can be significantly enhanced by this strategy of constructing O bonded Ni (Figs. 10(a)–10(e)).

Zhang et al. developed a novel theoretical calculation method named grand canonical quantum mechanics (GCQM), which is characterized by keeping the applied voltage constant, rather than keeping the number of electrons constant as usual quantum mechanics calculations, and thus can more accurately describe all

the reaction steps under applied potential including reactants, transition intermediates, and end products [171]. They also successfully introduced single center Co site on (210) surface of TiO₂ nanorods by co-doping strategy to synthesize stable Co-TiO₂ nanorod material without phase transition under alkaline OER conditions to get experimental data. Co-TiO₂ possesses almost the highest turnover frequencies among Co-based heterogeneous catalysts reported to date, achieving 6.6 ± 1.2 and 181.4 ± 28 s⁻¹ at 300 and 400 mV overpotentials, respectively. Based on the well-characterized structure of Co-TiO₂, the GCQM method was used to calculate its potential barriers of each catalytic step of OER under both AEM and LOM mechanisms. The theoretical calculation was found to be in exceeding agreement with the experimental results. The accuracy of the GCQM calculation method will contribute to the controlled synthesis of more advanced catalysts in future researches.

3.1.1.2 Multimetallic composites

According to the number of constituent elements, multimetallic composites can be divided into bimetallic, trimetallic, and tetrametallic systems. The combination of different metals provides possibility to adjust the physicochemical properties of valence electrons and electronic states of metal elements to produce favorable local coordination environment and more active centers due to the synergy effect between different metals [103, 172]. Thus, researchers are committed to synthesizing various multimetallic composites materials with satisfactory electrocatalytic performance [20, 57, 173]. For example, Zhuang et al. compounded monodisperse Au@Co₃O₄ with core-shell nanocrystal structure [174]. The Co element in the Co-based oxide was oxidized to a tetravalent state (Co^{IV}) before the start of water oxidation, which means that the formation of Co^{IV} centers is particularly important for OER. Therefore, when highly electronegative carriers such as Au atoms were doped into the catalyst, they can promote the oxidation of Co cations to a higher

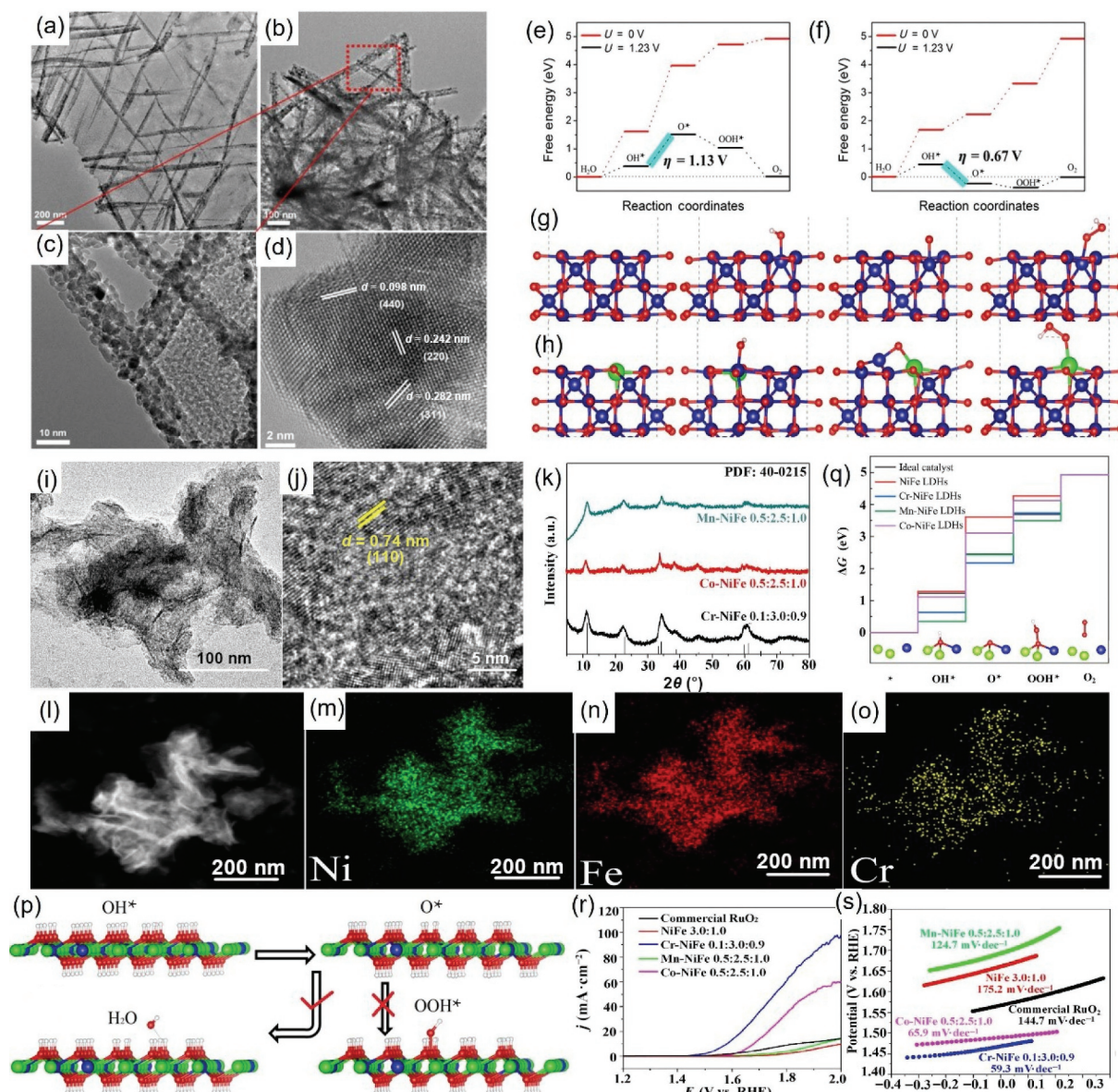


Figure 9 (a)–(c) TEM and (d) HRTEM images of the Zr- Co_3O_4 /NF. Energy spectrums of (e) Co_3O_4 and (f) Zr- Co_3O_4 . Schematic diagrams of theoretical adsorbent structures of (g) Co_3O_4 and (h) Zr- Co_3O_4 (red: O, blue: Co, green: Zr, and gray: H atoms). (i) TEM and (j) HRTEM images of Cr-NiFe LDHs (0.1:3.0:0.9). (k) X-ray diffraction (XRD) patterns of different transition metals doped NiFe LDHs. (l) HAADF-STEM image and (m)–(o) the corresponding elemental mappings of Cr-NiFe LDHs. (p) The OER progress of NiFe LDHs that the hydroxyl group at the active site firstly forms an OH^* intermediate, which then reacts with another hydroxyl group to form a H_2O molecule and adsorbed oxygen (O^*). The O^* group then combines with the hydroxyl group in solution to form a highly unstable OOH^* intermediate, which reacts with adjacent hydroxyl groups to regenerate O^* and water molecules which suggests that OER occurs only after terminal hydroxyl groups are converted to O^* . (q) Energy spectrums of un-doped/doped NiFe LDHs samples (red: un-doped, blue: Cr-doped, green: Mn-doped, purple: Co-doped NiFe LDHs, and black: ideal sample with energy barrier of 1.23 eV). (r) LSV curves. (s) Tafel plots. (a)–(h) Reproduced with permission from Ref. [158], © Elsevier B.V. 2021. (i)–(s) Reproduced with permission from Ref. [159], © Elsevier Inc. 2020.

state of Co^{IV} on the oxide surface and effectively elevate the catalytic activity. Contributed to this collaborative effect, the OER catalytic activity of $\text{Au}@\text{Co}_3\text{O}_4$ /NF is almost 7 times higher than the mixture of Au and Co_3O_4 nanocrystals, and 55 times as high as Au nanocrystals. Furthermore, Bell et al. investigated the theoretical overpotential for OER on Co_3O_4 and CoOOH surfaces by first-principles DFT calculations using the revised Perdew–Burke–Ernzerhof functional (RPBE) to describe the correlation and exchange [175]. The results showed that compared with pure Co (−1.17 eV), the d-band center of Co on Au substrate positively shifts by 0.74 eV, which results in a stronger Co–O bond and makes Co easier to be oxidized. Furthermore, the Hubbard-U corrected DFT calculations (DFT+U method) showed that both Co_3O_4 and $\beta\text{-CoOOH}$ are located at the weak binding branch of the OER volcano plot, which verifies the activity will be enhanced by this effect. The core–shell nanostructure can

provide “three-dimensional” close contact between metal core and oxide shell to maximize the interaction between doped precious metal Au atoms and Co_3O_4 . Furthermore, they also prepared Au NPs doped meso- Co_3O_4 ($\text{Au}/\text{meso-Co}_3\text{O}_4$) by nano casting using porous silica as hard template. Due to the high electronegativity and large specific surface area of doped noble metal Au as well as the preferential exposure of catalytic active lattice, the catalytic performance of the cobalt-based spinel structural material was significantly improved (Figs. 10(f)–10(i)).

However, the cost of doping noble metals like Au is relatively too high to be used on a large scale. Most studies are generally dedicated to reducing the number of precious metals, or even preparing transition metal-based catalysts to replace them. For example, Liu et al. rationally prepared an electrocatalyst with Fe doped layered nickel hydroxide nitrate nanosheets ($\text{Ni}_{3-x}\text{Fe}_x(\text{NO}_3)_2(\text{OH})_4$) via one-step solvothermal process [83]. As

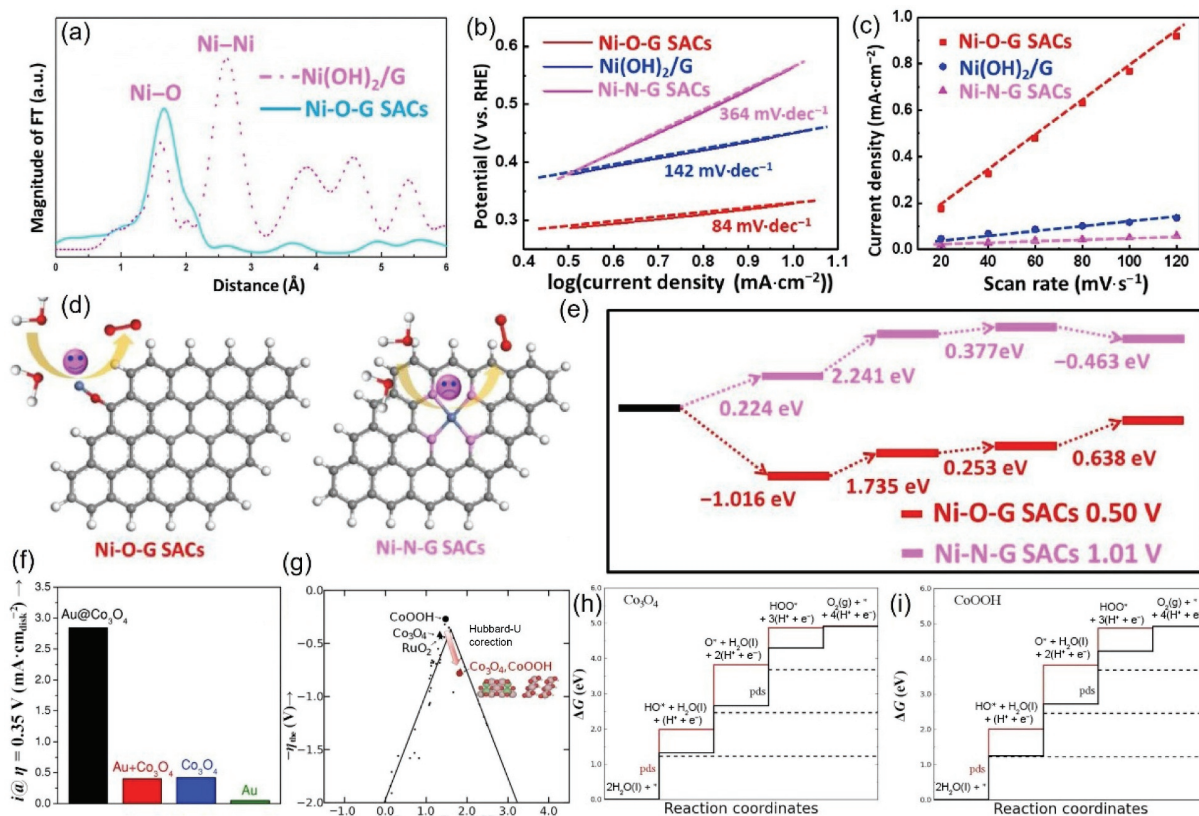


Figure 10 (a) K edge FT-EXAFS spectra of Ni. (b) Tafel plots. (c) Charging current density differences vs. scan rate. (d) Schematic diagram of different OER processes. (e) Calculated free-energy diagrams. (f) Catalyst activity at $\eta = 0.35$ V. (g) OER volcano plot. (h) Calculated OER free energy diagram with RPBE (black) and RPBE+U (red). (a)–(e) Reproduced with permission from Ref. [168], © Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences 2019. (f) Reproduced with permission from Ref. [174], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2014. (g)–(i) Reproduced with permission from Ref. [176], © American Chemical Society 2012.

shown in scanning electron microscope (SEM) and TEM images, the hierarchical architecture was loosely framed by adequately interconnected nanosheets like the well-defined flowers (2–5 μm) scattered by petals (Figs. 11(a) and 11(b)). The aggregated ultra-thin nanosheets with smooth surface grew unevenly towards messy directions enabling plenty of voids on the surface of the architectures, which is advantageous to electrocatalytic performance and the structure can be still maintained after Fe doping. The XPS spectra of Ni 2p and O 1s showed fractional phase structure change after OER, indicating that Ni species have been partially oxidized to OER-beneficial NiOOH. The beneficial synergistically electronic interaction between Ni and doping Fe in $\text{Ni}_{3-x}\text{Fe}_x(\text{NO}_3)_2(\text{OH})_4$ would gift the Ni-sites with high electron affinity, thus facilitating OH^- adsorption and favorable charge transfer. The η_{onset} of optimal $\text{Ni}_{2.85}\text{Fe}_{0.15}(\text{NO}_3)_2(\text{OH})_4$ (1.51 V vs. RHE) is much lower than $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (1.61 V vs. RHE) and IrO_2 (1.58 V vs. RHE). Furthermore, the η_{10} is 349 mV, which is 218 and 33 mV lower than that of $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ and IrO_2 , respectively. Moreover, the C_{dl} of $\text{Ni}_{2.85}\text{Fe}_{0.15}(\text{NO}_3)_2(\text{OH})_4$ (0.404 $\text{mF}\cdot\text{cm}^{-2}$) is significantly larger than pristine $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (0.132 $\text{mF}\cdot\text{cm}^{-2}$), suggesting its larger ECSA and more exposed catalytically active sites (Figs. 11(c) and 11(d)).

Besides bimetallic composites, recent studies have proved that the introduction of a third metal can further improve the OER catalytic activity [177–180]. For example, Yang et al. synthesized a trimetallic NiFeCr-LDH on conductive carbon paper (CP) through a straightforward one-step hydrothermal reaction (Fig. 11(e)) [181]. The unique micro-crystal structure of LDH material has both flexible and modular characteristics, which can realize the adjustment of electronic structure (Figs. 11(f) and 11(g)). Furthermore, the 3D CP substrate can provide larger specific

surface area to expose more effective reaction sites for the OER. It is easy to adjust the NiFeCr-LDH composition since Cr has a variety of oxidation states from +1 to +6 valence state and its multivalent nature provides more opportunities for strong electron binding and increases the synergy interaction among different metals. Since the addition of Cr atoms affected the electronic structure of Ni, the charge transfer ability of NiFe-based catalysts has been strikingly boosted as well [181–183]. When the ratio of the three element Ni:Fe:Cr was 6:2:1 (NiFeCr-6:2:1-LDH@CP), it exhibited the most satisfied OER catalytic activity. The η_{25} of NiFeCr-6:2:1-LDH@CP was as low as 225 mV and the Tafel slope was 69 $\text{mV}\cdot\text{dec}^{-1}$ in alkaline electrolyte (Fig. 11(h)). In addition, the catalyst microstructure and Cr were preserved in NiFeCr-LDH trimetallic composite after OER testing. However, many other metal elements, such as Ca, Zn, and Al, were easy to leach from the LDH structure with high reaction activity under the OER conditions, and therefore it is challenging to use these elements to prepare highly active electrocatalysts similar to NiFeCr-LDHs.

Michael et al. found Ni-Fe-Co mixed metal oxide (MMO) films as an OER catalyst with enhanced mass activity of 110 $\text{mA}\cdot\text{mg}^{-1}$ at 1.55 V (Figs. 11(i) and 11(j)) [46, 184]. For optimizing MMO morphology, the Ni-Fe-Co films with high specific surface area were loaded on Raney nickel carrier and sealed with aniline. MMO catalyst films supported on Raney Ni have better dispersed morphology, resulting in relatively high utilization rate of active sites. The *in-situ* X-ray absorption spectrum (XAS) analysis revealed that the function of Fe is to stabilize the 2+ oxidation state of Ni, while Co is to promote it to 3+ valence state, implying that the active site of OER is Fe not Ni. EXAFS results showed that the resulting Fe–O bond distance in $\text{Ni}_{1-x}\text{Fe}_x\text{OOH}$ is about 6%

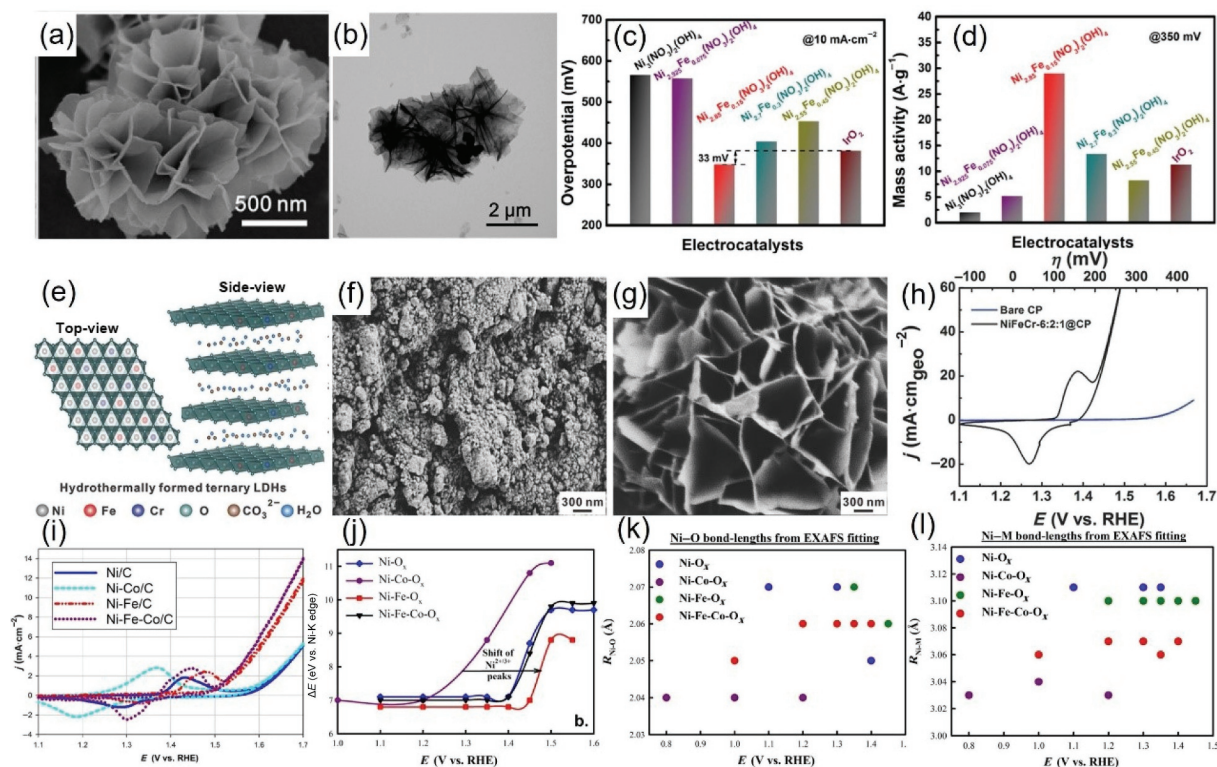


Figure 11 (a) SEM and (b) TEM images of $\text{Ni}_{2.85}\text{Fe}_{0.15}(\text{NO}_3)_2(\text{OH})_4$. Comparison of (c) η_{10} and (d) mass activity on $\text{Ni}_{3-x}\text{Fe}_x(\text{NO}_3)_2(\text{OH})_4$ with various x . (e) Schematic diagram of trimetal LDH crystal structure inserted with water and carbonate ions. SEM images of (f) NiFeCr-6:2:1 and (g) NiFeCr-6:2:1-F. (h) and (i) Polarization curves. (j) Graphical representation of shifts in Ni K-edge energy as a function of applied potential. Bond-lengths of (k) Ni-O and (l) Ni-M from EXAFS fitting. (a)–(d) Reproduced with permission from Ref. [185], © Hydrogen Energy Publications LLC 2019. (e)–(h) Reproduced with permission from Ref. [181], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018. (i)–(l) Reproduced with permission from Ref. [184], © American Chemical Society 2015.

smaller than that in the pure FeOOH lattice [46]. Therefore, the strain effect in MMO films due to the addition of Co shrinks the local geometry of Ni and Fe, resulting in an optimized binding energy between Fe and OER intermediates (Fe-OH/OOH bond strength) (Figs. 11(k) and 11(l)). Furthermore, since the conductive $\text{Ni}^{\text{III}}\text{OOH}$ phase could be formed due to the charge-transfer effect of Co, the Fe sites which are otherwise unattainable to transfer electrons in the uncondusive $\text{Ni}^{\text{II}}(\text{OH})_2$ host lattice are activated.

Highly active gelled FeCoW oxyhydroxide (G-FeCoW) was synthesized by Zhang et al. using a novel room-temperature sol-gel method, which is characterized by uniform mixing of precursors and controllable hydrolysis process that leads to the successful preparation of gelled oxyhydroxides materials with homogeneous distribution of metal atoms [186]. In addition to G-FeCoW, they also prepared gelled FeCo (G-FeCo) and annealed G-FeCoW (A-FeCoW) at 500 °C by the same method, and compared them with advanced LDH-NiFe and LDH-FeCo materials. Theoretical studies showed that W has diverse structures in its highest oxidation state and W doping enables to optimize the energy of OER intermediate, resulting in higher catalytic activity. The volcano diagram calculated by DFT+U indicated that the limit kinetic barrier of G-FeCoW is the smallest, and the tunability of the adsorption energy after alloying can significantly enhance the OER activity. In addition, total electron yield (TEY) XAS spectra revealed that the synergistic effect between W, Fe, and Co resulted in a favorable local coordination environment and electronic structure that optimizes the energetics of OER. These advantages make the η_{10} of G-FeCoW can attain ultra-low 191 mV, while its mass activity and TOF exhibited extremely high 1.5 s⁻¹ and 3,500 A g⁻¹, respectively, which are superior to other samples (Table 2).

Gao et al. prepared a multi-metal doped CeO_2 composite ($\text{CeO}_2/\text{NiFeCo}$) using homogeneous precipitation method (Fig.

12(a)) [187]. TEM and HRTEM images revealed that many distinct fish-scale lamellar structures are stacked, and the lamellar folds are uniform, leading to the formation of more active sites (Figs. 12(b) and 12(c)). NiFeCo multimetallic ions doping can optimize the chemical structure of CeO_2 , so that metal ions can be more simply embedded into the oxygen vacancies of CeO_2 and provide more active sites, leading to the improvement of electron transfer ability. In addition, the $\text{CeO}_2/\text{NiFeCo}$ composite exhibited metastable amorphous state and can be transformed into different active states during OER. The OER mechanism of amorphous materials is lattice oxygen oxidation mechanism (LOM), which can effectively avoid the adsorption process of intermediates in the adsorbate release mechanism, so as to promote the OER process in time. The η_{10} of $\text{CeO}_2/\text{NiFeCo}$ was 260 mV, which even has a competitive advantage over commercial RuO_2 catalysts (Figs. 12(d)–12(f)). Furthermore, Yang et al. used co-doping strategy to synthesize Ru-based catalysts $\text{Ni}_x\text{Co}_y\text{Ru}_{1-x-y}\text{O}_2$ with different molar ratios (1:1–1:1.5) of doped Ni and Co, which effectively reduced the amount of noble Ru (Fig. 12(g)) [188]. Compare with pure RuO_2 , the optimum sample $\text{NiCo}_{1.5}\text{Ru}-90$ shows superior OER electrocatalytic activity with Tafel slope of merely 32 mV-dec⁻¹ and better long-time stability, which can be attributed to the synergistic effect between the doped metal atoms in the catalyst lattice (Figs. 12(h)–12(j)). XRD, SEM, and TEM revealed that the lattice phase of RuO_2 did not change during the co-doping process, while the Ru vacancies and the valence state of Ru increased, resulting in the modification of the host metals, which led to a positive correlation between the catalytic performance and the molar ratio of Ni/Co (Figs. 12(k)–12(n)).

As for tetrametallic system, Yang et al. found that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ce}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) had excellent OER catalytic activity in alkaline media, even one order of magnitude higher than the most advanced iridium oxide. They selected the $\text{A}_{1-x}\text{A}'_x\text{B}_y\text{B}_{1-y}\text{O}_3$ perovskite structure (A or A' is rare earth metals or alkaline earth

Table 2 Comparison of OER performance on LDHs

Catalyst sample	Electrolyte	Current density (mA·cm ⁻²)	Overpotential (mV)	Tafel slope (mV·dec ⁻¹)	Ref.
NiFe-LDH/Co,N-carbon nanotubes	1 M KOH	50	~ 390	60	[134]
Cr-NiFe LDHs	1 M KOH	10	340	59.3	[159]
Co ₃ Fe ₃ Cr ₂ -LDH	1 M KOH	10	200	—	[163]
NiFeCr-6:2:1-LDHs	1 M KOH	10	280	131	[181]
NiFeCr-6:2:1-LDH@CP	1 M KOH	25	225	69	[181]
Ni-Fe LDH DSNCS	1 M KOH	20	246	71	[183]
Ni-Fe LDH SSNCs	1 M KOH	20	261	117	[183]
v-L-LDHs	1 M KOH	100	230	37.1	[229]
NiFe LDH@NiCoP/NF	1 M KOH	10	220	48.6	[232]
Ni _{2/3} Fe _{1/3} -rGO	1 M KOH	10	240	40	[233]
NiFe-LDH	0.1 M KOH	10	350	56	[234]
CoNiAl-LDH	1 MKOH	10	360	53.8	[235]
NiCoAl-LDH	0.1 M KOH	10	426	75.4	[236]
ZnCo LDH	1 M KOH	10	540	83	[237]
CoNi-LDH@PCPs	1 M KOH	10	350	58	[238]
NiCo ^{III} Fe-LDH/N-GO	0.1 M KOH	10	~ 310	56.8	[239]
FeCoNi hydroxide	1 M KOH	10	< 350	52.7	[240]
NiFeMn LDH/CP	1 M KOH	20	289	47	[241]
Ni ₃ FeAl _{0.91} -LDH@NF	1 M KOH	20	304	57	[242]
NiCoFe-LDH	0.1 M KOH	10	470	120	[243]
NiFe LDH@CNT/CP	1 M KOH	10	247	31	[244]
NiV LDH/GC	1 M KOH	10	318	50	[245]
NiGa LDH@CP	1 M KOH	10	450	117	[246]
CoCr LDH/GC	0.1 M KOH	10	340	81	[247]
Exfoliated NiCo LDH@CP	1 M KOH	10	367	40	[248]
Exfoliated NiFe LDH/GC	1 M KOH	10	300	40	[249]
Exfoliated CoCo LDH/GC	1 M KOH	10	350	45	[249]
Exfoliated NiCo LDH/GC	1 M KOH	10	330	41	[249]
NiFe hydroxide/GC	1 M KOH	10	240	39	[250]
Ni _x Co _{3-x} O ₄ nanowires/NF	1 M KOH	10	337	75	[251]
Fe-doped Co ₃ V ₂ O ₈ /GC	1 M KOH	10	307	36	[252]
NiFe-LDH/GP	1 M KOH	50	350	32	[253]
Ni-Fe LDH	1 M KOH	20	~ 330	48.4	[254]
CoFe LDHs-Ar nanosheets	1 M KOH	10	266	37.85	[255]
AE-CoFe LDH	1 M KOH	10	300	41	[256]
NiFe LDH/NiCo ₂ O ₄ /NF	1 M KOH	10	290	53	[257]
NiFe LDH@NiCo ₂ S ₄ /NF	1 M KOH	10	201	46.3	[258]
NiFe LDHs@FeOOH/NF	1 M KOH	10	208	42	[259]
NiFe LDH@Co _{0.85} Se/NF	1 M KOH	10	270	57	[260]
Ni-Fe LDH	1 M KOH	20	~ 295	56	[261]
Ni-Fe LDH nanosheets@defective graphene	1 M KOH	20	240	52	[262]
Fe ³⁺ -containing Ni-Fe LDH	1 M KOH	20	~ 255	40.3	[263]
Ru-doped Ni-Fe LDH	1 M KOH	20	~ 243	—	[264]
Dodecyl sulfate-intercalated Ni-Fe LDH	1 M KOH	20	~ 310	36	[265]
N-CoFe LDHs/NF	1 M KOH	10	233	—	[214]
FeNi-LDH/NF-1.0	1 M KOH	10	177	69.7	[223]
NiFe ₂ O ₄ /NiFe LDH-25	1 M KOH	100	190	21.5	[266]
CoMn-LDH/CFC-50	0.1 M KOH	10	258	49	[267]

(Continued)

Catalyst sample	Electrolyte	Current density ($\text{mA}\cdot\text{cm}^{-2}$)	Overpotential (mV)	Tafel slope ($\text{mV}\cdot\text{dec}^{-1}$)	Ref.
CoCo-LDH/CFC	0.1 M KOH	10	334	84	[267]
CoMn-LDH	1 M KOH	10	334	43	[268]
CoMn-LDH/CNT	0.1 M KOH	10	355	45	[269]
NiFe-LDH/Co,N-CNF	0.1 M KOH	10	312	60	[270]
$\text{Co}_3\text{Mn-LDH/MWCNT}$	1 M KOH	10	~ 300	73.6	[271]
n-NiFe LDH/NGF	0.1 M KOH	10	337	45	[272]
CoNi-LDH/Fe-PP-LBL	1 M KOH	10	264	37.6	[273]
FeNi_3Co_2 LDH	1 M KOH	10	~ 215	42	[274]
ZnCo-LDHnanosheets	0.1 M KOH	10	~ 480	101	[275]

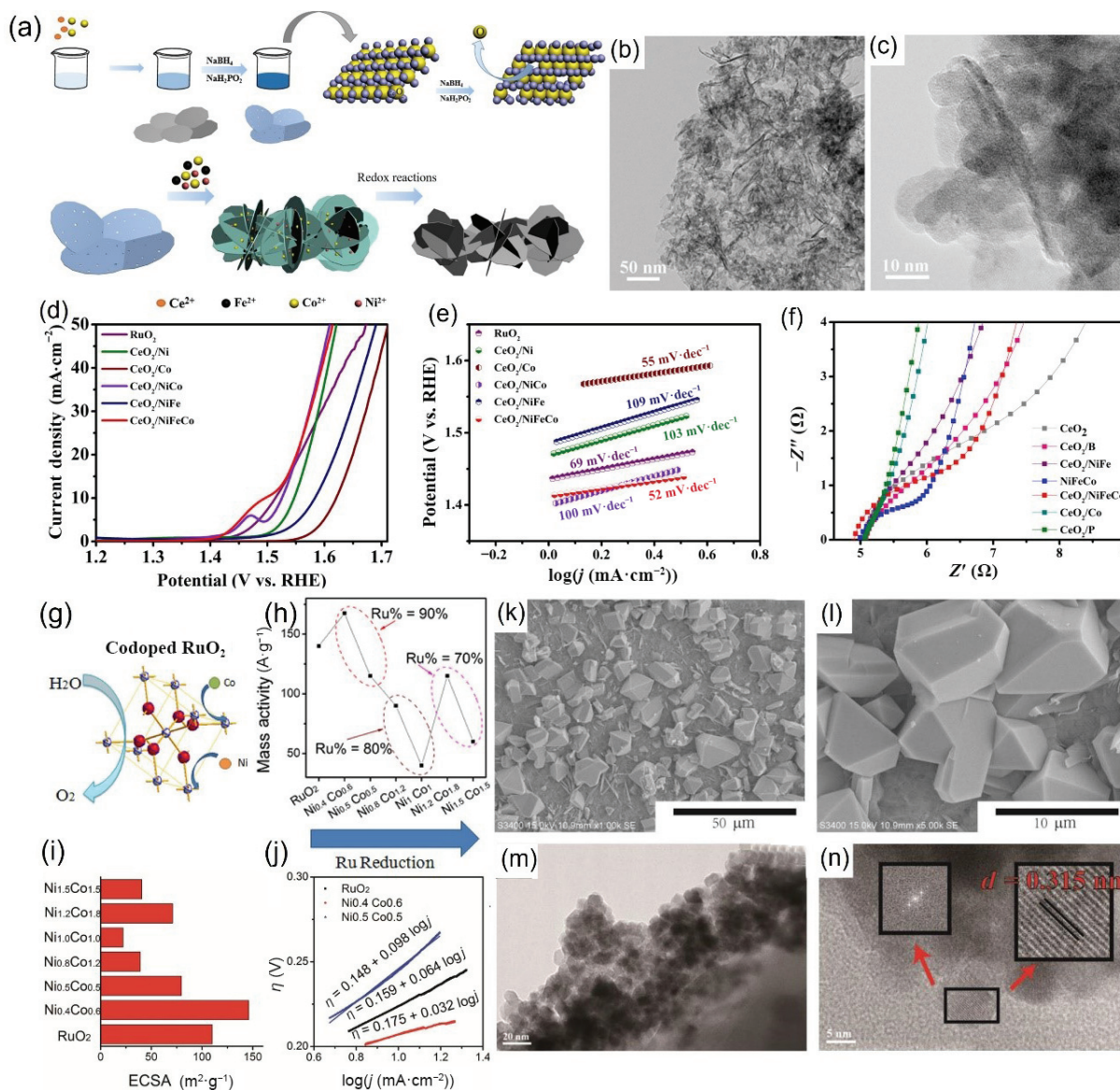


Figure 12 (a) Schematic diagram of synthetic process of CeO₂/NiFeCo. (b) TEM and (c) HRTEM images of fish-scale CeO₂/NiFeCo. (d) LSV curves, (e) Tafel plots, and (f) EIS spectra. (g) Illustration of Ni and Co co-doped RuO₂. (h) Mass activity at 1.7 V and (i) corresponding ECSA. (j) Tafel plots. (k) and (l) SEM and (m) and (n) TEM images of Ru_{0.9}(NiCo_{0.5})_{0.1}O₈ (inset in (n): fast Fourier transforms (FFTs), HRTEM, and the lattice fringe images of the selected regions). (a)–(f) Reproduced with permission from Ref. [187], © IOP Publishing Ltd. 2021. (g)–(n) Reproduced with permission from Ref. [188], © American Chemical Society 2019.

metals, and B or B' is transition metals) to systematically study more than 10 transition metal oxide perovskites, and successfully predicted the high catalytic activity of BSCF [189]. The results showed that the specific OER activity of perovskite oxides took on a volcanic shape with the filling of B cations on the surface. They reported a unique OER activity design principle that an almost

unified occupancy of the e_g orbital of surface transition metal ions and high covalency of bonding with oxygen can boost the intrinsic OER catalytic activity of perovskite metal oxides. The analysis was based on the molecular orbital bonding framework. Since the self-orbital of the surface transition metal ions was involved in bonding with the surface anionic adsorbents, its occupation can

greatly affect the binding of oxygen-related intermediates at the B site, thus affecting OER activity. For the right branch of the volcano, the RDS is at the B position ion ($B^{(m+1)+}-O^{2-} + OH^- \rightarrow B^{(m)+}-OOH^- + e^-$), whereas for the left branch of the volcano, the deprotonation of hydroxyl to form peroxide ions ($B^{(m)+}-OOH^- + OH^- \rightarrow B^{(m+1)+}-O_2^{2-} + H_2O + e^-$) may be the RDS. OER activity can be improved with increasing covalent mixing between B-site ions and O atoms of oxides under a constant e_g filling, where the active redox couple is located at the top of the O-2p band. Greater covalency between B-site and oxygen, where the active redox couple of the B-site ion has a larger O-2p character and promotes the charge transfer between adsorbates (like O_2^{2-} and O^{2-}) and surface cations in the RDSs of OER, results in superior OER activity. The above discussion shows that making e_g filling close to unity effectively promotes the RDS, resulting in higher OER activity.

3.1.2 Nonmetallic element doping

Besides metal atoms doping, nonmetallic heteroatoms doping provides another promising avenue to synthesize advantageous OER catalysts, which can substantially elevate catalytic activity, acid resistance, and durability [114, 190]. For example, Gao et al. doped N into MoS_2 by a simple hydrothermal method, and then performed surface reconstruction using electrochemical oxidation to construct $MoO_x@N$ -doped MoS_{2-x} with unique heterostructure and outstanding OER catalytic performance (Fig. 13(a)) [191]. Different content N-doping samples (N0- MoS_2 , N1- MoS_2 , N2- MoS_2 , and N3- MoS_2) were studied by changing the dosage of dicyandiamide, and results found that the η_{10} of $MoO_x@N3$ -doped MoS_{2-x} is merely 270 mV. N doping not only improves the conductivity of MoS_2 , but also promotes the charge transfer and makes Mo present a relative high state (Mo^{4+} – Mo^{6+}) (Fig. 13(b)), which is beneficial to the OER. Furthermore, the amorphous MoO_x formed in the outer layer of N- MoS_2 provides sufficient catalytic active sites, and the formed amorphous interface requires low interface energy, which is conducive to structural stability and charge transfer. DFT calculations revealed that since the charge of dopant (N) is different from that of host (S), while the crystal needs to be in equilibrium with no net charge, the substitution of S by N can weaken the adsorption energy barrier for the intermediates O^* and OH^* on the active site (Fig. 13(c)).

Li et al. prepared Co-based LDHs using polystyrene (PS) microspheres as template (PS@Co LDH) by a simple solvothermal method followed with annealing in argon atmosphere at 600 °C for C doping [192]. The unique hollow sphere structure endows multilayer C-Co/ Co_3O_4 with high specific surface area that can not only speed up the mass transfer rate, but also provide sufficient reactive sites. Furthermore, the metal Co and doped C atoms provide satisfactory electrical conductivity. Based on these advantages, the C-Co/ Co_3O_4 can achieve low η_{onset} (149 mV) and η_{10} (352 mV), which is even lower than that of commercial RuO_2 (η_{10} = 364 mV).

Simple hydrothermal treatment method was frequently carried out to dope carbon that makes defective carbon react with nitrogen-containing precursors such as a urea, ammonia, and so on. Nitrogen functional sites in the carbon skeleton can effectively adsorb metal precursors and promote the growth of metal oxide or hydroxide nanostructured particles or crystals on the surface [193–195]. Synthesized metal-carbon hybrid materials show a strong coupling effect, which can modulate the electronic and chemical structures between the metal active site and the carbon matrix, resulting in a synergistic effect in favor of OER. For example, in the Co_3O_4 embedded in graphitic carbon nitride (GCN) tubular nanostructure composite ($Co_3O_4@GCN$ TNS), the strong synergistic effect between Co_3O_4 and GCN led to higher

reaction activity and faster ion and electron conduction rate. $Co_3O_4@GCN$ TNS exhibited extremely low overpotential (0.12 V) and satisfactory current density (147 $mA\cdot cm^{-2}$) that are even better than commercial IrO_2 and RuO_2 . Furthermore, Yu et al. used solvothermal method to prepare 3D NiCoFe hydroxide/N-doped C (NiCoFe-NC) nanoplates (Fig. 13(d)) [196]. The typical morphology of ultra-thin nanoplates with an average particle size of 15–30 nm is shown in TEM and HRTEM images (Figs. 13(e) and 13(f)). The η_{10} of NiCoFe-NC is 250 mV, which can be even comparable to the benchmark RuO_2 (Figs. 13(g)–13(j)). Excellent catalytic performance can be attributed to synergistic effect between Fe^{III} species and Ni/Co metal centers in Ni-Co hydroxides. The addition of N-doped carbon hydrogel not only provided excellent multidimensional electrical conductivity, but also possessed high wettability, which facilitated the adsorption of water molecules, resulting in easier occurrence of OER.

Based on the theory of Butler–Volmer (BV) equation and the first principles, Li et al. performed DFT calculations to analyze the OER performance on Co_3O_4 doped with different elements (Figs. 14(a)–14(h)) [162, 192]. They used conductivity and band gap characteristics to describe the reaction energy barrier and catalytic activity of different materials. The results demonstrated that the band gap, electron/ion migration barrier, and ΔG of the adsorption to the reaction intermediates were significantly reduced after doping C atoms (Figs. 14(i)–14(r)). Additionally, they synthesized the optimal C- Co_3O_4 sample using a low-energy plasma injection method, which can regulate the vapor deposition process so that C atoms were doped in the appropriate sites to achieve optimal electrocatalytic performance. The C- Co_3O_4 exhibited an η_{10} of 235 mV, which is obviously lower than unmodified sample (423 mV).

As for graphene hydrogels, the functional groups such as –COOH and –OH can not only interact with water molecules through hydrogen bonding but also act as anchor sites to fix active nanoparticles [77]. Chen et al. prepared NiCo double hydroxides on N-doped graphene hydrogels (NG-NiCo) by hydrothermal treatment at 150 °C [197], which exhibited a 3D porous interconnected network. The η_{onset} of NG-NiCo (350 mV) was the most negative while its current density (145.3 $mA\cdot cm^{-2}$) at η = 400 mV was the highest among the tested samples. The functional groups of NG-NiCo can absorb water molecules efficiently in the first step, and the profoundly expanded electrode/electrolyte interface can provide more active sites for the second step and allow an effective oxygen evolution in the third step, thus resulting in boosted OER performance. Similarly, Chen et al. synthesized porous N-doped graphene-NiCo $_2O_4$ (PNG-NiCo) 3D hybrid film via similar process to NG-NiCo (Fig. 15(a)) [198]. The addition of NiCo $_2O_4$ between the graphene sheets could result in the formation of OER-beneficial out-of-plane pores (Fig. 15(b)), which facilitated mass transfer and infiltration of electrolyte, while small in-plane pores provided a high specific surface area and a shorter diffusion path length (Fig. 15(c)). The fractional porosity of PNG-NiCo was confirmed by nitrogen adsorption and methylene blue (MB) experiments (Fig. 15(d)). Fourier transform infrared (FTIR) spectrum of PNG-NiCo (Fig. 15(e)) showed functional groups of both graphene (–COOH and C–O(N)) and NiCo $_2O_4$ (Ni–O and Co–O), which resulted in double active site mechanism, contributing to the improvement of catalytic activity. The η_{onset} and η_5 of PNG-NiCo were 310 and 373 mV, respectively. Moreover, the anode current attenuation of PNG-NiCo was less than 10% after operation for 10 h.

Perovskite oxides have favorable structure and composition conducive to OER as well as preeminent intrinsic catalytic activity. Zhou et al. synthesized a tetragonal $SrCo_{0.95}P_{0.05}O_{3-\delta}$ perovskite (SCP) by non-metal P doping in $SrCoO_{3-\delta}$ (SC)

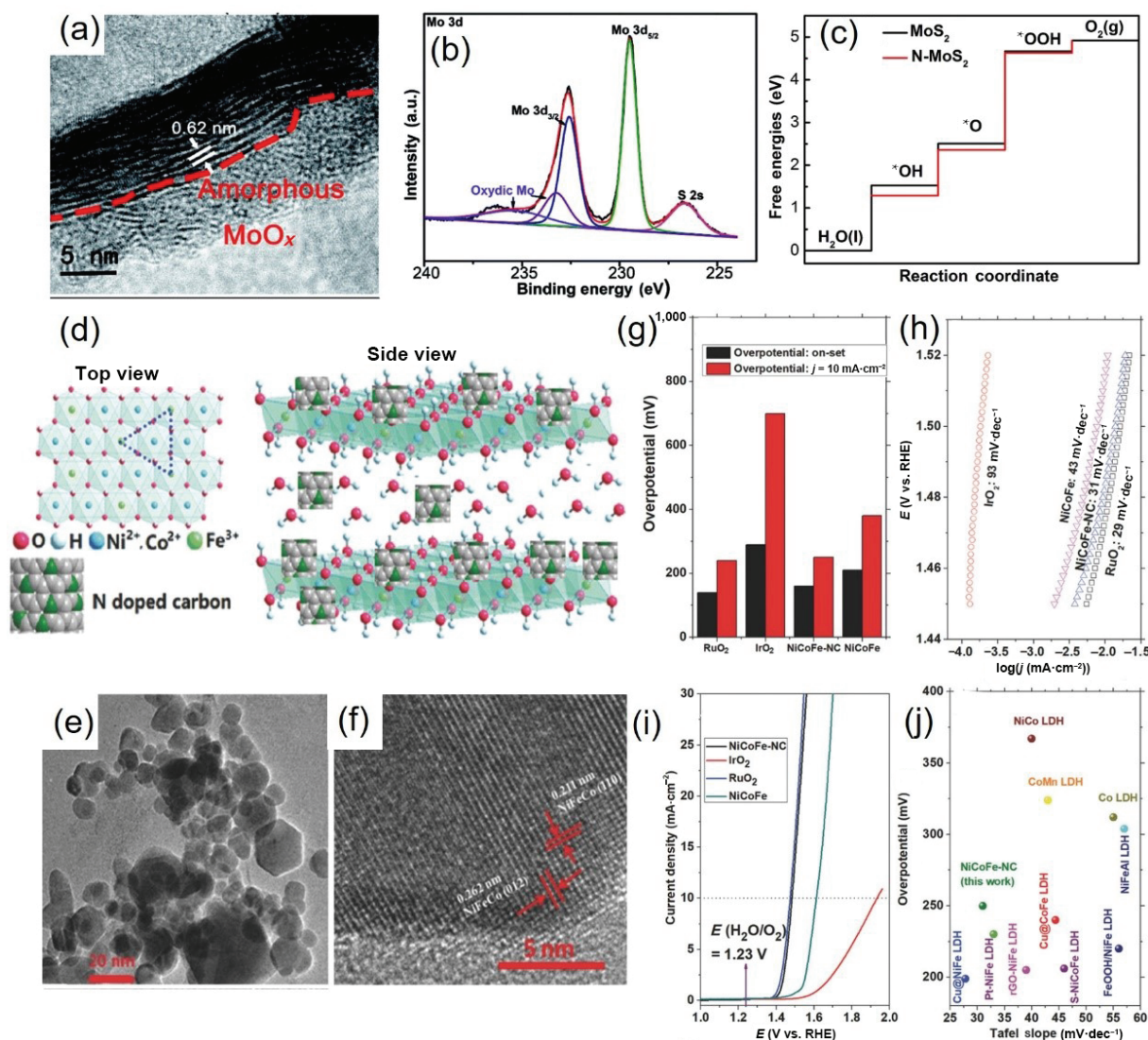


Figure 13 (a) HRTEM image and (b) XPS spectrum of Mo orbitals of $\text{MoO}_x\text{@N-doped MoS}_{2-x}$. (c) ΔG of the OER steps. (d) Crystal structure of NiCoFe-NC with intercalated H_2O and N-doped C. (e) TEM and (f) HRTEM images of NiCoFe-NC. (g) The η_{onset} and η_{10} histogram. (h) Tafel plots. (i) LSV curves. (j) Comparison image of η_{10} and Tafel slope. (a)–(c) Reproduced with permission from Ref. [191], © Royal Society of Chemistry 2019. (d)–(j) Reproduced with permission from Ref. [196], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018.

through solid-state reaction route (Figs. 15(f) and 15(g)) [199]. Compared to the undoped SC, SCP showed more outstanding OER performance, which can be attributed to higher electrical conductivity and larger amount of $\text{O}_2^{2-}/\text{O}^-$ species. Notably, the η_{10} and C_{dl} of SCP were 0.48 V and $1.53 \text{ mF}\cdot\text{cm}^{-2}$, respectively, which were lower than 0.52 V and $2.36 \text{ mF}\cdot\text{cm}^{-2}$ for SC, and the electrical conductivity of SCP ($\sim 312 \text{ S}\cdot\text{cm}^{-1}$) was remarkably higher than SC ($\sim 2 \text{ S}\cdot\text{cm}^{-1}$) at 25°C . During the 1,000 cycles accelerated durability test (ADT), SCP exhibited a unique activation process that results in enhanced activity (η_{10} decreased by $\sim 19 \text{ mV}$ and ECSA increased by $\sim 187\%$), while SC inactivated slightly (η_{10} increased by $\sim 18 \text{ mV}$ and ECSA increased by $\sim 89\%$). As confirmed by HRTEM, energy dispersive X-ray (EDX), and XPS analysis, the favorable activation phenomenon was closely related to the changes in their surface structure and composition during ADT. The formation of a very thick amorphous layer accompanied by massive leaching of Sr ions can be observed on the SC surface, while a relatively thin protective layer of active A-site (Sr) deletion was formed on the SCP surface, and the A-site defect effectively generated surface oxygen vacancies and Fe^{4+} species, which are mainly responsible for OER activation [200]. In addition, the stable tetragonal continuous structure inside SCP can prevent large loss of Sr ions from leaching and inactivation, and provide

conductive support for the surface A-site-deficient structure (Figs. 15(h)–15(k)). Furthermore, the unique activation process of SCP can also be observed in $\text{Sr}(\text{Co}_{0.8}\text{Fe}_{0.2})_{0.95}\text{P}_{0.05}\text{O}_{3-\delta}$ (SCFP) and $\text{SrCo}_{0.95}\text{S}_{0.05}\text{O}_{3-\delta}$ (SCS) and other P and S doped perovskite oxides [200–203].

3.1.3 Metallic and nonmetallic element dual doping

It is well known that the constitutive OER activity is mainly determined by the binding strength between electrocatalysts and O-containing reaction intermediates, which in turn is determined by the electronic structure of the active center. In this regard, element doping is considered to be a simple and effective method to adjust the electronic structure of the active center. Metal cationic doping can optimize the adsorption capacity of O-containing intermediates and promote the electrical conductivity, while the nonmetallic anion doping can not only optimize the adsorption energy of the reaction intermediates, but also ensure the durability of the electrocatalyst as well. Therefore, metal–nonmetal dual-doping strategy can be used to regulate the electronic structure and ensure the persistence more effectively through the synergistic effect between the cationic and anionic dopants, which is expected to further boost the OER electrocatalytic activity. For example, Zhao et al. constructed a

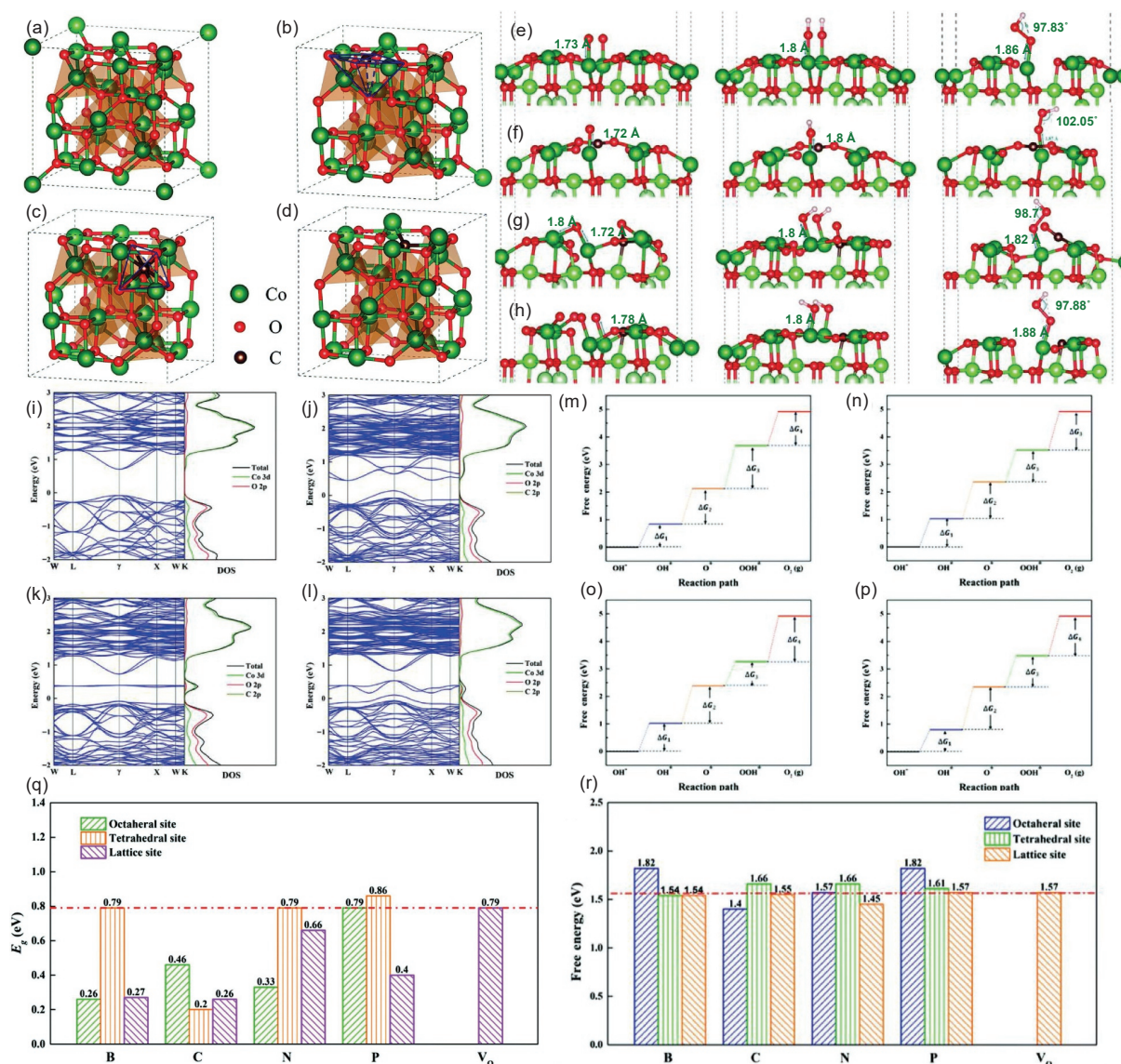


Figure 14 Schematic diagrams of relaxed configurations of (a) Co₃O₄ unit-cell and C occupying (b) an octahedral site, (c) a tetrahedral site, and (d) a lattice oxygen site. (e)–(h) Adsorbate configurations, (i)–(l) band structures and density of states (DOS), and (m)–(p) free energy diagrams of ((e), (i), and (m)) pure Co₃O₄, Co₃O₄ with C-doped in ((f), (j), and (n)) octahedral site, ((g), (k), and (o)) tetrahedral site, and ((h), (l), and (p)) Co₃O₄ with C replacing lattice oxygen atoms. (q) Calculated band gap and (r) RDS free energy value histograms of different heteroatoms doped Co₃O₄ samples. (a)–(r) Reproduced with permission from Ref. [162], © Royal Society of Chemistry 2019.

unique cactus-like Mn/N dual-doped Co₃O₄ on NF (N-Mn-Co₃O₄/NF) by hydrothermal synthesis and subsequent N₂ plasma treatment (Fig. 16(a)) [204]. To be specific, the traditional hydrothermal synthesis method was firstly used to doping Mn element, and the nanowire morphology (Figs. 16(b) and 16(c)) was prepared by optimizing the appropriate hydrothermal reaction time, which endowed the material with more accessible active reaction sites and outstanding mechanical stability. During the subsequent N₂ plasma treatment, N was successfully doped and Mn-doped cobalt carbonate hydroxide (CCH) was transformed into Mn-doped Co₃O₄. Due to the synergistic advantages of metal and non-metal doping, the intrinsic activity, conductivity, and mass/ion diffusion rate of the final N-Mn-Co₃O₄/NF electrode were further enhanced. These advantages enable the η_{50} and η_{100} of N-Mn-Co₃O₄/NF to achieve the ultra-low levels of 302 and 320 mV, respectively, while maintaining with no significant attenuation during stability tests of up to 40 h. Feng et al. focused on using Mn and S dual-doping strategy to optimize low-cost Co₃O₄ material (Mn-Co₃O₄/S) with ideal 3D electronic structure, and solved its disadvantages of poor electrical conductivity and few exposed active sites by the solution method

and ion exchange process (Fig. 16(d)) [205]. They found that the electronic structure of Co center was modified by Mn doping, which greatly increased the intrinsic activity of the active site in Co₃O₄. The introduction of S can enhance the conductivity of Co₃O₄, and provide sufficient proton adsorption sites. It is worth mentioning that the dual-doping of Mn and S also effectively increases the proportion of Co³⁺ and accelerates the dynamic process of four-electron transfer, thus improving the catalytic activity. The η_{10} , η_{100} , and η_{300} of the optimal Mn/S doped Co₃O₄ sample can be as low as 330, 407, 460 mV, respectively, and the outstanding catalytic performance can be well maintained after 20 h. Chen et al. co-doped Cr and N into earth-rich inverse spinel Fe₃O₄ nanoparticles on NF (Cr-Fe₃O₄-N/NF) by simple impregnation and calcination methods (Fig. 16(e)) [206]. The obtained Cr-Fe₃O₄-N/NF material has amazing catalytic performance, on which the η_{10} and R_{ct} can be reduced to 218 mV and 1.8 Ω , respectively, obviously better than commercial RuO₂ (Figs. 16(f)–16(i)). Notably, the Cr-Fe₃O₄-N/NF was able to continuously provide a high current density up to 50 mA·cm⁻² for more than 50 h (Figs. 16(j) and 16(k)). These amazing OER electrocatalytic performances can be attributed to the auxiliary

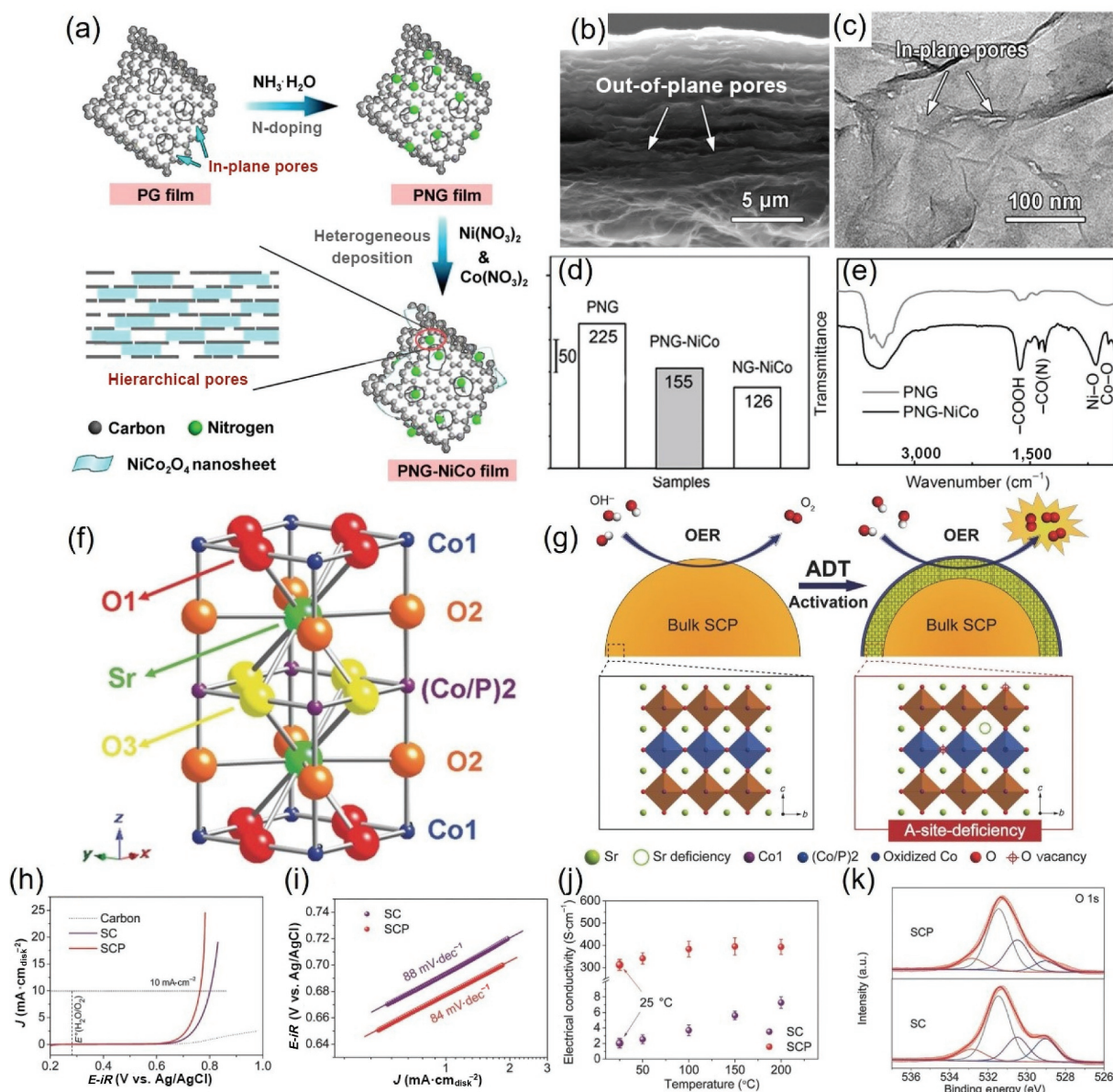


Figure 15 (a) Schematic diagram of the fabrication of 3D hybrid catalysts. (b) and (c) SEM images of PNG-NiCo. (d) Specific surface area. (e) FTIR spectra. Schematic diagrams of (f) tetragonal crystal structure of SCP and (g) capital sources of the OER activation for SCP during ADT. (h) LSV curves. (i) Tafel plots. (j) Temperature-dependent electrical conductivities. (k) XPS spectra of surficial O 1s species. (a)–(e) Reproduced with permission from Ref. [198], © American Chemical Society 2013. (f)–(k) Reproduced with permission from Ref. [199], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2016.

synergistic effect of Cr and N element doping in Fe_3O_4 . Specifically, the introduction of electron-deficient Cr atoms and highly electronegative N atoms can accelerate the dissociation process of water and serve as oxytropic sites. In addition, the co-doping can also optimize the electronic structure of Fe, improve its hydrogen bonding ability, reduce the impedance, and promote the charge transfer, thus significantly accelerating the adsorption and desorption of H_2O molecules and active intermediates.

In addition to metal–nonmetal doping of common Fe/Co oxides, some special materials have also been reported. Zhuang et al. developed a RuO_2 based material co-doped with metallic Fe cation and nonmetallic sulfate anion (S-RuFeO_x) [207]. The η_{10} of S-RuFeO_x in acidic electrolyte (0.1 M HClO_4) can achieve mere 187 mV, and its mass activity is even 20 times that of commercial RuO_2 . In addition, it can maintain stability up to 50 h during the CP test, which has obvious advantages over RuO_2 (Fig. 17(a)). The excellent catalytic performance can be attributed to the reason that the functionalization of the sulfate dopant weakens the adsorption of $^*\text{OO-H}$ intermediates, while the metal Fe dopant promotes the deprotonation of chemisorbed water molecules to form $^*\text{OOH}$,

both of which greatly boost the OER performance (Figs. 17(b) and 17(c)). Furthermore, sulfate also has the effect of efficiently stabilizing the lattice oxygen, resulting in more satisfactory OER durability. Transition metal carbonate hydroxide (TMCHs) is a promising OER electrocatalyst due to its excellent redox performance and lamellar structure, which greatly reduces the dead area in contact with the electrolyte. However, its intrinsic activity and conductivity are not ideal, and further optimization is necessary to reach the level of practical application. Accordingly, Cheng et al. synthesized another carbon nanotube material consisting of metal Fe and nonmetal P dual-doped nickel-hydrogen carbonate oxide (Fe, P-NiCH/CNTs) by a technically sophisticated solvothermal method [208]. The results of DFT calculations revealed that the Fe/P double doping can effectively optimize the electronic structure of the evolving NiOOH , reduce the energy barrier of RDS, and thus have the appropriate adsorption capacity for the O-containing intermediate species (Figs. 17(d)–17(h)). Furthermore, the modification of carbon nanotubes can enhance the electrical conductivity and the porous layered nanostructures can not only increase the exposure of

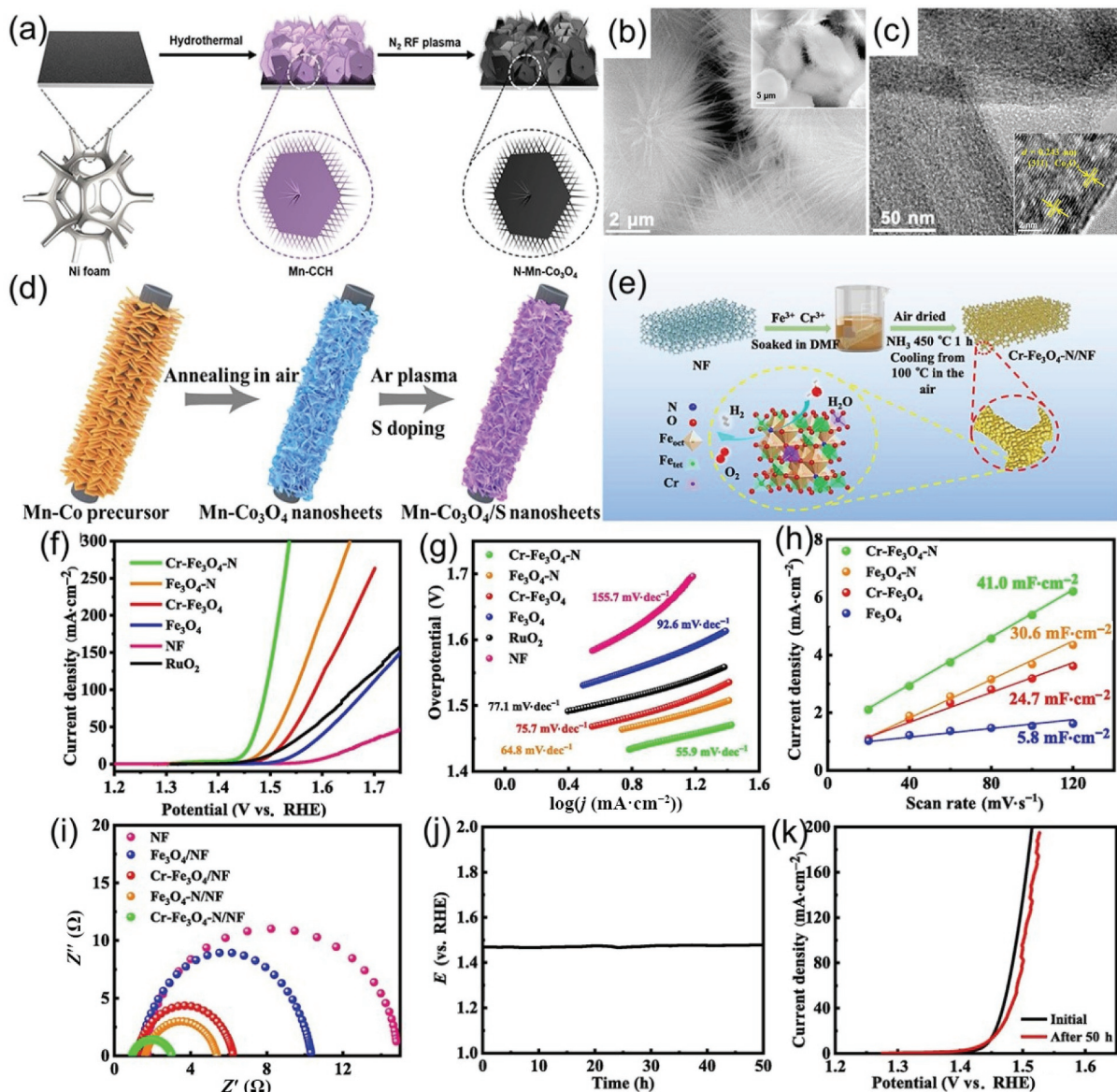


Figure 16 (a) Schematic diagram of the fabrication of cactus-like N-Mn-Co₃O₄/NF. (b) SEM and (c) TEM images of N-Mn-Co₃O₄/NF. Schematic diagram of the fabrication of (d) Mn-Co₃O₄/S nanosheet arrays on CC and (e) Cr-Fe₃O₄-N/NF. (f) LSV curves. (g) Tafel plots. (h) C_{dl} and (i) EIS plots. (j) Stability test. (k) LSV curves of Cr-Fe₃O₄-N/NF before and after stability experiments. (a)–(c) Reproduced with permission from Ref. [204], © Elsevier Inc. 2021. (d) Reproduced with permission from Ref. [205], © Elsevier Inc. 2019. (e)–(k) Reproduced with permission from Ref. [206], © Elsevier Inc. 2022.

active sites but also accelerate the mass transport. These factors endow the Fe, P-NiCH/CNTs with a significantly reduced value of η_{20} of 222 mV. Besides, using cobalt carbonate nanowire arrays (CoCH) as the precursor, Ji et al. prepared Ni-modified Fe/N co-doped nanosheets grown on porous CoO nanowire arrays by a sophisticated hydrothermal method [209]. During the high temperature reaction, the generated carbon dioxide can form small pores inside the nanowires. Then, Ni-modified Fe-ZIFs (ZIFs: zeolitic imidazolate frameworks) were *in situ* anchored on the CoO surface through the coordination between metal ions and imidazole ligands. The *in-situ* grown ZIFs can penetrate the holes on the CoO nanowires to form a continuous interlocking interface structure, which not only reduces the catalyst dead area but also enhances the structural stability. On the one hand, non-metallic N doping is beneficial to the adsorption of OH⁻ to generate active reactive species. On the other hand, the synergistic interaction between porous CoO and metallic Ni/Fe doped ions can enrich the number of active sites and enhance the ability of intrinsic electrocatalysis. Additionally, the open porous CoO nanowire array and vertically arranged NiFe-NC can form a 3D layered

structure, which is conducive to electrolyte penetration and rapid release of oxygen bubbles. Therefore, the best NiFe-NC@CoO sample exhibited a low η_{10} of 247.1 mV, and can maintain 25 mA·cm⁻² for 60 h without significant loss, showing remarkable stability.

Bessarabov et al. used DFT calculations to explore the effects of transition metal cations (TM: Cr, Mn, Fe, Mo, Ru, W, and Os) and non-metallic anions (X: F/S) doping on the surface activity of IrO₂ (110) plates [210]. The IrO₂ (110) model was planar to provide a clear understanding of the influence of TM doped atoms on OER intermediates (Figs. 18(a)–18(h)). Combined with the experiments, it was found that all the considered doping atoms on the IrO₂ surface led to the lattice distortion to a certain extent, and can effectively optimize the electronic structure and related bond length of the t_{2g} and e_g orbitals of Ir atoms. All the intermediate species of OER (O, OH, and OOH) can be stably adsorbed on different surface configurations. They also observed that the vertical movement distance of the non-metallic doped atoms in S_O and TM_{Ir} + S_O configurations was farther than that in F_O and TM_{Ir} + F_O configurations, indicating that the vertical movement of S-doped atoms at the O site was larger. Furthermore, considering

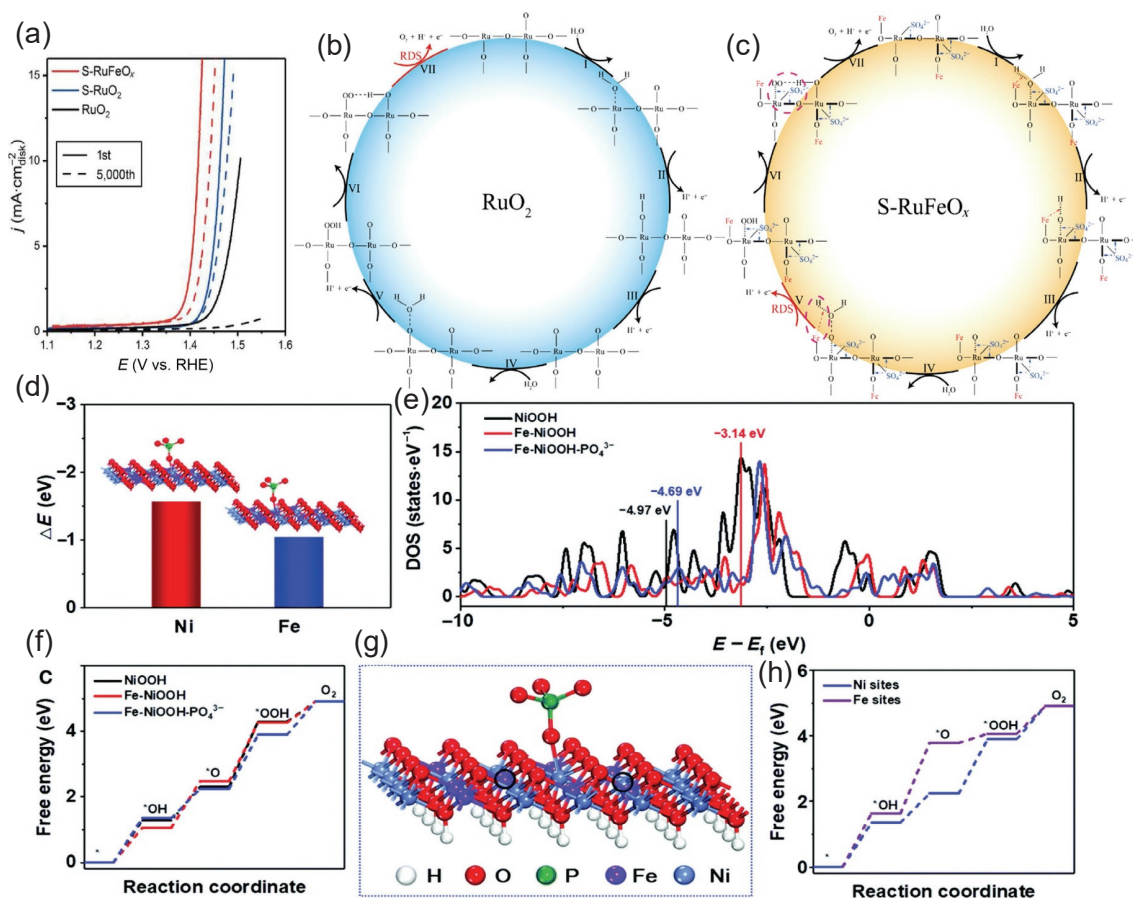


Figure 17 (a) OER polarization curves before and after 5,000 cycles. Schematic diagram of the OER mechanism in acid (b) on RuO_2 (110) and (c) on S-RuFeO_x (red line: the RDS). (d)–(h) DFT calculations. (d) Calculated adsorption energy of PO_4^{3-} on the Ni and Fe sites in Fe-NiOOH . (e) DOS curves of the Ni 3d orbitals. (f) Calculated OER energy pathway. (g) The atomic structure of $\text{Fe-NiOOH-PO}_4^{3-}$ (blank circle: the Fe and Ni sites) and (h) the corresponding OER energy pathway on the Ni and Fe sites in $\text{Fe-NiOOH-PO}_4^{3-}$. (a)–(c) Reproduced with permission from Ref. [207], © Wiley-VCH GmbH 2021. (d)–(h) Reproduced with permission from Ref. [208], © Royal Society of Chemistry 2022.

the change of bond length between OH and OOH intermediate species, they found that OOH intermediate adsorbed on the Os_{Ir} and $\text{W}_{\text{Ir}} + \text{F}_{\text{O}}$ configurations would be decomposed into O and OH species, which was not beneficial to the reaction. In contrast, considering the energy and structural parameters of OER intermediates, the metal–nonmetallic co-doped configuration of $\text{TM}_{\text{Ir}} + \text{F}_{\text{O}}$ can not only weaken the lattice distortion of IrO_2 , but also reduce the adsorption energy of active intermediate species. They also used the determined overpotential and electrochemical step symmetry index (ESSI) as the function of different configuration overpotential to further verify that the doping complexes without O and W are more suitable for OER reaction, and the co-doping configuration of $\text{Mn}_{\text{Ir}} + \text{S}_{\text{O}}$, $\text{Fe}_{\text{Ir}} + \text{F}_{\text{O}}$, and $\text{Cr}_{\text{Ir}} + \text{S}_{\text{O}}$ can endow the maximum improvement of OER activity (Fig. 18(i)). Their research provides valuable guidance for the design of more advanced metal–nonmetal co-doped catalysts.

3.2 Defect engineering

Due to thermodynamic factors, all solids have certain proportions and types of defects. Therefore, in the actual preparation of crystalline materials, controlling different concentrations and types of defects will lead to unusual changes in the electronic or chemical structure of the material for excellent OER catalytic performance [211]. Therefore, it is a very attractive direction to regulate the structure and electronic properties of catalyst materials through defect induction strategy to improve the conductivity, stability as well as catalytic activity [98, 212]. The defect engineering strategy can be subdivided into three types: doping defect, vacancy defect, and heterostructure defect.

3.2.1 Doping defect

Element doping can effectively tune the surface morphology and electronic structure of catalysts, which can produce defects and increase active sites, greatly improve conductivity, reduce the energy barrier of OER, and improve OER performance [213]. Wang et al. used nitrogen plasma to exfoliate bulk CoFe LDHs into ultrathin nanosheets and nitrogen doping and defects were simultaneously introduced into the final product [214]. In the process of nitrogen stripping and doping, the number of reactive sites was significantly enhanced. Since the nitrogen dopant influenced the arrangement of electrons surrounding reactive sites which is conducive to the adsorption of OER intermediates, the activity of reactive sites can be efficiently tuned by increasing the number of dangling bonds neighboring reactive sites and decreasing the coordination number of reactive sites via the introduction of defects. Similarly, Meng et al. synthesized highly reactive N-doped NiFeOOH (N- NiFeOOH) (Figs. 19(a)–19(e)) [215]. DFT calculations revealed that N-doping would adjust the d-band center of the surface metal atoms and enhance the adsorption ability of $^*\text{OH}$ on NiFeOOH , leading to the decrease in the OER overpotential (Figs. 19(h) and 19(i)). The η_{100} and Tafel slope of the N- NiFeOOH were 278 mV and 35.3 mV-dec^{-1} , respectively, which can be compared with the most remarkable non-noble catalysts (Figs. 19(j) and 19(k)).

Zhang et al. prepared cobalt manganese spinel oxides (CoMn_2O_4) doped with heteroatom sulfur ($\text{S-CoMn}_2\text{O}_4$) via simple sol-gel technique (Fig. 20(a)) [216], and found that the $\text{CoMn}_2\text{O}_4\text{-S}_2$ exhibited the highest OER activity with the smallest η_{10} of 350 mV. XPS spectra indicated that the S-doping can

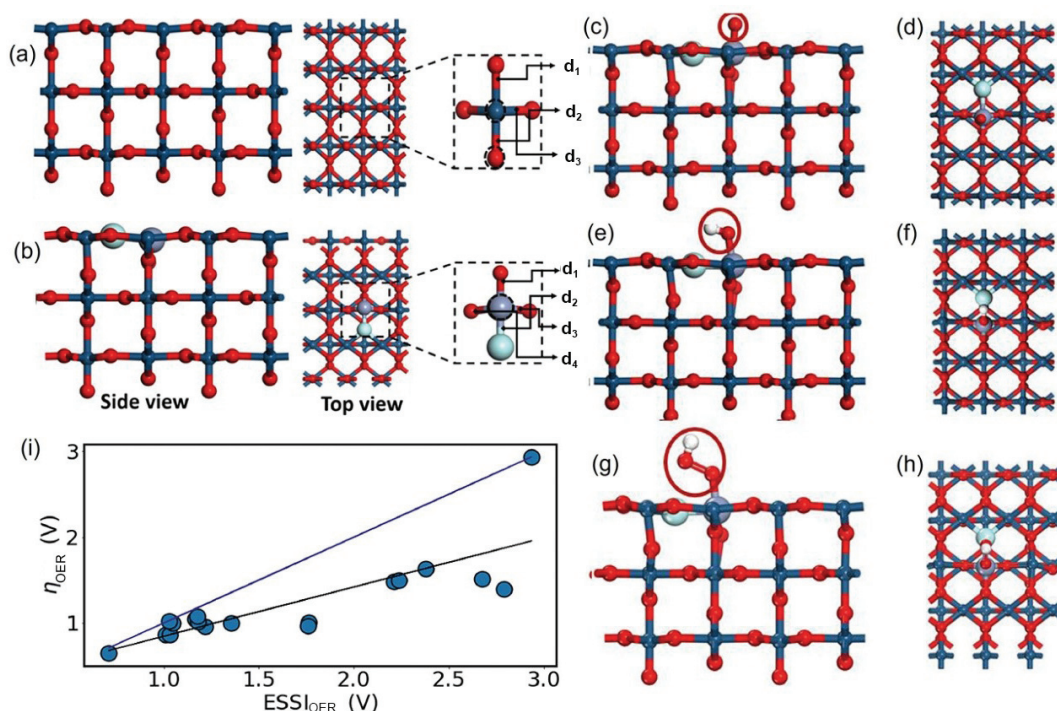


Figure 18 Schematic diagram of (a) pristine and (b) doped IrO_2 (110) rutile surfaces (blue: Ir, red: O, light green: TM_{Ir} , and purple: O_x atoms). Schematic diagram of the ((c), (e), and (g)) side and ((d), (f), and (h)) top view of IrO_2 (110) surfaces with ((c) and (d)) O atom, ((e) and (f)) OH molecule, and ((g) and (h)) OOH molecule on IrO_2 (110). (i) The η_{OER} as a function of the ESSl (black: the best linear fit, blue: the ideal catalyst (when $\eta_{\text{OER}} = \text{ESSl}$)). (a)–(i) Reproduced with permission from Ref. [210], © Elsevier Ltd. 2021.

obviously increase highly reactive Mn^{4+} , Co^{3+} , and oxygen defects. According to DOS diagrams, the boosted OER activities can be attributed to the enhancement of the shrinking energy difference between Co 3d–O 2p and Mn 3d–O 2p centers caused by the metal–oxygen covalency of $\text{S-CoMn}_2\text{O}_4$ (Figs. 20(b)–20(f)). In-depth researches have been done to illustrate the positive effects of *in situ* P doping into a NiO nanosheet shell to reconstruct the catalyst surface by Wang et al. [217]. DFT calculations demonstrated that the doped P atoms replaced O atoms in the subsurface of NiO(110), which weakened the binding strength between the catalyst surface and the reaction intermediates, and changed the RDS of OER to obtain a lower theoretical overpotential (Figs. 20(g)–20(j)). The synthesized P–NiO@NF electrode exhibited an η_{10} of 286 mV, significantly superior to the NiO@NF electrode ($\eta_{10} = 415$ mV) (Figs. 20(k) and 20(l)).

Zheng et al. used a facile solution reduction method to reduce mesoporous Co_3O_4 nanowires with NaBH_4 (Fig. 21(a)) [218]. DFT calculations demonstrated that the oxygen vacancies generated the novel defect states which were located in the band gaps and mainly showed the transition metal 3d characters, indicating the reduction effect. Moreover, the calculated E_{vac} suggested that the two electrons on the oxygen vacancy defect can be easily excited into the conduction band, resulting in a superior conductivity and enhanced electrochemical activity (Figs. 21(b)–21(e)). Compared to the original Co_3O_4 , the reduced Co_3O_4 nanowires showed significantly larger current density of $13.1 \text{ mA}\cdot\text{cm}^{-2}$ at 1.65 V (vs. RHE), higher capacitance of $978 \text{ F}\cdot\text{g}^{-1}$, and reduced charge transfer resistance (Figs. 21(f) and 21(g)). Recently, perovskite oxides are exploited as a research frontier for OER; however, their activity and stability are still far from desirable. Zhao et al. used anion defect engineering to dope different Cl concentrations into perovskite oxides to synthesize highly efficient $\text{LaFeO}_{3-3x}\text{Cl}_{0.15}$ OER electrocatalysts ($x = 0, 0.02, 0.05$, and 0.1 , denoted as LFO, LFOC2, LFOC5, and LFOC10, respectively) via sol-gel method (Figs. 21(h) and 21(i)) [219]. By generating anion defects, the Cl-doped $\text{LaFeO}_{2.85}\text{Cl}_{0.15}$ perovskite exhibited an η_{10} of 0.50 V, lower than the

pristine LaFeO_3 (0.59 V). In addition, the $\text{LaFeO}_{2.85}\text{Cl}_{0.15}$ showed better electrocatalytic stability than the original LaFeO_3 (Figs. 21(g)–21(l)). The enhanced OER activity can be resulted from the plentiful oxygen vacancies on the surface and reduced adsorption energy of H_2O molecule after the doping of Cl^- anion.

3.2.2 Vacancy defect

Introducing more vacancy defects into catalysts is considered to be an effective strategy for further improving the OER performance. The existence of vacancy defects not only helps to reduce the coordination number of adjacent reaction sites, but also affects the electronic structure of the catalyst to adjust the activity of reaction sites. After inducing vacancy defects, the structure and electronic properties of the material surface are regulated and optimized, which greatly improves the OER performance. Sun et al. used ethylene glycol to introduce oxygen defects into single-crystalline Co_3O_4 ultrathin nanosheets with O-terminated facets via moderate solvothermal reduction in alkaline environment [184]. Vacancy defects were formed under solvothermal conditions (Fig. 22(a)) [220]. The O-vacancy-rich Co_3O_4 (O- Co_3O_4) exhibited lower η_{onset} (220 mV vs. RHE) than pristine Co_3O_4 (P- Co_3O_4) (300 mV vs. RHE) which can be even comparable to the IrO_2 catalyst. The O- Co_3O_4 also showed outstanding stability with no obvious current recession after 1,000 CV cycles. DFT calculations revealed that the improved electrocatalytic activity can be attributed to the oxygen vacancies and the second-layered Co metal sites exposed consequently, resulting in the decreased OER activation energy of 2.26 eV and enhanced electron conductivity (Figs. 22(b)–22(e)). The moderate solvothermal reduction method provides an avenue to design advanced defect-based electrocatalysts.

Compared with anionic vacancies, cationic vacancy engineering is more challenging. Wang et al. prepared plentiful Sn vacancies on the surface of SnCoFe perovskite hydroxide precursor by Ar plasma [123]. XAS spectra verified that Sn vacancies could be firstly formed due to the weaker lattice energy as well as chemical bonds of $\text{Sn}(\text{OH})_4$. DFT calculations disclosed that the Sn

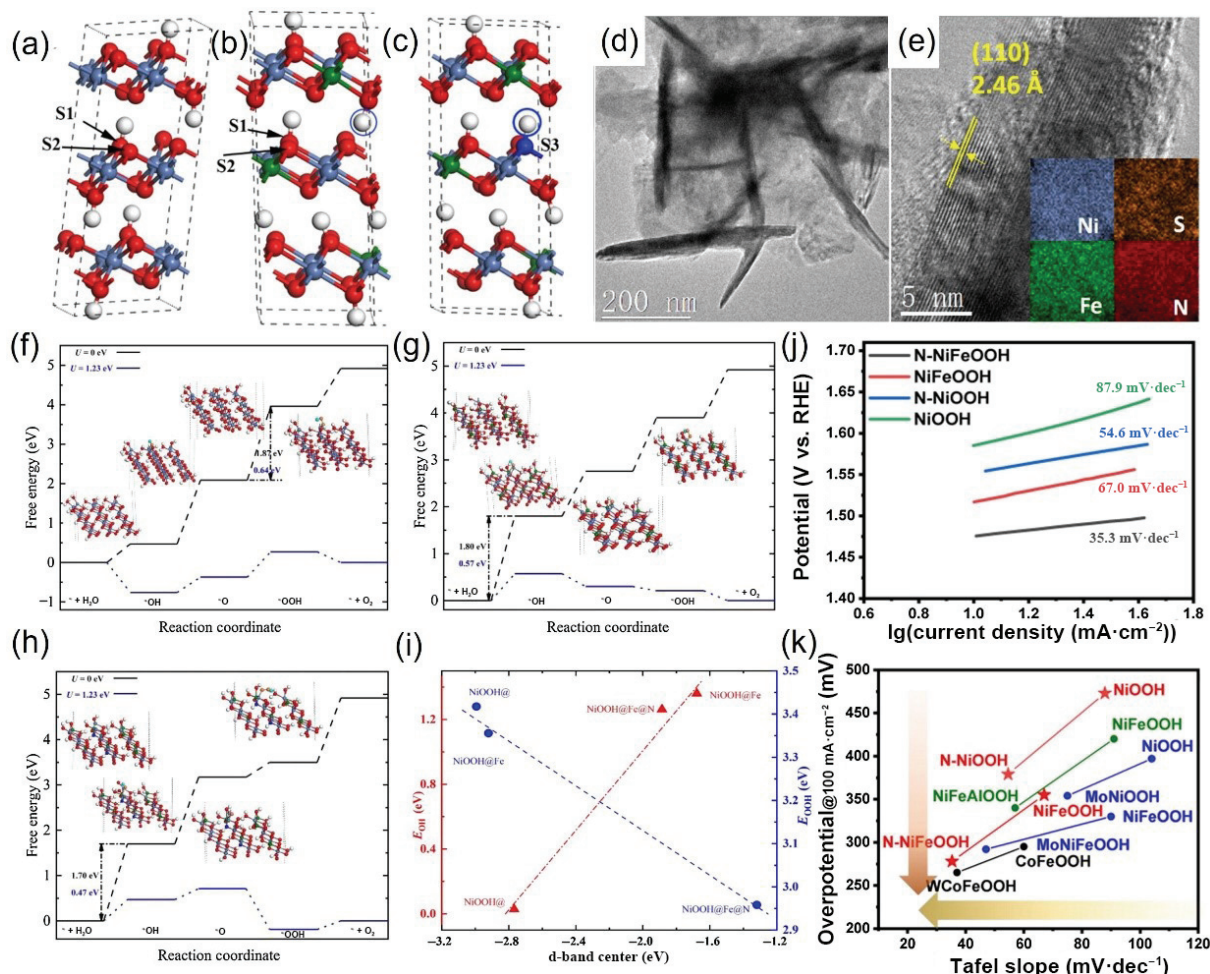


Figure 19 Atomic structure of (a) bulk NiOOH, (b) NiFeOOH, and (c) N-NiFeOOH (grey: Ni, green: Fe, red: O, blue: N, and white: H). (d) and (e) TEM images of N-(NiFe)₂S₂ (insert in (e): elemental mapping images). Free-energy diagram and intermediate products for OER on (01 $\bar{1}$ 2) surfaces of (f) NiOOH, (g) NiFeOOH, and (h) N-NiFeOOH. (i) d-band center of the Ni and Fe in top layer and formation energy of adsorbed OH/OOH. (j) Tafel slopes. (k) η_{100} and Tafel slope comparison diagram. (a)–(k) Reproduced with permission from Ref. [215], © Elsevier Inc. 2020.

vacancies can facilitate the exposure of active CoFe sites and the amorphous surface layer was simultaneously generated, thus modulating the conductivity and enhancing the OER catalytic performance. Based on these advantages, the η_{10} of Ar plasma etched SnCoFe (SnCoFe-Ar) was 270 mV, and the value of C_{dl} was 15.8 mF·cm⁻² (Figs. 23(a)–23(d)).

Recently, Wang et al. synthesized a typical LaNiO_3 perovskite (LNO) electrocatalyst using a sol-gel method [221]. Then the calcination was carried out at 700°C in a hydrogenation reduction atmosphere to prepare red-LNO-700 electrocatalyst, which showed an obviously lower η_{10} of 380 mV and superior OER durability than original LNO without calcination (Fig. 23(e)). XPS, O_2 -temperature-programmed desorption (O_2 -TPD), and HAADF-STEM revealed that high-density oxygen vacancy defects were formed on the surface of red-LNO-700 accompanied by the formation of a $\text{Ni}^{2+}/\text{Ni}^{3+}$ mixed valence state (Figs. 23(f) and 23(g)). DFT calculations and thermodynamic analysis revealed that the formation of oxygen vacancies was relatively easy on the low exponential LNO surface, which are more conducive to OER than those in the body, and the electronic band structure of LaNiO_3 perovskite changed to improve the conductivity, which led to the enhancement of catalytic activity of red-LNO-700 (Figs. 23(h)–23(k)).

However, the experimental conditions require reducing agents (H_2) and high temperature, which have the disadvantages of safety hazards, complexity, and time consuming. To solve these problems, Sun et al. used a fast (30 s) and facile (operated under environmental conditions) flame carving method to successfully

introduce abundant oxygen vacancy defects and hexagonal cavities with margins of (110) into NiFe-LDH, resulting in larger specific surface area, lower coordination number, and an electron-rich structure at the Ni and Fe sites as shown in SEM, TEM, and HRTEM images (Figs. 24(a)–24(e)) [222]. The flame-engraved NiFe-LDH exhibited higher OER performance than pristine NiFe-LDH with an ultra-low η_{onset} of 170 mV (vs. RHE). In addition, the relationship between TOF and g factor characterized by electron paramagnetic resonance (EPR) spectra at different flame treatment time confirmed that the electrocatalytic performance of Fe-LDH (30 s) was significantly better than that of the original Fe-LDH and Ir/C catalysts, and the OER catalytic activity decreased with the increase of g factor. As the number of O vacancy defect sites increased when the flame treatment time was less than 30 s, the g factor of etched Fe-LDH decreased with the increase of TOF, and the catalytic performance was improved, while over 30 s, the number of O vacancy defects decreased due to the formation of metal oxides, resulting in a negative correlation between g factor and TOF and the reduction of catalytic performance, indicating that the O vacancy defects have a crucial promotion effect on the electrocatalytic performance of NiFe-LDH (Figs. 24(f) and 24(g)).

Rui et al. developed introduced oxygen vacancies onto the surface of NiFe-LDH deposited on nickel foam (FeNi-LDH/NF) [223]. From TEM and HRTEM images, abundant vacancy defects could be distinctly observed (Fig. 25(a)). Since the O vacancy defects were caused by the insertion and removal of Na^+ , the O vacancy ratio in FeNi-LDH/NF can be adjusted by controlling the content of Na^+ in the reaction solution. The formed O vacancy

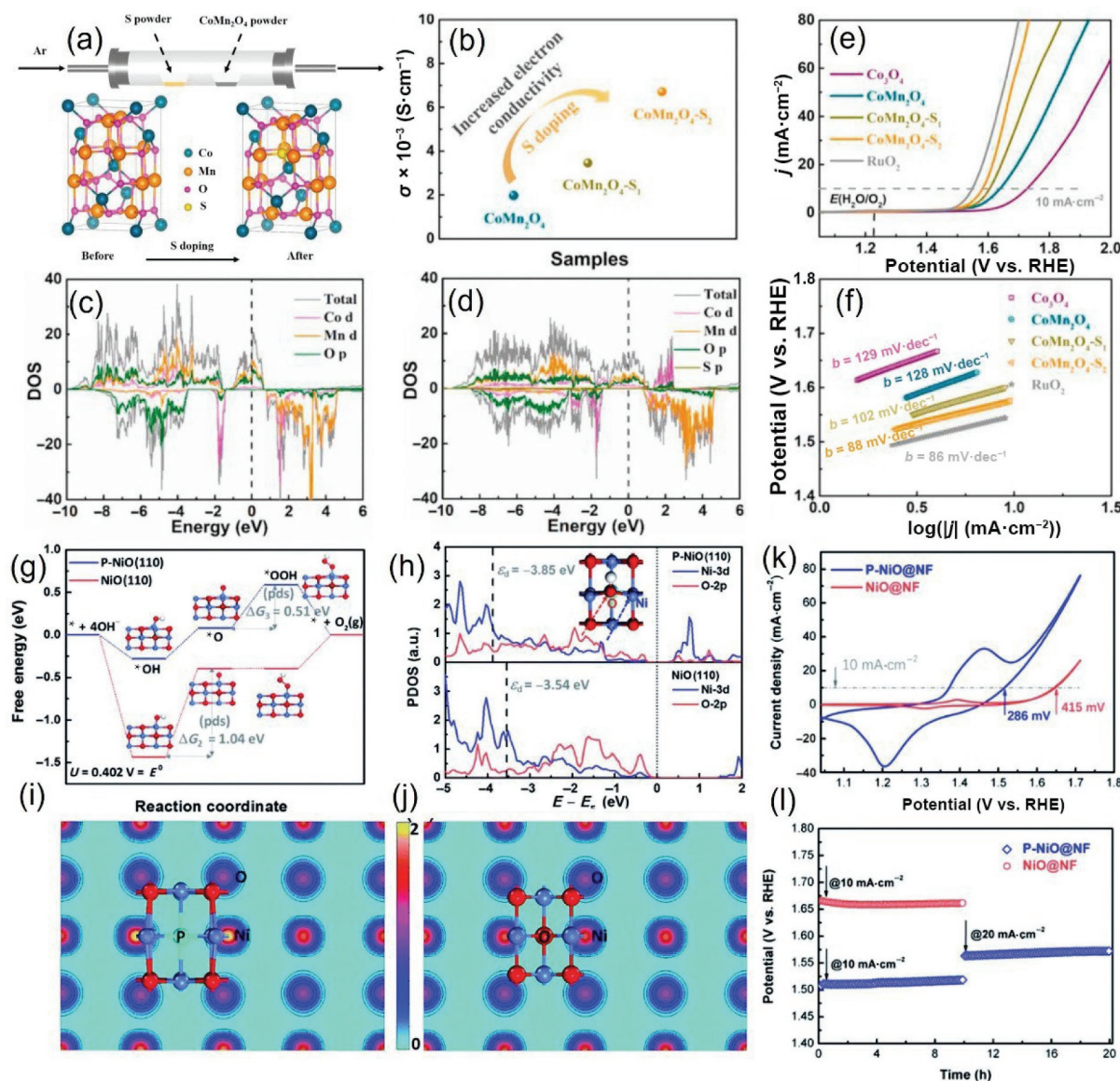


Figure 20 (a) Schematic diagram of S doped CoMn_2O_4 . (b) Electronic conductivity. DOS diagrams of (c) CoMn_2O_4 and (d) $\text{CoMn}_2\text{O}_4\text{-S}_2$. (e) LSV curves. (f) Tafel plots. (g) Free-energy diagrams for OER on (110) surface. (h) Projected DOS diagrams for the 3d orbital of Ni and the 2p orbital of the O atom in adsorbed OH (black line; d band centers). Calculated charge density diagrams for (i) P-NiO (110) and (j) pure Ni (110). (k) CV curves. (l) Chronopotentiometry test. (a)–(f) Reproduced with permission from Ref. [216], © Elsevier B.V. 2021. (g)–(l) Reproduced with permission from Ref. [217], © Royal Society of Chemistry 2021.

defects can improve the electronic conductivity, the wettability between the active site and electrolyte, the adsorption/activation ability to H_2O , and the disruption of H–OH bond. DFT calculations revealed that the OER electrocatalytic activity of FeNi-LDH/NF was volcanically dependent on the O vacancy ratio, and the delocalized electron content and the utilization efficiency of the active sites can reach the optimal balance, resulting in the best OER catalytic performance with the lowest η_{10} of 177 mV (Figs. 25(b)–25(e)).

3.2.3 Heterostructure defect

Electrocatalysts with particular heterostructure have been a research hotspot. In addition to the doping defect and vacancy defect, the defect site derived from the construction of particular morphologies can be defined as heterostructure defect. Heterojunction can be divided into homotype heterojunction (P–P or N–N) and heterotype heterojunction (P–N or P–N), and multilayer heterojunction is called heterostructure. Heterostructured electrocatalysts are those whose performance improvement comes simply from the unique structure. It is worth mentioning that not all specific configurations can derive defect

sites. One promising strategy to create defect sites is to grow targeted metal oxides and (oxy)hydroxides on various substrates with OER-beneficial heterostructures [37, 102, 109, 224, 225]. For example, many researchers used foam nickel, carbon cloth (CC), and other macro substrates to further expose active sites and enhance the conductivity of the catalysts. The edges of these materials can be more fully exposed, thus providing sufficient sites for the adsorption of OER intermediates. Furthermore, the durability of catalysts can also be enhanced to a certain extent through assembling different components in a specific structure. Taking the core–shell structure as an example, the surface of the material with high catalytic activity but poor stability is covered with a thin layer of stable species, which strikingly prolongs the service life. Additionally, due to the differences in electronegativity between different components, it may lead to electron transfer, which can be reflected in the movement of binding energy of a specific element orbital in the XPS spectrum. This will modulate the original electronic and energy band of the material, which makes the catalyst surface more conducive to the occurrence of OER.

Yu et al. used urea as carbon source and citric acid as chelating

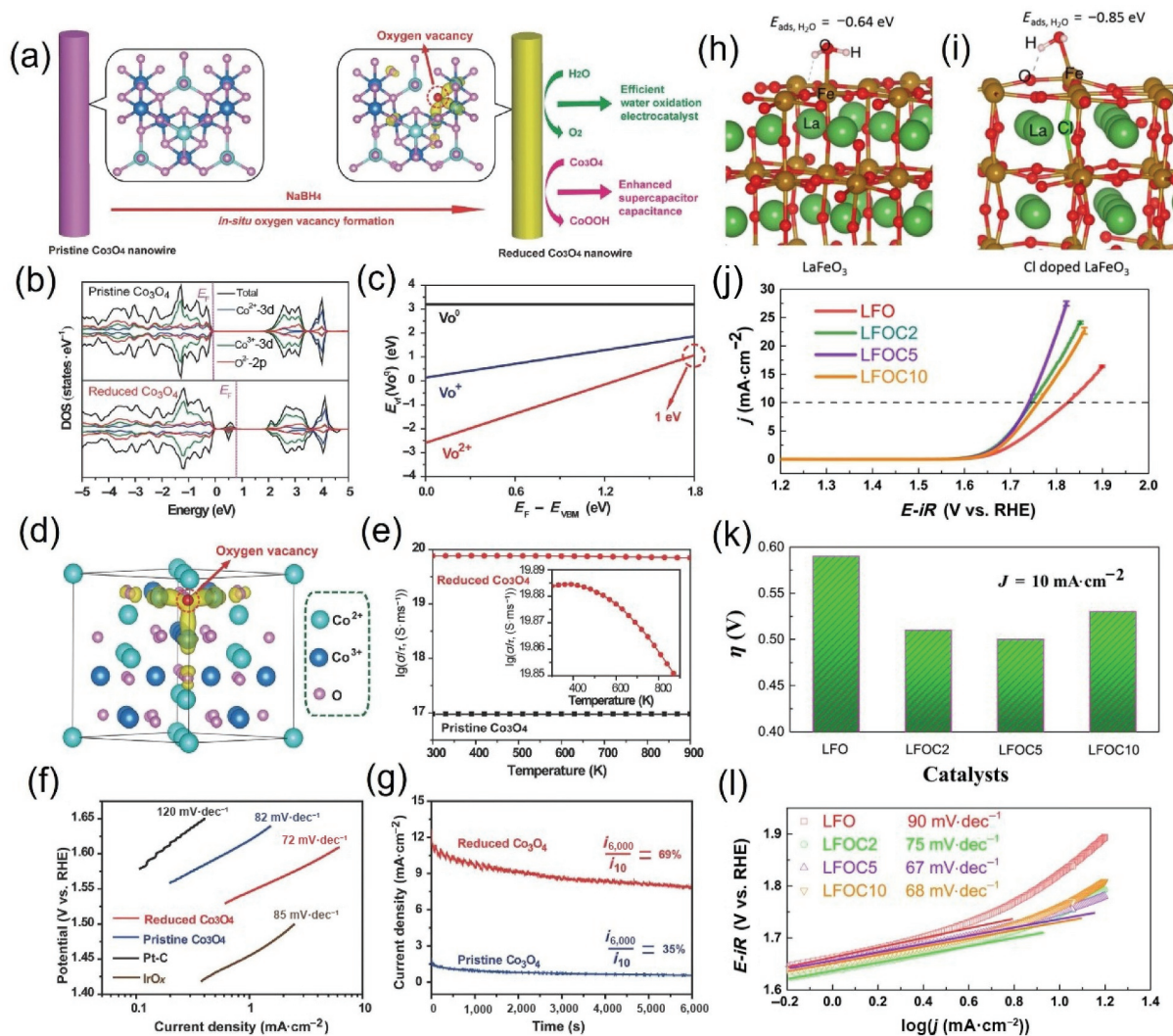


Figure 21 (a) Schematic diagram of O vacancy generation in Co_3O_4 nanowires. (b) Total densities of states (TDOS) and partial density of states (PDOS) diagrams. (c) Calculated E_{vac} for Co_3O_4 nanowires. (d) Partial charge density of the reduced Co_3O_4 . (e) Calculated conductivity. (f) Tafel plots. (g) Stability test. Schematic diagram of the adsorption of H_2O of (001) surface on (h) LaFeO_3 and (i) Cl-doped LaFeO_3 . (j) LSV curves. (k) η_{10} . (l) Tafel plots. (a)–(g) Reproduced with permission from Ref. [218], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2014. (h)–(l) Reproduced with permission from Ref. [219], © Hydrogen Energy Publications LLC. 2019.

agent to *in-situ* synthesize $\text{FeN}_{0.023}/\text{Mo}_2\text{C}/\text{C}$ heterostructure nanoparticles in N-doped carbon nanosheets using simple primary thermal reduction method (Fig. 26(a)) [226]. The material was formed by the coupling of two active components $\text{FeN}_{0.023}$ and Mo_2C , and abundant active defect sites existed in the heterogeneous interface, which promoted electron transfer and greatly boosted the catalytic activity (Figs. 26(b) and 26(c)). Moreover, the coupling effect optimized the binding energy of H atom and the reaction site, making the adsorption/desorption of the former much easier. In addition, as the carbon nanosheets wrapped the defection-rich heterostructure nanomaterials, the agglomeration of the latter was prevented and their oxidation and corrosion were also effectively prevented, which significantly improved the stability as well. The appeal advantage endowed $\text{FeN}_{0.023}/\text{Mo}_2\text{C}/\text{C}$ with extremely low η_{10} (227 mV) and excellent durability (lasts $10 \text{ mA}\cdot\text{cm}^{-2}$ up to 10 h). Zhang and his team reported a N-doped carbon (NC) coated Fe-Co-O/Co material grown on NF (Fe-Co-O/Co@NC-mNS/NF) with mesoporous nanosheet (mNS) morphology rich in defect sites derived from a MOF material [227]. Specifically, FeCo-Prussian blue analog (PBA) was used as a self-sacrificing template material and pyrolyzed in an Ar atmosphere of 800°C to prepare Fe-Co-O/Co@NC/NF precatalysts rich in oxygen vacancies. In the subsequent OER *in-situ* electrochemical oxidation process, Fe-Co-

O/Co@NC/NF evolved from micro-column structure to ultra-thin mesoporous nanosheet structure, and the hydroxyl oxides formed by surface oxidation acted as new reactive species, during which a large number of heterostructural defects were introduced, possessing an ultra-high ECSA and ideal number of active sites (Fig. 26(d)). To explore the causes of defects sites, they also carried out a series of morphology characterizations to detailedly study this evolution process. TEM, HRTEM, and FFT and inverse FFT (IFFT) images revealed that Fe-Co-O/Co@NC/NF has a typical core-shell shaped internal structure. During annealing in an inert atmosphere, the metal center of the MOF material was converted to metal/oxide, while the organic part containing N was converted to NC, which was then partially graphitized to encapsulate the core. After electrochemical OER treatment, the granular microcrystals were greatly reduced, indicating the formation of the internal structure and the existence of various defect points and lattice distortion which may be due to potential-related lattice stresses and strains *in-situ* generated during the potential cycle (Figs. 26(e)–26(w)). The mesoporous nanosheet structure with a large number of heterogeneous defects caused η_{10} of Fe-Co-O/Co@NC-mNS/NF plummeted to 257 mV, better than commercial RuO_2 loaded on NF (RuO_2/NF , 301 mV). Furthermore, Zhang et al. prepared NiO and CuO heterostructure nanosheets rich in defects on NF by similar electrical treatment

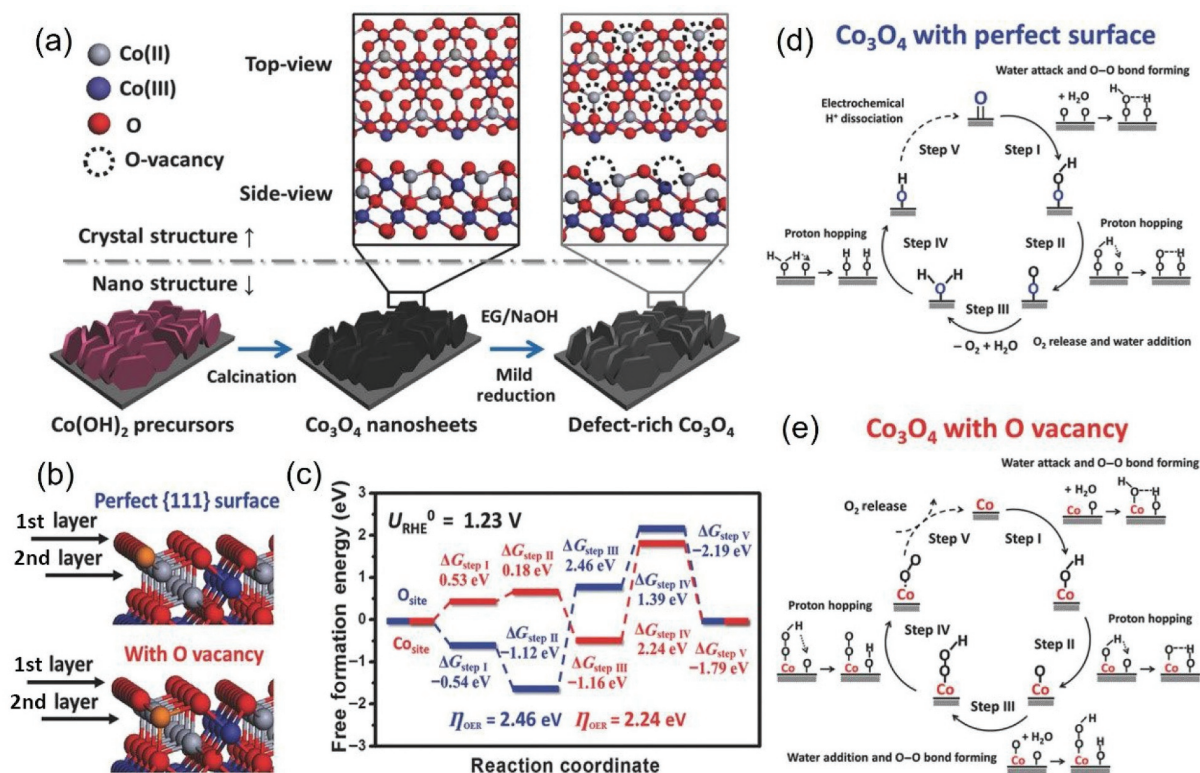


Figure 22 Schematic diagram of (a) the preparation of oxygen vacancy defects on the surface of Co_3O_4 nanosheets and (b) active sites. (c) Calculated free-energy diagrams. Mechanism of OER on (d) Co_3O_4 and (e) Co_3O_4 with O vacancies. (a)–(e) Reproduced with permission from Ref. [220], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.

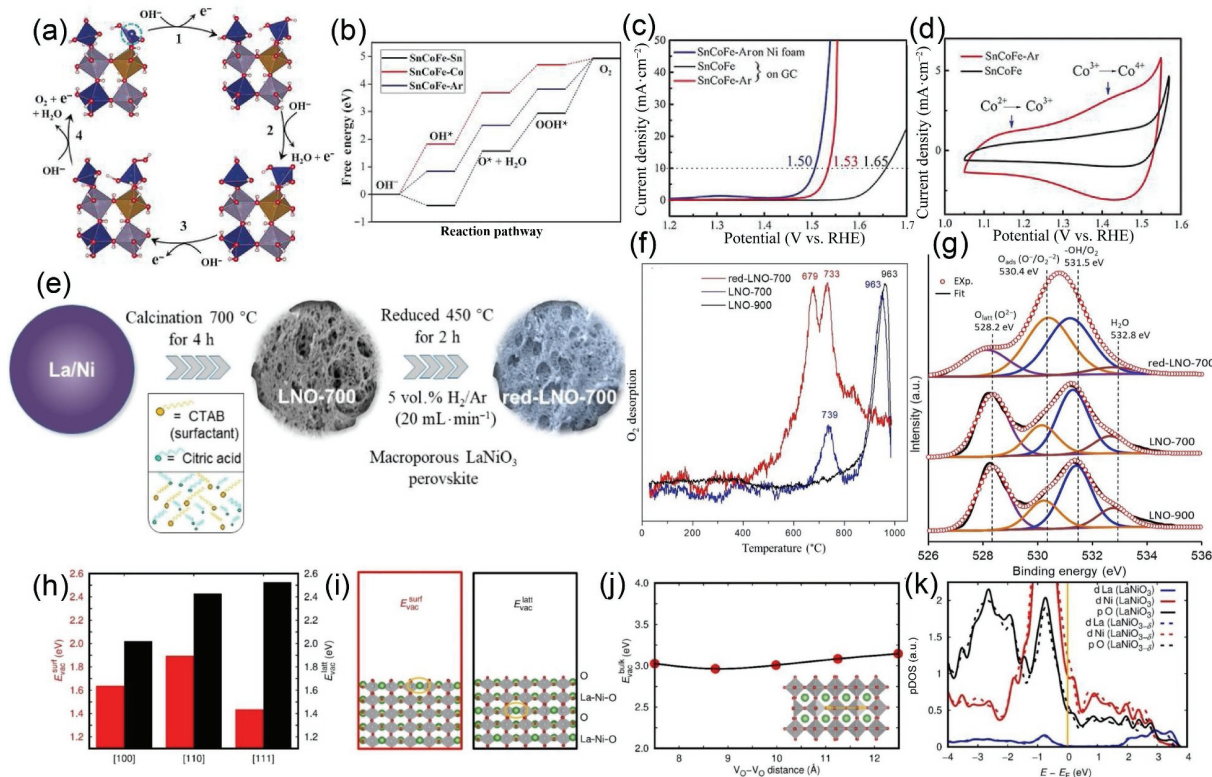


Figure 23 (a) OER mechanism on SnCoFe-Ar. (b) Calculated OER free-energy diagram. (c) LSV curves. (d) CV curves. (e) Schematic diagram of synthesis process of red-LNO-700. (f) O₂-TPD image. (g) O 1s XPS. (h)–(k) Calculated DFT results of LNO. (h) E_{vac} of surface/lattice O vacancies as a function of crystal orientation. (i) Schematic diagram of flat plate monomer model for E_{vac} calculation. (j) E_{vac} in bulk LNO as a function of the point defect distance. (k) Density of electronic states for d-Ni, p-O, and d-La orbitals. (a)–(d) Reproduced with permission from Ref. [123], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2018. (e)–(k) Reproduced with permission from Ref. [221], © Wiley-VCH GmbH 2021.

[228]. To expand, CuCl_2 was firstly converted to CuCl by replacement reaction with NF, followed by *in-situ* electrochemical oxidation to form $\text{NiO}/\text{CuO}/\text{Ni}$ foam. Due to the advantages of

heterogeneous structures, electrocatalysts have abundant active sites and outstanding proton/electron transport capabilities. The electronic interaction resulting from the interface effect between

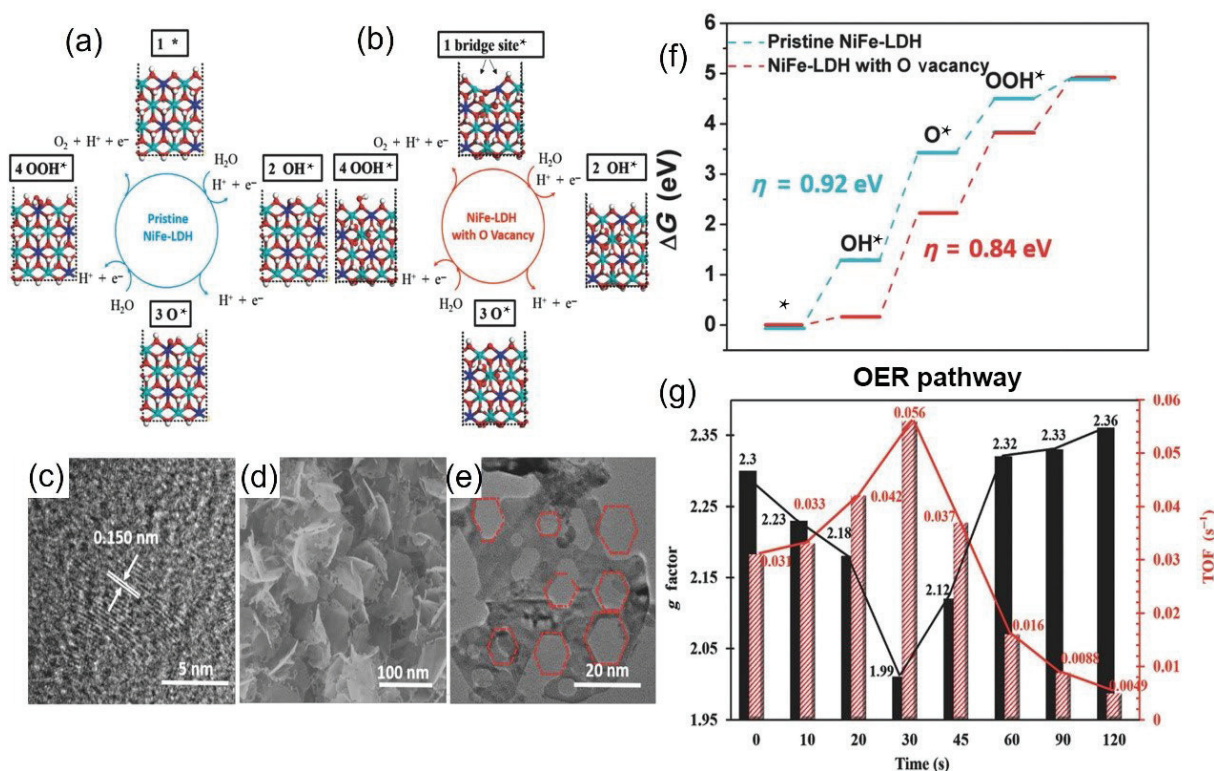


Figure 24 Schematic diagram of OER mechanism of (a) original LDH and (b) containing O vacancy LDH. (c) HRTEM, (d) SEM, and (e) calculated OER free energy. (f) Plots of g factor and TOF. (a)–(f) Reproduced with permission from Ref. [222], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018.

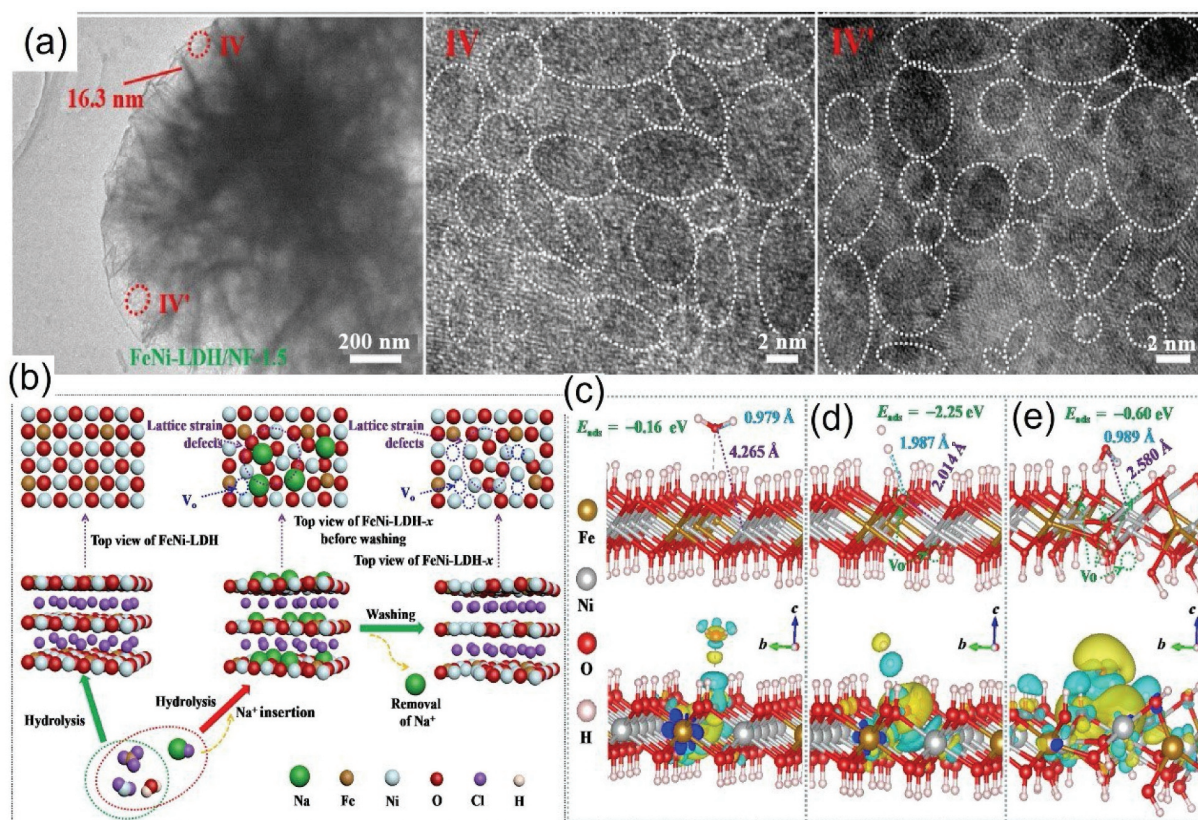


Figure 25 (a) TEM and HRTEM images of FeNi-LDH/NF-1.0. (b) Schematic diagram of the formation of O-vacancies in FeNi-LDH/NF- x . Calculated DFT results of the structures of H_2O adsorbed on the surface and the deformation charge density for FeNi-LDH/NF with O-vacancy of (c) 0, (d) 6.3%, and (e) 25%. (a)–(e) Reproduced with permission from Ref. [223], © Elsevier Ltd. 2019.

NiO and CuO can change the electronic structure of NiO, so that it has a suitable adsorption effect on intermediate species. The NiO and CuO components in NiO/CuO nanosheets existed in the form of many ultra-small nanocrystals, and therefore there were a large number of unsaturated coordination sites and strong

interconnection interfaces. These boundaries endow the catalyst with a large number of defects beneficial to OER, which can accelerate the catalytic kinetics and reduce η_{10} and R_{ct} to satisfactory 234 mV and 1.4 Ω , respectively, even far lower than those of commercial RuO_2 .

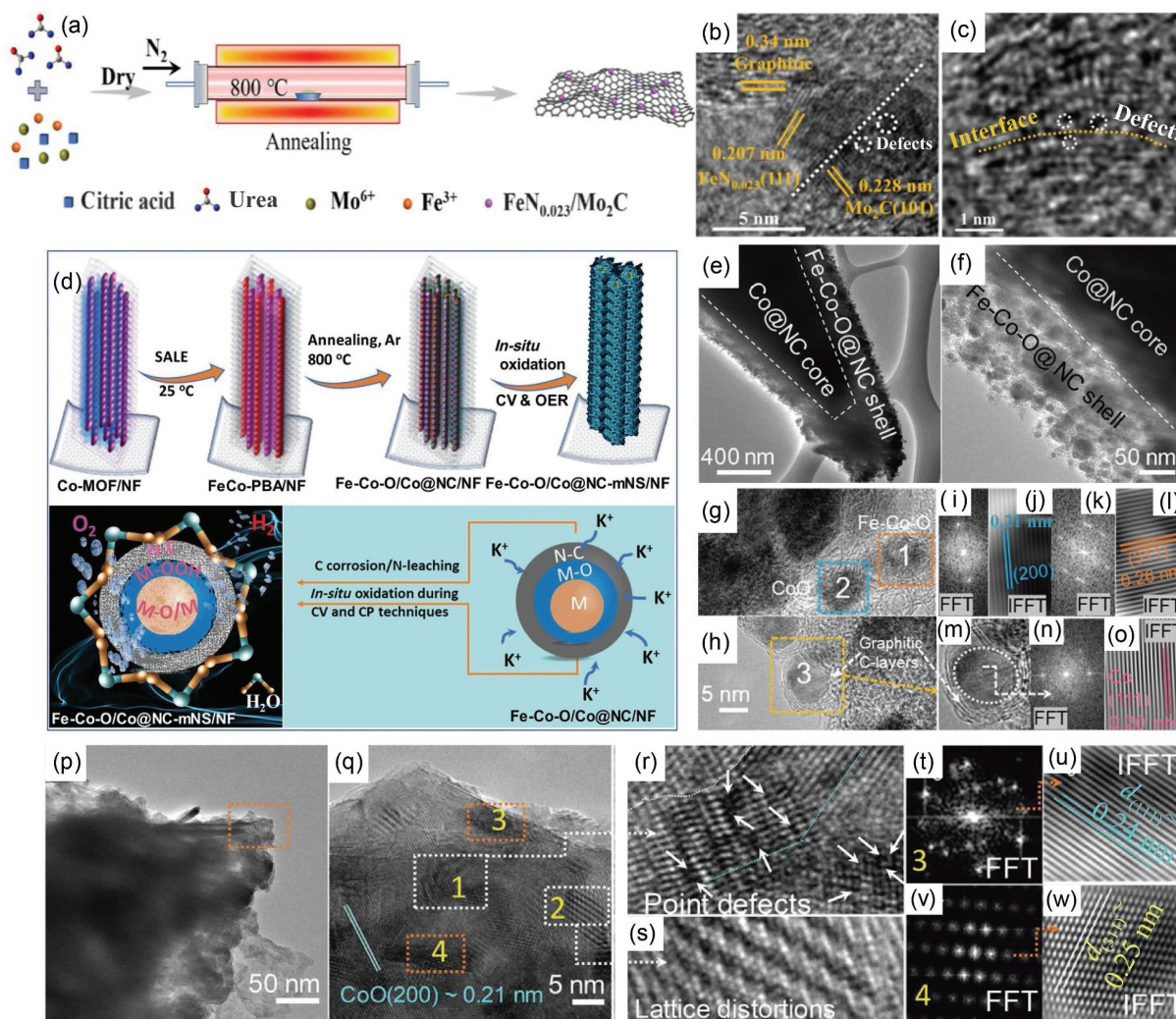


Figure 26 (a) Schematic diagram of preparing $\text{FeN}_{0.023}/\text{Mo}_2\text{C}/\text{C}$. (b) and (c) HRTEM images of $\text{FeN}_{0.023}/\text{Mo}_2\text{C}/\text{C}$. (d) Schematic diagram of preparing $\text{Fe-Co-O}/\text{Co@NC-mns}/\text{NF}$ from $\text{Co-MOF}/\text{NF}$ as the pre-catalyst and the reliable mechanism for the *in-situ* oxidation. ((e) and (f)) TEM, ((g) and (h)) HRTEM images, ((i)–(l)) FFT and the corresponding IFFT of regions 2 and 1 in (g), (m) magnified HRTEM image of region 3 in (h), and ((n) and (o)) FFT and the corresponding IFFT of region 3 in (h) for $\text{Fe-Co-O}/\text{Co@NC}/\text{NF}$. (p) TEM and (q) HRTEM images of $\text{Fe-Co-O}/\text{Co@NC-mns}/\text{NF}$. (r) and (s) Magnified HRTEM images of region 1 and 2 in (q). (t)–(w) FFT and the corresponding IFFT images of regions 3 and 4 in (q). (a)–(c) Reproduced with permission from Ref. [224], © Wiley-VCH GmbH 2022. (d)–(w) Reproduced with permission from Ref. [225], © American Chemical Society 2022.

LDHs are composed of positively charged brucite layers and interlayer regions containing charge balance anions and solvated molecules, which have been widely used as attractive OER electrocatalysts (Table 2). The interlayer bound anions, water, and various metal cations make LDHs have larger interlayer space and unique redox characteristics. However, the stacking structure of LDHs limits the exposure of active sites. The exfoliation can be used to solve this problem [190]. Wang et al. reported an interesting method to introduce heterostructure in LDHs to attain laminar NiFe-LDHs (v-L-LDHs) [229]. They demonstrated the promising OER activity by precisely introducing metal and oxygen multivacancies in NiFe-LDHs using the specific electron-withdrawing and atom-nabbing organic molecule methylisothiocyanate (CH_3NCS) (Figs. 27(a) and 27(b)). As shown in O 1s XPS spectra (Figs. 27(c) and 27(d)), the binding strength of oxygen vacancies and adsorbed water of v-NiFe LDH was significantly higher than that of NiFe LDH, which verified the existence of a large number of O vacancies and also explained that the formation of v-NiFe LDH was due to the ligand in NiFe LDH changed from hydroxide to sulfur complex, and was then washed out by ethanol. Compared with NiFe LDH, the coordination numbers of Ni-Ni/Ni-Fe and Fe-Fe/Fe-Ni shells of v-NiFe LDH are both reduced, which is caused by the rich Ni/Fe metal

vacancies in v-NiFe LDH (Figs. 27(e)–27(h)). These O and metal vacancies derived from heterostructure morphology provided sufficient defects for the OER. Remarkably, the optimized v-L-LDHs showed an η_{100} of 230 mV and Tafel slope of $37.1 \text{ mV} \cdot \text{dec}^{-1}$. DFT calculations unraveled that the boosted OER performance was contributed by the co-existence of M and O vacancies, which substantially enhanced the electroactivity for binding with adsorbates and electron transfer. Moreover, the Ni sites near the vacancies have been further activated and protected by the adjacent Fe sites to guarantee stable OER performance. Liu et al. prepared ultrathin CoFe-LDHs nanosheets with multi-defects via water-plasma-enabled exfoliation [190, 230]. The key point to exfoliate LDHs is to destroy the electrostatic interactions between the metal layers and the interlayer anions. Compared with the usual ultrasonication exfoliation, the as-developed water-plasma treatment in a dielectric barrier discharge (DBD) plasma reactor has much more advantages by producing highly active multivacancies and generating the fast exfoliation. Furthermore, multi-vacancies (O, Co, and Fe vacancies) were generated during the exfoliation process by the etching effect of water plasma, which can improve the electronic conductivity and facilitate the formation of more active CoOOH , thus boosting electrocatalytic OER activity. Compared to pristine CoFe-LDHs, the as-exfoliated

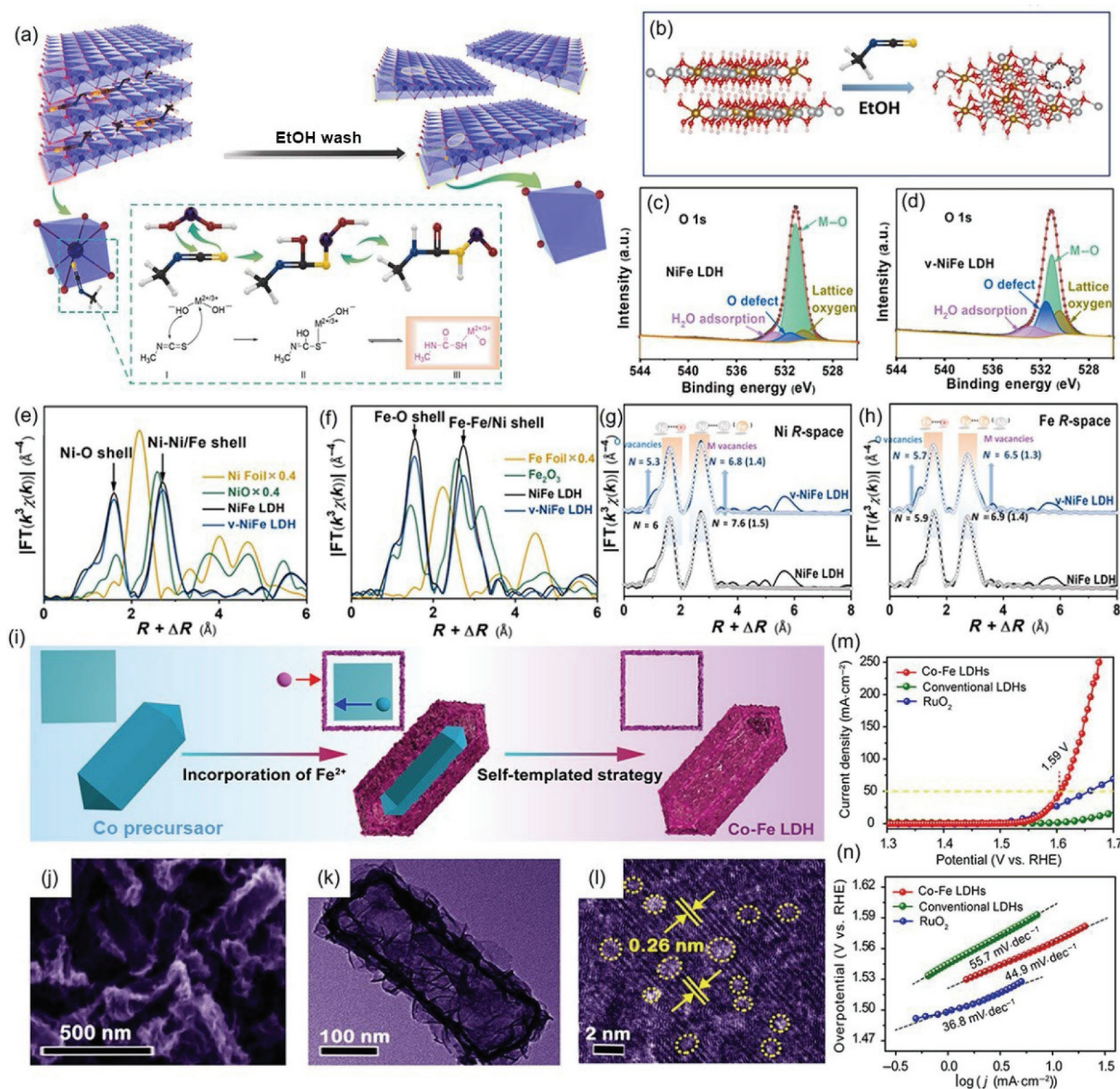


Figure 27 (a) The mechanism of target specific atoms to produce multiple vacancies. (b) Local structural models of NiFe LDH (left) and v-NiFe LDH (right) (orange: Fe, grey: Ni, red: O, white: H, black: C, blue: N, and yellow: S atoms). XPS spectra in O 1s regions of (c) NiFe LDH and (d) v-NiFe LDH. The k^3 -weighted FT spectra at the (e) Ni and (f) Fe K edges and corresponding fitted R -space plots at (g) Ni and (h) Fe K edges for original NiFe LDH and v-NiFe LDH. (i) Schematic diagram of preparation of defect-boosted Co-Fe LDHs. (j) Field emission SEM (FESEM) and ((k) and (l)) HRTEM images of Co-Fe LDHs. (m) Polarization curves. (n) Tafel plots. (a)–(h) Reproduced with permission from Ref. [229], © Elsevier Ltd. 2020. (i)–(n) Reproduced with permission from Ref. [231], © American Chemical Society 2019.

ultrathin CoFe-LDHs nanosheets exhibited lower η_{10} of 232 mV and outstanding kinetics (Tafel slope: 36 mV $\cdot$ dec $^{-1}$) (Table 2). Interestingly, the specific activity (current per Brunauer–Emmett–Teller (BET) area) (0.5034 mA $\cdot$ cm $^{-2}$ /BET) and the C_{dl} (11.71 mF $\cdot$ cm $^{-2}$) of water-plasma exfoliated CoFe-LDHs nanosheets are almost 5 times and 2.07 times higher than pristine CoFe-LDHs nanosheets, respectively. This work provides a novel strategy to exfoliate LDHs and to produce highly efficient OER electrocatalysts with multi-vacancies. In addition, Ye et al. used a very simple self-templated strategy to construct a unique prism-like Co-Fe based LDH material with abundant defects (Fig. 27(i)) [231]. They found that the prepared Co-Fe LDHs showed impressive electrocatalytic performance beneficial from the abundant micropore defects with a large number of active sites. The obvious inner cavity and hierarchical nanostructure of the material combined with observable abundant defects (Figs. 27(j)–27(l)) not only endowed the hierarchical prismatic Co-Fe LDHs with a large specific surface area of 294.1, enhanced charge/mass transfer capacity, and boosted OER kinetics, but also

ensured appropriate contact and wettability between its large exposed surface and the electrolyte solution. These advantages endow Co-Fe LDHs with an η_{50} of 350 mV (Figs. 27(m) and 27(n)).

3.3 Morphology control

It is well known that electrochemical reactions usually occur on the surface of the catalyst, and the morphology of the catalyst directly determines the size of the ECSA, and is closely related to the arrangement of the surface atoms and the electronic structure, which makes the morphology including size, shape, and even spacing distance become a crucial factor affecting the performance of catalysts. The unique nanostructure of catalysts usually provides a larger active reaction region and exposes more reaction sites [276]. In addition, these definite geometric structures can also promote the transmission of electrons and mass. These advantages make the reasonable construction of morphology, including low-dimensional nanoparticles and clusters, 2D nanosheets and nanoflowers structures, 3D core-shell, hierarchical porous and

nanotube structures, etc., become the research hotspot to improve the electrocatalytic performance. For example, 3D ordered microporous structure of LaFeO_3 perovskite synthesized by Shao et al. doubled its OER activity [277]. Qin et al. constructed $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF) with hierarchical porous surface morphology, which had a large surface area of $148 \text{ m}^2\text{g}^{-1}$ and showed OER activity superior to commercial IrO_2 [278]. In addition, the dual-perovskite $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5-\delta}$ material with fibrous structure designed by Wang et al. showed a nearly 20-fold increase in mass activity when the diameter of the fiber structure was reduced to about 20 nm [279].

3.3.1 Low-dimensional nanostructures

The reduction of catalyst size will significantly increase the atomic proportion on the surface, leading to the increase of ECSA, thus exposing more reactive sites for OER. Compared with bulk scale, nanomaterials generally have obvious advantages in catalytic performance. However, they are prone to agglomeration during the synthesis process, which has serious adverse effects on the material properties. Therefore, it is necessary to optimize the catalyst by morphology control to stabilize its catalytic performance at nano scale. In recent years, low-dimensional nanoparticles and nanowires with particular morphologies such as core-shell and hollow have been extensively studied.

Recently, core-shell structure becomes a research hotspot due to its unique advantages that the excellent electron conduction provided by the metal core extends throughout the oxide/hydroxide shell to provide sufficient OER active sites, and the shell in turn protects the metal core from suffering severe dissolution and oxidation especially in acidic electrolytes. For example, Qin et al. successfully synthesized core-shell nanoparticles with metal Ru as core and Ir oxide as shell (Ru@Ir-O) by liquid organic salt immersion method [280]. The oxygen-bound Ir shell can not only absorb electrons from the Ru core but also have tensile strain effect, which makes the material enable to carry more negative charges (Figs. 28(a)–28(e)). These factors make the band positions of the key intermediates O^* and HOO^* shift upward, thus enhancing their bonding strength on the surface. The η_{10} of Ru@Ir-O (238 mV) is much lower than that of pure IrO_2 (350 mV) and Ir (316 mV), and the mass activity of $1,169.0 \text{ A}\cdot\text{g}_{\text{metal}}^{-1}$ (1.55 V, 0.5 M H_2SO_4) is 5 and 78 times of conventional Ir and IrO_2 , respectively. Luo et al. prepared core-shell structured $\text{NiFeSn@NiFe (oxy)hydroxide}$ nanospheres using a general two-step electrochemical deposition strategy [281]. After electrochemical treatment, the surface of NiFe_2Sn alloy which is the core of the nanosphere was oxidized to form $\text{NiFe (oxy)hydroxide}$ amorphous shell (Figs. 28(f) and 28(g)). Similarly, the core can promote the electron transfer to the shell, which in turn can prevent the oxidation consumption of the former. This electrodeposition method is facile to regulate the proportion of Ni and Fe to optimize the OER activity of the final product with ease. In addition, Sn can selectively electrochemically etch larger surface area and abundant oxygen vacancies in alkaline solution, thus providing more active sites and more convenient mass and charge transfer pathways. To achieve better surface reconstruction and selective Sn etching, the alloy core material can be anodized for 2 h at $10 \text{ mA}\cdot\text{cm}^{-2}$ (denoted as $\text{NiFe}_{0.5}\text{Sn-A}$). The optimized sample of $\text{NiFe}_{0.5}\text{Sn-A}$ exhibited an outstanding OER activity with low η_{10} of 260 mV, high turnover frequency of 0.194 s^{-1} (300 mV), and good durability.

Hollow structure is another research hotspot. For example, to utilize the abundant Fe and Si elements in the earth and further reduce the cost while ensuring high catalytic performance, Meng et al. combined simple and experienced hydrothermal and metal deposition methods, and used the surface modification strategy to

decorate well-dispersed FeO_x on Co_2SiO_4 support to prepare $\text{Fe-Co}_2\text{SiO}_4$ composite materials with unique hollow nanospheres morphology (Figs. 29(a) and 29(b)) [282]. Under alkaline conditions, its η_{10} is 330 mV, and η_{100} is 390 mV (Figs. 29(c) and 29(d)). The good catalytic performance can be attributed to the synergistic effect between metal elements and the metal-carrier interaction that the appropriate dispersion of FeO_x provides abundant electrons to effectively boost the electron transfer of proton coupled multiple steps of OER, as well as the superior geometric effect of the hollow nanosphere morphology that its large ECSA and hollow structure provide sufficient active sites and speed up the mass transfer process. Furthermore, Wu et al. anchored Ru/RuO_2 nanoparticles on the fibrous ferrite $\text{La}_{0.9}\text{Fe}_{0.92}\text{Ru}_{0.08}\text{O}_{3-\delta}$ (LFRO) to synthesize final product (LFRO-H-O) with funny hollow nanofiber morphology (Figs. 29(e)–29(h)) [283]. In particular, LFRO nanofibers with hollow structure were prepared by optimized electrospinning method and the coated Ru and RuO_2 nanoparticles were constructed via *in-situ* growth strategy. The Kelvin probe force microscopy (KPFM) measurements showed that the low work function caused by a large number of oxygen vacancies can accelerate both mass and charge transfer, thus optimizing OER dynamics (Figs. 29(i)–29(n)). Additionally, the unique interaction between nanoparticles and perovskite materials and the abundant active sites provided by the hollow fiber structure endow the LFRO-H-O with an η_{10} of 380 mV, slightly higher than that of RuO_2 (340 mV). The multi-shell hollow structure provides larger surface areas to make better use of the internal space, which is more advantageous to the OER [67–69]. Furthermore, the interlayers can support each other for further enhancing their mechanical stability. Some studies reported that the layer-by-layer strategy based on hard template is an effective method to construct complex hollow structures with narrow size distribution [69]. However, the synthesis process is cumbersome that is not conducive to practical application. Gao et al. developed a simple strategy to prepare NiFe-LDH double-shelled nanocages (DSNCs) via simultaneous etching and coprecipitation using MIL-88A (spindle-like particles with metal-organic framework) as the precursor (Figs. 29(o)–29(s)) [183]. The shell number of Ni-Fe LDH DSNCs could be precisely regulated by adjusting the volume ratio. The special hollow structure endowed Ni-Fe-LDH DSNCs with significantly enhanced electrocatalytic activity with an η_{20} of 246 mV, which is 15 mV lower than Ni-Fe LDH SSNCs (Ni-Fe LDH single-shelled nanocages). The smaller semicircle in the EIS spectra indicated the decreased R_{ct} of Ni-Fe-LDH DSNCs and the current density of Ni-Fe-LDH DSNCs can be maintained up to 50 h without obvious fluctuation.

3.3.2 Two-dimensional nanostructure

The large specific surface area and rich edges of two-dimensional materials with different nanostructures, including nanofilms, nanosheets, and nanoflowers, endow them with abundant active sites for electrocatalytic reactions [284]. For example, $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4/\text{Ni}$ nanosheets array materials that can be directly applied without post-treatment were prepared using a one-step electrodeposition method that requires only a few minutes without template and annealing (Figs. 30(a)–30(e)) [285]. The controllability of composition and morphology can be achieved by adjusting the applied potential, electrical density, and time of electrodeposition operation to further optimize the OER performance. The η_{10} and η_{100} of the best sample are only 218 and 262 mV, respectively and it can maintain high catalytic activity for up to 220 h. The good OER performance can be attributed to the high ECSA of the 2D nanosheets arrays, which can expose sufficient active sites for the reactants, thus better matching the

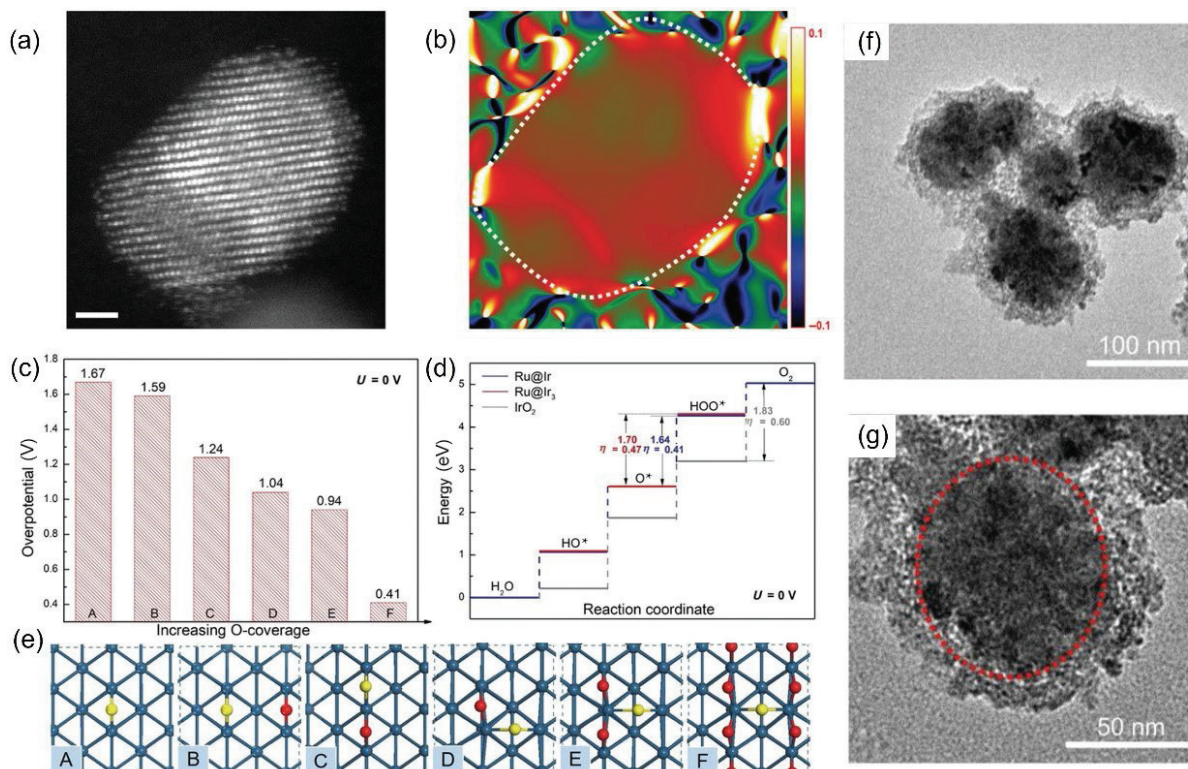


Figure 28 (a) Atomic resolution image and (b) corresponding GPA plot of Ru@Ir-O . DFT calculations of (c) OER overpotential and (d) OER energy profile of Ru@Ir-O , $\text{Ru@Ir}_3\text{-O}$, and IrO_2 under $U = 0$ V (represented by blue, red, and grey lines, respectively). (e) Surface structures of Ru@Ir-O varying with increasing oxygen coverage (cyan balls: Ir atoms, red balls: O atoms, and yellow balls: O^* with specific oxygen coverage reacting on the surface). (f) and (g) TEM images of $\text{NiFe}_{0.5}\text{Sn-A}$. (a)–(e) Reproduced with permission from Ref. [280], © Wiley-VCH GmbH 2022. (f) and (g) Reproduced with permission from Ref. [281], © Chen, M. X. et al. 2020.

Fermi energy level of $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ with the potential of O_2 generation. In addition, the low interfacial resistance between the catalyst and the substrate in the nanosheet structure is helpful for effective charge transfer at the electrode–electrolyte interface (Fig. 30(f)). Qi et al. reported the preparation of unique heterogeneous structures based on mature MOF template synthesis strategy to achieve precise control of both morphology and composition [286]. They converted the Co MOF on CC into an interesting mutually doped and heterogeneous $[(\text{Ru-Co})\text{O}_x]$ hollow nanosheets arrays by simple ion exchange and annealing operations in the air (Fig. 30(g)), which has unique composition and structural advantages, including the provision of richer active sites, optimized electronic structure, and ideal interfacial synergistic effect (Figs. 30(h)–30(j)). It showed remarkable OER activity with η_{10} as low as 171.2 mV and outstanding durability. Wei et al. reported a two-step etching-phosphorizing method for the preparation of $\text{Ni}_3\text{P}_4@\text{FeP}$ precatalyst on NF [287]. Under the electrochemical anode scanning, the surface of $\text{Ni}_5\text{P}_4@\text{FeP}$ was rapidly oxidized to amorphous and unstable NiFe_2O_4 , which was further reconstructed to Ni/FeOOH at high oxidation potential to obtain the final $\text{Ni/FeOOH@NiFe}_2\text{O}_4@\text{FeP}$ nanosheets (Figs. 30(k)–30(n)). The reconstructed amorphous $\text{Ni/FeOOH@NiFe}_2\text{O}_4$ intermediate was considered as a real OER active substance. Combining non-*in situ* characterization for capturing surface dynamic evolution and *in-situ* Raman spectroscopy, it was found that there was high structural reversibility between NiFe_2O_4 and $\text{Ni/FeOOH@NiFe}_2\text{O}_4$, and abundant amorphous interface hybrids between NiFe_2O_4 and $\text{Ni/FeOOH@NiFe}_2\text{O}_4$ had beneficial synergistic effects on OER activity in alkaline environment, resulting in the lower values of η_{10} (205 mV) and η_{100} (242 mV) on the $\text{Ni/FeOOH@NiFe}_2\text{O}_4@\text{FeP}$ nanosheets (Figs. 30(o) and 30(p)).

Besides the nanosheet structure, the nanoflower structure is also a research hotspot. For example, Gong et al. constructed a unique

electrocatalyst with nanoflower structure that consisted of NiFe_2O_4 nanoparticles and amorphous Ni-based nanosheets on porous iron foam (IF) substrate ($\text{Ni-ANS@NiFe}_2\text{O}_4/\text{IF}$) using a simple hydrothermal method (Fig. 31(a)) [288]. Morphological characterizations revealed the evolution process of the unique flower-like structure composed of nanosheets. The effect of Ni introduction on the OER activity was investigated, showing that both amorphous Ni-based nanosheets and NiFe_2O_4 formed by Ni introduction could act as active substances due to the synergistic effect between them, which further enhanced the catalytic activity. Additionally, the petal-like morphology of the final product has a very ideal large ECSA and shows more edge defects, exposing the active sites to a great extent and facilitating the adsorption of intermediate products (Figs. 31(b)–31(f)). The porous conductive IF substrate plays an auxiliary role in the diffusion of electrolytes and the release of oxygen. These advantages endow $\text{Ni-ANS@NiFe}_2\text{O}_4/\text{IF}$ with excellent OER performance, which can reach low overpotentials of 209, 251, and 270 mV for η_{10} , η_{100} , and η_{200} , respectively. Moreover, Jiang et al. synthesized a self-supported electrode with nanoflower-like morphology by using a three-step method [289]. The final product $\text{Ce-m-Ni(OH)}_2@\text{NiSe}_2$ has excellent electrocatalytic OER performance with η_{10} of 158 mV, which is mainly attributed to the appropriate composition and unique flower-like morphology (Figs. 31(g)–31(i)). Firstly, the NiSe_2 carrier has high conductivity that is conducive to electron transport. Secondly, the doping of Ce optimizes the energy barrier of OER intermediate, and the generated Ce(OH)_3 is beneficial to the exchange of oxygen and electrons (Figs. 31(j)–31(m)). Finally, the unique nanoflower morphology provides abundant open pore structures, making mass transfer much easier, thus greatly enhancing the catalytic ability.

3.3.3 Three-dimensional nanostructure

3D nanostructures have the characteristics of high openness, which is conducive to the adsorption of reaction intermediates, the

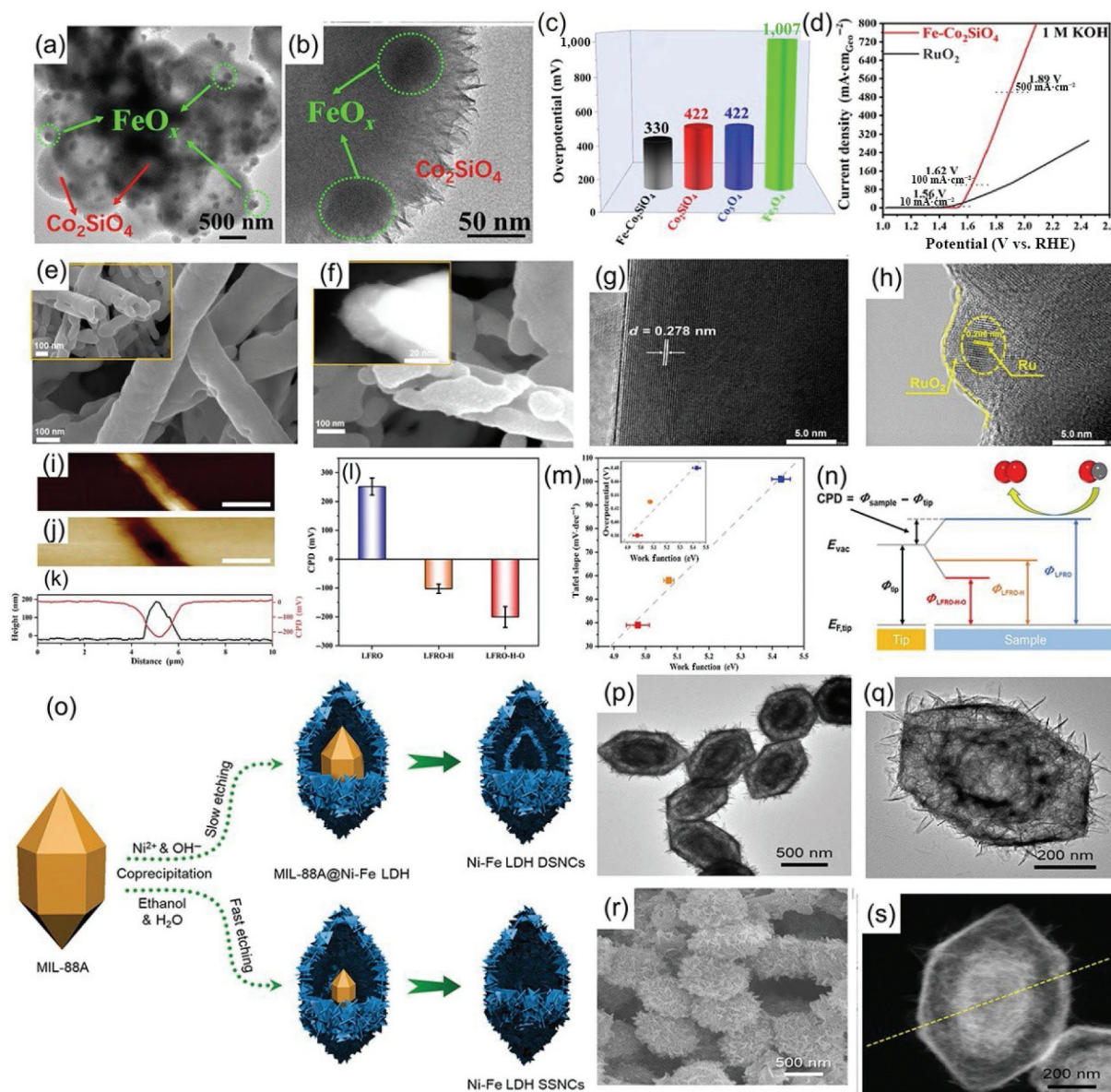


Figure 29 (a) and (b) TEM images of $\text{Fe-Co}_2\text{SiO}_4$. (c) Comparison of η_{10} . (d) LSV curves. ((e) and (f)) SEM and ((g) and (h)) HRTEM images of ((e) and (g)) LFRO-H-O and ((f) and (h)) exsolved nanoparticles (inset in (f): corresponding HRTEM image). (i)–(n) KPFM measurements. (i) Topography and (j) contact potential difference (CPD) images for LFRO-H-O. (k) The height (black) and CPD (red) profiles of LFRO-H-O. (l) CPD values for different samples. (m) Linear relation between the Tafel slopes (inset: overpotential) and work function values for LFRO (blue), LFRO-H (orange), and LFRO-H-O (red). (n) Diagram of energy levels (E_{vac} : vacuum level, E_{F} : Fermi level). (o) Schematic diagram of preparation of Ni-Fe LDH nanocages with tunable shells produced by self-templated strategy. ((p) and (q)) TEM, (r) FESEM, and (s) STEM images of Ni-Fe LDH DSNs. (a)–(d) Reproduced with permission from Ref. [282], © Elsevier Inc. 2021. (e)–(n) Reproduced with permission from Ref. [283], © Elsevier B.V. 2021. (o)–(s) Reproduced with permission from Ref. [183], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

penetration of electrolyte, and the transport of ions, which can achieve the maximum reduction of dead volume and further provide deep active sites. In recent years, a variety of 3D nanomorphologies have been reported, such as hierarchical porous structures, Janus, nanowire arrays, and so on. Due to unique double-sided structure and the asymmetric characteristics on both sides, Janus has become an emerging structure with great application prospect, attracting the attention of many researchers. Its nano-scale asymmetry has many surprising characteristics that are not possessed by uniform or symmetric structures. So far, a variety of synthetic strategies have been reported to prepare different Janus nanostructures. Wang et al. used an *in-situ* solution combustion method to tightly generate porous and amorphous $\text{Ni-Fe}_x\text{O}_y$ nanoparticle films on NF, followed by calcination, to obtain the final Janus nanostructured material composed of Ni-FeO_x and FeNi_3 ($\text{Ni-FeO}_x/\text{FeNi}_3$) (Fig. 32(a)) [290]. Morphology characterizations revealed that the high catalytic performance of the material can be attributed to the strong electron coupling effect

between FeO_x and FeNi_3 due to the asymmetric configuration of the Janus structure (Figs. 32(b)–32(e)), which can change the electronic structure of FeNi_3 and enhance the electrophilicity of Ni to promote the adsorbed $^*\text{O}$ to attract OH, causing the formation of $^*\text{OOH}$ more conducive. Due to the negative induction effect of electron absorption, $^*\text{OOH}$ intermediates are more facile to deprotonate to boost the generation of O_2 . These factors enable the η_{50} and η_{1000} of $\text{Ni-FeO}_x/\text{FeNi}_3$ to achieve low levels of 269 and 405 mV, respectively, while maintaining a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$ for up to 200 h. Zhang et al. reported a novel combination of electrostatic spinning and *in-situ* carbonization strategy to prepare 3D flexible Janus nanofibers with interesting core-shell hollow structures, which have efficient particle conduction pathways and high porosity (Figs. 32(f)–32(h)) [291]. The inner layer of the material is composed of N-doped NiFe alloy with excellent OER catalytic activity, which is coated with a conductive thin-walled carbon layer as an intermediate spacer. The morphology of the synthesized 3D flexible Ni-Fe-N-

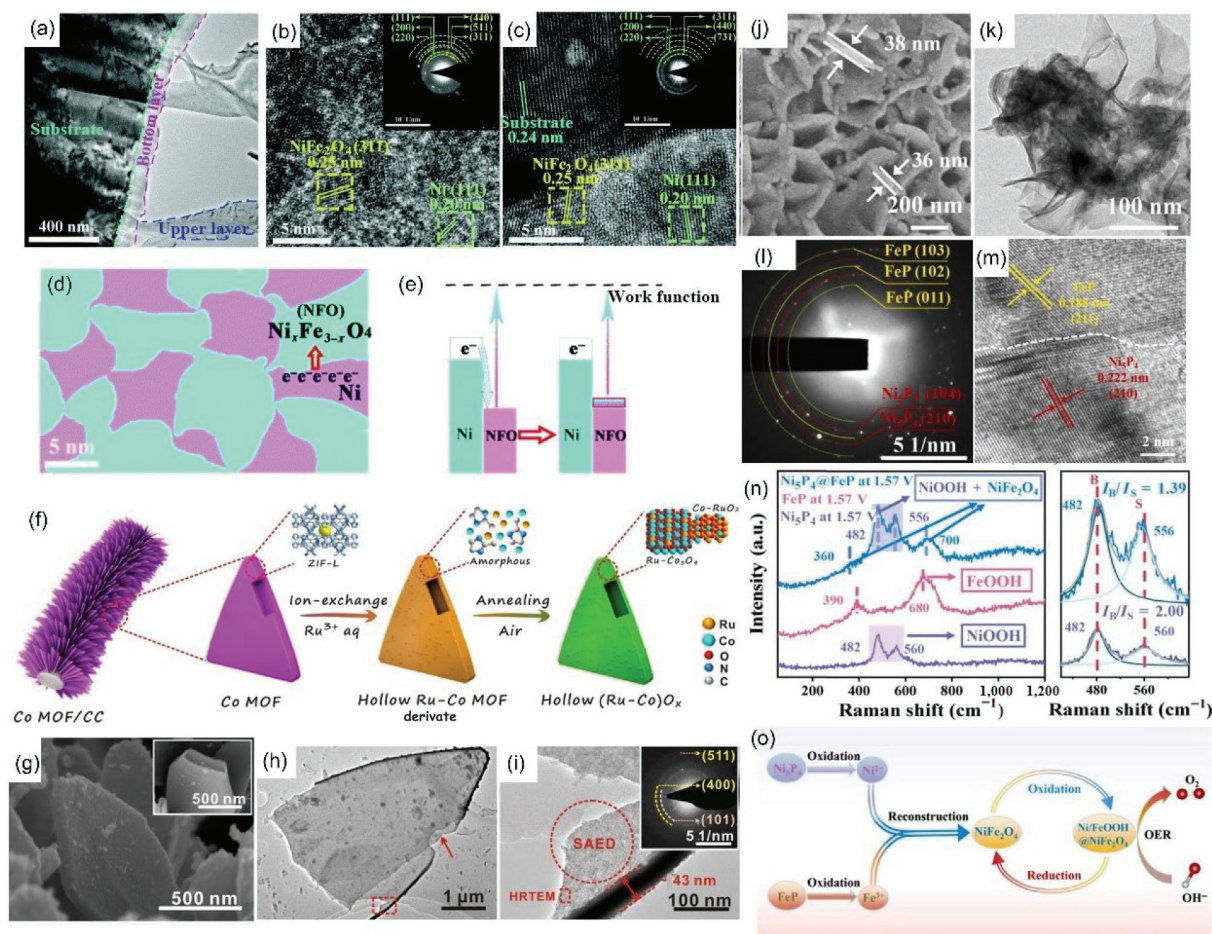


Figure 30 (a) TEM image, ((b) and (d)) HRTEM images, and ((c) and (e)) selected area electron diffraction (SAED) pattern of the ((b) and (c)) upper layer and ((d) and (e)) bottom layer of $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4/\text{Ni}$ hybrid NSA. (f) Schematic diagram of the electron transfer between Ni and $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$. (g) Schematic diagram of preparation, (h) SEM, and ((i) and (j)) TEM images of hollow $(\text{Ru-Co})\text{O}_x/\text{CC}$ (inset in (h): a broken hollow nanosheet, inset in (j): corresponding SAED pattern). (k) SEM, (l) TEM images, (m) SAED pattern, and (n) HRTEM image of $\text{Ni}_5\text{P}_4/\text{FeP}$ nanosheets. (o) OER Raman spectra from the 40th CV scan of Ni_5P_4 , FeP, and $\text{Ni}_5\text{P}_4/\text{FeP}$. (p) Schematic diagram of active Ni/FeOOH- NiFe_2O_4 layer formed by dynamic reconstruction on the surface of $\text{Ni}_5\text{P}_4/\text{FeP}$. (a)–(f) Reproduced with permission from Ref. [285], © Royal Society of Chemistry 2020. (g)–(j) Reproduced with permission from Ref. [286], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. (k)–(p) Reproduced with permission from Ref. [287], © Elsevier B.V. 2021.

C@C@Co-N-C Janus nanofibers (NiFe@C@Co CNFs) is easy to be precisely adjusted by optimizing the synthesis conditions. Benefiting from the unique open hollow Janus structure, the NiFe@C@Co CNFs not only exhibited a surface area of up to $209 \text{ m}^2\text{g}^{-1}$ to provide sufficient active sites and continuous ion diffusion paths, but also had excellent ORR and OER bifunctional catalytic properties in alkaline electrolytes. In addition, the material also had satisfactory mechanical flexibility that can be used as the flexible cathode for high-performance batteries.

Nanowire materials with unique configurations have also aroused feverish research interest. For example, Lin et al. adopted an ingenious top-down strategy and selected fluorinated NiMoO_4 nanowires as the precursor to construct a novel hollow $\text{MoO}_3/\text{NiF}_2$ heterogeneous nanowire material with abundant pore structures on NF ($\text{MoO}_3/\text{NiF}_2/\text{NF}$) (Fig. 33(a)) [292]. Reasonable fluorination can optimize the catalyst morphology and induce the precursor to generate disordered heterogeneous interfaces, which can adjust the electron properties. Remarkably, the porous hollow nanowires have large ECSA and can provide efficient paths for charge transport to greatly accelerate OER (Figs. 33(b)–33(d)). In addition, the heterogeneity without binder facilitates the release of generated O_2 bubbles on the surface of the self-supported electrode. These advantages enable the optimal sample to perform a remarkable η_{100} of 272 mV under suitable conditions and a high current density of $100 \text{ mA}\cdot\text{cm}^{-2}$ can be maintained for 50 h without significant activity loss. Furthermore, Yang et al.

constructed a novel binder-free electrode with hierarchical nanowire arrays by one-step chemical deposition assisted by uniform magnetic field [293]. Ultrathin amorphous Ni-Fe hydroxides as the shell with a thickness of 1–5 nm were *in-situ* grown on Ni-Fe alloys (denoted as $\text{Ni}_x\text{Fe}_{1-x}$ -AHNAs) (Fig. 33(e)). This material has the following highlights. Firstly, the $\text{Ni}_x\text{Fe}_{1-x}$ hydroxyl oxide layer, which is far thinner than that prepared by hydrothermal method, can be used as the internal high active phase of OER. Secondly, the chemical deposition method under magnetic field can reduce the impedance to a certain extent so as to accelerate the transmission of charge, and endow satisfactory mechanical stability that the prepared morphology is difficult to be destroyed. It is noteworthy that the layered nanowire array structure not only has the general effect of increasing ECSA, but also greatly expands the release area of generated O_2 bubbles, which is beneficial to ion/mass transfer (Figs. 33(f)–33(i)). These advantages result in $\text{Ni}_x\text{Fe}_{1-x}$ -AHNAs showing ultra-low η_{500} and η_{1000} of 248 and 258 mV, respectively (Figs. 33(j)–33(m)).

3.4 Development of binderless catalysts

Since a majority of multicomponent (oxy)hydroxides were synthesized as powder or particles in most cases, additional adhesives were required indispensably to fix these catalysts on the electrode surface. Complex post-treatment process was usually required to bond the catalytic material to the conductive substrate with the help of polymer adhesives such as Nafion. This process

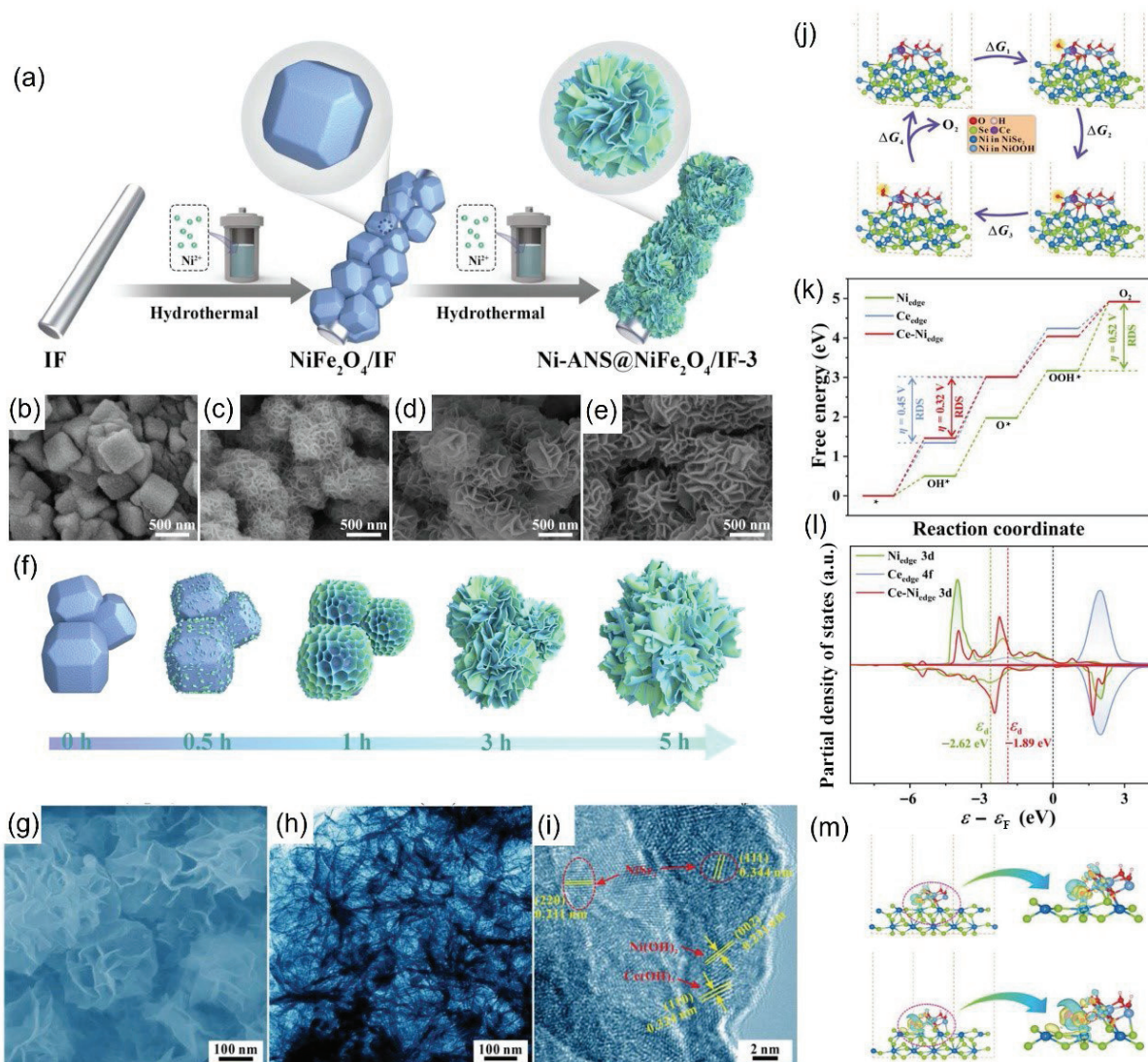


Figure 31 (a) Schematic diagram of preparation Ni-ANS@NiFe₂O₄/IF. SEM images of various growth time at (b) 0.5 h, (c) 1 h, (d) 3 h, and (e) 5 h. (f) Schematic illustration of nanoflower morphology evolution. (g) SEM, (h) TEM, and (i) high-resolution TEM images of Ce-m-Ni(OH)₂@NiSe₂. (j) Schematic diagram of adsorption atom configuration of Ce-Ni_{edge} site in each OER step. (k) Free energy diagrams. (l) PDOS diagrams. (m) The charge density difference between NiOOH@NiSe₂ and Ce-doped NiOOH@NiSe₂. (a)–(f) Reproduced with permission from Ref. [288], © Elsevier B.V. 2022. (g)–(m) Reproduced with permission from Ref. [289], © Wiley-VCH GmbH 2021.

inevitably reduces the contact area between electrolyte and catalytic active centers, increases the series resistance, blocks the active sites, inhibits the diffusion of electrolyte and gas products, and reduces the reactive activity, which is definitely detrimental to the electrocatalytic performance of the material [294]. In particular, in the case of high current density and severe gas evolution, the coated catalyst is easy to fall off from the substrate [295]. Therefore, researches adopted the method of growing OER active materials directly on the collector to solve the above problems.

Liu et al. anchored NiFe₂O₄ nanosheets on the surface of fibrous NiFe dendrite matrix (NiFe₂O₄@NFM) by simple electrodeposition and calcination oxidation, which not only realizes the multi-scale integrated assembly of substrates and functional materials, but also realizes the construction of 3D binder-free electrodes [296]. Moreover, choosing 3D dendrite substrate as support led to the improvement of the conductivity and durability of NiFe₂O₄ nanosheets. During the preparation of metal dendrites, the surface of the electrode overflowed a lot of gas discharged in the form of channels, which can be used as exhaust channels to prevent gas from flushing active substances. FESEM images revealed that the anchored NiFe₂O₄@NiFe exhibited

unique petal structure, resulting in more exposure of the active sites and the enhancement of ions diffusion as well as charge transfer (Figs. 34(a)–34(c)). The η_{10} of the NiFe₂O₄@NFM-3 was 234 mV and a high capacitance of 1,560 mF·cm⁻² was obtained at 1 mA·cm⁻² (Table 3).

The excellent properties of LDHs make them a hot topic in recent researches. Etesami et al. synthesized a series of self-supported bimetallic LDHs on NF via a simple ultra-fast electrodeposition technique [266, 297]. From SEM, TEM, and HRTEM images, the obtained bimetallic hydroxides were uniformly distributed on the NF substrate with short-range ordered crystalline or amorphous structures and 3D porous skeleton morphology, which are beneficial to OER (Figs. 34(d)–34(f)). In addition, the unique interaction between the LDHs and substrate NF resulted in outstanding OER activity even superior to RuO₂. Similarly, Chen et al. prepared a binderless NiFe₂O₄/NiFe LDH electrocatalyst by using a one-step chemical bath deposition (CBD) method under low temperature to blend the 2D heterostructure NiFe₂O₄ and NiFe-LDH firmly on a low-cost stainless steel mesh substrate [266]. The influence of component concentration on catalyst performance was studied. The η_{100} of the optimal NiFe₂O₄/NiFe LDH-25 sample was ultra-

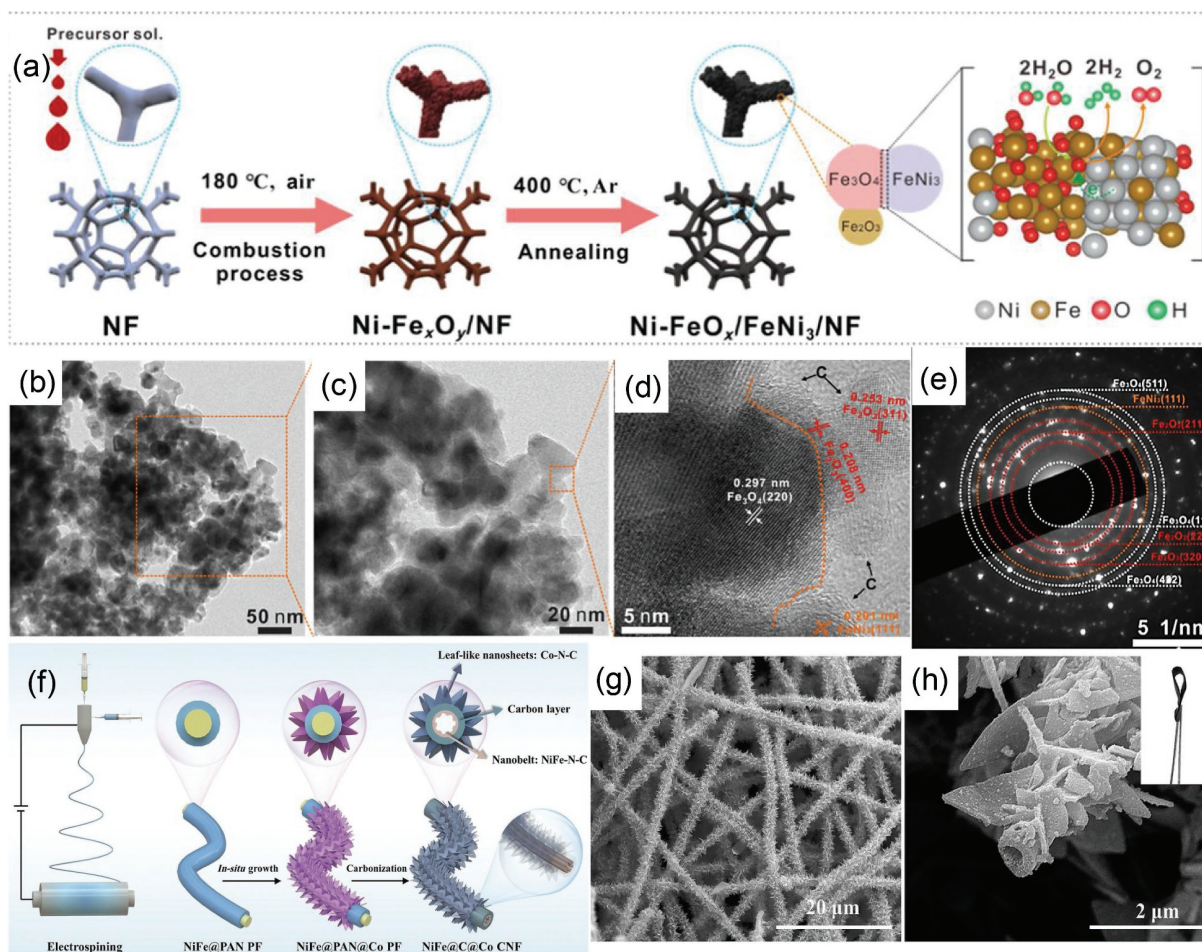


Figure 32 (a) Schematic diagram of preparation of Ni-FeO_x/FeNi₃, (b)–(d) TEM images, and (e) SAED pattern. (f) Schematic diagram of preparation of NiFe@C@Co CNFs and (b)–(d) SEM images. (a)–(e) Reproduced with permission from Ref. [290], © American Chemical Society 2022. (f)–(h) Reproduced with permission from Ref. [291], © Chen, X. et al. 2022.

low 190 mV, which surpassed most NiFe-based catalysts. The high OER activity can be attributed to the synergistic effect of NiFe LDHs and NiFe₂O₄. SEM and TEM images showed that the vertically arranged heterostructure sheets of NiFe₂O₄/NiFe LDH presented porous morphology, which provided abundant active edge sites directly attached to the highly conductive substrate, as well as efficient pathways for the transport of electrolyte ions and electrons, contributing to the significant improvement of electronic conductivity and electrocatalytic performance (Figs. 34(g)–34(i)) [266]. Gao et al. used electrodeposition method to rapidly prepare binderless CoMn-LDH nanosheets with a thickness of 1.9 nm on CFC substrate in 50 s, which exhibited an η_{10} of 258 mV [267]. The self-supported CoMn-LDH anode showed excellent stability even under the condition of high current density of 370 mA·cm⁻² and the bending degree of electrode was up to 180 degrees. The excellent OER performance can be contributed to the electron interaction between Mn and Co, the increase of electrochemical active area, and the decrease of charge transfer resistance. Atomic force microscopy (AFM) images and corresponding height profiles revealed that in the ultra-thin CoMn-LDH/CFC-50, the average thickness of CoMn-LDH nanosheets is about 1.9 nm, which is much smaller than that of CoCo-LDH/CFC nanosheets (2.5 nm), indicating that the addition of Mn can effectively reduce the thickness of Co-based LDHs (Figs. 34(j)–34(m)).

The similar one-step electrodeposition was used by Gong et al. to grow the Fe coordination polymer Fe(O_x)(H₂O)₂ nanorods on NF (Fe(O_x)(H₂O)₂/NF-(x)-y (x: deposition potential, y: time) (Fig. 35(a)) [298]. The best sample Fe(O_x)(H₂O)₂/NF-(-1.4)-15 is an

integrated binderless material with high OER catalytic efficiency that showed an η_{100} of 340 mV superior to most of MOF-based catalysts even after electrolysis for 80 h at 20 mA·cm⁻², showing satisfactory long-time durability. They studied the formation mechanism of Fe(O_x)(H₂O)₂ nanorods, and analyzed the influence of metal ions in MOFs on their morphology and OER properties. DFT calculations showed that the RDS on Fe(O_x)(H₂O)₂ and Ni(O_x)(H₂O)₂ was the formation of Fe⁺-OOH and Ni⁺-OH. Due to different electron configurations of Fe and Ni, their ΔG_{max} values were 1.628 and 1.71 eV, respectively, resulting in different D-band centers and different adsorbent affinities. Therefore, Fe compounds can avoid the particle aggregation in Ni compounds, so that more active sites were exposed to further improve the electrocatalytic activity (Figs. 35(b) and 35(c)).

Yu et al. used a corrosion method to prepare Fe-Ni-OH binderless hybrid NF electrode [299]. They immersed NF in a self-made piranha solution with 3:1 sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) as the reaction medium and integrated it with Fe(NO₃)₃ as the iron precursor into the final Ni-Fe based self-supported OER electrocatalyst with high activity and stability (Fig. 36(a)). The unique OER-beneficial microstructure could be observed in SEM and TEM images (Figs. 36(b)–36(k)). The researchers synthesized comparative samples under the same conditions using water and other solutions as reaction media named as NF-Fe-Y-Z (Y: reaction medium (W for water and PS for piranha solution), Z: reaction time in hour). According to various electrochemical evaluations, samples prepared in piranha solution had superior OER performance than those prepared in water, H₂SO₄, and H₂O₂. The former exhibited a low η_{10} of

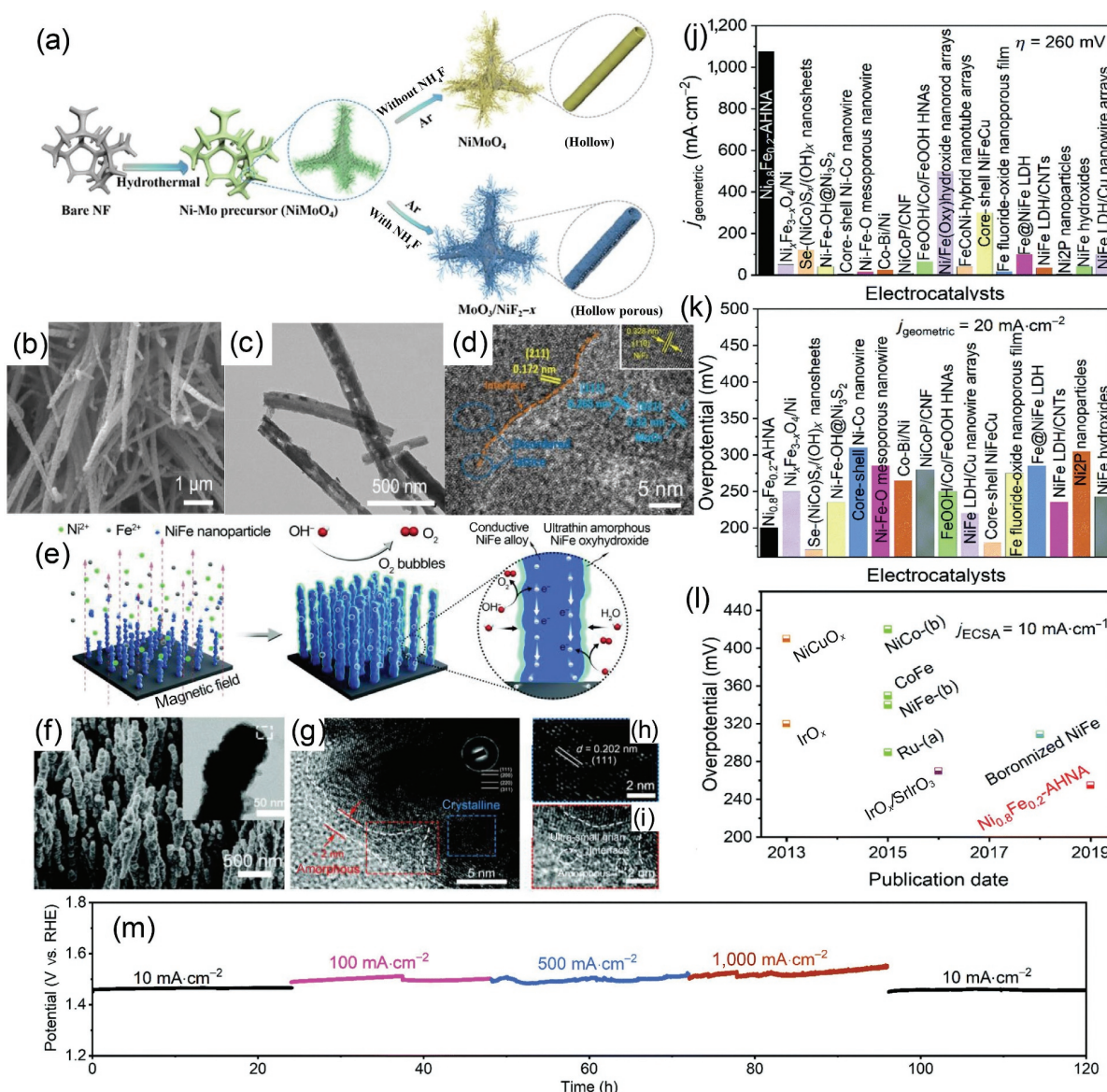


Figure 33 (a) Schematic diagram of preparation of $\text{MoO}_3/\text{NiFe}_2/\text{NF}$, (b) FESEM, (c) TEM, and (d) HRTEM images. (e) Schematic diagram of preparation of $\text{Ni}_{0.8}\text{Fe}_{0.2}$ -AHNAs, (f) SEM, and (g)–(i) HRTEM images. Comparison of (j) the current densities at 260 mV, (k) j_{20} , and (l) intrinsic OER catalytic activities of $\text{Ni}_{0.8}\text{Fe}_{0.2}$ -AHNAs and related OER catalysts. (l) Chronopotentiometric curves of $\text{Ni}_{0.8}\text{Fe}_{0.2}$ -AHNAs. (a)–(d) Reproduced with permission from Ref. [292], © Elsevier Ltd. 2021. (e)–(m) Reproduced with permission from Ref. [293], © Royal Society of Chemistry 2020.

245 mV, and can keep the η_{10} of 267 mV over 500 h, which can be attributed to the cooperative effect of Fe-Ni reciprocal hydroxides and the high specific surface area and low charge transfer resistance provided by the self-supported porous NF electrode. Interestingly, in the presence of piranha solution, the oxidation of NF was accelerated and Fe^{3+} ions were converted into amorphous Fe-hydroxide particles on NF, suggesting that sulfuric acid and hydrogen peroxide in piranha solution have a synergistic effect on the formation of active Fe/Fe-Ni hydroxide nanoparticles on the surface of NF. DFT calculations found that compared with bare $\text{Ni}(\text{OH})_2$, the adsorption free energy of OH^* and OOH^* decreased significantly when Fe was added to $\text{Ni}(\text{OH})_2$, which accelerated the OER, suggesting that Fe^{4+} plays a key role in reducing the RDS free energy of OER. Notably, OER activity did not decrease with the continuous decrease of active Fe species during the long-term reaction of NF-Fe-PS, suggesting that a small amount of Fe was sufficient to provide outstanding OER activity and stability (Figs. 36(l)–36(q)).

Chen et al. fabricated a non-binder OER electrode on the surface of NF using open hollow CuO_x nanocubes doped with Ni (hNC/NF) by simple spontaneous potentiometric replacement

followed by electrochemical voltammetry etching (Fig. 37(a)) [300]. This preparation method can be further used to design multi-layer porous electrocatalysts with open structure and high active region. Special face-selective etching was achieved by taking advantage of the unique structure of hollow nanocubes with large open ends, resulting in different accessibility to solution species on their tops and sides, which will advance the morphologic controllability of porous material preparation (Fig. 37(b)). Furthermore, the *in-situ* deposition nature of NF enabled the spontaneous doping of Ni. DFT calculations showed that adding Ni into CuO_x can optimize the energy barrier of OER and enhance the adsorption of oxygen intermediates. In addition, the hollow porous cubes have both large specific surface area and volume ratio, and shorten the transport distance of mass and ions. Therefore, the self-supported hNC/NF electrode showed the best OER electrocatalytic performance (η_{10} : 305 mV) among Cu-based electrocatalysts reported previously and preeminent long-term stability (Figs. 37(c) and 37(d)). Wang et al. used an optimized hydrothermal process to grow porous FeCo_2O_4 nanosheets with distinct layers on NF ($\text{FeCo}_2\text{O}_4/\text{NF}$) as a carbon-free and binderless electrode material for lithium-ion batteries (Figs.

Table 3 Comparison of electrochemical parameters between self-supporting binderless OER catalysts and other catalysts

Catalyst sample	Electrolyte	Current density ($\text{mA}\cdot\text{cm}^{-2}$)	Overpotential (mV)	Tafel slope ($\text{mV}\cdot\text{dec}^{-1}$)	Ref.
$\text{NiFe}_2\text{O}_4/\text{NFM}$ -3	0.1 M KOH	10	234	52	[296]
$\text{NiFe}_2\text{O}_4/\text{NiFe LDH}$ -25	1 M KOH	100	190	21.5	[266]
CoMn-LDH-50	0.1 M KOH	10	258	49	[267]
$\text{Fe}(\text{ox})(\text{H}_2\text{O})_2/\text{NF}$ -(-1.4)-15	1 M KOH	40	270	137	[298]
NF-Fe-PS	1 M KOH	10	245	82.9	[299]
hNC/NF	1 M KOH	10	305	72	[300]
$\text{Co}(\text{OH})_2/\text{MnO}_2\text{-CNAs}$	1 M KOH	10	340	114	[302]
NiCo_2O_4	1 M KOH	0	310	60.56	[303]
Fe-S-NiMoO ₄ /MoO ₃ @NF	1 M KOH	10	212	41	[304]
Co ₄ Mo ₈ /NF	1 M KOH	10	302.8	80.7	[305]
10S-CoMn ₂ O ₄ /FTO	0.1 M NaOH	10	300	26.28	[306]

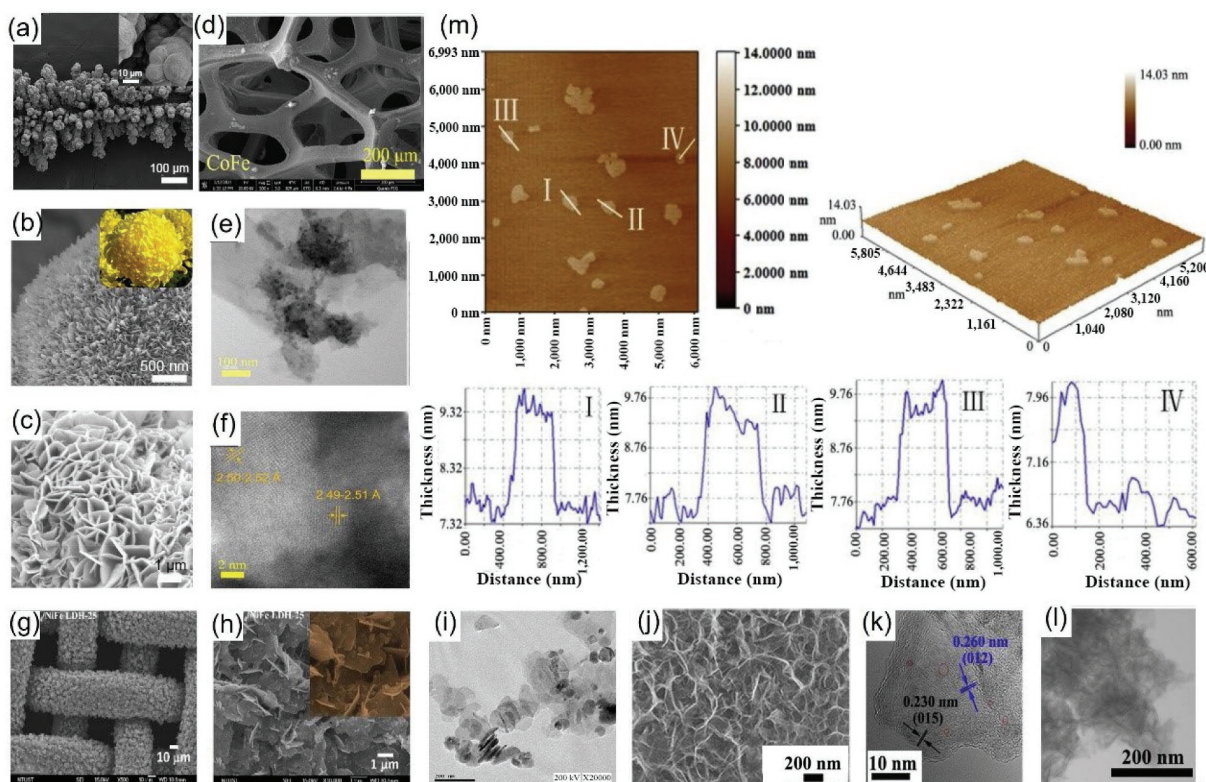


Figure 34 SEM images of (a) NFM, (b) $\text{NiFe}_2\text{O}_4/\text{NFM}$, and (c) $\text{NiFe}_2\text{O}_4/\text{NFM}$ prepared at 300 °C. (d) SEM, (e) TEM, and (f) HRTEM images of CoFe LDHs. ((g) and (h)) SEM and (i) TEM images of $\text{NiFe}_2\text{O}_4/\text{NiFe LDH}$ -25. (j) SEM, (k) HRTEM, (l) ADF STEM, and (m) AFM images and the corresponding height profiles of the nanosheets in the CoMn-LDH-50 anode. (a)–(c) Reproduced with permission from Ref. [296], © Elsevier B.V. 2019. (d)–(f) Reproduced with permission from Ref. [297], © Elsevier B.V. 2021. (g)–(i) Reproduced with permission from Ref. [266], © American Chemical Society 2020. (j)–(m) Reproduced with permission from Ref. [267], © Elsevier Ltd. 2018.

37(e)–37(i) [301]. In the OER, the discharge products began to decompose at 3.3 V, which can be attributed to the large open pores formed by the interconnecting of FeCo_2O_4 nanosheets to provide storage spaces for discharge products (Li_2O_2) and channels for O_2 diffusion as well as the mesopores distributed on nanosheets to provide abundant catalytic active sites.

Although self-supported 3D transition metal electrodes have the advantages of no binder and large ECSA, their poor electrical conductivity and difficulty in adjusting the electronic structure of (oxy)hydroxides limit their applications. To solve these problems, Wen et al. constructed 3D layered carbon nanoarrays through high temperature carbonization and hydrothermal treatment (Figs. 38(a)–38(c)) [302]. The surface of nanoarrays was coated with heterogeneous $\text{Co}(\text{OH})_2/\text{MnO}_2$ as an efficient OER electrocatalyst ($\text{Co}(\text{OH})_2/\text{MnO}_2\text{-CNAs}$). The $\text{Co}(\text{OH})_2/\text{MnO}_2\text{-}$

CNAs possessed higher conductivity and larger ECSA (approximately 2.6 times that of $\text{Co}(\text{OH})_2\text{-CNAs}$) that promoted electrolyte diffusion and ion transport. DFT calculations revealed that the formation of $\text{Co}(\text{OH})_2/\text{MnO}_2$ heterojunction structure reduced the valence state of Mn atoms, and increased the valence state of Co atoms to (Co^{III}), promoting the transformation of Co^{II} to Co^{III} in $\text{Co}(\text{OH})_2$ through the addition of MnO_2 , increasing the storage of oxidized charge in the catalyst, and resulting in the enhanced strength of Co–O bond, easier formation of O^* , and reduced free energy barrier of RDS in $\text{Co}(\text{OH})_2$ (Figs. 38(d)–38(g)). Furthermore, ultrathin porous NiCo_2O_4 nanosheets with oxygen vacancies were prepared as an efficient and independent cathode catalyst for Li– O_2 batteries [303]. A unique enhancement mechanism was established to explain its excellent OER electrocatalytic performance. Specifically, due to the strong

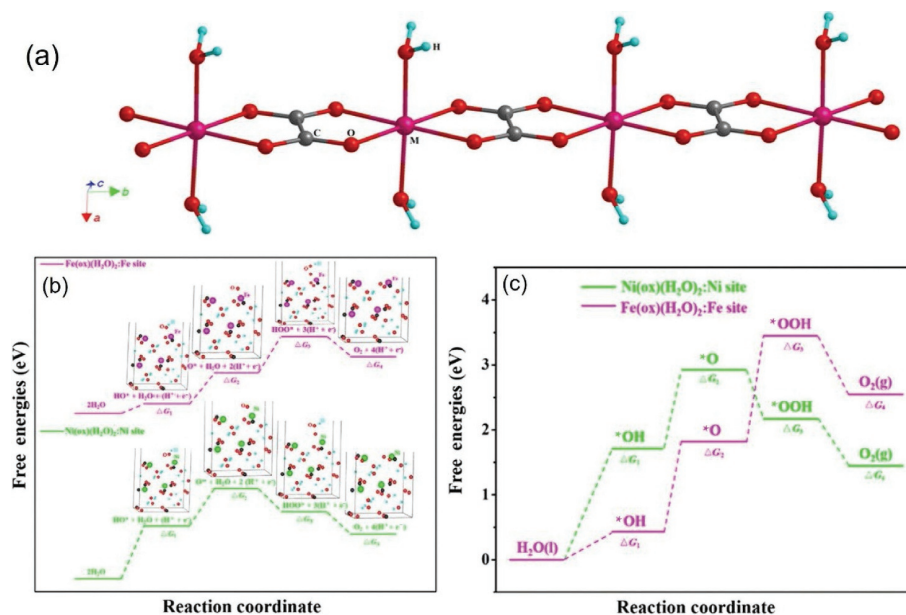


Figure 35 (a) Schematic structure of $M(Ox)(H_2O)_2$ ($M = Fe, Co, \text{ or } Ni$). (b) Optimized intermediate structures and ΔG of OER on (200) surfaces of $Ni(Ox)(H_2O)_2$ and $Fe(Ox)(H_2O)_2$. (c) Calculated Gibbs free energy diagrams. (a)–(c) Reproduced with permission from Ref. [298], © American Chemical Society 2021.

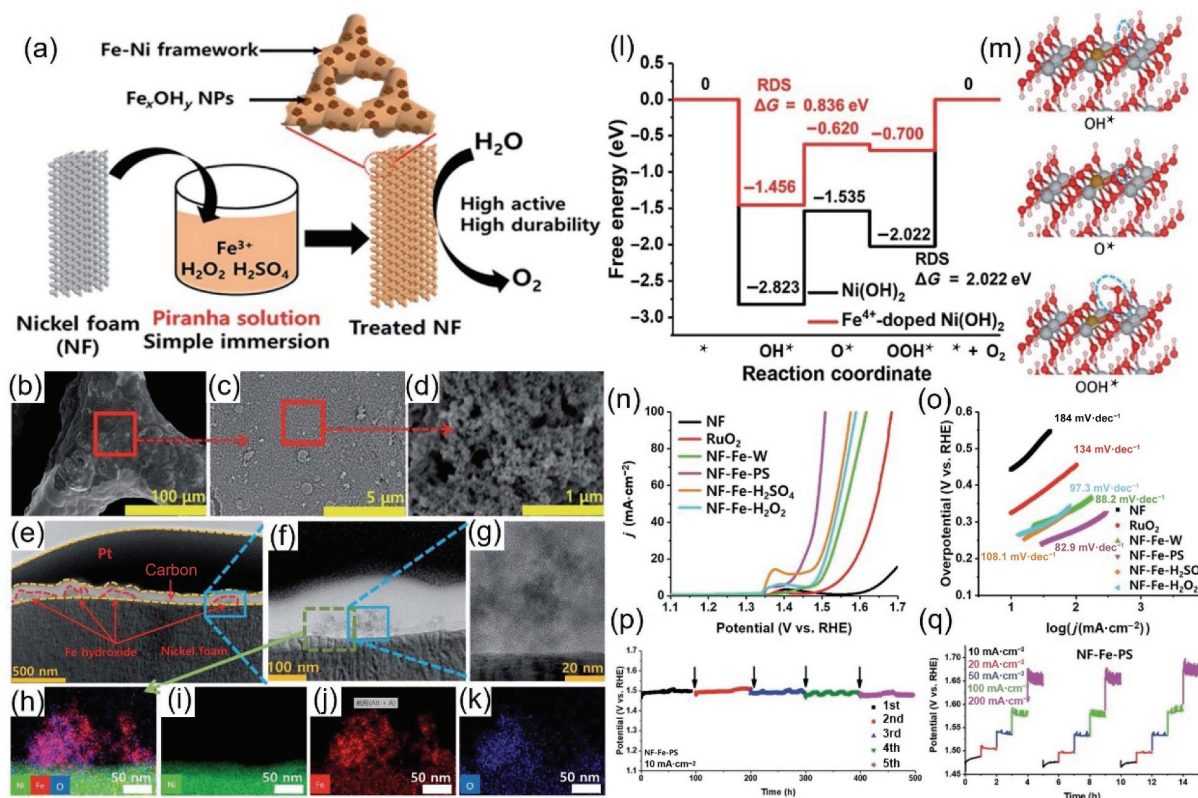


Figure 36 (a) Schematic diagram of the preparation of FeNi hydroxide on NF. ((b)–(d)) SEM, ((e)–(g)) TEM, and ((h)–(k)) element mapping images of NF–Fe–PS. (l) Calculated energies for each OER step. (m) Geometry of Fe–O coordination in NF–Fe–PS for each OER step. (n) LSV curves. (o) Tafel plots. (p) Long-term stability and (q) step stability test of NF–Fe–PS. (a)–(q) Reproduced with permission from Ref. [299], © Royal Society of Chemistry 2020.

adsorption strength between O_2 and $NiCo_2O_4$ nanosheets, smaller annular arrays were preferentially formed on the surface of $NiCo_2O_4$ nanosheets with low discharge depth. The torus less than 100 nm was in close contact with the cathode material and was easy to decompose during charging, which reduced the overpotential of OER and improved the cycling performance of the battery. As the discharge depth increased, larger ring products were grown on the smaller Li_2O_2 arrays by solution path, thus achieving extremely high discharge capacity (Figs. 38(h)–38(n)).

Doping non-metallic atoms into the binder-free multicomponent metal (oxy)hydroxides material can further

improve their catalytic performance. For example, Song et al. used a solvothermal method to uniformly grown binder-free Fe-S-NiMoO₄/MoO₃ on NF (Fe-S-NiMoO₄/MoO₃@NF) [304]. The free energy diagram indicated that each step of OER is well regulated under the influence of doped Fe atoms (Figs. 39(a)–39(f)). The PDOS diagrams of the local active Fe/Mo sites showed that the calculated ϵ_d (Fe) is -1.548 eV lower than ϵ_d (Mo) (Fig. 39(b)). According to d band center (ϵ_d) theory, ϵ_d level is positively correlated with adsorption capacity. Therefore, the band structure diagram of Fe@MoO₃ reflects that its weak adsorption ability leads to the facile desorption of adsorbed intermediates

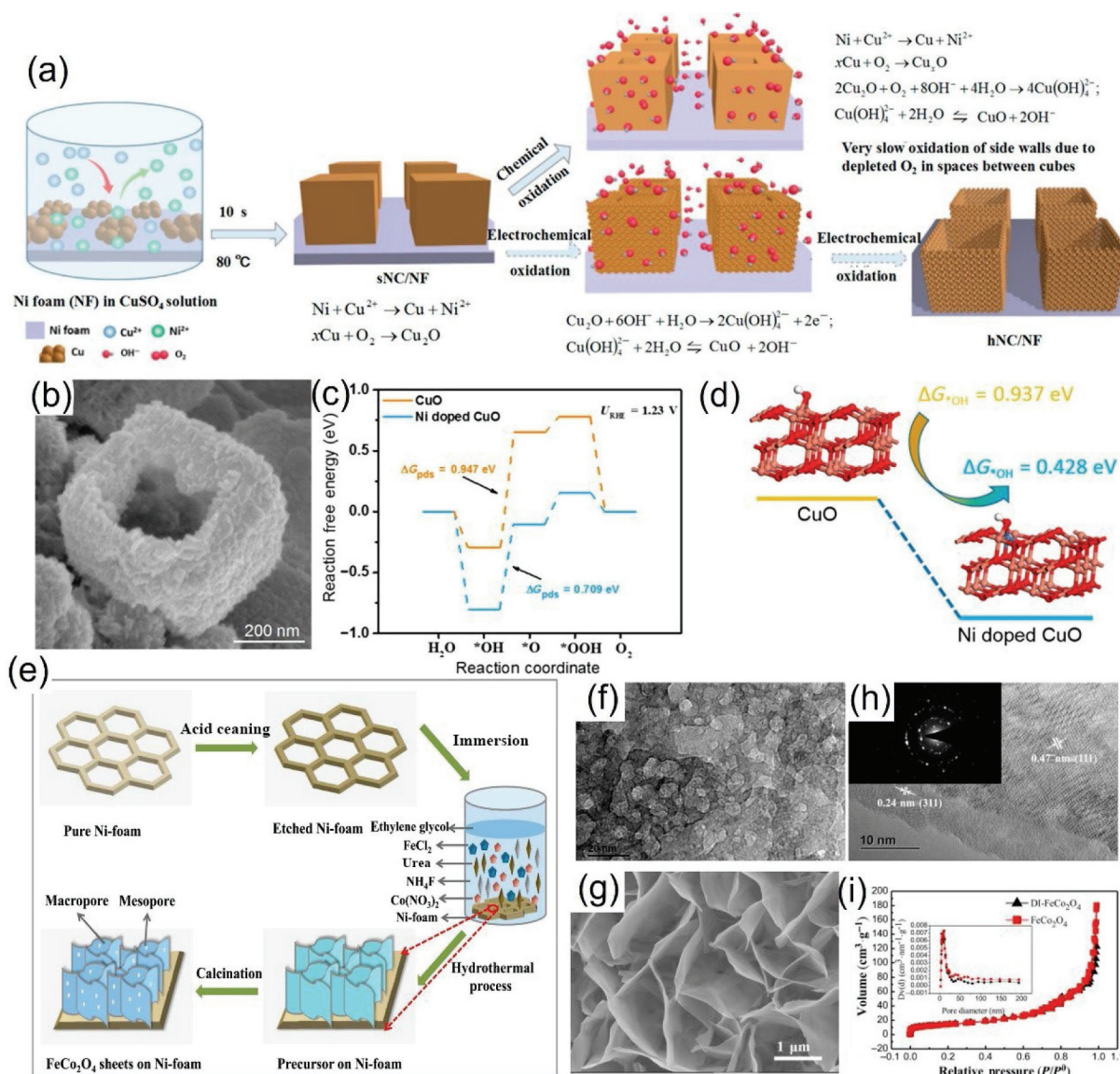


Figure 37 (a) Schematic diagram of the preparation of hNC/NF. (b) SEM image. (c) Calculated free energy diagram of each OER steps and (d) OH adsorption energies for Ni-doped CuO and CuO. (e) Schematic diagram of the preparation of hierarchical porous FeCo_2O_4 @Ni. (f) TEM, (g) FESEM, and (h) HRTEM images of FeCo_2O_4 @Ni. (i) N_2 adsorption/desorption isotherms and pore size distributions. (a)–(d) Reproduced with permission from Ref. [300], © American Chemical Society 2020. (e)–(i) Reproduced with permission from Ref. [301], © Elsevier B.V. 2018.

from its surface, which is consistent with the free energy coincides results (Figs. 39(c) and 39(d)). Furthermore, when more impurity energy levels of Fe is incorporated in the bandgap, the stable bonding of Fe and O forms. This O–Fe–O bridge can promote the rapid transmission of electrons in the catalyst, resulting in a significant decrease in the band gap (0.70 eV) of Fe@MoO_3 compared with that of the original MoO_3 (2.77 eV), which verifies that Fe@MoO_3 has enhanced conductivity. Therefore, Fe doping can adjust the crystal surface and electronic structure of MoO_3 , resulting in more stable electrode surface, improve electrical conductivity, and reduce reaction energy barrier. The obtained $\text{Fe-S-NiMoO}_4/\text{MoO}_3$ @NF electrode exhibited an ultra-low η_{500} of 271 mV and can operate stably at 50°C for over 100 h (Figs. 39(e) and 39(f)). Zhang et al. used facile solvothermal method to directly synthesize a novel binderless Co_4Mo_8 bimetallic coordination cluster supported with calixarene material on NF substrate (Figs. 39(g)–39(i)) [305]. During the preparation process, the sulfur-modified polyoxometalate Mo_8 clusters were successfully introduced into the Co_4Mo_8 /NF electrode. It is noteworthy that the intentional addition of S atoms to the lower edge of the Co_4Mo_8 clusters promotes adhesion between the clusters and

substrates, making the material more stable on NF even without binder that can continuously catalyze OER over 150 h under η_{40} of 366.8 mV. In addition, they synthesized similar binderless cluster materials with Ni (Ni_4Mo_8 /NF) or Zn (Zn_4Mo_8 /NF) replacing Co using same method for comparison, and found that the synergistic effect between Co–Mo metals endows Co_4Mo_8 /NF with an η_{10} of 302.8 mV (Figs. 39(j) and 39(k)).

Feng et al. directly synthesized CoMn_2O_4 material with S micro-peaks (S- CoMn_2O_4 -MSs) on its surface on the FTO substrate in chloride solution under low temperature and ambient atmosphere via a simple two-step electrodeposition technique (Fig. 39(l)) [306]. They found that the blocked surface layer results in inconvenient electrolyte contact and oxygen bubble release, which is a prerequisite for the performance of OER electrocatalyst. Thus, they further optimized the sulfured time to prepare the best final product. Compared with the original Mn_3O_4 (580 mV) and Co_3O_4 (410 mV), S- CoMn_2O_4 -MSs exhibited higher OER catalytic activity with an η_{10} of 300 mV, which could be attributed to the synergistic effect of Co and Mn as well as the large ECSA endowed by the unique micro-peak structure and the easily reactive low oxidation state of Co due to surface curing (Figs. 39(m) and

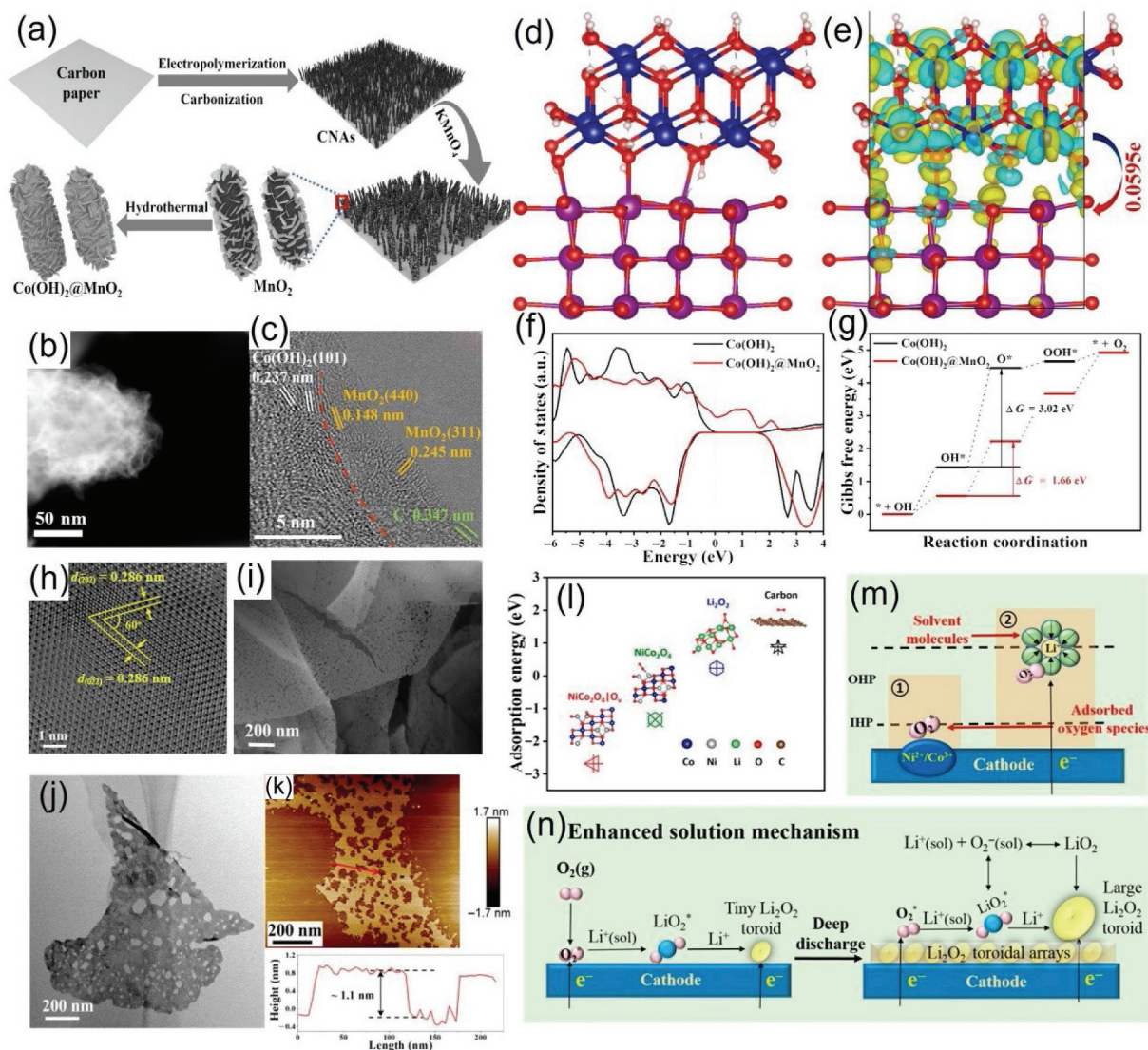


Figure 38 (a) Schematic diagram of the preparation of $\text{Co}(\text{OH})_2\text{@MnO}_2\text{-CNAs}$. (b) HAADF-STEM and (c) annular bright-field (ABF)-STEM images. (d) Schematic heterostructure of $\text{Co}(\text{OH})_2\text{@MnO}_2$. (e) Differential charge density of $\text{Co}(\text{OH})_2\text{@MnO}_2$. (f) DOS diagram. (g) Calculated free energy diagram. (h) HRTEM, (i) SEM, (j) TEM, and (k) AFM images and the amplitude profile of the red line of NiCo_2O_4 . (l) Calculated O_2 adsorption energy and corresponding adsorption configurations. (m) Schematic diagram of two-layer electrocatalysis of NiCo_2O_4 . (n) Schematic diagram of the possible mechanism of Li_2O_2 . (a)–(g) Reproduced with permission from Ref. [302], © The Electrochemical Society 2021. (h)–(n) Reproduced with permission from Ref. [303], © American Chemical Society 2019.

39(n)). In addition, the high adhesion of the S- $\text{CoMn}_2\text{O}_4\text{-MSs}$ to the electrode provided outstanding stability at $20 \text{ mA}\cdot\text{cm}^{-2}$ over 24 h.

4 Conclusions and perspectives

Notably, many researches have demonstrated that thin oxides or (ox) hydroxides *in situ* formed on the surface of catalysts should be the real active sites, and the electrocatalysts themselves act as precursors and conductive scaffolds. Therefore, the transition metal oxides/(oxy)hydroxides have been the hot topics in the electrocatalytic field. Understanding different material preparation strategies and gaining insight into the nature of how they improve catalytic performance are the essential prerequisite for rational design of excellent OER catalysts in the future. In this review, various electrocatalyst preparation strategies for promoting OER catalytic activity are comprehensively reviewed combined with theoretical achievements. However, the commercialization of high-performance and low-cost OER catalysts is still a great challenge. Therefore, further research is still needed to solve some related problems [307, 308].

4.1 Optimizing the type of metal centers

A large number of studies on non-noble-metal-based OER catalysts have been devoted to optimizing the types of metal centers. For example, 3d metal elements of group VIII, such as Fe, Co, and Ni, alone or in combination with other metals, can catalyze OER as effectively as noble metal Ir and Ru catalysts under alkaline conditions [8]. Therefore, the OER catalysts based on nonprecious transition metal elements as the metal center have attracted much attention. The related researches have achieved many achievements including single transition metal center catalysts, like Fe-, Ni-, and Co- based catalysts. On this basis, the element doping strategies can be used to dope different types of other elements into monometallic and bimetallic systems to obtain multi-metallic centers like Fe-Co, Ni-Fe, and Fe-Co-W or metal-nonmetallic centers like M-O, M-N, and N/M/O-C (M = Fe, Co, Ni) to improve OER performance [309]. However, more efforts should be made to further optimize the metal center, including exploring various combination types of different elements with outstanding OER catalytic activity, and developing more facile and efficient preparation methods to make the metal center have better conductivity, lower potential barrier, and faster

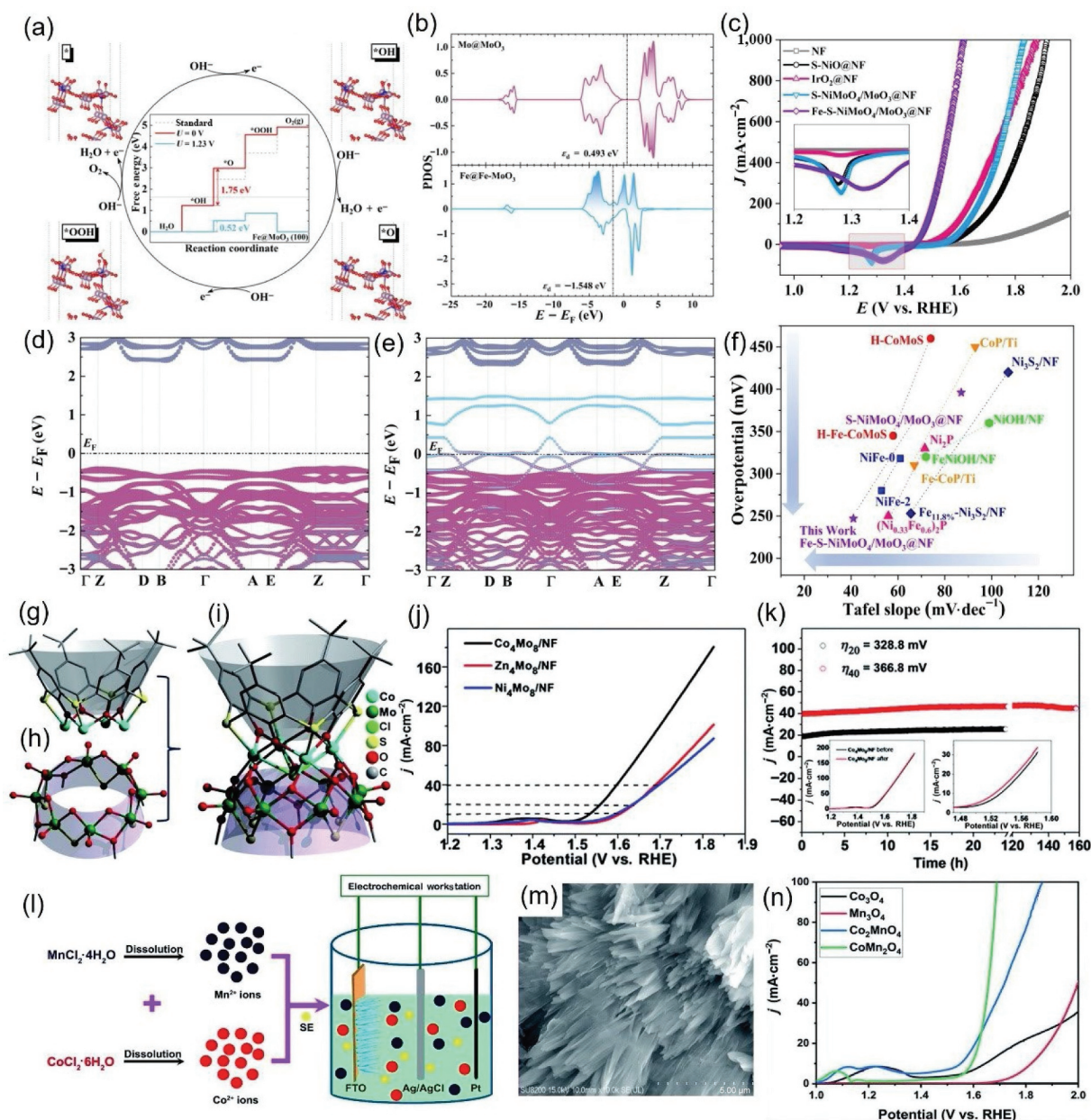


Figure 39 (a) Calculated OER free energy diagrams of Fe@MoO₃(100). (b) PDOS diagrams of Mo in MoO₃ and Fe in Fe@MoO₃. Band structures of (c) pristine MoO₃ and (d) Fe@MoO₃. (e) LSV curves. (f) The values of η_{100} and Tafel slope of various Fe-doped catalysts. Schematic diagrams of the structure of Co₄Mo₈ assembled with (g) a Co₄-TC4A unit, (h) an oxothiomolybdate Mo₈ unit, and (i) final product Co₄Mo₈/NF. (j) LSV curves. (k) Chronopotentiometry test. (l) Schematic diagrams of the synthesis of the S-CoMn₂O₄-MSS. (m) SEM image of the S-CoMn₂O₄-MSS. (n) LSV curves. (a)–(f) Reproduced with permission from Ref. [304], © Elsevier B.V. 2021. (g)–(k) Reproduced with permission from Ref. [305], © Royal Society of Chemistry 2019. (l)–(n) Reproduced with permission from Ref. [306], © Royal Society of Chemistry 2021.

reaction rate to further meet the actual needs of large-scale industrial application.

4.2 Improving the stability

The stability of electrocatalysts is an important aspect affecting their practical applications, which can be divided into two aspects: internal stability of catalyst itself and the stability during the catalytic reaction process. In the former, transition metal oxides usually show better stability than the corresponding hydroxides. In addition, the catalyst morphology is also a decisive factor and the stability of oxide catalysts with crystal structure is significantly better than that with amorphous structure, but the OER activity of the former is usually worse. Further optimization of catalyst composition and structure to meet industrial stability standards is still challenging. As for the stability during OER, many transition metal-based catalysts are synthesized in powder, which means that post-processing process and polymer binder are usually required

to bond the material to conductive substrate that may block some active sites and inhibit the diffusion of electrolyte and gaseous product. More seriously, the catalysts are facile to fall off in the case of high current density and rapid gas evolution, resulting in a significant reduction in catalytic activity. Although many studies are devoted to the *in-situ* preparation of self-supporting active OER materials on the substrate to avoid the use of binders, most of the laboratory stability tests of OER electrocatalysts focus on low current density of 10 mA·cm⁻² [310], while OER catalysts are generally required to maintain satisfactory stability at high current density of 800 mA·cm⁻² in practical industrial applications. Therefore, developing OER electrocatalysts with outstanding activity and excellent stability operated at high current density is still an arduous task in the future.

4.3 Morphology control

The OER catalytic activity is extremely dependent on the density

of active centers. High density of active centers such as unsaturated coordination atoms on catalyst surface can promote OER kinetics, thus improving electrocatalytic activity. In addition, the OER process involves multi-electron transfer, and hence the conductivity of materials is a decisive factor for the OER. In fact, catalytic materials with high density of active sites but low conductivity may exhibit poor overall catalytic performance. The main purpose of morphology control is to increase the specific surface area and active catalytic centers, shorten the charge or mass transfer path, and improve the conductivity and electrochemical performance. Reasonable design of unique morphologies, such as 1D nanowires/needles/rods/tubes, 2D nanosheets, and 3D assemblies/nanostructures, has shown great potential to improve electrical conductivity and ECSA.

4.4 Preparation of stable electrocatalysts under acidic conditions

Currently, most of the reported transition metal oxides and (oxy)hydroxides are generally examined in alkaline media. However, alkaline electrolyzers face the issues of relatively high energy consumption, high installation and maintenance cost, and low durability. Moreover, the process of OER in alkaline conditions requires a gas separation device and the reduced pH needs to be resolved by replenishing the alkaline electrolyte. Alkaline electrolytes rule out their application in proton exchange membrane (PEM) electrolytic cells. By contrast, acid electrolytes have much lower ohmic resistance and mature proton exchange membranes are commercially available, but transition metal based electrocatalysts are thermodynamically unstable under acidic conditions. Up to now, Ir-based electrocatalysts are the most stable ones applied in acidic environments. Therefore, the development of earth-abundant OER electrocatalysts in acidic media is an urgent challenge. Recent researches revealed that protecting active centers of OER using structurally stable elements such as Mn oxides and perovskites can achieve the goal [311]. For example, Li et al. synthesized γ -MnO₂ that can stably catalyze OER for up to 8,000 h in a strong acid environment with pH of 2 [310]. However, the Mn ions will be oxidized to MnO₄⁻ and dissolved into the electrolyte when the applied potentials are larger than 1.75 V, which limits its integration with the state of art PEM based water electrolyzers [59, 312]. Therefore, surface engineering and other methods should be developed to control the structure of catalysts to achieve satisfactory acidic OER activity and stability.

4.5 Improvement of characterization techniques

Most non-noble-metal-based catalysts undergo phase transition under OER conditions, including structure, valence state, and coordination environment. However, most of the current research adopts *ex situ* techniques, which can only give the characterization results before and after OER measurement. Furthermore, at high anodic potential of OER, the active center is dynamic during the operation, and because of the lack of advanced detection methods, structural evolution is often overlooked, making the correlation between structure and OER activity more difficult. Therefore, using *in situ* techniques to detect intermediates and their adsorption/desorption behaviors is essential to get firsthand experimental evidences for the proposed OER mechanisms. Recently, more and more *in situ* characterization techniques have been developed, such as *in situ* Raman spectroscopy, *in situ* ambient TEM, *in situ* XPS, etc. More excitingly, a general *operando* method using alcohol as a detection reagent enables to probe OER intermediates and discover intermediate bond energies that control OER dynamics under real working

conditions [313]. For example, Yao et al. reported direct observation of O-Ru₁-N₄ intermediates by manipulating XAS and *in situ* FTIR, providing deep insight into the reaction mechanism [83]. In future, *in situ* spectroscopies need to be further combined with other techniques and theoretical calculations to reveal the reaction mechanism more reliably. For example, using *in situ* TEM, real-time monitoring of changes in active intermediates can reveal the real course of OER, thus providing theoretical guidance for advancing design of novel and efficient catalysts.

4.6 Enhancing intrinsic activity beyond the scale relation

Although the scale relation in AEM is beneficial to rapidly screen catalysts, the scaling relationship between the OER intermediates HO* and HOO* in AEM imposes an upper limit on OER activity that the theoretical overpotential cannot exceed 0.37 V. Although several strategies have been devised to break the scale relations, such as stabilization of HOO*, independent of HO*, and introduction of proton receptors to alter the reaction pathway, breaking the ratio of HOO* to HO* sometimes may not lead to increased activity due to potentially inappropriate adsorption energies of the intermediates [314–316]. Future designs of enhanced OER catalysts should aim to optimize the free energy barrier of each OER step to approximate the equilibrium potential of 1.23 V as closely as possible. The synthesis of OER catalysts with the goal of breaking the HOO* and HO* relationship and independently optimizing the adsorption energy of various intermediates is challenging. Besides, converting OER paths to LOM can circumvent the scale relationship in the regular AEM to exceed the activity limits of the volcano map that the activation of LOM for direct O–O coupling bypassing the generation of *OOH intermediate is another effective approach. However, the competition between traditional AEM and LOM, that is, between cationic and anionic redox chemistry on catalyst surface, remains a major challenge to overcome. Other methods reported recently, such as coupling the catalyst to a non-thermal plasma [317] and changing the slope of the scale relationship by changing the oxygen reduction parameters rather than modifying the catalyst [318], are worthy of reference for future designs.

Acknowledgments

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References

- [1] Koper, M. T. M. Theory of multiple proton–electron transfer reactions and its implications for electrocatalysis. *Chem. Sci.* **2013**, *4*, 2710–2723.
- [2] Guan, J. Q.; Bai, X.; Tang, T. M. Recent progress and prospect of carbon-free single-site catalysts for the hydrogen and oxygen evolution reactions. *Nano Res.* **2022**, *15*, 818–837.
- [3] Devi, M. M.; Ojha, K. N.; Ganguli, A. K.; Jha, M. Transformation of waste tin-plated steel to iron nanosheets and their application in generation of oxygen. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 3669–3678.
- [4] Li, L. L.; Sun, H. N.; Hu, Z. W.; Zhou, J.; Huang, Y. C.; Huang, H. L.; Song, S. Z.; Pao, C. W.; Chang, Y. C.; Komarek, A. C. et al. *In situ/operando* capturing unusual Ir⁶⁺ facilitating ultrafast electrocatalytic water oxidation. *Adv. Funct. Mater.* **2021**, *31*, 2104746.
- [5] Zheng, F. Q.; Zhang, W. F.; Zhang, X. X.; Zhang, Y. L.; Chen, W. Sub-2 nm ultrathin and robust 2D FeNi layered double hydroxide nanosheets packed with 1D FeNi-MOFs for enhanced oxygen evolution electrocatalysis. *Adv. Funct. Mater.* **2021**, *31*, 2103318.

- [6] Kwon, J.; Han, H.; Jo, S.; Choi, S.; Chung, K. Y.; Ali, G.; Park, K.; Paik, U.; Song, T. Amorphous nickel-iron borophosphate for a robust and efficient oxygen evolution reaction. *Adv. Energy Mater.* **2021**, *11*, 2100624.
- [7] Zhang, Q. Q.; Guan, J. Q. Applications of atomically dispersed oxygen reduction catalysts in fuel cells and zinc-air batteries. *Energy Environ. Mater.* **2021**, *4*, 307–335.
- [8] Liu, N.; Wang, Y.; Zhang, Q. Q.; Guan, J. Q. Trifunctional iridium-based electrocatalysts for overall water splitting and Zn-air batteries. *Electrochim. Acta* **2021**, *380*, 138215.
- [9] Han, L.; Dong, S. J.; Wang, E. K. Transition-metal (Co, Ni, and Fe)-based electrocatalysts for the water oxidation reaction. *Adv. Mater.* **2016**, *28*, 9266–9291.
- [10] Wu, H. X.; Wang, Y. B.; Shi, Z. P.; Wang, X.; Yang, J. H.; Xiao, M. L.; Ge, J. J.; Xing, W.; Liu, C. P. Recent developments of iridium-based catalysts for the oxygen evolution reaction in acidic water electrolysis. *J. Mater. Chem. A* **2022**, *10*, 13170–13189.
- [11] Liu, N.; Cheng, Y.; Qi, H.; Hou, C. M.; Zhang, Q. Q.; Guan, J. Q. Promotion of the water oxidation activity of iridium oxide by a nitrogen coordination strategy. *Chem. Commun.* **2020**, *56*, 14909–14912.
- [12] Liu, N.; Duan, Z. Y.; Zhang, Q. Q.; Guan, J. Q. Insights into active species of ultrafine iridium oxide nanoparticle electrocatalysts in hydrogen/oxygen evolution reactions. *Chem. Eng. J.* **2021**, *419*, 129567.
- [13] Qin, F.; Zhao, Z. H.; Alam, M. K.; Ni, Y. Z.; Robles-Hernandez, F.; Yu, L.; Chen, S.; Ren, Z. F.; Wang, Z. M.; Bao, J. M. Trimetallic NiFeMo for overall electrochemical water splitting with a low cell voltage. *ACS Energy Lett.* **2018**, *3*, 546–554.
- [14] McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16977–16987.
- [15] Xu, K.; Ding, H.; Lv, H. F.; Tao, S.; Chen, P. Z.; Wu, X. J.; Chu, W. S.; Wu, C. Z.; Xie, Y. Understanding structure-dependent catalytic performance of nickel selenides for electrochemical water oxidation. *ACS Catal.* **2017**, *7*, 310–315.
- [16] Wu, Z. P.; Lu, X. F.; Zang, S. Q.; Lou, X. W. Non-noble-metal-based electrocatalysts toward the oxygen evolution reaction. *Adv. Funct. Mater.* **2020**, *30*, 1910274.
- [17] Han, Q. L.; Luo, Y. H.; Li, J. D.; Du, X. H.; Sun, S. J.; Wang, Y. J.; Liu, G. H.; Chen, Z. W. Efficient NiFe-based oxygen evolution electrocatalysts and origin of their distinct activity. *Appl. Catal. B: Environ.* **2022**, *304*, 120937.
- [18] Yan, D. Q.; Zhang, L.; Chen, Z. P.; Xiao, W. P.; Yang, X. F. Nickel-based metal-organic framework-derived bifunctional electrocatalysts for hydrogen and oxygen evolution reactions. *Acta Phys. Chim. Sin.* **2021**, *37*, 2009054.
- [19] Qiao, X. S.; Kang, H. J.; Li, Y.; Cui, K.; Jia, X.; Wu, X. H.; Qin, W. Novel FeNi-based nanowires network catalyst involving hydrophilic channel for oxygen evolution reaction. *Small* **2022**, *18*, 2106378.
- [20] Huang, W. Z.; Li, J. T.; Liao, X. B.; Lu, R. H.; Ling, C. H.; Liu, X.; Meng, J. S.; Qu, L. B.; Lin, M. T.; Hong, X. F. et al. Ligand modulation of active sites to promote electrocatalytic oxygen evolution. *Adv. Mater.* **2022**, *34*, 2200270.
- [21] Haase, F. T.; Rabe, A.; Schmidt, F. P.; Herzog, A.; Jeon, H. S.; Frandsen, W.; Narangoda, P. V.; Spanos, I.; Friedel Ortega, K.; Timoshenko, J. et al. Role of Nanoscale inhomogeneities in Co_2FeO_4 catalysts during the oxygen evolution reaction. *J. Am. Chem. Soc.* **2022**, *144*, 12007–12019.
- [22] Han, J. Y.; Zhang, M. Z.; Bai, X.; Duan, Z. Y.; Tang, T. M.; Guan, J. Q. Mesoporous Mn-Fe oxyhydroxides for oxygen evolution. *Inorg. Chem. Front.* **2022**, *9*, 3559–3565.
- [23] Anantharaj, S.; Ede, S. R.; Sakthikumar, K.; Karthick, K.; Mishra, S.; Kundu, S. Recent trends and perspectives in electrochemical water splitting with an emphasis on sulfide, selenide, and phosphide catalysts of Fe, Co, and Ni: A review. *ACS Catal.* **2016**, *6*, 8069–8097.
- [24] Li, J. H.; Wang, L. L.; He, H. J.; Chen, Y. Q.; Gao, Z. R.; Ma, N.; Wang, B.; Zheng, L. L.; Li, R. L.; Wei, Y. J. et al. Interface construction of NiCo LDH/NiCoS based on the 2D ultrathin nanosheet towards oxygen evolution reaction. *Nano Res.* **2022**, *15*, 4986–4995.
- [25] Xu, S. R.; Yu, X.; Luo, L.; Li, W. J.; Du, Y. S.; Kong, Q. Q.; Wu, Q. Multiscale manipulating induced flexible heterogeneous V-NiFe₂O₄@Ni₃P electrocatalyst for efficient and durable oxygen evolution reaction. *Nano Res.* **2022**, *15*, 4942–4949.
- [26] Gan, Y. H.; Cui, M. L.; Dai, X. P.; Ye, Y.; Nie, F.; Ren, Z. T.; Yin, X. L.; Wu, B. Q.; Cao, Y. H.; Cai, R. et al. Mn-doping induced electronic modulation and rich oxygen vacancies on vertically grown NiFe₂O₄ nanosheet array for synergistically triggering oxygen evolution reaction. *Nano Res.* **2022**, *15*, 3940–3945.
- [27] Liao, H. X.; Zhang, X. D.; Niu, S. W.; Tan, P. F.; Chen, K. J.; Liu, Y.; Wang, G. M.; Liu, M.; Pan, J. Dynamic dissolution and re-adsorption of molybdate ion in iron incorporated nickel-molybdenum oxyhydroxide for promoting oxygen evolution reaction. *Appl. Catal. B: Environ.* **2022**, *307*, 121150.
- [28] Xu, B. Y.; Zhang, Y.; Pi, Y. C.; Shao, Q.; Huang, X. Q. Research progress of nickel-based metal-organic frameworks and their derivatives for oxygen evolution catalysis. *Acta Phys. Chim. Sin.* **2021**, *37*, 2009074.
- [29] Shi, Z. P.; Wang, X.; Ge, J. J.; Liu, C. P.; Xing, W. Fundamental understanding of the acidic oxygen evolution reaction: Mechanism study and state-of-the-art catalysts. *Nanoscale* **2020**, *12*, 13249–13275.
- [30] Bai, X.; Wang, L. M.; Nan, B.; Tang, T. M.; Niu, X. D.; Guan, J. Q. Atomic manganese coordinated to nitrogen and sulfur for oxygen evolution. *Nano Res.* **2022**, *15*, 6019–6025.
- [31] Qin, R.; Wang, P. Y.; Lin, C.; Cao, F.; Zhang, J. Y.; Chen, L.; Mu, S. C. Transition metal nitrides: Activity origin, synthesis and electrocatalytic applications. *Acta Phys. Chim. Sin.* **2021**, *37*, 2009099.
- [32] Li, C. F.; Xie, L. J.; Zhao, J. W.; Gu, L. F.; Tang, H. B.; Zheng, L. R.; Li, G. R. Interfacial Fe-O-Ni-O-Fe bonding regulates the active Ni sites of Ni-MOFs via iron doping and decorating with FeOOH for super-efficient oxygen evolution. *Angew. Chem., Int. Ed.* **2022**, *61*, e202116934.
- [33] Wang, A. Y.; Niu, H.; Wang, X. T.; Wan, X. H.; Xie, L.; Zhang, Z. F.; Wang, J.; Guo, Y. Z. Two-dimensional metal-organic frameworks as efficient electrocatalysts for bifunctional oxygen evolution/reduction reactions. *J. Mater. Chem. A* **2022**, *10*, 13005–13012.
- [34] Liu, D.; Zhou, P. F.; Bai, H. Y.; Ai, H. Q.; Du, X. Y.; Chen, M. P.; Liu, D.; Ip, W. F.; Lo, K. H.; Kwok, C. T. et al. Development of perovskite oxide-based electrocatalysts for oxygen evolution reaction. *Small* **2021**, *17*, 2101605.
- [35] Bao, B.; Liu, Y. N.; Sun, M. Z.; Huang, B. L.; Hu, Y.; Da, P. F.; Ji, D. G.; Xi, P. X.; Yan, C. H. Boosting the electrocatalytic oxygen evolution of perovskite $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$ by the construction of yolk-shell nanostructures and electronic modulation. *Small* **2022**, *18*, 2201131.
- [36] Tang, L. N.; Yang, Y. L.; Guo, H. Q.; Wang, Y.; Wang, M. J.; Liu, Z. Q.; Yang, G. M.; Fu, X. Z.; Luo, Y.; Jiang, C. et al. High configuration entropy activated lattice oxygen for O_2 formation on perovskite electrocatalyst. *Adv. Funct. Mater.* **2022**, *32*, 2112157.
- [37] Peng, Y.; Huang, C. R.; Huang, J. L.; Feng, M.; Qiu, X. Z.; Yue, X.; Huang, S. M. Filling octahedral interstices by building geometrical defects to construct active sites for boosting the oxygen evolution reaction on NiFe_2O_4 . *Adv. Funct. Mater.* **2022**, *32*, 2201011.
- [38] Xiang, W. K.; Yang, N. T.; Li, X. P.; Linnemann, J.; Hagemann, U.; Ruediger, O.; Heidelmann, M.; Falk, T.; Aramini, M.; DeBeer, S. et al. 3D atomic-scale imaging of mixed Co-Fe spinel oxide nanoparticles during oxygen evolution reaction. *Nat. Commun.* **2022**, *13*, 179.
- [39] An, L.; Hu, Y.; Li, J. Y.; Zhu, J. M.; Sun, M. Z.; Huang, B. L.; Xi, P. X.; Yan, C. H. Tailoring oxygen reduction reaction pathway on spinel oxides via surficial geometrical-site occupation modification driven by the oxygen evolution reaction. *Adv. Mater.* **2022**, *34*, 2202874.
- [40] Ding, P.; Song, H. Q.; Chang, J. W.; Lu, S. Y. N-doped carbon dots coupled NiFe-LDH hybrids for robust electrocatalytic alkaline water and seawater oxidation. *Nano Res.* **2022**, *15*, 7063–7070.

- [41] Karmakar, A.; Karthick, K.; Sankar, S. S.; Kumaravel, S.; Madhu, R.; Bera, K.; Dhandapani, H. N.; Nagappan, S.; Murugan, P.; Kundu, S. Stabilization of ruthenium nanoparticles over NiV-LDH surface for enhanced electrochemical water splitting: An oxygen vacancy approach. *J. Mater. Chem. A* **2022**, *10*, 3618–3632.
- [42] Cai, Z. Y.; Wang, P.; Zhang, J. J.; Chen, A. Y.; Zhang, J. W.; Yan, Y.; Wang, X. Y. Reinforced layered double hydroxide oxygen-evolution electrocatalysts: A polyoxometallic acid wet-etching approach and synergistic mechanism. *Adv. Mater.* **2022**, *34*, 2110696.
- [43] Wang, Y. Z.; Yang, M.; Ding, Y. M.; Li, N. W.; Yu, L. Recent advances in complex hollow electrocatalysts for water splitting. *Adv. Funct. Mater.* **2022**, *32*, 2108681.
- [44] Yang, M.; Zhang, C. H.; Li, N. W.; Luan, D. Y.; Yu, L.; Lou, X. W. Design and synthesis of hollow nanostructures for electrochemical water splitting. *Adv. Sci. (Weinh)* **2022**, *9*, 2105135.
- [45] Li, Y.; Hu, X. S.; Huang, J. W.; Wang, L.; She, H. D.; Wang, Q. Z. Development of iron-based heterogeneous cocatalysts for photoelectrochemical water oxidation. *Acta Phys. Chim. Sin.* **2021**, *37*, 2009022.
- [46] Friebe, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M. J.; Sokaras, D.; Weng, T. C.; Alonso-Mori, R. et al. Identification of highly active Fe sites in (Ni, Fe)OOH for electrocatalytic water splitting. *J. Am. Chem. Soc.* **2015**, *137*, 1305–1313.
- [47] Fan, K.; Zou, H. Y.; Ding, Y. X.; Dharanipragada, N. V. R. A.; Fan, L. Z.; Inge, A. K.; Duan, L. L.; Zhang, B. B.; Sun, L. C. Sacrificial W facilitates self-reconstruction with abundant active sites for water oxidation. *Small* **2022**, *18*, 2107249.
- [48] Qian, Y.; Xu, X. L.; He, Y.; Lei, L. C.; Xia, Y. H.; Zhang, X. W. A novel monoclinic metal oxide catalyst for oxygen evolution reactions in alkaline media. *Inorg. Chem. Front.* **2022**, *9*, 941–949.
- [49] Zhang, B.; Wu, Z. H.; Shao, W. J.; Gao, Y.; Wang, W. W.; Ma, T.; Ma, L.; Li, S.; Cheng, C.; Zhao, C. S. Interfacial atom-substitution engineered transition-metal hydroxide nanofibers with high-valence Fe for efficient electrochemical water oxidation. *Angew. Chem., Int. Ed.* **2022**, *61*, e202115331.
- [50] Wang, M. H.; Lou, Z. X.; Wu, X. F.; Liu, Y. W.; Zhao, J. Y.; Sun, K. Z.; Li, W. X.; Chen, J. C.; Yuan, H. Y.; Zhu, M. et al. Operando high-valence Cr-modified NiFe hydroxides for water oxidation. *Small* **2022**, *18*, 2200303.
- [51] Guan, J. Q. Effect of coordination surroundings of isolated metal sites on electrocatalytic performances. *J. Power Sources* **2021**, *506*, 230143.
- [52] Rao, R. R.; Corby, S.; Bucci, A.; García-Tecedor, M.; Mesa, C. A.; Rossmeisl, J.; Giménez, S.; Lloret-Fillol, J.; Stephens, I. E. L.; Durrant, J. R. Spectroelectrochemical analysis of the water oxidation mechanism on doped nickel oxides. *J. Am. Chem. Soc.* **2022**, *144*, 7622–7633.
- [53] Wang, J.; Kim, S. J.; Liu, J. P.; Gao, Y.; Choi, S.; Han, J.; Shin, H.; Jo, S.; Kim, J.; Ciucci, F. et al. Redirecting dynamic surface restructuring of a layered transition metal oxide catalyst for superior water oxidation. *Nat. Catal.* **2021**, *4*, 212–222.
- [54] Shrestha, N. K.; Patil, S. A.; Han, J.; Cho, S.; Inamdar, A. I.; Kim, H.; Im, H. Chemical etching induced microporous nickel backbones decorated with metallic Fe@hydroxide nanocatalysts: An efficient and sustainable OER anode toward industrial alkaline water-splitting. *J. Mater. Chem. A* **2022**, *10*, 8989–9000.
- [55] Wu, C. C.; Zhang, X. M.; Xia, Z. X.; Shu, M.; Li, H. Q.; Xu, X. L.; Si, R.; Rykov, A. I.; Wang, J. H.; Yu, S. S. et al. Insight into the role of Ni-Fe dual sites in the oxygen evolution reaction based on atomically metal-doped polymeric carbon nitride. *J. Mater. Chem. A* **2019**, *7*, 14001–14010.
- [56] Görlin, M.; Chernev, P.; de Araújo, J. F.; Reier, T.; Dresch, S.; Paul, B.; Krähnert, R.; Dau, H.; Strasser, P. Oxygen evolution reaction dynamics, faradaic charge efficiency, and the active metal redox states of Ni-Fe oxide water splitting electrocatalysts. *J. Am. Chem. Soc.* **2016**, *138*, 5603–5614.
- [57] Kasian, O.; Grote, J. P.; Geiger, S.; Cherevko, S.; Mayrhofer, K. J. J. The common intermediates of oxygen evolution and dissolution reactions during water electrolysis on iridium. *Angew. Chem., Int. Ed.* **2018**, *57*, 2488–2491.
- [58] Man, I. C.; Su, H. Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **2011**, *3*, 1159–1165.
- [59] Reier, T.; Nong, H. N.; Teschner, D.; Schlögl, R.; Strasser, P. Electrocatalytic oxygen evolution reaction in acidic environments—reaction mechanisms and catalysts. *Adv. Energy Mater.* **2017**, *7*, 1601275.
- [60] Bai, X.; Duan, Z.; Nan, B.; Wang, L.; Tang, T.; Guan, J. Unveiling the active sites of ultrathin Co-Fe layered double hydroxides for the oxygen evolution reaction. *Chin. J. Catal.* **2022**, *43*, 2240–2248.
- [61] Rong, X.; Parolin, J.; Kolpak, A. M. A Fundamental relationship between reaction mechanism and stability in metal oxide catalysts for oxygen evolution. *ACS Catal.* **2016**, *6*, 1153–1158.
- [62] Rossmeisl, J.; Qu, Z. W.; Zhu, H.; Kroes, G. J.; Nørskov, J. K. Electrolysis of water on oxide surfaces. *J. Electroanal. Chem.* **2007**, *607*, 83–89.
- [63] Miao, X. B.; Zhang, L. F.; Wu, L.; Hu, Z. P.; Shi, L.; Zhou, S. M. Quadruple perovskite ruthenate as a highly efficient catalyst for acidic water oxidation. *Nat. Commun.* **2019**, *10*, 3809.
- [64] Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. The mechanism of water oxidation: From electrolysis via homogeneous to biological catalysis. *ChemCatChem* **2010**, *2*, 724–761.
- [65] Yao, Y. C.; Hu, S. L.; Chen, W. X.; Huang, Z. Q.; Wei, W. C.; Yao, T.; Liu, R. R.; Zang, K. T.; Wang, X. Q.; Wu, G. et al. Engineering the electronic structure of single atom Ru sites via compressive strain boosts acidic water oxidation electrocatalysis. *Nat. Catal.* **2019**, *2*, 304–313.
- [66] Grimaud, A.; Demortière, A.; Saubanière, M.; Dachraoui, W.; Duchamp, M.; Doublet, M. L.; Tarascon, J. M. Activation of surface oxygen sites on an iridium-based model catalyst for the oxygen evolution reaction. *Nat. Energy* **2017**, *2*, 16189.
- [67] Yoo, J. S.; Rong, X.; Liu, Y. S.; Kolpak, A. M. Role of lattice oxygen participation in understanding trends in the oxygen evolution reaction on perovskites. *ACS Catal.* **2018**, *8*, 4628–4636.
- [68] Macounova, K.; Makarova, M.; Krtil, P. Oxygen evolution on nanocrystalline RuO₂ and Ru_{0.9}Ni_{0.1}O_{2-δ} electrodes-DEMS approach to reaction mechanism determination. *Electrochem. Commun.* **2009**, *11*, 1865–1868.
- [69] Rincón, R. A.; Ventosa, E.; Tietz, F.; Masa, J.; Seisel, S.; Kuznetsov, V.; Schuhmann, W. Evaluation of perovskites as electrocatalysts for the oxygen evolution reaction. *ChemPhysChem* **2014**, *15*, 2810–2816.
- [70] Kang, Y. K.; Zhang, F. R.; Liu, B. W.; Sun, Y. Q.; Zhang, X.; Song, W. Y.; Wei, Y. C.; Zhao, Z.; Liu, J. Breaking the scaling relationship via dual metal doping in a cobalt spinel for the OER: A computational prediction. *Phys. Chem. Chem. Phys.* **2020**, *22*, 18672–18680.
- [71] Kasian, O.; Geiger, S.; Stock, P.; Polymeros, G.; Breitbach, B.; Savan, A.; Ludwig, A.; Cherevko, S.; Mayrhofer, K. J. J. On the origin of the improved ruthenium stability in RuO₂-IrO₂ mixed oxides. *J. Electrochem. Soc.* **2016**, *163*, F3099–F3104.
- [72] Chang, S. H.; Connell, J. G.; Danilovic, N.; Subbaraman, R.; Chang, K. C.; Stamenkovic, V. R.; Markovic, N. M. Activity–stability relationship in the surface electrochemistry of the oxygen evolution reaction. *Faraday Discuss.* **2014**, *176*, 125–133.
- [73] Shan, J. Q.; Zheng, Y.; Shi, B. Y.; Davey, K.; Qiao, S. Z. Regulating electrocatalysts via surface and interface engineering for acidic water electrooxidation. *ACS Energy Lett.* **2019**, *4*, 2719–2730.
- [74] Shang, C. Y.; Cao, C.; Yu, D. Y.; Yan, Y.; Lin, Y. T.; Li, H. L.; Zheng, T. T.; Yan, X. P.; Yu, W. C.; Zhou, S. M. et al. Electron correlations engineer catalytic activity of pyrochlore iridates for acidic water oxidation. *Adv. Mater.* **2019**, *31*, 1805104.
- [75] Yagi, S.; Yamada, I.; Tsukasaki, H.; Seno, A.; Murakami, M.; Fujii,

- H.; Chen, H.; Umezawa, N.; Abe, H.; Nishiyama, N. et al. Covalency-reinforced oxygen evolution reaction catalyst. *Nat. Commun.* **2015**, *6*, 8249.
- [76] Nong, H. N.; Reier, T.; Oh, H. S.; Gliech, M.; Paciok, P.; Vu, T. H. T.; Teschner, D.; Heggen, M.; Petkov, V.; Schlögl, R. et al. A unique oxygen ligand environment facilitates water oxidation in hole-doped IrNiO_x core-shell electrocatalysts. *Nat. Catal.* **2018**, *1*, 841–851.
- [77] Kim, J.; Shih, P. C.; Qin, Y.; Al-Bardan, Z.; Sun, C. J.; Yang, H. A porous pyrochlore Y₂[Ru_{1.6}Y_{0.4}]O_{7-δ} electrocatalyst for enhanced performance towards the oxygen evolution reaction in acidic media. *Angew. Chem., Int. Ed.* **2018**, *57*, 13877–13881.
- [78] Kim, J.; Shih, P. C.; Tsao, K. C.; Pan, Y. T.; Yin, X.; Sun, C. J.; Yang, H. High-performance pyrochlore-type yttrium ruthenate electrocatalyst for oxygen evolution reaction in acidic media. *J. Am. Chem. Soc.* **2017**, *139*, 12076–12083.
- [79] Sun, W.; Liu, J. Y.; Gong, X. Q.; Zaman, W. Q.; Cao, L. M.; Yang, J. OER activity manipulated by IrO₆ coordination geometry: An insight from pyrochlore iridates. *Sci. Rep.* **2016**, *6*, 38429.
- [80] Kuznetsov, D. A.; Naeem, M. A.; Kumar, P. V.; Abdala, P. M.; Fedorov, A.; Müller, C. R. Tailoring lattice oxygen binding in ruthenium pyrochlores to enhance oxygen evolution activity. *J. Am. Chem. Soc.* **2020**, *142*, 7883–7888.
- [81] Suntivich, J.; Hong, W. T.; Lee, Y. L.; Rondinelli, J. M.; Yang, W. L.; Goodenough, J. B.; Dabrowski, B.; Freeland, J. W.; Shao-Horn, Y. Estimating hybridization of transition metal and oxygen states in perovskites from O K-edge X-ray absorption spectroscopy. *J. Phys. Chem. C* **2014**, *118*, 1856–1863.
- [82] Retuerto, M.; Pascual, L.; Calle-Vallejo, F.; Ferrer, P.; Gianolio, D.; Pereira, A. G.; García, Á.; Torrero, J.; Fernández-Díaz, M. T.; Bencok, P. et al. Na-doped ruthenium perovskite electrocatalysts with improved oxygen evolution activity and durability in acidic media. *Nat. Commun.* **2019**, *10*, 2041.
- [83] Cao, L. L.; Luo, Q. Q.; Chen, J. J.; Wang, L.; Lin, Y.; Wang, H. J.; Liu, X. K.; Shen, X. Y.; Zhang, W.; Liu, W. et al. Dynamic oxygen adsorption on single-atomic Ruthenium catalyst with high performance for acidic oxygen evolution reaction. *Nat. Commun.* **2019**, *10*, 4849.
- [84] Laha, S.; Lee, Y.; Podjaski, F.; Weber, D.; Duppel, V.; Schoop, L. M.; Pielnhofer, F.; Scheurer, C.; Müller, K.; Starke, U. et al. Ruthenium oxide nanosheets for enhanced oxygen evolution catalysis in acidic medium. *Adv. Energy Mater.* **2019**, *9*, 1803795.
- [85] Kim, J.; Min, B. J.; Kwon, T.; Kim, T.; Song, H. C.; Ham, H. C.; Baik, H.; Lee, K.; Kim, J. Y. Facile one-step synthesis of Ru doped NiCoP nanoparticles as highly efficient electrocatalysts for oxygen evolution reaction. *Chem. Asian J.* **2021**, *16*, 3630–3635.
- [86] Chen, Y. B.; Li, H. Y.; Wang, J. X.; Du, Y. H.; Xi, S. B.; Sun, Y. M.; Sherburne, M.; Ager III, J. W.; Fisher, A. C.; Xu, Z. J. Exceptionally active iridium evolved from a pseudo-cubic perovskite for oxygen evolution in acid. *Nat. Commun.* **2019**, *10*, 572.
- [87] Binninger, T.; Mohamed, R.; Waltar, K.; Fabbri, E.; Levecque, P.; Kötzt, R.; Schmidt, T. J. Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts. *Sci. Rep.* **2015**, *5*, 12167.
- [88] Kötzt, R.; Lewerenz, H. J.; Stucki, S. XPS studies of oxygen evolution on Ru and RuO₂ anodes. *J. Electrochem. Soc.* **1983**, *130*, 825–829.
- [89] Hwang, J.; Rao, R. R.; Giordano, L.; Katayama, Y.; Yu, Y.; Shao-Horn, Y. Perovskites in catalysis and electrocatalysis. *Science* **2017**, *358*, 751–756.
- [90] Chen, Q. Q.; Hou, C. C.; Wang, C. J.; Yang, X.; Shi, R.; Chen, Y. Ir⁴⁺-doped NiFe LDH to expedite hydrogen evolution kinetics as a Pt-like electrocatalyst for water splitting. *Chem. Commun.* **2018**, *54*, 6400–6403.
- [91] Zhou, H. Q.; Yu, F.; Zhu, Q.; Sun, J. Y.; Qin, F.; Yu, L.; Bao, J. M.; Yu, Y.; Chen, S.; Ren, Z. F. Water splitting by electrolysis at high current densities under 1.6 volts. *Energy Environ. Sci.* **2018**, *11*, 2858–2864.
- [92] Balogun, M. S.; Qiu, W. T.; Yang, H.; Fan, W. J.; Huang, Y. C.; Fang, P. P.; Li, G. R.; Ji, H. B.; Tong, Y. X. A monolithic metal-free electrocatalyst for oxygen evolution reaction and overall water splitting. *Energy Environ. Sci.* **2016**, *9*, 3411–3416.
- [93] Liu, Y. X.; Bai, Y.; Han, Y.; Yu, Z.; Zhang, S. M.; Wang, G. H.; Wei, J. H.; Wu, Q. B.; Sun, K. N. Self-supported hierarchical FeCoNi-LTH/NiCo₂O₄/CC electrodes with enhanced bifunctional performance for efficient overall water splitting. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36917–36926.
- [94] Li, S. S.; Sun, J. R.; Guan, J. Q. Strategies to improve electrocatalytic and photocatalytic performance of two-dimensional materials for hydrogen evolution reaction. *Chin. J. Catal.* **2021**, *42*, 511–556.
- [95] Zhai, P. L.; Xia, M. Y.; Wu, Y. Z.; Zhang, G. H.; Gao, J. F.; Zhang, B.; Cao, S. Y.; Zhang, Y. T.; Li, Z. W.; Fan, Z. et al. Engineering single-atomic ruthenium catalytic sites on defective nickel-iron layered double hydroxide for overall water splitting. *Nat. Commun.* **2021**, *12*, 4587.
- [96] Liu, M. J.; Min, K. A.; Han, B.; Lee, L. Y. S. Interfacing or doping? Role of Ce in highly promoted water oxidation of NiFe-layered double hydroxide. *Adv. Energy Mater.* **2021**, *11*, 2101281.
- [97] Cai, Z. Y.; Bu, X. M.; Wang, P.; Su, W. Q.; Wei, R. J.; Ho, J. C.; Yang, J. H.; Wang, X. Y. Simple and cost effective fabrication of 3D porous core-shell Ni nanochains@NiFe layered double hydroxide nanosheet bifunctional electrocatalysts for overall water splitting. *J. Mater. Chem. A* **2019**, *7*, 21722–21729.
- [98] Zhang, B.; Shan, J. W.; Wang, X. Y.; Hu, Y. J.; Li, Y. Y. Ru/Rh cation doping and oxygen-vacancy engineering of FeOOH nanoarrays@Ti₃C₂T_x MXene heterojunction for highly efficient and stable electrocatalytic oxygen evolution. *Small* **2022**, *18*, 2200173.
- [99] Tang, Y. J.; Zou, Y.; Zhu, D. D. Efficient water oxidation using an Fe-doped nickel telluride-nickel phosphide electrocatalyst by partial phosphating. *J. Mater. Chem. A* **2022**, *10*, 12438–12446.
- [100] Peng, X. R.; Chen, X. C.; Liu, T.; Lu, C. F.; Sun, M. M.; Ding, F.; Wang, Y. Y.; Zou, P.; Wang, X. X.; Zhao, Q. B. et al. Rose-like nanocomposite of Fe-Ni phosphides/iron oxide as efficient catalyst for oxygen evolution reaction. *Chem. Asian J.* **2019**, *14*, 2744–2750.
- [101] Hu, L. Y.; Zeng, X.; Wei, X. Q.; Wang, H. J.; Wu, Y.; Gu, W. L.; Shi, L.; Zhu, C. Z. Interface engineering for enhancing electrocatalytic oxygen evolution of NiFe LDH/NiTe heterostructures. *Appl. Catal. B: Environ.* **2020**, *273*, 119014.
- [102] Hua, W.; Sun, H. H.; Jiang, M. W.; Ren, L. B.; Zhang, Y.; Wang, J. G. Cascading reconstruction to induce highly disordered Fe-Ni(O)OH toward enhanced oxygen evolution reaction. *J. Mater. Chem. A* **2022**, *10*, 7366–7372.
- [103] Peng, W. F.; Deshmukh, A.; Chen, N.; Lv, Z. X.; Zhao, S. J.; Li, J.; Yan, B. M.; Gao, X.; Shang, L.; Gong, Y. T. et al. Deciphering the dynamic structure evolution of Fe- and Ni-codoped CoS₂ for enhanced water oxidation. *ACS Catal.* **2022**, *12*, 3743–3751.
- [104] Wang, Y.; Li, X. P.; Zhang, M. M.; Zhang, J. F.; Chen, Z. L.; Zheng, X. R.; Tian, Z. L.; Zhao, N. Q.; Han, X. P.; Zaghbi, K. et al. Highly active and durable single-atom tungsten-doped NiS_{0.5}Se_{0.5} nanosheet@NiS_{0.5}Se_{0.5} nanorod heterostructures for water splitting. *Adv. Mater.* **2022**, *34*, 2107053.
- [105] Tahir, M.; Pan, L.; Zhang, R. R.; Wang, Y. C.; Shen, G. Q.; Aslam, I.; Qadeer, M. A.; Mahmood, N.; Xu, W.; Wang, L. et al. High-valence-state NiO/Co₃O₄ nanoparticles on nitrogen-doped carbon for oxygen evolution at low overpotential. *ACS Energy Lett.* **2017**, *2*, 2177–2182.
- [106] Chen, J. S.; Li, H.; Yu, Z. X.; Liu, C.; Yuan, Z. W.; Wang, C. J.; Zhao, S. L.; Henkelman, G.; Li, S. Z.; Wei, L. et al. Octahedral coordinated trivalent cobalt enriched multimetal oxygen-evolution catalysts. *Adv. Energy Mater.* **2020**, *10*, 2002593.
- [107] Hoa, V. H.; Tran, D. T.; Nguyen, D. C.; Kim, D. H.; Kim, N. H.; Lee, J. H. Molybdenum and phosphorous dual doping in cobalt monolayer interfacial assembled cobalt nanowires for efficient overall water splitting. *Adv. Funct. Mater.* **2020**, *30*, 2002533.
- [108] Li, Y. K.; Zhang, G.; Lu, W. T.; Cao, F. F. Amorphous Ni-Fe-Mo suboxides coupled with Ni network as porous nanoplate array on nickel foam: A highly efficient and durable bifunctional electrode for overall water splitting. *Adv. Sci. (Weinh)* **2020**, *7*, 1902034.
- [109] Wang, S.; Li, Q.; Sun, S. J.; Ge, K.; Zhao, Y.; Yang, K.; Zhang, Z.

- H.; Cao, J. Y.; Lu, J.; Yang, Y. F. et al. Heterostructured ferroelectric BaTiO₃@MOF-Fe/Co electrocatalysts for efficient oxygen evolution reaction. *J. Mater. Chem. A* **2022**, *10*, 5350–5360.
- [110] Balch, H. B.; Evans, A. M.; Dasari, R. R.; Li, H.; Li, R. F.; Thomas, S.; Wang, D. Q.; Bisbey, R. P.; Slicker, K.; Castano, I. et al. Electronically coupled 2D polymer/MoS₂ heterostructures. *J. Am. Chem. Soc.* **2020**, *142*, 21131–21139.
- [111] Huang, Y.; Zhang, S. L.; Lu, X. F.; Wu, Z. P.; Luan, D. Y.; Lou, X. W. Trimetallic spinel NiCo₂₋₃Fe₃O₄ nanoboxes for highly efficient electrocatalytic oxygen evolution. *Angew. Chem., Int. Ed.* **2021**, *60*, 11841–11846.
- [112] Li, R. C.; Hu, B. H.; Yu, T. W.; Chen, H. X.; Wang, Y.; Song, S. Q. Insights into correlation among surface-structure-activity of cobalt-derived pre-catalyst for oxygen evolution reaction. *Adv. Sci. (Weinh)* **2020**, *7*, 1902830.
- [113] Liu, Z.; Tang, B.; Gu, X. C.; Liu, H.; Feng, L. G. Selective structure transformation for NiFe/NiFe₂O₄ embedded porous nitrogen-doped carbon nanosphere with improved oxygen evolution reaction activity. *Chem. Eng. J.* **2020**, *395*, 125170.
- [114] Chen, X.; Wang, Q. C.; Cheng, Y. W.; Xing, H. L.; Li, J. Z.; Zhu, X. J.; Ma, L. B.; Li, Y. T.; Liu, D. M. S-doping triggers redox reactivities of both iron and lattice oxygen in FeOOH for low-cost and high-performance water oxidation. *Adv. Funct. Mater.* **2022**, *32*, 2112674.
- [115] Wang, K.; Du, H. F.; He, S.; Liu, L.; Yang, K.; Sun, J. M.; Liu, Y. H.; Du, Z. Z.; Xie, L. H.; Ai, W. et al. Kinetically controlled, scalable synthesis of γ -FeOOH nanosheet arrays on nickel foam toward efficient oxygen evolution: The key role of *in-situ*-generated γ -NiOOH. *Adv. Mater.* **2021**, *33*, 2005587.
- [116] Souza, A. S.; Bezerra, L. S.; Cardoso, E. S. F.; Fortunato, G. V.; Maia, G. Nickel pyrophosphate combined with graphene nanoribbon used as efficient catalyst for OER. *J. Mater. Chem. A* **2021**, *9*, 11255–11267.
- [117] Sheelam, A.; Balu, S.; Muneeb, A.; Bayikadi, K. S.; Namasivayam, D.; Siddharthan, E. E.; Inamdar, A. I.; Thapa, R.; Chiang, M. H.; Isaac Huang, S. J. et al. Improved oxygen redox activity by high-valent Fe and Co³⁺ sites in the perovskite LaNi_{1-x}Fe_{0.5x}Co_{0.5x}O₃. *ACS Appl. Energy Mater.* **2022**, *5*, 343–354.
- [118] Ran, J.; Wang, T.; Zhang, J.; Liu, Y.; Xu, C.; Xi, S.; Gao, D. Modulation of electronics of oxide perovskites by sulfur doping for electrocatalysis in rechargeable Zn-air batteries. *Chem. Mater.* **2020**, *32*, 3439–3446.
- [119] Wang, H.; Qi, J.; Yang, N. L.; Cui, W.; Wang, J. Y.; Li, Q. H.; Zhang, Q. H.; Yu, X. Q.; Gu, L.; Li, J. et al. Dual-defects adjusted crystal-field splitting of LaCo_{1-x}Ni_xO_{3- δ} hollow multishelled structures for efficient oxygen evolution. *Angew. Chem., Int. Ed.* **2020**, *59*, 19691–19695.
- [120] Qian, J. M.; Wang, T. T.; Zhang, Z. M.; Liu, Y. G.; Li, J. F.; Gao, D. Q. Engineered spin state in Ce doped LaCoO₃ with enhanced electrocatalytic activity for rechargeable Zn-air batteries. *Nano Energy* **2020**, *74*, 104948.
- [121] Li, Z. S.; Li, J. G.; Ao, X.; Sun, H. C.; Wang, H. K.; Yuen, M. F.; Wang, C. D. Conductive metal-organic frameworks endow high-efficient oxygen evolution of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ perovskite oxide nanofibers. *Electrochim. Acta* **2020**, *334*, 135638.
- [122] Xu, K. L.; Song, F.; Gu, J.; Xu, X.; Liu, Z. N.; Hu, X. Solvent-induced surface hydroxylation of a layered perovskite Sr₃FeCoO_{7- δ} for enhanced oxygen evolution catalysis. *J. Mater. Chem. A* **2018**, *6*, 14240–14245.
- [123] Chen, D. W.; Qiao, M.; Lu, Y. R.; Hao, L.; Liu, D. D.; Dong, C. L.; Li, Y. F.; Wang, S. Y. Preferential cation vacancies in perovskite hydroxide for the oxygen evolution reaction. *Angew. Chem., Int. Ed.* **2018**, *57*, 8691–8696.
- [124] Sun, H.; Chen, L.; Lian, Y. B.; Yang, W. J.; Lin, L.; Chen, Y. F.; Xu, J. B.; Wang, D.; Yang, X. Q.; Rümmerli, M. H. et al. Topotactically transformed polygonal mesopores on ternary layered double hydroxides exposing under-coordinated metal centers for accelerated water dissociation. *Adv. Mater.* **2020**, *32*, 2006784.
- [125] Zhao, S. L.; Tan, C. H.; He, C. T.; An, P. F.; Xie, F.; Jiang, S.; Zhu, Y. F.; Wu, K. H.; Zhang, B. W.; Li, H. J. et al. Structural transformation of highly active metal-organic framework electrocatalysts during the oxygen evolution reaction. *Nat. Energy* **2020**, *5*, 881–890.
- [126] Xu, H. J.; Shan, C. F.; Wu, X. X.; Sun, M. Z.; Huang, B. L.; Tang, Y.; Yan, C. H. Fabrication of layered double hydroxide microcapsules mediated by cerium doping in metal-organic frameworks for boosting water splitting. *Energy Environ. Sci.* **2020**, *13*, 2949–2956.
- [127] Zhou, L.; Zhang, C.; Zhang, Y. Q.; Li, Z. H.; Shao, M. F. Host modification of layered double hydroxide electrocatalyst to boost the thermodynamic and kinetic activity of oxygen evolution reaction. *Adv. Funct. Mater.* **2021**, *31*, 2009743.
- [128] Zhang, L. C.; Wang, J. Q.; Liu, P. Y.; Liang, J.; Luo, Y. S.; Cui, G. W.; Tang, B.; Liu, Q.; Yan, X. D.; Hao, H. G. et al. Ni(OH)₂ nanoparticles encapsulated in conductive nanowire array for high-performance alkaline seawater oxidation. *Nano Res.* **2022**, *15*, 6084–6090.
- [129] Singh, R. N.; Singh, J. P.; Lal, B.; Thomas, M. J. K.; Bera, S. New NiFe_{2-x}Cr_xO₄ spinel films for O₂ evolution in alkaline solutions. *Electrochim. Acta* **2006**, *51*, 5515–5523.
- [130] Huang, J. H.; Chen, J. T.; Yao, T.; He, J. F.; Jiang, S.; Sun, Z. H.; Liu, Q. H.; Cheng, W. R.; Hu, F. C.; Jiang, Y. et al. CoOOH nanosheets with high mass activity for water oxidation. *Angew. Chem., Int. Ed.* **2015**, *54*, 8722–8727.
- [131] Xiao, C. L.; Li, Y. B.; Lu, X. Y.; Zhao, C. Bifunctional porous NiFe/NiCo₂O₄/Ni foam electrodes with triple hierarchy and double synergies for efficient whole cell water splitting. *Adv. Funct. Mater.* **2016**, *26*, 3515–3523.
- [132] Zhang, Z. Y.; Liu, S. S.; Xiao, F.; Wang, S. Facile synthesis of heterostructured nickel/nickel oxide wrapped carbon fiber: Flexible bifunctional gas-evolving electrode for highly efficient overall water splitting. *ACS Sustainable Chem. Eng.* **2017**, *5*, 529–536.
- [133] Thenuwara, A. C.; Attanayake, N. H.; Yu, J.; Perdew, J. P.; Elzinga, E. J.; Yan, Q. M.; Strongin, D. R. Cobalt intercalated layered NiFe double hydroxides for the oxygen evolution reaction. *J. Phys. Chem. B* **2018**, *122*, 847–854.
- [134] Wang, T. Y.; Nam, G.; Jin, Y.; Wang, X. Y.; Ren, P. J.; Kim, M. G.; Liang, J. S.; Wen, X. D.; Jang, H.; Han, J. T. et al. NiFe (oxy)hydroxides derived from NiFe disulfides as an efficient oxygen evolution catalyst for rechargeable Zn-air batteries: The effect of surface S residues. *Adv. Mater.* **2018**, *30*, 1800757.
- [135] Zhou, D. J.; Wang, S. Y.; Jia, Y.; Xiong, X. Y.; Yang, H. B.; Liu, S.; Tang, J. L.; Zhang, J. M.; Liu, D.; Zheng, L. R. et al. NiFe hydroxide lattice tensile strain: Enhancement of adsorption of oxygenated intermediates for efficient water oxidation catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 736–740.
- [136] Kuai, C. G.; Zhang, Y.; Wu, D. Y.; Sokaras, D.; Mu, L. Q.; Spence, S.; Nordlund, D.; Lin, F.; Du, X. W. Fully oxidized Ni-Fe layered double hydroxide with 100% exposed active sites for catalyzing oxygen evolution reaction. *ACS Catal.* **2019**, *9*, 6027–6032.
- [137] Morales-Guio, C. G.; Liardet, L.; Hu, X. L. Oxidatively electrodeposited thin-film transition metal (oxy)hydroxides as oxygen evolution catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 8946–8957.
- [138] Guan, B. Y.; Yu, L.; Lou, X. W. General synthesis of multishell mixed-metal oxyphosphide particles with enhanced electrocatalytic activity in the oxygen evolution reaction. *Angew. Chem., Int. Ed.* **2017**, *56*, 2386–2389.
- [139] Xiao, Y.; Pei, Y.; Hu, Y. F.; Ma, R. G.; Wang, D. Y.; Wang, J. C. Co₂P@P-doped 3D porous carbon for bifunctional oxygen electrocatalysis. *Acta Phys. Chim. Sin.* **2021**, *37*, 2009051.
- [140] Zhu, H.; Gu, L.; Yu, D. N.; Sun, Y. J.; Wan, M.; Zhang, M.; Wang, L.; Wang, L. N.; Wu, W. W.; Yao, J. M. et al. The marriage and integration of nanostructures with different dimensions for synergistic electrocatalysis. *Energy Environ. Sci.* **2017**, *10*, 321–330.
- [141] Fu, G. T.; Yan, X. X.; Chen, Y. F.; Xu, L.; Sun, D. M.; Lee, J. M.; Tang, Y. W. Boosting bifunctional oxygen electrocatalysis with 3D

- graphene aerogel-supported Ni/MnO particles. *Adv. Mater.* **2018**, *30*, 1704609.
- [142] Du, J.; Chen, C. C.; Cheng, F. Y.; Chen, J. Rapid synthesis and efficient electrocatalytic oxygen reduction/evolution reaction of CoMn_2O_4 nanodots supported on graphene. *Inorg. Chem.* **2015**, *54*, 5467–5474.
- [143] Zhu, H.; Yu, D. N.; Zhang, S. G.; Chen, J. W.; Wu, W. B.; Wan, M.; Wang, L. N.; Zhang, M.; Du, M. L. Morphology and structure engineering in nanofiber reactor: Tubular hierarchical integrated networks composed of dual phase octahedral CoMn_2O_4 /carbon nanofibers for water oxidation. *Small* **2017**, *13*, 1700468.
- [144] Yu, X. W.; Zhao, J.; Johnsson, M. Interfacial engineering of nickel hydroxide on cobalt phosphide for alkaline water electrocatalysis. *Adv. Funct. Mater.* **2021**, *31*, 2101578.
- [145] Xing, M.; Kong, L. B.; Liu, M. C.; Liu, L. Y.; Kang, L.; Luo, Y. C. Cobalt vanadate as highly active, stable, noble metal-free oxygen evolution electrocatalyst. *J. Mater. Chem. A* **2014**, *2*, 18435–18443.
- [146] Cao, L. M.; Wang, J. W.; Zhong, D. C.; Lu, T. B. Template-directed synthesis of sulphur doped NiCoFe layered double hydroxide porous nanosheets with enhanced electrocatalytic activity for the oxygen evolution reaction. *J. Mater. Chem. A* **2018**, *6*, 3224–3230.
- [147] Lu, B. G.; Cao, D. X.; Wang, P.; Wang, G. L.; Gao, Y. Y. Oxygen evolution reaction on Ni-substituted Co_3O_4 nanowire array electrodes. *Int. J. Hydrogen Energy* **2011**, *36*, 72–78.
- [148] Huang, L. L.; Chen, R.; Xie, C.; Chen, C.; Wang, Y. Y.; Zeng, Y. F.; Chen, D. W.; Wang, S. Y. Rapid cationic defect and anion dual-regulated layered double hydroxides for efficient water oxidation. *Nanoscale* **2018**, *10*, 13638–13644.
- [149] Muthurasu, A.; Maruthapandian, V.; Kim, H. Y. Metal-organic framework derived $\text{Co}_3\text{O}_4/\text{MoS}_2$ heterostructure for efficient bifunctional electrocatalysts for oxygen evolution reaction and hydrogen evolution reaction. *Appl. Catal. B* **2019**, *248*, 202–210.
- [150] Zhuang, L. Z.; Jia, Y.; Liu, H. L.; Li, Z. H.; Li, M. R.; Zhang, L. Z.; Wang, X.; Yang, D. J.; Zhu, Z. H.; Yao, X. D. Sulfur-Modified oxygen vacancies in iron-cobalt oxide nanosheets: Enabling extremely high activity of the oxygen evolution reaction to achieve the industrial water splitting benchmark. *Angew. Chem., Int. Ed.* **2020**, *59*, 14664–14670.
- [151] Lu, S. S.; Shi, Y. M.; Zhou, W.; Zhang, Z. P.; Wu, F.; Zhang, B. Dissolution of the heteroatom dopants and formation of orthoquinone moieties in the doped carbon materials during water electrooxidation. *J. Am. Chem. Soc.* **2022**, *144*, 3250–3258.
- [152] Kim, Y.; Kim, S.; Shim, M.; Oh, Y.; Lee, K. S.; Jung, Y.; Byon, H. R. Alteration of oxygen evolution mechanisms in layered LiCoO_2 structures by intercalation of alkali metal ions. *J. Mater. Chem. A* **2022**, *10*, 10967–10978.
- [153] Cao, L.; Ma, Y. H.; Song, A. L.; Bai, L.; Zhang, P. P.; Li, X. H.; Shao, G. J. Stable composite of flower-like NiFe-layered double hydroxide nucleated on graphene oxide as an effective catalyst for oxygen reduction reaction. *Int. J. Hydrogen Energy* **2019**, *44*, 5912–5920.
- [154] Wu, Y. Z.; Zhao, Y. Y.; Zhai, P. L.; Wang, C.; Gao, J. F.; Sun, L. C.; Hou, J. G. Triggering lattice oxygen activation of single-atomic Mo sites anchored on Ni-Fe oxyhydroxides nanoarrays for electrochemical water oxidation. *Adv. Mater.* **2022**, *34*, 2202523.
- [155] Zhang, Q. Q.; Guan, J. Q. Applications of single-atom catalysts. *Nano Res.* **2022**, *15*, 38–70.
- [156] Lin, C.; Zhao, Y. H.; Zhang, H. J.; Xie, S. H.; Li, Y. F.; Li, X. P.; Jiang, Z.; Liu, Z. P. Accelerated active phase transformation of NiO powered by Pt single atoms for enhanced oxygen evolution reaction. *Chem. Sci.* **2018**, *9*, 6803–6812.
- [157] Tian, B. L.; Shin, H.; Liu, S. T.; Fei, M. C.; Mu, Z. Y.; Liu, C.; Pan, Y. H.; Sun, Y. M.; Goddard III, W. A.; Ding, M. N. Double-exchange-induced *in situ* conductivity in nickel-based oxyhydroxides: An effective descriptor for electrocatalytic oxygen evolution. *Angew. Chem., Int. Ed.* **2021**, *60*, 16448–16456.
- [158] Yang, G. J.; Zhu, B. T.; Fu, Y. J.; Zhao, J.; Lin, Y. N.; Gao, D. Q.; Li, J. Y. High-valent zirconium-doping modified Co_3O_4 weave-like nanoarray boosts oxygen evolution reaction. *J. Alloys Compd.* **2021**, *886*, 161172.
- [159] Liu, X. M.; Fan, X.; Huang, H.; Lin, H. P.; Gao, J. Z. Electronic modulation of oxygen evolution on metal doped NiFe layered double hydroxides. *J. Colloid Interface Sci.* **2021**, *587*, 385–392.
- [160] Chen, J. S.; Li, H.; Chen, S. M.; Fei, J. Y.; Liu, C.; Yu, Z. X.; Shin, K.; Liu, Z. W.; Song, L.; Henkelman, G. et al. Co-Fe-Cr (oxy)hydroxides as efficient oxygen evolution reaction catalysts. *Adv. Energy Mater.* **2021**, *11*, 2003412.
- [161] Abellán, G.; Carrasco, J. A.; Coronado, E.; Romero, J.; Varela, M. Alkoxide-intercalated CoFe-layered double hydroxides as precursors of colloidal nanosheet suspensions: Structural, magnetic and electrochemical properties. *J. Mater. Chem. C* **2014**, *2*, 3723–3731.
- [162] Xu, A. N.; Dong, C. F.; Wu, A. J.; Li, R. X.; Wang, L.; Macdonald, D. D.; Li, X. G. Plasma-modified C-doped Co_3O_4 nanosheets for the oxygen evolution reaction designed by Butler-Volmer and first-principle calculations. *J. Mater. Chem. A* **2019**, *7*, 4581–4595.
- [163] Bo, X.; Li, Y. B.; Chen, X. J.; Zhao, C. High valence chromium regulated cobalt-iron-hydroxide for enhanced water oxidation. *J. Power Sources* **2018**, *402*, 381–387.
- [164] Yan, W. N.; Bian, W. Y.; Jin, C.; Tian, J. H.; Yang, R. Z. An efficient Bi-functional electrocatalyst based on strongly coupled CoFe_2O_4 /carbon nanotubes hybrid for oxygen reduction and oxygen evolution. *Electrochim. Acta* **2015**, *177*, 65–72.
- [165] Kargar, A.; Yavuz, S.; Kim, T. K.; Liu, C. H.; Kuru, C.; Rustomji, C. S.; Jin, S.; Bandaru, P. R. Solution-processed CoFe_2O_4 nanoparticles on 3D carbon fiber papers for durable oxygen evolution reaction. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17851–17856.
- [166] Nsanzimana, J. M. V.; Peng, Y. C.; Xu, Y. Y.; Thia, L.; Wang, C.; Xia, B. Y.; Wang, X. An efficient and earth-abundant oxygen-evolving electrocatalyst based on amorphous metal borides. *Adv. Energy Mater.* **2018**, *8*, 1701475.
- [167] Grewe, T.; Deng, X. H.; Tüysüz, H. Influence of Fe doping on structure and water oxidation activity of nanocast Co_3O_4 . *Chem. Mater.* **2014**, *26*, 3162–3168.
- [168] Xu, Y. Q.; Zhang, W. F.; Li, Y. G.; Lu, P. F.; Wu, Z. S. A general bimetal-ion adsorption strategy to prepare nickel single atom catalysts anchored on graphene for efficient oxygen evolution reaction. *J. Energy Chem.* **2020**, *43*, 52–57.
- [169] Lee, S.; Bai, L. C.; Hu, X. L. Deciphering iron-dependent activity in oxygen evolution catalyzed by nickel-iron layered double hydroxide. *Angew. Chem., Int. Ed.* **2020**, *59*, 8072–8077.
- [170] Lin, Y. C.; Tian, Z. Q.; Zhang, L. J.; Ma, J. Y.; Jiang, Z.; Deibert, B. J.; Ge, R. X.; Chen, L. Chromium-ruthenium oxide solid solution electrocatalyst for highly efficient oxygen evolution reaction in acidic media. *Nat. Commun.* **2019**, *10*, 162.
- [171] Liu, C.; Qian, J.; Ye, Y. F.; Zhou, H.; Sun, C. J.; Sheehan, C.; Zhang, Z. Y.; Wan, G.; Liu, Y. S.; Guo, J. et al. Oxygen evolution reaction over catalytic single-site Co in a well-defined brookite TiO_2 nanorod surface. *Nat. Catal.* **2021**, *4*, 36–45.
- [172] Uyama, T.; Okazaki, Y.; Kawaguchi, S.; Yamada, I. Positive and negative synergistic effects of Fe-Co mixing on the oxygen and hydrogen evolution reaction activities of the quadruple perovskite $\text{CaCu}_2\text{Fe}_{4-x}\text{Co}_x\text{O}_{12}$. *ACS Appl. Energy Mater.* **2022**, *5*, 214–226.
- [173] Jin, D.; Kang, J.; Prabhakaran, S.; Lee, Y.; Kim, M. H.; Kim, D. H.; Lee, C. Chromium-rich $\text{Cr}_x\text{Ir}_{1-x}\text{O}_2$ wire-in-tube alloys for boosted water oxidation with long standing electrocatalytic activity. *J. Mater. Chem. A* **2022**, *10*, 13803–13813.
- [174] Zhuang, Z. B.; Sheng, W. C.; Yan, Y. S. Synthesis of monodisperse $\text{Au}@\text{Co}_3\text{O}_4$ core-shell nanocrystals and their enhanced catalytic activity for oxygen evolution reaction. *Adv. Mater.* **2014**, *26*, 3950–3955.
- [175] Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421.
- [176] García-Mota, M.; Bajdich, M.; Viswanathan, V.; Vojvodic, A.; Bell, A. T.; Nørskov, J. K. Importance of correlation in determining electrocatalytic oxygen evolution activity on cobalt oxides. *J. Phys. Chem. C* **2012**, *116*, 21077–21082.
- [177] Dionigi, F.; Zeng, Z. H.; Sinev, I.; Merzdorf, T.; Deshpande, S.; Lopez, M. B.; Kunze, S.; Zegkinoglou, I.; Sarodnik, H.; Fan, D. X.

- et al. *In-situ* structure and catalytic mechanism of NiFe and CoFe layered double hydroxides during oxygen evolution. *Nat. Commun.* **2020**, *11*, 2522.
- [178] Bo, X.; Li, Y. B.; Hocking, R. K.; Zhao, C. NiFeCr hydroxide holey nanosheet as advanced electrocatalyst for water oxidation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 41239–41245.
- [179] Castro, A. J. R.; Marques, S. P. D.; Soares, J. M.; Filho, J. M.; Saraiva, G. D.; Oliveira, A. C. Nanosized aluminum derived oxides catalysts prepared with different methods for styrene production. *Chem. Eng. J.* **2012**, *209*, 345–355.
- [180] Li, X. H.; Walsh, F. C.; Pletcher, D. Nickel based electrocatalysts for oxygen evolution in high current density, alkaline water electrolyzers. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1162–1167.
- [181] Yang, Y.; Dang, L. N.; Shearer, M. J.; Sheng, H. Y.; Li, W. J.; Chen, J.; Xiao, P.; Zhang, Y. H.; Hamers, R. J.; Jin, S. Highly active trimetallic NiFeCr layered double hydroxide electrocatalysts for oxygen evolution reaction. *Adv. Energy Mater.* **2018**, *8*, 1703189.
- [182] Ouyang, D.; Xiao, J. Y.; Ye, F.; Huang, Z. F.; Zhang, H.; Zhu, L.; Cheng, J. Q.; Choy, W. C. H. Strategic synthesis of ultrasmall NiCo₂O₄ NPs as hole transport layer for highly efficient perovskite solar cells. *Adv. Energy Mater.* **2018**, *8*, 1702722.
- [183] Zhang, J. T.; Yu, L.; Chen, Y.; Lu, X. F.; Gao, S. Y.; Lou, X. W. Designed formation of double-shelled Ni-Fe layered-double-hydroxide nanocages for efficient oxygen evolution reaction. *Adv. Mater.* **2020**, *32*, 1906432.
- [184] Bates, M. K.; Jia, Q. Y.; Doan, H.; Liang, W. T.; Mukerjee, S. Charge-transfer effects in Ni-Fe and Ni-Fe-Co mixed-metal oxides for the alkaline oxygen evolution reaction. *ACS Catal.* **2016**, *6*, 155–161.
- [185] Liu, Y. Y.; Han, N.; Jiang, J.; Ai, L. H. Boosting the oxygen evolution electrocatalysis of layered nickel hydroxidenitrate nanosheets by iron doping. *Int. J. Hydrogen Energy* **2019**, *44*, 10627–10636.
- [186] Zhang, B.; Zheng, X. L.; Voznyy, O.; Comin, R.; Bajdich, M.; Garcia-Melchor, M.; Han, L. L.; Xu, J. X.; Liu, M.; Zheng, L. R. et al. Homogeneously dispersed multimetal oxygen-evolving catalysts. *Science* **2016**, *352*, 333–337.
- [187] You, H. H.; Wang, B.; Wang, Y. Z.; Cao, Y. P.; Wei, K.; Gao, F. M. Efficient fish-scale CeO₂/NiFeCo composite material as electrocatalyst for oxygen evolution reaction. *Nanotechnology* **2021**, *32*, 365403.
- [188] Wu, Y. Y.; Tariq, M.; Zaman, W. Q.; Sun, W.; Zhou, Z. H.; Yang, J. Ni-Co codoped RuO₂ with outstanding oxygen evolution reaction performance. *ACS Appl. Energy Mater.* **2019**, *2*, 4105–4110.
- [189] Suntivich, J.; May, K. J.; Gasteiger, H. A.; Goodenough, J. B.; Shao-Horn, Y. A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. *Science* **2011**, *334*, 1383–1385.
- [190] Yang, S. L.; Zhang, T. R.; Li, G. C.; Yang, L. Q.; Lee, J. Y. Facile synthesis of N/M/O (M = Fe, Co, Ni) doped carbons for oxygen evolution catalysis in acid solution. *Energy Storage Mater.* **2017**, *6*, 140–148.
- [191] Wang, Y. Z.; Liu, S. S.; Hao, X. F.; Luan, S. R.; You, H. H.; Zhou, J. S.; Song, D. D.; Wang, D.; Li, H.; Gao, F. M. Surface reorganization engineering of the N-doped MoS₂ heterostructures MoO_x@N-doped MoS_{2-x} by *in situ* electrochemical oxidation activation for efficient oxygen evolution reaction. *J. Mater. Chem. A* **2019**, *7*, 10572–10580.
- [192] Hang, L. F.; Sun, Y. Q.; Men, D. D.; Liu, S. W.; Zhao, Q.; Cai, W. P.; Li, Y. Hierarchical micro/nanostructured C doped Co/Co₃O₄ hollow spheres derived from PS@Co(OH)₂ for the oxygen evolution reaction. *J. Mater. Chem. A* **2017**, *5*, 11163–11170.
- [193] Zeng, M.; Liu, Y. L.; Zhao, F. P.; Nie, K. Q.; Han, N.; Wang, X. X.; Huang, W. J.; Song, X. N.; Zhong, J.; Li, Y. G. Metallic cobalt nanoparticles encapsulated in nitrogen-enriched graphene shells: Its bifunctional electrocatalysis and application in zinc-air batteries. *Adv. Funct. Mater.* **2016**, *26*, 4397–4404.
- [194] Liang, Y. Y.; Li, Y. G.; Wang, H. L.; Zhou, J. G.; Wang, J.; Regier, T.; Dai, H. J. Co₃O₄ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nat. Mater.* **2011**, *10*, 780–786.
- [195] Lv, Q.; Wang, N.; Si, W. Y.; Hou, Z. F.; Li, X. D.; Wang, X.; Zhao, F. H.; Yang, Z.; Zhang, Y. L.; Huang, C. S. Pyridinic nitrogen exclusively doped carbon materials as efficient oxygen reduction electrocatalysts for Zn-air batteries. *Appl. Catal. B: Environ.* **2020**, *261*, 118234.
- [196] Liu, W. J.; Hu, X.; Li, H. C.; Yu, H. Q. Pseudocapacitive Ni-Co-Fe hydroxides/N-doped carbon nanoplates-based electrocatalyst for efficient oxygen evolution. *Small* **2018**, *14*, 1801878.
- [197] Chen, S.; Duan, J. J.; Jaroniec, M.; Qiao, S. Z. Three-dimensional N-doped graphene hydrogel/NiCo double hydroxide electrocatalysts for highly efficient oxygen evolution. *Angew. Chem., Int. Ed.* **2013**, *52*, 13567–13570.
- [198] Chen, S.; Qiao, S. Z. Hierarchically porous nitrogen-doped graphene-NiCo₂O₄ hybrid paper as an advanced electrocatalytic water-splitting material. *ACS Nano* **2013**, *7*, 10190–10196.
- [199] Zhu, Y. L.; Zhou, W.; Sunarso, J.; Zhong, Y. J.; Shao, Z. P. Phosphorus-doped perovskite oxide as highly efficient water oxidation electrocatalyst in alkaline solution. *Adv. Funct. Mater.* **2016**, *26*, 5862–5872.
- [200] Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y. Synthesis and activities of rutile IrO₂ and RuO₂ nanoparticles for oxygen evolution in acid and alkaline solutions. *J. Phys. Chem. Lett.* **2012**, *3*, 399–404.
- [201] Wygant, B. R.; Jarvis, K. A.; Chemelewski, W. D.; Mabayoje, O.; Celio, H.; Mullins, C. B. Structural and catalytic effects of iron- and scandium-doping on a strontium cobalt oxide electrocatalyst for water oxidation. *ACS Catal.* **2016**, *6*, 1122–1133.
- [202] Han, B. H.; Risch, M.; Lee, Y. L.; Ling, C.; Jia, H. F.; Shao-Horn, Y. Activity and stability trends of perovskite oxides for oxygen evolution catalysis at neutral pH. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22576–22580.
- [203] Xiao, L.; Wang, Z.; Guan, J. 2D MOFs and their derivatives for electrocatalytic applications: Recent advances and new challenges. *Coord. Chem. Rev.* **2022**, 472.
- [204] Wang, P. Y.; Zhang, L.; Wang, Z.; Bu, D. C.; Zhan, K.; Yan, Y.; Yang, J. H.; Zhao, B. N. and Mn dual-doped cactus-like cobalt oxide nanoarchitecture derived from cobalt carbonate hydroxide as efficient electrocatalysts for oxygen evolution reactions. *J. Colloid Interface Sci.* **2021**, *597*, 361–369.
- [205] Qi, J. L.; Wang, H. H.; Lin, J. H.; Li, C.; Si, X. Q.; Cao, J.; Zhong, Z. X.; Feng, J. C. Mn and S dual-doping of MOF-derived Co₃O₄ electrode array increases the efficiency of electrocatalytic generation of oxygen. *J. Colloid Interface Sci.* **2019**, *557*, 28–33.
- [206] Meng, S. C.; Sun, S. C.; Liu, Y.; Lu, Y. K.; Chen, M. Synergistic modulation of inverse spinel Fe₃O₄ by doping with chromium and nitrogen for efficient electrocatalytic water splitting. *J. Colloid Interface Sci.* **2022**, *624*, 433–442.
- [207] Xue, Y. R.; Fang, J. J.; Wang, X. D.; Xu, Z. Y.; Zhang, Y. F.; Lv, Q. Q.; Liu, M. Y.; Zhu, W.; Zhuang, Z. B. Sulfate-functionalized RuFeO_x as highly efficient oxygen evolution reaction electrocatalyst in acid. *Adv. Funct. Mater.* **2021**, *31*, 2101405.
- [208] Ye, Q.; Liu, J.; Lin, L.; Sun, M.; Wang, Y. F.; Cheng, Y. L. Fe and P dual-doped nickel carbonate hydroxide/carbon nanotube hybrid electrocatalysts for an efficient oxygen evolution reaction. *Nanoscale* **2022**, *14*, 6648–6655.
- [209] He, J.; Hu, Z. F.; Zhao, J. L.; Liu, P.; Lv, X. B.; Tian, W.; Wang, C. H.; Tan, S.; Ji, J. Y. Ni-decorated Fe-/N- co-doped carbon anchored on porous cobalt oxide nanowires arrays for efficient electrocatalytic oxygen evolution. *Chem. Eng. Sci.* **2021**, *243*, 116774.
- [210] Obodo, K. O.; Ouma, C. N. M.; Bessabov, D. First principles evaluation of the OER properties of TM-X (TM = Cr, Mn, Fe, Mo, Ru, W and Os, and X = F and S) doped IrO₂ (110) surface. *Electrochim. Acta* **2022**, *403*, 139562.
- [211] Li, D. G.; Park, E. J.; Zhu, W. L.; Shi, Q. R.; Zhou, Y.; Tian, H. Y.; Lin, Y. H.; Serov, A.; Zulevi, B.; Baca, E. D. et al. Highly quaternized polystyrene ionomers for high performance anion

- exchange membrane water electrolyzers. *Nat. Energy* **2020**, *5*, 378–385.
- [212] Tang, T. M.; Wang, Z. L.; Guan, J. Q. A review of defect engineering in two-dimensional materials for electrocatalytic hydrogen evolution reaction. *Chin. J. Catal.* **2022**, *43*, 636–678.
- [213] Zhou, B. H.; Gao, R. J.; Zou, J. J.; Yang, H. M. Surface design strategy of catalysts for water electrolysis. *Small* **2022**, *18*, 2202336.
- [214] Wang, Y. Y.; Xie, C.; Zhang, Z. Y.; Liu, D. D.; Chen, R.; Wang, S. Y. *In situ* exfoliated, N-doped, and edge-rich ultrathin layered double hydroxides nanosheets for oxygen evolution reaction. *Adv. Funct. Mater.* **2018**, *28*, 1703363.
- [215] Li, J. W.; Song, J. D.; Huang, B. Y.; Liang, G. E.; Liang, W. L.; Huang, G. J.; Jin, Y. Q.; Zhang, H.; Xie, F. Y.; Chen, J. et al. Enhancing the oxygen evolution reaction performance of NiFeOOH electrocatalyst for Zn-air battery by N-doping. *J. Catal.* **2020**, *389*, 375–381.
- [216] Zhang, Z. M.; Sun, H. N.; Li, J. F.; Shi, Z. H.; Fan, M. H.; Bian, H. Q.; Wang, T.; Gao, D. Q. S-doped CoMn_2O_4 with more high valence metallic cations and oxygen defects for zinc-air batteries. *J. Power Sources* **2021**, *491*, 229584.
- [217] Dai, W. J.; Bai, X. W.; Zhu, Y. A.; Zhang, Y.; Lu, T.; Pan, Y.; Wang, J. L. Surface reconstruction induced *in situ* phosphorus doping in nickel oxides for an enhanced oxygen evolution reaction. *J. Mater. Chem. A* **2021**, *9*, 6432–6441.
- [218] Wang, Y. C.; Zhou, T.; Jiang, K.; Da, P. M.; Peng, Z.; Tang, J.; Kong, B.; Cai, W. B.; Yang, Z. Q.; Zheng, G. F. Reduced mesoporous Co_3O_4 nanowires as efficient water oxidation electrocatalysts and supercapacitor electrodes. *Adv. Energy Mater.* **2014**, *4*, 1400696.
- [219] Zhang, J.; Cui, Y. X.; Jia, L. C.; He, B. B.; Zhang, K.; Zhao, L. Engineering anion defect in $\text{LaFeO}_{2.85}\text{Cl}_{0.15}$ perovskite for boosting oxygen evolution reaction. *Int. J. Hydrogen Energy* **2019**, *44*, 24077–24085.
- [220] Cai, Z.; Bi, Y. M.; Hu, E. Y.; Liu, W.; Dwarica, N.; Tian, Y.; Li, X. L.; Kuang, Y.; Li, Y. P.; Yang, X. Q. et al. Single-crystalline ultrathin Co_3O_4 nanosheets with massive vacancy defects for enhanced electrocatalysis. *Adv. Energy Mater.* **2018**, *8*, 1701694.
- [221] Arandiyah, H.; Mofarah, S. S.; Wang, Y.; Cazorla, C.; Jampaiah, D.; Garbrecht, M.; Wilson, K.; Lee, A. F.; Zhao, C.; Maschmeyer, T. Impact of surface defects on LaNiO_3 perovskite electrocatalysts for the oxygen evolution reaction. *Chem. —Eur. J.* **2021**, *27*, 14418–14426.
- [222] Zhou, D. J.; Xiong, X. Y.; Cai, Z.; Han, N. N.; Jia, Y.; Xie, Q. X.; Duan, X. X.; Xie, T. H.; Zheng, X. L.; Sun, X. et al. Flame-engraved nickel-iron layered double hydroxide nanosheets for boosting oxygen evolution reactivity. *Small Methods* **2018**, *2*, 1800083.
- [223] Li, J. W.; Lian, R. Q.; Wang, J. Y.; He, S.; Jiang, S. P.; Rui, Z. B. Oxygen vacancy defects modulated electrocatalytic activity of iron-nickel layered double hydroxide on Ni foam as highly active electrodes for oxygen evolution reaction. *Electrochim. Acta* **2020**, *331*, 135395.
- [224] Cui, T. T.; Wang, Y. P.; Ye, T.; Wu, J.; Chen, Z. Q.; Li, J.; Lei, Y. P.; Wang, D. S.; Li, Y. D. Engineering dual single-atom sites on 2D ultrathin N-doped carbon nanosheets attaining ultra-low-temperature zinc-air battery. *Angew. Chem., Int. Ed.* **2022**, *61*, e202115219.
- [225] You, H. H.; Wu, D. S.; Si, D. H.; Cao, M. N.; Sun, F. F.; Zhang, H.; Wang, H. M.; Liu, T. F.; Cao, R. Monolayer NiIr-layered double hydroxide as a long-lived efficient oxygen evolution catalyst for seawater splitting. *J. Am. Chem. Soc.* **2022**, *144*, 9254–9263.
- [226] Han, N. N.; Luo, S. W.; Deng, C. W.; Zhu, S.; Xu, Q. J.; Min, Y. L. Defect-Rich $\text{FeN}_{0.023}/\text{Mo}_2\text{C}$ Heterostructure as a highly efficient bifunctional catalyst for overall water-splitting. *ACS Appl. Mater. Interfaces* **2021**, *13*, 8306–8314.
- [227] Singh, T. I.; Rajeshkhanna, G.; Pan, U. N.; Kshetri, T.; Lin, H.; Kim, N. H.; Lee, J. H. Alkaline water splitting enhancement by MOF-derived Fe-Co-Oxide/Co@NC-mNS heterostructure: Boosting OER and HER through defect engineering and *in situ* oxidation. *Small* **2021**, *17*, 2101312.
- [228] Yin, H. J.; Yuan, K.; Zheng, Y. L.; Sun, X. C.; Zhang, Y. W. *In situ* synthesis of NiO/CuO nanosheet heterostructures rich in defects for efficient electrocatalytic oxygen evolution reaction. *J. Phys. Chem. C* **2021**, *125*, 16516–16523.
- [229] Wang, Y. Q.; Tao, S.; Lin, H.; Wang, G. P.; Zhao, K. N.; Cai, R. M.; Tao, K. W.; Zhang, C. X.; Sun, M. Z.; Hu, J. et al. Atomically targeting NiFe LDH to create multivacancies for OER catalysis with a small organic anchor. *Nano Energy* **2021**, *81*, 105606.
- [230] Liu, R.; Wang, Y. Y.; Liu, D. D.; Zou, Y. Q.; Wang, S. Y. Water-plasma-enabled exfoliation of ultrathin layered double hydroxide nanosheets with multivacancies for water oxidation. *Adv. Mater.* **2017**, *29*, 1701546.
- [231] Ye, C.; Wang, M. Q.; Bao, S. J.; Ye, C. H. Micropore-boosted layered double hydroxide catalysts: EIS analysis in structure and activity for effective oxygen evolution reactions. *ACS Appl. Mater. Interfaces* **2019**, *11*, 30887–30893.
- [232] Zhang, H. J.; Li, X. P.; Hähnel, A.; Naumann, V.; Lin, C.; Azimi, S.; Schweizer, S. L.; Maijenburg, A. W.; Wehrspohn, R. B. Bifunctional heterostructure assembly of NiFe LDH nanosheets on NiCoP nanowires for highly efficient and stable overall water splitting. *Adv. Funct. Mater.* **2018**, *28*, 1706847.
- [233] Ma, W.; Ma, R. Z.; Wang, C. X.; Liang, J. B.; Liu, X. H.; Zhou, K. C.; Sasaki, T. A superlattice of alternately stacked Ni-Fe hydroxide nanosheets and graphene for efficient splitting of water. *ACS Nano* **2015**, *9*, 1977–1984.
- [234] Li, J.; Gao, X.; Liu, B.; Feng, Q. L.; Li, X. B.; Huang, M. Y.; Liu, Z. F.; Zhang, J.; Tung, C. H.; Wu, L. Z. Graphdiyne: A metal-free material as hole transfer layer to fabricate quantum dot-sensitized photocathodes for hydrogen production. *J. Am. Chem. Soc.* **2016**, *138*, 3954–3957.
- [235] Wang, J. J.; Zeng, H. C. Three-dimensional hierarchical multimetal-LDH nanoflakes and their derived spinel oxides for efficient oxygen evolution. *ACS Appl. Energy Mater.* **2018**, *1*, 4998–5007.
- [236] Khan, S. B.; Khan, S. A.; Asiri, A. M. A fascinating combination of Co, Ni and Al nanomaterial for oxygen evolution reaction. *Appl. Surf. Sci.* **2016**, *370*, 445–451.
- [237] Li, Y.; Zhang, L.; Xiang, X.; Yan, D. P.; Li, F. Engineering of ZnCo-layered double hydroxide nanowalls toward high-efficiency electrochemical water oxidation. *J. Mater. Chem. A* **2014**, *2*, 13250–13258.
- [238] Wang, W. X.; Lu, Y.; Zhao, M. L.; Luo, R. J.; Yang, Y.; Peng, T.; Yan, H. L.; Liu, X. M.; Luo, Y. S. Controllable tuning of cobalt nickel-layered double hydroxide arrays as multifunctional electrodes for flexible supercapattery device and oxygen evolution reaction. *ACS Nano* **2019**, *13*, 12206–12218.
- [239] Zhou, D. J.; Cai, Z.; Lei, X. D.; Tian, W. L.; Bi, Y. M.; Jia, Y.; Han, N. N.; Gao, T. F.; Zhang, Q.; Kuang, Y. et al. NiCoFe-layered double hydroxides/N-doped graphene oxide array colloid composite as an efficient bifunctional catalyst for oxygen electrocatalytic reactions. *Adv. Energy Mater.* **2018**, *8*, 1701905.
- [240] Zhang, Q. R.; Bedford, N. M.; Pan, J.; Lu, X. Y.; Amal, R. A fully reversible water electrolyzer cell made up from FeCoNi (oxy)hydroxide atomic layers. *Adv. Energy Mater.* **2019**, *9*, 1901312.
- [241] Lu, Z. Y.; Qian, L.; Tian, Y.; Li, Y. P.; Sun, X. M.; Duan, X. Ternary NiFeMn layered double hydroxides as highly-efficient oxygen evolution catalysts. *Chem. Commun.* **2016**, *52*, 908–911.
- [242] Liu, H. X.; Wang, Y. R.; Lu, X. Y.; Hu, Y.; Zhu, G. Y.; Chen, R. P.; Ma, L. B.; Zhu, H. F.; Tie, Z. X.; Liu, J. et al. The effects of Al substitution and partial dissolution on ultrathin NiFeAl trinary layered double hydroxide nanosheets for oxygen evolution reaction in alkaline solution. *Nano Energy* **2017**, *35*, 350–357.
- [243] Qian, L.; Lu, Z. Y.; Xu, T. H.; Wu, X. C.; Tian, Y.; Li, Y. P.; Huo, Z. Y.; Sun, X. M.; Duan, X. Trinary layered double hydroxides as high-performance bifunctional materials for oxygen electrocatalysis. *Adv. Energy Mater.* **2015**, *5*, 1500245.
- [244] Gong, M.; Li, Y. G.; Wang, H. L.; Liang, Y. Y.; Wu, J. Z.; Zhou, J. G.; Wang, J.; Regier, T.; Wei, F.; Dai, H. J. An advanced Ni-Fe layered double hydroxide electrocatalyst for water oxidation. *J. Am. Chem. Soc.* **2013**, *135*, 8452–8455.
- [245] Fan, K.; Chen, H.; Ji, Y. F.; Huang, H.; Claesson, P. M.; Daniel, Q.;

- Philippe, B.; Rensmo, H.; Li, F. S.; Luo, Y. et al. Nickel-vanadium monolayer double hydroxide for efficient electrochemical water oxidation. *Nat. Commun.* **2016**, *7*, 11981.
- [246] Liang, H. F.; Li, L. S.; Meng, F.; Dang, L. N.; Zhuo, J. Q.; Forticaux, A.; Wang, Z. C.; Jin, S. Porous two-dimensional nanosheets converted from layered double hydroxides and their applications in electrocatalytic water splitting. *Chem. Mater.* **2015**, *27*, 5702–5711.
- [247] Dong, C. L.; Yuan, X. T.; Wang, X. Y.; Liu, X. Y.; Dong, W. J.; Wang, R. Q.; Duan, Y. H.; Huang, F. Q. Rational design of cobalt-chromium layered double hydroxide as a highly efficient electrocatalyst for water oxidation. *J. Mater. Chem. A* **2016**, *4*, 11292–11298.
- [248] Liang, H. F.; Meng, F.; Cabán-Acevedo, M.; Li, L. S.; Forticaux, A.; Xiu, L.; Wang, Z. C.; Jin, S. Hydrothermal continuous flow synthesis and exfoliation of NiCo layered double hydroxide nanosheets for enhanced oxygen evolution catalysis. *Nano Lett.* **2015**, *15*, 1421–1427.
- [249] Song, F.; Hu, X. L. Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis. *Nat. Commun.* **2014**, *5*, 4477.
- [250] Zhang, W.; Wu, Y. Z.; Qi, J.; Chen, M. X.; Cao, R. A thin NiFe hydroxide film formed by stepwise electrodeposition strategy with significantly improved catalytic water oxidation efficiency. *Adv. Energy Mater.* **2017**, *7*, 1602547.
- [251] Yan, X. D.; Li, K. X.; Lyu, L.; Song, F.; He, J.; Niu, D. M.; Liu, L.; Hu, X. L.; Chen, X. B. From water oxidation to reduction: Transformation from $\text{Ni}_3\text{Co}_{3-x}\text{O}_4$ nanowires to NiCo/NiCo_x heterostructures. *ACS Appl. Mater. Interfaces* **2016**, *8*, 3208–3214.
- [252] Gao, T. T.; Jin, Z. Y.; Liao, M.; Xiao, J. L.; Yuan, H. Y.; Xiao, D. A trimetallic V-Co-Fe oxide nanoparticle as an efficient and stable electrocatalyst for oxygen evolution reaction. *J. Mater. Chem. A* **2015**, *3*, 17763–17770.
- [253] Zhao, Y. F.; Zhang, X.; Jia, X. D.; Waterhouse, G. I. N.; Shi, R.; Zhang, X. R.; Zhan, F.; Tao, Y.; Wu, L. Z.; Tung, C. H. et al. Sub-3 nm ultrafine monolayer layered double hydroxide nanosheets for electrochemical water oxidation. *Adv. Energy Mater.* **2018**, *8*, 1703585.
- [254] Yuan, Z. J.; Bak, S. M.; Li, P. S.; Jia, Y.; Zheng, L. R.; Zhou, Y.; Bai, L.; Hu, E. Y.; Yang, X. Q.; Cai, Z. et al. Activating layered double hydroxide with multivacancies by memory effect for energy-efficient hydrogen production at neutral pH. *ACS Energy Lett.* **2019**, *4*, 1412–1418.
- [255] Wang, Y. Y.; Zhang, Y. Q.; Liu, Z. J.; Xie, C.; Feng, S.; Liu, D. D.; Shao, M. F.; Wang, S. Y. Layered double hydroxide nanosheets with multiple vacancies obtained by dry exfoliation as highly efficient oxygen evolution electrocatalysts. *Angew. Chem., Int. Ed.* **2017**, *56*, 5867–5871.
- [256] Zhou, P.; Wang, Y. Y.; Xie, C.; Chen, C.; Liu, H. W.; Chen, R.; Huo, J.; Wang, S. Y. Acid-etched layered double hydroxides with rich defects for enhancing the oxygen evolution reaction. *Chem. Commun.* **2017**, *53*, 11778–11781.
- [257] Wang, Z. Q.; Zeng, S.; Liu, W. H.; Wang, X. W.; Li, Q. W.; Zhao, Z. G.; Geng, F. X. Coupling molecularly ultrathin sheets of NiFe-layered double hydroxide on NiCo₂O₄ nanowire arrays for highly efficient overall water-splitting activity. *ACS Appl. Mater. Interfaces* **2017**, *9*, 1488–1495.
- [258] Liu, J.; Wang, J. S.; Zhang, B.; Ruan, Y. J.; Lv, L.; Ji, X.; Xu, K.; Miao, L.; Jiang, J. J. Hierarchical NiCo₂S₄@NiFe LDH heterostructures supported on nickel foam for enhanced overall-water-splitting activity. *ACS Appl. Mater. Interfaces* **2017**, *9*, 15364–15372.
- [259] Chi, J.; Yu, H. M.; Qin, B. W.; Fu, L.; Jia, J.; Yi, B. L.; Shao, Z. G. Vertically aligned FeOOH/NiFe layered double hydroxides electrode for highly efficient oxygen evolution reaction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 464–471.
- [260] Hou, Y.; Lohe, M. R.; Zhang, J.; Liu, S. H.; Zhuang, X. D.; Feng, X. L. Vertically oriented cobalt selenide/NiFe layered-double-hydroxide nanosheets supported on exfoliated graphene foil: An efficient 3D electrode for overall water splitting. *Energy Environ. Sci.* **2016**, *9*, 478–483.
- [261] Andronesco, C.; Barwe, S.; Ventosa, E.; Masa, J.; Vasile, E.; Konkana, B.; Möller, S.; Schuhmann, W. Powder catalyst fixation for post-electrolysis structural characterization of NiFe layered double hydroxide based oxygen evolution reaction electrocatalysts. *Angew. Chem., Int. Ed.* **2017**, *56*, 11258–11262.
- [262] Jia, Y.; Zhang, L. Z.; Gao, G. P.; Chen, H.; Wang, B.; Zhou, J. Z.; Soo, M. T.; Hong, M.; Yan, X. C.; Qian, G. R. et al. A heterostructure coupling of exfoliated Ni-Fe hydroxide nanosheet and defective graphene as a bifunctional electrocatalyst for overall water splitting. *Adv. Mater.* **2017**, *29*, 1700017.
- [263] Cai, Z.; Zhou, D. J.; Wang, M. Y.; Bak, S. M.; Wu, Y. S.; Wu, Z. S.; Tian, Y.; Xiong, X. Y.; Li, Y. P.; Liu, W. et al. Introducing Fe²⁺ into nickel-iron layered double hydroxide: Local structure modulated water oxidation activity. *Angew. Chem., Int. Ed.* **2018**, *57*, 9392–9396.
- [264] Chen, G. B.; Wang, T.; Zhang, J.; Liu, P.; Sun, H. J.; Zhuang, X. D.; Chen, M. W.; Feng, X. L. Accelerated hydrogen evolution kinetics on NiFe-layered double hydroxide electrocatalysts by tailoring water dissociation active sites. *Adv. Mater.* **2018**, *30*, 1706279.
- [265] Dang, L. N.; Liang, H. F.; Zhuo, J. Q.; Lamb, B. K.; Sheng, H. Y.; Yang, Y.; Jin, S. Direct synthesis and anion exchange of noncarbonate-intercalated NiFe-layered double hydroxides and the influence on electrocatalysis. *Chem. Mater.* **2018**, *30*, 4321–4330.
- [266] Kashale, A. A.; Yi, C. H.; Cheng, K. Y.; Guo, J. S.; Pan, Y. H.; Chen, I. W. P. Binder-free heterostructured NiFe₂O₄/NiFe LDH nanosheet composite electrocatalysts for oxygen evolution reactions. *ACS Appl. Energy Mater.* **2020**, *3*, 10831–10840.
- [267] Yan, F.; Guo, D.; Kang, J. Y.; Liu, L. N.; Zhu, C. L.; Gao, P.; Zhang, X. T.; Chen, Y. J. Fast fabrication of ultrathin CoMn LDH nanorarray as flexible electrode for water oxidation. *Electrochim. Acta* **2018**, *283*, 755–763.
- [268] Song, F.; Hu, X. L. Ultrathin cobalt-manganese layered double hydroxide is an efficient oxygen evolution catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 16481–16484.
- [269] Liu, Z. B.; Yu, C.; Han, X. T.; Yang, J.; Zhao, C. T.; Huang, H. W.; Qiu, J. S. CoMn layered double hydroxides/carbon nanotubes architectures as high-performance electrocatalysts for the oxygen evolution reaction. *ChemElectroChem* **2016**, *3*, 906–912.
- [270] Wang, Q.; Shang, L.; Shi, R.; Zhang, X.; Zhao, Y. F.; Waterhouse, G. I. N.; Wu, L. Z.; Tung, C. H.; Zhang, T. R. NiFe layered double hydroxide nanoparticles on Co, N-codoped carbon nanoframes as efficient bifunctional catalysts for rechargeable zinc-air batteries. *Adv. Energy Mater.* **2017**, *7*, 1700467.
- [271] Jia, G.; Hu, Y. F.; Qian, Q. F.; Yao, Y. F.; Zhang, S. Y.; Li, Z. S.; Zou, Z. G. Formation of hierarchical structure composed of (Co/Ni)Mn-LDH nanosheets on MWCNT backbones for efficient electrocatalytic water oxidation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14527–14534.
- [272] Tang, C.; Wang, H. S.; Wang, H. F.; Zhang, Q.; Tian, G. L.; Nie, J. Q.; Wei, F. Spatially confined hybridization of nanometer-sized NiFe hydroxides into nitrogen-doped graphene frameworks leading to superior oxygen evolution reactivity. *Adv. Mater.* **2015**, *27*, 4516–4522.
- [273] Zhang, C.; Zhao, J. W.; Zhou, L.; Li, Z. H.; Shao, M. F.; Wei, M. Layer-by-layer assembly of exfoliated layered double hydroxide nanosheets for enhanced electrochemical oxidation of water. *J. Mater. Chem. A* **2016**, *4*, 11516–11523.
- [274] Long, X.; Xiao, S.; Wang, Z. L.; Zheng, X. L.; Yang, S. H. Co intake mediated formation of ultrathin nanosheets of transition metal LDH—An advanced electrocatalyst for oxygen evolution reaction. *Chem. Commun.* **2015**, *51*, 1120–1123.
- [275] Qiao, C.; Zhang, Y.; Zhu, Y. Q.; Cao, C. B.; Bao, X. H.; Xu, J. Q. One-step synthesis of zinc-cobalt layered double hydroxide (Zn-Co-LDH) nanosheets for high-efficiency oxygen evolution reaction. *J. Mater. Chem. A* **2015**, *3*, 6878–6883.
- [276] Bai, X.; Guan, J. Q. MXenes for electrocatalysis applications: Modification and hybridization. *Chin. J. Catal.* **2022**, *43*, 2057–2090.
- [277] Dai, J.; Zhu, Y. L.; Zhong, Y. J.; Miao, J.; Lin, B. W.; Zhou, W.;

- Shao, Z. P. Enabling high and stable electrocatalytic activity of iron-based perovskite oxides for water splitting by combined bulk doping and morphology designing. *Adv. Mater. Interfaces* **2019**, *6*, 1801317.
- [278] Yu, H. R.; Chu, F. Q.; Zhou, X.; Ji, J. L.; Liu, Y.; Bu, Y. F.; Kong, Y.; Tao, Y. X.; Li, Y. X.; Qin, Y. A perovskite oxide with a tunable pore-size derived from a general salt-template strategy as a highly efficient electrocatalyst for the oxygen evolution reaction. *Chem. Commun.* **2019**, *55*, 2445–2448.
- [279] Cheng, X.; Fabbri, E.; Yamashita, Y.; Castelli, I. E.; Kim, B.; Uchida, M.; Haumont, R.; Puente-Orench, I.; Schmidt, T. J. Oxygen evolution reaction on perovskites: A multieffect descriptor study combining experimental and theoretical methods. *ACS Catal.* **2018**, *8*, 9567–9578.
- [280] Zhang, J. H.; Fu, X. B.; Xia, F. J.; Zhang, W. Q.; Ma, D. S.; Zhou, Y.; Peng, H.; Wu, J. S.; Gong, X. Q.; Wang, D. et al. Core-shell nanostructured Ru@Ir-O electrocatalysts for superb oxygen evolution in acid. *Small* **2022**, *18*, 2108031.
- [281] Chen, M. X.; Lu, S. L.; Fu, X. Z.; Luo, J. L. Core-shell structured NiFeSn@NiFe (oxy)hydroxide nanospheres from an electrochemical strategy for electrocatalytic oxygen evolution reaction. *Adv. Sci. (Weinh)* **2020**, *7*, 1903777.
- [282] Mu, Y.; Zhang, Y. F.; Pei, X. Y.; Dong, X. Y.; Kou, Z. K.; Cui, M.; Meng, C. G. Dispersed FeO_x nanoparticles decorated with Co₂SiO₄ hollow spheres for enhanced oxygen evolution reaction. *J. Colloid Interface Sci.* **2022**, *611*, 235–245.
- [283] Fu, L.; Zhou, J.; Zhou, L. K.; Yang, J. M.; Liu, Z. R.; Wu, K.; Zhao, H. F.; Wang, J. K.; Wu, K. Facile fabrication of exsolved nanoparticle-decorated hollow ferrite fibers as active electrocatalyst for oxygen evolution reaction. *Chem. Eng. J.* **2021**, *418*, 129422.
- [284] Tang, T. M.; Li, S. S.; Sun, J. R.; Wang, Z. L.; Guan, J. Q. Advances and challenges in two-dimensional materials for oxygen evolution. *Nano Res.*, in press, <https://doi.org/10.1007/s12274-022-4575-0>.
- [285] Li, D. J.; Liu, S. Q.; Ye, G. Y.; Zhu, W. W.; Zhao, K. M.; Luo, M.; He, Z. One-step electrodeposition of Ni_xFe_{3-x}O₄/Ni hybrid nanosheet arrays as highly active and robust electrocatalysts for the oxygen evolution reaction. *Green Chem.* **2020**, *22*, 1710–1719.
- [286] Wang, C.; Qi, L. M. Heterostructured inter-doped ruthenium-cobalt oxide hollow nanosheet arrays for highly efficient overall water splitting. *Angew. Chem., Int. Ed.* **2020**, *59*, 17219–17224.
- [287] Li, Y.; Wu, Y. Y.; Hao, H. R.; Yuan, M. K.; Lv, Z.; Xu, L. L.; Wei, B. *In situ* unraveling surface reconstruction of Ni₃P₄@FeP nanosheet array for superior alkaline oxygen evolution reaction. *Appl. Catal. B: Environ.* **2022**, *305*, 121033.
- [288] Zhang, Y. Q.; Ye, L.; Zhang, M. L.; Ma, L. F.; Gong, Y. Q. A nanoflower composite catalyst *in situ* grown on conductive iron foam: Revealing the enhancement of OER activity by cooperating of amorphous Ni based nanosheets with spinel NiFe₂O₄. *Appl. Surf. Sci.* **2022**, *589*, 152957.
- [289] Zai, S. F.; Gao, X. Y.; Yang, C. C.; Jiang, Q. Ce-modified Ni(OH)₂ nanoflowers supported on NiSe₂ octahedra nanoparticles as high-efficient oxygen evolution electrocatalyst. *Adv. Energy Mater.* **2021**, *11*, 2101266.
- [290] Qayum, A.; Peng, X.; Yuan, J. F.; Qu, Y. D.; Zhou, J. H.; Huang, Z. L.; Xia, H.; Liu, Z.; Tan, D. Q.; Chu, P. K. et al. Highly durable and efficient Ni-FeO_x/FeNi₃ electrocatalysts synthesized by a facile *in situ* combustion-based method for overall water splitting with large current densities. *ACS Appl. Mater. Interfaces* **2022**, *14*, 27842–27853.
- [291] Chen, X.; Pu, J.; Hu, X. H.; Yao, Y. C.; Dou, Y. B.; Jiang, J. J.; Zhang, W. J. Janus hollow nanofiber with bifunctional oxygen electrocatalyst for rechargeable Zn-Air battery. *Small* **2022**, *18*, 2200578.
- [292] Jiang, X. L.; Tang, M. Y.; Tang, L.; Jiang, N.; Zheng, Q. J.; Xie, F. Y.; Lin, D. M. Hornwort-like hollow porous MoO₃/NiF₂ heterogeneous nanowires as high-performance electrocatalysts for efficient water oxidation. *Electrochim. Acta* **2021**, *379*, 138146.
- [293] Liang, C. W.; Zou, P. C.; Nairan, A.; Zhang, Y. Q.; Liu, J. X.; Liu, K. W.; Hu, S. Y.; Kang, F. Y.; Fan, H. J.; Yang, C. Exceptional performance of hierarchical Ni-Fe oxyhydroxide@NiFe alloy nanowire array electrocatalysts for large current density water splitting. *Energy Environ. Sci.* **2020**, *13*, 86–95.
- [294] Gou, Y.; Liu, Q.; Liu, Z. A.; Asiri, A. M.; Sun, X. P.; Hu, J. M. FeMoO₄ nanorod array: A highly active 3D anode for water oxidation under alkaline conditions. *Inorg. Chem. Front.* **2018**, *5*, 665–668.
- [295] Qian, M. M.; Cui, S. S.; Jiang, D. C.; Zhang, L.; Du, P. W. Highly efficient and stable water-oxidation electrocatalysis with a very low overpotential using FeNiP substitutional-solid-solution nanoplate arrays. *Adv. Mater.* **2017**, *29*, 1704075.
- [296] Zhang, X. L.; Liu, R. L.; Tao, C. Y.; Wu, S. S.; Huang, F.; Wang, H. W. 3D metal dendrite-derived petaloid shaped NiFe₂O₄@ NFM as binderless electrode for oxygen evolution reaction and electrochemical energy storage. *J. Alloys Compd.* **2020**, *813*, 152219.
- [297] Etesami, M.; Mohamad, A. A.; Nguyen, M. T.; Yonezawa, T.; Pornprasertsuk, R.; Somwangthanaroj, A.; Kheawhom, S. Benchmarking superfast electrodeposited bimetallic (Ni, Fe, Co, and Cu) hydroxides for oxygen evolution reaction. *J. Alloys Compd.* **2021**, *889*, 161738.
- [298] Hai, Y.; Liu, L.; Gong, Y. Iron coordination polymer, Fe(oxalate)(H₂O)₂ nanorods grown on nickel foam via one-step electrodeposition as an efficient electrocatalyst for oxygen evolution reaction. *Inorg. Chem.* **2021**, *60*, 5140–5152.
- [299] Shin, C. H.; Wei, Y.; Park, G. S.; Kang, J.; Yu, J. S. High performance binder-free Fe-Ni hydroxides on nickel foam prepared in piranha solution for the oxygen evolution reaction. *Sustainable Energy Fuels* **2020**, *4*, 6311–6320.
- [300] Wang, W.; Jiang, Y. L.; Hu, Y. C.; Liu, Y. C.; Li, J.; Chen, S. L. Top-open hollow nanocubes of Ni-doped Cu oxides on Ni foam: Scalable oxygen evolution electrode via galvanic displacement and face-selective etching. *ACS Appl. Mater. Interfaces* **2020**, *12*, 11600–11606.
- [301] Wang, H.; Chen, H. Z.; Wang, H. J.; Wu, L.; Wu, Q. X.; Luo, Z. K.; Wang, F. Hierarchical porous FeCo₂O₄@Ni as a carbon- and binder-free cathode for lithium-oxygen batteries. *J. Alloys Compd.* **2019**, *780*, 107–115.
- [302] Zheng, T. L.; He, J.; Cai, P. W.; Liu, X.; Wu, D. J.; Song, L. T.; He, Q. G.; Tang, Y. Z.; Wang, G. J.; Gu, M. et al. Enhanced oxygen evolution reaction electrocatalysis on Co(OH)₂@MnO₂ decorated carbon nanoarrays: Effect of heterostructure, conductivity and charge storage capability. *J. Electrochem. Soc.* **2021**, *168*, 114515.
- [303] Guo, X.; Zhang, J. Q.; Zhao, Y. F.; Sun, B.; Liu, H.; Wang, G. X. Ultrathin porous NiCo₂O₄ nanosheets for lithium-oxygen batteries: An excellent performance deriving from an enhanced solution mechanism. *ACS Appl. Energy Mater.* **2019**, *2*, 4215–4223.
- [304] Zhang, Y.; Guo, H. R.; Ren, J. K.; Li, X. P.; Ren, W. L.; Song, R. MoO₃ crystal facets modulation by doping heteroatom Fe from polyoxometalate for quasi-industrial oxygen evolution reaction. *Appl. Catal. B: Environ.* **2021**, *298*, 120582.
- [305] Zhang, M.; Chen, M. W.; Bi, Y. F.; Huang, L. L.; Zhou, K.; Zheng, Z. P. A bimetallic Co₄Mo₈ cluster built from Mo₈ oxothiomolybdate capped by a Co₄-thiacalix[4]arene unit: The observation of the Co-Mo synergistic effect for binder-free electrocatalysts. *J. Mater. Chem. A* **2019**, *7*, 12893–12899.
- [306] Bahadur, A.; Hussain, W.; Iqbal, S.; Ullah, F.; Shoaib, M.; Liu, G. C.; Feng, K. J. A morphology controlled surface sulfurized CoMn₂O₄ microspike electrocatalyst for water splitting with excellent OER rate for binder-free electrocatalytic oxygen evolution. *J. Mater. Chem. A* **2021**, *9*, 12255–12264.
- [307] Xie, X. H.; Du, L.; Yan, L. T.; Park, S.; Qiu, Y.; Sokolowski, J.; Wang, W.; Shao, Y. Y. Oxygen evolution reaction in alkaline environment: Material challenges and solutions. *Adv. Funct. Mater.* **2022**, *32*, 2110036.
- [308] Guo, T. Q.; Li, L. D.; Wang, Z. C. Recent development and future perspectives of amorphous transition metal-based electrocatalysts for oxygen evolution reaction. *Adv. Energy Mater.* **2022**, *12*, 2200827.
- [309] Tang, T. M.; Wang, Z. L.; Guan, J. Q. Optimizing the

- electrocatalytic selectivity of carbon dioxide reduction reaction by regulating the electronic structure of single-atom M-N-C materials. *Adv. Funct. Mater.* **2022**, *32*, 2111504.
- [310] Li, A. L.; Ooka, H.; Bonnet, N.; Hayashi, T.; Sun, Y. M.; Jiang, Q. K.; Li, C.; Han, H. X.; Nakamura, R. Stable potential windows for long-term electrocatalysis by manganese oxides under acidic conditions. *Angew. Chem., Int. Ed.* **2019**, *58*, 5054–5058.
- [311] Huynh, M.; Ozel, T.; Liu, C.; Lau, E. C.; Nocera, D. G. Design of template-stabilized active and earth-abundant oxygen evolution catalysts in acid. *Chem. Sci.* **2017**, *8*, 4779–4794.
- [312] Frydendal, R.; Paoli, E. A.; Chorkendorff, I.; Rossmeisl, J.; Stephens, I. E. L. Toward an active and stable catalyst for oxygen evolution in acidic media: Ti-stabilized MnO₂. *Adv. Energy Mater.* **2015**, *5*, 1500991.
- [313] Tao, H. B.; Xu, Y. H.; Huang, X.; Chen, J. Z.; Pei, L. J.; Zhang, J. M.; Chen, J. G.; Liu, B. A general method to probe oxygen evolution intermediates at operating conditions. *Joule* **2019**, *3*, 1498–1509.
- [314] Govindarajan, N.; García-Lastra, J. M.; Meijer, E. J.; Calle-Vallejo, F. Does the breaking of adsorption-energy scaling relations guarantee enhanced electrocatalysis? *Curr. Opin. Electrochem.* **2018**, *8*, 110–117.
- [315] Zhao, Z. J.; Liu, S. H.; Zha, S.; Cheng, D. F.; Studt, F.; Henkelman, G.; Gong, J. L. Theory-guided design of catalytic materials using scaling relationships and reactivity descriptors. *Nat. Rev. Mater.* **2019**, *4*, 792–804.
- [316] Pérez-Ramírez, J.; López, N. Strategies to break linear scaling relationships. *Nat. Catal.* **2019**, *2*, 971–976.
- [317] Mehta, P.; Barboun, P.; Herrera, F. A.; Kim, J.; Rumbach, P.; Go, D. B.; Hicks, J. C.; Schneider, W. F. Overcoming ammonia synthesis scaling relations with plasma-enabled catalysis. *Nat. Catal.* **2018**, *1*, 269–275.
- [318] Pegis, M. L.; Wise, C. F.; Koronkiewicz, B.; Mayer, J. M. Identifying and breaking scaling relations in molecular catalysis of electrochemical reactions. *J. Am. Chem. Soc.* **2017**, *139*, 11000–11003.