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Review

Perspective of hydrogen energy and recent progress in electrocatalytic water splitting



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ABSTRACT

As a secondary energy with great commercialization potential, hydrogen energy has been widely studied due to the high calorific value, clean combustion products and various reduction methods. At present, the blueprint of hydrogen energy economy in the world is gradually taking shape. Compared with the traditional high-energy consuming methane steam reforming hydrogen production method, the electrocatalytic water splitting hydrogen production stands out among other process of hydrogen production owing to the mild reaction conditions, high-purity hydrogen generation and sustainable production process. Basing on current technical economy situation, the highly electric power cost limits the further promotion of electrocatalytic water splitting hydrogen production process. Consequently, the rational design and development of low overpotential and high stability electrocatalytic water splitting catalysts are critical toward the realization of low-cost hydrogen production technology. In this review, we summarize the existing hydrogen production methods, elaborate the reaction mechanism of the electrocatalytic water splitting reaction under acidic and alkaline conditions and the recent progress of the respective catalysts for the two half-reactions. The structure–activity relationship of the catalyst was deep-going discussed, together with the prospects of electrocatalytic water splitting and the current challenges, aiming at provide insights for electrocatalytic water splitting catalyst development and its industrial applications.

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1. Introduction

Ever-increasing energy consumption and increasingly serious environmental pollution have necessitated the development of new energy sources to replace fossil energies [1–3]. Hydrogen is a new energy that has attracted much attention in the process of the world energy crisis in the 21st century [4,5]. As a bridge connecting different energies, hydrogen can complement and synergize with the power system, and is an ideal interconnection medium for collaborative optimization across energy networks. The extremely excellent characteristics as follow: (1) The combustion of hydrogen has a high calorific value, and the product of combustion is water, without the pollutants and carbon emissions generated by the use of traditional energy. Therefore, hydrogen is the cleanest energy and can replace fossil energy to achieve a green development path with zero carbon emissions in energy utilization. (2) Hydrogen can be widely used in transportation, industry,

construction and other fields, which can not only provide high-efficiency raw materials, reducing agents, and high-quality heat sources for refining, steel, metallurgy and other industries, but also can be used in automobiles, rail transit, and ships through fuel cell technology to reduce the dependence of long-distance and high-load traffic on oil and natural gas. In addition, hydrogen can also be applied to distributed power generation to provide protection for residential and commercial electricity. (3) As a secondary energy, hydrogen can be produced in various ways, including fossil energy steam reforming, biomass pyrolysis, photolysis of water, and electrochemical water splitting, etc [6].

Among a variety of industrial hydrogen production methods, methane steam reforming is currently the main hydrogen production industrial process [7]. However, the methane steam reforming has disadvantages such as high energy consumption and large carbon emissions. In comparison, the reaction conditions for hydrogen production by electrochemical water splitting are mild, and the production process is green and sustainable. Therefore, the electrochemical water splitting is considered to be the most promising energy development system [8]. The water produced by the combustion of hydrogen can be used to electrochemical water splitting

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to produce hydrogen, forming a virtuous cycle. In particular, combining with renewable energy (solar energy, wind energy, waterpower, tidal energy and geothermal energy *etc.*) power generation system can provide sufficient power guarantee for electrochemical water splitting to achieve green and clean industry cycle, and further expand the application of renewable energy power generation.

Although the electrochemical water splitting has significant advantages, high-efficiency hydrogen production requires durable and excellent active catalysts to overcome kinetic obstacles to promote reaction kinetics [9]. The electrochemical water splitting is mainly divided into the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. Metal catalysts are the main development materials for electrochemical catalysts because of their excellent conductivity. At present, platinum (Pt) is the best solid electrocatalyst for HER [10], and noble metals iridium (Ir), ruthenium (Ru) and their oxides (IrO_2 and RuO_2) are excellent OER catalysts [11–13]. However, the low reserves and high cost of noble metals limit the industrial application of noble metal catalysts in electrochemical water splitting. Therefore, researchers have been committed to the development of non-noble metal electrocatalysts with high activity, durable and low cost in recent years to promote the industrial development of electrochemical water splitting.

Nanoengineering provides new opportunities for the design and development of electrochemical catalysts. Researchers are able to design complex nanostructures of catalysts at the atomic level (surface and interface engineering design), so that catalysis can expose as many electrocatalytic active sites as possible, thereby improving the intrinsic kinetics of the electrochemical reaction. In recent years, our group has focused on the design and synthesis of functional nanomaterials, and developed a series of electrochemical catalysts for electrochemical water splitting reactions. In this report, we summarized the research results and progress of nanomaterial electrocatalysts in electrochemical water splitting in order to provide feasible ideas for the future research and development of electrocatalysts in electrochemical water splitting, and promote the development and application of hydrogen (Fig. 1).

2. Hydrogen Production Method

There are many hydrogen production methods, including hydrogen production from coal, biological hydrogen production, thermochemical decomposition hydrogen production, and hydrogen production by electrolysis of water, as summarized in Fig. 2.

2.1. Hydrogen production by electrolysis of water splitting

The raw material for the production of hydrogen by electrolysis of water is water, which does not produce pollutants during the preparation process. It is a green hydrogen production technology. At present, the production of hydrogen produced by electrolysis of water splitting has reached 4% of the total production of hydrogen in the world. With the development of hydrogen technology, its application prospects will become better [13]. The positive and negative electrodes are inserted into water and direct current is applied. Hydrogen ions in the water undergo reduction reaction at the cathode to produce hydrogen, and hydroxide ions undergo oxidation reaction at the anode to produce oxygen. According to different electrolytes, it can be divided into alkaline electrolysis, proton membrane electrolysis and solid oxide electrolysis [14]. The electric energy required for hydrogen production by electrolysis needs to be converted from thermal energy or other forms of energy, and the general thermoelectric conversion efficiency can only reach about 30%–40%. In this way, the total efficiency of

changing from primary energy to hydrogen energy is only about 25%–34%. If the use of water resources, wind resources and solar energy resources to generate electricity is combined with water electrolysis for hydrogen production, the rational use and complementarity of resources can be realized, which is of great significance to the economy and the environment.

2.2. Hydrogen production from coal

The principle of hydrogen production from coal is to generate hydrogen and other gas components through the coking of coal (or high-temperature dry distillation) and the gasification of coal. Hydrogen production from coal coking is to produce coke from coal at about 1000 °C under the isolation of air. The gas phase by-product produced in the process is coke oven gas, and the hydrogen content accounts for about 55%–60% of the total. Coal gasification uses temperature and pressure to cause the organic matter in the coal to undergo chemical reactions such as coal pyrolysis, gasification and combustion with the gasification agent, thereby converting solid coal into gas. In the process, gaseous products such as CO_2 , CO and H_2 are obtained. On the one hand, directly purifying, separating, and purifying the gas products obtained by coal gasification can obtain a certain purity of hydrogen; on the other hand, the CO in the coal gas can be used to produce hydrogen through the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) [15]. These materials are generally gasified at higher temperatures than 900 °C [16] by applying the following techniques: (1) fixed bed gasification, (2) moving bed gasification, (3) fluidized bed gasification, (4) entrained flow gasification and (5) plasma gasification. Among these gasification processes, the entrained and plasma gasification of coal may generally be carried out at higher temperatures between 1200 °C and 1700 °C, respectively [17–19]. However, the others may require lower operating temperatures than 1200 °C. The water–gas shift reaction is also an important reaction to produce hydrogen from fossil fuels and biomass. It is widely used in the hydrogen production industry and is currently a relatively inexpensive hydrogen production technology. The development of efficient and stable water–gas shift reaction catalysts is of great significance to the production of hydrogen and the application of hydrogen to fuel cells.

2.3. Biological hydrogen production

Biological hydrogen production uses microorganisms to produce hydrogen from biomass (wheat straw, rice straw, *etc.*) through cracking or enzyme-catalyzed reactions. According to statistics, the world's annual biomass production is about 30 billion tons, but only 4% of that is used as energy, and the resource potential for hydrogen production is great. The application of biological processes for hydrogen production was initially described in 19th century [20]. In this process, the two enzymes hydrogenase and nitrogenase play a key role, and microorganisms convert water molecules and organic substrates into hydrogen through the two catalytic activities [21]. Biological hydrogen production can be produced through the following processes, including photocatalytic water splitting, photo-fermentation, and dark-fermentation. In the photocatalytic decomposition of water, both photosynthetic bacteria and algae need to decompose water to produce hydrogen under certain light conditions. Photo-fermentation hydrogen production is carried out by purple non-sulfur bacteria from various carbon sources using light energy. In dark-fermentation, anaerobic bacteria generate hydrogen from organic matter using food or agricultural wastes and wastewater [22].

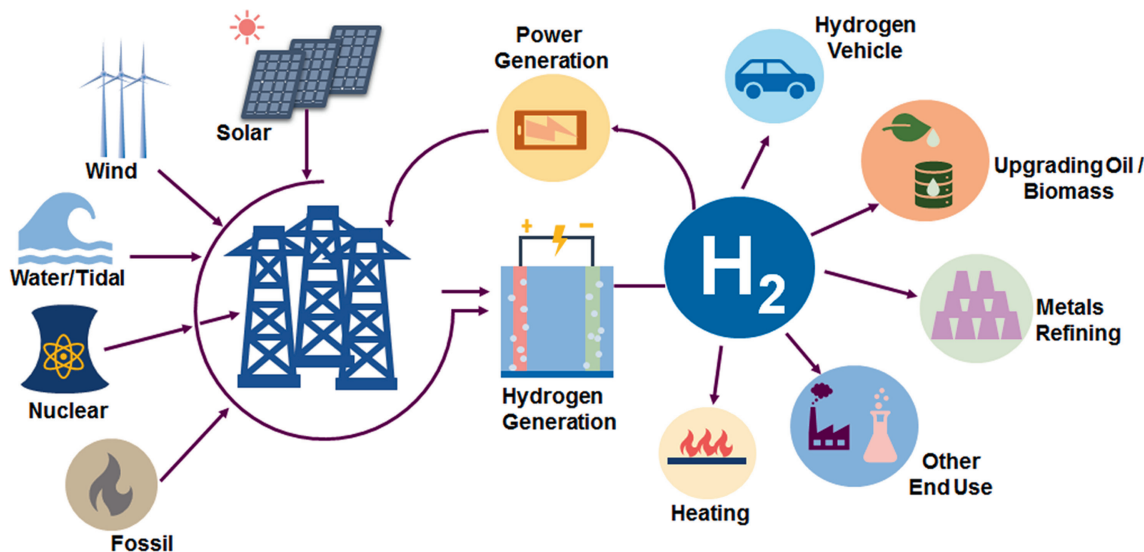


Fig. 1. Schematic illustration of electrochemical water splitting connecting hydrogen energy production and application.

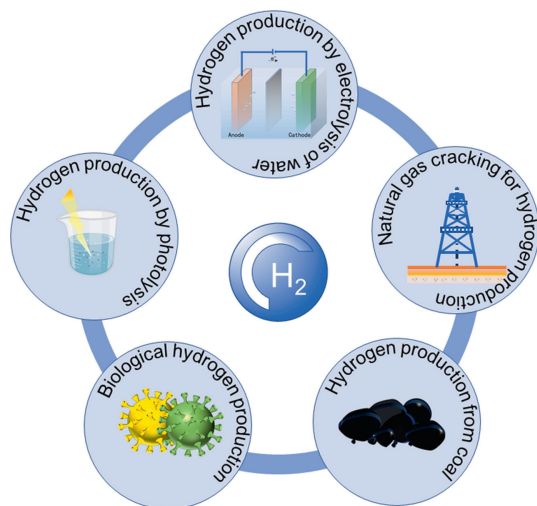


Fig. 2. Typical hydrogen production methods.

2.4. Hydrogen production by photolysis

Using the energy of solar incident light can cause water molecules to undergo oxidation–reduction reactions to generate hydrogen, that is, photocatalytic decomposition to produce hydrogen. More and more researchers are focusing on the research of visible light water splitting catalysts. The development of photocatalysts with visible light response, high catalytic activity, good stability and low cost has always been a research hotspot. When developing new types of visible light catalytic materials, it is important to consider whether the materials can effectively absorb visible light and whether the photocatalytic water splitting meets the thermodynamic requirements. Once the visible light-catalyzed decomposition of water to produce hydrogen has achieved a major breakthrough, the ultimate dream of human energy may be realized.

2.5. Natural gas cracking for hydrogen production

Thermal catalytic cracking of methane technology directly cracks methane into carbon and hydrogen ($CH_4(g) \rightarrow C(s) + H_2(g)$ $\Delta H = 75.6 \text{ kJ} \cdot \text{mol}^{-1}$), which can achieve zero CO_2 emission while

producing hydrogen. There are methods such as thermal catalytic cracking, plasma cracking and molten metal cracking to produce hydrogen from natural gas cracking. The choice of catalyst in the thermal catalytic cracking of methane technology is particularly important. According to its type, it can be divided into carbonaceous catalysts and metal catalysts. Carbon catalysts are resistant to high temperature, sulfur poisoning, and have stable catalytic activity. Among them, activated carbon has the highest activity in thermal catalytic cracking of methane. Among the metal catalysts, $Ni-CeO_2/SiO_2$ can achieve a higher methane conversion rate at a lower synthesis temperature. After experiment, catalytic methane cracking at 580°C , the conversion rate of methane is as high as 90%, and high methane conversion rate is achieved while lowering the reaction temperature [23].

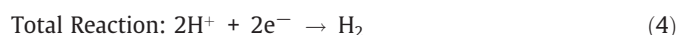
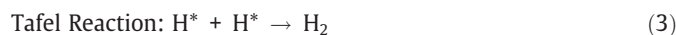
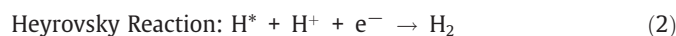
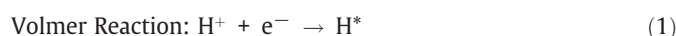
Hydrogen production from coal has serious pollution and other environmental protection issues. It is necessary to comprehensively improve the technical level on the existing basis in order to meet the strategic needs of sustainable development. The system energy consumption and greenhouse gas emissions caused by the natural gas hydrogen production reaction operation process are relatively large. Therefore, it is necessary to improve the reaction conditions and reduce the energy loss of the reaction process to improve the overall environmental protection effect of the system. Hydrogen production by photolysis directly uses primary energy without waste due to energy conversion, and it is theoretically simple and efficient. However, this hydrogen production method is still in the initial stage of research and development. The current difficulty in the technology is the development of catalysts, and there are problems such as low hydrogen production efficiency (less than 4%). Biological hydrogen production raw materials have complex composition, many impurities in the initial product, difficult purification process, and large area, which is not suitable for large-scale production. The process of producing hydrogen by electrolysis of water is relatively simple, can be fully automated, easy to operate, and its hydrogen purity is relatively high (generally up to 99%–99.9%).

3. Reaction Mechanism of Electrocatalytic Water Splitting

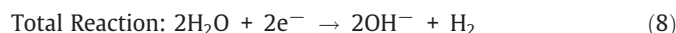
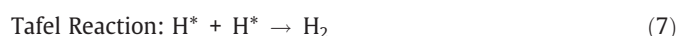
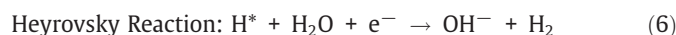
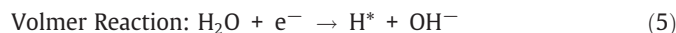
3.1. Hydrogen evolution reaction mechanism

Hydrogen evolution reaction is a key half-reaction of the cathode to produce hydrogen in the total hydrolysis of water. It

involves a two-electron transfer process that reduces protons or water to hydrogen molecules (H_2) when an external potential or electrochemical energy is applied. This HER mechanism is highly dependent on environmental conditions [24]. HER can be carried out in acidic or alkaline solutions, and the electrolyte is generally a certain concentration of potassium hydroxide solution or sulfuric acid solution. The mechanism of acidic HER is shown in Fig. 3(a), while the mechanism of alkaline HER is shown in Fig. 3(b). Generally, the surface of the catalyst in an acidic medium involves two consecutive steps [25]. First, the H atom combines with the active sites on the catalyst to form H^* , and the corresponding process is the Volmer step or the discharge step (Eq. (1)). Next, H^* combines with H and electrons (e^-) to form H_2 molecules. The corresponding process is Heyrovsky step or electrochemical desorption step (Eq. (2)). In addition, the two H^* on the surface of the catalyst can also be combined into H_2 , and the corresponding process is the Tafel step (Eq. (3)). The overall HER is expressed by the formula (Eq. (4)).



Since the alkaline electrolyte does not contain H^+ , the HER reaction begins with the dissociation of H_2O molecules to provide protons [26]. This process involves the Volmer step (Eq. (5)) and Heyrovsky step (Eq. (6)), corresponding to the Tafel step (Eq. (7)) and the same as the acid solution. The entire reaction equation is formula (8).



For HER activity in an alkaline medium, adsorption and hydroxy must be weighed against water separation [27], while maintaining a moderate hydrogen absorption can promote the water dissociation process.

Theoretical analysis shows that HER activity is related to hydrogen adsorption (H_{ad}). The free energy of hydrogen adsorption (ΔG_H) is considered to be the main parameter of hydrogen evolution materials, and a moderate hydrogen binding energy will help

the HER process [28]. At present, Pt is the best HER catalyst with the best hydrogen adsorption energy in both media, and exhibits the highest exchange current density. The activity of HER in alkaline media is generally lower than in acidic media [29]. This is mainly because the reaction is hindered by the slow water dissociation step, which reduces the reaction rate by 2–3 orders of magnitude. With the development of *in-situ* characterization methods, the HER mechanism in alkaline media has been further studied, locally generated hydronium ions are observed in alkaline HER. Qiao *et al* found that a unique H_3O^+ intermediate layer that creates an acidic environment on the catalyst's surface was first identified under high $[OH^-]$ conditions [30,31]. This H_3O^+ intermediate layer was found to be responsible for an anomalous acid-like HER activity of nanostructured electrocatalysts in alkaline electrolytes. More electrochemical analysis and *in situ* Raman characterizations have indicated that these H_3O^+ are generated by high-rate water dissociation process that promotes desorption of H^* on the surface of electrocatalysts.

3.2. Oxygen evolution reaction mechanism

The oxygen evolution reaction requires the transmission of four electrons, including the breaking of the O–H bond and the formation of the O–O bond, therefore, OER is a thermodynamically unfavorable process and requires a high potential to overcome the kinetic energy barrier [32]. So far, OER is still the bottleneck of water splitting. The reaction mechanism of the OER could be changed according to the pH of the electrolyte [33]. The reaction process of OER is different in acidic environment and alkaline environment. The mechanism of acidic OER is shown in Fig. 4(a), while the mechanism of alkaline OER is shown in Fig. 4(b). In acidic electrolyte, two water molecules are oxidized, and an oxygen molecule is produced through four proton-coupled electron transfer steps (Eq. (14)) [34]. Firstly, H_2O is adsorbed on the active site (*), and H_2O is converted into adsorbed hydroxyl (OH^*) by losing a proton and an electron (Eq. (9)). Then, the OH^* continues to lose a proton and an electron, thereby producing adsorbed oxygen (O^*) (Eq. (10)). There are two ways to generate O_2 from O^* . One is to generate O_2 through the direct combination of two O^* , releasing free active site (Eq. (11)). The other way is the interaction between O^* and H_2O [35]. By losing protons and electrons, a hydroperoxide intermediate (OOH^*) is produced (Eq. (12)). After further loss of a proton and an electron, OOH^* release O_2 , and realize the regeneration of the active site (*) (Eq. (13)).

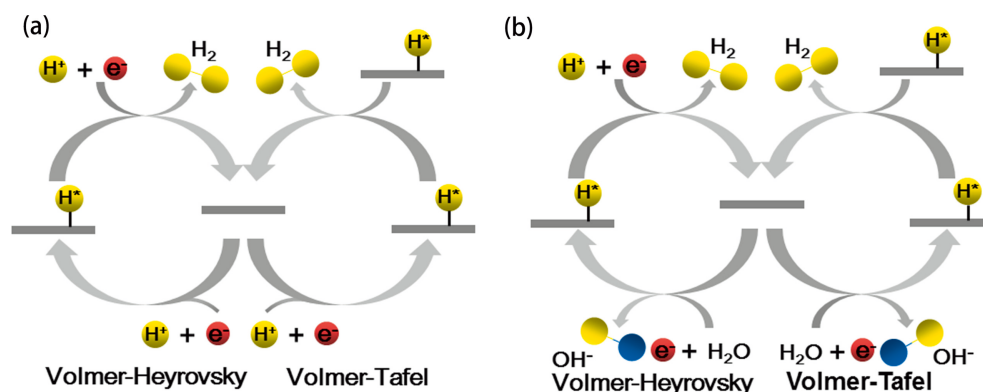


Fig. 3. Schematic diagram of HER reaction mechanism. (a) in acid electrolyte. (b) in alkaline electrolyte.

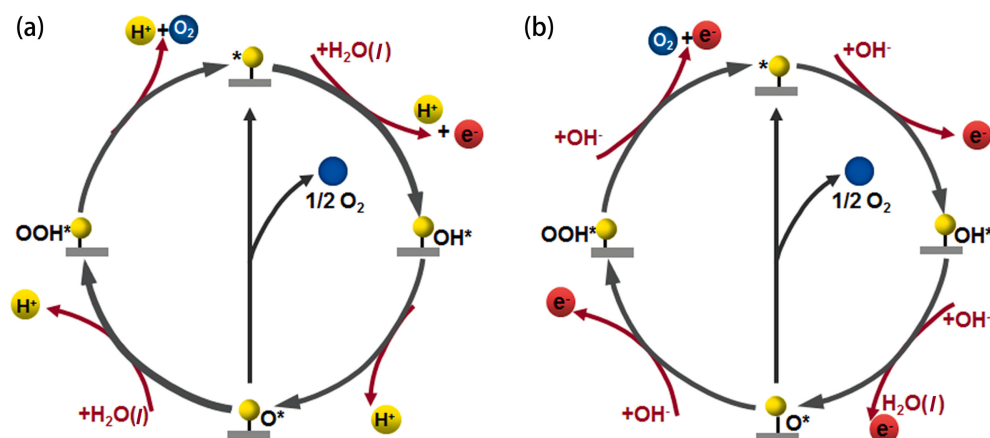
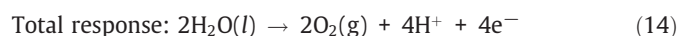
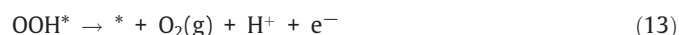
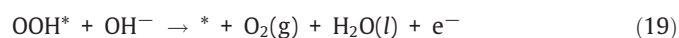
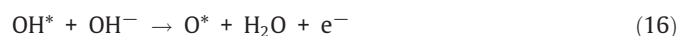


Fig. 4. Schematic diagram of OER reaction mechanism. (a) in acidic environment. (b) in alkaline environment.



where * represents the reactive sites on the surface of the electrocatalyst, (g) represents the gas phase, (l) represents the liquid phase, and OH*, O* and OOH* represent the substances adsorbed on the active sites. Unlike under acidic conditions, in alkaline electrolytes, oxygen molecules are produced by the conversion of the OH⁻ through four electron transfer steps [36]. In addition, the water molecule is also produced (Eq. (20)). Firstly, the OH⁻ is adsorbed on the active site (*) to obtain OH* by releasing an electron (Eq. (15)). Subsequently, the generated OH* interacts with the OH⁻ to obtain O* by losing an electron (Eq. (16)). Similar to acidic electrolytes, there are also two different ways to generate O₂ in alkaline electrolytes. One is that two O* directly combine to produce O₂ and release free active site (*) (Eq. (17)). The other way is to nucleophilic attack on O* by OH⁻ to generate intermediate (OOH*) (Eq. (18)). The further proton-coupled electron transfer of OOH* leads to the production of O₂ and at the same time realizes the active site (*) The regeneration (Eq. (19)).



where the symbol is the same as Eqs. (9)–(14).

Generally, whether under acidic conditions or alkaline conditions, each basic step has a specific free energy as the corresponding intermediate combination [37]. The step with the largest free energy difference becomes the rate limiting step (RDS), and determines the theoretical point of the reaction ($\eta = G/\text{e} - 1.23 \text{ V}$).

The *in situ* and operando characterization techniques has been well developed for revealing the actual active sites and capturing dynamic structural evolution of surficial active phase. For the

OER reaction catalyzed by transition metal-based materials, the actual active sites for OER are normally recognized as the metal oxyhydroxides. Chala *et al* intentionally introduce guest anions (Br⁻ and Cl⁻) into NiMn-layered double hydroxides (LDHs), which exhibit the superior OER performance (onset overpotential of 0.17 V and overpotential of 0.24 V at 10 mA·cm⁻²) [38]. The fundamental mechanistic insights and active phases during the OER process are characterized by *in situ* X-ray diffraction, *in situ* Raman spectroscopy and *in situ* X-ray absorption spectroscopy, revealing that the Ni site constitutes the OER activity active phase is the actual dynamically generated NiOOH. They also prove that Ni sites undergo a reversible oxidation state under the working conditions to create active NiOOH species which catalyze the water to generate oxygen.

4. Research Progress of Catalysts for Electrocatalytic Water Splitting

4.1. Research progress of HER catalysts

As an efficient and environmentally friendly process, water splitting is expected to be used for sustainable hydrogen production. Water splitting is related to the reaction of two half-cells: HER and OER. Both of these reactions require highly efficient electrocatalysts, such as platinum group metals (PGMs), 3d transition metals, and 3d transition metal-based materials, such as carbides [39], nitrides [40], phosphides [41], sulfides [42], and hydroxide [43].

4.1.1. Noble-metal based alloy

Although the conversion of water to hydrogen in acidic and alkaline media has been extensively studied, the technology still has many challenges, especially the slow kinetics in alkaline electrolytes. Among various electrocatalysts, platinum group metals, such as Pt, Ir and their alloys, have been widely used as effective electrocatalysts for HER due to their low onset potential and low Tafel slope. However, high cost, scarcity and low toxicity resistance have largely hindered their wide application.

One strategy to increase the HER activity of platinum group metal-based catalysts is to increase the intrinsic activity of each site. Lv *et al.* synthesized an ultra-thin, curved PdIr alloy nanosheet with a thickness of about five atoms to achieve superior electrocatalytic hydrogen evolution performance [44]. PdIr alloy nanosheets show a very high electrochemically active surface area (ECSA, (127.5 ± 10.8) m²·(g Pd+Ir)⁻¹) and a unique surface electronic structure, resulting in the HER showing excellent electrocatalytic

performance. When it is $10 \text{ mA}\cdot\text{cm}^{-2}$, only 34 mV is required. DFT calculations confirm that the excellent HER properties are derived from the surface strain effect of the optimized PdIr nanosheets, which endows the PdIr nanosheets in the micro-active area with higher electrical activity. The excellent modulation ability of the surface electronic structure. Zhu *et al.* synthesized hollow IrAg nanotubes (Ir_6Ag_9 NTs) with enriched Ir shells by selective etching [45]. Ir_6Ag_9 NTs showed low HER overpotential (in $0.5 \text{ mol}\cdot\text{L}^{-1}$ and $0.05 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 , only 20 mV and 34 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$). More importantly, when Ir_6Ag_9 NTs/C is used as a dual-function electrocatalyst, it only needs to apply a voltage of 1.55 V at $10 \text{ mA}\cdot\text{cm}^{-2}$ in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 and has excellent durability. IrAg nanotube catalyst enhanced HER performance is attributed to their large surface area and abundant oxidized Ir species on the surface of the nanotubes.

Among them, alloying platinum group metals with transition metals not only reduces the loading of platinum group metals, but also improves electrochemical performance on the atomic scale. Our group designed and synthesized a series of ultra-small hollow ternary alloy nanostructures, including hollow PtNiCu nanoparticles, hollow PtCoCu nanoparticles and hollow CuNiCo nanoparticles [46]. Used for the research of electrocatalytic hydrogen evolution performance. The results of performance evaluation for HER are shown in Fig. 5 (a) – (c). Alloying platinum group metals with transition metals not only reduces the loading of platinum group metals, but also improves electrochemical performance on the atomic scale, and at the same time can save costs, which is a cost-effective strategy. In particular, the electrocatalytic HER activity and stability of ultra-small hollow PtNiCu nanoparticles with low Pt (10%) content in alkaline solutions are much better than commercial Pt/C. Hollow PtNiCu nanoparticles have an overpotential of 28 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ and a mass activity of $4.54 \text{ A}\cdot(\text{mg Pt})^{-1}$ at -70 mV , which is 5.62 times that of commercial Pt/C. Through the analysis of the bonding and anti-bonding orbitals, DFT calculations show that the bonding strength between different metals and hydrogen intermediates (H^*) is $\text{Pt} > \text{Co} > \text{Ni} > \text{Cu}$. The excellent HER

performance of hollow PtNiCu nanoparticles is derived from the moderate synergistic interaction of the three metals and H^* . Liu *et al.* prepared a RuNi alloy nanostructure composed of multilayer nanosheets [47], achieving a low overpotential of 15 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ and a Tafel slope of $28 \text{ mV}\cdot\text{dec}^{-1}$ at $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH. Surpasses commercial Pt/C and Ru/C catalysts. The reason for the enhancement of HER performance comes from the large electrochemically active surface area produced by the two-dimensional RuNi alloy nanostructure and the electronic effect of nickel alloying. Lv *et al.* reported a one-pot synthesis of IrNi polycrystalline nanocrystals with a 3D flower-like structure as a highly efficient bifunctional electrocatalyst for HER and OER in acidic electrolytes [48]. When Ir is alloyed with Ni, the hydrogen bonding energy on Ir is greatly weakened. The prepared IrNi catalyst shows the best HER activity, with a low Tafel slope of $29.7 \text{ mV}\cdot\text{dec}^{-1}$ and an overpotential of 25 mV at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ in acid, which is higher than the commercial Ir/C ($29.7 \text{ mV}\cdot\text{dec}^{-1}$, 44 mV) is much better. In addition, when IrNi NFs is used as a dual-function electrocatalyst for the cathode and anode of the water splitting device, a low battery voltage of 1.60 V can be achieved at $10 \text{ mA}\cdot\text{cm}^{-2}$ in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 . Cheng *et al.* synthesized defect-rich RhCu nanotubes through a wet chemical strategy and used it as a highly active electrocatalyst for overall water splitting under all pH conditions [49]. In acidic, neutral and alkaline media, to achieve a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, the overpotentials of RhCu NTs are 12 mV, 57 mV and 8 mV, which are better than Pt/C catalysts. Experiments and DFT calculations show that the unique hollow structure can expose more active sites on the inner and outer walls of the nanotubes, promote electron transfer, and make full use of the active centers.

4.1.2. Non-precious alloy materials

Nickel-based materials are replacing platinum-based materials because of their low cost and excellent HER catalytic performance. Tian *et al.* used a solution consisting of $0.2 \text{ mol}\cdot\text{L}^{-1}$ NiSO_4 , $0.3 \text{ mol}\cdot\text{L}^{-1}$ $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, and $0.02 \text{ mol}\cdot\text{L}^{-1}$ Na_2MoO_4 to

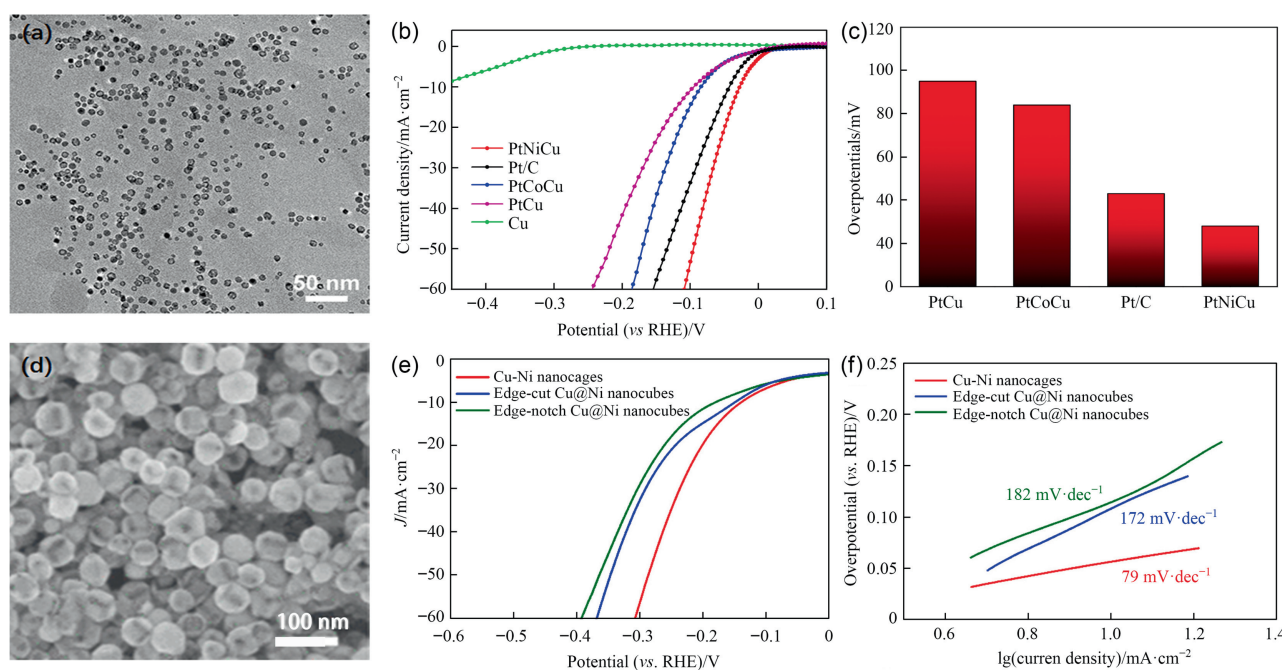


Fig. 5. (a) Transmission electron microscopy (TEM) image of hollow PtNiCu nanoparticles. (b) The HER polarization curves of hollow PtNiCu nanoparticles, commercial Pt/C, hollow PtCoCu nanoparticles, hollow PtCu nanoparticles and Cu nanoparticles in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH aqueous solution at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. (c) Overpotentials at a current density of $10.0 \text{ mA}\cdot\text{cm}^{-2}$ of hollow PtNiCu nanoparticles, commercial Pt/C, hollow PtCoCu nanoparticles and hollow PtCu nanoparticles. (d) Scanning electron microscopy (SEM) image of Cu–Ni nanocages. (e) Polarization curves of edge-cut Cu@Ni nanocubes, edge-notched Cu@Ni nanocubes, and Cu–Ni nanocages. (f) Tafel plots of edge-cut Cu@Ni nanocubes, edge-notched Cu@Ni nanocubes, and Cu–Ni nanocage.

electrodeposit NiMo alloy hollow nanorod array on Ti mesh (NiMo HNRs/TiM) [50]. In the evaluation of HER activity and stability in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte, NiMo alloy hollow nanorods materials showed a low onset potential of 60 mV (overpotential of 92 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$) and Tafel slope of $76 \text{ mV}\cdot\text{dec}^{-1}$, and maintained catalytic activity for at least 15 h. In addition to NiMo alloy, Ni can also form alloys with other metals to improve catalytic activity. Hong *et al.* Synthesized NiW alloy materials on a Cu foil substrate by using a co-electrodeposition method [51]. By changing the ratio of Ni^{2+} and W^{6+} in the electrolyte, Synthesized NiW alloys with different element content ratios. Among these, $\text{Ni}_{59}\text{W}_{41}$ materials exhibited the better activity of overpotential of 122 mV in $6.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte. This result showed that alloying effect of Ni and Mo caused the surface area to become larger, and enlarged hydrogen active sites led to excellent HER activity. Zhang *et al.* synthesized composite porous foam NiZn alloy by a combination of electrolytic deposition, heat treatment and hydrochloric acid corrosion [52]. Compared with nickel foam, the NiZn alloy with porous structure exhibited better HER catalytic activity in 30% (mass fraction) KOH (overpotential of 306 mV at $200 \text{ mA}\cdot\text{dm}^{-2}$).

In addition to nickel-based materials, copper-based materials are widely used in electrochemical catalysis and other fields due to their low price and high performance. Our group reported CuNi materials with different structures fabricated by the solvothermal one-pot method (solution containing $\text{Cu}(\text{acac})_2$, $\text{Ni}(\text{acac})_2$ and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) [53]. They controlled the synthesis temperature, time and the amount of solvent to fabricate unique edge-cut Cu@Ni nanocubes, edge-notched Cu@Ni nanocubes, and mesoporous Cu-Ni nanocages. The results of performance evaluation for HER are shown in Fig. 5 (d)–(f). The synergistic effect of copper and nickel and the hollow structure bring greater surface area and active sites, giving rise to enhanced intrinsic activity. As a result, Mesoporous Cu-Ni nanocage with an average size of 62 nm exhibited the best geometric activity with an over-potential of approximately 140 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ and Tafel slope of $79 \text{ mV}\cdot\text{dec}^{-1}$. The overpotential at $10 \text{ mA}\cdot\text{cm}^{-2}$ of CuNi was in the order of Mesoporous Cu-Ni nanocage (140 mV) < edge-notched Cu@Ni nanocubes (155 mV) < edge-cut Cu@Ni nanocubes (183 mV), Tafel slope of CuNi was in the order of Mesoporous Cu-Ni nanocage ($79 \text{ mV}\cdot\text{dec}^{-1}$) < edge-cut Cu@Ni nanocubes ($172 \text{ mV}\cdot\text{dec}^{-1}$) < edge-notched Cu@Ni nanocubes ($182 \text{ mV}\cdot\text{dec}^{-1}$). In the subsequent stability test of 2000 cycles, Activity of Mesoporous Cu-Ni nanocage was not significantly reduced, and maintained catalytic activity for about 8 h. In addition to binary alloys, SoumenSaha *et al.* synthesized the ternary CuFeNi materials using microemulsion [54] three alloy materials: CuFeNi, CuFe_2Ni and CuFeNi_2 were synthesized by controlling the concentration of Cu, Ni, Fe in the microemulsion. In the evaluation of HER activity and stability in $6.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte, CuFeNi exhibited better HER catalytic performance with an overpotential of 545 mV at a high value of current density ($228 \text{ mA}\cdot\text{cm}^{-2}$).

Co-based materials have attracted the attention because of their corrosion resistance and excellent electrical conductivity. CoMo alloys are more researched in cobalt-based alloy materials [55]. Fan *et al.* measured the HER activity in the presence of 30 w/o KOH after fabricating CoMo by the electrodeposition method [56]. The CoMo catalyst showed about a low overpotential of 182 mV at $100 \text{ mA}\cdot\text{cm}^{-2}$ and Tafel slope of $116 \text{ mV}\cdot\text{dec}^{-1}$. Santos *et al.* synthesized CoMo and CoMoCu by using a rapid electrodeposition process [57]. In the evaluation of HER activity in $6.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte. The CoMo catalyst showed catalytic activity (overpotential of 156 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$, overpotential of 247 mV at $100 \text{ mA}\cdot\text{cm}^{-2}$ and Tafel slope of $83 \text{ mV}\cdot\text{dec}^{-1}$). Cu was added during the electrodeposition of CoMo, and the co-deposition of Cu increased the surface area which resulted in

enhanced catalytic activity of the ternary CoMoCu alloys containing 23% of Cu (overpotential of 119 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$, overpotential of 200 mV at $100 \text{ mA}\cdot\text{cm}^{-2}$ and Tafel slope of $82 \text{ mV}\cdot\text{dec}^{-1}$). Similarly, it was also due to addition of Cu leading to better catalytic performance. Kim *et al.* changed the crystal structure from hexagonal close-packed (hcp) to face-centered cubic (fcc) by controlling the content of Cu in the CoCu alloys [58]. In the evaluation of HER activity and stability in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 electrolyte, $\text{Co}_{59}\text{Cu}_{41}$ exhibited high catalytic activity (overpotential of 342 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ and Tafel slope of $103 \text{ mV}\cdot\text{dec}^{-1}$) among the CoCu alloy catalysts, maintained excellent catalytic activity in 12 h.

Due to their abundance and low cost, Fe alloys are also very promising. Addition of Mo promoted the formation of fine cracks on the surface of the alloy, which was the reason for the enhanced catalytic activity. Safizadeh *et al.* used citrate-based electrolyte to electrodeposit FeMo alloy, which exhibited a low onset overpotential (395 mV at $250 \text{ mA}\cdot\text{cm}^{-2}$) and Tafel slope ($151 \text{ mV}\cdot\text{dec}^{-1}$) of the HER [59]. Forming an amorphous structure is also one of the methods to enhance the activity of Fe-based materials. Chu *et al.* performed high-pressure torsion (HPT) treatment on the melt-spun amorphous $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$ alloy to improve the performance of the alkaline HER. In the subsequent work [60], the samples synthesized by changing different HPT turns (including 1, 2, 5, 10) were labeled HPT-1 N, HPT-2 N, HPT-5 N, HPT-10 N, respectively. The HPT treatment induced some structural defects of the amorphous alloy, which enhanced the catalytic performance. The HPT-5 N sample exhibited the best catalytic performance, with a low onset overpotential (174 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$) and Tafel slope ($199 \text{ mV}\cdot\text{dec}^{-1}$) in $1.0 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte. Moreover, it was established that the HPT-treated amorphous alloy Maintained good performance after 1000 cycles.

4.1.3. Others

Currently, the most advanced HER electrocatalyst is Pt. However, scarcity and high cost limit its application [61]. Therefore, it is very hopeful to develop an earth-rich and efficient HER electrocatalyst. Recently, the binding of transition metals and non-metallic elements (N, O, S, C, P) has become a promising choice for replacing precious metals. Transition metal sulfides (TMSs) has received great attention in electrochemical applications due to its good compatibility with solution phase synthesis technology [62]. Due to the low cost and the preparation method, the metal sulfide is expected to be the most common catalyst candidate [63]. In addition, molybdenum sulfide (MoS_2) is one of the most old and oldest sulfide candidates [64]. Norskoff *et al.* showed that the free energy of atomic hydrogen bonds on the edge of molybdenum disulfide is close to that of platinum [65]. This discovery indicates that molybdenum disulfide is a promising HER electrocatalyst. When molybdenum disulfide was first used as a catalyst, it was found that the electrochemically assisted HER had a linear relationship with the number of edge positions of MoS_2 , which led to further indepth research. The electrocatalytic HER activity linearly depends on the number of edge sites of the molybdenum disulfide catalyst. Inspired by this understanding, various strategies have been proposed to expose active sites to increase HER activity, for example, Li *et al.* synthesized molybdenum disulfide nanoparticles by selective solvothermal on a reduced graphene oxide (RGO) sheet suspended in a solution [66]. The obtained molybdenum disulfide/RGO hybrid material has nano-scale several layers of molybdenum disulfide structure, and a large number of exposed edges are stacked on graphene. Compared with other molybdenum disulfide catalysts, the molybdenum disulfide/RGO hybrid material is undergoing hydrogen evolution. The reaction showed excellent electrocatalytic activity. The Tafel slope of the molybdenum disulfide catalyst measured in HER for the first time is $41 \text{ mV}\cdot\text{dec}^{-1}$; this far exceeds the activity of the

previous molybdenum disulfide catalyst due to the abundant catalytic activity on the molybdenum disulfide nanoparticles. Edge sites and excellent electrical coupling with the underlying graphene network. Geng *et al.* developed a vertically arranged molybdenum disulfide nanosheet array on a graphene-mediated three-dimensional nickel network, and synthesized a powerful and highly active alkaline solution HER system [67]. Several layers of MoS₂ nanosheets on the three-dimensional graphene/nickel structure can expose their edge positions to the maximum on the atomic scale and exhibit excellent catalytic activity for hydrogen production. Transition metal nitrides (TMNs) are often referred to as interstitial alloys, in which nitrogen atoms are inserted into the interstices of the transition metal lattice [68]. The density of states in the d-band of the corresponding metal is adjusted by nitrogen atoms, and therefore, smaller defects in the d-band occupancy are realized. Therefore, these transition metal nitrides can exhibit electron-donating ability equivalent to that of noble metals [69]. Due to its high electrochemical stability, it is a potential substitute for active metal electrocatalysts. Showed superior physical properties, including their high melting point, it has become an interesting active material for electrodes, and also exhibits high electrical conductivity and chemical stability. These aspects make metal nitrides become very attractive catalysts. Tong *et al.* synthesized Ni nanosheets doped with nitrogen and vanadium on self-supporting conductive carbon paper [70]. Compared with Ni/CP, NV Ni/CP showed better HER performance with 95 mV (10 mA·cm⁻²) low overpotential, small Tafel slope (140 mV·dec⁻¹) and excellent long-term stability. Its excellent HER performance is attributed to the increase in active sites and the increase in conductivity. To achieve facile and large-scale synthesis of a family of 2D layered TMNs (MoN_{1.2}, WN_{1.5}, and Mo_{0.7}W_{0.3}N_{1.2}) Qiao *et al.* employed alkali molten salts as catalysts under atmospheric pressure [71]. *Ex-situ* experiments reveal that the molten salt can lower the formation energy of 2D layered TMNs by assuring a liquid–gas synthesis and forming a TMN-salt-TMN superstructure as an intermediate. Since TMNs have excellent electron conductivity and noble metal-like electronic structure, 2D TMNs exhibit good catalytic performance in HER [72,73]. At the current density of 10 mA·cm⁻², the 2D Mo_{0.7}W_{0.3}N_{1.2} exhibits the lowest overpotential of 129 mV in acidic electrolyte and 122 mV in alkaline electrolyte, which are significantly lower than those for MoN_{1.2} and WN_{1.5}, individually. This activity enhancement can be attributed to the optimized W sites induced by the doping process. Importantly, the unique metal-nitrogen bonds can guarantee a noble-metal-like electronic structure of transition-metal nitrides.

Transition metal oxides (TMOs) are made of oxygen atoms bounded with a central TM forming different lattice or crystal structures. Molybdenum diselenide (MoSe₂) is widely considered to be one of the most promising hydrogenation reaction catalysts. However, the lack of active sites and the difference in conductivity of molybdenum selenide severely limit its HER performance. Jian *et al.* by introduced a layer of molybdenum dioxide on molybdenum foil, a molybdenum dioxide/molybdenum dioxide hybrid nanofila sheet in the surface of molybdenum foil [74]. Metal MoO₂ can increase the charge transport efficiency of MoSe₂/MoO₂, thereby increasing the overall HER performance. Zhao *et al.* synthesized an amorphous lithium cobalt oxide nanowire array (CoMoO₄NWA/Ti) on a titanium grid by a simple two-step hydrothermal method [75]. As a three-dimensional hydrogen evolution electrode, CoMoO₄NWA/Ti shows excellent catalytic activity in 1.0 mol·L⁻¹ potassium hydroxide, and only needs 81 and 243 mV overpotentials to reach currents of 10 and 100 mA·h·cm⁻², respectively. It is worth noting that it also has long-term electrochemical durability. This research not only provides an attractive rare earth

catalyst material for hydrogen production by electrolysis under alkaline conditions, but also provides a new direction for the development of metal molybdate nanoarray applications.

Among carbon nanomaterials, graphene, carbon fiber, carbon nanotubes and other carbon nanomaterials have the advantages of high conductivity, easy functionalization, and corrosion resistance, *etc.*, and are often used as structural carriers to disperse catalysts, and at the same time to increase their electron transport capacity. For example, Li *et al.* synthesized graphene-supported MoS₂ particles by solvothermal method by suspending go flakes in solution [66]. The introduction of graphene effectively inhibited agglomeration of MoS₂ particles, making MoS₂ have more exposed edges. Thus, the electrocatalytic activity of HER was improved. The as small as Tafel slope is 41 mV·dec⁻¹. The HER electrocatalytic activity of MoS₂ synthesized by this method is much higher than that synthesized by annealing. This is due to the good coupling between MoS₂ and graphene. In addition, Liu *et al.* also obtained good electrocatalytic performance of HER by modifying carbon nanotubes with CoP [76].

In addition, the introduction of transition metals can be used to regulate the electronic structure, regulate the electrocatalytic activity and optimize the electrocatalytic performance of nano-carbon materials. Transition metal carbides also exhibit properties and activities similar to platinum due to the special electronic structure properties of the d-band center movement, and have been widely studied and applied in the field of traditional catalysis. Tungsten carbide (WC) is one of the more promising alternative materials. HER electrocatalytic activity is comparable to that of platinum. Schroder and colleagues compared 18 different transition metal compounds (carbides, nitride, sulfides, silicides, and borides) [77], and they proved that WC can provide the best electrocatalytic performance of HER, and they proposed that WC should not be an independent electrocatalyst, but should be used as a substrate to support Pt. Esposito *et al.* reduced the cost by loading a single layer of platinum on tungsten carbide, it showed activity comparable to that of bulk platinum [78]. Moreover, they demonstrated that the surface electrons and chemical properties of a single layer of platinum loaded on the tungsten carbide were very similar to those of a lump of platinum, thus demonstrating the possibility that all but the outer layer of platinum on the catalyst could be replaced by tungsten carbide. Tungsten carbide is a good base for supporting platinum because of its excellent electrochemical stability. However, the mechanism of the coordination between platinum and tungsten has not yet been studied, which is a problem that needs more researchers to explore.

Metal phosphating is a kind of compound formed by metal and phosphorus. It has good electron conduction property and chemical stability. Therefore, phosphide is also widely used in HER. In 2005, Liu and Rodriguez *et al.* calculated by density functional theory (DFT) that Ni₂P has a crystal structure and electronic structure similar to that of NiFe hydrogenase [79], envisaging Ni₂P to be a highly active catalyst toward the HER. This theory has greatly promoted the research of metal phosphides as electrocatalyst. For example, Tian *et al.* synthesized FeP nanoparticle films on carbon cloth at low temperature [80]. The FeP/CC catalyst has high catalytic activity similar to that of commercially produced Pt/C, and it has good durability in strong acid medium. Because Fe and carbon cloth are relatively cheap, this catalyst can be applied to the electrolysis of water to produce hydrogen on a large scale. Yang *et al.* synthesized Urchin-like CoP nanocrystals by a simple method [81]. When it was applied to HER reaction, the catalyst showed excellent catalytic activity of HER. When the current density was 100 mA·cm⁻², only an overpotential of 180 mV was required. The electrocatalytic activity of metal phosphating can be further

improved by doping other elements appropriately. Zhang *et al.* increased the electron density of Ni and Co by replacing the O atoms in NiCoP with less electronegative N elements [82]. The increase of the electron cloud density of Ni and Co elements promoted the charge transfer of the catalyst, thus improving its HER catalytic activity. Therefore, compared with NiCoP, N-NiCoP has an overpotential of 149 mV in acidic media and 162.5 mV in alkaline media. N doping provides a promising way to improve HER electrocatalytic performance of NiCoP. However, metal phosphide has a good catalytic activity of HER, but there is still a gap between it and the actual application, because the surface of metal phosphide catalyst is prone to form negatively charged P site and passivation layer, thus separating the catalytic reaction. Therefore, the technology of applying metal phosphide to HER still needs further research.

4.2. Research progress of OER catalysts

Electrochemical water splitting is a highly efficient and sustainable way to produce hydrogen, and is considered an effective method for the production, storage and use of renewable energy in the future. Electrolytic water consists of two half reactions, namely the cathode HER and the anode OER [83,84]. Among them, the process of OER reaction needs to transfer $4e^-$, which is a very slow process in kinetics [85]. To drive the reaction, a very high overvoltage needs to be applied. Therefore, in the OER reaction, it is often necessary to introduce an effective catalyst to reduce the overpotential, thereby improving the energy conversion efficiency. At present, the most efficient OER catalysts are precious metal catalysts, such as iridium and ruthenium oxides (IrO_2 and RuO_2 , *etc.*), but these precious metals are limited by their scarcity and high cost and cannot be applied on a large scale [86]. Therefore, in recent decades, a lot of research has focused on finding low-cost, high-stability non-noble metal materials, such as layered double hydroxides (LDHs), metal oxide and non-metal oxide, hierarchical porous activated carbon (HPAC), graphene nanoribbons (GNR), $\text{C}_6\text{H}_4\text{NO}_2/\text{g-C}_3\text{N}_4$ complexes, metal chalcogenides, metal organic frameworks, *etc* [87,88].

4.2.1. Layered double hydroxides (LDHs)

LDHs is a kind of metal hydroxide composed of two or more metal elements. The structure is composed of the main layer and the interlayer anions and water molecules overlapping each other. Because the composition (type and proportion of metal ions on the laminate, the type of anion, *etc.*) is easy to adjust, the structure (number of layers, layer spacing, *etc.*) is easy to cut, and it is easy to combine with other materials to achieve functionalization and other advantages. LDHs show good application prospects in energy conversion and electrochemical energy storage such as supercapacitors, secondary batteries and electrocatalysis. However, the disadvantages of LDHs materials as catalysts: dense packing of the layered structure of LDHs materials; insufficient conductivity; electrons are not conducive to transport between products, *etc.* which will reduce the activity of LDHs-based electrocatalysts, and thus cannot make full use of its active area. In order to optimize the LDHs-based OER catalyst, researchers have done a lot of work to improve the overall performance of the catalyst.

Our group designed a new hybrid nanostructure using *in-situ* co-precipitation method. They directly grew two-dimensional cerium-doped NiFe layered double hydroxide nanosheets on the surface of two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXene to form NiFeCe-LDH/Mxene [89]. Through the synergistic effect of Ce doping and MXene coupling, the prepared NiFeCe-LDH/MXene hybrid material presents a hierarchical nanoporous structure, high conductivity and strong interface connection. Fig. 6 shows the synthesis process of the catalyst and its excellent catalytic activity for OER. In an alka-

line medium, when the current density is $10 \text{ mA}\cdot\text{cm}^{-2}$, the initial overpotential is 197 mV, and the overpotential is 260 mV, which is much lower than its pure LDH counterpart and IrO_2 catalyst. In addition, the catalyst also exhibits fast reaction kinetics and remarkable stability and durability.

In order to improve the OER activity of the catalyst and at the same time overcome the shortcomings of poor stability of Co-LDH, our group designed the interface engineering heterojunction between ZIF-67 and LDH [90]. The interface is composed of the oxygen (O) of Co-LDH and the nitrogen (N) of the 2-methylimidazole ligand in ZIF-67, which regulate the local electronic structure of the catalytic active center. Density functional theory calculations show that the interfacial interaction can enhance the strength of the Co-O_{OUT} bond in Co-LDH, which makes the H-O_{OUT} bond more likely to break, and leads to a low change in the free energy of the potential determining step at the heterogeneous interface during the OER process. Fig. 7 shows the synthesis process of the catalyst and that Co-LDH@MOF exhibits superior OER activity at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, with a low overpotential of 187 mV and an electrochemical stability over 50 h.

Lu *et al.* found that if the Co nanoparticles can be uniformly distributed inside and on the surface of carbon nanofibers (CNFs), the surface roughness of CNFs can be increased, which is beneficial to the growth of NiFe LDH nanosheets [91]. Therefore, they designed a simple electrospinning, carbonization and electrodeposition process, using cobalt carbon nanofibers to support NiFe LDH nanosheets to form a core-shell structure (Co-C@NiFe LDH). The core-shell structure of the catalyst Co-C@NiFe LDH constructs a three-dimensional network, which has the advantages of large specific surface area, abundant exposed active sites and full contact with electrolyte. Moreover, the efficient electron transfer between Co nanoparticles and NiFe LDH nanosheets and the high conductivity of CNFs can further improve OER efficiency. Therefore, the OER performance of the Co-C@NiFe LDH nanofiber catalyst with a three-dimensional core-shell structure is outstanding. In $1 \text{ mol}\cdot\text{L}^{-1}$ KOH solution, when the current density is $10 \text{ mA}\cdot\text{cm}^{-2}$, the overpotential is 249 mV, the Tafel slope is only $57.9 \text{ mV}\cdot\text{dec}^{-1}$. And the durability is very good, after the 190 h stability test, there is almost no obvious degradation. Liao *et al.* designed a sulfate ion (SO_4^{2-}) modulation strategy, using SO_4^{2-} to modify NiFe (oxy) hydroxide to prepare a catalyst. The specific method is to dissolve thiourea in the electrolyte, and then perform expandable anodic oxidation of the NiFe foam to obtain SO_4^{2-} modified NiFe (oxygen) hydrogen oxidation catalyst (called NF-SO.15) [92]. The catalyst can accelerate the electrochemical reconstruction of the pre-catalyst and stabilize the reaction intermediate OOH^* , thereby increasing the OER activity of NiFe (oxy) hydroxide. Through experimental and theoretical studies, they found that SO_4^{2-} leaching is beneficial to electrochemical reconstitution under OER conditions to form active NiFeOOH. At the same time, the residual SO_4^{2-} adsorbed on the surface can stabilize the OOH^* intermediate, thereby improving OER performance, and realizing the dual effect of SO_4^{2-} on the improvement of OER performance. In $1 \text{ mol}\cdot\text{L}^{-1}$ KOH solution, when the current density is $50 \text{ mA}\cdot\text{cm}^{-2}$, NF-SO.15 can achieve an ultra-low potential of 234 mV, and the Tafel slope is only $27.7 \text{ mV}\cdot\text{dec}^{-1}$. And NF-SO.15 also exhibits excellent durability over 100 h at a high current density of $100 \text{ mA}\cdot\text{cm}^{-2}$.

In general, LDH-based OER electrocatalyst materials have high energy conversion efficiency and environmental friendliness, and have received extensive attention from researchers. It provides an opportunity to find efficient substitutes for precious metal catalysts and realize efficient and economical energy conversion.

4.2.2. Metal oxide and non-metal oxide

Recently, various non-noble metal oxides have been developed as next-generation OER catalysts, which have high and stable OER

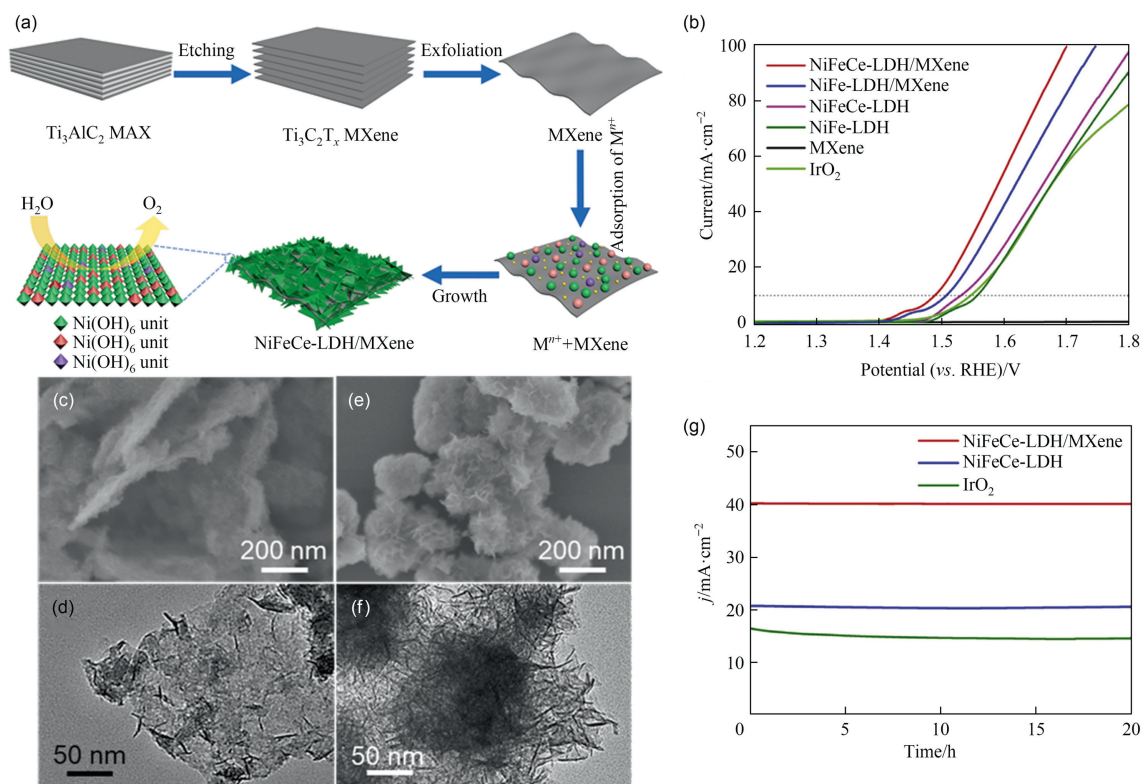


Fig. 6. (a) Schematic illustration of the synthetic procedure of NiFeCe-LDH/MXene hybrid. (b) Polarization curves of NiFeCe-LDH/MXene, NiFe-LDH/MXene, NiFeCe-LDH, NiFe-LDH, pristine MXene and IrO_2 . (c, d) SEM and TEM images of NiFeCe-LDH/MXene hybrid. (e, f) SEM and TEM images of pure NiFeCe-LDH. (g) Chronoamperometry response of NiFeCe-LDH/MXene, NiFeCe-LDH, and IrO_2 catalysts at a constant potential of 1.574 V vs. RHE over 20 h.

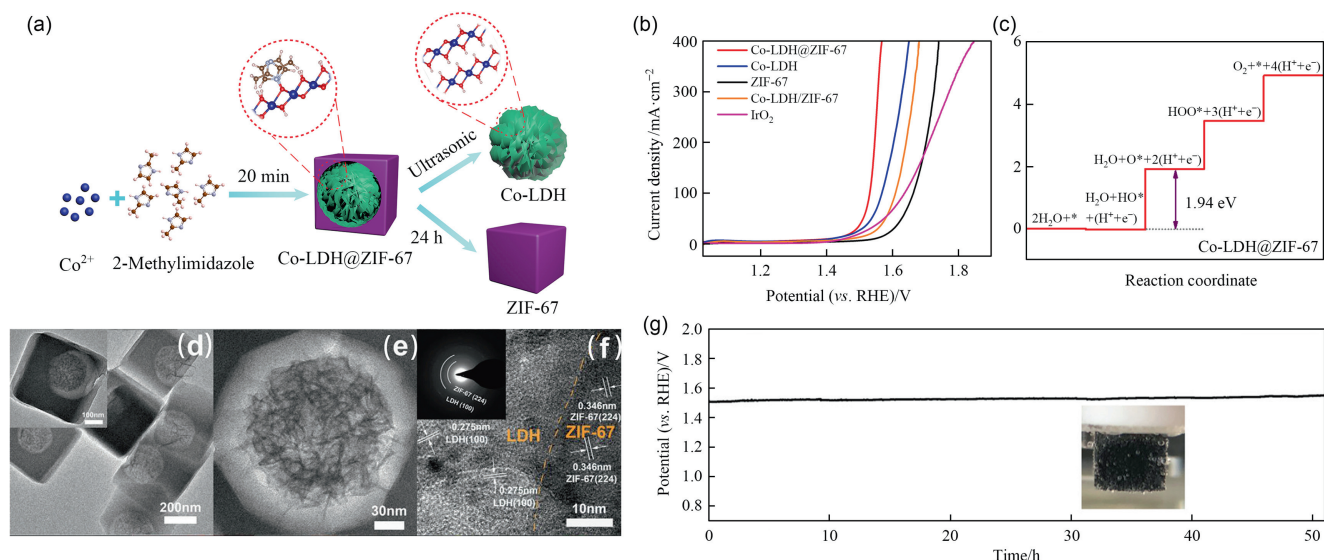


Fig. 7. (a) Schematic illustration of growth pathway to prepare Co-LDH@ZIF-67, Co-LDH, and ZIF-67. (b) Electrochemical properties of Co-LDH@ZIF-67, Co-LDH, ZIF-67, Co-LDH/ZIF-67, and IrO_2 for OER. (c) The Gibbs free energy diagram for OER on Co-LDH@ZIF-67. (d, e) TEM image of Co-LDH@ZIF-67. (f) HRTEM image of Co-LDH@ZIF-67. (g) Long-term stability test of Co-LDH@ZIF-67 carried out under a constant current density of 30 mA cm^{-2} (inset: the production of O_2 bubbles on the carbon cloth with Co-LDH@ZIF-67 as the electrode).

activity in alk alkaline electrolytes, but they are unstable in acidic solutions. At present, acid electrolytes are still widely used in industrial applications, such as polymer electrolyte membrane (PEM) water electrolyzers, which have the advantages of high operating current, high voltage efficiency, and compact system design. For applications using acidic electrolytes, in order to reduce

the cost of precious metal oxides as OER catalysts, researchers are developing IrO_2 -based and RuO_2 -based nanoparticles (NPs) with high specific surface area to mass ratio. At the same time, distributing the catalyst NPs on a stable conductive support material helps to prevent the catalyst NPs from accumulating and provide higher conductivity, thereby maximizing the effective catalytic surface

area exposed to the electrolyte, which is useful for improving the OER of noble metal oxides [93]. The mass activity of the catalyst is significance. To test the practical supporting performance of antimony-doped tin oxide (ATO) particles, Han *et al.* tested the capacitance and OER activity change of RuO₂ OER catalysts supported by commercial ATO (ATO-C) or synthesized ATO (ATO-S), which was compared with the unsupported RuO₂ and RuO₂ supported by Acetylene Black (AB) carbon [94]. All samples were loaded on fluorine doped tin oxide (FTO) glass. The loading of RuO₂ was 100 $\mu\text{g}\cdot\text{cm}^{-2}$, and the loading of support material (ATO or carbon) was also 100 $\mu\text{g}\cdot\text{cm}^{-2}$. After mixing RuO₂ with these support materials, the initial total capacitance increased from ~ 0.6 mF (no support) to ~ 1.1 mF (with ATO-C or ATO-S) or ~ 1.6 mF (with carbon), due to the contribution of effective surface areas from the support materials. Meanwhile, the initial OER activity of RuO₂ did not deviate much from $\sim 2.5 \text{ A}\cdot(\text{g RuO}_2)^{-1}$ at 1.5 V_{RHE} after mixing with the carbon or ATO-C. However, after mixing with the ATO-S particles, the OER activity rose to $\sim 6 \text{ A}\cdot(\text{g RuO}_2)^{-1}$ at 1.5 V_{RHE}. The improved OER activity could result from a more uniform distribution of RuO₂ that increased the effective surface area exposed to the electrolyte.

Also reported in the literature, the synthesis of RuO₂ loaded CeO₂ with varying amount of Ru loading with enhanced amount of Ce³⁺ and surface area, through synthesis of CeO₂ using cerium ammonium carbonate complex as procure followed by Ru loading by impregnation and calcination at 300 °C, is presented. Corresponding characterizations by XRD, SEM, TEM, XPS of all the samples reveal the formation of highly crystalline mesoporous CeO₂ nanoparticles with uniformly dispersed RuO₂ particles on the CeO₂ surface having approximately 45% Ce³⁺. All the samples were utilized as OER catalyst for electrocatalytic H₂ generation through water electrolysis. Electrocatalytic experiments reveal that synthesized 1 % (mass) RuO₂ loaded CeO₂ (1-RuO₂/CeO₂) showed superior OER activity. A quite low over-potential of 350 mV is required to attain a current density of 10 mA $\cdot\text{cm}^{-2}$ (η_{10}), with a Tafel slope of 74 mV $\cdot\text{dec}^{-1}$ for OER in 1 mol $\cdot\text{L}^{-1}$ KOH solution. The synthesized 1-RuO₂/CeO₂ electrocatalyst also exhibited superior long term stability in basic medium and redox atmosphere [95].

There is an urgent need for cheap, stable and abundant photoelectrochemical water splitting catalyst materials. Manganese oxide is an interesting OER catalyst, but the minimum thickness of the manganese oxide film has not been determined [96]. Studies have found that MnO_x films with a thickness of less than 1.5 nm do not have OER activity. X-ray photoelectron spectroscopy shows that This is because the electrostatic catalyst-support interaction prevents the electrochemical oxidation of manganese ions near the interface of the support. In thicker films, after oxidation and electrochemical treatment, Mn^{III} and Mn^{IV} oxide layers appear as OER active catalysts. According to our investigation, it can be concluded that a single layer of Mn^{III, IV}-O is sufficient to form oxygen evolution under alkaline conditions. In this work, an ultra-thin (<10 nm) manganese oxide film was grown on silicon by atomic layer deposition to study the source of OER activity under alkaline conditions. It is found that a minimum MnO_x thickness of 1.5 nm is required to obtain an OER active film, and a thickness of >2 nm is required for the film to stably exceed the first cyclic voltammogram. The highest OER current is in the 4–6 nm MnO_x film. The OER current of the thick film decreases, which can attribute to the increase in fill resistance. XPS analysis showed that before OER, the oxidation state of manganese ions changed from II to III/IV. We found that the number of oxidized Mn (II) ions corresponds to 0.19 nm MnO_x (~ 1 monolayer), which is consistent with previous reports. This indicates that the single layer of MnO_x should already be very active. However, the high electronegativity of silicon atoms in the substrate affects adjacent manganese ions and increases their binding energy. Therefore, manganese ions

are more difficult to oxidize at a distance of 1 nm from the Si/MnO interface than Mn ions farther from the interface. This explains why films smaller than 1.5 nm do not have OER activity. In order to avoid this limitation, the electronegativity of the support should be less than that of the OER catalyst to allow the manganese ions near the catalyst/support interface to be easily oxidized. These insights illustrate the importance of catalyst/support interaction in electrocatalysis and provide useful design guidelines for ultra-thin MnO_x-based OER catalysts [97].

Transition metal oxides (mainly perovskites) have received widespread attention as effective catalysts for OER in alkaline media. Here, Kirsanova *et al.* introduced that YBaCo₄O_{7.3} oxide with tetrahedral coordination Co₂/Co₃ is a brand new OER catalyst. YBaCo₄O_{7+ δ} demonstrates the ability to reversibly intercalate impressive amounts of oxygen at temperatures ranging from 270–350 °C, making it a promising oxygen storage material as well. The oxygen-storage capacity (OSC) of YBaCo₄O_{7+ δ} (OSC $\approx 2450 \mu\text{mol O}\cdot\text{g}^{-1}$) substantially exceeds that reported for conventional oxygen-storage materials, *e.g.* CeO₂–ZrO₂ (OSC $\approx 1500 \mu\text{mol O}\cdot\text{g}^{-1}$). At an overpotential of 400 mV, its OER activity is 1.18 mA $\cdot\text{cm}^{-2}$, which exceeds that of the LaNiO₃ benchmark catalyst in addition. Here, we successfully prepared an OER catalyst with excellent electrochemical performance through a simple anion doping. Firstly, a stable cubic perovskite SrCoO_{3- δ} was prepared by anion F-doping instead of traditional A and/or B site doping. Secondly, SrCoO_{2.85- δ} F_{0.15} demonstrates excellent OER activity superior to its parent hexagonal compound H-Sr₂Co₂O₅ and those perovskites prepared via complicated A- and/or B-site doping. DFT calculations and XPS investigations reveal that the cubic structure and the highly oxidative oxygen species (O₂²⁻/O⁻) via F-doping jointly contribute to the better OER properties of SrCoO_{2.85- δ} F_{0.15} [98].

4.2.3. Others

In the past few years, despite extensive research on HER, OER is limited. The chemistry in OER is more complex, involving irreversible surface oxidation of these materials and converting them to the corresponding oxide/hydroxyl groups. Interestingly, these *in-situ* changes have been widely observed, resulting in better performance and higher activity catalysts [99]. The design and development of low-cost, high-efficiency, and stable electrocatalysts to replace precious metal catalysts for OER remains a major challenge. The size of nanoparticles in single-atom-supported catalytic materials has been reduced to the atomic scale, with extremely high metal utilization. This structure not only reduces the usage of noble metals but also improves the mass activity of catalytic materials. Qiao *et al* created a new type of hybrid structure by integrating noble metal atoms into the lattice of transition metal oxides [100]. This study shows that iridium single atoms can be accommodated into the cationic sites of cobalt spinel oxide with short-range order. The resultant Ir_{0.06}Co_{2.94}O₄ catalyst exhibits much higher electrocatalytic activity than the parent oxide by 2 orders of magnitude toward the challenging oxygen evolution reaction under acidic conditions. This work eliminates the “close-packing” limitation of noble metals and offers promising opportunity to create analogues with desired topologies for various catalytic applications. Although noble metal-based materials (IrO₂ and RuO₂) are considered to be the most advanced OER catalysts, their high prices, long-term instability, and scarcity have also promoted the exploration of alternative materials, which are relatively in the natural world. It is cheap and has abundant reserves, and can be used to develop electrolyzers suitable for hydrogen production. The metal-free catalyst has the advantages of no pollution, economy, stable catalytic performance, etc., and can be used in various redox reactions. OER has attracted much attention because it can be used to produce clean energy. Hierarchical porous activated car-

bon (HPAC) shows the potential applications of OER. Yu and his colleagues used KOH and/or K_2CO_3 as the activator to prepare HPAC extracted from fallen leaves (ash tree). Characterization shows that HPAC in the KOH/ K_2CO_3 system has a high specific surface area and abundant hierarchical pores, which is beneficial to the mass transfer and charge transfer in the OER. The acid-washed HPAC shows relatively low activity, and electrochemical tests indicate that the ash content may contribute to OER. HPAC is a potential carbon-based catalyst with significant OER activity and durability. Souza and his colleagues reported the development and application of a new type of hybrid catalyst, which is heat-treated from a mixture of GNR and nickel pyrophosphate (β - $Ni_2P_2O_7$) [101]; Chemical materials have obvious improved properties, including easy charge transfer, high electroactive specific surface area, high activity and effective resistance to OER corrosion in alkaline media. The highly dispersed β - $Ni_2P_2O_7$ -30 % (mass) is in direct contact with GNR-70 % (mass), coupled with the application of heat treatment, to ensure the partial enrichment of nickel in the GNPi350N catalyst, which helps to produce excellent and excellent performance under alkaline conditions. High-efficiency material that stabilizes OER activity. Compared with the most advanced IrO_2 (300 mV), when fixed on a carbon paper electrode, GNPi350N catalyst needs about 320 mV of overpotential to reach $10\text{ mA}\cdot\text{cm}^{-2}$ current density. Pan HaoLi and his colleagues used density functional theory calculations to combine polar nitrobenzene molecules with g- C_3N_4 monolayer compounds to design a series of $C_6H_4NO_2$ /g- C_3N_4 complexes [102]. During the OER, due to the redistribution of electrons on the g- C_3N_4 substrate, the electrocatalytic performance is significantly improved. The lowest OER overpotential of a composite sample is 0.14 V, and the OER overpotential of the most stable composite sample is 0.27 V. The number of active electrons in active atoms is used as a descriptor of catalytic activity, which can accurately estimate the OER activity of metal-free electrocatalysts. This modification strategy will be extended to the design of high-efficiency metal-free electrocatalysts. Water electrolysis is a promising strategy for producing green hydrogen. However, expensive electrode costs and slow OER kinetics hinder this process. Therefore, it is necessary to develop an efficient and low-cost OER electrocatalyst. Du and his colleagues anneal iron-doped cobalt-based coordination polymers in an NH_3 atmosphere, N and Fe co-doped CoO nanoparticles (Co_x-Fe_yO-N) rich in O vacancies and the CoO/Co_xN interface were successfully prepared [103]. The ratio of Co^{2+} and Fe^{3+} is systematically changed, and $Co_{0.89}Fe_{0.11}O-N$ has the highest OER activity in $1.0\text{ mol}\cdot\text{L}^{-1}$ KOH. In addition, through the growth of the generated $Co_{0.89}Fe_{0.11}O-N$. On foamed nickel, when the current density is $50\text{ mA}\cdot\text{cm}^{-2}$ and the overpotential is 360 mV, the corresponding OER activity can be further enhanced. The superior OER activity of $Co_{0.89}Fe_{0.11}O-N$ is due to the existence of oxygen vacancies and the CoO/Co_xN interface. During the reaction, $CoO-N$ is partially oxidized to Co_3O_4 , and Co_3O_4 and CoO jointly catalyze OER. Yue and his colleagues reported the synthesis of a binary transition metal phosphide ($Co_xFe_{1-x}P$) with a yolk shell structure [104]. Different Co/Fe ratios are obtained through the phosphating process with cobalt ferrite as the precursor. In addition, the synthesized $Co_xFe_{1-x}P$ catalyst is used for OER. The whole egg yolk shell structure $Co_xFe_{1-x}P$ catalysts with different Co/Fe ratios showed better performance than solid catalysts. The study found that the formation of Co oxide on the catalyst surface and the optimal Co/Fe ratio during the OER process are critical to its activity. Among the prepared $Co_xFe_{1-x}P$ catalysts, the Co/Fe ratio of 0.47/0.53 ($Co_{0.47}Fe_{0.53}P$) showed the best performance. Carbon dioxide. $Co_{0.47}Fe_{0.53}P$ has an overpotential of 277 mV when the current density is $10\text{ mA}\cdot\text{cm}^{-2}$, and has excellent stability in alkaline media. Its excellent performance is due in part to the transfer of valence electrons from Co to P and Fe. The excellent conductive substrate of

$Co_{0.47}Fe_{0.53}P$ and the stable iron phosphate on the surface of the catalyst also help to improve OER performance. In addition, the egg yolk shell structure of $Co_{0.47}Fe_{0.53}P$ increases the contact area between the electrolyte and the catalyst. These characteristics of $Co_{0.47}Fe_{0.53}P$ improved the performance of OER. This optimized binary transition metal phosphide will provide a new method for the design of non-noble metal electrocatalysts. Inspired by Lego games, Bai and his colleagues prepared CoP nanoarrays by combining negatively charged carbon quantum dots (CDs) with positively charged Co and Cd ions in the layered CdP_2 -CDs-CoP zone [105]. Due to the low evaporation temperature of Cd, the solubility product (K_{sp}) of $Cd(OH)_2$ is relatively high, and trace amounts of CdP_2 are captured in the nanoarray on the surface of CdP_2 -CDs-CoP. When coupled with CDs, CdP_2 enriches the defects and active centers of the catalyst. The CdP_2 -CDs-CoP zone nanoarray serves as a robust OER electrocatalyst, providing an overpotential of 285 mV to drive a current density of $10\text{ mA}\cdot\text{cm}^{-2}$, demonstrating the advantages over commercial RuO_2 . He Fan and his colleagues used spin-polarized density functional theory calculations, and they systematically studied several kinds of palladium (Pd_n , $n = 1-6$, and 13) anchored in experimentally available single vacancies with S (Pd_n/MoS_2) Defective nanoclusters on MoS_2 monolayer, used for OER [106]. The results show that due to the strong interaction between the palladium clusters and the suspended molybdenum atoms and sulfur atoms around the vacancies, the Pd_n/MoS_2 materials studied have high stability, with the binding energy of each palladium atom ranging from -3.12 to -4.36 eV . Interestingly, the OER catalytic activity of these Pd_n/MoS_2 catalysts largely depends on the size of the anchored Pd clusters: Pd_2/MoS_2 has been identified as the best OER catalyst due to its ultra-low overpotential of 0.32 V. In order to obtain more light wavelengths to improve the photo-assisted electrochemical water splitting ability, Yao and his colleagues developed a new three-dimensional (3D) flower-like CuS structure heterostructure, which is accompanied by SnS_2 nanoparticles and reduction oxidation Graphene (rGO) aerogel has excellent photo-assisted electrocatalytic OER performance and good stability [107]. The results show that the $CuS/SnS_2/rGO$ (CSr) heterostructure has good catalytic kinetics, effective visible light capture and fast charge transfer. The overpotential ($264\text{ mV}@10\text{ mA}\cdot\text{cm}^{-2}$) is 20% lower under light-assisted conditions than under light-cutting conditions. SnS_2 can obtain more light wavelengths, which enhances its intrinsic activity. However, as the content of SnS_2 increases, OER activity decreases. The combination of CS heterostructure and rGO conductive aerogel achieves rapid charge transfer. In addition, the possible mechanism of light-assisted electrocatalytic OER is also proposed. In general, this work provides new insights for the simple and scalable manufacturing of high-efficiency, low-cost and stable non-noble metal-based electrocatalysts. CoS-related catalysts usually have good OER activity, but require a very complicated preparation process. Guo and his colleagues prepared NiCo-150 composite catalyst by a simple two-step electrodeposition method, and its excellent OER performance is 145 mV at $10\text{ mA}\cdot\text{cm}^{-2}$ and 337 mV at $50\text{ mA}\cdot\text{cm}^{-2}$. The Ni-150 composite catalyst shows good OER performance, but the OER performance is further improved after electrodeposition of CoS, which is better than the simple CoS/NF composite catalyst [108]. The experimental results show that this pre-deposition *in-situ* growth technology effectively reduces the internal resistance of the electrochemical process and significantly increases the electrochemical active centers by controlling the morphology. As an important carbon neutral technology, people have great expectations for the electrochemical decomposition of water to produce hydrogen. This technology aims to solve the global energy crisis and greenhouse gas problems. However, the OER process must be catalyzed with high output energy for a long time, which brings challenges to the efficient and stable processing of

practical electrodes. The design of new supramolecular complexes and metal organic frameworks (MOFs) as water oxidation catalysts requires stability studies, because many metal organic compounds will decompose under the harsh conditions of water oxidation. Metal organic frameworks have been widely reported as catalysts for water splitting to produce hydrogen. Salmanion and his colleagues studied the stability of the NiFe MOF during OER [109]. In the Raman spectrum, the peaks related to C—C and C—O in 1100–1550 cm^{-1} became weaker after OER, indicating that the carboxylic acid functional group was reduced. Comparing the energy dispersion spectra of MOF before and after OER shows that the carbon content is reduced, but the oxygen content is increased. Similar to the results of linear sweep voltammetry, energy dispersion spectroscopy shows that the MOF surface changes to an oxide structure after OER. Transmission electron microscopy also showed some new crystallized regions after OER. The crystal area indicates that the lattice spacing is 0.21–0.23 nm, which corresponds to the (012) plane of the NiFe layered double hydroxide. In summary, these experiments show that in the OER process, MOF is converted to NiFe oxide, and there are obvious defects and defects in the regular geometric arrangement of ions. NiFe oxide is a candidate material for catalyzing OER. This discovery may be a roadmap for progress in the field of sustainable catalysis. Fang Wenhui reported a new hybrid electrocatalyst: iron-cobalt modified nitrogen-doped carbon/reduced graphene oxide-700 °C (Fe-Co-CN/rGO-700) [110]. The catalyst exhibited good electrocatalytic performance for OER in alkaline solution. When the current density is 10 $\text{mA}\cdot\text{cm}^{-2}$, the overpotential is 0.308 V. The catalyst has excellent durability (after 45 h). The activity is mainly due to the highly dispersed iron/cobalt species, the high-porosity flake structure, the improvement of the electronic structure of nitrogen-doped carbon, and the high conductivity of rGO. Combined with density functional theory calculations, the improvement of OER performance is also attributed to the adsorption/desorption equilibrium of hydrogen-containing and oxygen-containing intermediates, and the increase in the density of electronic states near the Fermi level. This work provides a novel and simple strategy for the synthesis of porous carbon electrocatalyst materials using metal organic framework as the precursor, which has high activity and strong stability for OER. Ma prepared Fe-MOF nanosheet arrays on foam nickel by doping with rare earth erbium ($\text{Er}_{0.4}\text{Fe-MOF/NF}$) and used it as an electrocatalyst [111]. $\text{Er}_{0.4}\text{Fe-MOF/NF}$ can generate 248 mV overpotential at a current density of 100 $\text{mA}\cdot\text{cm}^{-2}$, and has a long-term electrochemical durability of 100 h. At high current densities of 500 and 1000 $\text{mA}\cdot\text{cm}^{-2}$, the overpotentials of 297 mV and 326 mV are reached, respectively, showing its potential in industrial applications. This enhancement is attributed to the synergistic effect of Fe and Er sites, and Er plays a supporting role in the engineering of the electronic state of Fe sites, making them have enhanced OER activity. This strategy of designing the OER activity of Fe-MOF by doping with rare earth ions has paved a new way for the design of other MOF catalysts for industrial OER applications.

5. Perspectives and Challenges

In this article, we summarized the existing hydrogen production methods and the reaction mechanism of the two half reactions of electrolytic water splitting, as well as the recent research progress of the electrocatalytic water splitting. Researchers explored the structure–activity relationship of the catalyst by regulating the material structure and composition, realized the accurate construction of the catalyst, and effectively improved the catalytic activity of the electrocatalytic water splitting. It provides a new idea for the development and utilization of hydrogen energy. Tak-

ing the factors of carbon emission reduction into account, the hydrogen production by electrocatalytic water splitting has higher social effect results benefit than that of fossil fuel. But we must be soberly aware that we still face grave challenges in further industrial application. Firstly, from the perspective of technical economy, the economic competitiveness of electrocatalytic water splitting hydrogen production technology still needs to be strengthened. Except for reducing the power cost of electrocatalytic water splitting, improving the performance of the catalyst will be the main research direction in the future. Secondly, the cathode reaction-OER of electrocatalytic water splitting is a slow four electron transfer process, while the anode reaction-HER is a relatively fast two electron transfer process. The cask theory inspired us that in order to enhance the energy conversion efficiency as much as possible, we need to develop a catalyst that can effectively reduce the activation energy of the two half reactions at the same time. However, the current research is still focused on the catalyst performance improvement of the single OER or HER. Finally, owing to acid-base corrosion, acidic or alkaline electrolytes are harmful to the long-term operation of industrial equipment, which hinders further industrial application. Therefore, the investigation of high-efficiency catalysts in a neutral electrolyte will be a promising direction. In summary, the application prospect of hydrogen energy faces both rare opportunities and severe challenges. But, there is no doubt that hydrogen production by electrocatalytic water splitting driven by renewable energy will be one of the most promising alternative energy strategies, and the rapid development of nano-catalysts will greatly promote the industrialization process of large-scale electrocatalytic water splitting hydrogen production.

Declaration of Competing Interest

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

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