

Surface Structure Engineering of FeNi-Based Pre-Catalyst for Oxygen Evolution Reaction: A Mini Review

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Abstract: Oxygen evolution reaction (OER) is a significant half-reaction for water splitting reaction, and attention is directed to the high-performance non-precious catalysts. Iron nickel (FeNi)-based material is considered as the most promising pre-catalyst, that will be transferred to the real active phase in the form of high valence state metal species. Even so, the catalytic performance is largely influenced by the structure and morphology of the FeNi pre-catalysts, and lots of work has been done to optimize and tune the structure and chemical environment of the FeNi-based pre-catalysts so as to increase the catalytic performance. Herein, based on our work, a mini review is proposed for the surface structure engineering of FeNi-based pre-catalyst for OER. The reaction mechanism of alkaline OER is firstly presented, and then the strategies in surface engineering of FeNi-based pre-catalyst for improving OER performance are discussed in terms of heteroatom doping, surface composition modification, selective structural transformation, surface chemical state regulation, heterostructure construction, and support effect. It can be concluded that the surface structure, morphology, and the chemical states of Fe/Ni in the system will significantly influence the final catalytic performance, though all of them were transferred into the active phase state of high valence state metal species. In other words, the catalytic performance of FeNi-based catalysts is also determined by the property of their pre-catalysts. To carefully design and maximize the synergistic effect of Fe and Ni is necessary to boost the catalytic performance. We hope this topic will be a good and timely complement to the study of FeNi-based catalysts for OER in the water-splitting technique.

Key words: FeNi-based catalyst; surface structure engineering; oxygen evolution reaction; water splitting reaction; catalysis

1 Introduction

Water electrolysis is a clean and reliable technology that can convert renewable energy into chemical energy and store them in the form of hydrogen. The overall water electrolysis includes the anodic oxygen evolution reaction (OER) and the cathodic hydrogen evolution reaction (HER)^[1]. Compared with HER, OER undergoes more sluggish kinetics with a complex four-electron transfer process that requires more energy input^[2]. To drive OER smoothly, highly efficient catalysts are required; the Ru/Ir/Rh and transition metal (Fe/Co/Ni/Mn) based materials are the pre-

vailing catalysts^[3]. As shown in Figure 1a, during the catalysis process, the catalyst as denoted as M will be re-constructed involving the high valence state M species formations such as the M-O and M-OOH. Therefore, a consensus is made that the freshly prepared catalysts are called the pre-catalyst and the real active catalyst is the high valence state metal species *in situ* formed during the electrocatalysis process driven by the high potentials^[4]. Since the OER is a multi-step proton-coupled electron transfer process involving several intermediates^[5], the catalytic activity and kinetics are dependent on many factors like the ad-

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sorption/desorption energy, activation barriers, and charge transferability. These characteristics are closely related to the catalyst surface structure and electronic structure which can induce favorable interactions with reactants and optimize the reaction pathway.

By combining the experimental results with the theoretical calculations, the volcano plot was proposed to describe and predict the structure-activity relationship^[6-8]. Too strong and too weak interactions between the intermediates and catalyst are both detrimental to the catalytic activity as shown in Figure 1b, whereas the catalysts located at the top of the volcano plot represent superior catalytic ability^[9]. Thus, designing OER electrocatalysts with moderate interactions should be an efficient way to improve the catalytic activity, which can be realized through the surface engineering strategies to achieve the favorable adsorption/desorption energy with reactants. The noble metal-based catalysts of Ru, Ir, and Rh have outstanding intrinsic activity for OER, but their large-scale application has been restricted by the scarce reserves and the instability during the electrolysis^[10]. Fortunately, in the alkaline electrolyte, FeNi-based catalysts are also very promising for OER due to the FeNi synergistic effect^[11]. The catalytic mechanism of the FeNi-based catalyst for OER is still in debate, namely, the active sites are still not clear^[12], while that the co-action of Fe and Ni can promote OER compared to the individual Fe and Ni species is well confirmed, and even with a trace amount of Fe that can promote the catalytic performance of Ni^[13]. In FeNi system, the *in situ* generated FeNi oxyhydroxide or Fe-doped β -NiOOH as observed in some spectroscopic studies were found to be significant for the enhanced activity^[14, 15]. The relevant discussion can be seen in some perspective comments^[16], here we will not discuss them. Some FeNi-based catalysts even showed competitive and better activity for OER compared with noble metal catalysts in alkaline electrolytes like FeNi alloy^[17], NiFe layered double hydroxides (LDHs)^[18], Ni₃FeN^[19], and FeNiP^[20]. Many modification methods including morphological designing,

components optimization, defects creation, and heteroatom doping have been devoted to improving their OER activity^[21]. Several reviews have been done to summarize the advance of FeNi-based catalysts for OER in terms of catalyst preparation, theoretical calculation, performance optimization, and performance deciphering^[22]. And recently, the intrinsic activity modulation and structural design of NiFe alloy have been critically discussed to understand the mechanism of OER in an alkaline medium^[23].

Though all the pre-catalysts will be transferred to the real active phase of high valence state metal species, the rational design of pre-catalysts is vital for surface reconstruction and active species formation, which will certainly impact the OER catalytic performance^[24]. Herein, combined with our work, we pay attention to the surface structure engineering of FeNi-based pre-catalyst for OER. The mechanism is briefly shown firstly to help understand the structural evolution of the catalysts, and then some commonly used strategies to tune the surface structure of FeNi-based pre-catalysts are summarized in terms of heteroatom doping, surface composition modification, selective structural transformation, surface chemical state regulation, heterostructure construction, and support effect. Finally, we propose the challenges and perspective comments, and suggestions for the development of FeNi-based catalysts for OER. Compared with other reviews, we concentrate on the surface structure engineering strategies of FeNi-based pre-catalyst as well as their structure-activity relationship for OER. Hopefully, this review will give some novel understanding in the structure-activity relationship of FeNi-based pre-catalyst for OER in alkaline electrolytes.

2 Reaction Mechanism of OER

The oxygen is generally evolved on the surface of metal oxide or hydroxyl oxide derived from the pre-catalyst^[25]. The specific mechanism may vary with the change of catalyst surface structure^[26, 27], and different reaction kinetics would be met even with the catalysts possessing the same compositions^[28, 29]. Whereas a general mechanism for OER in an alkaline medium

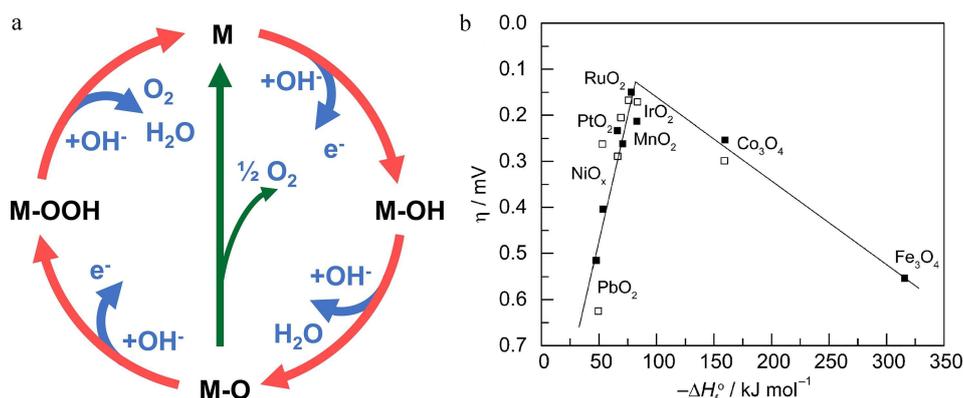
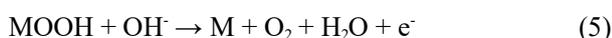


Figure 1 (a) The OER mechanism in alkaline conditions. (b) Volcano plot showing activity for O₂ production on catalysts surfaces versus the enthalpy changes of catalysts in acidic (■) and basic (□) solutions^[6]. (color on line)

involving the catalyst re-configuration is well recognized as shown in Figure 1a and the specific reaction steps can be described as follows^[30]:



In the initial stage, OH⁻ adsorbs on M site and loses one electron to form M-OH; Then another OH⁻ reacts with MOH to generate H₂O and MO intermediate by coupling with a proton and removing an electron. The final molecular O₂ can be obtained via two possible pathways, one is the direct combination of two MO, and the other approach is mediated by the formation of intermediate MOOH. In specific, the nucleophilic attack of OH⁻ on M-O produces MOOH, where the third electron is involved in the reaction circuit. Finally, an OH⁻ attacks the MOOH intermediate and releases the fourth electron to form O₂. The specific Gibbs free energy (ΔG) of these elementary steps has been studied by density functional theory (DFT) calculations. The catalyst with the optimal ΔG difference between the intermediates (ΔG_{HOO*} - ΔG_{O*}) was proved to have the best OER activity and the lowest overpotential^[31]. Thus, the optimization of the binding energy of the intermediates greatly influences the overall reaction kinetics. Tuning the surface structure and chemical environment of the FeNi-based

pre-catalyst would be an efficient approach to improve the OER performance.

As for the mechanism of OER catalyzed by FeNi-based materials, many atomic-scale analyses and *in situ* characterizations have been performed^[32-34]. For instance, a “Ni-O-Fe” bond was proposed to mediate the charge transfer between Fe and Ni, which promoted the formation of the high valent metal element and contributed to the high OER catalytic performance^[35]. In another research, the NiOOH lattice was believed to have the function of stabilizing Fe⁴⁺ as detected by operando Mossbauer spectroscopy, the Fe-doped NiOOH lattice synergistically improved the OER activity^[36]. Some other literatures emphasized the effect of Fe on Ni. Lena et al. for the first time proved that the impurities of Fe dramatically increased the OER activity of Ni_{1-x}Fe_x(OH)₂/Ni_{1-x}Fe_xOOH catalyst^[37], the author attributed this enhanced activity to the partial-charge-transfer activation effect of Ni by Fe incorporation. Furthermore, the Fe substitution into metal Ni was also demonstrated to improve the OER activity because the Fe lengthened the Ni-O bond within oxyhydroxides and facilitated the decomposition of *OOH intermediates into O₂^[38]. It can be seen that whether the active center is Fe or Ni is still controversial in FeNi-based catalysts. Therefore, more advanced techniques, accurate characterizations, and further comprehensive studies are in great need to identify the specific reaction mechanism and real active sites for OER.

3 Surface Structure Engineering of FeNi-Based Pre-Catalysts

3.1 Heteroatom Doping

Though FeNi-based catalysts are considered as the substitutes for noble metal catalysts, their catalytic performance has been still restricted by the relatively low conductivity and poor corrosion resistance in alkaline solutions. In general, element doping could induce favorable properties like electronic structure redistribution, morphological modification, and intrinsic conductivity improvement, thereby enhancing the catalytic ability^[39,40]. As far as we know, doping can be directly realized in the active catalyst and the catalyst support. Several non-metal elements like N, P, S, and B have been explored for doping FeNi-based catalysts^[41,42]. Sulfur-incorporated NiFe₂O₄ over nickel foam (S-NiFe₂O₄/NF) was fabricated through the thiourea-assisted electrodeposition and calcination method, and the formation of metal-sulfur bonds and unsaturated coordination sulfur ions around the surface and

defect area were confirmed (Figure 2a)^[43]. A low overpotential of 267 mV at 10 mA · cm⁻² was achieved to drive OER (Figure 2b), and the enhanced performance was attributed to the synergism of S-doping and 3D morphology where the adsorption energy of intermediates and the conductivity were optimized by incorporation of S. The heteroatom (P, B, and S) doped FeNi-based porous nanocubes were evaluated for OER (Figure 2c), and much superior performance than those of the pristine Fe-Ni-O and Ir/C catalysts was observed for all the doped catalysts (Figure 2d)^[44]. The incorporation of P, or B, or S was able to adjust the electronic structure and promote the formation of high valent Ni active species. Therein, the Ni-Fe-O-P exhibited the larger active area and current density as well as the smaller charge transfer resistance and Tafel slope compared with Ni-Fe-O-B and Ni-Fe-O-S. However, the specific origin of the difference in OER catalytic performance of the three doped catalysts was not explained. A future study to explore the dif-

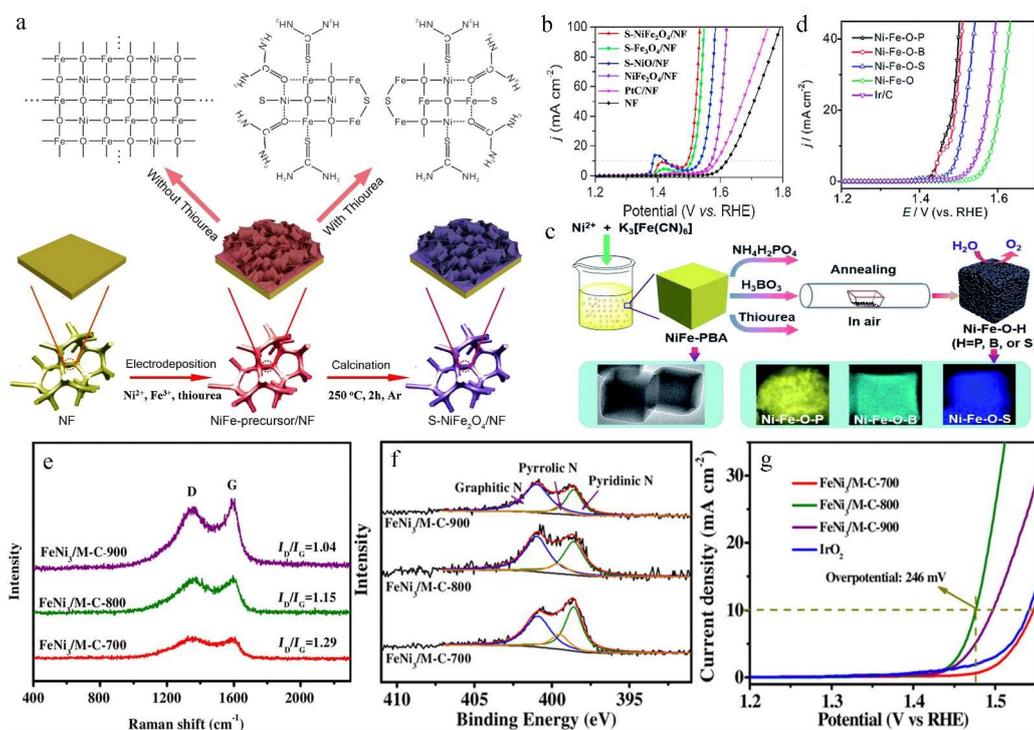


Figure 2 (a) Schematic illustration of the confined growth of S-NiFe₂O₄/NF. (b) OER polarization curves of all the samples in 1.0 mol · L⁻¹ KOH^[43]. (c) Schematic illustration of the synthesis of Ni-Fe-O-H catalysts. (d) LSV curves of all the samples at a scan rate of 5 mV · s⁻¹^[44]. (e) Raman spectra and (f) XPS spectra of N 1s for the FeNi₃/M-C-700, FeNi₃/M-C-800, and FeNi₃/M-C-900. (g) Polarization curves of all the samples^[45]. (color on line)

ference induced by the different doping atoms might be interesting.

To increase the catalytic activity, the conductive carbon-supported or encapsulated FeNi system was developed, and the catalytic efficiency and durability could be further increased by heteroatoms doping into the carbon materials^[46]. For example, the nitrogen and fluorine co-doped carbon-supported FeNi catalyst with the optimum ratio of Fe/Ni possessed high catalytic properties for OER^[47]. The FeNi nanoparticles embedded in N-doped graphitized carbon shells were reported to have high durability and activity for OER due to the tuned lattice and electronic structures of the metal core^[48]. We investigated the oxygen evolution performance of FeNi₃ nanoparticles immobilized in S, N co-doped carbon (FeNi₃/M-C) for OER via the pyrolysis of the *in situ* formed metal-complex from low-cost precursors^[45]. The sample obtained at the pyrolysis temperature of 800 °C (FeNi₃/M-C-800) exhibited suitable defects and graphitization degree as indicated by the Raman spectrum (Figure 2e) and the moderate graphitic-N/pyridinic-N ratio as revealed by X-ray photoelectron spectroscopic (XPS) spectrum (Figure 2f). This catalyst thus showed high active sites exposure and conductivity improvement due to the balance of defects and graphitization, which delivered 10 mA · cm⁻² at a low overpotential of 246 mV, exceeding the commercial IrO₂ catalyst (Figure 2g). Besides, the local electronic environment of the catalyst can be alerted by the different doping types of N (p-type and n-type) and the distinct sp² electronic configuration of C-N bond, the electron-donating graphitic-N and electron-withdrawing pyridinic-N could promote the transfer of oxygen evolution intermediates to the final products^[49]. In addition, FeNi alloy was proved to have the most sufficient synergistic effect with the single layer graphene shell compared with other 3d transition metal nanoparticles^[50]. The encapsulated FeNi needed a small overpotential of 280 mV to achieve 10 mA · cm⁻² accompanied by good durability up to 10000 cycles. As stated above, the combination of FeNi active sites and multi-non-metal elements doped conductive carbon material can

synergistically induce local electronic redistribution, improve charge transfer ability, and promote catalytic activity. If finely optimizing the composition and structure, the catalytic performance can be further improved. Note that the properties of the parent precursors have a big influence on the composition and structure of the carbonized substrate, it is still a challenge to develop highly active transition metals incorporated in heteroatom-doped carbon hybrid materials.

3.2 Surface Composition Modification

The active sites for OER are generally considered to be in the surface metal oxide layer, in which they will further turn into *OOH and produce O₂ through deprotonation^[51]. The surface content of FeNi thus would also influence the catalytic performance, and preparing such a metal oxide layer is promising but in great challenge. In one typical work, the FeNi alloy/S, N-doped carbon (FeNi/SN-C) was firstly prepared by thermal annealing the Fe/Ni complex, and the surface composition of FeNi/SN-C obtained at 800 °C was then modified to promote OER using the Kirkendall effect^[52]. Because of the different diffusion rates and oxygen coupling ability between Fe and Ni^[53], a core-shell structure of Fe-rich Fe-Ni oxide shell and Fe-Ni alloy core was successfully formed during the thermal annealing process in air at 400 °C (FeNi/SN-C-800-400) (Figure 3a-b). A core-shell structure was formed where the interconnected nanocrystals of a Fe-Ni oxide shell with a Fe-rich composition covered over the Fe-Ni alloy core; and the shell thickness was around 25 nm with the clear lattice fringes of Fe₂O₃ and the (111) interface of the FeNi alloy in the core (Figure 3c-d). Due to the loss of carbon by oxidation in air, the surface composition of the catalyst was changed; the content of Fe was increased from 1.77 to 10.95at% and the content of Ni was also increased from 2.27 to 9.09at% as confirmed by the XPS spectra (Figure 3e). The ratio of Fe to Ni on the surface was increased from 0.78 to 1.2 due to Fe diffusion to the shell and Ni-enrichment in the center. As a result, the resultant catalyst showed an overpotential of 230 mV to deliver 10 mA · cm⁻², ca. 30 mV less than that of pristine catalyst without surface composition mod-

ification (Figure 3f). Theoretical calculations have proved that Fe sites are more active for water oxidation than Ni sites in FeNi alloy^[54]. Hence, the Fe-rich Fe-Ni oxide shell of FeNi/SN-C-800-400 can provide more oxide active sites to enhance the OER, meanwhile, the conductive Fe-Ni core is endowed with high electrical conductivity, as a result, they synergistically improved the OER catalytic performance. This research also revealed that the highly ordered crystal structure of metal alloy is unfavorable for OER, but the catalytic ability can be improved by surface composition modification. Similarly, a series of FeNi-based pre-catalysts with different structures of NiO_x/FeO_x alloy, FeO_x-NiO_x core-shell, and NiO_x-FeO_x/NiO_x core-mixed shell were rationally designed^[55]. As expected, the shell composition of mixed FeO_x/NiO_x composition over the NiO_x core contributed to the best catalytic activity for OER, confirming the significance of catalyst surface composition modification. A similar conclusion was also verified in other studies, for example, the nickel phosphide with a metal oxide shell displayed much higher OER activity than the pure metal oxide phase^[56].

3.3 Selective Structural Transformation

Besides the surface composition modification, in-

creasing the catalytic activity of FeNi-based pre-catalyst by structural transformation and exposing more active sites were also an effective approach. In a representative study, the selective structural transformation was proposed on the FeNi alloy/NiFe₂O₄ hybrid catalyst embedding the porous N-doped carbon nanosphere (FeNi-FeNiO/CNS) by a low-temperature phosphating process, where the FeNi alloy was transformed to the FeNi phosphate by forming a novel metal phosphate/NiFe₂O₄ hybrid (P-FeNiO/CNS) (Figure 4a)^[57]. The structural transformation was well supported by the XRD pattern, where the FeNi alloy peaks disappeared after the phosphating process (Figure 4b), and an amorphous metal phosphate layer over the NiFe₂O₄ nanoparticle was observed by the high-resolution TEM images and the linear elements profile distribution. By transforming the FeNi alloy to the more active amorphous metal phosphate, a largely improved OER performance was achieved that required a very low overpotential of 220 mV to drive 10 mA·cm⁻², which was about 66 mV less than that of the pristine FeNiO/CNS catalyst (Figure 4c). DFT calculations revealed the more suitable adsorption energy toward the intermediates during the catalytic process, thereby facilitating the reaction kinetics for

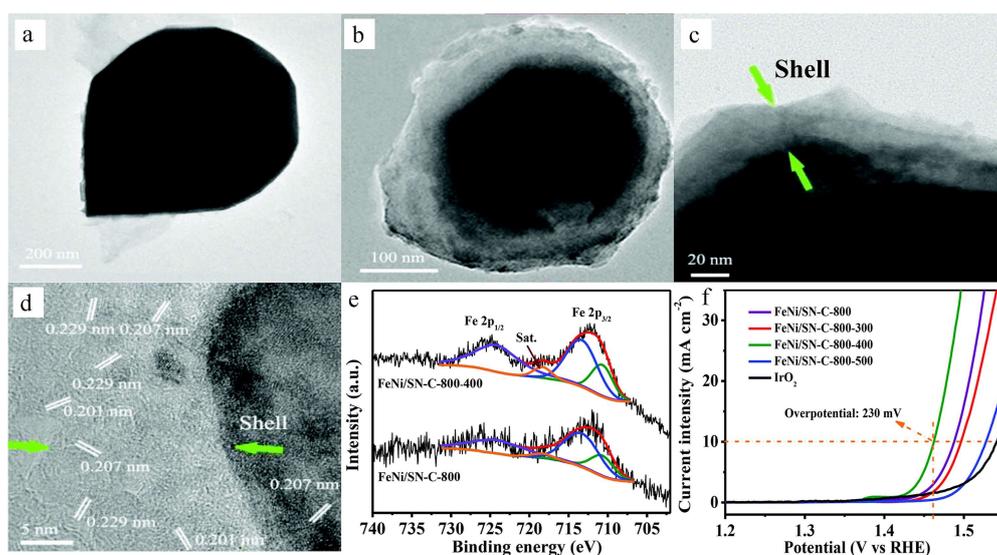


Figure 3 (a) TEM image of FeNi/SN-C-800 nanoparticle. (b-c) TEM and (d) HRTEM images of FeNi/SN-C-800-400. (e) High resolution XPS spectra for Fe 2p of FeNi/SN-C-800-400 and FeNi/SN-C-800. (f) Polarization curves of all the samples at a scan rate of 5 mV·s⁻¹ in 1 mol·L⁻¹ KOH^[52]. (color on line)

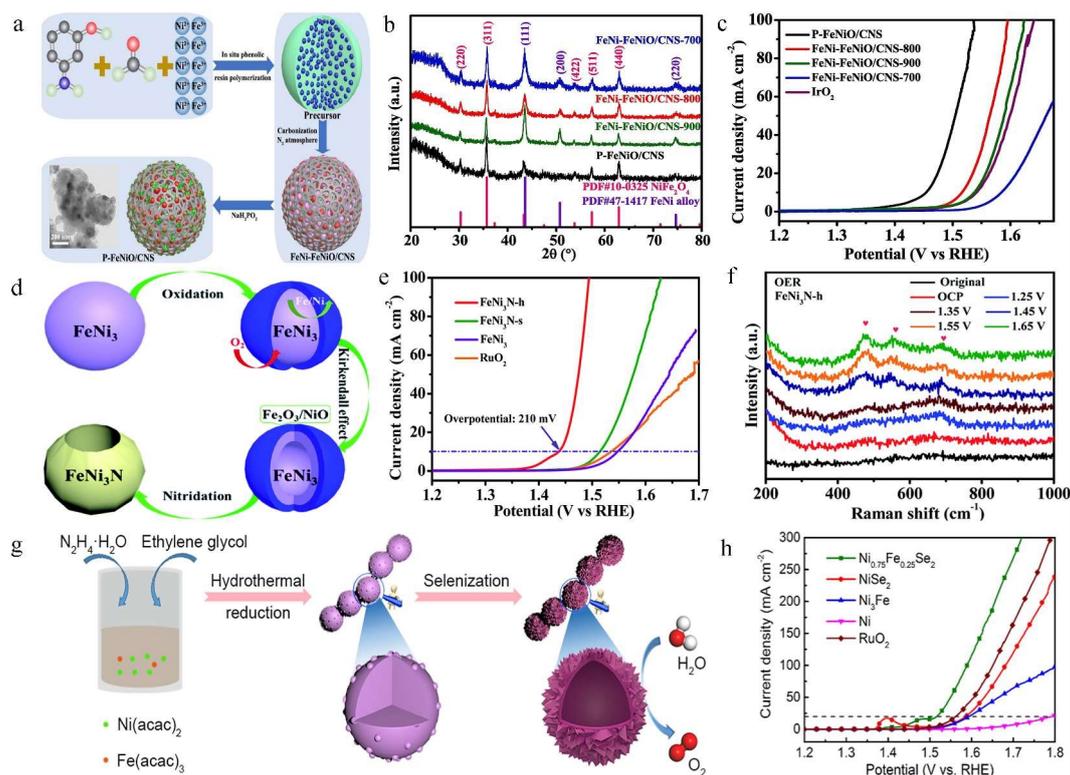


Figure 4 (a) Schematic diagram for the catalyst fabrication. (b) XRD patterns of all the samples. (c) Polarization curves of the as-prepared catalysts^[57]. (d) Schematic illustration for the fabrication of the FeNi₃N nanoparticles with hollow interiors. (e) Polarization curves of FeNi₃, FeNi₃N-h, FeNi₃N-s, and RuO₂ at a scan rate of 5 mV · s⁻¹ in 1 mol · L⁻¹ KOH. (f) Raman spectra of FeNi₃N-h at various potentials for the OER^[58]. (g) Schematic illustration showing the processing of NiFe diselenide hollow nanochains. (h) Polarization curves of Ni_{0.75}Fe_{0.25}Se₂, NiSe₂, Ni₃Fe, Ni and RuO₂ catalysts^[59]. (color on line)

oxygen evolution.

The transition metal nitrides exhibited good catalytic performance for the electrocatalysis reaction due to the inherent metallic features, unique electron construction, high electrical conductivity, and strong corrosion resistance^[60, 61]. Most importantly, the energy barriers of metal nitrides for electrocatalysis can be reduced because of the larger electron density near the Fermi level caused by d-band contraction^[62, 63]. Therefore, the structural transformation from FeNi-based materials to their nitrides has attracted increasing attention^[64]. By optimizing the bulk composition and tuning the electronic state, the catalytic performance for OER was found to be largely increased^[65, 66]. For example, the 3D Ni₃FeN nanoparticles supported on the reduced graphene oxide (Ni₃FeN/r-GO) were synthesized by nitridation in NH₃ at 700 °C^[19]. They showed high activity for OER with a small overpo-

tential of 270 mV to reach 10 mA · cm⁻². In addition, a strong electronic interaction between Ni₃FeN and r-GO was proved by DFT calculations, which accounted for the improved OER catalytic performance. It should be mentioned that the bulk metal nitrides have a low surface area, and increasing the exposure of their active sites would be helpful to performance improvement^[67]. Therefore, the hollow FeNi₃N (FeNi₃N-h) nanoparticles were constructed to improve the intrinsic activity of OER by combined oxygen-etching and nitridation methods (Figure 4d)^[58]. An enhanced performance was obtained with a low overpotential of 210 mV to reach 10 mA · cm⁻² for OER, much lower than those of FeNi and solid FeNi₃N (FeNi₃N-s) catalysts (Figure 4e). This promotion effect was due to the morphological modification and selective structural transformation from FeNi alloy to nitride that led to the increased active surface area, faster reaction

kinetics, and efficient charge transfer. Meanwhile, an amorphous metal (oxy)hydroxide layer was also detected by *in situ* Raman spectroscopy during the catalytic reaction, which was believed to be significant for OER (Figure 4f). Transition metal selenides are also broadly studied due to their merits of high metallic character, electrical conductivity, and low band gaps^[68]. The structural transformation from FeNi alloy to metal diselenide hollow nanochains ($\text{Ni}_{0.75}\text{Fe}_{0.25}\text{Se}_2$) was realized via a two-step hydrothermal method and evaluated for OER (Figure 4g)^[59]. An improved OER performance was found for some good characteristics like low overpotential (267 mV at $10 \text{ mA} \cdot \text{cm}^{-2}$) (Figure 4h), small Tafel slope ($67 \text{ mV} \cdot \text{dec}^{-1}$), and good durability.

Fluorine, as the most electronegative element, is also used for the structural transformation of FeNi-based catalysts. Fluorine-containing catalysts have been reported to be efficient for active phase formation due to the increased ionic bonds and the exposure of active sites caused by the fluorine etching effect^[69]. A novel concept of selective fluoridation of metal alloy/oxide hybrid was firstly proved active for OER^[70]. The structure of FeNi₃ alloy/oxide was transferred into metal fluoride as FeNiF via a low-temperature fluoridation, and an enhanced OER activity was obtained. We found that the high surface area and roughness were caused by the high-temperature annealing of the FeNi precursor, but the low-temperature fluoridation accounted for the increased performance by forming a new Metal-F structure and phase. In another typical research, the OER catalytic performance of FeNi layer double hydroxides (LDHs) could be largely boosted via a facile and controllable fluoridation method^[71]. The morphology was changed from nanosheet to nanorod via fluoridation, and meanwhile, significant improvements in catalytic activity and stability were also observed. A low overpotential of 225 mV at $10 \text{ mA} \cdot \text{cm}^{-2}$ and a small Tafel slope of $79 \text{ mV} \cdot \text{dec}^{-1}$ were reported, which outperformed the noble IrO_2 catalyst and most of the similar FeNi-based catalysts. This outstanding OER catalytic performance was attributed to the structural transfor-

mation from Metal-O bond in FeNi LDHs to Metal-F bond after fluoridation, which was much easier to form the real active sites of Fe-doped high valence Ni (oxy)hydroxide.

3.4 Surface Chemical State Regulation

For the FeNi catalysis system, the high valent metal (oxy)hydroxides generated during the reaction process were more active for OER, and their amount was increased with the prolonged electrochemical cycling^[72]. The strategies of composition and structure modification have been employed to facilitate the formation of surface oxide while they were less active than the *in situ* produced (oxy)hydroxides metal species^[73]. Therefore, the regulation of the surface chemical state by forming a more reduction state on the pre-catalyst surface might facilitate the subsequent *in situ* oxidation that might be conducive to the improvement of OER. To verify this hypothesis, we have done a series of thermal oxidation and/or reduction treatments to investigate the influence of the surface chemical state of FeNi-based catalysts for OER^[74]. As shown in Figure 5a, the FeNi samples with different surface chemical states were prepared by treating the FeNi precursor (FeNi-P) in different conditions like the thermally reduced (FeNi-H) and oxidized (FeNi-O) samples as well as the further oxidized (FeNi-H/O) and reduced samples (FeNi-O/H). As expected, the different chemical states largely influenced the catalytic performance for OER. We found that the completely oxidized FeNi as metal oxide and the completely reduced FeNi as metal alloy showed very low performance for OER; the samples with a good synergistic chemical state of metal oxide and metallic state on the surface could effectively catalyze the reactions. As shown in the polarization curves (Figure 5b), the FeNi-P catalyst required an overpotential of 340 mV to offer $10 \text{ mA} \cdot \text{cm}^{-2}$, while the reduced overpotentials of 290 mV and 320 mV for the FeNi-H and FeNi-O samples; the best catalytic activity with the lowest overpotential of 230 mV was found on FeNi-O/H catalyst to drive $10 \text{ mA} \cdot \text{cm}^{-2}$ by further reducing the FeNi-O sample. The first step of

low-temperature O₂ etching could increase the surface roughness, and the following H₂ reduction treatment resulted in an obvious defect layer by generating more reduced metal on the surface that can contribute to the formation of the active site during the catalysis process (Figure 5c). High valence state Fe/Ni species synergism was revealed by the post and *in situ* Raman spectrum analysis (Figure 5d)^[75, 76]. Therefore, the catalytic performance was closely determined by the chemical states of the pre-catalyst, and that is why the varied catalytic performance is always observed for the catalyst with the same composition but varied chemical states prepared by different approaches.

3.5 Heterostructure Construction

Unlike general composite, the heterostructure usually contains an obvious interface between the different components which can induce desirable properties due to the interface interaction^[77, 78]. The heterostructure of FeNi-based material with other materials have also been explored intensively^[79, 80]. For instance,

the layer of Fe₃Ni₄S₈ (FNS) could be *in situ* formed at the interface of MoS₂ nanosheet vertically grown on the FeNi substrate during the synthesis process (Figure 6a)^[81]. A strong electronic interaction between MoS₂ and FNS was found, as a result, the adsorptions of both H atoms and OH groups could be facilitated on the heterointerface between MoS₂ and FNS (Figure 6b). Finally, the enhanced overall water splitting performance was observed, that required an ultra-small overpotential of 204 mV to drive 10 mA · cm⁻² for OER (Figure 6c). An example of FeNi-based heterostructure composing of FeNi₂Se₄-FeNi LDH was prepared by a combined hydrothermal and partial selenization method^[82]. The heterointerface between FeNi₂Se₄ and FeNi LDH facilitated the electronic interaction and accelerated the charge transfer, thereby optimizing the intermediate adsorption energy, improving the conductivity, and boosting the water electrolysis. It can be seen that the catalytic performance of heterostructure is usually superior to the samples with single-phase. Therefore, heterostructure

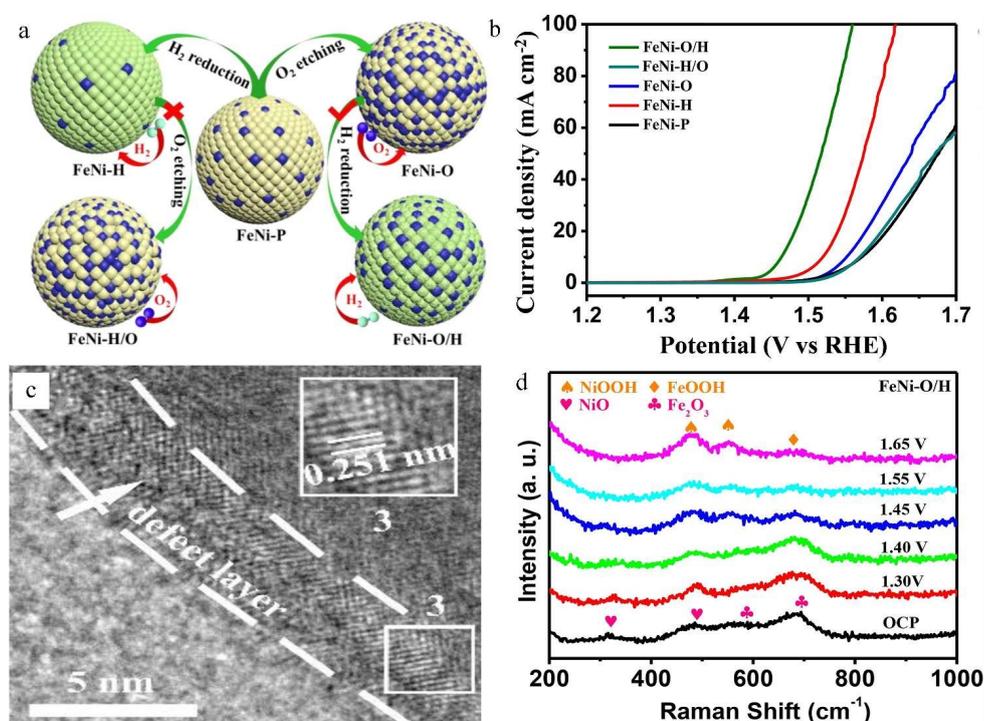


Figure 5 (a) Schematic illustration showing the synthesis of FeNi-based nanoparticles. (b) Polarization curves of FeNi-P, FeNi-O, FeNi-H, FeNi-O/H, and FeNi-H/O. (c) HRTEM image of FeNi-O/H. (d) Raman spectra of FeNi-O/H for OER at different potentials in 1 mol · L⁻¹ KOH^[74]. (color on line)

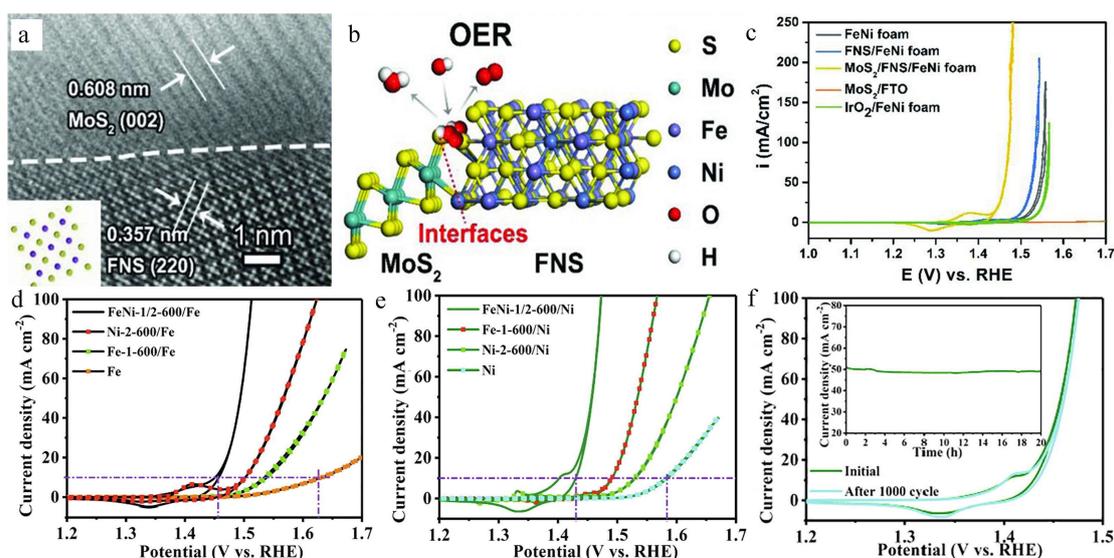


Figure 6 (a) Atomic-resolution HAADF-STEM image of MoS₂/FNS interface. (b) The mechanisms of MoS₂/FNS coupling interfaces acting on OER. (c) CV curves of all the samples in 1 mol·L⁻¹ KOH aqueous electrolyte^[81]. (d) Cyclic voltammetric curves of FeNi-1/2-600/Fe, Fe-1-600/Fe, Ni-2-600/Fe and Fe slice. (e) Cyclic voltammetric curves of FeNi-1/2-600/Ni, Fe-1-600/Ni, Ni-2-600/Ni and Ni slice. (f) The stability test of FeNi-1/2-600/Ni^[83]. (color on line)

construction is a promising and cost-efficient way to fabricate OER electrocatalyst.

3.6 Support Effect

In addition to the catalytic active phase, support is also vital in the catalyst system. Active species alone are usually confronted with the problems of aggregation, inactivation, and instability. For FeNi-based catalysts in OER, many substrates like carbon materials, metal-organic frameworks, metal foam, and Prussian blue analog have all been employed to support FeNi active components^[84-86]. Several studies confirmed that the FeNi-based catalysts deposited on certain supports have higher catalytic activity than the unsupported ones^[87]. For example, the FeNi LDH immobilized on the reduced graphene oxide (rGO) was reported to have better OER performance compared with the unsupported catalyst and traditional planer electrode^[88]. At the same time, some problems also arise when using support including the contamination of carbon support and the activity overestimation of rigid metal foam^[89]. Thus, it is necessary to explore the influence of support in the whole catalyst system. We conducted a study to probe the support effect and Fe/Ni synergistic effect where the amorphous FeNi

hydroxide was electrodeposited on the plane metal foil electrodes^[83]. For specific, the influence of the Fe and Ni foil support electrode and the electrolyte containing different amounts of Fe and Ni were investigated. Experimental results revealed that the FeNi supported on the Ni foil possessed much better OER performance than the Fe foil supported catalyst in the condition of similar chemical states of Fe and Ni. Moreover, the synergism of FeNi was also verified by observing the different redox peaks of Ni species on different Fe/Ni electrodes as reflected in cyclic voltammetric curves (Figure 6d and e). The surface roughness and electrochemical surface area were also altered resulting from the support effect. Finally, the optimized electrode delivered a current density of 10 mA·cm⁻² at an ultralow overpotential of ca. 200 mV (Figure 6f) accompanying with outstanding durability in 20 h long-term stability test. To sum up, the rational design of support can be an efficient strategy to improve the catalytic performance of FeNi-based catalyst for OER. Further study of the relationship and interaction between active phases and support may provide useful guidance to the development of FeNi-based catalysts.

4 Conclusions and Perspectives

FeNi-based materials have been regarded as the most promising alternatives to noble metal catalysts for OER due to their low cost, high catalytic activity, rich active phases, and various composition tuning. Though the real active phase was the *in situ* formed high valence state of Fe/Ni species based on the catalytic mechanism, the property of FeNi-based pre-catalyst largely influences their catalytic performance. It can be concluded that by carefully designing the surface structure and tuning the chemical environment, the interactions between reactant and catalyst can be enhanced, thereby improving the OER electrocatalysis performance. The surface structure engineering of FeNi-based pre-catalyst for OER can be realized by engineering strategies including element doping, composition modification, structure transformation, chemical state tuning, heterostructure construction, and support utilizing. As a result, the adsorption energy of intermediates and charge transfer ability can be improved via the electronic effect and synergistic effect; and the facile formation of metal (oxy)hydroxides active phase imparts these catalysts with high OER catalytic performance. It should be mentioned that the structural transformation from the low intrinsic FeNi alloy to other species with high intrinsic activity would be more direct and useful for the high-performance catalyst design and fabrication. These functionalization treatments like phosphorization, nitridation, and selenization, etc. can alter the polarity of chemical bonds, cause lattice distortion, and facilitate the *in situ* generations of metal (oxy)hydroxides, thereby greatly enhancing the OER catalytic activity.

Though a variety of surface engineering strategies have been employed to finely design the FeNi-based catalysts and remarkable progress has been made, there are still several problems and challenges that need to be emphasized.

(1) Catalyst modification: (i) Since the structural transformation of FeNi-based materials by incorporating nonmetal elements to form a new compound significantly improves the OER catalytic perfor-

mance, more nonmetal elements are desired. For example, the formation of fluoride has been proved to increase the polarity of chemical bonds which can facilitate the bond fracture and the generation of active intermediate species. (ii) Single-atom catalyst is believed to expose more active sites and improve the utilization rate of catalysts; thus, the dual FeNi single atoms system is also worth studying to fully take advantage of their synergistic effect. (iii) Apart from the modification of surface chemical properties, the physical properties (such as superoleophobicity surface, etc.) of catalyst surface also need to be improved to optimize the gas evolution behavior.

(2) Mechanism study: (i) High valent FeNi (oxy) hydroxides are widely known as the active species for OER, nevertheless, the clear reaction pathway, and the relationship between Fe and Ni still need to be identified, especially for the FeNi-based pre-catalysts with different structures. Recently, machine learning (ML) attracts much attention in many science and engineering fields, including catalysis. ML can build models from data to deeply understand the relevance between material property and catalytic activity. Thus, ML can be combined with *in situ* techniques, atomic-scale characterizations, and DFT calculations to clarify the specific reaction mechanism. It should be noted that each *in situ* characterization has its limitation and application range, the combination of multiple advanced detection techniques should be helpful to provide more information about the reaction mechanism. (ii) Many efforts have been devoted to improving the catalytic activity, however, the corrosion of harsh electrolytes and electrochemical cycle instability largely impede the OER performance of FeNi-based catalysts. It is urgent to improve the mechanical and electrochemical stabilities to meet the demand of the real application. Moreover, the surface structure reconstruction and deactivation mechanism should be carefully studied so as to guide the design of FeNi-based OER electrocatalysts. (iii) The field-effect has been employed to modify the catalysis conditions. Electric field and magnetic field have been reported to facilitate electron transfer and electron

spin polarization, respectively, which improve water oxidation. Especially as a magnetic material, the catalytic behavior of FeNi-based catalysts under the influence of a magnetic field is worth studying. Thus, applying an external driving field to the FeNi-based catalyst system may be an efficient strategy to boost the OER activity. (iv) To narrow the gap between laboratory testing and practical device performance, the change of dynamic, mass transfer, local pH value, and bubble evolution rate should be fully explored.

(3) Large-scale production and practical application: (i) The synthesis method of FeNi-based catalysts needs to be further optimized, and a good design and fabrication approach should meet the demands of large-scale production, environmental friendliness, and recyclability. (ii) FeNi-based OER catalysts are mainly tested in an alkaline medium, thus the development of an alkaline water electrolyzer equipped with an anion exchange membrane (AEM) is significant in their practical application for OER. Nevertheless, the supported catalyst faces the problem of dissolution and poisoning effect under the conditions of high working current density and harsh electrolyte in the AEM electrolyzer. Besides, the issues of substrate corrosion and passivation, as well as the ionomer binders degradation, should be taken into account. (iii) One thing should be mentioned that nowadays water splitting demands ultrapure electrolytes to avoid side reactions and contaminations, considering the extreme situations and underdeveloped areas, the robust FeNi-based catalyst that can resist the impurities in the electrolyte needs future exploration.

Notes

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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 re-

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析氧反应铁镍基预催化剂的表界面调控与进展

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摘要: 析氧反应(OER)是水分解中重要的半反应, 为提高其催化性能, 开发高效非贵金属催化剂已成为当前的研究重点。铁镍(FeNi)基材料被认为是最好的预催化剂, 在催化过程中, 它们的表面将转变成高价态金属氧化物或氢氧化物作为真正的活性物质。FeNi 基预催化剂的结构和形貌在很大程度上影响了其催化性能, 因此, 优化和调整 FeNi 基预催化剂的结构和化学环境可以提高电催化性能。基于我们的研究工作, 我们撰写了 FeNi 基预催化剂的表面结构调控促进电化学析氧反应的研究进展。我们首先介绍了碱性 OER 的反应机理, 然后从杂原子掺杂、表面成分改性、选择性结构转变、表面化学状态调节、异质结构构建和载体效应等方面讨论了 FeNi 基预催化剂表面调控对析氧反应性能的影响。尽管在 OER 反应中 FeNi 都被认为转变成高价态的金属活性物质, Fe/Ni 体系的表面结构、形貌和化学状态仍然能够显著影响其最终的催化性能, 即 FeNi 基预催化剂的性质会影响析氧反应的催化性能。通过精细设计并尽量提高 Fe 和 Ni 的协同作用将有利用提升氧析出的催化性能。我们希望本综述能够对 FeNi 基预催化剂的制备和表界面性质调控与电催化析氧反应性能的理解有所帮助。

关键词: 铁镍基催化剂; 表面结构调控; 析氧反应; 水分解反应; 催化作用