



# Engineering of Self-Supported Electrocatalysts on a Three-Dimensional Nickel Foam Platform for Efficient Water Electrolysis

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## Abstract

Economical water electrolysis requires highly active non-noble electrocatalysts to overcome the sluggish kinetics of the two half-cell reactions, oxygen evolution reaction, and hydrogen evolution reaction. Although intensive efforts have been committed to achieve a hydrogen economy, the expensive noble metal-based catalysts remain under consideration. Therefore, the engineering of self-supported electrocatalysts prepared using a direct growth strategy on three-dimensional (3D) nickel foam (NF) as a conductive substrate has garnered significant interest. This is due to the large active surface area and 3D porous network offered by these electrocatalysts, which can enhance the synergistic effect between the catalyst and the substrate, as well as improve electrocatalytic performance. Hydrothermal-assisted growth, microwave heating, electrodeposition, and other physical methods (i.e., chemical vapor deposition and plasma treatment) have been applied to NF to fabricate competitive electrocatalysts with low overpotential and high stability. In this review, recent advancements in the development of self-supported electrocatalysts on 3D NF are described. Finally, we provide future perspectives of self-supported electrode platforms in electrochemical water splitting.

**Keywords** Nickel foam · Water splitting · Surface modification · Hydrothermal method · Microwave-assisted method · Electrodeposition · Chemical vapor deposition · Plasma treatment

## Introduction

The limited reserves of traditional fossil energy sources and many environmental problems resulting from their use have prompted many researchers to search for efficient and clean renewable energy sources. Among various clean energy technologies, electrochemical water splitting from renewable power is one of the most promising strategies to produce sustainable hydrogen as a green chemical fuel and energy carrier [1, 2]. However, the slow kinetics of the two half-cell reactions, namely the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) at the electrode interfaces, remain the major obstacle to hydrogen economy [3, 4]. Thus, extensive attention has been paid to design highly active electrocatalysts for overall water splitting. Noble metal-based electrocatalysts, specifically Ru/Ir- and Pt-based materials, are still the most employed electrocatalysts for OER and HER, respectively, but their high cost and scarce elemental reserves restrict their further applications [5, 6]. Transition metal-based catalysts have

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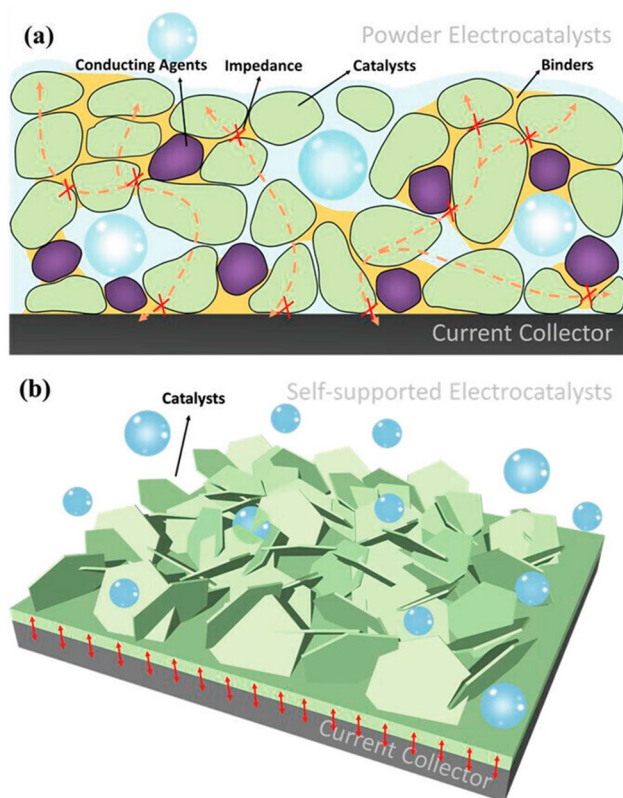
components with a rich modulation range, including hydroxides [7], oxides [8], carbides [9], sulfides [10], phosphides [11], and nitrides [12]. Although they are easily fabricated and cheap, their electrocatalytic activity and long-term stability need improvement [13].

Different types of electrocatalysts are often prepared in the form of powder particles and developed with binders (i.e., Nafion) and conductive agents (i.e., carbon black) to form a slurry-like paste, which is then coated on the conductive substrates or known as current collectors (Fig. 1a) [14], which are utilized to prepare electroactive substrates. However, binders can clog the active sites and hinder electron transfer processes [15, 16]. Conductive agents oxidize at higher operating potentials and limit the mass transfer of reactants [17]. Moreover, under prolonged scouring of the gas bubbles produced by water electrolysis, the electrocatalytic coating tends to detach from the electrode surfaces, resulting in a decrease in or even the disappearance of catalytic activity [18]. To overcome these issues, binder-free self-supported electrocatalysts have been developed, which can be directly grown on conductive substrates (Fig. 1b) [14]. The main advantages of fabricating such self-supported electrocatalysts over powdery-coated ones are as follows:

1. Simple electrode preparation steps can be performed while reducing the manipulating cost and loading mass [19, 20].
2. More active sites are exposed at the interface without using binders or conductors [21, 22].
3. The catalyst particles are firmly attached to the current collector, which significantly reduces the possibility of mechanical detachment [23].
4. Stability and catalytic activity can be further improved by forming hydrophilic/hydrophobic interfaces by modulating the morphology and microstructure of the active substances [24, 25].

These abovementioned advantages make self-supported electrocatalysts more applicable for practical engineering applications. Therefore, various conductive substrates have been used for growing many self-supported electrocatalysts, such as carbon paper [26], titanium foil [27], stainless steel [28], nickel foam (NF) [29], and copper foam [30]. Among them, NF is the most preferred conductive substrate because of its high electrical conductivity, large specific surface area for high catalyst loading and good dispersion, and continuous porous structure that facilitates mass transfer and gas bubble diffusion [31].

In fact, detailed reviews on self-supported electrocatalysts and conductive substrates have been published [14, 19, 23, 32–39]. However, no systematic review has reported surface modification strategies and related research progress on NF substrates. In this brief review, we put emphasis on several surface modification strategies commonly utilized for the direct growth of self-supported electrocatalysts on NF substrates, such as hydrothermal- and microwave-assisted growth, electrodeposition, chemical vapor deposition (CVD), and plasma treatment. Finally, we offer perspectives and challenges regarding self-supported electrode materials in water electrolysis.



**Fig. 1** **a** Schematic illustration of coated powdery-type electrocatalysts; **b** schematic illustration of self-supported electrocatalyst. Reproduced with permission from Ref. [14]. Copyright © 2021, Wiley

## Hydrothermal-Assisted Growth of Nanostructured Materials on the NF

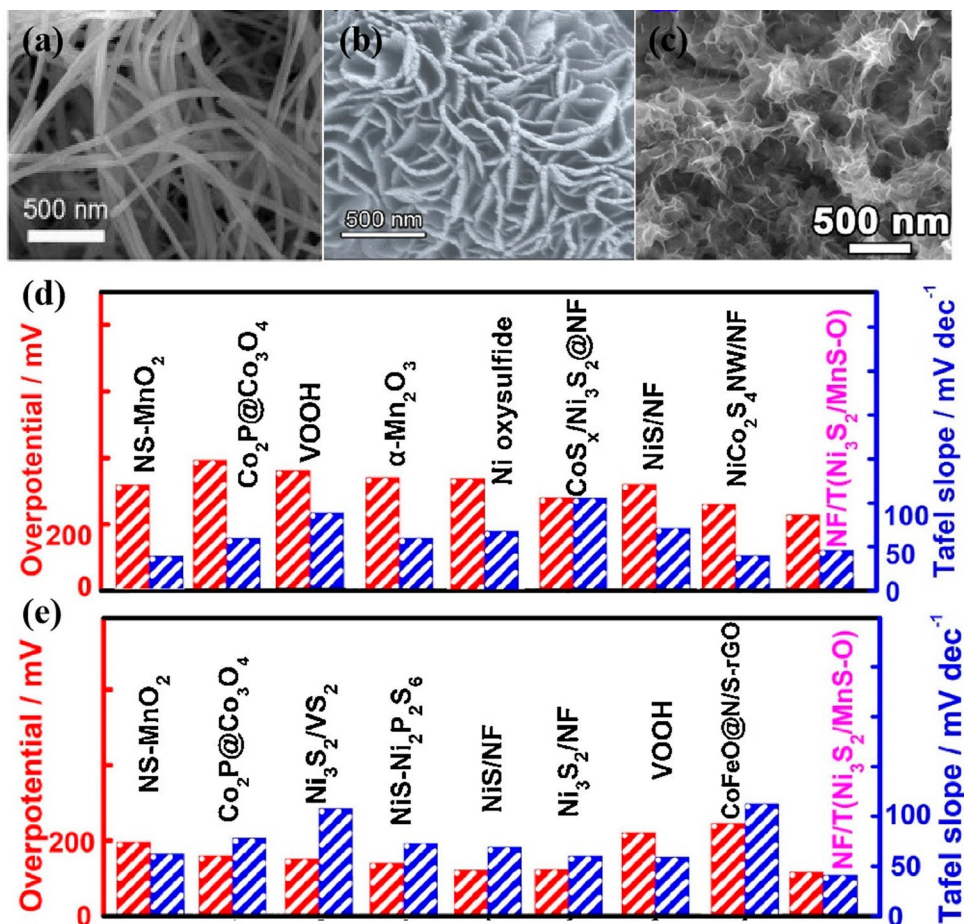
The hydrothermal strategy is defined as the formation of materials in aqueous solutions using consecutive steps of dissolution and recrystallization in a closed system at high temperature and high pressure [40].

Therefore, volatilization of reactants at high temperatures, stress-induced defects, and mutual reaction between phases can be avoided. Further, the reaction conditions, such as composition, time, and temperature, can be easily controlled, thereby controlling the structure, size, morphology, and crystallinity of the resulting products [41, 42]. High-purity nanoparticles with good dispersibility, uniform morphology, and complete grain boundaries can be obtained

[43]. These benefits make the hydrothermal strategy a promising method for the direct growth of electroactive catalysts on NF substrates. Tang et al. [44] prepared NiSe nanowires grown on NF by one-step hydrothermal treatment of NF using NaHSe as the selenium source (Fig. 2a). NiSe/NF presented remarkable bifunctional electrocatalytic activity in an alkaline 1.0 mol/L KOH electrolyte with an OER overpotential ( $\eta_{20}$ ) of 270 mV at 20 mA/cm<sup>2</sup> and HER overpotential ( $\eta_{10}$ ) of 96 mV at 10 mA/cm<sup>2</sup>. Moreover, NiSe/NF exhibited good stability for overall water splitting after 20 h by applying a cell voltage of 1.74 V to deliver 20 mA/cm<sup>2</sup>. The corresponding Raman spectroscopy analysis disclosed the formation of an electroactive layer of NiOOH on the surface of NiSe nanowires during the electrolysis process. Thus, the authors concluded that the generation of the oxy-hydroxide phase (-OOH) might be the key factor for the outstanding bifunctional catalytic activity of NiSe/NF [45, 46]. Dinh et al. [47] also applied a one-step hydrothermal method for the in-situ growth of porous ultrathin NiFeV-LDH nanosheets on NF substrates (Fig. 2b). By preparing different molar ratios of Ni:Fe:V solutions and comparing the electrochemical efficiency, they

observed that remarkable electrocatalytic performance can be realized using a molar ratio of 6:1:1 for the preparation of Ni<sub>0.75</sub>Fe<sub>0.125</sub>V<sub>0.125</sub>-LDHs/NF. The polarization curves of Ni<sub>0.75</sub>Fe<sub>0.125</sub>V<sub>0.125</sub>-LDHs/NF revealed an overpotential for OER at 231 mV and that for HER at 125 mV at a current density of 10 mA/cm<sup>2</sup> in 1.0 mol/L KOH, which could be stabilized at 30 mA/cm<sup>2</sup> for 15 h. The remarkable catalytic performance of Ni<sub>0.75</sub>Fe<sub>0.125</sub>V<sub>0.125</sub>-LDHs/NF is mainly due to the synergistic effect of the ternary metal system, which improves the intrinsic electrocatalytic activity, besides the ultrathin porous character, which increases the surface area and number of active sites. Zhang et al. [48] synthesized binary sulfides of Ni<sub>3</sub>S<sub>2</sub>/MnS nanosheets on NF by two-step hydrothermal treatment using KMnO<sub>4</sub> and Na<sub>2</sub>S precursors, followed by electro-oxidation of the Ni<sub>3</sub>S<sub>2</sub>/MnS/NF substrate at 1.6 V vs. RHE to produce NF/T(Ni<sub>3</sub>S<sub>2</sub>/MnS-O) with ultrathin nanosheets and abundant oxygen vacancies (Fig. 2c). The abundant oxygen vacancies and hierarchical porous nanosheet structure not only provide enough space for penetration and diffusion of the electrolyte but also increase the number of active sites and accelerate the charge transfer process. Compared with other reported metal oxides

**Fig. 2** **a** High-magnification SEM images of NiSe/NF. Reproduced with permission from Ref. [44]. Copyright © 2015, Wiley; **b** field-emission SEM images of Ni<sub>0.75</sub>Fe<sub>0.125</sub>V<sub>0.125</sub>-LDHs/NF. Reproduced with permission from Ref. [47]. Copyright © 2018, Wiley; **c** SEM images of NF/T(Ni<sub>3</sub>S<sub>2</sub>/MnS-O); **d** comparison of overpotential and Tafel slope of OER between the NF/T(Ni<sub>3</sub>S<sub>2</sub>/MnS-O) and reported metal oxide and sulfide catalysts; **e** comparison of overpotential and Tafel slope of HER between the NF/T(Ni<sub>3</sub>S<sub>2</sub>/MnS-O) and reported metal oxide and sulfide catalysts. Reproduced with permission from Ref. [48]. Copyright © 2018, Elsevier



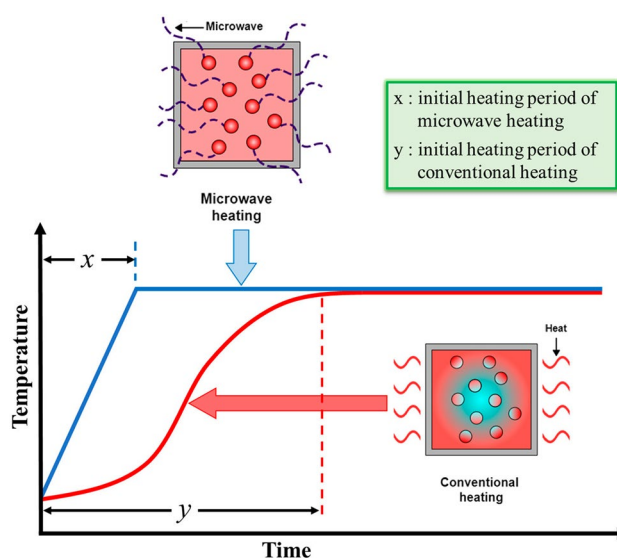
and sulfides [49–61], NF/T(Ni<sub>3</sub>S<sub>2</sub>/MnS–O) showed promising electrocatalytic activity due to its low OER and HER overpotentials and small Tafel slopes (Fig. 2d, e).

Further improvement in the catalytic performance of self-supported electrode materials can be achieved by doping of nonmetallic elements via multistep processes. For instance, Lu et al. [62] built CoMoN<sub>x</sub> nanosheet arrays on NF by one-step hydrothermal treatment followed by nitridation in an NH<sub>3</sub>/Ar atmosphere. For the optimal CoMoN<sub>x</sub>-500 nanosheet arrays (NSAs)/NF (CoMoN<sub>x</sub>-500 NSAs/NF) at a current density of 10 mA/cm<sup>2</sup>, the 3D interconnected NSAs and the synergistic effect between Co<sub>2</sub>N and Mo<sub>2</sub>N improved the charge transfer process and further decreased the overpotentials of OER and HER to 231 mV and 91 mV, respectively. Using the CoMoN<sub>x</sub>-500 NSAs/NF as an electrolyzer for overall water splitting, a current density of 10 mA/cm<sup>2</sup> was delivered by applying a cell voltage of 1.55 V. Similarly, Chen et al. [63] synthesized P-doped FeNiRh nanosheet arrays on NF by one-step hydrothermal treatment and continuous phosphatization. The prepared P-FeNiRh/NF demonstrated an OER overpotential of 226 mV at 30 mA/cm<sup>2</sup> and an HER overpotential of 73 mV at 10 mA/cm<sup>2</sup>. It can be noted that, the P-FeNiRh/NF can be efficiently utilized for overall water splitting, with a cell voltage of 1.62 V required to realize a current density of 10 mA/cm<sup>2</sup>.

### Microwave-Assisted Growth of Nanostructured Materials on the NF

Microwave-assisted growth is a common method for in situ growth of nanostructured materials on NF. It uses microwave arrays, which are a type of electromagnetic wave in the frequency range of 900 MHz–2.45 GHz, for controlling the heating process [64]. As an alternative heating source, microwave arrays transfer energy by causing dipole polarization and ion migration without changing the molecular structure [65]. Moreover, microwave arrays can uniformly heat the reactant at different depths, thus refining the crystal size and morphology of the nanomaterials [40]. Compared with the conventional hydrothermal method, the microwave-assisted method has a shorter initial heating period, which significantly speeds up the heating process and decreases the reaction time, whereas the hydrothermal method has a slow heat transfer mechanism, longer initial heating period, and nonconstant rate of heating (Fig. 3) [66, 67]. Thus, high material yield and pure and uniform nanoparticles with desired morphology can be easily fabricated using the microwave-assisted method [66].

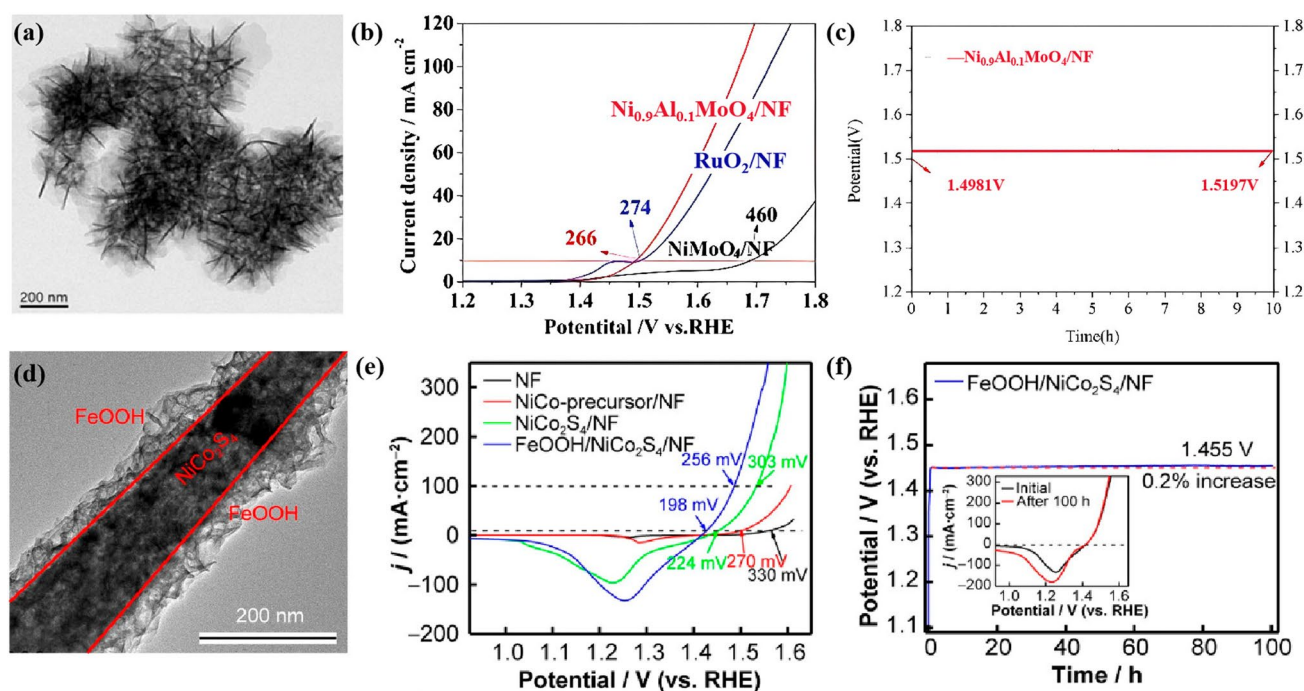
With regard to monofunctional self-supported electrode materials, Duan et al. [68] employed a microwave-assisted solvothermal method to grow trimetallic molybdate



**Fig. 3** Schematic diagrams and initial heating periods of microwave-assisted and conventionally-heated hydrothermal synthesis. Reproduced with permission from Refs. [66, 67]. Copyright © 2014, MDPI

nanoflowers on NF (Fig. 4a). The high specific surface area of the nanoflower-like structure and the synergistic effect between the multimetals increased the number of active sites and electrocatalytic activity. The OER overpotential of the prepared Ni<sub>0.9</sub>Al<sub>0.1</sub>MoO<sub>4</sub>/NF at 10 mA/cm<sup>2</sup> was 266 mV, which is lower than that of the commercial RuO<sub>2</sub>/NF electrode material (274 mV) (Fig. 4b). Furthermore, Ni<sub>0.9</sub>Al<sub>0.1</sub>MoO<sub>4</sub>/NF also showed good stability for actual water splitting at a cell voltage of 1.52 V, which can deliver a current density of 10 mA/cm<sup>2</sup> for 10 h (Fig. 4c). Furthermore, Guo et al. [69] utilized two-step hydrothermal treatments followed by microwave-assisted irradiation to grow the FeOOH/NiCo<sub>2</sub>S<sub>4</sub> core-shell nanorod morphology on NF. It was found that the nanosheets formed by FeOOH uniformly covered the NiCo<sub>2</sub>S<sub>4</sub> surface (Fig. 4d). The strongly coupled interface consisting of Ni/Co–S–Fe not only modulated the electronic structure of the active elements but also decreased the adsorption free energy of the reaction intermediates, which improved the catalytic activity of this electrode material. Compared with the hydrothermally synthesized NiCo<sub>2</sub>S<sub>4</sub>/NF, the microwave-irradiated FeOOH/NiCo<sub>2</sub>S<sub>4</sub>/NF showed a lower OER overpotential  $\eta_{10}$  of 198 mV, a Tafel slope of 62 mV/dec, and an outstanding stability with only 0.2% reduction after 100 h of operation at 1.49 V. (Fig. 4e, f).

Regarding bifunctional self-supported electrode materials, Ren et al. [70] prepared RuCoMo<sub>y</sub>O<sub>x</sub>/NF using coprecipitation and microwave-assisted heating (Fig. 5a). The ratio of amorphous (RuCoMoO<sub>x</sub>) to crystalline (CoMoO<sub>4</sub> and CoO) regions was affected by changing the reaction time, which



**Fig. 4** **a** TEM images of the  $\text{Ni}_{0.9}\text{Al}_{0.1}\text{MoO}_4/\text{NF}$ ; **b** LSV curves of  $\text{Ni}_{0.9}\text{Al}_{0.1}\text{MoO}_4/\text{NF}$ ,  $\text{NiMoO}_4/\text{NF}$ , and  $\text{RuO}_2/\text{NF}$ ; **c** Stability test of the  $\text{Ni}_{0.9}\text{Al}_{0.1}\text{MoO}_4/\text{NF}$  ( $10 \text{ mA}/\text{cm}^2$ ,  $1 \text{ mol}/\text{L}$  KOH). Reproduced with permission from Ref. [68]. Copyright © 2021, Wiley; **d** TEM images with of the  $\text{FeOOH}/\text{NiCo}_2\text{S}_4/\text{NF}$ ; **e** LSV curves of NF, NiCo-

precursor/NF,  $\text{NiCo}_2\text{S}_4/\text{NF}$ , and  $\text{FeOOH}/\text{NiCo}_2\text{S}_4/\text{NF}$  under 85% IR compensation; **f** Stability test of the  $\text{FeOOH}/\text{NiCo}_2\text{S}_4/\text{NF}$  ( $10 \text{ mA}/\text{cm}^2$ ,  $1 \text{ mol}/\text{L}$  KOH). Reproduced with permission from Ref. [69]. Copyright © 2023, Springer Link

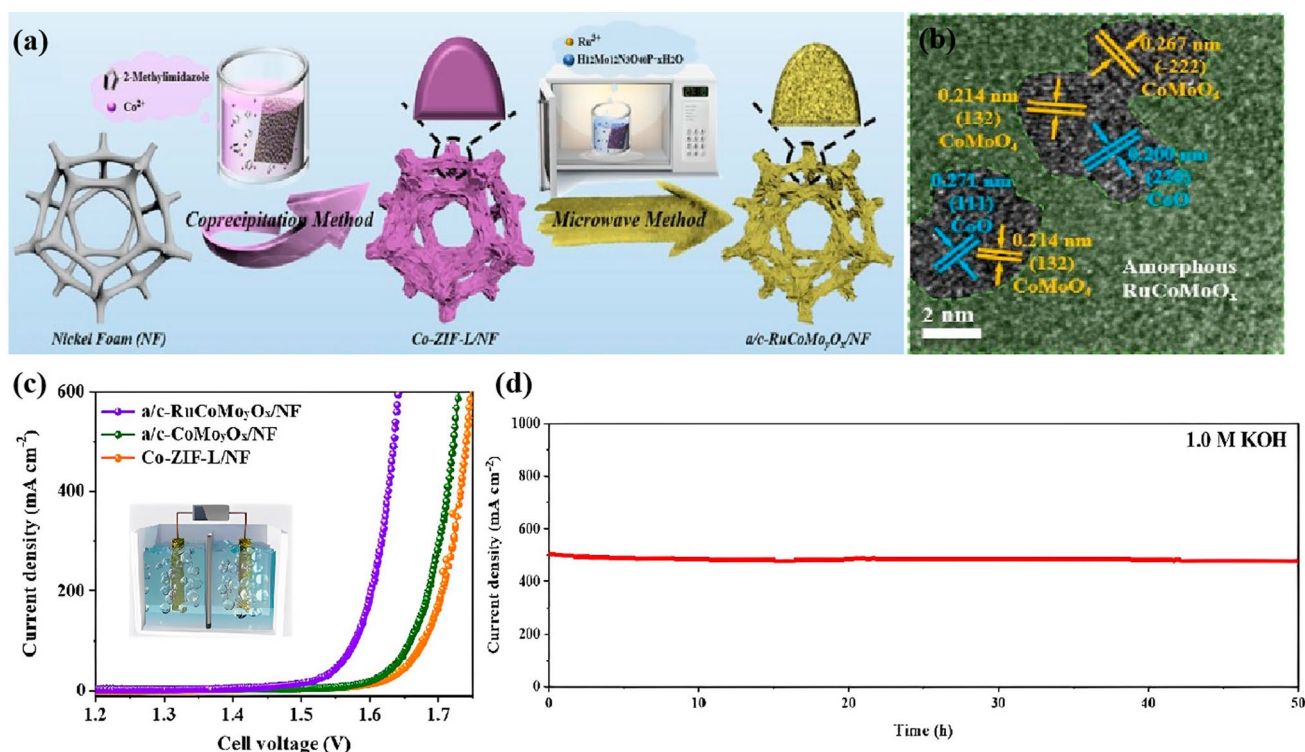
resulted in the formation of numerous amorphous/crystalline (a/c) heterointerfaces in  $\text{RuCoMo}_y\text{O}_x/\text{NF}$  (Fig. 5b). The amorphous phase in the a/c heterointerface has remarkable structural flexibility due to the disordered arrangement of internal atoms, which is suitable for the reconstruction of the surface structure of the electrocatalyst and the improvement of corrosion resistance during the electrocatalytic process [71]. Concurrently, many unsaturated ligand bonds in the a/c heterointerface are involved in the construction of active sites [72]. The a/c- $\text{RuCoMo}_y\text{O}_x/\text{NF}$  heterointerfaces showed remarkable bifunctional electrocatalytic activity with HER and OER overpotentials of 39 mV and 166 mV, respectively, at  $10 \text{ mA}/\text{cm}^2$ . Furthermore, the a/c- $\text{RuCoMo}_y\text{O}_x/\text{NF}$  could achieve a current density of  $100 \text{ mA}/\text{cm}^2$  in the overall water splitting system at a voltage of only 1.58 V and could continuously output an industrial-grade current density ( $500 \text{ mA}/\text{cm}^2$ ) for 50 h at a constant voltage of 1.64 V (Fig. 5c, d).

In this context, Nadarajan et al. [73] constructed a heterointerface structure consisting of multiple CoMo oxides ( $\text{CoO}/\text{CoMoO}_3/\text{Co}_2\text{Mo}_3\text{O}_8$ ) on NF using microwave-assisted heating followed by annealing. The multiphase heterointerface composition was optimized by changing the molar ratio of cobalt/molybdenum and annealing time to enhance its bifunctional electrocatalytic activity, which required 51 mV for HER and 293 mV

OER at  $10 \text{ mA}/\text{cm}^2$ . By maintaining the ratio of Co:Mo at 1.25:1, followed by annealing at  $450 \text{ }^\circ\text{C}$  for 2 h, the  $\text{CoMoO-1.25}/\text{NF}$  electrolyzer exhibited high durability for 500 h in the water splitting process at an operating cell voltage of 1.63 V, which could deliver a current density of  $10 \text{ mA}/\text{cm}^2$ .

Although hydrothermal- or microwave-assisted growth of self-supported electrodes has been broadly applied for producing novel electrocatalysts, they have some limitations summarized as follows:

1. Expensive autoclaves consist of a high-strength alloy shell and a polytetrafluoroethylene (PTFE) liner to withstand high temperatures and pressures (Fig. 6a) during the reaction and protect the autoclave body from corrosion by chemical solutions [66, 74].
2. The hydrothermal- or microwave-assisted reaction mechanism is unclear because the chemical reaction occurs in a closed system. Therefore, it is difficult to follow the nucleation and growth mechanisms [75, 76].
3. The desired morphology, size, and composition of the final products, particularly in the nanosized dimension, cannot be easily controlled.
4. There is a lack of control the catalyst quantity grown on the conductive substrate because the active substrates can



**Fig. 5** **a** Schematic diagram of the preparation of the a/c-RuCoMo<sub>x</sub>O<sub>y</sub>/NF; **b** HRTEM image of the a/c heterointerface; **c** LSV curve of the a/c-RuCoMo<sub>x</sub>O<sub>y</sub>/NF to the overall water splitting; **d** Stability

test of the a/c-RuCoMo<sub>x</sub>O<sub>y</sub>/NF (1.64 V, 1 mol/L KOH). Reproduced with permission from Ref. [70]. Copyright © 2023, Elsevier

interact with the reaction medium and form undesirable composite materials.

5. The undesired products or impurity species cannot be easily removed from the obtained self-supported electrocatalysts.

6. Hydrothermal- and microwave-assisted reactions take a long time.

## Electrodeposition of Nanostructured Materials on the NF

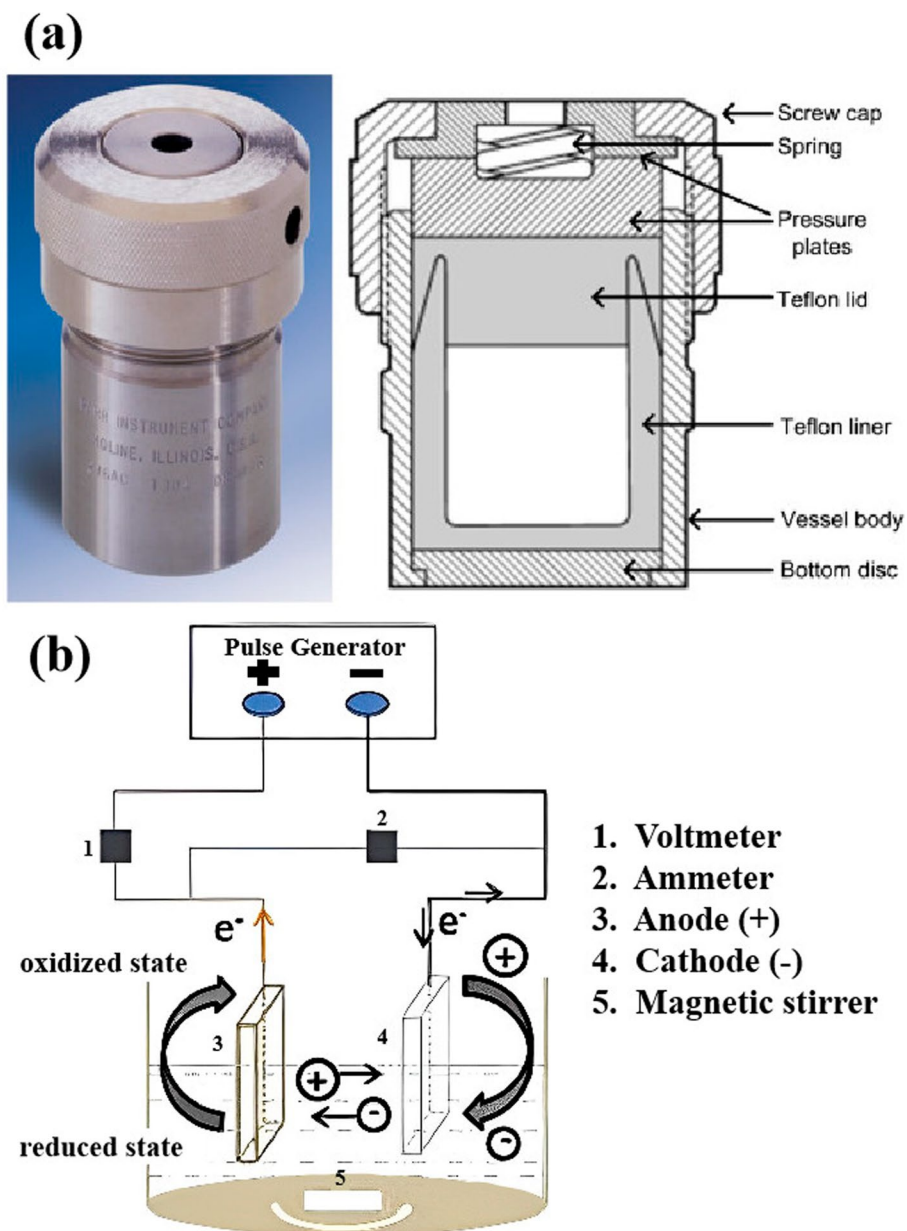
On the other hand, the electrodeposition strategy has garnered more and more attention because it provides a short time consumption, easy operation, and easy optimization of the loading quality on the electrode surface (Fig. 6b) [77]. Thus, the resulting electrocatalysts have high purity and strong bond energies with the substrates, which increases electron mobility and overall electrocatalytic activity [78, 79].

The design of uniformly stable and mutually coupled multiphase structures of electrocatalysts on NF conductive substrates can be easily performed by electrodeposition. For instance, Lee et al. [80] synthesized hollow CoS<sub>x</sub> triangular nanoarrays on NF using the coprecipitation–solvochemical

method and then electrodeposited the CoS<sub>x</sub> nanoarrays with NiFe-LDH nanosheets to obtain a unique heterostructure H-CoS<sub>x</sub>@NiFe-LDH/NF (Fig. 7a). This unique heterointerface not only offers numerous active sites but also enhances the mass transfer and exhaust rates during water electrolysis. Meanwhile, the synergistic coupling effect between CoS<sub>x</sub> and NiFe-LDH stimulated the bifunctional electrocatalytic activity and realized HER and OER overpotentials at 95 mV and 250 mV to deliver 10 mA/cm<sup>2</sup>, respectively. Also, the actual water splitting voltage of the water electrolyzer with H-CoS<sub>x</sub>@NiFe-LDH/NF as the electrode material is only 1.59 V at 10 mA/cm<sup>2</sup>, and it can be operated stably for 100 h at a constant current density of 50 mA/cm<sup>2</sup>, demonstrating good stability (Fig. 7b, c).

Similarly, Yang et al. [81] prepared a NiFe-LDH@CoS<sub>x</sub>/NF self-supported electrode material by combining hydrothermal and electrodeposition methods to fabricate an amorphous CoS<sub>x</sub> phase on the surface of the hydrothermally synthesized NiFe-LDH nanosheets. The heterointerface constructed from CoS<sub>x</sub> and NiFe-LDH and their synergistic effects effectively promoted charge transfer and improved the bifunctional electrocatalytic activity. As a consequence, the HER and OER overpotentials of NiFe-LDH@CoS<sub>x</sub>/NF were 136 and 206 mV at 10 mA/cm<sup>2</sup>, respectively. The NiFe-LDH@CoS<sub>x</sub>/NF-based water

**Fig. 6 a** Structure diagram of a typical autoclave. Reproduced with permission from Ref. [74]. Copyright © 2019, Elsevier; **b** Schematic diagram of electro-deposition principle. Reproduced with permission from Ref. [77]. Copyright © 2022, Elsevier



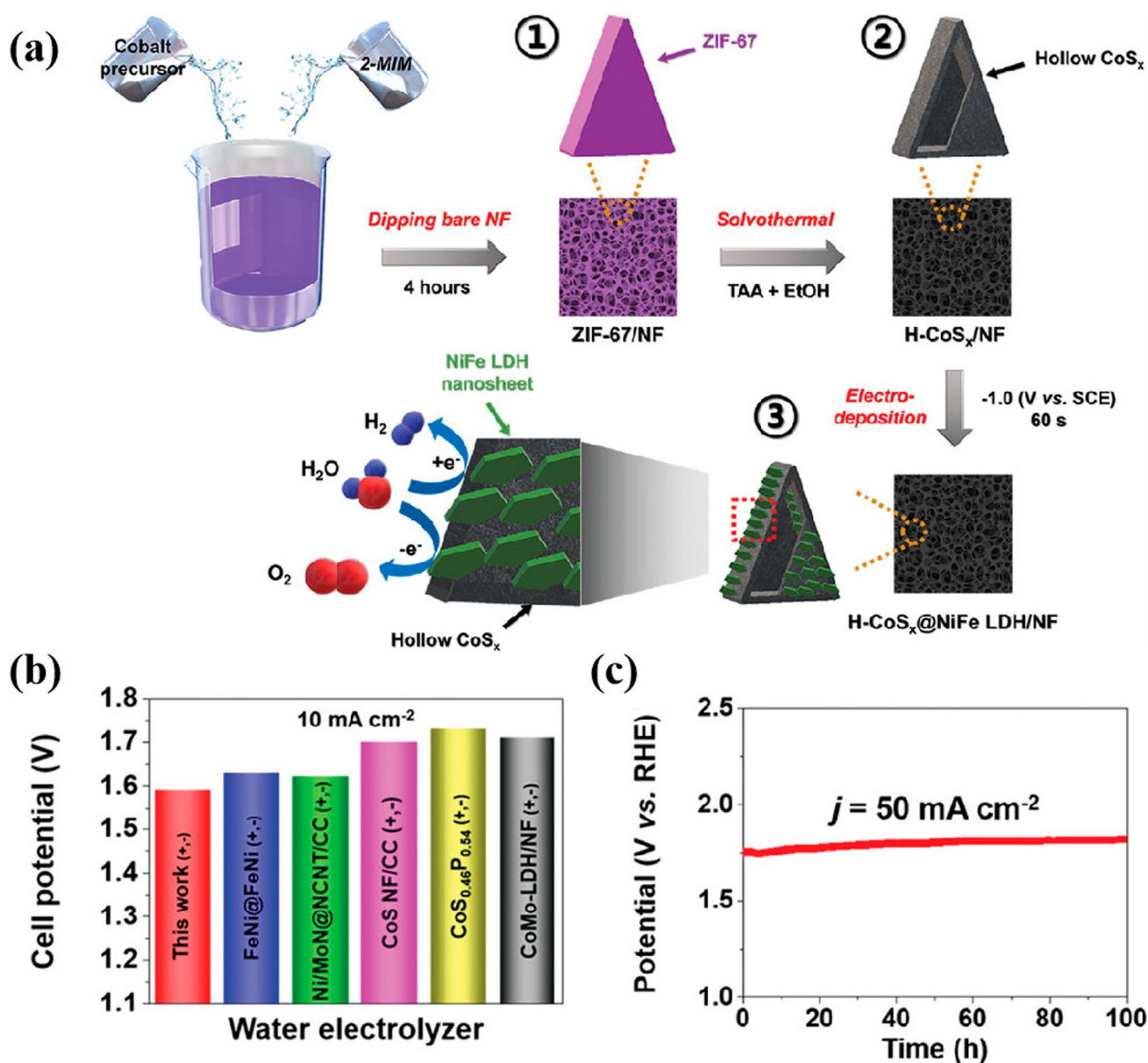
electrolyzer had an actual water splitting voltage as low as 1.537 V at 10 mA/cm<sup>2</sup> and demonstrated good stability for 25 h. The CoFe-LDH@NiFe-LDH/NF synthesized by Zhou et al. [82] by a similar strategy also presented outstanding bifunctional catalytic activity and stability. The CoFe-LDH@NiFe-LDH/NF-based water electrolyzer had an actual water splitting voltage of only 1.59 V at 10 mA/cm<sup>2</sup> and could be operated for 25 h.

## Other Methods for Growing Nanostructured Materials on NF

### CVD

CVD is a process in which a solid material is deposited from a vapor phase by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface (Fig. 8) [83].

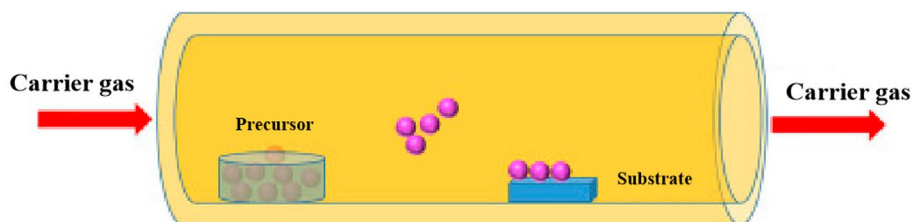
To prepare self-supported electrode materials, CVD is often combined with the above methods to dope



**Fig. 7** a Schematic illustration of the fabrication process for the H-CoS<sub>x</sub>@NiFe-LDH/NF; b Comparison of voltage values at 10 mA/cm<sup>2</sup> for the H-CoS<sub>x</sub>@NiFe-LDH/NF with other reported electrode

materials; c Stability test of the H-CoS<sub>x</sub>@NiFe-LDH/NF (50 mA/cm<sup>2</sup>, 1 mol/L KOH). Reproduced with permission from Ref. [80]. Copyright © 2022, Wiley

**Fig. 8** Schematic diagrams of a typical CVD process. Reproduced with permission from Ref. [83]. Copyright © 2021, Elsevier





nonmetallic elements onto the surface of the conductive substrate. The introduction of nonmetals, such as P, S, and NN, can further improve the catalytic activity of self-supported electrode materials, mainly because of the better adsorption properties of nonmetals for specific reaction intermediates compared with their metallic elements [84–87]. Sun et al. [88] grew NiO/CoO hydrothermally with nanorod and nanosheet morphologies on NF. Then, the surface of the NiO/CoO was phosphatized by plasma-enhanced CVD to produce NiCo phosphides with nanorod arrays (NiCo-P/NF), as illustrated in Fig. 9a. The doping of P elements onto NiO/CoO exhibited an outstanding HER activity with overpotentials of 78 and 80 mV at a current density of 10 mA/cm<sup>2</sup> in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> and 1.0 mol/L KOH, respectively. Feng et al. [89] made Mn–Co–P nanosheets on an NF electrode with a porous network by electrodeposition followed by CVD (Fig. 9b). Mn–Co–P/NF presented excellent electrocatalytic activity and stability with HER and OER overpotentials of 63 mV and 310 mV at 10 mA/cm<sup>2</sup>, respectively. The electrodes were used to construct an electrolyzer device that provided high stability for 25 h and required only 1.70 V to generate a current density of 20 mA/cm<sup>2</sup>.

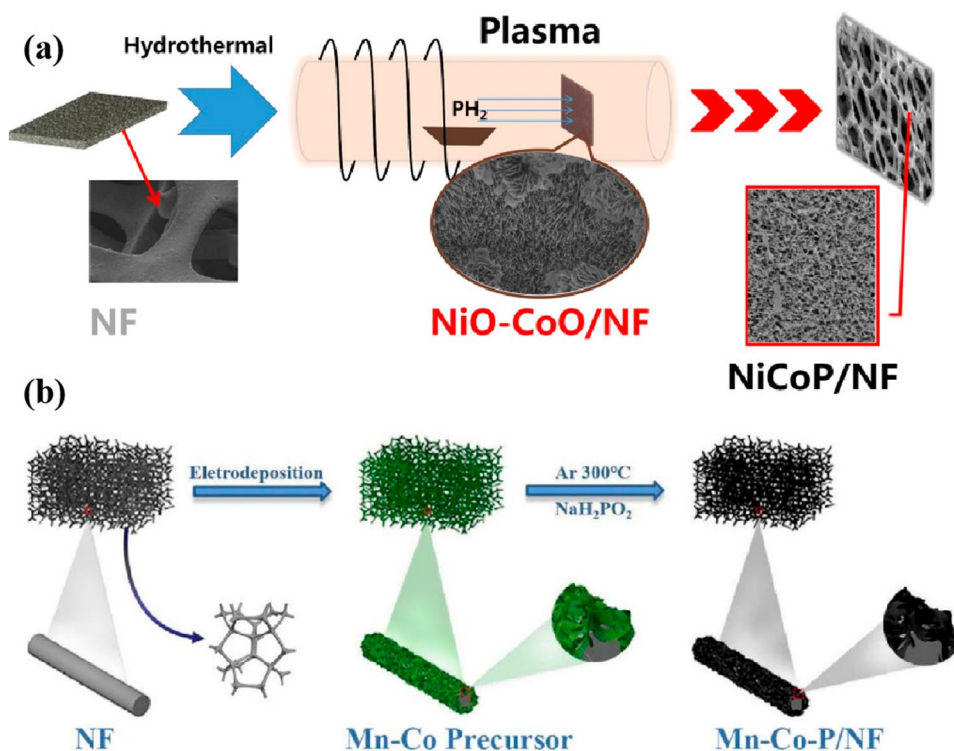
### Plasma Treatment

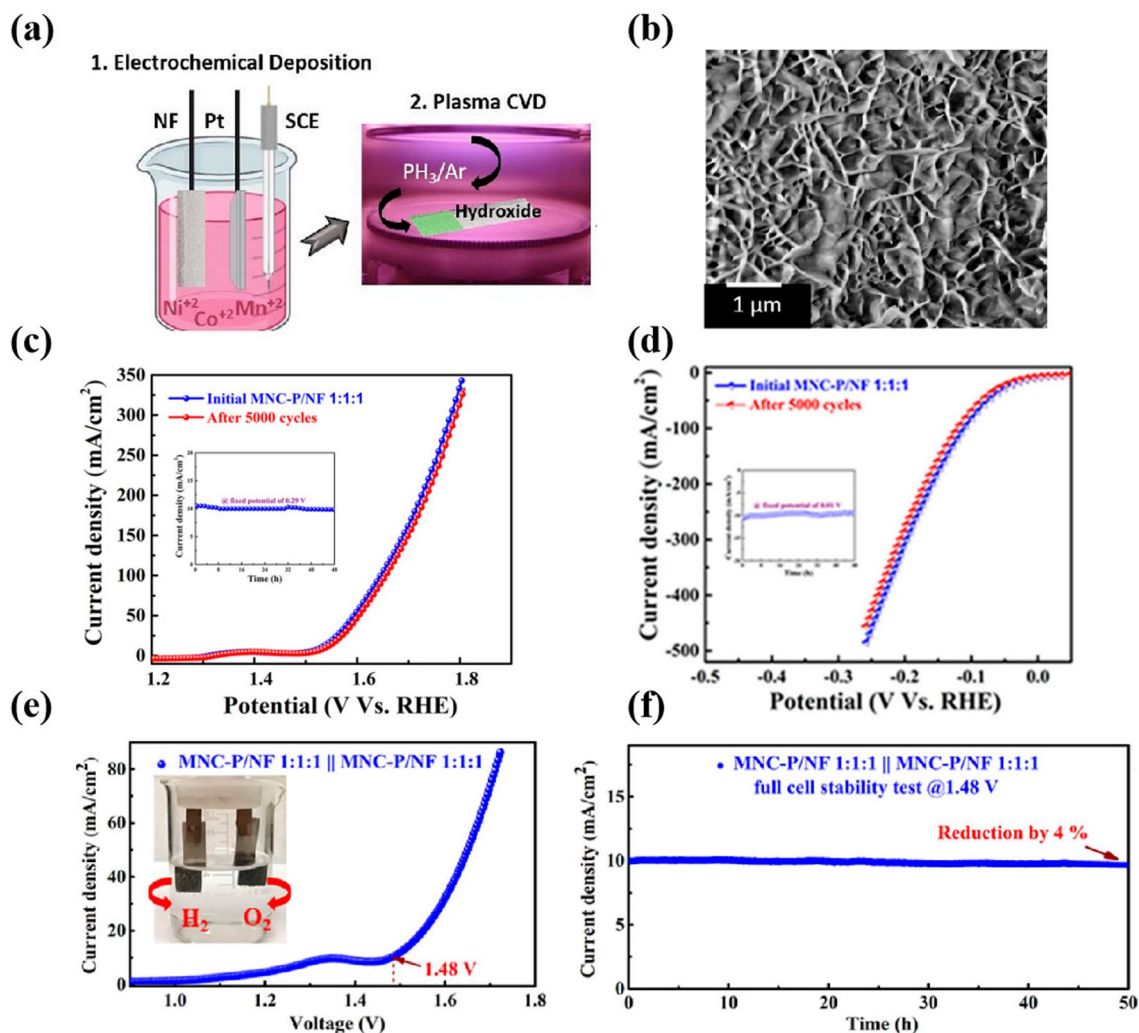
Plasma treatment is another physical surface treatment process that is often utilized as a subsequent process to

hydrothermal growth or electrodeposition steps to dope nonmetallic elements on the conductive substrate surface. For example, Salem et al. [90] used a combined electrodeposition and plasma treatment method to prepare MnNiCo-P with nanoflower-like morphology (MnNiCo-P/NF) on NF (Fig. 10a, b), with an OER overpotential of 289 mV at 10 mA/cm<sup>2</sup> in 1.0 mol/L KOH and HER overpotential as low as 14 mV. This electrode performed better than the commercially available Pt/C catalyst, and the LSV curves remained stable after 5000 cycles (Fig. 10c, d). Interestingly, the MnNiCo-P/NF-based water electrolyzer delivered a current density of 10 mA/cm<sup>2</sup> at a cell voltage of only 1.48 V and maintained 96% of the current density after 50 h, exhibiting extremely high stability (Fig. 10e, f).

Similarly, Fan et al. [91] synthesized NiVFe-LDHs/NFF with nanoflower hydrothermally on Ni–Fe foam (NFF). Then, the catalyst surface was simultaneously nitrated and phosphatized by plasma treatment to obtain N-NiVFeP/NFF with nanosheet arrays. Motivated by the synergistic effects of the multiphase heterointerface, numerous active sites provided by the nanosheet arrays, and increased conductivity after doping with N and P elements, N-NiVFeP/NFF showed remarkable bifunctional catalytic activity with HER and OER overpotentials of 79 mV and 229 mV at 10 mA/cm<sup>2</sup>, respectively. N-NiVFeP/NFF required only 1.52 V to produce a current density of 10 mA/cm<sup>2</sup> in the overall water splitting system and could be operated stably for 100 h.

**Fig. 9** **a** Schematic illustration of the synthesis process for the NiCo-P/NF. Reproduced with permission from Ref. [88]. Copyright © 2020, Elsevier; **b** Schematic illustration of the synthesis process for the Mn–Co–P/NF. Reproduced with permission from Ref. [89]. Copyright © 2021, Elsevier





**Fig. 10** **a** Schematic illustration of the synthesis process for the MnNiCo-P/NF; **b** FESEM images of the MnNiCo-P/NF; **c** OER cycling stability for the MnNiCo-P/NF before and after 5000 cycles; **d** HER cycling stability for the MnNiCo-P/NF before and after 5000

cycles; **e** LSV curve of the MnNiCo-P/NF to the overall water splitting; **f** Stability test of the MnNiCo-P/NF (1.48 V, 1 mol/L KOH). Reproduced with permission from Ref. [90]. Copyright © 2023, Wiley

Generally, CVD and plasma treatment are effective in doping nonmetallic elements onto the NF surface, but they cannot be used alone to grow nanostructured materials on NF. These methods are often used as after-treatments for hydrothermal-assisted growth, microwave-assisted growth, and electrodeposition growth to improve the adsorption of reaction intermediates and further enhance the intrinsic catalytic activity of self-supported electrode materials.

## Conclusions and Future Perspectives

The design of efficient non-noble metal electrocatalysts via self-supported strategies on 3D NF substrates has been reported in the literature to enhance their bifunctional

activity and stability and compete with commercially available noble metal-based electrodes. Various surface modification methods, such as hydrothermal-assisted growth, microwave-assisted growth, electrodeposition growth, CVD, and plasma treatment, have been employed to achieve self-supported strategies. The advantages and disadvantages of these methods are summarized in Table 1.

Briefly, no single method for constructing self-supported electrocatalysts is universally superior in catalytic activity to other methods. Researchers often propose composite process strategies to obtain self-supported electrocatalysts with higher performance. Based on the design principle of “coating, loading, and then doping,” multiphase heterostructures consisting of metal compounds are first grown on the conductive substrate by a

**Table 1** Comparison between commonly used surface modification methods for self-supported electrode materials

Methods	Synthetic cost	Synthetic time	Catalyst morphology	Mechanical stability (substrate)	Chemical stability (catalyst)
Hydrothermal-assisted growth	Relatively low	Long	Relatively good	Unstable	Stable
Microwave-assisted growth	Relatively low	Relatively long	Good	Relatively unstable	Stable
Electrodeposition	Low	Short	Relatively good	Stable	Relatively stable
Chemical vapor deposition	Relatively high	Relatively short	Relatively poor	Relatively stable	Relatively stable
Plasma treatment	Relatively high	Relatively short	Relatively poor	Relatively stable	Relatively stable

hydrothermal, microwave, or electrodeposition method and then doped with nonmetallic elements by CVD or plasma treatment, finally producing self-supported electrode materials with a homogeneous and stable nanostructure. However, such self-supported electrode materials still face several challenges:

1. The synergy between the grown electrocatalysts and substrate materials is unpredictable, and a deep understanding of particular active sites is still lacking. Thus, theoretical studies and predictions of new structural compositions will be beneficial for the application of NF in water electrolysis.
2. The true number of active sites for the self-supported electrocatalyst that participates in OER and HER requires a deep understanding of the role of surface species, which remains unclear.
3. The instability of the NF-based electrode in acidic media is a significant issue that should be overcome. Thus, the development of acid-resistant NF electrode materials is imperative.
4. Scaling up electrolyzers for commercial applications is still difficult.

To solve these shortcomings, researchers need to pay more attention to understanding the mechanisms of nucleation and growth of self-supported electrode materials and enhance their OER and HER performance in practical industrial environments. An in-depth study of the reaction mechanism can help in constructing self-supported electrode materials with higher activity and stability. Testing and improving actual devices can help realize the commercial value of such self-supported electrocatalytic materials.

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## Declarations

**Conflicts of interest** The authors declare there is no conflict of interests.

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