

## Recent advances of modified Ni (Co, Fe)-based LDH 2D materials for water splitting

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**Abstract:** Water splitting technology is an efficient approach to produce hydrogen ( $H_2$ ) as an energy carrier, which can well address the problems of environmental deterioration and energy shortage, as well as establishment of a clean and sustainable hydrogen economy powered by renewable energy sources due to the green reaction of  $H_2$  with  $O_2$ . While the efficiency of  $H_2$  production by water splitting technology is intimately related with the reactions on electrode. Nowadays, the efficient electrocatalysts in water splitting reactions are the precious metal-based materials, i.e., Pt/C,  $RuO_2$  and  $IrO_2$ . Ni (Co, Fe)-based layered double hydroxides (LDH) two-dimensional (2D) materials are the typical non-precious metal-based materials in water splitting with advantages of low cost, excellent electrocatalytic performance and simple preparation methods, which exhibits a great potential for the substitution for precious metal-based materials. This review summarizes the recent progress of Ni (Co, Fe)-based LDH 2D materials for water splitting, which mainly focuses on discussing and analyzing the different strategies to modify LDH materials towards high electrocatalytic performance. We also discuss the recent achievements including their electronic structure, electrocatalytic performance, catalytic center, preparation process and catalytic mechanism. Furthermore, the characterization progress in revealing electronic structure and catalytic mechanism of LDH is highlighted in this review. Finally, we put forward some future perspectives related to design and explore advanced LDH catalysts in water splitting.

**Keywords:** Water splitting; LDH materials; Hydrogen evolution reaction; Oxygen evolution reaction; Electrocatalytic performance

## 1. Introduction

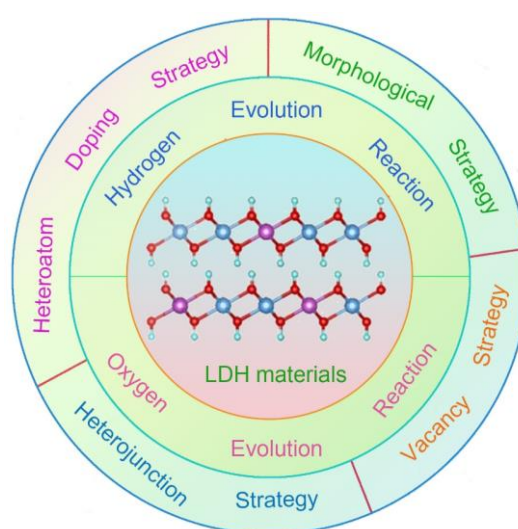
Water splitting technology to produce hydrogen ( $H_2$ ) as an energy carrier is always regarded as an efficient approach to address the problems of environmental deterioration and energy shortage, which can establish a clean and sustainable hydrogen economy powered by renewable energy sources due to the high-energy capacity of  $H_2$  and green reaction of  $H_2$  with  $O_2$  [1-3]. This technology contains two important reactions in electrolytic cell. The first one is hydrogen evolution reaction (HER,  $2H^+ + 2e^- \rightarrow H_2$ ) on cathode, and second one is oxygen evolution reaction (OER,  $2H_2O \rightarrow 4H^+ + 4e^- + O_2$ ) on anode [3,4]. These two reactions are all needed the catalysts to accelerate. Nowadays, the most efficiently active HER and OER electrocatalysts are precious metal-based materials, e.g., Pt/C,  $RuO_2$  and  $IrO_2$ , which possess the high exchange current density ( $j_0$ ), small Tafel slope and low overpotential [3,5]. However, their prohibitive cost and scarcity greatly hinder the large-scale application of water splitting. Therefore, developing non-precious metal-based HER and OER electrocatalysts are of significance and important for large-scale application of water splitting technology to  $H_2$  generation.

The HER rate is dependent on  $H^*$  adsorption condition over the surface of catalysts, which closely relates with the electronic structure of catalysts [6,7]. In general, an advanced HER electrocatalyst should possess a suitable  $H^*$  adsorption energy which is neither too strong or too weak, i.e.,  $\Delta G_{H^*}$ , as reflected by the commercial Pt/C catalyst with  $|\Delta G_{H^*}|$  being of near to zero. OER involves a four-electron transfer process, which means that the transfer of  $4e^-$  and  $4H^+$  from two water ( $H_2O$ ) molecules can generate one oxygen molecule. Due to this point, OER generally possesses the larger overpotential than that of HER because of its lower sluggish reaction kinetics, which directly determines the efficiency of electrolyser technologies and is also regarded as the bottleneck reaction of water splitting technology [8,9]. Similar to HER, the precious metal-based oxides, i.e.,  $RuO_2$  and  $IrO_2$ , have also been regarded as the benchmarks of OER catalysts which possess the excellent OER activity in a wide range of pH values. However, OER over  $RuO_2/IrO_2$  involves a lattice oxygen insertion and removal process (i.e., the insertion/removal of O in and out of lattice, renamed as lattice oxygen evolution reaction (LOER)), which results in a collapse of crystal structure and leaching Ru/Ir species, thus losing the OER activity [10]. This important problem also restricts the large-scale application of water

splitting to generate H<sub>2</sub> energy. Based on these analysis, design non-precious metal-based compounds is of great significance to replace the commercial precious metals and reduce the cost of water splitting to H<sub>2</sub> generation.

Nowadays, a large number of non-precious metal-based materials have been widely developed in water splitting technology including carbon materials, metals, metal oxides/hydroxides, sulfides and phosphides [3,9,11-17]. Among these non-precious metal-based materials, metal-based layered double hydroxides (LDH) exhibit the great promising potential to substitution for precious metal-based catalysts due to their low cost, simple preparation methods and excellent electrocatalytic performance in water splitting, as well as the easier tunable chemistry in regulating electrocatalytic activity [12,18]. LDHs is a layered hydrotalcite-like compound composed of octahedral MO<sub>6</sub> stacked layers sharing the edge. Among them, [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup> (M usually refers to the transition metal in the first row) represents positively charged metal hydroxide layers, and [A<sub>x/n</sub>•H<sub>2</sub>O]<sup>n-</sup> represents water molecules and anions (CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, VO<sub>4</sub><sup>-</sup>, etc.) for balancing positive charges between layers. LDH materials (such as NiFe-, NiCo-, CoFe-hydroxides, etc.) have become one of the most promising abundant earth-transition metals-based electrocatalysts because of its adjustable and changeable interlayer anions. For metal sulfides and phosphides, their structures are not stable and easily reconstruct into metal hydroxides due to their sensitive ability of O species during water splitting reactions, especially for the OER [11,19]. Then the new formed metal hydroxides can efficiently catalyze OER and HER. Similar, non-precious metals are also sensitive to O species and easier oxidized [20,21], then forming metal hydroxides in OER and HER. In the most studies, metal hydroxides are inevitable during OER and HER, which are also widely regarded as highly active catalytic sites with superior activity of current density. Ni (Co, Fe)-based LDH materials featured by 2D morphology are the most typical hydroxides as HER and OER catalysts with high performance, rich sources in earth and convenient preparation methods, which have grown into a category of non-precious metal-based electrocatalysts for substituting precious metal materials [12,22,23]. Nowadays, with the advantages of high current density (reaching up to 1000 mA cm<sup>-2</sup>) and superior stability (1000 hours), the Ni (Co, Fe)-based LDH materials exhibit a promising potential of substitution for commercial precious metal-based materials, and also have achieved more attention in water splitting technology. As

well known, an excellent electrocatalyst should possess the high conductivity which endows the fast electron transfer from internal catalyst to its surface to participate the reaction with reactants. While the Ni (Co, Fe)-based LDH materials have a low conductivity which greatly hinders their application in electrocatalysis. In the last several decades, a large number of Ni (Co, Fe)-based LDH materials have been constructed as electrocatalysts in water splitting [24]. Therefore, a comprehensive and systematical review focusing on summarizing these achievements on Ni (Co, Fe)-based LDH 2D materials is very important for moving forward the development of non-precious metal-based materials. This review summarizes the recent progress of Ni (Co, Fe)-based LDH materials for water splitting, which mainly focuses on discussing and analyzing the different strategies to modify LDH materials towards high electrocatalytic performance (Figure 1). This is highlighted in the area of water electrolysis, where Ni (Co, Fe)-based LDH have exhibited great promise to achieve high OER and HER activities through forming highly-intrinsic catalytic-sites *via* different strategies. We also discuss the recent achievements including electronic structure, electrocatalytic performance, catalytic center and preparation process. Furthermore, the characterization progress in revealing electronic structure and catalytic mechanism of LDH is also summarized in details. Finally, we put forward some future perspectives related to design and explore advanced LDH catalysts in water splitting.



**Figure 1.** Modification strategies of Ni (Co, Fe)-based LDH materials as water splitting electrocatalysts.

## 2. Heteroatom doping strategy

Heteroatoms incorporated into crystal structure of Ni (Co, Fe)-based LDH materials can induce the electron distribution of host atoms due to the formed new chemical bonds between heteroatoms and host atoms, which leads to generate new highly active catalytic sites for water splitting. Therefore, doping with the impurity atom in metallic hydroxides has been widely regarded as an effective strategy to construct high electrocatalytic performance of LDH-based electrocatalysts. Doping with heteroatoms can easily produce a large number of oxygen vacancies ( $V_O$ ) due to the broken crystal structure, which can increase the conductivity of LDH as presented electronic states near Fermi level and also make more active sites exposed in electrolyte, thus leading to easily electron transfer during reactions and more ratios of catalytic sites reacting with intermediates. Simultaneously, the generated  $V_O$  and heteroatoms jointly regulate the electronic states of catalytic sites, thus optimizing the adsorption energies of intermediates. In this section, we will summarize the achieved recently progress of doping strategy in promoting electrocatalytic performance of LDH materials including their preparation methods, characterizations, catalytic mechanism and theoretical studies.

### 2.1 Precious metal doping

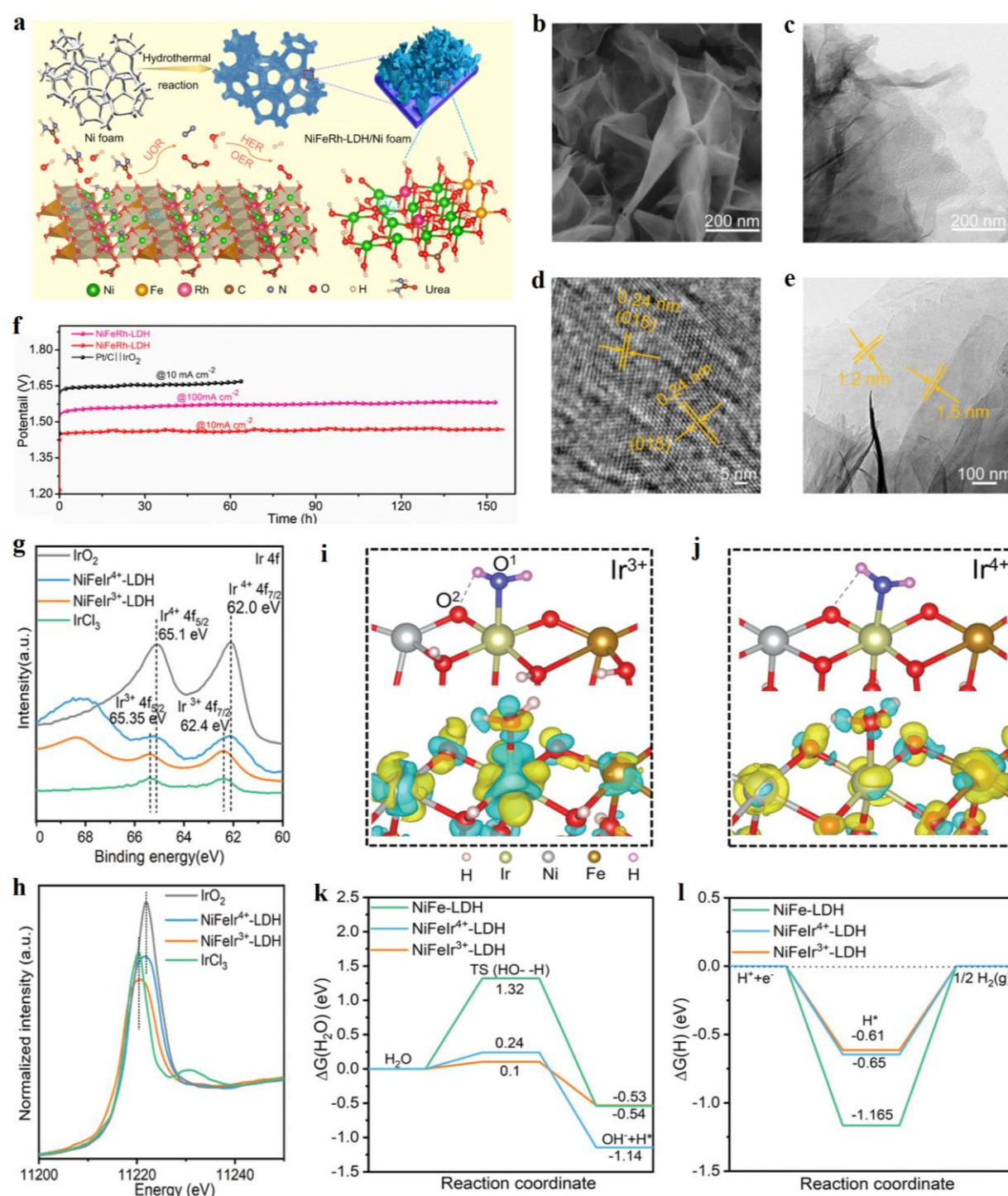
Precious metals, such as Pt, Ru and Ir, are the important compositions to form highly-intrinsic catalytic sites for OER and HER, which possess the optimized intermediate adsorption energies during reactions, thus exhibiting the low overpotentials [25,26]. Recently, Precious metal doping LDH can construct the highly-catalytic sites for HER and OER, which develops a large number of excellent LDH catalysts in water splitting [27-32], such as Ag, Ru, Rh, Ir, Pt. Wang et al. prepared Ni foam supporting Rh doped NiFe-LDH material by hydrothermal method which exhibited the bifunctional electrocatalytic activities for HER and OER, as well as urea oxidation reaction (UOR) [30]. The Rh-NiFe-LDH material, featured with thin layers of 1.2-1.5 nm (Figure 2a-e), exhibited an excellent HER and OER performance including a low overpotential of 24 mV at 10 mA cm<sup>-2</sup> for HER and 204 mV at 10 mA cm<sup>-2</sup> for OER. This Rh-NiFe-LDH catalysts also showed an excellent stability in water splitting cell in the continuous 155 hours test (Figure 2f). In addition, this hydrothermal method was also well applied in constructing Ir-NiFe-LDH using the ethylene glycol as solvent. Fan and co-workers reported

that an atomic Ir doped NiCo-LDH showed better HER and OER properties than these of commercial Pt/C and Ir/C electrodes, respectively [31]. In water splitting cell, Ir-NiCo-LDH achieved the current density of  $10 \text{ mA cm}^{-2}$  at the ultra-low voltage of 1.45 V, showing excellent water-splitting performance, which was superior to many recent state-of-the-art bifunctional water-splitting catalysts. Single Ir atom incorporated into NiCo-LDH could generate a large number of Vo vacancies which tuned the electron states, thus forming the highly active sites for HER and OER activities to lower their overpotentials.

The valence state of single precious metal can efficiently tune the electrocatalytic performance of LDH materials. Wang et al. synthesized NiFe-LDH doped with Ir ions with different valence states by simple hydrothermal method [32]. X-ray photoelectron spectra (XPS) and Ir L-edge X-ray absorption near edge structure (XANES) spectra showed two categories of Ir-NiFe-LDH materials with  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  species by choosing the different Ir precursors (Figure 2g,h). The low-valence  $\text{Ir}^{3+}$ -NiFe-LDH exhibited the superior HER and OER activities to  $\text{Ir}^{4+}$ -NiFe-LDH material, including the low overpotentials of HER (312 mV at  $500 \text{ mA cm}^{-2}$ ) and OER (207 mV at  $10 \text{ mA cm}^{-2}$ ). Density functional theory (DFT) calculation revealed that the adsorption sites changed from Ni sites to  $\text{Ir}^{3+}/\text{Ir}^{4+}$  sites after Ir ions being doped into NiFe-LDH (Figure 2i,j). On the one hand, compared with NiFe-LDH and  $\text{Ir}^{4+}$ -NiFe-LDH,  $\text{Ir}^{3+}$ -NiFe-LDH had the lowest adsorption energy for water molecules, thus promoting the adsorption of water molecules and accelerating the Volmer reaction of HER (Figure 2k). On the other hand,  $\text{Ir}^{3+}$  could provide more electrons to react with  $\text{H}_2\text{O}$  molecules, thus weakening the O-H bond in water molecules and promoting the dissociation of water molecules, which facilitated the kinetics of OER process (Figure 2i,j). In addition, the incorporation of  $\text{Ir}^{3+}/\text{Ir}^{4+}$  into NiFe-LDH obviously reduced the water-dissociation energy barriers and the energy barrier for the desorption of  $\text{H}^*$  species (Figure 2k,l). This work well demonstrates that the valence state of heteroatoms plays a critical role in tuning the electrocatalytic performance of LDH, and also provides an efficient approach to construct advanced LDH material through regulating the electron states of precious metal. At present, rational design of advanced HER electrocatalysts should consider from two points of the dissociation of water molecules and  $\text{H}^*$  adsorption energy. Nowadays, precious metal doping strategy has been widely applied in constructing excellent electrocatalysts in water splitting [33-35], which can form the optimized catalysts



sites with a best free energy profile, thus leading to an ultrahigh mass activity-based on precious metals.



**Figure 2.** Characterizations and theoretical studies of precious metal doped LDH. (a) Schematic illustration of the preparation process of Rh-NiFe-LDH on nickel foam. (b) Scanning electron microscope (SEM) image of Rh-NiFe-LDH. (c-e) Transmission electron microscope (TEM)

image of Rh-NiFe-LDH. (f) Durability tests of Rh-NiFe-LDH as bifunctional catalysts in water splitting cells at different current densities. (g) XPS spectra of Ir. (h) Ir L-edge XANES spectra of serial materials. (i, j) Atomic model (top) and differential-charge density (down) for H<sub>2</sub>O molecule adsorbed on Ir<sup>3+</sup>-NiFe-LDH (i) and Ir<sup>4+</sup>-NiFe-LDH. Note: yellow and blue regions represent excess and depletion of charge density, respectively. (k, l) Calculated adsorption free energy diagrams for Volmer step (k) and Tafel step (l) on serial catalysts. (a-f) Reproduced with permission [30]. Copyright 2021, Elsevier. (g-l) Reproduced with permission [32]. Copyright 2021, Wiley-VCH.

## 2.2 Non-precious metal doping

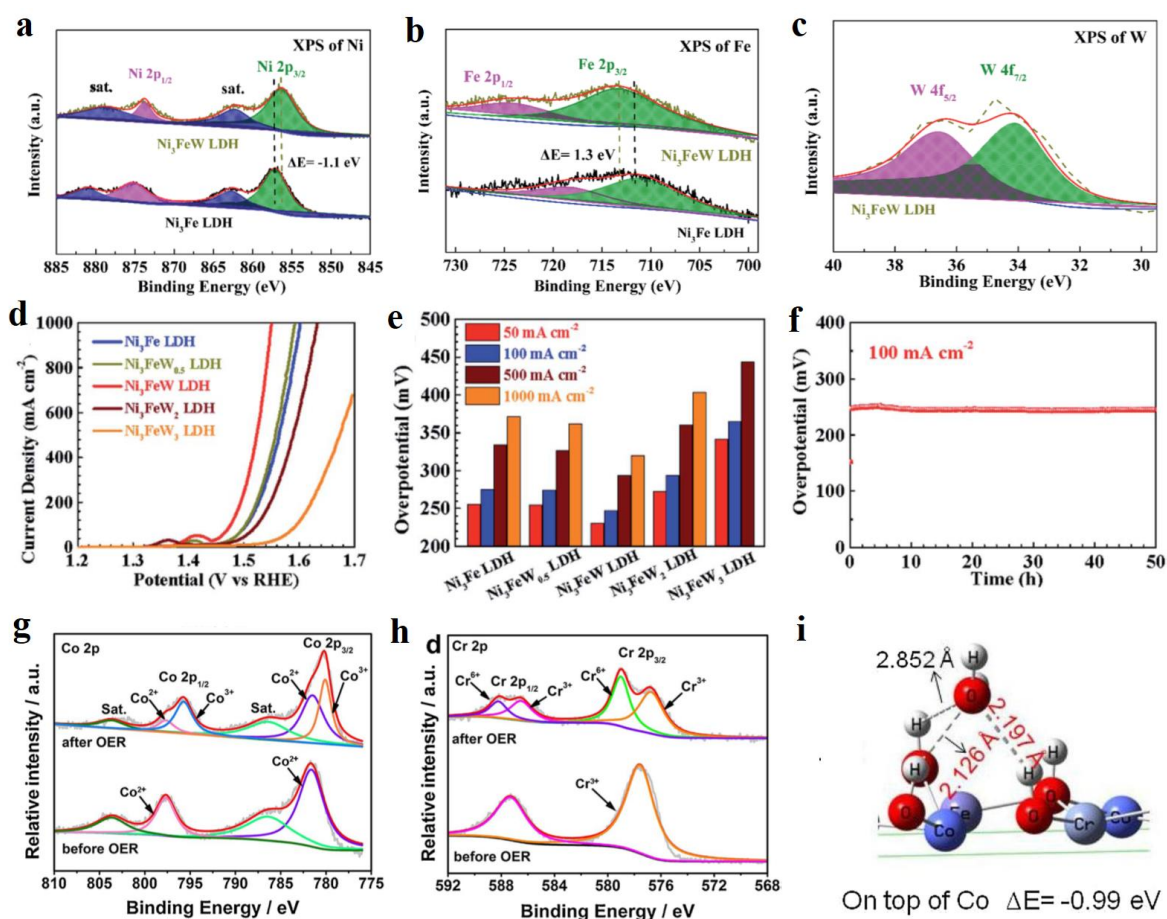
Recently, a large number of non-precious metal doping LDH also can construct high-performance electrocatalysts in water splitting, including Fe, V, Cr, W, Mo and Ce [36,37]. This kind of LDH materials usually exhibit the bifunctional electrocatalytic performance in OER and HER activities. Li et al. reported a V doped NiFe-LDH material by H<sub>2</sub> plasma reduction treatment and cation doping methods, which showed high HER and OER performance due to the synergistic effect of oxygen and metal vacancies, as well as V dopant [38]. The V dopant played a regulator to activate its neighboring Ni atoms in NiFe-LDH, thus leading to the optimized energy profiles of HER and OER. Vacancy defect engineering is widely regarded as the promising strategy to activate the intrinsic electrocatalytic activity of electrocatalysts, which can regulate the electronic structure of materials, thus leading to formed optimal free energy profiles [39,40]. Zhou and co-workers reported a general method of preparation of Fe doped Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub> nanosheets with abundant active sites by a simple cation-exchange process, which performed extraordinary OER [41]. The enhanced OER activity of Ni<sub>0.83</sub>Fe<sub>0.17</sub>(OH)<sub>2</sub> on NiFe-LDH was attributed to the defect-rich hole basal plane of Ni<sub>0.83</sub>Fe<sub>0.17</sub>(OH)<sub>2</sub> generated by the cation exchange process. Firstly, the nanoporous structure and abundant Ni and O vacancies formed during the chemical etching process in the containing Fe<sup>3+</sup> solution, which easily generated more exposed active sites. The O vacancies could effectively tune the valence states of Ni and Fe, thus regulating electrocatalytic activity. Secondly, Ni<sub>0.83</sub>Fe<sub>0.17</sub>(OH)<sub>2</sub> exhibited the better wettability than NiFe-LDH and original Ni(OH)<sub>2</sub>, which resulted in the easier electrolyte permeation and accelerating the migration of



hydroxyl groups and the release of oxygen. Due to the above points, the  $\text{Ni}_{0.83}\text{Fe}_{0.17}(\text{OH})_2$  exhibits the high OER performance with a low overpotential of 245 mV at  $10 \text{ mA cm}^{-2}$ .

The valence state of single metal atom is also a regulator to tune the electrocatalytic performance of LDH materials. Wu's group prepared the W doped  $\text{Ni}_3\text{Fe-LDH}$  as OER catalyst with high current densities of 100 and  $1000 \text{ mA cm}^{-2}$  at the low overpotentials of 247 and 320 mV, respectively [42]. In this material system, the W dopant with +6 valence state resulted in the negatively shift of 1.1 eV for Ni and positive shift of 1.3 eV for Fe in W- $\text{Ni}_3\text{Fe-LDH}$  compared to pure  $\text{Ni}_3\text{Fe-LDH}$  (Figure 3a-c). Such shift indicated Ni being of low valence state and Fe being of high valence state in W- $\text{Ni}_3\text{Fe-LDH}$ , which were favorable for high OER activity with high current density (Figure 3d). In details, the OER activity depends on the content of W dopant as presenting the first increase of OER activity and then decrease (Figure 3e). The excessive content of W would lead to the increased charge-transfer resistance, which was the main reason of decreased OER activity for W- $\text{Ni}_3\text{Fe-LDH}$  with high amount of W dopant. In long time test, W- $\text{Ni}_3\text{Fe-LDH}$  exhibited the superior stability in the continuous 50 h test (Figure 3f). Such dopant regulating engineering strategy to enhance OER activity is also demonstrated by the Cr dopant in  $\text{CoFe-LDH}$  [43]. As well known, the electrochemical activation is a general process before obtaining the electrocatalytic test. After OER test, the Cr and Co species in Cr- $\text{CoFe-LDH}$  material exhibited a higher valence state compared to pure  $\text{CoFe-LDH}$  (Figure 3g,h), which indicated that the formed Co and Cr species with high valence state are the highly active catalytic sites for OER. DFT calculation exhibited that the Co site in Cr- $\text{CoFe-LDH}$  material possessed a strong ability of  $\text{H}_2\text{O}$  dissociation with a short chemical bond between H and OH in  $\text{H}_2\text{O}$  compared to other adsorption configurations over Cr and Fe sites (Figure 3i), thus greatly enhancing the reaction of water splitting into  $\text{OH}^*$  that was favorable for  $\text{O}_2$  generation. Recently, Kundu's group reported that Ce as the dopant incorporated into  $\text{NiCo-LDH}$  to realize the goal of greatly enhancing OER activity [44]. The Ce dopant generated the higher ratio of  $\text{Ni}^{3+}$  species to  $\text{Ni}^{2+}$  in Ce- $\text{NiCo-LDH}$  compared to pure  $\text{NiCo-LDH}$ , indicating more  $\text{Ni}^{3+}$  sites existed in  $\text{NiCo-LDH}$ , thus increasing the number of highly active catalytic sites of  $\text{Ni}^{3+}$  as OER catalytic center. Nowadays, more and more non-precious metal doped LDH have been developed as superior electrocatalysts in water splitting, such as W- $\text{Ni}(\text{OH})_2/\text{NiOOH}$  [45], Mo- $\text{NiCo-LDH}$  [46], Fe- $\text{NiCo-LDH}$  [47], Ta-FeNi-LDH

[48]. Due to the plentiful non-precious metals and its amount regulation engineering on electrocatalytic performance, non-precious metal doping strategy provides a vast opportunity to develop excellent electrocatalysts in water splitting.

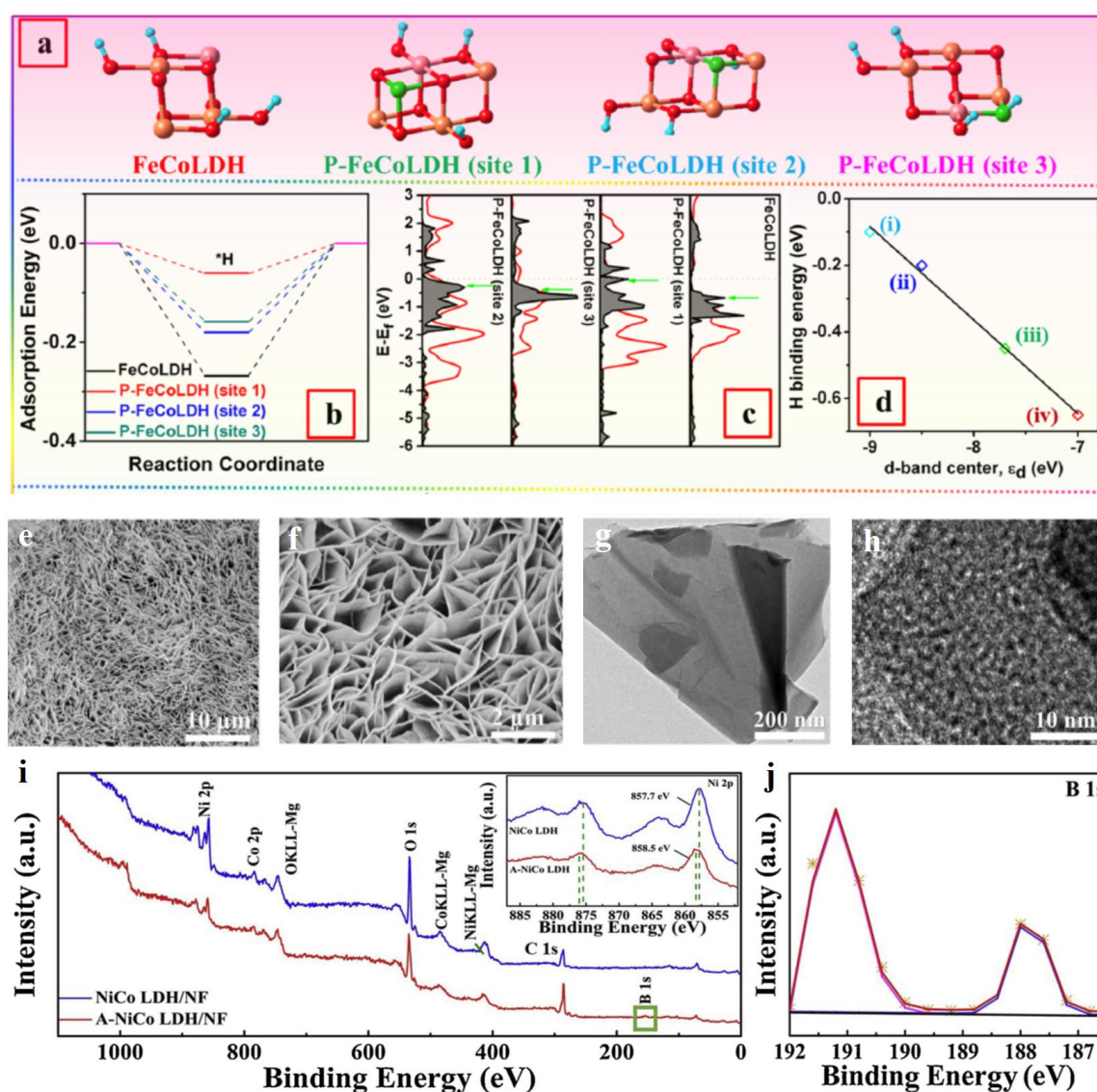


**Figure 3.** Chemical state characterizations, OER performance and theoretical studies non-precious metal doped LDH materials. (a) Ni 2p XPS of W-Ni<sub>3</sub>Fe-LDH and Ni<sub>3</sub>Fe-LDH. (b) Fe 2p XPS of W-Ni<sub>3</sub>Fe-LDH and Ni<sub>3</sub>Fe-LDH. (c) W 4f XPS of W-Ni<sub>3</sub>Fe-LDH. (d) Linear sweep voltammetry (LSV) curves of serial Ni<sub>3</sub>Fe-LDH with different W contents. (e) Comparison of OER performance of serial materials at different current densities. (f) Long-time stability of W-Ni<sub>3</sub>Fe-LDH at 100 mA cm<sup>-2</sup>. (g) Co 2p XPS of Cr-CoF-LDH before and after OER. (h) Cr 2p XPS of Cr-CoF-LDH before and after OER. (i) Theoretical model of H<sub>2</sub>O adsorbed on Co site in Cr-CoF-LDH and its adsorption energy. (a-f) Reproduced with permission [42]. Copyright 2020, Royal Society of Chemistry. (g-i) Reproduced with permission [43]. Copyright 2020, Elsevier.

## 2.3 Non-metal doping

Except the metal doping enhancing the electrocatalytic performance of LDH, non-metal atom dopant also can form highly active catalytic sites due to their different electronegativities compared to oxygen atoms [49, 50], such as F, S, P and B [51-54]. These non-metal atoms bonding with metal atoms induce the different electron states on metals compared to pure LDH and simultaneously generate some vacancy defects, which realize the tuned electron density of LDH aiming to optimize the adsorption energies of intermediates, thus exhibiting the enhanced electrocatalytic performance.

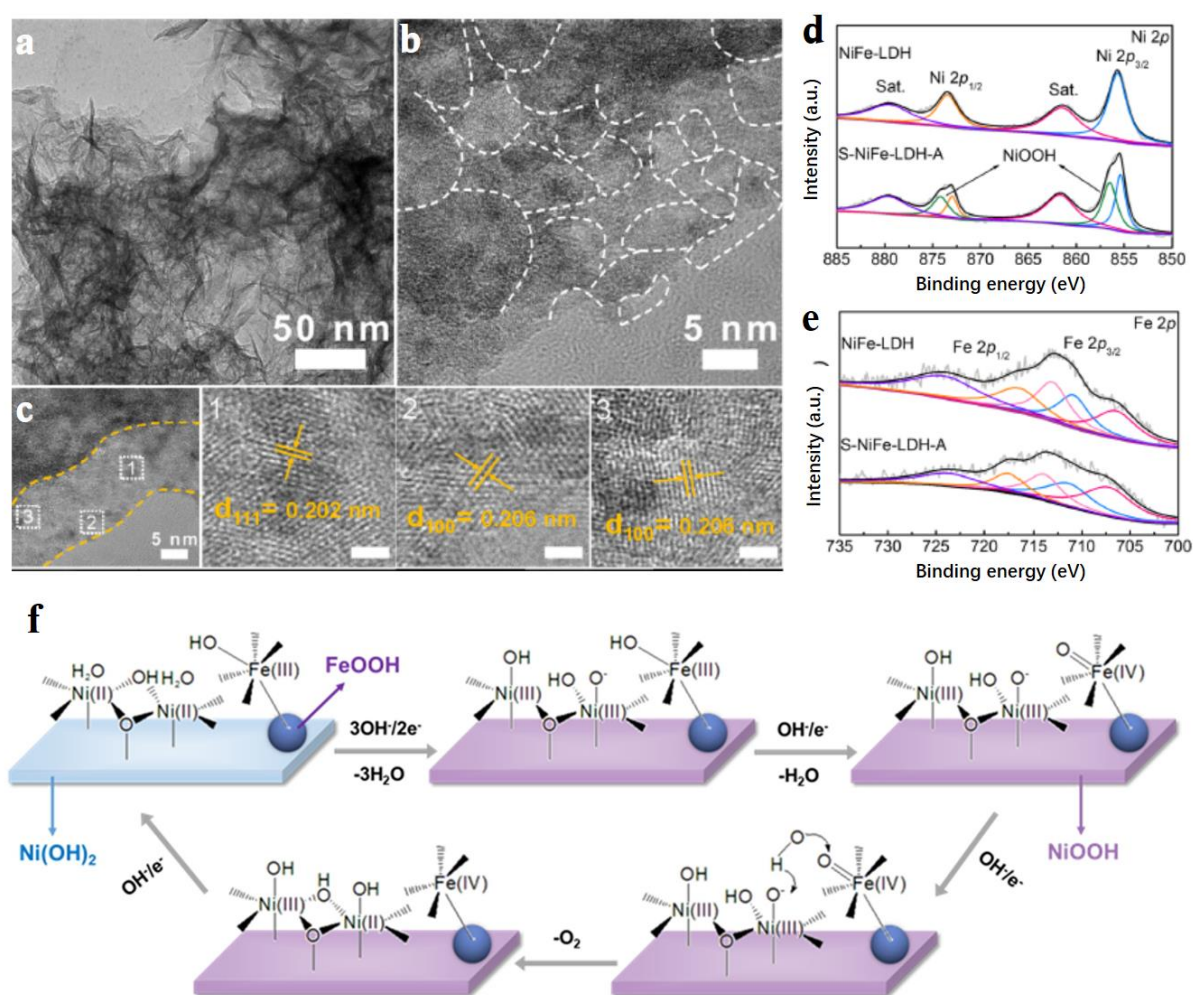
Tang et al. prepared P doped FeCo-LDH (P-FeCoLDH) supported on Cu foam using  $\text{NaH}_2\text{PO}_4$  as precursor at 350 °C heat treatment [51]. P dopant could increase the electrochemical catalytic surface area (ECSA) and conductivity of FeCo-LDH, which significantly enhanced the number of catalytic sites and facilitated the electron transfer process during HER, respectively. Simultaneously, P-FeCoLDH possessed a lowest  $\Delta G_{\text{H}^*}$  (-0.27 eV) value, indicating its best  $\text{H}^*$  adsorption state which facilitated the  $\text{H}_2$  formation. Such best  $\text{H}^*$  adsorption state of P-FeCoLDH resulted from the tuned *d*-band center near to the anti-bonding orbital  $\sigma^*$  of  $\text{H}^*$  species. Because of a lower electronegativity for P compared to O, P-FeCoLDH exhibited a lower static contact angle in the water, which indicated that P atoms facilitated the adsorption of  $\text{H}_2\text{O}$  molecule, thus promoting the dissociation of water (Figure 4a-d). This phenomenon is also demonstrated by B doped NiCo-LDH (B-NiCo-LDH) to realize high catalytic performance of HER with a low overpotential being of 381 mV at high current density of 1000  $\text{mA cm}^{-2}$ , better than that of Pt/C catalyst [52]. B atom could be introduced into LDH lattice in the form of borate ( $\text{BO}_3$  species), which led to the generated amorphous NiCo-LDH. Such new formed phase would generate a large number of defects, such as  $\text{V}_\text{O}$ , unsaturated atoms, exposed more active sites and enhanced electrical conductivity (Figure 4e-j). Meanwhile, the existed  $\text{BO}_3$  species easily reacted with hydroxyl in alkaline electrolyte to form four-coordinated  $\text{BO}_4$ . The formed  $\text{BO}_4$  groups with a strong proton accepting ability promoted the dissociation of adsorbed  $\text{H}_2\text{O}$  molecule through adsorbing H atoms and then transferred onto the nearby metal atoms.  $\text{H}_2$  molecules could be released after two H atoms combining with each other over metal atoms.



**Figure 4.** Theoretical studies and characterizations of non-metal atom doped LDH catalysts. (a) The theoretical structure models and (b) H\* adsorption free energy of various sites over P-FeCoLDH. (c) Local density of states projected for the adsorbed H atom (H-DOS, dark shaded area). (d) The relationship of DFT-based hydrogen adsorption energies ( $\Delta E$ ) and metal  $d$ -band center positions on four different surficial sites, (i) P-FeCoLDH (site 1), (ii) P-FeCoLDH (site 3), (iii) P-FeCoLDH (site 2), and (iv) FeCoLDH. (e, f) SEM images of B-NiCo-LDH. (g, h) TEM images of B-NiCo-LDH. (i) Full XPS spectrum of B-NiCo-LDH. (j) B 1s spectrum of B-NiCo-LDH. (a-d) Reproduced with permission [51]. Copyright 2021, Elsevier. (e-j) Reproduced with permission [52]. Copyright 2020, Elsevier.

Non-metal atoms doping is also an efficient method to enhance OER activity of LDH. Chai's group prepared S doped NiFe-LDH (S-NiFe-LDH) on MoNi foam support by the electrochemical metallic deposition method in a thioacetamide (TAA) solution [53]. In this system, TAA provided the S dopant incorporated into NiFe-LDH during the deposition, meanwhile the released  $S^{2-}$  species reacted with  $Ni^{2+}$  and  $Fe^{2+/3+}$  to generate more exposed edges of LDH. In such preparation process, the S-NiFe-LDH featured with property of the large active surface area, more exposed active sites and long-term robustness (Figure 5a-c), jointly contributing to high OER performance including a low overpotential of 270 mV at  $50 \text{ mA cm}^{-2}$  and favorable durability. S atoms incorporated into NiFe-LDH facilitated the formation of high valence states of Ni and Fe (Figure 5d,e), which were highly active catalytic sites for OER with favorable process of O species transfer cycling. This corrosive condition for preparing LDH is also reflected in F doped  $Co_3Fe$ -LDH system [54]. Wang et al. synthesized F doped  $Co_3Fe$ -LDH (F- $Co_3Fe$ -LDH) by  $CHF_3$ -plasma etching method. During the  $CHF_3$ -plasma process, F atoms replacing the O atoms and the metal vacancies ( $V_M$ ) generated at the same time. Simultaneously, the generated O atoms would also result in a strong interaction between Co and Fe atoms with an octahedral coordination, thus forming highly active catalytic sites for OER with a low energy barrier. F atom attracted more electrons from metal sites due to its high electronegativity being of 4.0, which resulted in higher oxidation states of Co and Fe compared to pure  $Co_3Fe$ -LDH as demonstrated by XPS and XANES spectra. As well known, the Co (Ni, Fe etc) metallic sites with high valence state possess the highly intrinsic OER activity [55,56]. Therefore, F- $Co_3Fe$ -LDH exhibited a low overpotential of 276 mV at  $10 \text{ mA cm}^{-2}$  due to the optimized free energy profile for OER from the F dopant and more exposed active sites. Nowadays, the doping with nonmetallic elements has been regarded as an efficient approach to improve electrocatalytic performance of LDH by utilization of their different electronegativities compared to O [57,58], which mainly generated  $V_O$ ,  $V_M$ , unsaturated atoms, exposed more active sites and enhanced electrical conductivity, as well as new formed high-catalytic sites with low theoretical energy barriers for HER and OER.





**Figure 5.** Characterization and OER mechanism of S-NiFe-LDH. (a) TEM image. (b,c) High resolution (HR) TEM image. (d) Ni 2p XPS spectra of S-NiFe-LDH and NiFe-LDH. (e) Fe 2p XPS spectra of S-NiFe-LDH and NiFe-LDH. (f) OER mechanism over Fe and Ni sites in S-NiFe-LDH. (a-f) Reproduced with permission [53]. Copyright 2021, Elsevier.

### 3. Heterojunction strategy

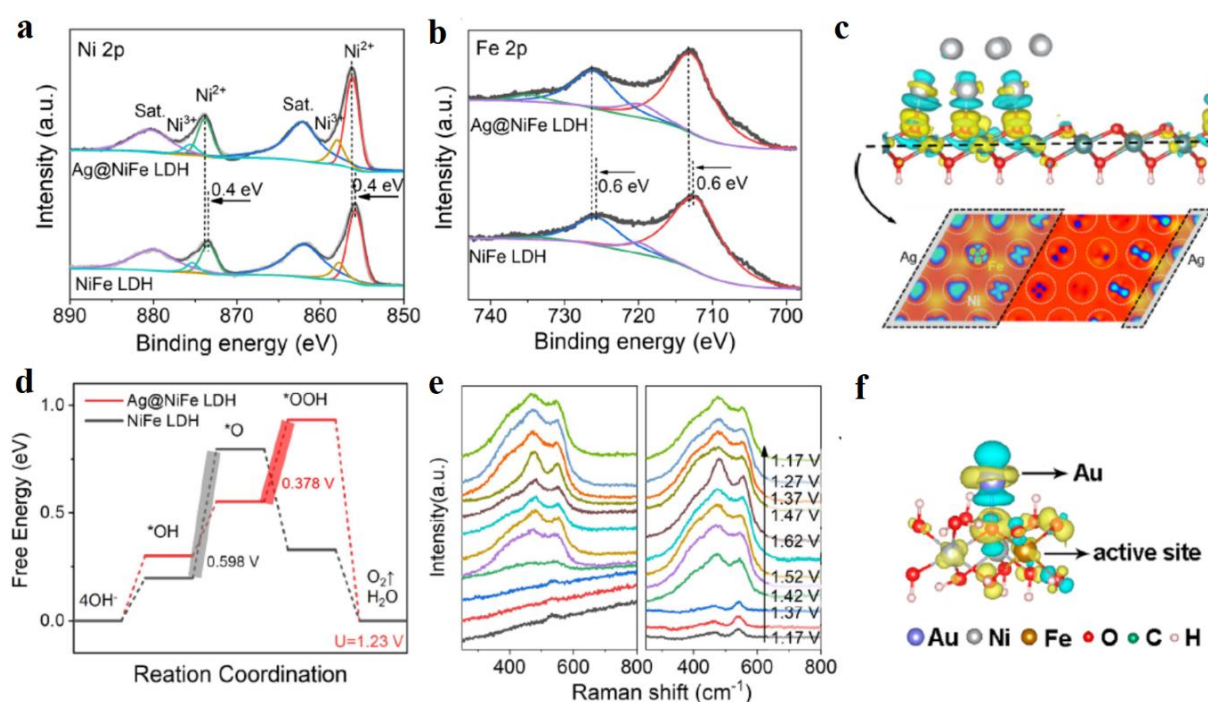
It is an efficient approach to enhance the electrocatalytic performance of LDH by constructing the heterojunction of LDH with other compounds. In this kind of material system, new highly active catalytic sites can be formed in interface between two compounds due to their strong chemical interaction which generates new chemical bonds and tunes electronic state of individual compounds. Generally, there exists two functions of heterojunction to realize the high electrocatalytic performance of LDH-based catalysts. Firstly, the enhanced conductivity

of LDH-based materials can be obtained through hybridizing with high conductive metal compounds, which efficiently improve the electron transfer rate between reactants and catalysts, thus greatly facilitating the reaction dynamics. Secondly, new catalytic sites are formed between the two compounds, which can optimize the free energy profiles of reactions, thus lowering the overpotentials. In this section, we will summarize the recent progress in heterojunction strategy for constructing LDH-based catalysts hybridized by other compounds, including metals, metal compounds, carbon and organic materials, which also involves their preparation methods, characterizations, electrocatalytic performance and theoretical studies.

### 3.1 Metals

Metals and their alloys possess the excellent conductivity, which not only greatly improve the electron transfer during reactions over LDH-based materials, but also form the new highly catalytic centers with low overpotentials. Nowadays, the metals and their alloys hybridized with LDH are mainly precious metals, such as Ag, Pt, Au, PtNi alloy [59-65]. Of course, some non-precious metals also can form a heterojunction with LDH, for example, CuNi alloy [66]. Song et al. skillfully combined the negatively charged Ag nanoparticles with positively charged different kinds of hydroxides (NiFe-LDH, CoFe-LDH,  $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ) through the electrostatic adsorption principle to construct advanced OER electrocatalysts [59]. In these Ag nanoparticles modified LDH materials, Ag-NiFe-LDH exhibited the best OER activity with overpotential of 246 mV at  $10 \text{ mA cm}^{-2}$ , as well as a long-time stability in the water splitting cell at  $500 \text{ mA cm}^{-2}$  in continuous 110 h test. Ag nanoparticles resulted in the increase of valence state for Ni and Fe in Ag-NiFe-LDH (Figure 6a,b), indicating the strong chemical interaction between Ag nanoparticles and LDH as well demonstrated by the differential charge densities over Ni, Fe and Ag elements (Figure 6c). Ni species with high valence state of +3 is widely regarded as highly active catalytic sites for OER with a low theoretical overpotential of OER energy profile (Figure 6d), which is the main result of high OER performance of Ag-NiFe-LDH. *In situ* Raman spectra exhibited that the new peak at  $549 \text{ cm}^{-1}$  assigned to  $\text{Ni}^{3+}\text{-O}$  species appeared at a low overpotential of 1.42 V while the stretching vibration of  $\text{Ni}^{2+}\text{-OH}$  ( $452 \text{ cm}^{-1}$ ) and  $\text{Ni}^{2+}\text{-O}$  ( $531 \text{ cm}^{-1}$ ) diminished over Ag-NiFe-LDH (Figure 6e), indicating that Ag nanoparticles facilitated the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  oxidation with a lower applied potential compared to

NiFe-LDH, thus leading to high OER activity. Meanwhile, Ag-NiFe-LDH material possessed a 0.378 eV energy barrier in the limited step of  $O^*$  to  $OOH^*$  during OER, much lower than that of 0.598 eV from  $OH^*$  to  $O^*$  over NiFe-LDH, which indicated that Ag hybridized NiFe-LDH successfully formed the highly-catalytic sites for OER. Such new formed catalytic site was also demonstrated by the appearance of electron states of Ni and Fe near the Fermi level. Metal nanoparticles generating the high valence state of atoms on LDH is also well demonstrated by the Pt clusters on NiFe-LDH [60]. Generally, the new formed high species of atom between LDH materials and metals usually possess the optimized energy profiles of electrocatalytic reactions [61]. Sun et al. used a layered triboelectric nanogenerator (TENG) as a power source to generate a pulsed direct current with high voltage to electrodeposit Pt nanoclusters with being of 2 nm onto NiFe-LDH nanosheets (Pt-NiFe-LDH) [62]. The as-synthesized Pt-NiFe-LDH electrocatalyst exhibited the superior electrocatalytic activities to NiFe-LDH loaded with Pt nanoparticles prepared by the traditional  $NaBH_4$  reduction method. The current density of  $50 \text{ mA cm}^{-2}$  could be reached at the ultra-low overpotential of 86 mV for HER. By controlling the working frequency and deposition time of layered TENG, the size of Pt nanoclusters was easily tuned. High electrocatalytic performance of Pt-NiFe-LDH was attributed to the synergistic effect between Pt nanoclusters and NiFe-LDH which greatly promoted the fracture of  $H-O-H$  and optimized the adsorption energies of intermediates. This unique strategy of preparing heterojunction electrocatalyst easily tuned the valence state of metal atoms in LDH making partial  $Fe^{3+}$  into  $Fe^{2+}$ , and thus realized the electronic regulation. Considering the high cost of noble metal electrocatalysts, Zhang's group prepared nano-sized Au atom modified NiFe-LDH (Au-NiFe-LDH) to reduce the cost of electrocatalysts and improve the utilization efficiency of metal atoms [63]. The prepared catalyst delivered 6 times higher current density at overpotential of 280 mV than that of NiFe-LDH, which resulted from the new formed Fe sites constructed by single Au atoms (Figure 6f). Because of this point, the reaction step of  $O^*$  to  $OOH^*$  could be optimized, thus exhibiting superior OER activity over Au-NiFe-LDH.

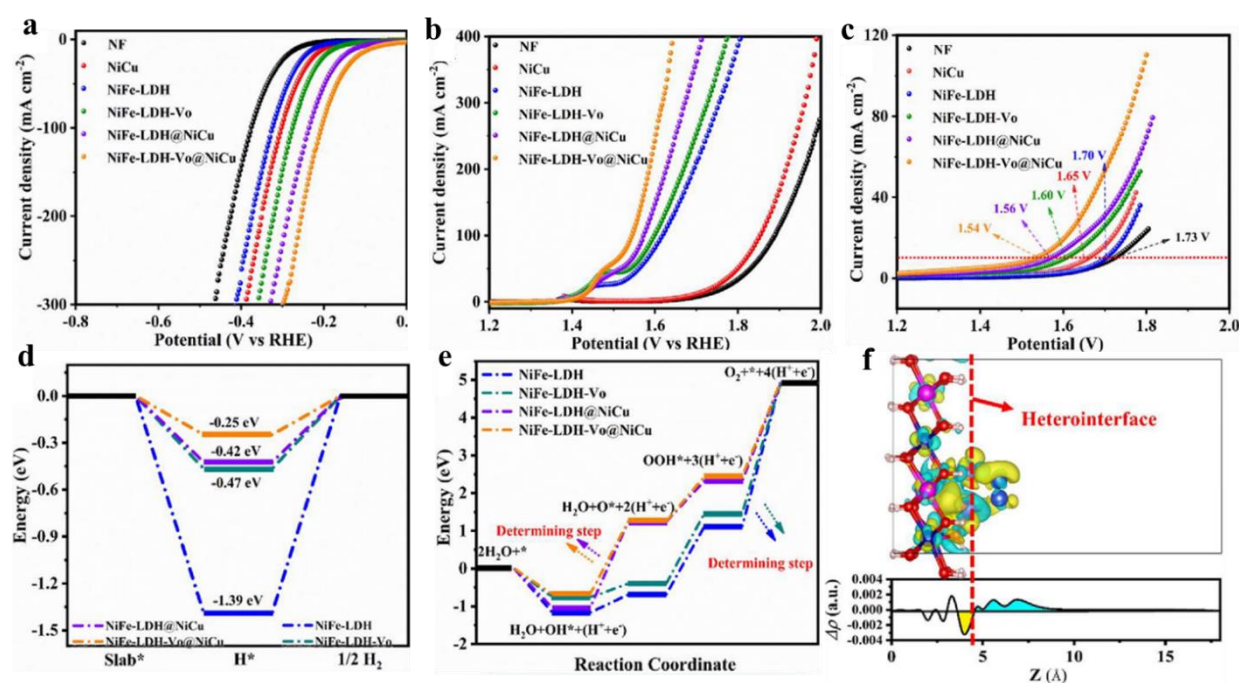


**Figure 6.** Characterizations and theoretical studies of heterojunction for LDH materials. (a,b) Ni 2p (a) and Fe 2p (b) XPS spectra for Ag@NiFe-LDH. (c) Side view (up) and 2D view (bottom) of differential charge density of Ag@NiFe-LDH. (d) OER energy profiles of NiFe-LDH and Ag@NiFe-LDH. (e) *In situ* Raman spectra of NiFe-LDH and Ag@NiFe-LDH. (f) Differential charge densities of NiFe-LDH with Au atom when one O atom is adsorbed on the Fe site. Iso-surface value is 0.004 eÅ<sup>-3</sup>. Yellow and blue contours represent electron accumulation and depletion, respectively. (a-e) Reproduced with permission [59]. Copyright 2022, Elsevier. (f) Reproduced with permission [63]. Copyright 2018, American Chemical Society.

Except for above analyzed of precious metal nanoparticles/clusters can form the heterojunction to enhance the electrocatalytic performance of LDH, transition metals (Ni, Cu and their alloys) with low cost have been reported as substitutes for precious metals to hybridize with LDH to form the heterojunction. Lei et al. reported that NiFe-LDH modified by NiCu alloy exhibited an excellent electrocatalytic performance in water splitting cell [66]. Firstly, NiFe-LDH was treated with H<sub>2</sub>O<sub>2</sub> at 120 °C for 6 h to generate the oxygen vacancies (V<sub>O</sub>). Secondly, the electrodeposition method was performed at negative potential to construct NiFe-LDH-NiCu



heterojunction. The  $V_O$  generated by  $H_2O_2$  etching effectively tuned the electronic structure of the composites and expose more active sites. NiFe-LDH- $V_O$ -NiCu delivered the current density of  $50 \text{ mA cm}^{-2}$  with only 166 mV overpotential for HER and current density of  $50 \text{ mA cm}^{-2}$  with only 244 mV overpotential for OER (Figure 7a,b). In a water splitting cell under alkaline conditions, NiFe-LDH- $V_O$ -NiCu acted as both cathode and anode catalysts exhibited the current density of  $10 \text{ mA cm}^{-2}$  at 1.54V (Figure 7c). Due to the generation of oxygen vacancies and the deposition of NiCu, the electronic structure of NiFe-LDH was well tuned. DFT studied showed that NiFe-LDH- $V_O$ -NiCu had the value of  $|\Delta G_{H^*}|$  near zero, indicating that the adsorption energy of  $H^*$  for NiFe-LDH was successfully optimized by introduction of  $V_O$  and NiCu alloy (Figure 7d). For OER, the existence of  $V_O$  and NiCu optimized the energy profile of OER during reaction as presenting the lowest energy barriers (Figure 7e). According to Bader's charge density, the most intense electron movement occurred at the coupling interface between NiFe-LDH and NiCu, and the electrons of NiFe-LDH was captured by NiFe (Figure 7f). Nowadays, metals and their alloys hybridized with LDH has been widely applied in constructing advanced electrocatalysts due to their convenient methods.



**Figure 7.** Electrocatalytic performance and theoretical studies of NiFe-LDH- $V_O$ -NiCu. (a) LSV curves of HER. (b) LSV curves of OER. (c) LSV curves in water splitting cell. (d) Calculated



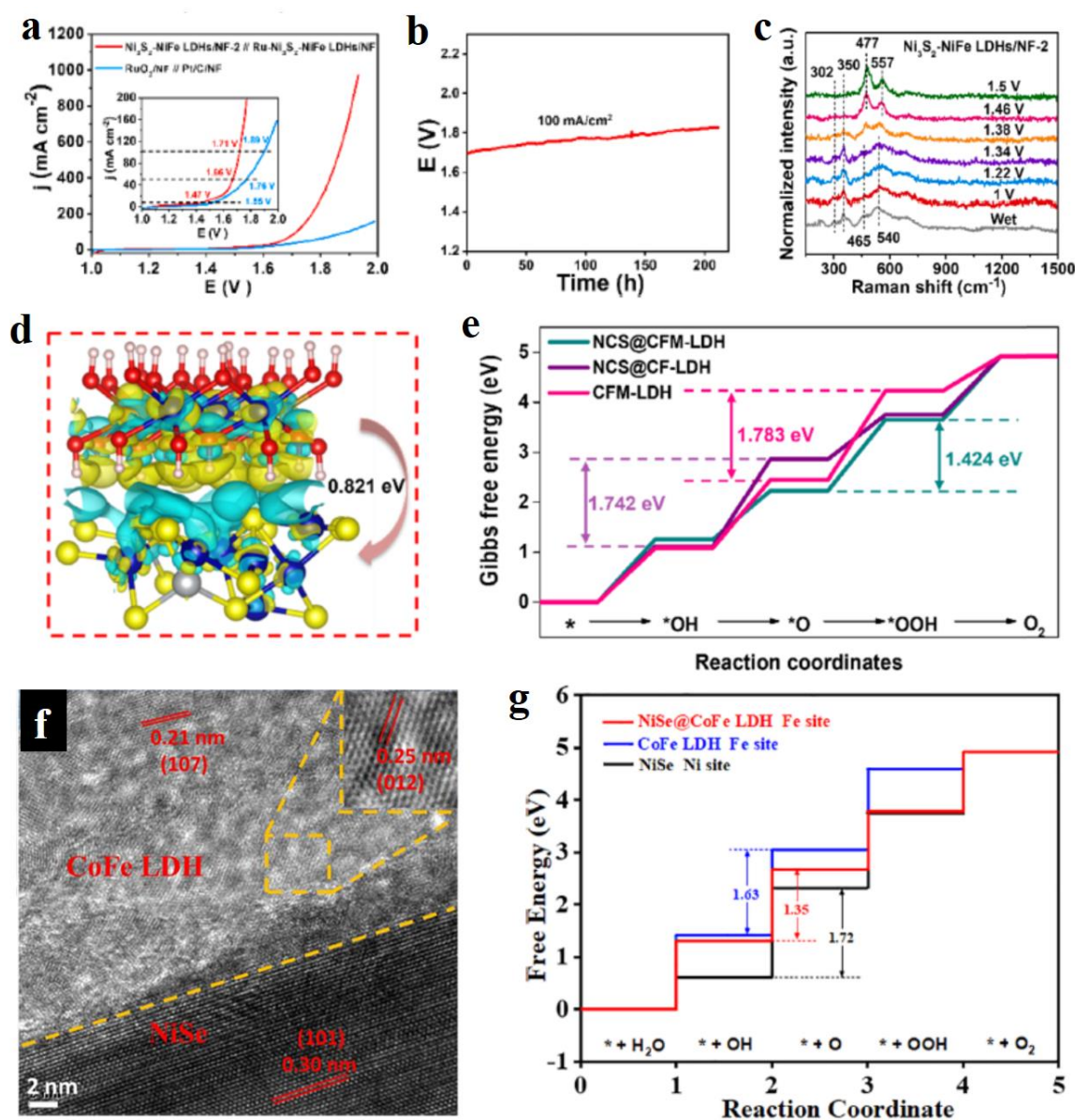
free energy diagram of HER. (e) Calculated free energy diagram of OER intermediates at zero potential ( $U = 0$ ). (f) The differential charge density diagram of NiFe-LDH-Vo-NiCu diagram. (a-f) Reproduced with permission [66]. Copyright 2022, Elsevier.

### 3.2 Metal compounds

Due to the plentiful combination modes of metal and non-metal atoms, a large number of heterojunctions constructed by LDH and metal compounds have been developed as water splitting electrocatalysts, including metal oxides, chalcogenides, phosphides and carbides. These metal compounds featured with their unique electronic structures have been widely utilized as efficient regulators to enhance electrocatalytic performance of LDH materials. Li et al. reported a novel  $\text{Ni}_3\text{S}_2$ -embedded NiFe-LDH heterogeneous structured porous nanosheets on Ni foam ( $\text{Ni}_3\text{S}_2$ -NiFe-LDHs/NF), which was synthesized via a simple one-pot solution method at room temperature for only 15 minutes [67]. In this preparation process, NaHS played a vital role in synthesizing this material. It not only reacted with metal cations to produce sulfides, but also hydrolyzed to produce  $\text{OH}^-$  which provided condition for the growth of LDH. The as-prepared catalyst possessed rich coupling interfaces and enhanced charge transfer capability, as well as the porous nanosheet structure endowed its more exposed active sites, which jointly contributed to excellent OER activity. In details, the current densities of 50, 500 and  $1000 \text{ mA cm}^{-2}$  could be realized at the low overpotentials of 230, 285 and 303 mV, respectively. Furthermore, the water splitting cell constructed by  $\text{Ni}_3\text{S}_2$ -NiFe-LDHs/NF exhibited the high current densities of 100 and  $500 \text{ mA cm}^{-2}$  at low voltages of 1.71 and 1.85 V, respectively, much better than that of cell formed by Pt/C and  $\text{RuO}_2$  (Figure 8a), as well as possessed the excellent stability in continuous more than 200 h test (Figure 8b). In this work, the authors used in situ Raman spectra to investigate the dynamic surface chemistry of  $\text{Ni}_3\text{S}_2$ -NiFe-LDHs. With increase of applied potential during OER, the characteristic Raman peaks of  $\text{Ni}_3\text{S}_2$  at 302 and  $350 \text{ cm}^{-1}$  were gradually decreased and then disappeared at 1.46 V vs. RHE, while the Raman peaks of 477 and  $557 \text{ cm}^{-1}$  assigned to  $\text{Ni}^{3+}$ -O vibrations emerged and were transferred from 465 and  $540 \text{ cm}^{-1}$  assigned to  $\text{Ni}^{2+}$ -O (Figure 8c). This resulted well demonstrated that  $\text{Ni}^{3+}$  species was the highly active catalytic sites for OER, and the  $\text{Ni}_3\text{S}_2$  was not stable and easily transformed into metal hydroxides. Feng et al. reported a unique cactus-

like morphology of NiCo<sub>2</sub>S<sub>4</sub>-NiFe LDH heterostructure, which performed long-term stability and better OER activity than commercial IrO<sub>2</sub> [68]. The enhanced OER activity was attributed to the strong interaction between NiCo<sub>2</sub>S<sub>4</sub> and NiFe-LDH. In addition, NiFe-LDH with nano-sheet and nano-wire structure well inhibited the collapse of NiCo<sub>2</sub>S<sub>4</sub> hollow nanospheres, and thus protected NiCo<sub>2</sub>S<sub>4</sub> from chemical corrosion to ensure its super stability. Nowadays, many other metal sulfides have been reported as the components to hybridize with LDH for developing excellent electrocatalysts, such as FeNi<sub>2</sub>S<sub>4</sub> [69], NiCo<sub>2</sub>S<sub>4</sub> [70], NiS<sub>x</sub> [71]. Generally, this kind of heterojunction exists the clearly electron transfer process between the individual component, which greatly optimizes the energy profiles of reactions, thus leading to low overpotentials. For instance, electrons accumulated at interface between CoFe-LDH and NiCo<sub>2</sub>S<sub>4</sub> (Figure 8d), thus forming the highly active catalytic sites for OER with an optimized energy profile (Figure 8e) [70]. For OER, the more electron states accumulated over Fermi level facilitate to react with reactants due to the fast electron transfer process, which is the guidance of design OER materials towards high electrocatalytic activity.

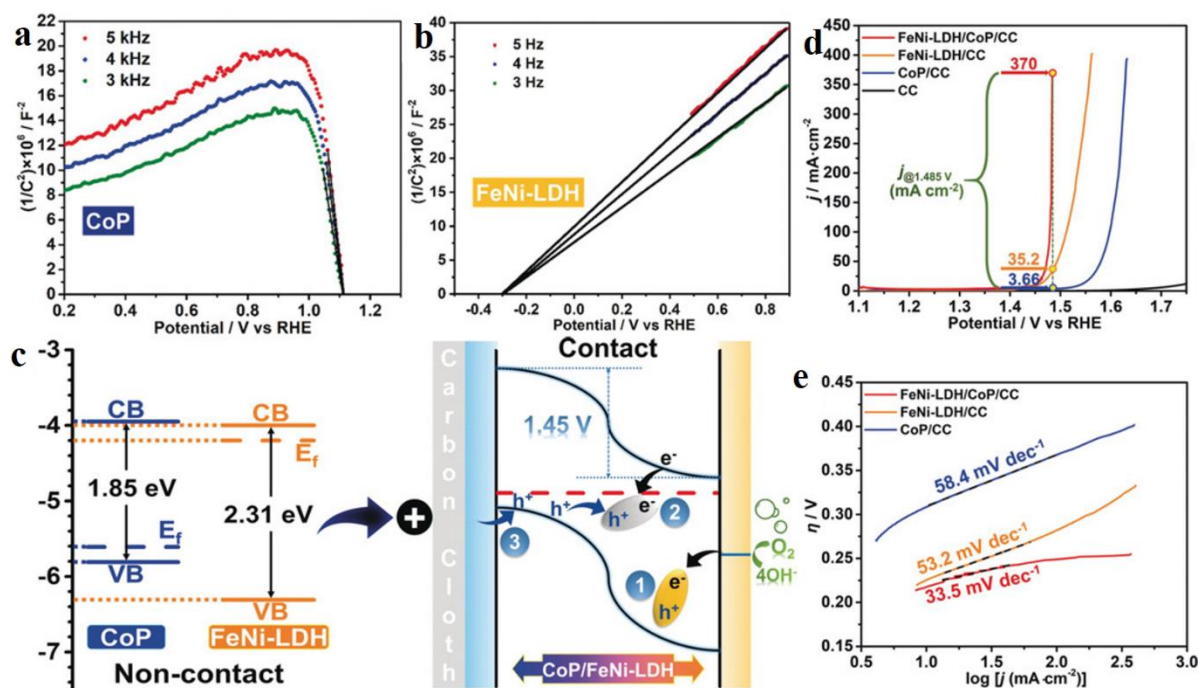
Similar to the case of metal sulfides, metal selenides also hybridize with LDH to form high performance of heterojunction catalysts. Peng et al. prepared FeNi<sub>2</sub>Se<sub>4</sub>-FeNi-LDH heterostructure by in-situ growth of FeNi-LDH nanosheet array on nickel foam conductive substrate and subsequent partial selenization treatment, which performed the low overpotentials of 205 mV for OER and 106 mV for HER at current density of 10 mA cm<sup>-2</sup> [72]. In water splitting cell, FeNi<sub>2</sub>Se<sub>4</sub>-FeNi-LDH acted as a bifunctional catalyst to drive the cell in voltage of 1.56 V at 10 mA cm<sup>-2</sup> which is lower than that of cell constructed by Pt/C and RuO<sub>2</sub> (1.58 V), indicating its great potential in substituting for precious metal catalysts. NiSe-CoFe-LDH nanoarrays were prepared by first selenization method and then electrodeposition path [73]. Due to the intimate contact of NiSe and CoFe-LDH (Figure 8f), the electronic interaction between NiSe and CoFe-LDH was easily observed in XPS spectra. Such interaction resulted in the formed highly active catalytic sites for OER with low theoretical overpotentials (Figure 8g). Metal selenides hybridized with LDH have been more and more demonstrated that LDH can strongly interact with metal selenides to form highly active catalytic sites, which is also an efficient candidate to improve electrocatalytic performance of LDH, e.g., Cu<sub>2</sub>Se-NiFe-LDH nanosheets [74], NiSe-FeNi-LDH [75].



**Figure 8.** Electrocatalytic performance and theoretical studies of LDH hybridized with metal sulfides and selenides. (a) LSV curves of water splitting cell over  $\text{Ni}_3\text{S}_2\text{-NiFe-LDHs}$ . (b) Stability of  $\text{Ni}_3\text{S}_2\text{-NiFe-LDHs}$  in water splitting cell. (c) Raman spectra in water splitting cell using  $\text{Ni}_3\text{S}_2\text{-NiFe-LDHs}$  as catalyst. (d) Charge density difference at the  $\text{NiCo}_2\text{S}_4\text{-CoFe-LDH}$  interface, and the charge depletion and accumulation are in yellow and blue, respectively. (e) Calculated free energy diagram of OER. (f) TEM images of  $\text{NiSe-CoFe-LDH}$ . (g) Calculated free energy diagram of OER. (a-c) Reproduced with permission [67]. Copyright 2022, Elsevier.

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Metal phosphides ( $MP_x$ ) have been widely applied in electrocatalysis due to their multifunctional active sites, tunable structures and compositions, as well as plentiful electronic properties [76]. Liu et al. reported a FeNi-LDH-CoP n-p junction structure composed of amorphous n-type FeNi-LDH and p-type CoP nanoarrays, which exhibited the excellent OER performance with 231 mV overpotential at 20 mA cm<sup>-2</sup> [77]. From Mott-Schottky (M-S) plots of FeNi-LDH and CoP, it was easily observed that FeNi-LDH was a n-type semiconductor with a positive slope of Tauc plot and CoP was a p-type semiconductor with a negative slope of Tauc plot (Figure 9a,b). The flat band (FB) potentials for FeNi-LDH and CoP were -0.3 and 1.11 V vs. RHE, respectively. Therefore, the band structures of FeNi-LDH and CoP could be obtained as shown in Figure 9c (Left) when they were not contact. Due to the different Fermi levels of two semiconductors, electrons over CoP transferred to FeNi-LDH when they were contact (Figure 9c (Right)). Such electron transfer process could be easily observed in XPS data of serial catalysts, which led to enhanced OER activity of CoP-FeNi-LDH with a low Tafel slope of 33.5 mV dec<sup>-1</sup> (Figure 9d,e). The excellent OER performance of CoP-FeNi-LDH junction was attributed to the positively charged FeNi-LDH site possessing a strong ability for adsorbing OH<sup>-</sup>, thus greatly facilitating the OER dynamics with a low energy barrier. This work provides an efficient approach to develop advanced electrocatalysts through constructing n-p and p-p junction with a strong ability of OH<sup>-</sup> adsorption [78,79]. In a short word, metal phosphides hybridized with LDH usually possess the excellent electrocatalytic performance in water splitting with several hundred current densities up to 300 mA cm<sup>-2</sup>, especially for their superior OER activities [78,80,81].

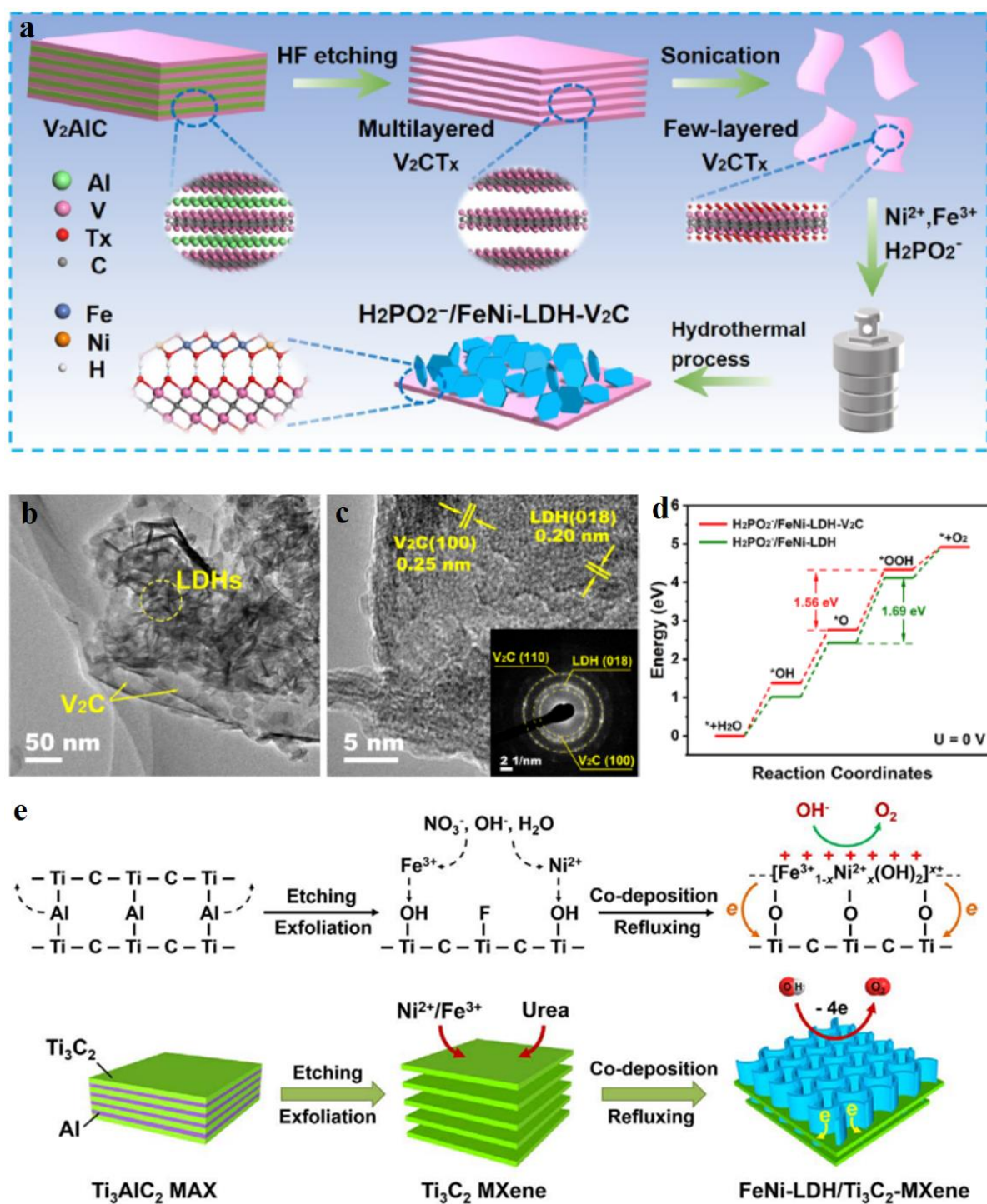


**Figure 9.** Characterizations and electrocatalytic performance of CoP-FeNi-LDH junction. (a) Mott-Schottky plots of CoP. (b) Mott-Schottky plots of FeNi-LDH. (c) The energy diagrams of CoP and FeNi-LDH and the proposed mechanism for electrocatalyzing OER in the FeNi-LDH-CoP p-n junction under the condition of applied potential. (d) LSV curves of OER over serial catalysts. (e) Tafel slopes of catalysts. (a-e) Reproduced with permission [77]. Copyright 2019, Wiley-VCH.

In recent years, two-dimensional (2D) metal carbides and nitrides (MXenes) as a promising electrocatalyst in energy conversion field, have achieved more and more attention from researches due to their high specific surface area, good electrical conductivity, superior mechanical strength, and tunable surface chemistry [82]. Metal carbides and nitrides have also been well demonstrated as an efficient candidate to hybridize with LDH aiming to obtain high performance electrocatalysts [82,83]. Hou et al. coupled a few-layer  $\text{V}_2\text{C}$  nanosheets and FeNi LDH nanosheets with  $\text{H}_2\text{PO}_2^-$  intercalation to form  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH-V}_2\text{C}$  hybrid material for enhancing OER with 250 mV overpotential at  $10 \text{ mA cm}^{-2}$  and a small Tafel slope of  $46.5 \text{ mV dec}^{-1}$  [84]. This heterojunction was prepared by combining the chemical etching and hydrothermal method (Figure 10a). Due to the 2D morphology structures of  $\text{V}_2\text{C}$  and NiFe-



LDH materials, the  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH-V}_2\text{C}$  possessed the intimate contact between the individual components (Figure 10b,c), which led to electron transfer between them as demonstrated by the shifts of their elements' XPS and XAS spectra. Such electron transfer generated the new highly catalytic OER sites with optimized energy profile with a theoretical overpotential of 1.56 eV, much lower than that of  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH}$  being of 1.69 eV (Figure 10d). In this material system, the  $\text{H}_2\text{PO}_2^-$  acted as an anion intercalation to adjust the intrinsic electronic structure of pristine NiFe-LDH, which also played a synergistic role in enhancing OER activity, much better than that of  $\text{CO}_3^{2-}$  reference. DFT results showed that the  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH-V}_2\text{C}$  heterojunction owned a higher electron state than that of  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH}$  which facilitated the electron transfer process during OER, thus leading to a low energy barrier. Qiu et al. developed a hierarchical NiFe LDH/ $\text{Ti}_3\text{C}_2$ -MXene nanohybrid as an efficient OER catalyst [85].  $\text{Ti}_3\text{C}_2$  was synthesized by etching  $\text{Ti}_3\text{AlC}_2$  with LiF and HCl to form  $\text{Ti}_3\text{C}_2$  with 2D morphology structure and plentiful superficial  $\text{OH}^-$  chemical groups. For NiFe-LDH growth,  $\text{Ni}^{2+}/\text{Fe}^{3+}$  tended to combine with  $\text{OH}^-$  groups on  $\text{Ti}_2\text{C}_3$  due to the electrostatic adsorption, and then subsequent hydrolysis and oxidation of  $\text{MO}_6$  groups provided support for the growth of LDH on  $\text{Ti}_2\text{C}_3$  (Figure 10e). In this process, LDH could be firmly anchored on the surface of  $\text{Ti}_2\text{C}_3$ , efficiently preventing its agglomeration, thus endowing its excellent stability during OER. Meanwhile, the strong interaction between them promoted the oxidation-reduction process of LDH for OER and effectively electron transferred between the NiFe-LDH and  $\text{Ti}_2\text{C}_3$  due to the high conductivity of  $\text{Ti}_2\text{C}_3$ . Generally, two-dimensional metal carbides and nitrides are the big family materials to hybridized with LDH materials due to its tunable and plentiful surficial chemical groups which provide the ideal sites for LDH growth with uniform dispersion. Simultaneously, the high conductive property of metal carbides and nitrides endows the fast electron transfer between the reactants and catalytic sites, thus facilitating the dynamics of reactions during electrocatalysis. Therefore, more and more MXenes-LDH heterojunction catalysts have been reported as excellent electrocatalysts in water splitting [82,83,86-88], especially for their superior OER performance.

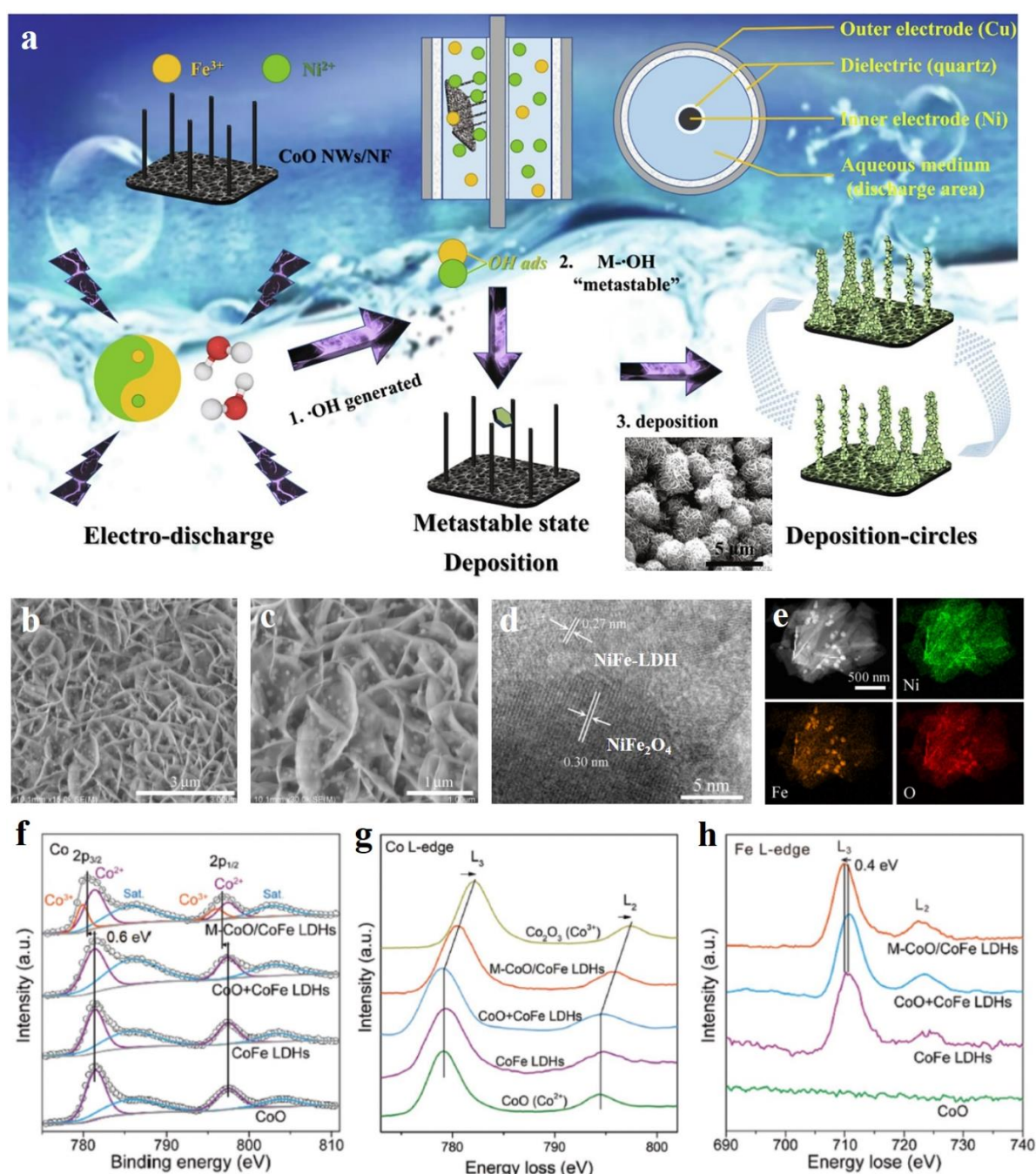


**Figure 10.** Schematic illustration, characterizations and electrocatalytic performance of MXene hybridized with LDH. (a) Preparation process of  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH-V}_2\text{C}$ . (b, c) TEM images of  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH-V}_2\text{C}$ . (d) Calculated energy profile of OER over  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH-V}_2\text{C}$  and  $\text{H}_2\text{PO}_2^-/\text{NiFe-LDH}$  at  $U=0$  V. (e) Preparation process of  $\text{NiFe-LDH-Ti}_3\text{C}_2$ . (a-d) Reproduced with permission [84]. Copyright 2021, Elsevier. (e) Reproduced with permission [85]. Copyright 2018, Elsevier.

Transition metal oxides featured by their low cost, high stability and excellent electrocatalytic activity, also have been as the candidates for hybridizing with LDH to construct excellent catalysts [89]. Huang et al. prepared CoO-NiFe-LDH/NF electrocatalysts with 3D open structure via a novel Dielectric Barrier Discharge (DBD) microplasma [90]. This unique preparation method possesses the three advantages in guiding material formation (Figure 11a): (1) Due to the higher plasma chemical reactivity, BDB microplasma had higher density of free radicals, which was favorable for the formation of  $\bullet\text{OH}$  in the aqueous solution of BDB reactor; (2) The integration of electric work endowed the metal ions and OH in aqueous solution with enough energy to keep them in a "metastable state" to ensure the nucleation and growth of NiFe-LDH; (3) Cyclic deposition can ensure that NiFe LDH was uniformly distributed on CoO/NF. Such unique 3D open structure of CoO-NiFe-LDH/NF was favorable for reactants diffusion and products release, thus exhibiting an enhanced OER activity. Gao et al. used one-step solvothermal method to prepare the  $\text{NiFe}_2\text{O}_4$  nanoparticles loaded on NiFe-LDH nanosheets.  $\text{NiFe}_2\text{O}_4$  nanoparticles were uniformly dispersed on the NiFe-LDH nanosheets (Figure 11b-e), which provided more exposed actives for OER [91]. In details, the large current densities of 500 and 1000  $\text{mA cm}^{-2}$  for OER could be obtained under the small overpotentials of 242 and 265 mV, respectively, as well as long time stability in continuous 20 h test under the current density of 500  $\text{mA cm}^{-2}$ . The superior electrocatalytic performance of  $\text{NiFe}_2\text{O}_4$ -NiFe-LDH was attributed to the strong interface coupling between  $\text{NiFe}_2\text{O}_4$  and NiFe-LDH, which endowed the composite with better electron mobility and more catalytic active sites to participate reactions. Strong chemical interaction between metal oxides and LDH has also been well supported on the CoO nanoclusters on CoFe-LDH support [92]. XPS and XAS spectra showed that the Co-O-Fe bond formed at the strong coupling interface of heterostructure contributed to the electron transfer from CoO to CoFe-LDH and the formation of a large amount of  $\text{Co}^{3+}$  (Figure 11f-h), thus leading to enhanced OER activity. Similar, the NiO nanoparticles supported on NiFe-LDH nanosheets with intimate contact were also successfully prepared by the hydrothermal and post calcination method as efficient OER catalyst [93]. Zhao et al. used the  $-\text{NH}_2$  group to modify the surface of NiFe-LDH, in which the  $-\text{NH}_2$  group provided the sites for  $\text{Ir}^{4+}$  adsorption and  $\text{IrO}_2$  growth [94]. Due to this point,  $\text{IrO}_2$  nanoparticles with a uniform size of 5 nm were loaded on NiFe-LDH, thus leading to a low overpotential of 274 mV at a

current density of  $10 \text{ mA cm}^{-2}$ , a low Tafel slope of  $59 \text{ mV dec}^{-1}$  and superior stability in the continuous 35 h test. Nowadays, metal oxides have been developed the big family candidates for constructing heterojunction with LDH, e.g., CuO-CoOOH [95], CuO-FeCoNi-LDH [96],  $\text{Co}_3\text{O}_4$ -FeOOH [97]. In these heterojunctions, the electron transfer between the individual components is the main reason of their high electrocatalytic performance, and the heterojunctions are usually p-n type [95,96]. Recently, carbonate hydroxides have been reported as another component to hybridize with LDH materials to form high-performance OER and HER materials [98], which also opens other method to modify LDH materials by using metal carbonate hydroxides.





**Figure 11.** Schematic illustration and characterizations of metal oxides hybridized with LDH. (a) Schematic illustration of preparing CoO-NiFe-LDH. (b, c) SEM images of NiFe<sub>2</sub>O<sub>4</sub>/NiFe-LDH. (d) High resolution TEM image of NiFe<sub>2</sub>O<sub>4</sub>/NiFe-LDH. (e) Dark field TEM and elemental mapping images of NiFe<sub>2</sub>O<sub>4</sub>/NiFe-LDH. (f) Co 2p XPS spectra of serial Co-based materials. (g) Co EELS spectra of serial Co-based materials. (h) Fe EELS spectra of serial Co-based materials. (a) Reproduced with permission [90]. Copyright 2021, Elsevier. (b-e) Reproduced with permission [91]. Copyright 2018, American Chemical Society. (f-h) Reproduced with permission [92]. Copyright 2018, Wiley-VCH.

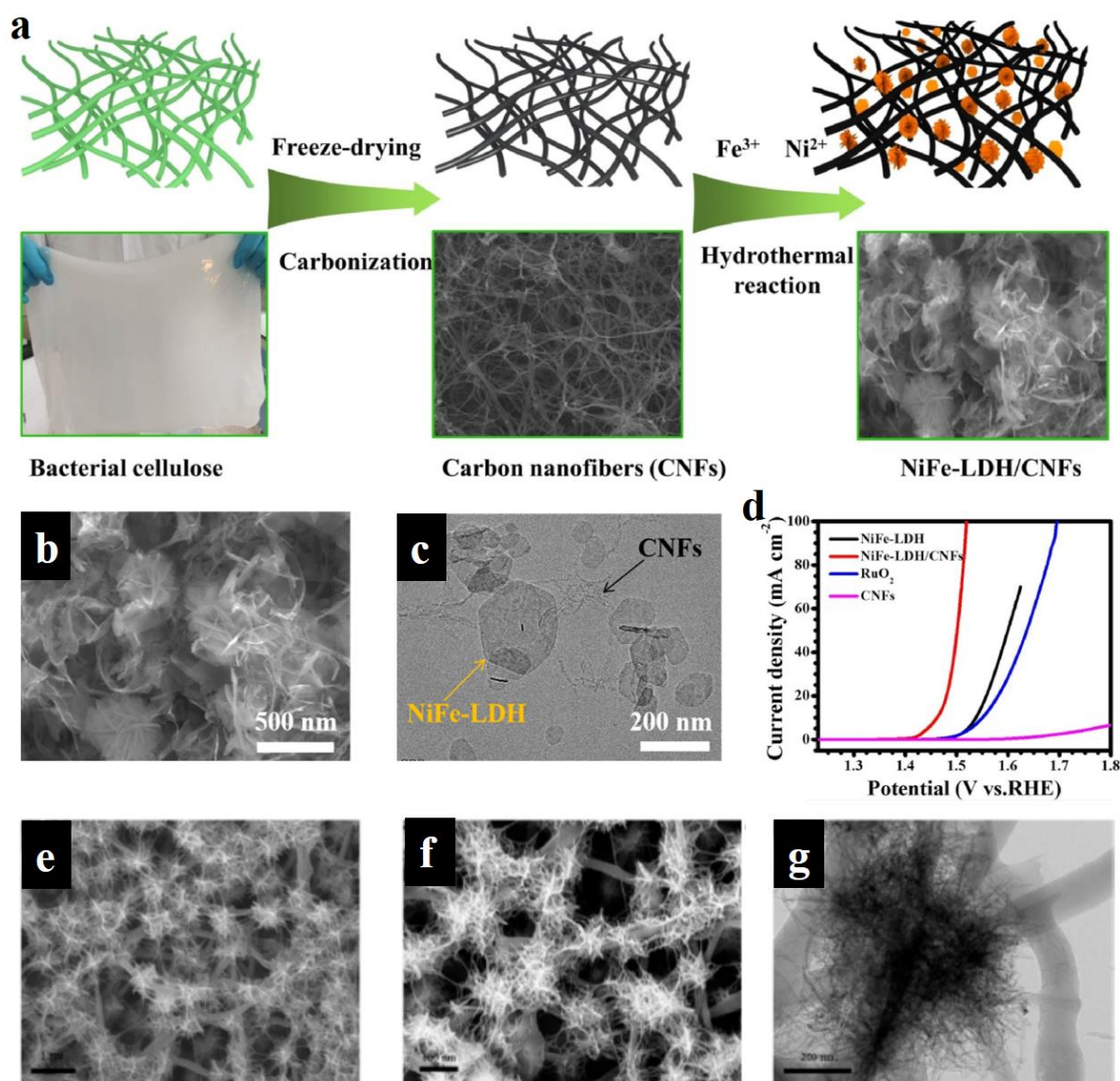


### 3.3 Carbon materials

As one of the huge reserve resources, carbon-based materials have been widely applied in field of energy conversion and storage, due to their high specific surface area, low cost, high conductivity, tunable chemical modification (e.g., heteroatom doping) and variable morphological features (e.g., 1D, 2D and 3D morphologies) [99-102]. As well known, the poor conductivity of LDH greatly restricts the electron transfer between the bulk catalysts and reactant species, thus leading to high overpotential of reactions [103]. Carbon materials featured by high conductivity are widely regarded as efficient candidates for hybridizing LDH to construct excellent electrocatalysts. Simultaneously, their porous structure endows LDH intimately contact with carbon materials, and also provides the more active sites exposed in electrolyte, as well as facilitates the reactants and products diffusion. Liu et al. used the bacterial cellulose as carbon source to obtain carbon nanofibers by carbonization method, and then FeNi-LDH were loaded on carbon nanofibers using hydrothermal method (Figure 12a) [104]. From SEM and TEM images as shown in Figure 12b,c, carbon nanofibers as the binder efficiently linked the FeNi-LDH, thus well establishing the 3D morphological feature. This FeNi-LDH/carbon nanofibers exhibited superior OER activity (230 mV overpotential at  $10 \text{ mA cm}^{-2}$ ) to commercial  $\text{RuO}_2$  and pure FeNi-LDH materials (Figure 12d). This work well demonstrates that the conductivity of catalysts is important for enhancing their electrocatalytic performance. Xu et al. successfully assembled the Ni-based LDHs/graphene quantum dots (GQDs) heterojunction catalyst on the foam nickel conductive skeleton by employing the electrostatic adsorption principle [105]. Combined with DFT theoretical calculation, XPS analysis and OER test results, it could be revealed that the pristine electronic structure of the prepared heterojunction catalyst was changed due to the strong interaction of heterojunction interface, and thus the adsorption energy of reaction intermediates was optimized. The electrons over LDH transferred to GQDs, which increased the valence state of metal cations in LDH and improved the adsorption capacity of  $\text{OH}^-$  in order to ensure the charge balance in LDH. This work suggests that valence state of LDH can be tuned by carbon materials, thus optimizing the adsorption energies of intermediates towards lowering reaction energy barriers.

3D morphology of NiFe-LDH/carbon fiber heterojunction was easily prepared by first carbonization of polyacrylonitrile (PAN) and iron phthalocyanine (FePc) and second

hydrothermal method [106]. NiFe-LDH was uniformly dispersed on carbon fibers with nanosheet morphology (Figure 12e-g). This morphological feature facilitated the reactants diffusion, thus improving the OER dynamics. Now, heterojunction composed by carbon materials and LDH have been more and more developed in recent years, such as NiCo-LDH/GO-CNTs [107], NiCo-LDH/fullerene dots [108], FeNiOOH/carbon dots [109], NiCo-LDH/graphite felt [110]. As one of the traditional carbon dots (CDs), fullerene quantum dot (FQD) has attracted attention from researchers. Wang et al. designed a three-dimensional layered structure on foamed nickel by simple self-assembly strategy, which consisted of CoNi-LDH modified by FQDs. FQDs/CoNi-LDH/NF with exhibiting excellent HER and OER properties was attributed to FQDs being anchored in the interlayer and surface of NiCo-LDH to accelerate electron and mass transport [108]. In water splitting cell, the prepared FQD/CoNi-LDH/NF catalyst could be used as cathode and anode to drive overall water-splitting reaction, and the cell voltage of 1.59 V could reach 10 mA cm<sup>-2</sup>.



**Figure 12.** Schematic illustration, characterizations and electrocatalytic performance of carbon materials hybridized with LDH. (a) Schematic illustration of preparing FeNi-LDH/carbon nanofibers. (b, c) SEM (b) and TEM (c) images of FeNi-LDH/carbon nanofibers. (d) LSV curves of serial catalysts. (e-g) SEM (e, f) and TEM (g) images of NiFe-LDH/carbon fibers. (a-d) Reproduced with permission [104]. Copyright 2022, Elsevier. (e-g) Reproduced with permission [106]. Copyright 2022, American Chemical Society.

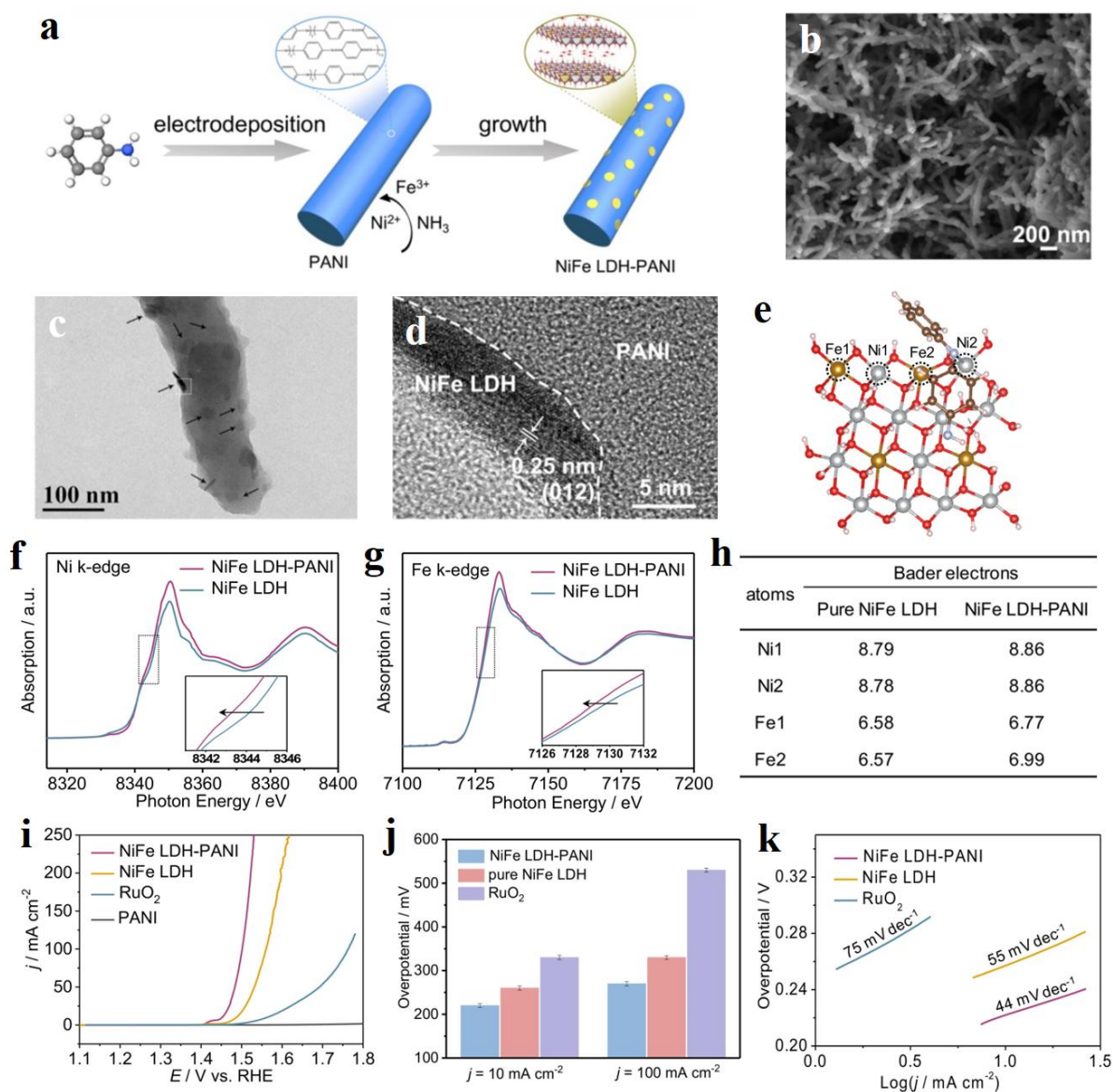
### 3.4 Organic materials

Due to the easier adjustability of interlayer spacing, the interlayer metal ions of LDHs are capable of coordinating with organic ligands including the conductive polymers and metal-

organic framework to construct organic/LDHs heterojunctions to enhance electrocatalytic activity of LDH [111-114]. Huang et al. prepared the electron-rich NiFe-LDH loaded on carbon paper modified by polyaniline (PANI) via the first electrodeposition and followed by hydrothermal method (Figure 13a) [113]. SEM and TEM images showed that NiFe-LDH nanodisks grew on the surface of PANI nanorods with intimate contact (Figure 13b-d). Due to this point, the strong chemical interaction between NiFe-LDH and PANI resulted in the changed electron state of Ni and Fe sites in NiFe-LDH. In details, Ni and Fe gathered more electrons from PANI, leading to the negative shift of pre-edge for Ni and Fe compared to pure NiFe-LDH (Figure 13f,g) and lower binding energies in their XPS spectra. Bader charge analysis showed that Ni and Fe sites in NiFe-LDH-PANI had higher electron density compared to pure NiFe-LDH (Figure 13e,h), and higher DOS near Fermi level. Because of this point, NiFe-LDH-PANI possessed a more moderate energy for the formation of  $\ast\text{OH}$  and a lower energy for the formation of  $\ast\text{O}$ , thus lowering the energy barrier of reaction and accelerating the kinetics of OER. Finally, NiFe-LDH-PANI delivered an excellent OER performance including the low overpotentials of 220 and 270 at 10 and 100  $\text{mA cm}^{-2}$ , respectively (Figure 13i), much better than that of commercial  $\text{RuO}_2$  (Figure 13j), as well as a low Tafel slope of 44  $\text{mV dec}^{-1}$  (Figure 13k).

In addition, metal organic framework (MOF) also can form the heterojunction with LDH materials to enhance catalytic performance [112,115,116]. Chen' group prepared a heterogeneous array of 2D NiFe-LDH nanosheets packed with 1D NiFe MOF (NiFe-LDH/MOF) with extraordinary OER performance in carbon fiber cloth [115]. During the preparation process, NiFe-LDHs were partially converted into NiFe MOFs *via* template sacrifice method. In the formation process of the catalyst, 2,5-dihydroterephthalic acid ( $\text{H}_4\text{DOBDC}$ ) coordinated with NiFe-LDHs, which led to *in-situ* phase reconstruction and nanocrystalline growth. With the increase of reaction time, the pristine NiFe-LDHs gradually transformed into ultrathin NiFe-LDH nanosheets and Fe/Ni-based MOF. This unique method endowed the intimate contact of NiFe-LDH nanosheets and Fe/Ni-based MOF, thus delivering superior OER performance including a low overpotential of 72  $\text{mV}$  100  $\text{mA cm}^{-2}$  and high stability in 36 continuous test and 10000 potential cycles. In this material system, the unsaturated porous NiFe MOFs provided the abundant metal active sites and facilitated to form

the ultrathin NiFe-LDHs, which made more OER active sites exposed in electrolyte. This work also provides an efficient approach to construct advanced electrocatalysts to decrease the size in thickness of LDH via a template sacrifice method.



**Figure 13.** Preparation, characterizations and OER performance of NiFe-LDH-PANI (a) Schematic illustration of the synthesis of NiFe-LDH-PANI. (b) SEM, (c, d) TEM images of NiFe LDH-PANI. (e) The structural model of NiFe-LDH-PANI. Gray, yellow, red, brown, light blue, and pink spheres present Ni, Fe, O, C, N and H atoms, respectively. (f) Ni K-edge and (g) Fe K-edge XANES spectra. (h) Bader charges for Ni and Fe atoms at the surface of pure NiFe-LDH and the interface of NiFe-LDH-PANI. (i) LSV curves of serial catalysts. (j) Overpotentials



at different current densities. (k) Tafel slope. (a-k) Reproduced with permission [113]. Copyright 2021, Elsevier.

## 4. Morphological strategy

The electrocatalytic performance of catalysts is closely related with their morphologies which involves the number of active sites, electron transfer process between bulk catalysts and reactants, as well as reactant and product diffusion. Nowadays, some reported morphological strategies of LDH have been reported to enhance the activity of LDH materials. In this section, the recent advances of morphological strategy on enhancing electrocatalytic performance will be summarized including preparation methods, characterizations, electrocatalytic performance and reaction mechanism.

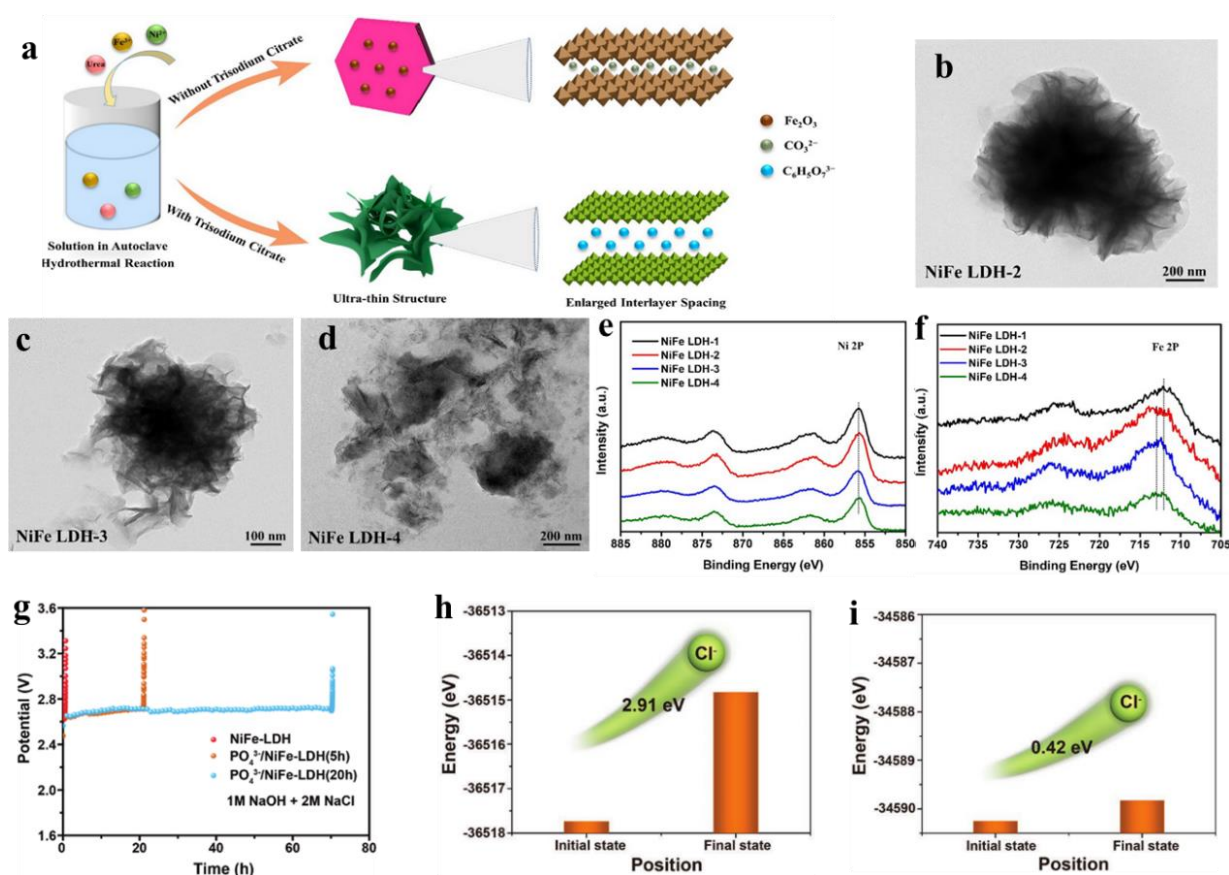
### 4.1 Intercalation

Due to the weak interaction of layers for LDH, the anions are easily incorporated into layers of LDH, thus tuning its interlayer spacing distance and enhancing their ECSA. In general, the large interlayer spacing facilitates to form LDHs nanosheets with high specific surface area and exposed density of active sites, as well as forming anion defects, thus further improving the electrocatalytic performance of LDHs. In addition, when the spacing between layers exceeds a certain threshold, it is helpful for LDHs to peel off and form ultrathin nanosheet structure with smaller size.

Gu et al. realized the preparation of intercalation-induced partial exfoliation of NiFe-LDHs with abundant active edge sites by utilizing the one-pot hydrothermal method [117]. In the preparation process, trisodium citrate was as intercalation agent to replace the  $\text{CO}_3^{2-}$  ion intercalation in the traditional NiFe-LDH material, which endowed it being of a large interlayer spacing and formed an obviously different morphological structure (Figure 14a). The morphology of NiFe-LDH changed from the flower-like structure composed of nanosheets to the ultrathin nanosheets structure with the increase of trisodium citrate content, which suggested that more active sites were exposed on the surface of LDH (Figure 14b-d). XPS data showed that the electronic structure of Fe sites on NiFe-LDH surface changed with a positive shift after introducing citrate anion, which the Ni sites kept a stable structure without clear changes

(Figure 14e,f). Because of existing above changes after intercalation of citrate anion, the modified NiFe-LDH exhibited an enhanced OER activity. What's more, anion intercalation also can improve the stability of LDH. For instance, Sun et al. prepared NiFe-LDH with  $\text{PO}_4^{3-}$  intercalation, which efficiently inhibited the corrosion of Ni conductive substrate by  $\text{Cl}^-$  in seawater due to the existed electrostatic repulsion between highly negatively charged  $\text{Cl}^-$  ions and highly negatively charged  $\text{PO}_4^{3-}$ , and thus significantly improved the stability of NiFe-LDH in seawater electrolyte [118].  $\text{PO}_4^{3-}$  intercalated NiFe-LDH maintained a high current of  $400 \text{ mA cm}^{-2}$  after continuous 72 h test in simulated seawater solution with high NaCl concentration (1M NaOH+2M NaCl), and its stability was 100 times higher than that of pure NiFe-LDH (40 min) (Figure 14g). DFT calculation showed that NiFe-LDH with  $\text{PO}_4^{3-}$  intercalation had a higher migration energy barrier of  $\text{Cl}^-$  than that of pure NiFe-LDH, which proved that  $\text{Cl}^-$  had a weaker migration ability in NiFe-LDH with  $\text{PO}_4^{3-}$  intercalation (Figure 14h,i). Therefore, the excellent stability of NiFe-LDH intercalated with  $\text{PO}_4^{3-}$  could be attributed to the fact that the introduction of  $\text{PO}_4^{3-}$  was conducive to reduce the corrosion of  $\text{Cl}^-$  on the foam nickel conductive substrate and the shedding of NiFe-LDH without  $\text{Cl}^-$  corrosion. This work well provides a new idea for designing efficient and stable seawater electrolysis catalysts through the anion intercalation of LDH materials. Nowadays, anion intercalation has been developed as an efficient approach to improve electrocatalytic performance of LDH [119-121], which leads to LDH with a thin layer structure, more exposed catalytic sites and tuned electronic densities of metals. Because of these advantages, LDH with anion intercalation always exhibits an excellent activity and stability in water splitting. The layer distance between LDH materials can be also easily tuned by the organic small molecules, in which the organic small molecules efficiently weaken the interlayer interaction of LDH materials, thus leading to the enhanced electrocatalytic activity [122-124]. Gao's group reported that CoFe-LDH materials with a large interlayer distance of 0.6 nm were prepared in the ethanol solution using ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) as a pH regulator [122].  $\text{NH}_4\text{HCO}_3$  was decomposed into  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , thus leading to forming CoFe-LDH materials with adsorbing ethanol molecules and a large interlayer distance being of 0.6 nm. CoFe-LDH material featured by a large interlayer distance possessed the more cation defects supported by XAS spectra of Co and Fe compared to CoFe-LDH material without ethanol, and low impedance of electron transfer, as well as a

large ECSA, which jointly contribute to the enhanced OER activity. Recently, Sun's group have prepared a benzoate (BZ) anions-intercalated NiFe-LDH (BZ-NiFe-LDH) nanosheet [123]. Due to the resistance of BZ to  $\text{Cl}^-$  over NiFe-LDH, the BZ-NiFe-LDH nanosheet exhibited a superior OER activity and stability in seawater splitting. In details, the decreased OER activity for BZ-NiFe-LDH nanosheet is about 28% in the continuous 100 h test, much lower than that of NiFe-LDH being of 79%. This important work provides a promising method to construct advanced OER catalysts with superior stability though the organic molecule intercalation in LDH materials, and extends the application of LDH materials to seawater electrolysis.



**Figure 14.** Preparation illustration, characterizations and theoretical studies of LDH intercalated by anion. (a) Schematic illustration of the synthesis process of the NiFe-LDH without and with trisodium citrate. (b-d) TEM images of (b) NiFe LDH-2, (c) NiFe LDH-3, and (d) NiFe LDH-4. (e) Ni 2p and (f) Fe 2p XPS spectra of NiFe LDH-1, NiFe LDH-2, NiFe LDH-3 and NiFe LDH-4. (g) Durability tests of the NiFe-LDH and the  $\text{PO}_4^{3-}/\text{NiFe-LDH}$  with

different intercalation times under the current density of  $400 \text{ mA cm}^{-2}$ . (h,i) Energy barrier for  $\text{Cl}^-$  migration in the  $\text{PO}_4^{3-}/\text{NiFe-LDH}$  (h) and pure  $\text{NiFe-LDH}$  (i). (a-f) Reproduced with permission [117]. Copyright 2022, Elsevier. (g-i) Reproduced with permission [118]. Copyright 2022, Wiley-VCH.

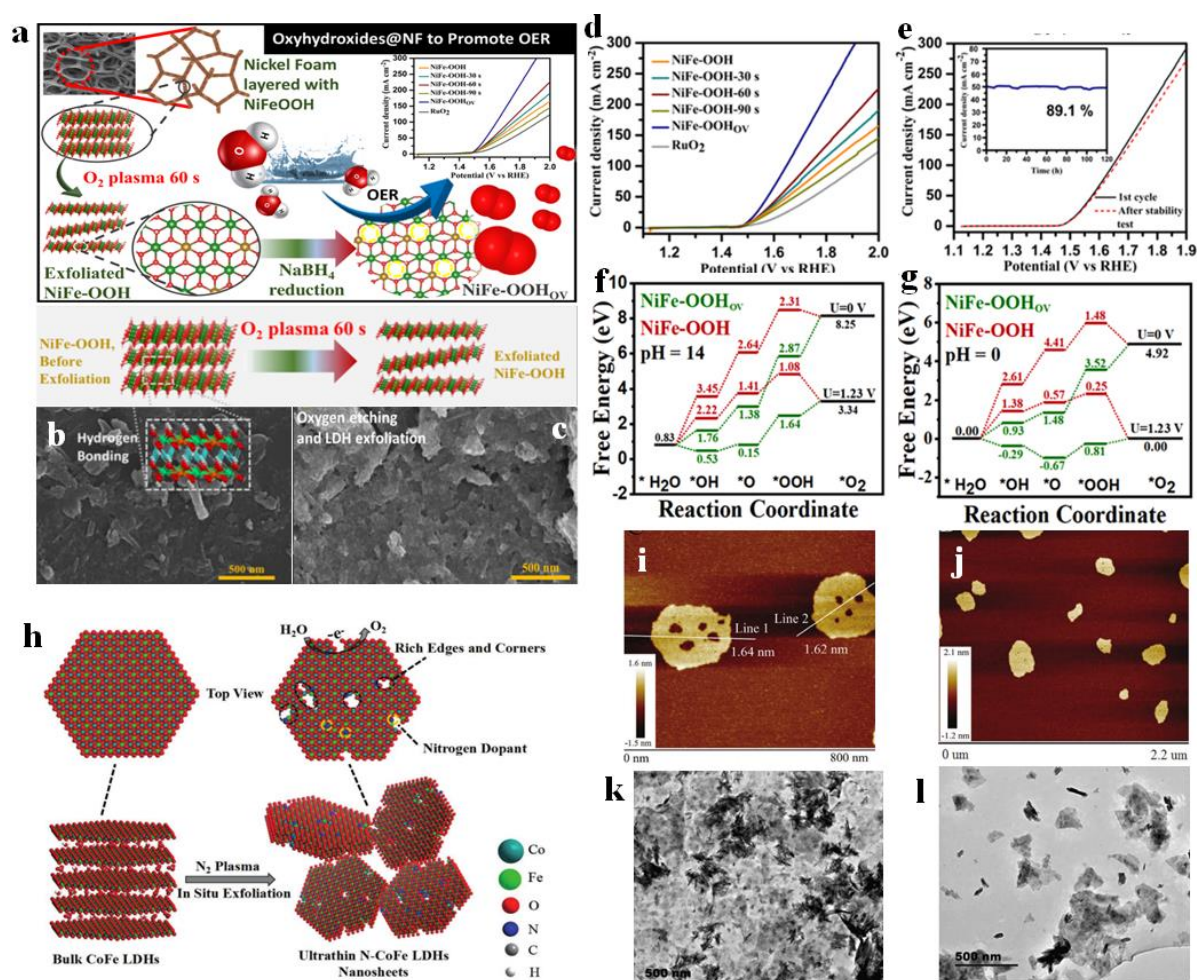
## 4.2 Exfoliation

In general, the traditional LDHs are layered stacked structures, which not only shield a large number of catalytic active sites, but also inhibit the electron and mass transfer during electrocatalytic reactions over catalyst. Therefore, it can be stripped into ultrathin nanosheets with smaller size by exfoliation strategy to significantly enhance electrocatalytic performance [125-129]. The peeled single-layer ultra-thin LDHs nanosheets provide large surface area and more electrochemically active sites, thus facilitating to react with reactants.

Bagchi et al. stripped  $\text{NiFe-LDH}$  by analogy with graphene stripping technology and prepared ultra-thin  $\text{NiFeOOH}$  nanosheets with oxygen vacancies by subsequent reduction treatment [125]. In the synthesis process, layered LDHs were firstly stripped by oxygen plasma method, and then reduced by  $\text{NaBH}_4$  at room temperature, which not only produced vacancies, but also inhibited the formation of hydrogen bonds connecting the layers together, which was conducive to the stripping of LDH (Figure 15a). Compared with pure  $\text{NiFe-OOH}$ ,  $\text{NiFe-OOH}$  after treated O-plasma for 60 s ( $\text{NiFe-OOH 60 s}$ ) showed the thinner fragment structure (Figure 15b,c), thus leading to the excellent OER performance. It delivered a current density of  $50 \text{ mA cm}^{-2}$  with a low overpotential of 330 mV for OER, and also maintained an ultra-high stability of 120 h at this current density (Figure 15d,e). The DFT calculation at different PH values revealed that  $\text{NiFe-OOH 60 s}$  was prone to adsorb  $\text{O}^*$ ,  $\text{OH}^*$  and  $\text{OOH}^*$  than pristine  $\text{NiFe-OOH}$ , and the free energy profile of OER steps was optimized due to the existence of oxygen defects (Figure 15f,g). In this material system, the  $\text{V}_\text{O}$  vacancy facilitated the electron transfer process during reactions, thus leading to the fast electron transfer to participate reactions. Meanwhile,  $\text{NiFe-OOH}_{\text{V}_\text{O}}$  material possessed a large ECSA, indicating its more exposed active sites in electrolyte, which also facilitated the electrocatalytic reactions. Wang et al. prepared vacancy-rich N-doped ultrathin  $\text{CoFe-LDH}$  nanosheets by  $\text{N}_2$  plasma etching technology, as shown in Figure 15h [126]. The AFM image of the sample showed that the stripped N-CoFe

LDH had a thickness of only 1.6 nm (Figure 15i,j). At the same time, many atomic-sized pores were observed on the basal plane of N-CoFe LDH due to plasma treatment, which proved the structural characteristics of the catalyst with rich edge sites, and the atomic-sized pores were helpful to improve the electrocatalytic activity of the catalyst due to the exposure of more electrocatalytic active sites as presented a lower resistance ( $21.4 \Omega$ ) than that of CoFe LDH ( $94.9 \Omega$ ). Meanwhile, the formed atomic-sized pores resulted in the generated Co and Fe with a low valence state ( $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$ ) which facilitated the adsorption of  $\text{H}_2\text{O}$  molecules, thus enhancing OER activity. Benefiting from the unique structural characteristics, N-CoFe LDHs/NF showed excellent electrocatalytic activity, and only an ultra-low overpotential of 233mV was needed to achieve the geometric catalytic density of  $10 \text{ mA cm}^{-2}$ . What's more, the ultrasonic treatment is one of the indispensable methods to peel off 2D layered materials. Zheng et al. explored the effect of exfoliating NiFe-LDH on the performance of catalyst OER under different ultrasonic conditions (including suspension concentration, sonification times and amplification in water) [127]. TEM images showed that the stacked NiFe-LDH nanolayers were peeled off into ultra-thin layered structures, and the thickness could even reach 0.227 nm (Figure 15k,l). Because of this point, NiFe-LDH showed excellent OER activity with the overpotential of 250 mV at  $10 \text{ mA cm}^{-2}$  in alkaline solution. In addition, the ratio of Fe with +3 valence state in NiFe-LDH with 0.227 nm in thickness was large than that of bulk NiFe-LDH material, which is widely regarded as highly active catalytic sites for OER, thus facilitating the OER reaction steps. In general, exfoliation is an efficient method to generate the thin NiFe-LDH layer with abundant exposed sites and accompanied by generated some defect vacancies to form highly active catalytic sites, thus providing more sites for reaction and exhibiting high-electrocatalytic performance.





**Figure 15.** Preparation illustration, characterizations and theoretical studies of LDH Exfoliation.

(a) Schematic illustration of structural tuning in NiFe-OOH grown on Ni Foam as the substrate to fabricate NiFe-OOH<sub>OV</sub> catalyst for OER. (b,c) SEM images of (b) NiFe-OOH and (c) NiFe-OOH after 60 s of O-plasma exposure (NiFe-OOH 60 s). (d) OER polarization curves of NiFe-OOH<sub>OV</sub>, NiFe-OOH-30 s, NiFe-OOH-60 s, NiFe-OOH-90 s, and NiFe-OOH catalysts compared to RuO<sub>2</sub> in 1.0 M KOH electrolyte. (e) OER polarization curves for NiFe-OOH<sub>OV</sub> before and after long-term stability test. The inset shows the chronoamperometric response at a current density of 50 mA cm<sup>-2</sup> for 120 h. (f,g) Free energy diagrams of NiFe-OOH and NiFe-OOH<sub>OV</sub> for the OER at different pH: (f) pH=0 and (g) pH=14. (h) Illustration of the exfoliation of bulk CoFe-LDHs into ultrathin CoFe-LDHs nanosheets by N<sub>2</sub> plasma. (i,j) AFM images of the ultrathin N-CoFe LDHs nanosheets. (k,l) TEM of (k) NiFe LDH and (l) Exf NiFe-LDH with 15 min. (a-g) Reproduced with permission [125]. Copyright 2021, American Chemical

Society. (h-j) Reproduced with permission [126]. Copyright 2018, Wiley-VCH. (k,l) Reproduced with permission [127]. Copyright 2021, Elsevier.

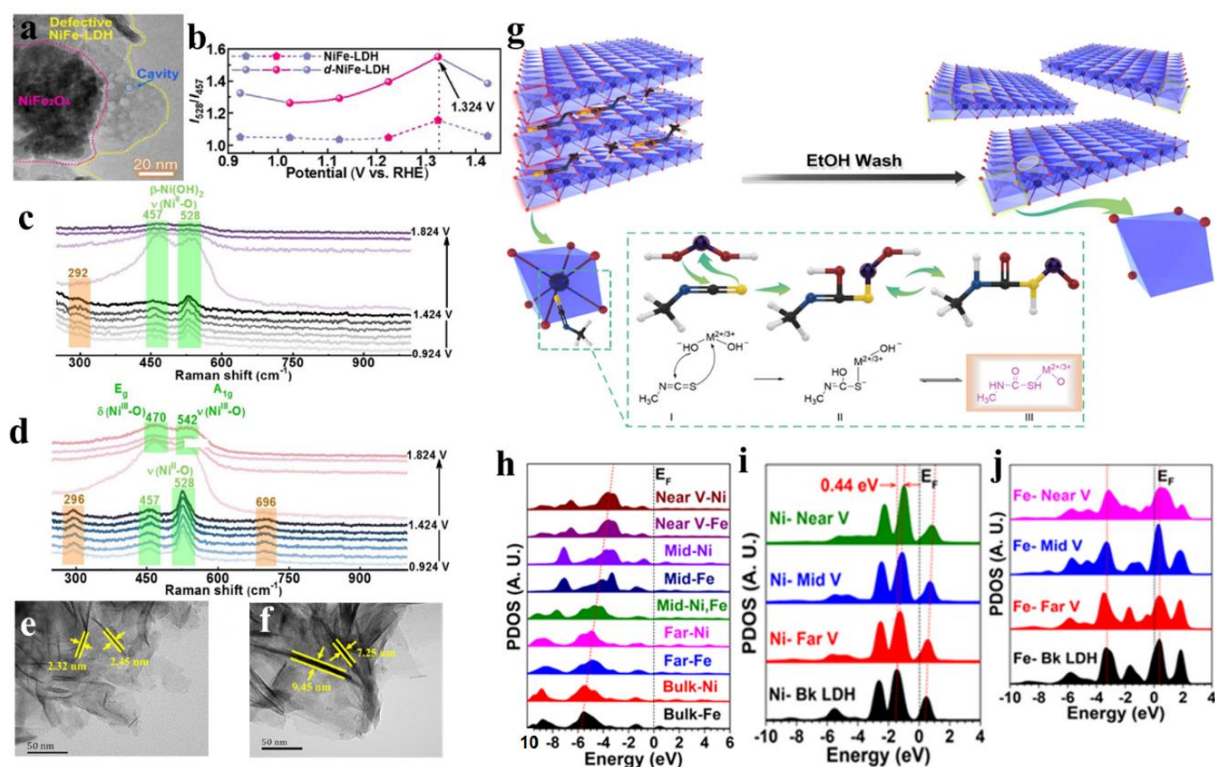
## 5. Vacancy strategy

Currently, vacancy strategy is also recognized as an indispensable approach to improve the initial electrocatalytic performance of Ni (Co)-based LDH materials. Generally, vacancy regulation of LDHs includes cation vacancy (e.g.,  $M^{2+}/M^{3+}$ , where M is metal cation) regulation and anion vacancy (e.g., oxygen vacancies) regulation. The generation of oxygen vacancies means the generation of a large number of unsaturated atoms, which can significantly enhance the surface adsorption energy of LDHs for anions ( $OH^-$ ) in electrolyte and reduce the activation energy of the full reaction steps. The existence of metal vacancies can provide a large number of unsaturated coordination atoms, which regulates the electronic configuration near the active metal sites, thus promoting HER/OER activity.

Heteroatom doping and plasma treatment are the main methods to generate vacancies [31, 41, 125, 126, 130]. Furthermore, Li et al reported a defective NiFe-LDH with metal vacancies (d-NiFe-LDH), which was prepared by dissolving metal cations from NiFe-LDH with polar aprotic solvent [131]. In the synthesis process, part of  $Ni^{2+}$  and  $Fe^{3+}$  were dissolved in the high-temperature solvent heat treatment of mixed solution of ethanol, water and N, N-dimethylformamide, and then the weak alkaline environment generated by DMF hydrolysis made the two cations re-deposit on the remaining LDH in the form of  $NiFe_2O_4$ . TEM images clearly showed the formation of  $NiFe_2O_4$  and some cavities left by cation dissolution (Figure 16a). In-situ Raman spectroscopy revealed that with the increase of applied voltage,  $I_{528}/I_{457}$  (the intensity ratio of the characteristic peaks at  $528$  and  $457\text{cm}^{-1}$ ) regarded as the index of the fraction of defective or disordered  $Ni(OH)_x$  species increased (Figure 16b-d). the cation vacancy  $V_M$  initially generated in the prepared samples gradually transformed into  $V_M\text{-OH}$  configuration, and then further transformed into  $V_M\text{OH-H}$  configuration with the most active thermodynamic properties, which proved that the formation of vacancies promoted the structural transformation of NiFe-LDH during the OER reaction.

In addition, vacancies can also be generated by electron-withdrawing organic small molecules. Yang et al. used small organic molecule methyl isocyanate ( $CH_3NCS$ ) to create

multiple vacancies of metal and oxygen on the edge and basal surface of LDH, which successfully enhanced the catalytic activity of LDHs for OER [132]. In the process of synthesis, the electron-withdrawing organic small molecule  $\text{CH}_3\text{-N}=\text{C}=\text{S}$  entered the LDH interlayer as an anchoring agent, which caused the LDH to peel off (Figure 1g). Then,  $\text{CH}_3\text{NCS}$  anchored on the specific atoms (oxygen and metal atoms) of  $\text{MO}_6$  unit in LDH, and removed the oxygen and metal atoms in LDH, thus forming multiple vacancies of oxygen and metal in LDH. TEM showed that the thickness of the modified NiFe-LDH nanosheets was reduced from 8 nm to 2.5 nm, which was helpful to expose more unsaturated catalytic active sites (Figure 1e,f). At the ultra-low overpotential of 260 mV, the current for OER of  $50 \text{ mA cm}^{-2}$  could be delivered, and its performance was better than that of most reported recent state-of-the-art catalysts. DFT revealed that the interaction of metal vacancies and O vacancies in NiFe-LDH promoted electron transfer (Figure 1h-j). Such a composite defect region was not only beneficial to the electrical activity of the intermediate product, but also was beneficial to the stability of the intermediate product. The modulated electronic environment determined the superior OER performance. Based on the above analysis, it is easily concluded that vacancy strategy is an efficient approach to enhance electrocatalytic performance of LDH materials, which also has developed as a convenient method to construct superior LDH materials [133,134].



**Figure 16.** Characterization and DFT results for the vacancy strategy to enhance electrocatalytic performance of LDH materials. (a) TEM images of d-NiFe-LDH. (b) In situ Raman spectroscopy measurements of the evolution of  $I_{528}/I_{457}$  versus potential. (c) The Raman spectra of pristine NiFe-LDH under different applied potentials. (d) The Raman spectra of pristine d-NiFe-LDH under different applied potentials. (e,f) TEM images of (e) NiFe LDH and (f) v-NiFe LDH. (g) The mechanism of the NiFe-LDH with metal and oxygen multivacancies. (h) The site-dependent PDOSs of O-2p orbitals. (i) The site-dependent PDOSs of Ni-3d orbitals. (j) The site-dependent PDOSs of Fe-3d orbitals. (a-d) Reproduced with permission [131]. Copyright 2021, Wiley-VCH. (e-j) Reproduced with permission [132]. Copyright 2020, Elsevier.

## 6. Summary and perspective

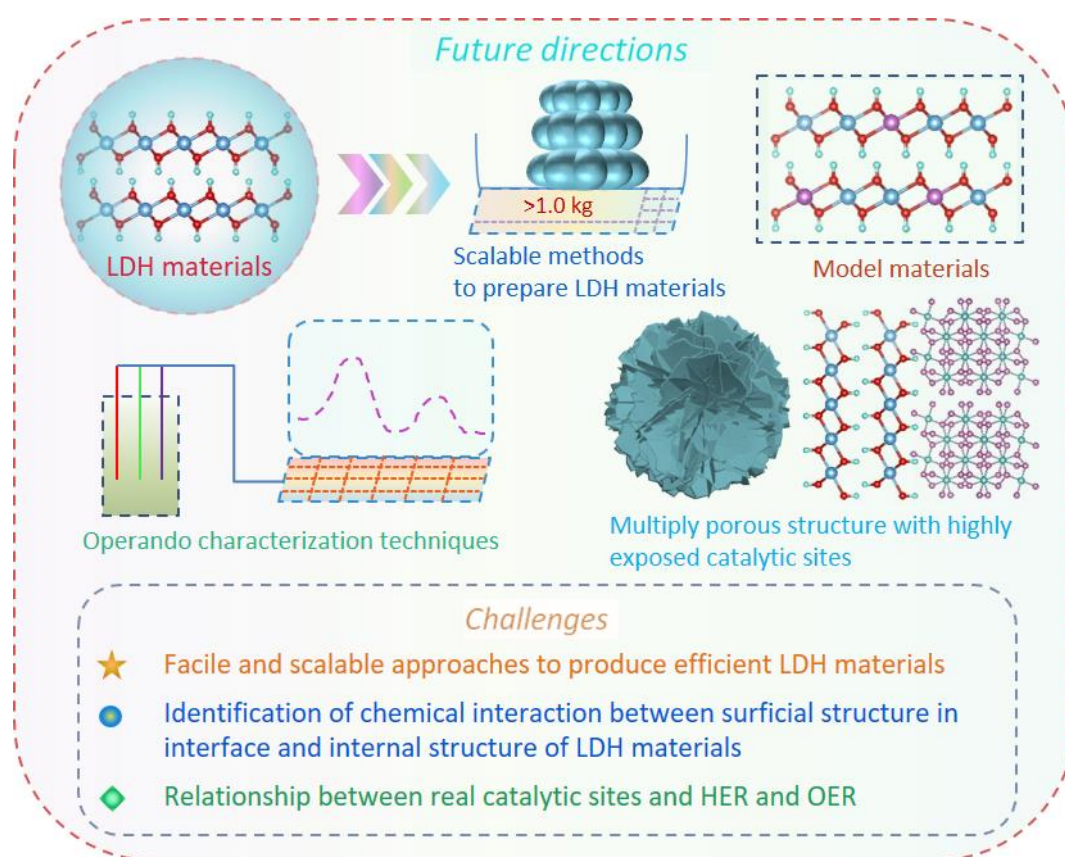
This review elaborates the comprehensive achievements of Ni (Co, Fe)-based LDH 2D materials for water splitting, including their preparation methods and strategies, electrocatalytic performance, characterizations and electrocatalytic mechanism over catalysts. For chemical modification over Ni (Co, Fe)-based LDH 2D materials, there are mainly three strategies to



modify LDH materials towards highly electrocatalytic performance in water splitting. The first one is the heteroatom doping strategy which can effectively tune the electron distribution of host atoms due to the formed new chemical bonds between heteroatoms and host atoms. Meanwhile, doping with heteroatoms can easily produce a large number of oxygen vacancies ( $V_O$ ) due to the broken crystal structure, which can increase the conductivity of LDH and also make more active sites exposed in electrolyte, thus leading to easier electron transfer during reactions and increased number of catalytic sites reacting with intermediates. What's more, the generated  $V_O$  and heteroatoms jointly regulate the electronic states of catalytic sites, thus optimizing the adsorption energies of intermediates. In general, the heteroatom doping contains the precious metal, non-precious metal and non-metal doping three categories, and these heteroatoms leads to generate new highly active catalytic sites for water splitting.

The second one is the heterojunction strategy which can generate new highly active catalytic sites in interface between two compounds due to their strong chemical interaction. Such strong chemical interaction also tunes electronic state of individual compounds compared to pure compound. In general, there exists two functions of heterojunction to realize the high electrocatalytic performance of LDH-based catalysts. Firstly, the enhanced conductivity of LDH-based materials can be obtained through hybridizing with high conductive metal compounds, which efficiently improve the electron transfer rate between reactants and catalysts, thus greatly facilitating the reaction dynamics. Secondly, new catalytic sites are formed between the two compounds, which can optimize the free energy profiles of reactions, thus lowering the overpotentials. Nowadays, heterojunction strategy for constructing LDH-based catalysts hybridized by other compounds includes the metals, metal compounds, carbon and organic materials, which can be also as bifunctional catalytic sites for HER and OER. The third one is the morphology strategy to regulate the size of LDH in thickness, which can efficiently increase the number of active sites, enhance electron transfer process between bulk catalysts and reactants, as well as facilitate reactant and product diffusion, and thus greatly enhance the electrocatalytic performance of water splitting.





**Figure 17.** Major challenges and future directions in the design of advanced LDH materials for water splitting.

Nowadays, with the development of characterization instruments, the microstructures of LDH, as well as evolution of chemical environmental changes during reactions have been solidly established by combining multiply characterization technologies. Simultaneously, the reaction mechanism over electrocatalysts can be also reasonably proposed, especially for the intermediate detection, e.g.,  $\text{OOH}^*$ ,  $\text{OH}^*$  and  $\text{H}^*$  species. Despite the rapid progress in water splitting for LDH materials, several major challenges still need to be addressed for the construction of advanced LDH materials to enable their application in water splitting (Figure 17). Here, the current critical issues and possible future directions in water splitting field of LDH are highlighted in the following parts.

1. The practicality of convenient and scalable approaches is a prerequisite for the implementation of high-performance LDH materials with precisely tuned electronic structure for water splitting. The target of substituting precious-metal based electrocatalysts with abundant transition metals should be achieved through the convenient and scalable synthetic strategies to satisfy the large market demands of water splitting technology to obtain hydrogen

energy. Despite the promising electrocatalytic performance compared to commercial precious metal-based materials, Ni (Co, Fe)-based LDH materials have not been widely applied in industrial water splitting technology, presumably due to the difficulty in large-scalable synthesizing LDH and does not satisfy the demand of large-scale application of water splitting.

2. The chemical interaction between surficial structure in interface and internal structure of LDH materials is critical for design and construction of LDH materials to realize the excellent electrocatalytic performance including activity and stability. Although the chemical states of metal atoms in LDH materials can be clearly observed during reactions, the amount of new formed metal sites can be not quantized, as well as the difficulty in revealing the detailed information in interface between individual component. Therefore, the new formed species in interface should be considered carefully in tailoring electrocatalytic activity, which involves the formation of highly active catalytic sites and electronic changes of LDH.

3. Model catalysts with a precisely stable microstructure are explored to investigate the reaction mechanism, which provide the reaction rate limiting step of HER and OER over catalysts. Guided by this principle, the Ni (Co, Fe)-based LDH can be easily constructed, even in design bifunctional HER and OER materials. In many cases, the local structure of LDH is an average result due to the difficulty in distinguishing the ratios of each structure, e.g., OH\* or O\* bonded with metal. Therefore, it is highly desired to develop model catalysts to probe the structural evolution of LDH during water splitting reactions through *in situ*/operando characterization techniques.

4. Multiply porous structures with highly exposed single atoms is preferred to realize the mostly all metals to participate reaction, fast reactant transport and efficient gas product dissociation. HER and OER are the three-phase reactions referring to gas, liquid and solid surface of catalysts. Porous structure with highly exposed single metal atoms is conducive to the reactant chemical-acting with catalytic site as soon as possible, meanwhile facilitates the gas product dissociation and reactant transport, thus endowing high efficiency of H<sub>2</sub> production from water splitting as presenting high current density. The generated strain in porous structure likely tailors the chemical environments of LDH, thus regulating its catalytic performance.

Ni (Co, Fe)-based LDH materials in water splitting have been achieved much progresses including their preparation methods, catalytic mechanism and electrocatalytic performance. In

this review, we categorize the three strategies to modify LDH according to their formation and regulation mechanisms, which involves their preparation methods, microstructure, catalytic mechanism and electrocatalytic performance. The joint effort between experimental and theoretical groups will offer new viewpoints in principle to develop highly efficient LDH in water splitting. The increased intensively researches will help to address the critical challenges and thus accelerates the development of new LDH with high activity and stability in water splitting.

### **Acknowledgements**

This work was supported by the National Natural Science Foundation of China (11974276 and 22078261), Natural Science Basic Research Program of Shaanxi (2020JM-422), Key Science and Technology Innovation Team of Shaanxi Province (2022TD-33), National innovation and entrepreneurship training program for college students (202210697148, 202210697069), Qin Chuangyuan project of Shaanxi Province (QCYRCXM-2022-213).

### **Conflict of Interest**

The authors declare no conflict of interest.

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