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Advances in Hybrid Electrocatalysts for Oxygen Evolution Reactions: Rational Integration of NiFe Layered Double Hydroxides and Nanocarbon

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The oxygen evolution reaction (OER) has attracted tremendous explorations in both fundamental and application fields recently, due to its core status in next-generation energy conversion and storage technologies, such as water splitting and metal-air batteries. Transition metal-based compounds, especially the NiFe layered double hydroxides (NiFe LDHs) have been wellestablished as the most effective and cost-efficient electrocatalysts to boost the sluggish water oxidation and improve the energy efficiency. Nevertheless, a favorable substrate is highly required to expose the poorly conductive active phases and enhance reactivities of OER. In this review, the recent advances concerning synthetic strategies, hierarchical structures, and OER performances of NiFe LDH/nanocarbon hybrid electrocatalysts are summarized. A brief description of OER catalysis, LDHs, and nanocarbon materials is presented firstly, followed by a thorough overview of various investigations according to their synthetic methods and structural characters. The development of high-performance OER catalysts is covered by both a short summary and a presentation of future prospects. This review provides stimulatory knowledge and sheds fresh light into the development of advanced functional materials with a wise hybridization of active phases and conductive substrates.

1. Introduction

Discovering sustainable energy sources and efficient energy storage technologies has become one of the most urgent and pivotal challenges in such an era that the social development and daily life rely heavily on energy, while the conventional sources face a looming crisis.^[1] Promisingly alternative to the diminishing energy sources based on fossil fuels, the clean and abundant "hydrogen economy" has rapidly emerged and come under intense scrutiny.^[2–9] H₂ can be potentially produced via water splitting by renewables such as nuclear, solar, or the electricity generated from renewable sources, and then

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fuel cells or cleanly combusted in air.^[8] A competent water electrolyzer is prerequisite for this cycle to produce hydrogen at the cathode, with the evolution of oxygen at the anode. Generally, the hydrogen evolution reaction (HER, $2H^+ + 2e^- \rightarrow H_2$, in acid) with two-electron transfer is facile, while the oxygen evolution reaction (OER, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, in acid), is kinetically sluggish with a high overpotential and thereby low energy efficiency, limiting the practical promotion of water splitting.^[4,6] Additionally, OER is also the central reaction to metal-air batteries, such as aqueous Zn-air and nonaqueous Li-air batteries, processing at the air cathode during charging.^[10-12] Metalair batteries are regarded as the next-generation energy storage technologies with extremely high theoretical energy densities, and have attracted intense investigation, aiming at practical applications in portable electric devices, electric vehicles, or large-scale smart grids. OER involves

efficiently transformed into electricity in

four-step proton-coupled electron transfer and the formation of oxygen-oxygen bonding,^[13,14] which requires catalysts to boost this process, with high catalytic activity, excellent durability, and favorable earth-abundance. Therefore, it is of vital significance to develop high-effective and cost-efficient catalysts for OER.

To date, the noble metal oxides, such as IrO₂ and RuO₂ are demonstrated as the state-of-the-art electrocatalysts for OER in both acidic and alkaline mediums, whereas their high cost and scarce resource limit the industrial applications.^[5,15–17] Recently, transition-metal-based materials (Ni, Fe, Co, Mn, etc.), as a family of earth-abundant alternatives, have been widely investigated and discovered to exhibit considerable electrocatalytic activity towards OER.^[18-21] The resultant performances in metal-air batteries or water splitting devices can be significantly influenced by their chemical composition, crystal structure, size distribution, hierarchical porosity, electrical conductivity, surface chemistry, electrode architecture and so on. Among various candidates, the strongly coupled nickel iron layered double hydroxide/nanocarbon (NiFe LDH/NC) hybrids have attracted the most interest since the pioneer work reported by Dai et al. in 2013.^[22] NiFe LDHs are believed to serve as superior active

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phases with excellent intrinsic electrocatalytic activity and durability despite the controversy on their underlying mechanism,^[18,23–30] while NC substrates provide an interconnected conductive framework, which is crucial to the poorly conductive LDH materials. The strongly coupled interface renders a smooth electron transfer from active sites to the current collector, and even alters the local electron structure of NiFe LDHs with an enhanced activity. With plenty of research in this field, various NiFe LDH/NC composites have been proposed and demonstrated to possess satisfactory performances for OER.^[22,31–40] Besides, the understanding of the activity origin of NiFe LDHs, the role of NC materials, the interfacial effect, and the relationship between structure and performance has been remarkably enriched.

Several excellent reviews focusing on the design of OER catalysts,^[2,10–12] the synthesis and application of LDHs,^[41,42] and even the LDH/NC hybrids^[43,44] have recently appeared, however, no systematic and specific review on NiFe LDH/NC hybrids for OER electrocatalysts has been reported yet, which we believe is of great significance to oxygen electrochemistry and also inspiring for the development of other analogous functional composites.

In this review, we highlight the advances in the investigation of NiFe LDH/NC catalysts for OER, primarily since 2013. Brief descriptions of OER catalysis, LDHs, and nanocarbon materials are presented firstly, followed by a short introduction to NiFe LDH/NC catalysts. Then, recent advances in this field are reviewed according to their synthetic methods and structural characters. Finally, a short summary is provided and future prospects are discussed. This review will provide stimulatory knowledge in developing superior OER catalysts with further optimization of NiFe LDH/NC hybrids and also shed novel light into the design and synthetic strategies towards advanced functional materials.

2. Mechanism and Catalysts for OER

2.1. OER Catalysis

The OER catalysis is sluggish with complex reaction pathways. O₂ molecular generally inclines to generate from metal oxide surfaces, which is much more intricate than bare metals.^[11,15] Thereby, the understanding of detailed mechanisms is elusive and always depended on the specific systems. Normally, the four-step proton-coupled electron transfer paths are considered to occur as follows,

$$^{*}+H_{2}O \rightleftharpoons OH^{*}+H^{+}+e^{-}$$
(1)

$$OH^* \rightleftharpoons O^* + H^+ + e^-$$
 (2)

 $O^* + H_2 O \rightleftharpoons OOH^* + H^+ + e^-$ (3)

$$OOH^* \rightleftharpoons^* + O_2 + H^+ + e^-$$
(4)

where *stands for an active site, and O*, OH*, OOH* represent adsorbed intermediates respectively.



These elemental steps are widely adopted for the first-principle calculations with density functional theory (DFT),^[17,45–48] whereas most non-precious metal oxides are unstable under oxidation potentials in acidic mediums.^[5] Consequently, the research hitherto reported dominantly focuses on the preciousmetal-free catalysts for OER in alkaline conditions. In this case, the reaction process can be described using the following elementary steps:

$$^{*}+OH^{-} \rightleftharpoons OH^{*} + e^{-}$$
 (5)

$$OH^* + OH^- \rightleftharpoons O^* + H_2O + e^-$$
(6)

$$O^* + OH^- \rightleftharpoons OOH^* + e^-$$
(7)

$$OOH^* + OH^- \rightleftharpoons^* + O_2 + H_2O + e^-$$
(8)

The free energy diagram is usually employed to investigate the activation energy and thermochemical overpotential of OER.^[47] As illustrated in Figure 1a, the staircase curves indicate energetics of a real or ideal catalyst with sequential steps corresponding to different intermediates. The ΔG_i denotes the free reaction energy of each elementary reaction step. The step with the highest ΔG_i is the last step to go downhill when the applied potential increased (Figure 1a), and it is regarded as the potential-determining step, which controls the activation energy for OER. For an ideal catalyst, the ΔG_i of four electron transfer steps should be the same (4.92 eV/4 = 1.23 eV), leading to an equilibrium potential (E0), 1.23 V vs RHE (reversible hydrogen electrode, all the potential mentioned hereinafter is relative to RHE unless otherwise specified) for OER at all pHs. However, there is no real catalyst that can facilitate each steps with the exactly same reaction free energies, hence rendering an overpotential.

Figure 1b reproduces the typical polarization curve for OER which is always obtained using the rotating disk electrode (RDE) apparatus. With the increase of applied potential, the current density (per geometric area) first maintains zero before activation, and then bursts with a rapid rise after the onset potential. While the onset potential is very useful to derive mechanistic information from specific systems, it is imprecise to determine the values, especially for such gas-evolving systems,^[49] and also complex to estimate the relationship between structure and property.

Another parameter is Tafel slope, which is also considered as system-specific and potential-dependent, and is not recommended to serve as a merit for comparing electrocatalytic performances.^[5] McCrory and Peters proposed a benchmarking protocol for evaluating OER catalysts under conditions relevant to integrated solar water-splitting devices.^[5] It focuses on the activity and stability. The overpotential required to achieve 10.0 mA cm⁻², approximately corresponding to 10% efficient solar water-splitting devices,^[3,5] represents the catalytic activity, and the overpotential for 10 mA cm⁻² after 2.0 h is adopted as a measure of stability. Though other applications such as water electrolyzers or metal-air batteries have different operation parameters, this figure of merit considering the activity and stability is referential.



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Figure 1. (a) Typical free energy diagram for OER, indicating the reactive species and intermediates. The dashed lines display downhill energetics for all steps at the electrode potential which is called "thermochemical overpotential"; ΔG_i denotes the free reaction energy of each elementary reaction step. Reproduced with permission.^[47] Copyright 2010, Wiley-VCH. (b) A schematic polarization curve for OER. The equilibrium potential (E^0) is 1.23 V vs RHE, and the potential required for a current density of 10.0 mA cm⁻² (E_{10}) is generally adopted as a critical figure of merit for OER catalysts. The stability is another key point for superb electrocatalysts in water oxidation.

2.2. NiFe LDHs

LDHs are a class of lamellar hydroxides, also known as hydrotalcite-like materials, whose structure is derived from the brucite $(Mg(OH)_2)$ layers.^[41,42] This large family of materials is commonly referred to as anionic clays, vividly indicating the architecture of positive charged layers and compensating interlayer anions, which can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x} (OH)_{2}][An^{-}_{x/n}] \cdot mH_{2}O$. The M^{2+} and M^{3+} are divalent (Mg²⁺, Ni²⁺, Co²⁺, Zn²⁺, Fe²⁺, Cu²⁺, etc.) and trivalent metals (e.g., Al³⁺, Fe³⁺, Cr³⁺, Mn³⁺, etc.), respectively, with a molar ratio (*x*) of $M^{3+}/(M^{2+}+M^{3+})$ generally ranging from 0.2 to 0.33. An⁻ are the exchangeable inorganic or organic anions present in the interlayer galleries. The LDH structure, as illustrated



Figure 2. (a) The idealized structure of carbonate-intercalated LDHs. Metal hydroxide octahedras stacks along the crystallographic c-axis, with tunable M^{2+}/M^{3+} molar ratios, while water and anions are present in the interlayer region. Reproduced with permission.^[50] Copyright 2014, Royal Society of Chemistry. (b) Proposed OER pathway for NiFe LDHs. The catalyst transforms into $\gamma Ni_{1-x}Fe_xOOH$ during OER potential, and this model illustrates the interaction between intermediates (HO*, O*, OOH*) and active sites (the substituted Fe surface atom in $\gamma NiOOH$). Reproduced with permission.^[27] Copyright 2015, American Chemical Society.

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in Figure 2a, is remarkably attractive with several advantages. Firstly, a large number of metal can be atomically dispersed in the LDH flakes with a well-defined arrangement, fully exposed active sites, and various high-performance metal/oxide/(oxy) hydroxide catalysts can be derived from LDHs.^[50] Besides, the anion exchange properties and facile exfoliation into monolayer sheets provide abundant opportunities for nano-engineering and assembly towards functional nanocomposites.^[51] A plenty of synthetic techniques such as coprecipitation, electrodeposition, and sol-gel synthesis, make it feasible to integrate the fabrication of LDHs and other components together.^[42] Therefore, LDH materials have been widely investigated and applied in various fields, such as heterogeneous catalysis, energy storage and conversion, nanocomposite materials, healthcare, environmental protection, and so on.[41,42,44,50]

It can be traced back to the early last century that the very common metal Ni and its oxide were discovered to exhibit activity for OER in alkaline conditions.^[52,53] Then the incidental Fe impurities in the nickel hydroxides were found to lower the OER overpotential during the studies of Ni-based alkaline batteries,[53-55] thereby leading to systematic investigation of the role of iron contamination. Incidental or intentional Fe incorporation are both demonstrated to have similar effect in decreasing the overpotential, even with an ultra-low Fe concentration (0.01%).^[23,24,56,57] Generally, the NiFe-based compounds,^[22] including NiFe alloys,^[21,58,59] oxides,^[5,23,25,26,60] and (oxy)hydroxides,^[18,19,24,27–30,61,62] have been considered as the most promising earth-abundant catalysts for OER in alkaline electrolytes.[22,27]

Metal oxides and hydroxides often have higher oxidation states, such as +2/+3/+4, which renders changeable valance states of metal sites, and it is remarkably beneficial for OER due to the optimal interaction between metal ions and oxygen intermediates.^[10] The hydroxides, especially NiFe LDHs are more attractive due to the unique features with lamellar structures, tunable compositions, and facile intercalation, resulting in excellent OER activities. Taken NiFe (oxy)hydroxides as instance, Bell and co-workers^[27] found that at potentials well below the onset potential, a LDH structure was observed, with Ni²⁺ and Fe³⁺ presented (Figure 2b). As the potential raised, the hydroxide was oxidized into $\gamma Ni_{1-x}Fe_xOOH$ (when x < 25%) below the onset potential, which can be regarded as the Fedoped y-NiOOH structure. Notably, the Fe substitution attributed to the replacement of more covalent Ni-O bonds with more ionic Fe-O bonds, resulting in a shift in their binding energies of oxygen intermediates toward optimal values. Another firstprinciple study suggested the more favorable generation of O2 from OOH* species on NiFe LDHs, and the Fe sites exhibited higher activity than the Ni(OH)₂ framework.^[63] Other LDH materials, such as NiCo LDHs, [64-68] CoFe LDHs, [69] CoMn LDHs,^[70] NiFeMo LDHs,^[71] ZnCo LDHs,^[72,73] NiTi LDHs,^[74] NiCoFe LDHs,^[75,76] TiO2@CoAl LDHs,^[77] are also demonstrated to exhibit remarkable reactivity for OER, and even photocatalytic OER.[78]

However, the research in this field remained stagnant for a long time due to the low conductivity of LDHs. Conductive substrates or additive, such as nanocarbon materials, are urgently required to make the potential active sites work efficiently.^[22]

2.3. Nanocarbon Materials

Fullerenes, carbon nanotubes (CNTs), graphene (G), carbon quantum dots (CQDs) and their hybrids, exhibiting a conjugated all-carbon structure, dominantly constitute a large family of nanocarbon materials, which attract increasing interest recently.^[79,80] Nanocarbon materials, always possessing unprecedented intrinsic properties, especially the high electrical and thermal conductivity, mechanical strength, as well as the adjustable structure and surface chemistry, have triggered a tremendous research aiming at a wide range of applications, such as functional composites, energy conversion and storage, photonics and optoelectronics, biotech and nanomedicine, heterogeneous catalysis and so on.^[81-83]

Specifically, a novel field of "carbocatalysis"^[84-86] or metalfree carbon catalysts^[83] has emerged and developed rapidly, employing nanocarbon or their derivatives as catalysts for various reactions. Compared with conventional carbonaceous catalysts, such as active carbon, the nanocarbon catalysts have several advantages, including better pore structure, more uniform characteristics, less defects and impurities, enhanced oxidative resistance, and better electron or heat transport.^[82] The nanocarbon materials can serve as multi-functional substrates with higher conductivity, strongly coupled interfaces,^[43] and electron-transfer induced change to enhance the catalytic behavior. In addition, modified nanocarbon with functionalities or defects typically lead to electron rearrangement and thereby generate highly active sites themselves.^[81-84,86] More interestingly, the unique porosities of nanocarbon materials afford effective scaffolds to stabilize nano-sized catalytic particles or nanoconfinement effects, which is well-established to largely influence the catalytic reactivity.^[82]

So far, there are several reports of metal-free nanocarbon catalysts for OER, such as N-doped G/CNT hybrids,[87] CNT@ NCNT,^[88] N-doped carbon,^[89] N, O co-doped G-CNT hydrogel film,^[90] N, P co-doped mesoporous nanocarbon foam,^[48] P-doped graphitic carbon nitrides,^[91] etc. Nevertheless, it is unfavorable that the catalytic nanocarbon materials, which always contain defects or functional groups, tend to suffer from carbon oxidation under the high potential of OER, leading to a limited durability.^[92]

Therefore, to our knowledge, nanocarbon materials are more suitable to serve as frameworks supporting more active and stable phase, such as NiFe LDHs in the case of OER. The latter is responsible for the catalytic activity dominantly, while nanocarbon mainly contributes to an interconnected electron pathway, hierarchical porosity for free mass transfer, fully assessable active sites, strongly coupled interfaces, as well as the regulation of active phases. The ingenious hybridization of the promising active phase (NiFe LDHs) and multi-contribute substrate (NC) will no doubt result in significantly enhanced catalytic performances.

2.4. NiFe LDH/NC Hybrid Catalysts

A key to such NiFe LDH/NC hybrid catalysts for OER is the scrupulous design of promising hierarchical nanostructures and effective strategies to fabricate ideal composites.^[44] Due to the various types of NC materials and complex interaction between LDH and NC components, the hybrid structures can be classified according to the structural features of NC materials,



as illustrated in **Figure 3**. Zero-dimensional (0D) CQDs, onedimensional (1D) CNTs, two-dimensional (2D) graphene, threedimensional (3D) porous graphene layers or frameworks, and the 3D freestanding configuration are taken into account, with different contact modes and scales.

In the next section, we will review some recent advances in NiFe LDH/NC catalysts for OER, with various hybrid structures mostly illustrated in Figure 3. However, another thread is provided below considering the fabrication strategies, which is believed to be more inspiring for further development. **Table 1** summarizes the various NiFe LDH/NC catalysts compared according to their composition, synthesis methods, and OER performances. The discussion of relationship between structure and performance is also included, nevertheless, we don't intend to make it comprehensive with very detailed and in-depth insights on the mechanism, which is important but complex.

3. NiFe LDH/NC Hybrid Catalysts for OER

3.1. Growth of LDHs on NC Support

3.1.1. Two-Step Nucleation and Growth

The most common method to fabricate LDHs is the co-precipitation of target metal cations from their precursor solutions. If selected NC materials with certain affinity towards the cations were introduced into the precursor solution in advance, the LDHs were expected to nucleate on the adsorption sites of the NC substrate, and then directly grow on it. With a fine regulation of the precipitation conditions, such as pretreatment, composition, temperature, and duration, NiFe LDHs can be in situ grown on NC substrates with different morphologies.^[44]

The first work reported in this aspect was conducted by Dai's group, and it has stimulated a large number of investigations on NiFe LDH-based catalysts for OER since 2013.^[22] For the first time, they synthesized a crystalline NiFe LDH phase with high OER activity in basic solution, and devised an effective strategy for the nucleation and growth of nano-sized NiFe LDHs on CNTs with enhanced performance (Figure 4a). A three-step process was proposed for the fabrication, including the mild oxidization of CNTs, hydrolysis and nucleation of metal precursors on the mildly oxidized CNTs at a low temperature (85 °C), and then solvothermal growth at a high temperature (160 °C) for the crystallization of LDHs and partial reduction of oxidized CNTs. As shown in Figure 4b, nano-sized NiFe LDH plates were uniformly grown on a gently oxidized CNT network. When casted onto a glassy carbon (GC) electrode with an areal loading of ca. 0.20 mg cm^{-2} , the hybrid material delivered an onset potential about 1.50 V in 0.10 M KOH and 1.45 V in 1.0 M KOH. If loaded on carbon fiber paper (CFP,



Figure 3. Scheme of hierarchical NiFe LDH/NC hybrid electrocatalysts with different nanostructures classified according to the dimensionality of NC materials. (a) The possible hybrids of LDH flakes and 0D NC materials, such as CQDs. (b) The hybridization of LDHs and 1D NC components, typically CNTs, with LDH flakes attached or insert on the surface, or the CNTs grown from LDH sheets. (c) Different structures for LDHs hybridized with 2D NC materials, dominantly graphene: LDH uniformly decorated or vertically grown on graphene layers, the hetero-assembly or layer-by-layer self-assembly of exfoliated monolayer LDHs and graphene. (d) 3D NC substrates, such as the porous graphene layers or frameworks with a spatial confinement for LDH growth. The 3D freestanding electrode fabricated onto a 3D substrate is important to proof the concept of hierarchical 3D structure from microto meso- and macroscale.

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Table 1. Comparison of NiFe LDH/NC hybrid electrocatalysts for OER.

NC Туре	Mole Ratio of Ni/Fe	Electrolyte (KOH)	Catalyst Loading (mg cm ⁻²) ^{a)}	$\eta_{ m onset}$ (mV) ^{b)}	η_{10} (mV) ^{c)}	TOF (s ⁻¹) ^{d)}	Tafel Slope (mV dec ⁻¹)	Stability	Synthesis Methods ^{e)}	References
oCNT	5	0.10 M	0.20	~270	~315		35	1000 s at 2.5 mA cm ⁻² (~100%)	DMF/H ₂ O Ni(OAc) ₂ , Fe(NO ₃) ₃ 85 °C, 4 h; 120 °C, 12 h; 160 °C, 2 h	[18]
		1.0 M		~220	235	0.56 ^{f)}	31			
GO	5	1.0 M	1.02	~220	245			1000 cycles between 1.10 and 1.85 V (~100%)	DMF/H ₂ O + hydrazine Ni(OAc) ₂ , Fe(NO ₃) ₃ 120 °C, 18 h; 160 °C, 2 h	[30]
GO	5	0.10 M	0.20	~250	~300		33	4000 s at 2.5 mA cm ⁻² (~99%)	DMF/H ₂ O Ni(OAc) ₂ , Fe(NO ₃) ₃ 120 °C, 12 h; 160 °C, 2 h	[31]
NGF	3	0.10 M	0.25	<270	337		45	12000 s at 350 mV (~97%)	NMP/H ₂ O Ni(NO ₃) ₂ , Fe(NO ₃) ₃ 100 °C, 6 h	[26]
₀GSH	3	0.10 M	0.25	240	350	-	54	10000 s at 1.0 mA cm ⁻² (~100%)	NMP/H ₂ O Ni(NO ₃) ₂ , Fe(NO ₃) ₃ 100 °C, 6 h	[29]
CQD	5	0.10 M	0.20	260	305		35	3000 s at 2.5 mA cm ⁻² (~100%)	DMF/H ₂ O Ni(OAc) ₂ , Fe(NO ₃) ₃ 85 °C, 4 h; 120 °C, 12 h; 160 °C, 2 h	[24]
		1.0 M		210	235		30			
RGO	3	1.0 M	0.25 ^{g)}	195	206	~1.0	39	28800 s at 10 mA cm ⁻² (~100%)	FeCl ₃ , NiCl ₂ 150 °C, 24 h delamination, several days	[27]
RGO	2	1.0 M	0.25	<170	~210	~0.1	40	36000 s at 10 mA cm ⁻² (~99%)	FeCl ₃ , NiCl ₂ delamination, several days	[25]
G/Nickel foam	3	0.10 M	2.18 ^{h)}	240	325		44	8000 s at 10 mA cm ⁻² (~92%)	Methanol/H ₂ O Ni(NO ₃) ₂ , Fe(NO ₃) ₃ 180 °C, 23 h	[28]
RGO	4	1.0 M	0.14	~190	259		39	7200 s at 260 mV (~90%)	H ₂ O Ni(NO ₃) ₂ , Fe(NO ₃) ₃ -1.2 V, 10 s	[33]
MWCNT sheet	4	1.0 M	90 wt% @ MWCNT	~220	~260 255 ⁱ⁾		21	86400 s at 240 mV (~99%)	Ni(NO ₃) ₂ , Fe(NO ₃) ₃ NaOH/H ₂ O, quickly added drop-casted	[32]

^{a)}The catalyst loading represents the areal loading of catalysts on GC electrodes unless otherwise specified; ^{b)} η_{onset} denotes the onset overpotential (mV); ^{c)} η_{10} denotes the overpotential (mV) required for a current density of 10 mA cm⁻²; ^{d)}TOF values are calculated based on the current at an overpotential of 300 mV and assuming all the metal ions as active sites; ^{e)}Synthesis methods are compared concerning the solvents, the metal precursors, the temperature and duration; ^{f)}This TOF value is based on the current texted on CFP electrodes, while other values are calculated based on the tests on GC electrodes; ^{g)}This column results are based on the test with catalysts loaded onto nickel foam substrates; ^{h)}This column results are based on the test with catalysts loaded onto nickel foam substrates; ^{h)}The 260 mV is η_{10} for the NiFe LDH catalysts loaded on GC electrode (0.05 mg cm⁻²), and the 255 mV is the overpotential required for a current density of 180 mA cm⁻² for NiFe LDH/CNT fiber electrodes.

loading ~0.25 mg cm⁻²), a current density of 5.0 mA cm⁻² can be achieved at an overpotential of 250 mV, with a low Tafel slope of 31 mV dec⁻¹ and high durability. A high turnover frequency (TOF) of 0.56 s⁻¹ was achieved at an overpotential of 300 mV in 1.0 M KOH (Figure 4c), which was comparable with high-performance perovskite materials.^[93]

They found that the high OER activity was mainly attributed to the NiFe LDH phase, but the enhancement of electronic conductivity due to the hybridization of CNTs was also important. Additionally, X-ray absorption near-edge structure (XANES) results revealed a drastic increase of carbonyl π^* peak intensity for NiFe LDH/CNT samples (Figure 4d), indicating the formation of M–O–C (M = Ni, Fe) bonding and facilitated charge transport.

Besides the 1D CNT, 2D graphene, especially the graphene oxides (GO), can also serve as favorable substrates for the twostep nucleation and growth of NiFe LDHs.^[42] GO materials, commonly prepared by Hummer's method, possess abundant



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Figure 4. (a) Scheme of the NiFe LDH/NC hybrids and LDH structure. Reproduced with permission.^[22] Copyright 2013, American Chemical Society (b) TEM image of the hybrid, showing individual LDH nanoplates and smaller iron oxide particles on CNTs. Reproduced with permission.^[22] Copyright 2013, American Chemical Society (c) IR-compensated polarization curves of NiFe LDH/CNT hybrid, compared with other samples, loaded on CFP with an areal loading of 0.25 mg cm⁻² in 1.0 m KOH. Reproduced with permission.^[22] Copyright 2013, American Chemical Society. (d) C K-edge XANES profile of NiFe LDH/CNT (black) and pure CNT (red) without the hybridization of LDH. Reproduced with permission.^[22] Copyright 2013, American Chemical Society.

oxygen-containing functional groups on the lamellar surface and an extraordinary dispersing performance, which is beneficial for the adsorption and anchor of metal precursors. Mixing the GO solution and metal precursors together, Lee et al. reported the facile fabrication of NiFe LDH/reduced GO (NiFe/ RGO) composites by a solvothermal treatment at 120 °C for 18.0 h and then 160 °C for 2.0 h.[37] The transmission electron microscopy (TEM) image indicated a high crystallization and well dispersion of LDHs on RGO layers (Figure 5a). The overpotential required for 10.0 mA cm⁻² was about 245 mV in 1.0 M KOH, with a catalyst loading of ca. 1.02 mg cm⁻² (Figure 5c). Remarkably, it was demonstrated that the NiFe/ RGO sample exhibited a significantly reduced sheet resistance, about 10³ times lower than that of bare NiFe LDHs, and the charge-transfer resistance revealed by electrochemical impedance spectroscopy was also much lower (Figure 5c). The capacitance value of NiFe/RGO was 2.4 times higher than that of bare NiFe LDHs, indicating a much higher active surface area. Therefore, it was concluded that the introduction of RGO provided a better electron pathway and higher surface area for the loaded NiFe LDHs, leading to the significantly enhanced performances.

Most recently, Kang et al. reported a similar work with the same mole ratio of Ni/Fe precursors (5:1).^[38] However, with much lower catalyst loading (~0.20 mg cm⁻²), lower LDH mass ratio, and lower pH of electrolyte (0.10 \times KOH) compared

with that reported by Lee et al., the OER activity was surprisingly outstanding. A small overpotential of \sim 300 mV was required for a current density of 10.0 mA cm⁻² in 0.10 M KOH (Figure 5d).

3.1.2. One-Step Spatially Confined Growth

In addition to the high conductivity of NC materials, one of their main advantages is the diverse hierarchical porous structure. In particular, various hierarchical porous graphene materials with controllable in-plane micropores, wrinkled mesopores, and strutted macropores have been fabricated via a multistep process with multiscale templates, showing promising performances in lithium-ion batteries,^[94] lithium-sulfur batteries,^[95–98] supercapacitors,^[99–101] and fuel cells.^[102,103] This suggests that the NC materials with unique porosities can provide multifunctional frameworks for active particles loading with effective interfacial coupling, spatial confinement in the microscale and even the nanoconfinement effects.

To take full advantage of the NC substrates, our group proposed a novel nitrogen-doped graphene framework (NGF) for the in situ growth and decoration of nanometer-sized NiFe LDHs (nNiFe LDHs) as shown in **Figure 6**a.^[33] The NGF was catalytically deposited on mesoporous MgO templates

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Figure 5. (a) TEM image of NiFe/RGO and (b) the corresponding OER polarization curves, and (c) Nyquist plots with an equivalent circuit. All three panels are reproduced with permission.^[37] Copyright 2015, Elsevier. The inset high resolution TEM image in Figure a exhibits the lattice of LDHs and RGO. The empty circles and rectangles in Figure b denote the current densities after 1000 repeated potential cycling of each catalyst between 1.10 and 1.85 V. (d) The polarization curves of RGO-NiFe LDH compared with other samples. Reproduced with permission.^[38] Copyright 2016, Elsevier.

with NH3 introduced as nitrogen source. The nNiFe LDH/ NGF was fabricated via a one-step urea-assisted precipitation with NGF as the substrate. No additional treatment, such as pre-oxidization of the NC materials was required. It was found that the nitrogen dopant and topology-induced defects of NGF contributed to the adsorption of metal cations and anchored nucleation, and then the in-plane mesopores served as nanoreactors for a spatially confined growth of nNiFe LDHs (Figure 6b). The X-ray photoelectron spectroscopy (XPS) results of nNiFe LDH/NGF indicated a ca. 0.7 eV shift of Ni 2p spectra to higher binding energy, suggesting the formation of C-N···Ni-O bonding. As a result, the hierarchical NiFe LDH/graphene structure demonstrated an enhanced activity and durability for oxygen evolution under alkaline conditions, among the most kinetically active candidates for the water-splitting (Figure 6c). Based on this material platform, a phase evolution from Fe doped Ni(OH)₂/ NiO(OH) to Ni doped FeO(OH) was demonstrated with increased Fe. This kind of moderate guest-metal substitution into host (oxy)hydroxide frameworks (either Fe into Ni or Ni into Fe) can enhance the resultant OER performance due to an optimized metal-oxygen bond length and intermediate adsorption.^[104]

Furthermore, a mildly oxidized graphene/single-walled carbon nanotube hybrid (oGSH) was introduced to regulate and control the hybridization of NiFe LDHs via the one-step precipitation.^[36] The oxygen functionalities and defects were demonstrated to anchor the nucleation and the hierarchical



pores in hybrid NC materials led to in situ growth of dual-sized LDHs, with ca. 100 nm plates in the strutted caves and ca. 5 nm nanoplates on the oGSH surface. This hierarchical structure and dual-sized distribution of LDHs contributed to a porous framework for smooth mass diffusion, intimate interfaces for rapid charge transfer, and efficiently utilized active sites (Figure 6d).

The direct growth of NiFe LDHs on NC supports gives rise to an uniform distribution and effective hybridization of the active phase on conductive substrates with a strongly coupled interface.^[43] The NC materials can serve as a conducting framework with significantly enhanced charge transport for electrochemical applications. Besides, the carbon surface, usually exhibiting various oxygen-containing groups can tune the morphology and size of active particles, leading to fully exposed active sites. The synthetic conditions have a significant influence on the resultant morphology and performances. For the two-step method with a hydrolysis-induced nucleation and thermal treatment for crystallization, the preoxidization of NC materials, the temperature, solvent type, and reaction duration are important to adjust the size and phase. However, the reaction conditions can be more facile for the single-step strategy with spatially confined effect. The hierarchical porosity

contributes a lot to regulate the hybridization of LDHs, in additional to the defective sites on the surface.

3.2. Decoration of NC on LDHs

The post-growth of NiFe LDH plates on different NC substrates can decorate the poorly conductive LDH materials onto a hierarchical carbon scaffold with much enhanced conductivity and thereby better performance. However, the working active sites dispersed all over the LDH plates, rather than the active phase, might not be totally linked into the conductive network due to different contact modes (Figure 3). Contrastively, if the active LDHs serve as the substrate, and certain NC materials are decorated in a microscale, better interconnections and full demonstration of active sites are expected.

Carbon nanodots (CDs), including CQDs and graphene quantum dots are emerged as the most recent members in the NC family and have generated enormous excitement due to their unique structure and properties.^[105–108] Generally, the 0D CDs exhibit a size below 10 nm with abundant functional groups on the surface. Their supernal conductivity, rapid electron transfer, excellent electron reservoir property, and high solubility make them advantageous to form nanocomposites and enhance the activity of original materials. To decorate CQDs onto the NiFe LDH plates, Kang et al. designed a three-step process using the CQD dispersion and metal salt solution as precursors.^[31] The two solutions were firstly mixed

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Figure 6. (a) TEM image of nNiFe LDH/NGF hybrids, exhibiting a uniform decoration of nNiFe LDHs into the graphene framework. The inset indicates the spatially confined growth of LDHs in the nano-sized graphene pores. Reproduced with permission.^[33] Copyright 2015, Wiley-VCH. (b) High-resolution TEM images of nNiFe LDH/NGF electrocatalysts. Reproduced with permission.^[33] Copyright 2015, Wiley-VCH. (c) The evaluation of OER performances considering both kinetics (Tafel slope) and activity (the overpotential required for 10.0 mA cm⁻²). All measurements were conducted in 0.10 m KOH electrolyte. Reproduced with permission.^[33] Copyright 2015, Wiley-VCH. (d) TEM image of NiFe LDH/oGSH hybrids with a dual-sized distribution of NiFe LDH plates. Reproduced with permission.^[36] Copyright 2015, Royal Society of Chemistry.

together with vigorously stirring at 85 °C for 4.0 h, and then transferred to solvothermal reaction at 120 °C for 12.0 h, followed by additional solvothermal treatment at 160 °C for 2.0 h. Graphitic CQDs with an average size of 5 nm were uniformly decorated on the as-grown NiFe LDH sheets (**Figure 7**a-c). The FT-IR spectra of CQD/NiFe LDH composite exhibited a slight shift of some dominant peaks compared with pristine CQDs, indicating the electrostatic interactions between NiFe LDHs and CQDs. Thereby, a greatly enhanced activity for OER was observed, with a low overpotential of ~235 mV in 1.0 M KOH and ~305 mV in 0.10 M KOH for 10.0 mA cm⁻² (Figure 7d). The ultra-small size of CQDs and the direct integration of LDHs with CQDs were demonstrated to be vital for the enhanced performance.

Calcination and reduction of NiFe LDHs can transform them into mixed metal oxides with uniformly dispersed metal nanoparticles (NPs), which were proven as excellent catalysts for the growth of CNTs.^[44] The CNTs grown out from the NPs on LDH flakes were demonstrated to connect all the active sites into the conductive network via "point-line-point" contacts, thereby

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giving rise to a more effective catalyst,^[109] as illustrated in Figure 3b.

3.3. Heteroassembly of LDH/NC

As discussed above, one of the most interesting advantages of LDHs is the facile delamination property, which can lead to monolayer LDH flakes. The facile exfoliation of NiFe LDHs can generate more active sites and higher conductivity, thereby dramatically increasing the activity and durability.^[110] Consequently, if replacing the bulk NiFe LDHs with exfoliated ones, it is expected to achieve much better OER performances for NiFe LDH/NC hybrids.

Yang et al. demonstrated a synthetic route for preparing strongly coupled NiFe LDH/GO hybrids by an anion exchange step to expand the interlayer space, followed by the exfoliation of LDHs and assembly with GO sheets, as shown in Figure 8a.^[34] The as-obtained NiFe LDH/GO hybrid exhibited an alternative stacking of exfoliated LDH layers and GO along the x axis, resulting in largely exposed active surface and decreased charge transfer resistance (Figure 8b). Further improvement can be achieved by reducing the assembled GO into RGO via a chemical route. For the NiFe LDH/RGO hybrids, the overpotential required for 10.0 A cm⁻² was as low as 195 mV, and the TOF value at an overpotential of 300 mV approached 1.0 s⁻¹, even higher than the NiFe LDH/CNT sample (Figure 8c).^[22] Besides, the catalysts delivered an excellent durability, with nearly constant potential for 8.0 h operating at 10.0 mA cm⁻². The superior OER performance was ascribed

to the assembling catalytic active materials and NC at the molecular level with a synergistic effect.

A similar superlattice structure of NiFe LDH and GO was fabricated by Sasaki's group via a facile delamination strategy (Figure 8d).^[32] The NiFe LDH/RGO hybrid exhibited an remarkable OER efficiency with a small overpotential of 210 mV for 10.0 mA cm⁻², and stable for a prolonged testing time up to 36000 s. It was also revealed that the increase of Fe content in NiFe LDH was beneficial for enhancing the catalytic activity (Figure 8e). Additionally, the NiFe LDH/RGO catalyst was demonstrated to be effective for HER, which was the first report on the bifunctional OER/HER catalyst based on NiFe LDH/NC composites.

All the above-mentioned strategies, including the growth of LDHs on NC, the decoration of NC on LDHs or the heteroassembly of LDH/NC, provide effective methods to hybrid active LDHs and conductive NC together with different morphologies and contact modes, thereby leading to diverse performances. The LDH phase delivers high intrinsic activities, while the NC material serves as a good electron-conducting matrix.



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Figure 7. (a) TEM image of the CQD/NiFe LDH composite. Reproduced with permission.^[31] Copyright 2014, American Chemical Society. (b) Schematic illustration of the hybridization of CQDs and NiFe LDHs, especially showing the interaction and role of CQDs. Reproduced with permission.^[31] Copyright 2014, American Chemical Society. (c) High resolution TEM image exhibits the lattices of CQD and NiFe LDH. Reproduced with permission.^[31] Copyright 2014, American Chemical Society. (d) IR-corrected polarization curves of CQD/NiFe LDHs and control samples, with a loading of 0.20 mg cm⁻² on GC electrode, in 0.10 M KOH. Reproduced with permission.^[31] Copyright 2014, American Chemical Society.

NC materials with different porosities can also help to regulate and stable the nanostructured LDH particles. Furthermore, the strong interaction via electron rearrangement or even covalent bonds between these two subunits is demonstrated to generate enhanced activity and stability. Specifically, the size and thickness of LDH plates, the type and pretreatment of NC materials, the composition of hydroxides and the mass ratio of LDH/NC, as well as the reaction conditions are several important parameters that determine the eventual products and their electrocatalytic performances.

3.4. 3D Freestanding Electrode

In spite of the significant advances in highly active and stable catalysts, there is still a long way to go before meeting the requirements of practical applications. One of the crucial factor is the configuration and fabrication of electrodes in real devices, rather than the direct dripping onto GC electrodes during test. The heterogeneous OER catalysis occurs only at triple-phase boundary regions, where the electron, electrolyte, and oxygen gas can contact with each other.^[111] Therefore, in addition to the inherent activity of the powered catalysts, the formation of stable triple-phase boundary regions can substantially influence the overpotential, power density, and durability during practical operation. Especially for nanocomposites, the interactions between separated particles, the constructions of



interconnected porous structure, and the adhesions on the electrode substrate against gas bubble generation are the main issues required to be well addressed.^[39]

The design of 3D freestanding electrodes with a self-supported and binder-free configuration is a favorable alternative.^[66,91,112] In practice, the catalyst ink prepared with binder has been drop-dried onto metal foams^[34] or CFP substrates^[22] to form the macroscale electrodes, exhibiting excellent activity and durability. Ulteriorly, the in situ deposition and anchor of active particles onto 3D conductive substrates or the direct fabrication of catalysts into freestanding films is expected to be more attractive. The most direct and efficient idea is to grow active phases on a 3D conductive scaffold, such as nickel foam (NF),^[113] graphene hydrogel,^[66] CFP,^[91] etc. In situ growth of nitrogen-doped NiFe LDHs on a NF substrate was also reported a very low overpotential of 0.23 V at 10 mA cm⁻² and a high Faradaic efficiency of ca. 98%.^[114]

In the case of NF, the grown LDH sheets are easily packed and banked on the Ni surface, resulting in a limited electron transportation and utilization of the outside LDHs. Recently, we found that a thin layer of graphene deposited on the NF in advance can provide a more hydrophobic surface and modulate the growth of NiFe LDHs with

better dispersion (**Figure 9a** and b).^[35] The graphene connected all LDH flakes with a strong coupled interface as indicated by the XPS results (Figure 9c). Therefore, a high utilization efficiency of active phases was achieved, resulting in enhanced activity with a low overpotential of 325 mV for 10.0 mA cm⁻² in 0.10 \times KOH.

3D graphene frameworks with open porous structure, high conductivity, adjustable surface defects, lightweight, and flexibility are promising for the deposition of NiFe LDHs. Shi et al. presented a two-step method to fabricate a novel NiFe LDH/3D-electrochemically reduced graphene oxide (NiFe/3D-ErGO) electrode.^[40] The 3D-ErGO supported on Au electrode was firstly obtained by electrochemical reduction of GO/electrolyte solutions, and then NiFe LDH nanoplates were electrochemically deposited into the 3D-ErGO scaffolds (Figure 9d and e). The synergistic effect of NiFe LDHs and 3D-ErGO substrates rendered an outstanding OER activity with an ultra-low overpotential of 259 mV (at 10.0 mA cm⁻²) and low Tafel slope of 39 mV dec⁻¹. Furthermore, the role of Fe in the Ni-Fe phase was demonstrated to be critical, with a significant decrease of Tafel slope and overpotential upon Fe doping (Figure 9f). Very recently, Zhang and co-workers proposed a facile one-step hydrothermal process to fabricate NiFe LDHs into a 3D rGO framework, with conductive CNT additions.^[115] Feng and coworkers reported a 3D strongly coupled ternary hybrid electrode through in situ growth of Co_{0.85}Se nanosheets vertically aligned on exfoliated graphene foil with following formation of NiFe



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Figure 8. (a) Illustration of the synthetic process of NiFe LDH/GO hybrids. Reproduced with permission.^[34] Copyright 2014, Wiley-VCH. (b)TEM image of the as-fabricated NiFe LDH/GO hybrid and (c) the corresponding OER performance with a catalyst loading of 0.25 mg cm⁻². The dot line exhibited the polarization curve after chronopotentiometry measurement at a current density of 10.0 mA cm⁻² for about 8.0 h. Reproduced with permission.^[34] Copyright 2014, Wiley-VCH. (d) TEM image of NiFe LDH/GO composites and the HRTEM image showing the alternatively stacked LDH and GO sheets. Reproduced with permission.^[32] Copyright 2015, American Chemical Society. (e) IR-corrected polarization curves of NiFe LDH/GO with different Ni/Fe ratios or the reduction of GO. Reproduced with permission.^[32] Copyright 2015, American Chemical Society.

LDHs by a facile hydrothermal treatment with superb OER activity.^[116] A small potential of 1.51 V is required to achieve a current density of 250 mA cm⁻².

Most recently, Liu and co-workers reported a novel microfiber electrode for OER composed of colloidal NiFe LDH NPs and multi-walled CNT (MWCNT) sheets. As illustrated in Figure 9g, the colloidal NiFe LDH NPs were firstly prepared by rapid coprecipitation followed by sonication, and then drop-casted onto a MWCNT sheet. After that, the NiFe LDH/MWCNT sheet was twisted into a fiber with LDH NPs immobilized both inside and outside of the CNT bundles (Figure 9h). Contributed from the nanosized NiFe LDHs (~33 nm) with high intrinsic activity and hybrid fiber configuration with strong connection, the flexible NiFe LDH/MWCNT electrode exhibited superior activity and stability for OER in 1.0 \times NaOH. A small overpotential of 255 mV was required for 180 mA cm⁻², and the fiber electrode can retain the OER activity over 24 h of continuous reaction at around 38 mA cm⁻² (Figure 9i).

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Alternatively, the layer-by-layer (LBL) self-assembly process is regarded as a versatile and effective technique for the fabrication of multilayer and multi-component flexible films.^[44] This strategy provides more opportunities to constructive 3D freestanding electrodes composed by 2D subunits, such as graphene oxides and exfoliated LDH sheets as schematically illustrated in Figure 3c.^[112] Based on the increasing fundamental knowledge of the activity origins of NiFe LDHs and their hybrids, the next step for NiFe LDH/NC catalysts is expected to be the development and implementation of 3D freestanding electrodes aiming at practical applications.

4. Summary and Outlook

The rational integration of NiFe LDH and NC materials has been demonstrated as a versatile and effective strategy for promising OER catalysts with high activity and durability in alkaline conditions. Systematic effort has been devoted to design and develop highperformance NiFe LDH/NC hybrids since the pioneering work reported by Dai in 2013, leading to a vast range of candidates with different precursors and nanostructures. The NiFe LDHs provide high intrinsic activity, while NC material is introduced to improve the electrical conductivity. Additional effects such as stabilization of the active NPs and interfacial coupling are expected with favorable interaction modes.

It is notable that the dimensionality of NC materials, the pre-treatment of components, and the fabrication conditions are main factors to regulate the resultant structures and performances. Towards practical applications,

however, the direct formation of 3D freestanding electrodes is also of significant importance, especially for a very low overpotential and enhanced durability. Despite the great advances, further improvements are required to make the NiFe LDH/ NC catalysts really competitive and promising for metal-air batteries and water splitting.

Fundamentally, the objective and veritable evaluation of the activity and durability is the prerequisite for systematic development aiming at promising energy conversion technologies. In the case of NiFe LDH and their hybrids, the onset potential and Tafel slope are difficult to confirm due to the overlap of Ni²⁺/Ni³⁺ redox current and OER current. Another important activity metric, TOF, is also diverse on account of the indetermination of real active sites. Additionally, since the densities of LDHs and carbon materials differ greatly, different mass ratios of LDHs and NC in the composites induce disparate activities even at the same catalyst loading. Therefore, detailed statement and comparison is strongly recommended.



Figure 9. (a) Scheme and (b) SEM image of LDH/G/Ni hybrid electrocatalyst. Reproduced with permission.^[35] Copyright 2015, Royal Society of Chemistry. (c) High resolution Ni 2p spectra of LDH/G/Ni showing a slight shift compared with LDH/Ni. Reproduced with permission.^[35] Copyright 2015, Royal Society of Chemistry. (d) Fabrication steps of NiFe/3D-ErGO and (e) its scanning electron microscopy (SEM) image. Reproduced with permission.^[40] Copyright 2015, Royal Society of Chemistry. (f) The relationship between overpotential (at 10.0 mA cm⁻²), Tafel slope and the Ni/Fe ratios. Reproduced with permission.^[40] Copyright 2015, Royal Society of Chemistry. (g) Illustration of the fabrication of NiFe LDH/MWCNT fibers. Reproduced with permission.^[39] Copyright 2016, Royal Society of Chemistry. (h) SEM image of the fiber electrode, and corresponding polarization curves before and after 24 h test. Reproduced with permission.^[39] Copyright 2016, Royal Society of Chemistry.

The advent of advanced in situ or in operando techniques, such as X-ray absorption near-edge spectra, high-resolution electron microscopy imaging coupled with electron energy loss spectra, online scanning flow cell/inductively coupled plasma mass spectrometry, and scanning electrochemical cell microscopy make it possible for in-depth investigation and in operando analysis of the working catalysts. Any fresh insight on the underlying catalytic origin of NiFe LDHs, the interfacial couple effect, the degradation mechanism and the relationship between structure and performances can provide powerful instructions on the further optimization. For example, the systematic theoretical study of the catalytic pathway and working active sites of NiFe LDHs considering the various compositions and physical structures, and the advanced online and in operando investigation of the degradation of a model NiFe LDH/NC composite are strongly expected.

Furthermore, the material chemistry is worthy to be enriched with new structure design and more versatile synthesis methods. It will open great opportunities for the precise modulation of the composition, size and thickness of NiFe LDHs, and the effective fabrication of hierarchical porous NC materials with multi-functionalities. As well-demonstrated, the interfacial bondings between NiFe LDHs and NC are not only beneficial for enhancing activity but also significant for the improvement of stability, however, the knowledge and strategy in this aspect is still an open question. Besides, further attempts on the fabrication of freestanding electrode and efficient integration of catalysts into potential devices are believed to be a considerable direction.

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