Synergistic coupling of NiFeZn-OH nanosheet network arrays on a hierarchical porous NiZn/Ni heterostructure for highly efficient water splitting

Qiuxia Zhou¹, Caixia Xu^{1*}, Yaxin Li¹, Ximiao Xie¹, Hong Liu^{1,2*} and Shishen Yan^{1*}

ABSTRACT Efficient and economical electrocatalysts should be developed for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) to split water for an extensive application prospect of green and clean hydrogen energy. Here, we develop highly efficient OER and HER electrocatalysts through the scalable fabrication of NiFeZn hydroxide nanosheets firmly arrayed on a hierarchical porous intermetallic NiZn and Ni heterojunction over nickel foam (NiFeZn-OH/NiZn-Ni/NF). One bimodal porous NiZn intermetallic/Ni layer is *in situ* constructed on the nickel foam surface to maximize the exposure of catalytic sites and build firm NiFeZn-OH nanosheets *via* the redox reaction with FeCl₃. NiFeZn-OH/NiZn-Ni/NF shows low overpotentials of $\eta_{50/600}$ around 235/284 mV for OER and $\eta_{50/600}$ around 73/212 mV for HER, small Tafel slopes of 46.1 and 41.1 mV dec⁻¹, and prolonged catalytic durability in an alkaline medium because of the strong synergistic effects of Zn doping, multiple interface engineering, and integral three-dimensional free-standing scaffold. As bifunctional catalysts, NiFeZn-OH/NiZn-Ni/NF required a low electrolytic voltage of 1.49 V at 20 mA cm⁻² (1.61 V at 100 mA cm⁻²) with a sustained and stable output for 40 h during water splitting. This work might provide insights into the exploration of low-cost and highly efficient intermetallic/multimetallic hydroxide heterostructured electrocatalysts for practical overall water splitting.

Keywords: NiFeZn hydroxide, heterostructure, hydrogen evolution reaction, oxygen evolution reaction, overall splitting water

INTRODUCTION

Water electrolysis produces hydrogen and oxygen; it is a readily available mode, and water is an abundant resource, so this process has been widely explored [1]. Unfortunately, water splitting involves oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), which are considered limiting factors because the multistep proton-coupled electron transfer in electrolysis commonly leads to a high energy barrier and sluggish reaction kinetics [2,3]. Noble metal-based electrocatalysts, such as Ru/Ir-based materials for OER and Pt-based materials for HER, possess excellent electrocatalytic performances. How-

ever, high prices and rare reserves have seriously impeded their widespread practical applications in water electrolysis [4]. For this reason, various economic transition metal-based compounds, such as oxides [5], hydroxides [6], phosphides [7], sulfides [8], carbides [9], and selenides [10], have been developed for water splitting. Although OER and HER activities have been remarkably enhanced, forceful energy output cannot be easily obtained using different electrocatalysts in overall water splitting because the catalytic performance of most HER and OER electrocatalysts is commonly mismatched in the same media; consequently, the catalytic efficiency decreases. Therefore, highly active bifunctional electrocatalysts should be explored to achieve large-scale hydrogen production with cost-effective and efficient processes.

Among various transition-metal compound electrocatalysts, NiFe-based hydroxides have received great concerns because of their low overpotentials toward OER and abundant sources [2,11]. Introducing a third nonprecious metal (such as Mn [12], Ce [13], Zn [14], Zr [15], and Co [16]) into NiFe-based hydroxides can further decrease the overpotential and enhance the catalytic efficiency of OER because of the maximization of catalytic sites and modification of local coordination environment and electronic structures. Lim *et al.* [14] reported that the doping of Zn²⁺ into NiFeO_xH_y dramatically enhances its OER activity and durability. They proposed that the type of strong Lewis acid species can modulate the electronic property of NiFe hydroxide to achieve a more appropriate intermediate binding during oxygen evolution. At present, NiFe-based hydroxides have been regarded as a class of active nonprecious OER electrocatalysts in alkaline media because of their strong multimetallic synergistic effects [15]. However, their relatively inferior performance toward HER severely hampers their applications as bifunctional catalysts in water splitting. If the high HER performance can be achieved for NiFe-based hydroxides, such low-cost and widely available systems may open up broad opportunities for overall water splitting to hydrogen production. Few studies have found that incorporating extrinsic nonprecious metal NiFe-based hydroxides can yield acceptable bifunctional activities toward both OER and HER [16,17]. For example, Dinh *et al.* [17] reported that porous ultrathin ternary NiFeV layer double hydroxide nanosheets grown on nickel foam (NiFeV-LDH/NF) deliver an enhanced bifunctional activity with over-

¹ Institute for Advanced Interdisciplinary Research (iAIR), Spintronics Institute, Collaborative Innovation Center of Technology and Equipment for Biological Diagnosis and Therapy in Universities of Shandong, University of Jinan, Jinan 250022, China

² State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

* Corresponding authors (emails: chm_xucx@ujn.edu.cn (Xu C); ifc_liuh@ujn.edu.cn (Liu H); shishenyan@sdu.edu.cn (Yan S))

potentials of 231 and 125 mV for OER and HER, respectively, at 10 mA cm⁻² in 1.0 mol L⁻¹ KOH electrolyte compared with that of NiFe-LDH/NF and NiV-LDH/NF. These findings suggest that novel bifunctional NiFe-based multimetallic hydroxides should be developed for overall water splitting with a stable operation and lower overpotentials in alkaline media.

Aside from incorporating a third nonprecious metal into NiFe hydroxide, well-defined microstructures can further improve the electrocatalytic activity and durability of water splitting [18]. Ternary metallic hydroxide nanomaterials are usually prepared through a wet chemical method using metallic salts as precursors with a common powder-type morphology [12,13]. Constructing self-supporting electrocatalysts on three-dimensional (3D) porous metal substrates is an effective and popular approach to avoid polymer binders from reducing electrocatalytic efficiency [19]. A 3D porous substrate is preferred to provide a highly conductive pathway and robust mechanical stability and increase the accessibility of catalytic sites [13,20]. Therefore, highly active bifunctional NiFe-based hydroxide electrocatalysts should be rationally designed for water splitting by incorporating a third metal and engineering nanostructure.

This study was performed to develop self-supported ternary NiFeZn hydroxide nanosheets using intermetallic NiZn and Ni heterojunction on a nickel foam surface (NiFeZn-OH/NiZn-Ni/NF) as a 3D substrate and precursor *via* a scalable electrodeposition-annealing-dealloying strategy. The bimodal intermetallic NiZn and Ni heterojunction on the NF surface were prepared through dealloying by electroplating Zn on NF, which functioned as a high-surface-area precursor to construct ternary NiFeZn hydroxide *in situ* through a one-step redox reaction with FeCl₃ [21]. The bimodal NiZn/Ni heterojunction precursor could provide high-density reaction sites and participate in the multi-interface regulation of NiFeZn hydroxide to obtain a superior catalytic activity. Moreover, the self-supported architecture with abundant voids and channels was beneficial to the rapid mass transport and accelerated reaction kinetics during HER and OER electrocatalysis. With a robust 3D architecture, smooth mass transfer, and modulated electron structure between NiZn/Ni and NiFeZn hydroxide interface, the as-made NiFeZn-OH/NiZn-Ni/NF showed a high electrocatalytic performance with low overpotentials and small Tafel slopes in OER and HER. NiFeZn-OH/NiZn-Ni/NF as a highly active bifunctional catalyst required a low cell voltage to afford a high overall current density with a stable output. Thus, this work proposed a scalable and facile strategy to design highly active and stable intermetallic/multimetallic hydroxides for practical overall water splitting. This strategy presented the advantages of high reproducibility and cost-effective mass production.

EXPERIMENTAL SECTION

Chemicals

RuO₂ nanoparticles and commercial Pt/C were purchased from Sigma Aldrich Chemical Reagent Co., Ltd. Other agents were bought from Shanghai Sinopharm Chemical Reagent Ltd., Co., China. All agents with analytical purity were used directly without further purification.

Preparation of NiFeZn-OH/NiZn-Ni/NF

Zn was electroplated for 1 h, annealed, and etched to prepare NiZn-Ni/NF with the ratio of intermetallic NiZn and Ni of

approximately 55.94:44.06 [21]. NiZn-Ni/NF was soaked in 20 mL of 25 mmol L⁻¹ FeCl₃ solution at 25 ± 1°C for 4 h to obtain NiFeZn-OH/NiZn-Ni/NF. For comparison, NiFe hydroxide nanosheets on NF (NiFe-OH/NF) were also made by immersing NF (1 cm × 2 cm) in 20 mL of 100 mmol L⁻¹ FeCl₃ solution at 25 ± 1°C for 7 h. The calculated loading mass of NiFeZn-OH/NiZn-Ni/NF was ~2.2 mg cm⁻².

Characterization

X-ray diffraction (XRD, Bruker D8 advanced) was conducted with Cu Kα radiation (λ = 1.5418 Å) at a step rate of 0.02° s⁻¹. The microstructures and compositions of all samples were determined using a field-emission scanning electron microscope (SEM, Hitachi Regulus 8100) and an X-ray energy dispersive X-ray spectrometer (Oxford INCA). Electron backscatter diffraction (EBSD) was performed with an SEM (Quanta FEG 450) coupled with an EBSD acquisition system (Oxford Instruments). Transmission electron microscopy (TEM) was carried out on a JEOL JEM-ARF200F. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB MK II X-ray photoelectron spectrometer. The components were identified through inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer Optima 8300).

Electrochemical tests

All electrochemical tests (Supplementary information, SI) were carried out on a CHI 760E electrochemical workstation (Shanghai Chenhua Co., China).

RESULTS AND DISCUSSION

Preparation and characterization

NF was chosen as the substrate because of its low cost, good electrical conductivity, and ample macropores. However, it has a micron-sized porous structure with a small specific surface area. As such, a dealloying strategy was first utilized to construct a new layer of a bimodal structure composed of intermetallic NiZn and Ni on the NF surface to further enlarge its specific surface area and synchronously introduce Zn by electrodeposition, annealing, and dissolving partial Zn atoms (Fig. 1). Then, NiZn-Ni/NF with Zn residues was immersed in the FeCl₃ solution to grow ternary hydroxides *in situ* based on the redox reaction of Ni, Zn, and Fe³⁺.

Fig. S1 illustrates the structural evolution of the smooth-surface NF backbone to the rough NiZn alloy layer on NF with a Zn atomic content of 78.22 (Fig. S2). After NiZn/NF was etched, numerous uniform pores and channels (1 μm) formed (Fig. 2a and inset). Many nanoscale ligaments/pores with a typical size of around 7 nm were newly formed (Fig. 2b), indicating the formation of a trimodal porous architecture consisting of an initial micron-scale 3D skeleton from NF and bimodal nanoscale ligaments/pores from the surface alloy layer of the NF skeleton. Fig. S3 shows the EBSD images, demonstrating that the intermetallic NiZn and Ni intercrossed through the porous surface with a molar ratio of ~55.94:44.06. The element mapping images revealed that Ni and Zn were uniformly distributed with an atomic ratio of around 70.45:29.55 on the surface of NiZn-Ni/NF (Fig. S4). Along with hydrolysis coprecipitation, the redox reaction of Fe³⁺ with the surface Ni and Zn subsequently produced NiFeZn hydroxide nanosheets. Furthermore, 2D curly nanosheet subunits with a thickness of dozens of nanometers

Figure 1 Schematic of the fabrication of a NiFeZn hydroxide nanosheet network grown on NiZn-Ni/NF.

Figure 2 (a and inset) SEM and (b) TEM images of NiZn-Ni/NF. (c) SEM and (d, e) cross-section SEM images of NiFeZn-OH/NiZn-Ni/NF. (f) TEM and (g) HRTEM images of NiFeZn hydroxide nanosheets. (h1–h4) Corresponding enlarged parts of the square regions. (i) SAED pattern of NiFeZn hydroxide nanosheets.

interlaced to form one layer of a 3D multilevel nanosheet network array with embedded rich pores and channels (Fig. 2c). The thickness of the nanosheet network array was around 1 μm , and this array had a firm and integral anchor on the bimodal porous NiZn-Ni/NF to produce a high-surface-area interface (Fig. 2d, e). The TEM image in Fig. 2f further supported the structure of the hierarchical nanosheet network, where the bright region came from the pores, and the dark region could be ascribed to the interlaced nanosheets.

The high-resolution TEM (HRTEM) image in Fig. 2g presents the detailed texture of one nanosheet, where numerous ordered grains, whose main size was as small as 4 nm, were randomly

dispersed in the amorphous matrix, thereby forming a disordered/ordered crosslinking ensemble. Additionally, different kinds of lattice fringes could be identified, as marked by squares. The lattice fringes from different regions had a spacing of 0.240, 0.248, 0.290, and 0.231 nm (Fig. 2h1–h4), which could be ascribed to the (101), (330), (206), and (002) crystal planes of $\text{Fe}(\text{OH})_2$, $\text{FeO}(\text{OH})$, $\text{Zn}(\text{OH})_2$, and $\text{Ni}(\text{OH})_2$, respectively. In the corresponding selected area electron diffraction (SAED) pattern (Fig. 2i), where some of the characteristic diffraction points such as $\text{Fe}(\text{OH})_2$ (003), $\text{FeO}(\text{OH})$ (400), $\text{Zn}(\text{OH})_2$ (202), and $\text{Ni}(\text{OH})_2$ (110) can be clearly seen as denoted. Moreover, the diffuse rings with circular diffraction spots further verified the amorphous

nature with numerous dispersed nanocrystals. This finding was also consistent with the XRD result shown below. The amorphous body is preferred to the crystallized state because of its superior activity [22]. Elemental mapping (Fig. S5) revealed the homogeneous distribution of Ni, Fe, Zn, and O in the nanosheet network array peeled off by ultrasonic treatment. ICP analysis indicated that the atomic ratio of Ni, Fe, and Zn was 29.98:53.12:16.90 in the hydroxide nanosheets. NiFe-OH/NF also had a well-distributed nanosheet network structure anchored on NF via a one-step redox reaction between NF and FeCl₃ solution (Fig. S6). The whole reaction was expressed as follows: $\text{Zn} + 2\text{Fe}^{3+} \rightarrow \text{Zn}^{2+} + 2\text{Fe}^{2+}$ (1), $\text{Ni} + 2\text{Fe}^{3+} \rightarrow \text{Ni}^{2+} + 2\text{Fe}^{2+}$ (2), $4\text{Fe}^{2+} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^-$ (3), $\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Ni}^{2+} + \text{Zn}^{2+} + \text{OH}^- \rightarrow \text{NiFeZn-OH}$ (4). During the reaction, Ni and Zn uniformly distributed on NF were oxidized by Fe³⁺. The generated metallic ions underwent hydrolysis and grew together to form a uniform nanosheet network. The whole preparation was simple and highly reproducible. Furthermore, it had a high yield, could be used for mass production, and did not require any extra agents at ambient temperature. The effects of the FeCl₃ solution concentration and reaction time on the resulting structure were explored (Fig. S7). A detailed description is provided in the SI.

XRD was applied to investigate the evolution of phase structures and components during the formation of the NiFeZn-OH/NiZn-Ni/NF sample. After Zn was electroplated on NF, the diffraction peaks of Zn appeared (Fig. S8a), and many diffraction peaks of intermetallic β_1 -NiZn and γ -NiZn₃ newly emerged on NF after annealing (Fig. 3a) [23]. β_1 -NiZn intermetallic residues formed as the diffraction peaks of metallic Ni emerged upon dealloying (Fig. 3b). No evident diffraction peaks related to NiFeZn hydroxide occurred upon redox reaction because of its

amorphous matrix despite the existence of many structurally ordered nanoscale domains, as observed in the HRTEM image [24]. NiFe hydroxide in NiFe-OH/NF also had low crystallinity (Fig. S8b) [11].

XPS was conducted to further investigate the surface chemical states of NiZn-Ni/NF, NiFe-OH/NF, and NiFeZn-OH/NiZn-Ni/NF. From the Ni 2p_{3/2} region in NiZn-Ni/NF, the peaks can be assigned to metallic Ni and Ni²⁺ species (Fig. 3c) [25]. The bond energy of Ni⁰ in NiZn-Ni/NF negatively shifted by 0.36 eV compared with that of pure Ni. For Zn 2p (Fig. 3d), the 2p_{3/2} peak at 1021.60 eV could be assigned to metallic Zn with a positive shift of 0.43 eV compared with that of pure Zn [26]. The bond energy shifts of Ni and Zn stemmed from the formation of intermetallic NiZn. After the redox reaction with FeCl₃, the 2p_{3/2} and 2p_{1/2} of the Ni²⁺ peak suffered from slight negative shifts of about 0.16 and 0.09 eV (Fig. 3e). This result indicated a change in the electronic structure of Ni after Zn incorporation. For the Fe 2p in Fig. 3e, the peaks at 710.44 and 723.80 eV could be ascribed to Fe(OH)₂ [27], and the peaks at 713.04 and 726.99 eV could be attributed to FeOOH [28]. The binding energies of Fe²⁺ 2p_{3/2} and 2p_{1/2} negatively shifted by 0.13 and 0.12 eV after Zn introduction. These negative shifts confirmed the influence of Zn doping and intense electronic interactions between the interfaces of NiZn-Ni/NF and NiFeZn-OH. From the Zn 2p core level of NiFeZn-OH/NiZn-Ni/NF in Fig. 3d, two peaks at 1021.57 and 1044.62 eV could be assigned to Zn²⁺ from Zn(OH)₂ [29]. From the O 1s in Fig. 3f, the peaks centered at 529.16 and 530.84 eV came from the metal-oxygen bonds (M-O) and the bound hydroxide groups (M-OH) [30], and the peak at 532.46 eV is possibly related to water adsorbed on the sample surface [27]. By comparison, the bond energy of O shifted to a lower direction than those of NiZn-Ni/NF and

Figure 3 XRD patterns of (a) NiZn/NF, (b) NiZn-Ni/NF, and NiFeZn-OH/NiZn-Ni/NF samples. XPS data of (c) Ni 2p, (d) Zn 2p, (e) Fe 2p, and (f) O 1s for NiFeZn-OH/NiZn-Ni/NF, NiFe-OH/NF, and NiZn-Ni/NF.

NiFe-OH/NF. The negative shifts for Ni, Fe, and O indicated the strong interfacial electronic interactions between NiZn-Ni and NiFeZn hydroxide, and such interactions are necessary to accelerate the charge transfer in water splitting. Based on these observations, XPS data further confirmed the successful formation of ternary hydroxide and modulated electronic structures compared with the NiFe-OH/NF sample, which is more favorable for the fast reaction kinetics.

Electrocatalytic activity tests

Fig. 4a shows the linear sweep voltammetry (LSV) curves of OER with iR correction for all comparative samples. NiFeZn-OH/NiZn-Ni/NF displays an optimal electrocatalytic activity with a lower onset potential and a larger current density at the same overpotential. Notably, it can deliver a current density as high as 600 mA cm^{-2} with the required overpotential of only 284 mV, which is valuable regarding the industrial need for the large current density output. In addition, it has output current densities of 50 and 100 mA cm^{-2} under the overpotentials of 235

and 254 mV, which are obviously lower than those of other samples (Fig. 4b). By comparison, ternary NiFeZn hydroxide constructed on the NiZn-Ni/NF surface serves as active sites for an excellent OER performance, which is also superior to the performance of many representative analogs (Table S1) [2,11,12,15,20,29,31–39]. These results indicated that the as-designed materials with an integrated 3D nanosheet network could achieve a high electrocatalytic performance toward oxygen evolution.

Among the samples, NiFeZn-OH/NiZn-Ni/NF had the smallest Tafel slope of 46.1 mV dec^{-1} (Fig. 4c), further suggesting its high intrinsic activity for OER [22]. It also had the smallest charge transfer resistance (R_{ct} ; Fig. 4d, e), implying a much faster charge transfer during the electrocatalytic process, possibly because of the rapid mass and electron transport along the integrated interface between the well-conductive NiZn-Ni/NF substrate and NiFeZn-OH nanosheet network. The catalytic behavior of one electrocatalyst is considered to be closely related to its electrochemical active surface area (ECSA). Therefore,

Figure 4 (a) LSV curves, (b) overpotentials at 50 and 100 mA cm^{-2} , and (c) Tafel plots of NiFeZn-OH/NiZn-Ni/NF, NiZn-Ni/NF, NiFe-OH/NF, RuO_2 , and NF toward OER in 1.0 mol L^{-1} KOH solution with iR compensation at a scan rate of 5 mV s^{-1} . (d) Electrochemical impedance spectroscopy (EIS) data at the overpotential of 300 mV for the as-made samples and (e) an enlarged image of the dashed frame. (f) Capacitive current at 1.174 V vs. reversible hydrogen electrode (RHE) at different scan rates for NiFeZn-OH/NiZn-Ni/NF, NiFe-OH/NF, NiZn-Ni/NF, and NF. (g) LSV curves of NiFeZn-OH/NiZn-Ni/NF at a scan rate of 5 mV s^{-1} before and after the test for 4000 CV cycles. (h) Current-time curves of NiFeZn-OH/NiZn-Ni/NF under the potentials of 1.498, 1.556, and 1.658 V for 20 h, respectively.

cyclic voltammetry (CV) tests were conducted at different scanning rates to obtain double-layer capacitance (C_{dl}) (Fig. S9), which is directly proportional to the ECSA [2]. Among all samples, NiFeZn-OH/NiZn-Ni/NF had the largest C_{dl} of 167.8 mF cm^{-2} , which was 18.6, 1.5, and 22.7 times those of NiFe-OH/NF, NiZn-Ni/NF, and NF, respectively (Fig. 4f). This result confirmed that the *in situ* construction of ternary NiFeZn hydroxide on bimodal porous NiZn/Ni could generate many exposed active sites and greatly enhance the OER performance.

Apart from excellent catalytic activities, long-term durability is an important criterion for electrocatalysts in practical water splitting. In this study, the polarization curves of NiFeZn-OH/NiZn-Ni/NF nearly overlapped with each other before and after 4000 CV cycles (Fig. 4g). After constant oxygen evolution for 20 h under different fixed potentials, the current densities remained at 99.3%, 98.0%, and 97.2% compared with the initial density, respectively, further indicating the high catalytic durability of NiFeZn-OH/NiZn-Ni/NF (Fig. 4h).

In alkaline media, OER is a surface process involving a four-step proton-coupled electron transfer [39]: $M + OH^- \rightarrow MOH + e^-$ (1), $MOH + OH^- \rightarrow MO + H_2O + e^-$ (2), $MO + OH^- \rightarrow MOOH + e^-$ (3), and $MOOH + OH^- \rightarrow M + O_2 + H_2O + e^-$ (4). Bonding interactions (M–O) are vital for the catalytic behavior of these intermediates during an OER process, so the surface structure of one catalyst can strongly affect the electrocatalytic performance [35]. Our results showed that NiFeZn-OH/NiZn-Ni/NF possessed ideal catalytic kinetics and dramatically enhanced the OER activity. Besides the highly efficient mass transfer from structural superiorities, the accelerated oxygen-evolving kinetics and distinct OER performance of NiFeZn-OH/NiZn-Ni/NF were successfully obtained through electron structure modulation through interface engineering and Zn

doping.

The electrocatalytic performance of all catalysts toward HER was further assessed in the same media. As indicated by the LSV curves in Fig. 5a, the current density of NiFeZn-OH/NiZn-Ni/NF at the same overpotential was higher than that of the other samples, and the onset overpotential of the former was lower than that of the latter, as observed in the OER. It only required an overpotential of only 212 mV at 600 mA cm^{-2} . Besides, it achieved the current densities of 50 and 100 mA cm^{-2} at lower overpotentials of 73 and 99 mV (Fig. 5b), respectively. However, in the same case, larger overpotentials of 260/301, 121/144, and 288/344 mV were needed for NiFe-OH/NF, NiZn-Ni/NF, and NF, respectively. In our previous study, NiZn-Ni/NF has a high HER activity [21]. Herein, the enhanced HER activity of NiFeZn-OH/NiZn-Ni/NF verified that the introduction of NiFeZn hydroxide improved the HER activity. Therefore, NiZn-Ni heterojunction and NiFeZn-OH act together as active sites toward hydrogen evolution. The HER activity of NiFeZn-OH/NiZn-Ni/NF is not as good as that of Pt/C in the region of current densities lower than 170 mA cm^{-2} ; however, it outperforms Pt/C when a much higher current density is required because Pt/C commonly peels off from the NF as a result of the generation of massive bubbles at high current densities. This phenomenon also demonstrates that a self-supporting structure is preferable for high-output hydrogen production at an industrial scale. The HER activity of NiFeZn-OH/NiZn-Ni/NF is comparable to that of a Pt/C catalyst, even superior to numerous nonprecious metal compound electrocatalysts, as shown in Table S2 [20,29,36,39–49].

The HER process in an alkaline solution can be expressed in the following reaction mechanism [50]: $H_2O + e^- + M \rightarrow H-M + OH^-$ (Volmer step, 120 mV dec^{-1}), $H-M + H_2O + e^- \rightarrow H_2 +$

Figure 5 (a) LSV curves, (b) overpotentials at 50 and 100 mA cm^{-2} , and (c) Tafel plots of NiFeZn-OH/NiZn-Ni/NF, NiFe-OH/NF, NiZn-Ni/NF, Pt/C, and NF toward HER in 1.0 mol L^{-1} KOH solution with iR compensation at a scan rate 5 mV s^{-1} . (d) EIS data at the overpotential of 250 mV for the as-made samples. (e) LSV curves of NiFeZn-OH/NiZn-Ni/NF at a scan rate of 5 mV s^{-1} before and after the test for 4000 CV cycles. (f) Current-time curves of NiFeZn-OH/NiZn-Ni/NF under the potentials of -0.087 , -0.176 , and -0.255 V for 20 h, respectively.

$\text{OH}^- + \text{M}$ (Heyrovsky step, 40 mV dec^{-1}), and $\text{H-M} + \text{H-M} \rightarrow \text{H}_2 + 2\text{M}$ (Tafel step, 30 mV dec^{-1}). A Tafel slope determines the rate-limiting step of the HER pathway as an inherent property of electrocatalysts. Therefore, when the Volmer reaction is the rate-limiting step of HER, the Tafel slope should be 120 mV dec^{-1} . Conversely, when the Heyrovsky or Tafel reaction is the rate-limiting step, the Tafel slope should be 40 or 30 mV dec^{-1} . In Fig. 5c, the Tafel slope of NiFeZn-OH/NiZn-Ni/NF for HER was 41.1 mV dec^{-1} , which was close to 37.6 mV dec^{-1} of Pt/C. This result indicated that the Heyrovsky reaction was the rate-determining step, which was the advantageous kinetics of HER.

The R_{ct} of NiFeZn-OH/NiZn-Ni/NF was smaller (0.5Ω) than those of NiFe-OH/NF (10.5Ω), NiZn-Ni/NF (0.6Ω), and NF (17.1Ω). This finding revealed its faster charge transfer during HER (Fig. 5d). Its electrocatalytic activity had almost no evident decline after 4000 CV cycles (Fig. 5e). Moreover, current-time curves at different fixed potentials further showed its prolonged catalytic durability with almost no current loss upon a continuous reaction for 20 h (Fig. 5f).

With the outstanding OER and HER performance of NiFeZn-OH/NiZn-Ni/NF, the electrolyzer of the overall water splitting was developed and used as the cathode and anode in a two-electrode system. As shown in Fig. 6a, only a voltage of 1.49 V was required to achieve a current density of 20 mA cm^{-2} , which was lower than those of NiFeZn-OH/NiZn-Ni/NF (+)||NiZn-Ni/NF (-) (1.53 V) and commercially available RuO_2 (+)||Pt/C (-)

(1.64 V). Besides, it can deliver the current density of 100 mA cm^{-2} under the potential of 1.61 V for this electrode, which was much lower than those of the two other electrolyzers. In addition, the as-constructed target device showed negligible decay after 40 h of long-term continuous testing at 1.52 V (Fig. 6b). It also had the most optimal output stability among the three electrolyzers. The electrocatalytic performance of NiFeZn-OH/NiZn-Ni/NF was better than most similar electrocatalysts for overall water splitting (Fig. 6c and Table S3), indicating its remarkable superiority as a bifunctional catalyst [5,20,27,36,39,41,42,44–48,51].

The cause of the exceptional catalytic durability of NiFeZn-OH/NiZn-Ni/NF in water electrolysis was explored using the OER anode as a representative. The SEM image after the stability test (Fig. S10a) indicated that the structure of the nanosheet network was mostly retained. Our comparison revealed that the nanosheet network is slightly dissolved and aggregated, which usually occurs in NiFe-based hydroxides [1,2]. In alkaline solutions, OH^- can diffuse into hydroxide nanosheet interlayers and stimulate the local acidic surroundings; consequently, OH^- dissolves [1]. ICP analysis confirmed that the atomic ratio of Ni, Fe, and Zn in the post-test hydroxide nanosheets was approximately 34.02:47.95:18.03. Compared with that of the fresh sample, the Fe content slightly decreased, whereas the Ni and Zn contents increased. This result might be attributed to the relatively severe dissolution of Fe from NiFeZn hydroxides in the

Figure 6 (a) LSV curves of the overall water splitting of NiFeZn-OH/NiZn-Ni/NF, NiFeZn-OH/NiZn-Ni/NF (+)||NiZn-Ni/NF (-), and RuO_2 (+)||Pt/C (-) in a two-electrode device. (b) Current-time curves of NiFeZn-OH/NiZn-Ni/NF, NiFeZn-OH/NiZn-Ni/NF (+)||NiZn-Ni/NF (-), and RuO_2 (+)||Pt/C (-) at constant potentials of 1.52, 1.55, and 1.65 V in a two-electrode configuration, respectively. (c) Cell voltage ($@10 \text{ mA cm}^{-2}$) comparison of recently reported bifunctional electrocatalysts in Table S3.

electrolyte. In addition, the residual elements in the electrolyte were measured after the stability test. Ni, Fe, and Zn were almost undetected in the resulting electrolyte, possibly because the relatively large amounts of electrolytes were used during long periods of the stability test. During the test, the slight dissolution of the catalyst yielded a low concentration in the electrolyte, so the dissolved ions could not be detected. The XRD pattern obtained after the stability test showed that the amorphous nature of NiFeZn-OH/NiZn-Ni/NF was still preserved upon the continuous electrocatalytic reaction (Fig. S10b). The XPS in Fig. S11a indicated that the Ni²⁺ content in the Ni 2p region slightly reduced as the Ni³⁺ species emerged; as such, Ni(OH)₂ was slightly oxidized during oxygen evolution. The change in Zn 2p and Fe 2p could be disregarded compared with the fresh sample (Fig. S11b, c). For O 1s in Fig. S11d, the M–O bond obviously increased after the stability test, implying that hydroxide was partially oxidized to M–O–OH under oxidative conditions, which is usually thought to be the real catalytically active sites for water splitting [22]. These results suggested that NiZn-Ni/NF could robustly adhere to the NiFeZn-OH nanosheet network. The bulky integral 3D architecture possessed high corrosion resistance and mechanical stability under strong oxidizing environments.

Our study demonstrated that NiFeZn-OH/NiZn-Ni/NF as a bifunctional electrocatalyst exhibited an outstanding catalytic activity, high structural stability, and exceptional device performance in alkaline electrolytes. Its outstanding OER and HER performances were likely attributed to its structural and compositional originalities. A highly conductive 3D scaffold with microscale hollow channels and rich voids embedded in the nanosheet network could accelerate the evolution/release of gas molecules during HER and OER, thus promoting the reaction kinetics. The 2D thin nanosheet subunits and rich voids as reservoirs could provide high-density active sites and enough contact with electrolytes. The assembly between the bulky multilevel 3D scaffold and nanosheet network had high corrosion resistance and robust structural stability, resulting in high structural stability and device performance. In addition, the synergistic effects of Ni, Fe, and Zn hydroxides and modulation of electron structures through interface engineering and Zn doping could create multiple active sites with high activity; thus, the electrocatalytic kinetics of NiFeZn-OH/NiZn-Ni/NF could be modified for OER and HER. Lastly, an amorphous texture with numerous ordered nanoscale grains of NiFeZn hydroxide possibly contributed to the adsorption/desorption of reactants and superior bifunctional activity.

CONCLUSIONS

In summary, a ternary NiFeZn hydroxide nanosheet network anchored on the hierarchical porous NiZn/Ni and having remarkable electrocatalytic activities toward water splitting was successfully prepared by dealloying and a redox reaction. With a crosslinking hydroxide nanosheet array, a hierarchical porous substrate, interface engineering, and synergistic effects of Ni, Fe, and Zn species, NiFeZn-OH/NiZn-Ni/NF exhibited lower overpotentials at high current densities, smaller Tafel slopes, and stable catalytic durability toward OER and HER. In particular, its constructed electrolyzer possessed an outstanding performance toward the overall water splitting with a smaller required cell voltage and prolonged output. Our work provided insights into the development of novel and highly active bifunctional

electrocatalysts for practical and economic hydrogen production *via* water splitting.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Qiuxia Zhou received her bachelor's and master's degrees from the University of Jinan in 2014 and 2017, respectively. Currently, she is a doctoral student in Prof. Shishen Yan's group at the Spintronics Institute, University of Jinan. Her research focuses on the design and preparation of nanomaterials and their catalytic and electrocatalytic activities, including electrochemical sensing and water splitting.

Caixia Xu received her doctoral degree in 2009 from Shandong University. At present, she is a professor at the Institute for Advanced Interdisciplinary Research (IAIR), University of Jinan. Her research focuses on the preparation of nanomaterials and their catalytic and electrocatalytic activities in some small molecules to develop useful advanced materials for fuel cell-related technology, electrochemical sensing, and heterogeneous industrial catalysis.

Hong Liu is a professor at the State Key Laboratory of Crystal Materials, Shandong University. He received his doctoral degree in 2001 from Shandong University (China). His current research mainly focuses on the chemical processing of nanomaterials for energy-related applications, including photocatalysis and tissue engineering, especially interactions between stem cells and nanostructures of biomaterials and nonlinear optical crystals.

Shishen Yan is a professor at the State Key Laboratory of Crystal Materials, Shandong University. He received his doctoral degree in 1996 from Shandong University (China). His current research focuses on spintronics, including the spin flow generation, transport, regulation and detection, electric field regulation, magnetism, magnetoresistance, rectifier magnetic resistance, spin Hall effect, and spin-orbit coupling.

NiFeZn-OH纳米片网络阵列与多层次多孔NiZn/Ni异质结协同耦合实现高效全水分解

周秋霞¹, 徐彩霞^{1*}, 李雅馨¹, 解西淼¹, 刘宏^{1,2*}, 颜世申^{1*}

摘要 开发高效、经济的析氧反应(OER)和析氢反应(HER)电催化剂,在绿色和清洁氢能方面具有广阔的应用前景. 本工作中,我们在泡沫镍负载的多层次多孔NiZn金属间化合物/Ni异质结上原位构筑NiFeZn氢氧化物纳米片阵列(NiFeZn-OH/NiZn-Ni/NF)用作高效的OER和HER电催化剂. 首先,在泡沫镍表面构筑一层双峰多孔NiZn金属间化合物/Ni,获得最大程度的催化位点暴露,然后与FeCl₃氧化还原反应生长牢固的NiFeZn-OH纳米片阵列. 由于Zn掺杂、多界面工程以及三维一体化导电骨架的协同效应, NiFeZn-OH/NiZn-Ni/NF对于OER和HER显示出低的过电势,在电流密度为50/600 mA cm⁻²时分别约为235/284 mV和73/212 mV,其Tafel斜率分别为46.1和41.1 mV dec⁻¹,在碱性介质中显示出高的催化耐久性. 作为双功能催化剂, NiFeZn-OH/NiZn-Ni/NF在全水分解中达到20 mA cm⁻²仅需1.49 V (100 mA cm⁻²时需1.61 V),且能持续、稳定运行40 h. 这项工作有助于探索设计低成本、高效的金属间化合物/多金属氢氧化物异质结电催化剂,为其在全水分解的实际应用提供启示.