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Self-supported NiFe-LDH@CoS_x nanosheet arrays grown on nickel foam as efficient bifunctional electrocatalysts for overall water splitting HPSTAR

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ABSTRACT

Electrocatalytical water splitting to produce hydrogen energy is a promising green technology to solve energy crisis and environmental issues. The development of highly efficient and low-cost electrocatalysts is crucial for mass hydrogen production from water splitting. We newly assemble the self-standing 3D NiFe-LDH@CoS_x/NF bifunctional electrocatalysts, *via* the electrodeposition of amorphous CoS_x on two-dimensional (2D) NiFe-LDH anosheets which are supported by porous nickel foam (NF). The integration of HER-active electrocatalyst of CoS_x with outstanding OER catalyst of NiFe-LDH guarantees the bifunctional electrocatalytic activity. Furthermore, the formation of the constructed interfaces between amorphous CoS_x and NiFe-LDH manosheets synergistically favors the electron transfer. Therefore, this novel NiFe-LDH@CoS_x/NF hierarchical assembly needs ultralow overpotentials of 136 mV (for HER) and 206 mV (for OER) to afford the 10 mA cm⁻² current density in alkaline medium (1 M KOH). An electrolyzer based on the NiFe-LDH@CoS_x/NF produces an extremely low cell voltage (1.537 V) and good durability. This study offers a promising strategy for facile fabrication of low-cost electrocatalystic performance for overall water splitting.

1. Introduction

With the increasingly serious energy crisis and environmental problems, renewable clean energy has been explored on a large scale in the past few decades [1]. Hydrogen energy is regarded as ideal alternative energy due to its zero carbon emission and high energy density [2]. Electrolysis of water is seen as one of the most promising and effective pathways to produce hydrogen. The process of electrochemical water splitting is driven by two half reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [3]. However, the large overpotentials and slow kinetics of HER and OER severely hinder the practical application of the water splitting [4,5]. In this regard, it is very necessary to utilize highly efficient electrocatalysts to decrease the overpotentials and improve the water splitting efficiency [6]. Up to now, noble metal catalysts (Pt, RuO₂ and IrO₂, et al.) hold the highest

electrochemical activity for HER and OER [7,8]. While the high price of the precious metals impede their large-scale commercial applications [9,10]. Therefore, the design and construction of cheap while highly efficienct electrocatalysts become particularly important.

Currently, transition metal-based catalysts, for example, the metal oxides [11], hydroxides [12], phosphates [13], sulfides [14,15], selenides [16] and nitrides [17] of Fe, Co, Ni, Mn and Mo, have attracted intensive interest. But the most reported electrocatalysts only showed acceptable activity and stability toward one of the two half-reactions (HER or OER), and thus they can be individually optimized [18]. Considering lowering cost and simplifying device for industrial applications, designing bifunctional non-noble electrocatalysts which can simultaneously catalyze both HER and OER is an urgent requirement [2].

For OER, NiFe layered double hydroxides (NiFe-LDHs) have shown

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excellent electrocatalytic performance in alkaline media according to pioneering reports [19–21]. In NiFe-LDHs, it was found the Fe ions normally work as the active sites during the OER process [22]. For HER, due to the weak binding property between Fe³⁺ and hydrogen, there still is a large kinetic energy barrier for Volmer step and hence a sluggish HER kinetics for NiFe-LDH catalysts [23,24], although the Ni²⁺ possesses favorable adsorption ability toward water molecules. Therefore, how to functionalize NiFe-LDHs to improve the HER catalytic performance while maintain or optimize OER property so as to work as effective dual-function catalysts utilized in water splitting, is of critical importance.

Coupling NiFe-LDH with certain HER-active substances can be expected to improve the HER performance of the resulting composites. For HER, MoS₂ is quite prospective for replacing Pt [25-28], due to its low Gibbs free energy of hydrogen adsorption [29]. However, MoS₂ exhibits preferable electrocatalytic activity for HER only in acidic electrolytes [30,31], and its catalytic performance is not up to the mark in alkaline medium [32]. Electrolytic HER under alkaline conditions is more favorable than under acid media in industrial applications because of its economic and effective advantages [33]. Actually, prior studies revealed that amorphous CoS_x exhibited highly catalytic activity toward HER in alkaline solutions, thanks to its isotropic property and disordered structure [34,35]. Furthermore, some researches indicated that abundant unsaturated sulfur atoms along the cobalt sulfide edges in amorphous CoS_x can work as the active sites to accelerate the adsorption of proton, which is beneficial for HER activity [35,36]. Integration of amorphous CoS_x and NiFe-LDH may endow the composite favorable HER and OER activity, which is suitable for use as dual-function electrocatalysts, while there is no report focused on this.

With the hope that the newly assembled system is highly active for both HER and OER in alkaline conditions, for the first time, to our knowledge, we assemble the hierarchical structure consisted of amorphous CoS_x layers on NiFe-LDH nanosheets using a facile hydrothermal method followed by electrodeposition. The nickel foam (NF) acts directly as nickel source to produce the NiFe-LDH structure, which saves the operation step of adding Ni sources and reduces raw material cost. The resulting NiFe-LDH@CoSx/NF assembly can function efficiently as both the HER and OER catalysts. As expected, the NiFe-LDH@CoSx/NF displays superior electrocatalytic performance toward water splitting with an ultra-low cell voltage of 1.537 V to yield the 10 mA cm⁻² current density. The results demonstrate that the largely enhanced catalytic activity of NiFe-LDH@CoSx/NF is ascribed to the synergistic effect of CoS_x and NiFe-LDH. At the same time, the electron transfer from Ni to Co may also makes a significant contribution to the improved electrocatalytic performance.

2. Experimental section

2.1. Preparation of NiFe-LDH/NF

The NiFe-LDH/NF was fabricated by a facile one-step hydrothermal reaction [37]. Typically, NF was cut into pieces $(2 \times 3 \text{ cm}^2)$ and pretreated sequentially with HCl solution (1 M), water, and ethanol to remove the oxidation layers. Then, the cleaned NF was weighed after being dried in vacuum oven. Subsequently, 0.808 g (2 mmol) Fe $(NO_3)_3$ ·9H₂O and 0.601 g (10 mmol) urea were added into 36 mL deionized water. The resulting solution was transferred into a Teflon-lined autoclave (50 mL). A piece of pretreated NF was immersed in the above-mentioned solution and reacted at 100 °C for 8 h, and then cooled down to room temperature. The tan product was collected after being rinsed with water and ethanol several times, dried at 40 °C in vacuum overnight.

2.2. Preparation of NiFe-LDH@CoSx/NF

The electrodeposition of CoSx on NiFe-LDH/NF was based on a

literature method [38] with some modification. The electrodeposition experiments were performed on a CHI750E electrochemical workstation with a three-electrode configuration (a graphite rod as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the as-prepared NiFe-LDH/NF (1 \times 1 cm²) as working electrode). The 0.58 g (2 mmol) of Co(NO₃)₂·6H₂O and 15.2 g (200 mmol) of thiourea were dissolved in 100 mL deionized water to form a solution, and 45 mL abovementioned solution was used as deposition electrolyte. The amorphous CoS_x film was deposited onto NiFe-LDH/NF nanosheets by cyclic voltammetry (CV) in a potential range from -1.2 to 0.2 V (vs. SCE) with a scan rate of 5 mV s^{-1} at room temperature for 10 cycles. After that, the resulting samples were washed carefully with water and ethanol for several times to remove surface metal ions before dried in a vacuum oven at 40 °C overnight. To optimize the NiFe-LDH@CoSx/NF catalyst, 5, 10 and 15 cycles of cyclic voltammetry were conducted, and the as-obtained composites were denoted as NiFe-LDH@CoSx/NF-5C, NiFe-LDH@CoSx/NF-10C and NiFe-LDH@CoSx/NF-15C, respectively. Unless particular clarification, NiFe-LDH@CoSx/NF is used to denote the NiFe-LDH@CoSx/NF-10C sample in this paper. The mass loadings of the products are shown in Table S1.

2.3. Preparation of CoS_x/NF and CoS_x/CC (carbon cloth)

The CoS_x/NF electrode was deposited as a control sample using the same electrodeposition method as for NiFe-LDH@CoS_x/NF except for changing the NiFe-LDH/NF (1 \times 1 cm²) to NF (1 \times 1 cm²) itself as the working electrode when the electrodeposition experiment was performed. To be a control sample for X-ray absorption fine structure (XAFS) analysis, CoS_x/CC (CC is carbon cloth) was prepared using the same method of CoS_x/NF except that NF was replaced by CC.

2.4. XAFS measuments

The Co, Ni and Fe K-edges XANES were recorded in transmission mode at beamline 01C1 of the National Synchrotron Radiation Research Center (NSRRC). The photon energies were calibrated to the first inflection point of the K edge from cobalt metal foil at 7709 eV, or iron - metal foil at 7112 eV, or nickel metal foil at 8333 eV, respectively. All data were processed using the Ifeffit-based Athena programs with the theoretical standards calculated using FEFF8 [39].

3. Results and discussions

3.1. Structural and morphological characterization

A typical designed and assembled approach to NiFe-LDH@CoSx/NF is displayed in Scheme 1. The resulting samples were characterized by Xray diffraction (XRD). From Fig. 1a-A, CoS_x/NF shows obvious diffraction peaks at 44.5° , 51.8° , and 76.4° (labeled as '#'), assigned to (111), (200), and (220) facets of Ni metals (JCPDS No. 04-0850) of NF. Note that there is no diffraction which can be indexed to CoS_x, meaning that it may exist in an amorphous state. For NiFe-LDH/NF (see Fig. 1a-B), a series of Bragg reflections at $2\theta = 10.8^{\circ}$ (d = 0.81 nm), 22.6° (d = 0.39 nm), 34.3° (d = 0.25 nm) and 38.6° (d = 0.23 nm) are observed, which can be indexed to (003), (006), (012) and (015) planes of NiFe-LDH (labeled as '*') [40]. Besides, the peak at 60.8° (d = 0.15 nm) corresponds to the characteristic (110) plane of the LDH layers. After electrodepositon of CoS_x onto NiFe-LDH, the XRD pattern for the resulting NiFe-LDH@CoSx/NF (Fig. 1a-C) exhibits diffraction peaks ascribed to NF and NiFe-LDH, with the absence of diffractions of CoS_x. Though SEM mapping discussed below verified the presence of cobalt sulfides, no diffraction peaks related to any kind of CoS_x can be detectable in NiFe-LDH@CoS_x/NF and CoS_x/NF, suggesting the amorphous nature of the electrodeposited CoS_x. To investigate the structural nature, the NiFe-LDH/NF is analyzed by the FT-IR spectra (Fig. 1b). The IR band at 1630 \mbox{cm}^{-1} corresponds to the bending vibration of interlayer H_2O of

Table 1

Comparison of OER performance of NiFe-LDH@CoS_x/NF with other reported electrocatalysts.

Catalysts	Loading(mg cm ⁻²)	η ₁₀ (mV)	References
NiFe-LDH@CoS _x /NF	1.48	206	This work
NF/Ni _{0.8} Fe _{0.2} LDH	0.5	231	Small 2018 [62].
δ -FeOOH NSs/NF	0.16	265	Adv. Mater. 2018
NiFe LDH@NiCoP/NF	2	220	Adv. Funct. Mater.
High-index faceted Ni ₃ S ₂	1.6	260	J. Am. Chem. Soc.
CoFe-LDH	-	250	Appl. Catal. B-
			Environ. 2019 [66].
Ni _{0.7} Fe _{0.3} S ₂ /NF	3.0	198	J. Mater. Chem. A 2017 [67].
FePO ₄ /NF	0.29	218	Adv. Mater. 2017
Ni _{0 75} Fe _{0 125} V _{0 125} -LDHs/NF	1.42	231	Small 2018 [69].
Co ₅ Mo _{1.0} O NSs@NF	-	270	Nano Energy 2018
FeOOH/CeO2 HLNTs-NF	0.44	210	Adv. Mater. 2016
NiFe/Ni(OH) ₂ /NiAl foil	_	246	Adv. Sci. 2017 [72]
NiFe-LDH/NF	-	240	Science 2014 [73].

LDH [41]. The obvious absorption peak at 1384 cm⁻¹ is ascribed to vibration of NO_3^- [42]. Notably, a shoulder at 1354 cm⁻¹ assigned to vibration of CO_3^{2-} [43] suggests co-presence of CO_3^{2-} . The 670 cm⁻¹ band is assigned to the stretching vibration of Ni/Fe-O (metal-O) [44], and the 511 cm⁻¹ one is assigned to O-metal-O vibration [45]. All these FT-IR results indicate formation of typical NiFe-LDH structure with NO_3^- and some CO_3^{2-} as interlayer anions to compensate the charge.

The structure and morphology of the designed catalysts were investigated by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). When CoS_x was electrodeposited on NF directly, the SEM images of CoS_x/NF (see Fig. 2a and 2b) revealed that NF was covered closely and uniformly by the ultrathin CoS_x nanosheets. In comparison, the NiFe-LDH/NF showed thicker and much bigger nanosheets with a thickness of ~ 10 nm (Fig. 2c, 2d). After electrodepositing CoS_x onto NiFe-LDH nanosheets (Fig. 2e, 2f), the obtained NiFe-LDH@CoSx/NF still displayed the morphology of nanosheets, with a thickness of ~ 20 nm which was thicker than both CoS_x and NiFe-LDH, implying that electrodeposited CoS_x film is decorated onto the NiFe-LDH nanosheets. Furthermore, the NiFe-LDH@CoSy sheets appeared to be vertically grown on the NF substrate and spatially interconnected, forming a three-dimensional hierarchical porous structure (Fig. 2f). Such flake shape with a large surface area maximizes the exposure of active sites and porous structure guarantees a large contact area between electrolyte and catalyst. The NiFe-LDH@CoSx/NF-5C



Scheme 1. Schematic illustration of synthetic process of NiFe-LDH@ CoS_x/NF .



Fig. 1. (a) XRD patterns of (A) CoS_x/NF, (B) NiFe-LDH/NF, (C) NiFe-LDH@CoS_x/NF, and (b) FT-IR spectra of NiFe-LDH/NF.



Fig. 2. SEM images of (a, b) CoS_x/NF, (c, d) NiFe-LDH/NF, and (e, f) NiFe-LDH@CoS_x/NF. (g-k) SEM image and elemental mapping of NiFe-LDH@CoS_x/NF.

(Fig. S1a) has a similar morphology with NiFe-LDH@ $CoS_x/NF-10C$ (that is, NiFe-LDH@ CoS_x/NF) except the formed nanosheets are thinner. With longer electrodeposition time, the as-prepared NiFe-LDH@ $CoS_x/NF-15C$ depicted rougher and curvier nanosheets due to more electrodeposited CoS_x on NiFe-LDH (Fig. S1b). The Energy Dispersive Spectroscopy (EDS) mapping images (Fig. 2h-k) of NiFe-LDH@ CoS_x/NF (its SEM see Fig. 2g) show the uniform distribution of Co, S, Ni, and Fe elements throughout the material, and the existence of Co and S further confirms the formation of cobalt sulfides. The HRTEM image of CoS_x/NF (Fig. 3a) disclosed the amorphous nature of the electrodeposited CoS_x , in agreement with the corresponding fast Fourier transformation (FFT) (see Fig. 3b) of selected area of Fig. 3a. As depicted in Fig. 3c, TEM image of NiFe-LDH@ CoS_x /NF confirmed its nanosheet-like morphology. HRTEM image of NiFe-LDH@ CoS_x /NF composite (Fig. 3d) exhibited a 0.25 nm spacing which is assigned to the (012) plane of NiFe-LDH. From Fig. 3d, distinct interfaces between the amorphous CoS_x and the NiFe-LDH crystalline phase can be clearly observed, showing a wrapped structure with a close contact of the two phases.



Fig. 3. (a) HRTEM image of CoS_x/NF , (b) corresponding FFT on the selected box area marked with red line in (a), and (c) TEM and (d) HRTEM images of NiFe-LDH@CoS_x/NF.



Fig. 4. XPS spectra for (a) Fe 2p and (b) Ni 2p of NiFe-LDH/NF and NiFe-LDH@CoS_x/NF and (c) Co 2p and (d) S 2p of CoS_x/NF and NiFe-LDH@CoS_x/NF, respectively.

3.2. Electronic states characterization

X-ray photoelectron spectroscopy (XPS) was performed to probe chemical states and electron interactions of elements between FeNi-LDH and CoS_x in the electrocatalysts. In NiFe-LDH/NF, for Fe 2p (see Fig. 4a), the two peaks with binding energies of 725.91 and 712.77 eV correspond to Fe(III) $2p_{1/2}$ and Fe(III) $2p_{3/2}$, respectively [46], revealing the + 3 oxidation state of Fe. In NiFe-LDH@CoS_x/NF, the very similar Fe 2p peaks at 725.90 and 712.78 eV indicate the electrodeposition of CoS_x does not change the valence of Fe and its coordination environment. The Ni 2p region of NiFe-LDH/NF and NiFe-LDH@CoSx/NF could be resolved into four peaks (Fig. 4b). For NiFe-LDH/NF, the binding energies of Ni 2p1/2 and Ni 2p3/2 of 872.93 and 855.45 eV, respectively, are in good agreement with the reported data of Ni^{2+} in NiFe-LDH [47]. After the electrodeposition of CoS_x , both Ni $2p_{1/2}$ and Ni $2p_{3/2}$ present higher binding energies of 873.51 and 855.62 eV, respectively, suggesting the interactions between NiFe-LDH and CoS_x. Fig. 4c displays the Co2p spectra. For CoS_x/NF, the energies of 794.32 and 778.37 eV are respectively assignable to Co $2p_{1/2}$ and Co $2p_{3/2}$ of Co³⁺ [48], while the 797.67 and 781.92 eV correspond to Co^{2+} [49]. Based on the integral peak area, the molar ratio of $Co^{2+}:Co^{3+}$ is determined to be 1.79:1 in the amorphous CoS_x . By comparing with the CoS_x/NF , the peaks of Co2p in NiFe-LDH@CoSx/NF have a down-shift to 793.92 and 778.02 eV for Co^{3+} and 796.62 and 781.62 eV for Co^{2+} , further proving the interactions between the two phases of NiFe-LDH and CoS_x.

X-ray absorption near edge structure (XANES) is performed to further investigate the interactions between CoS_x and NiFe-LDH. To avoid influence by Ni element in the nickel foam (NF), the CoS_x was electrodeposited on carbon cloth to work as a control sample (denoted as

CoS_x/CC). The Co K-edge XANES spectra of CoS_x/CC and NiFe-LDH@CoS_x/NF are displayed in Fig. 5a. The edge position is determined by the maximum first derivative of the normalized XANES spectra [50]. The edge position of Co K-edge in NiFe-LDH@CoSx/NF shift to lower energy than that of CoS_x/CC (insets of Fig. 5a), suggesting the lower valence state of Co species in the NiFe-LDH@CoSx/NF composite. For the Co in NiFe-LDH@CoS_x/NF sample, another phenomenon is that the intensity of the white line peak decrease. The lower white line peak implies the lower valence state of Co in NiFe-LDH@CoSx/NF [51]. In contrast, the edge position of Ni K-edge in NiFe-LDH@CoSx/NF has an obviously shift to higher energy compared to NiFe-LDH (inset of Fig. 5b), suggesting valence state of Ni in NiFe-LDH@CoSx/NF gets higher after integration. Also, the intensity of white line peak of Ni in NiFe-LDH@CoS_x/NF is higher than that of NiFe-LDH/NF, indicating that Ni in NiFe-LDH@CoS_x/NF presents an electron deficiency [52]. The two curves of Fe K-edge in NiFe-LDH@CoSx/NF and NiFe-LDH/NF display very similar features and almost can overlap (Fig. 5c), meaning that neither the valence state nor the chemical environment of Fe has changed after the electrodeposition of CoS_x. This matches well with our XPS results. After formation of the interfaces, CoS_x, a p-type semiconductor [53], tend to be an electron-acceptor site resulting in negative shifts to lower energy. While NiFe-LDH has an up-shift with the energy of Ni K-edge owing to its property of n-type semiconductor [42,54,55], leading to the electron transfer from Ni to Co.

This Ni \rightarrow Co electron transfer would cause more positive valence state of Ni and negative valence state of Co. As known the valence change may affect the electron density and electronic structure, which influences the adsorption states and is beneficial for the enhancement of the electrocatalytical activity. Based on the Yang's principle and



Fig. 5. XANES spectra of (a) Co K-edge of CoS_x/CC and NiFe-LDH@CoS_x/NF, (b) Ni K-edge of NiFe-LDH/NF and NiFe-LDH@CoS_x/NF, and (c) Fe K-edge of NiFe-LDH/NF and NiFe-LDH@CoS_x/NF. Insets of (a) and (b) show the enlarged absorption edge, demonstrating the charge transfer from Ni to Co.

previous reports [56-58], the occupancy of e_g orbital is a key factor for the electrocatalytical performance of 3d transition metals, because the σ -bonding e_g orbital has a stronger overlap with the oxygen-related adsorbate than does the π -bonding t_{2g} orbital, and thus can more directly promote electron transfer between surface cation and adsorbed reaction intermediates [59]. Electrocatalysts having too high or too low eg occupancy (2 or 0, respectively) will bind oxygen-related adsorbate too strongly or weakly, respectively, thus leading to unsatisfactory performance for water splitting [60]. According to previous reports [57,59], the optimal e_g filling is 1.2 for better catalytical performance. In the present work, the Ni^{2+} has a $t_{2g}^6 e_g^2$ electronic configuration while the Co^{2+} is with a $t_{2g}^5 e_g^2$ configuration [58]. For Ni, the electron transfer causes the decrease in its e_g occupancy, approaching to optimal $e_g^{1.2}$ filling from e_g^2 . For Co, due to the acquisition of electrons, the terrific configuration of $t_{2g}^6 e_g^1$ (near to $e_g^{1,2}$) of Co^{2+} for ideal OER electrocatalysts may be formed [57]. Therefore, the optimal eg filling of Ni and Co will both contribute to the improvement of OER activity. For HER, it was reported that the electronic structure of Co²⁺ and Ni³⁺-rich configurations may lower down the ΔG_{H^*} for HER [58]. In the present NiFe-LDH@CoS_x/NF, the Ni \rightarrow Co electron transfer causes the increase of Ni valence (forming $Ni^{2+\sigma}$) and decrease of Co valence (having more $Co^{2+\sigma}$) relative to Co^{3+}), which are beneficial to the improvement of HER activity.

3.3. Electrocatalytic HER performance

HER performance of the as-obtained materials were tested with a typical three electrode cell in 1 M KOH electrolytes, during which the materials acted directly as working electrodes. The commercial Pt/C (20 wt%) loaded on bare NF was also measured for contrast. As shown in Fig. 6a, the CoS_x/NF requires a lower overpotential of 200 mV to reach 10 mA cm $^{-2}$ ($\eta_{10}=200$ mV) in comparison to the NiFe-LDH/NF ($\eta_{10}=$ 368 mV), indicating the amorphous CoS_x is, as expected, more active toward HER than NiFe-LDH. Remarkably, the NiFe-LDH@CoSx/NF shows the highest activity with the lowest η_{10} value of 136 mV among the as-prepared materials. To investigate the effect of different deposited amounts of CoSx on the catalytical performance, we also tested the samples which are prepared with different numbers of CV cycles when CoS_x was electrodeposited. As illustrated in Fig. S2a, the η_{10} of NiFe-LDH@CoS_x/NF-10C is 64 and 42 mV smaller than those of NiFe-LDH@CoS_x/NF-5C ($\eta_{10} = 200 \text{ mV}$) and NiFe-LDH@CoS_x/NF-15C ($\eta_{10} =$ 178 mV), respectively, indicating that optimal coating amounts of CoS_x on NiFe-LDH would effectively enhance the catalytical activity. To obtain a further insight into the electrocatalytic HER kinetics, the Tafel plots were calculated by fitting the Tafel equation $(\eta = b\log i + a, where \eta)$ is overpotential, *b* is Tafel slope, and *j* is current density). As shown in Fig. S2b, NiFe-LDH@CoS_x/NF has a Tafel slope of 73 mV dec⁻¹, indicating its rate limiting step follows the Volmer-Heyrovsky mechanism [4]. Moreover, the NiFe-LDH@CoS_x/NF shows the lowest Tafel slope among the control samples, where a smaller slope means faster escalation of HER rate [61]. Electrochemical impedance spectroscopy (EIS) was carried out to reveal ionic and charge transport rate during HER. The semicircle in the high-frequency range of Nyquist plot is related to charge-transfer resistance (Rct). As displayed in Fig. 6b, based on the fitting equivalent circuit model, the NiFe-LDH/NF and CoS_x/NF have R_{ct} of 38.58 and 24.31 Ω (see Table S2), respectively. When NiFe-LDH is integrated with CoS_x, the as-obtained NiFe-LDH@CoS_x/NF composite exhibits a much smaller R_{ct} (8.02 Ω), implying the rapid electron transport for hydrogen evolution on the electrode. These results verify that NiFe-LDH@CoSx/NF possesses outstanding HER performance in alkline electrolytes.

3.4. Electrocatalytic OER performance

The electrocatalytic OER activity of NiFe-LDH/NF, CoS_x/NF and NiFe-LDH@ CoS_x/NF was evaluated in 1 M KOH as well. Fig. 6c shows

typical OER polarization curves of the as-prepared catalysts. The NiFe-LDH/NF ($\eta_{10} = 226$ mV) shows a better OER performance than $CoS_x/$ NF ($\eta_{10} = 277$ mV). When CoS_x was electrodeposited onto NiFe-LDH/ NF, the required overpotential of NiFe-LDH@CoSx/NF is reduced to a much lower value of 206 mV ($\eta_{10} = 206$ mV), even smaller than the benchmark of RuO₂ ($\eta_{10} = 223$ mV). This demonstrates the NiFe-LDH@CoSx/NF exhibits an outstanding OER performance, which is better or comparable to most reported Fe/Co/Ni-based materials as listed in Table 1 [62–73]. The electrodeposition of CoS_x on NiFe-LDH/ NF scaffold was optimized by varying the cycles of electrodeposition and measuring their OER performance (Fig. 6d). Similar to HER, the NiFe-LDH@CoSx/NF-10C shows relatively smaller overpotential for OER than NiFe-LDH@CoS_x/NF-5C ($\eta_{10} = 228$ mV) and NiFe-LDH@CoS_x/NF-15C ($\eta_{10} = 277$ mV). Furthermore, the Tafel slopes originated from corresponding polarization curves were applied to investigate the OER kinetics (Fig. 6e). The Tafel slope of 62 mV dec⁻¹ of NiFe-LDH@CoSx/NF is much smaller than those of NiFe-LDH/NF (85 mV dec⁻¹) and CoS_x/NF (93 mV dec⁻¹). The low Tafel slope of the NiFe-LDH@CoS_v/NF implies its favorable OER kinetics. Furthermore, NiFe-LDH@CoS_x/NF also exhibits good durability during the OER. As illustrated in Fig. 6f, the chronoamperometric test reveals that NiFe-LDH@CoS_v/NF can maintain a constant current density of 15 mA cm⁻² for nearly 24 h. It can be seen from these data that, after the combination of the two components of NiFe-LDH and CoS_x, both the HER and OER performance are improved compared to the two original components. This indicates that the electron transfer between Ni and Co is beneficial for the performance improvement of the electrocatalysts.

3.5. Overall water splitting

Considering the excellent catalytic activity of NiFe-LDH@CoSx/NF toward both HER and OER, a water electrolyzer was assembled using NiFe-LDH@CoSx/NF as both the cathode and anode in 1.0 M KOH. From Fig. 7a, we can see the electrolyzer (NiFe-LDH@CoSx/NF||NiFe-LDH@CoSx/NF) requires a fairly low overpotential of 1.537 V to afford the current density of 10 mA cm⁻², in contrast to 1.661 V for CoS_x/NF|| CoS_x/NF electrodes and 1.718 V for NiFe-LDH/NF||NiFe-LDH/NF electrodes. Impressively, such an extremely low cell voltage (1.537 V) of the NiFe-LDH@CoSx/NF catalyst for overall water splitting is comparable or even superior to Pt/C||RuO₂ (1.633 V) and those recently reported highly active materials [46,49,72,74-76], as depicted in Fig. 7b. Additionally, the long-term durability of this two-electrode configuration was also tested. As shown in Fig. 7c, the chronoamperometry curve of NiFe-LDH@CoS_x/NF shows a slightly degradation of current density after a long-term test, indicating its good stability. Moreover, the NiFe-LDH@CoS_x/NF exhibits a similar polarization curve after the long period of tests with the initial one (inset of Fig. 7c), confirming its good stability.

To further validate the better performance of NiFe-LDH@CoS_x/NF composite than the control samples of NiFe-LDH/NF and CoS_x/NF, their comparative stability tests were conducted at the voltage of 1.75 V (see Fig. S3). As shown, the current density of NiFe-LDH@CoS_x/NF maintains at ~ 20 mA cm⁻² for 24 h, while the current density of NiFe-LDH/NF and CoS_x/NF is decreased to ~ 5 mA cm⁻² after the first 3 h. These results highlight the excellent electrocatalytic activity and good stability of the NiFe-LDH@CoSx/NF.

3.6. Characterizations for NiFe-LDH@CoS_x/NF after stability test

In order to further gain insights into the reaction mechanism, both the cathode (for HER) and anode materials (for OER) of NiFe-LDH@ CoS_x /NF were characterized by SEM, XRD and XPS after the longterm stability test for water splitting. As shown in the inset of Fig. S3, the SEM image after HER reveals no obvious change of the nanosheet-like morphology, while the surface of the nanosheets after OER gets rougher. The XRD patterns (Fig. S4) of the samples indicate the main



Fig. 6. Electrocatalytic activity of the samples for OER and HER in 1 M KOH: (a) iR corrected polarization curves for HER; (b) EIS Nyquist plots at a potential of -0.12 V (vs. RHE), the inset is the fitting model; (c) iR corrected OER polarization curves for different samples and (d) the composites in which CVs were applied with different numbers of cycles when CoS_x was electrodeposited; (e) Tafel plots for OER and (f) OER chronoamperometry tests of NiFe-LDH@ CoS_x /NF evaluated at 20 mA cm⁻² without iR compensation.

structure of NiFe-LDH@CoS_x/NF after HER and OER remains nearly identical as before. Besides, after the long-term HER testing, the XPS spectra (Fig. 8) for NiFe-LDH@CoS_x/NF are very similar to those before the stability test, which is consistent with the previous report [77]. For OER, the XPS spectra substantially change except that Fe 2p spectrum

stay the same as before. As shown in Fig. S5a, after OER electrolysis, the presence of two new peaks at 856.02 and 873.70 eV indicates that Ni²⁺ is partially oxidized into Ni³⁺ [78]. In the Co 2p spectrum of NiFe-LDH@CoS_x/NF after OER (Fig. S5b), the binding energies at 778.02 and 781.60 eV can be assigned to Co(III) and Co(II) which belong to the



Fig. 7. (a) Polarization curves of NiFe-LDH@CoS_x/NF||NiFe-LDH@CoS_x/NF, NiFe-LDH/NF||NiFe-LDH/NF, CoS_x/NF||CoS_x/NF, and RuO₂/NF||Pt/C/NF in 1.0 M KOH. (b) Comparison of required voltages at the current density of 10 mA cm⁻² for the NiFe-LDH@CoS_x/NF catalyst in this work with other state-of-the-art transition metal catalysts. (c) Chronoamperometry curves of NiFe-LDH@CoS_x/NF tested in a two-electrode configuration. Inset: polarization curves of NiFe-LDH@CoS_x/NF||NiFe-LDH@CoS_x/NF in 1.0 M KOH before and after chronoamperometry operation. References cited in panel (b): Cu@NiFe LDH/CF[46], CoS_x/Ni₃S₂@NF [49], NiFe/Ni(OH)₂/NiAl [72], NiFe-LDH/NiCo₂O₄/NF [74], NiCo₂S₄ NW/NF [75], EG/Co_{0.85}Se/NiFe-LDH [76].



Fig. 8. XPS spectra of (a) Fe 2p, (b) Ni 2p and (c) Co 2p for NiFe-LDH@CoS_x/NF before and after HER/OER durability testing (24 h).

remaining cobalt sulfide after OER test, while the appearance of new peaks at 780.60 and 782.80 eV can be indexed to cobalt oxyhydroxide [79] and hydroxide [80] transformed from CoS_x. The formation of hydroxides and oxyhydroxides explains the presence of rough surface in the SEM image after OER. The generated hydroxides and oxyhydroxides on the surface of electrocatalyst are most likely the actual catalytic active sites for water oxidation [77,81].

In addition, the dissolution of Co, Ni and Fe in the electrolyte was investigated by ICP-AES after 24 h durability tests for overall water splitting. As shown in Table S3, compared with CoS_x/NF and NiFe-LDH/NF, the NiFe-LDH@CoS_x/NF has the much lower dissolution rates of Co, Ni and Fe (at the level of ppb/h), further confirming its good stability.

4. Conclusions

In summary, a self-standing 3D NiFe-LDH@CoSx/NF assembly is fabricated by electrodepositing amorphous CoSx onto NiFe-LDH nanosheet arrays which are vertically aligned on nickel foam (NF). The NF is used as nickel source to achieve the preparation of NiFe-LDH, which therefore simplifies the operation step and reduces raw material cost. The optimized NiFe-LDH@CoSx/NF electrocatalyst is highly active for catalyzing both HER ($\eta_{10} = 136 \text{ mV}$) and OER ($\eta_{10} = 206 \text{ mV}$). The synergistic effect of CoS_x and NiFe-LDH and charge transfer through the interfaces have effectively enhanced both the HER and OER performance, proving an excellent dual-function electrocatalyst. Furthermore, the nanosheets arrays of NiFe-LDH@CoSx directly grow on NF, forming a hierarchical porous material which can directly work as binder-free electrode with more exposed active sites, smooth mass diffusion, and intimate contact for rapid charge transfer. This novel composite of NiFe-LDH@CoSx/NF only needs a 1.537 V cell voltage to obtain the 10 mA cm⁻² current density for overall water splitting. Our work shows the significance of interface and synergistic effect between two individual components which is only active to catalyze HER or OER, which can offer a new viewpoint for the rational design of highly active and lowcost electrocatalysts applied on overall water-splitting.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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