# Supporting Information for

Hafnium incorporation modulating the electronic structure of NiFe

layered double hydroxide for effective oxygen evolution

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## **1. Experimental**

#### **1.1 Chemicals and Materials**

Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O; 98%, Alfa Aesar), iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O; 99.95%, Macklin), hafnium(IV) chloride (HfCl<sub>4</sub>; 99.5%, Macklin), urea (CH<sub>4</sub>N<sub>2</sub>O; 99%, Aladdin), iridium dioxide (IrO<sub>2</sub>; 99.9%, Macklin), potassium hydroxide (KOH; 90%, Macklin), ethanol (C<sub>2</sub>H<sub>5</sub>OH; 98%, Sinopharm), and Nafion solution (5%, Sigma-Aldrich) were analytical grade and used without further purification. Ultrapure water ( $\geq$ 18.2 M $\Omega$  cm) was purified by an Ulupure UPR-III-10T (Sichuan YOUPU Ultrapure Technology Corporation) system. Nickel foam (NF, thickness ~1.5 mm) was purchased from Kunshan Lvchuang Electronic Technology Corporation.

#### **1.2** Synthesis of LDH Catalysts

#### 1.2.1 Synthesis of NiFeHf LDH Powders

The NiFeHf LDH powder, serving as a representative sample, was synthesized through a straightforward one-step hydrothermal method. Specifically, 174.5 mg of Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ , 39.8 mg of FeCl<sub>2</sub>· $4H_2O$ , 32.0 mg of HfCl<sub>4</sub>, and 270.3 mg of urea were dissolved in 20 mL of ultrapure water to create a clear, transparent, yellow-brown precursor solution. Subsequently, this solution was transferred to a Teflon-lined stainless steel autoclave and heated at 120 °C for 6 h.

#### 1.2.2 NiFeHf LDH Grown on Nickel Foam (NiFeHf LDH@NF)

Firstly, hydrophilic treatment of nickel foam (NF) was carried out, and the specific treatment method of nickel foam was referred to Yang *et al.*<sup>[S1]</sup>

The NiFeHf LDH nanostructures were directly grown on foam nickel (NiFeHf LDH@NF) using the same preparation conditions above. The pretreated NF (1 cm × 4 cm) was dipped into the 15 mL of precursor solution in the Teflon container. At the end of a synthetic process, the NiFeHf LDH@NF electrode was washed with ultrapure water and ethanol, and finally below dried on nitrogen flow.

## **1.3 Materials Characterization**

Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance spectrometer with a Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) in the 2 $\theta$  range from 5–70° at a scan rate of 5° min<sup>-1</sup>. Fourier-transform infrared (FT-IR) spectra were acquired using a VECTOR-22 (Bruker) infrared spectrophotometer in the wavenumber range of 400–4000 cm<sup>-1</sup>. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) were collected on ZEISS Sigma 300 at the acceleration voltages of 3–15 kV, respectively. High resolution transmission electron microscopy (HRTEM) images, selected area electron diffraction (SAED) patterns, and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded on JEM 2100F machine at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were collected using an ESCALAB 250Xi (ThermoFisher) device featuring an Al K $\alpha$  X-ray source. Inductively coupled plasma optical emission spectrometer (ICP-OES) were carried out by using an IRIS Intrepid II (ThermoFisher) instrument.

#### **1.4 Electrochemical Characterization**

*The Fabrication of the Working Electrodes*: Initially, 5 mg of NiFeHf LDH powder was dispersed in a mixed solvent comprising 600  $\mu$ L of deionized water, 400  $\mu$ L of ethanol, and 20  $\mu$ L of a 5% Nafion solution. The mixture was then sonicated to form a homogeneous ink. Subsequently, 5  $\mu$ L of this ink was deposited onto the surface of a polished glassy carbon electrode (GCE), ensuring a mass loading of approximately 130  $\mu$ g cm<sup>-2</sup>, and was allowed to dry slowly under infrared light. For the NiFeHf LDH nanostructures grown directly on nickel foam (NiFeHf LDH@NF), the material was used as an integrated 3D working electrode. The mass loading was determined to be approximately 2.45 mg cm<sup>-2</sup> by measuring the weight difference between the unsupported and supported electrodes.

*OER Activity and Performance Evaluations*: Electrochemical measurements were conducted at room temperature in a three-electrode system using a CHI760E electrochemical workstation equipped with a rotating disk electrode (RDE, Pine Research

Instrument) in a 1.0 M KOH electrolyte. The LDH catalysts were loaded onto a glassy carbon (GC, AFE5T050GC, 0.196 cm<sup>2</sup> geometric area) electrode, which served as the working electrode. A platinum wire and a Hg/HgO/1 M KOH (Gaoss Union) electrode were used as the counter and reference electrodes, respectively. All potentials reported in this study were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation:  $E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098$  V. In 1.0 M KOH electrolyte (pH  $\approx$ 13.86). The pH of the electrolyte was determined as the average of three independent measurements using a PHS-3E pH meter (INESA Scientific Instrument). High-purity O<sub>2</sub> (99.999%) was purged on the electrolyte during the whole electrochemical test. Linear sweep voltammetry (LSV) curves were collected on a range on 0.2–0.8 V (vs. Hg/HgO) at a scan rate of 5 mV s<sup>-1</sup>. The polarization curves in this study were manually corrected for solution resistance at 95%. Electrochemical impedance spectroscopy (EIS) measurements were operated at 1.516 V (vs. RHE) in a frequency range of 700–45 kHz with an amplitude of 10 mV. The double-layer capacitance (Cdl) was measured in the non-Faradaic zone at the range of 0.2–0.3 V (vs. Hg/HgO) using different scan rates from 20 to 120 mV s<sup>-1</sup>. The plot of  $\Delta j = (j_a - j_c) / 2$  at 0.25 V (vs. Hg/HgO) against the scan rate revealed a linear relationship. The current density was determined by the geometric area of the electrode. The measurements of constant current at 10 mA cm<sup>-2</sup> were operated on modified GC and 3D electrodes for 8 and 24 h, respectively. The magnetic stirring was used to prevent the collection of oxygen bubbles on the surface of 3D electrode. The rotating ring disk electrode (RRDE, AEF7R9GCPT), consisted of a GC disk, a Pt ring, and a thin PTFE gap  $(320 \,\mu\text{m})$ , was applied to study the OER kinetics and Faradic efficiency (FE) at a rotation speed of 1600 rpm. The FE measurement was performed on an N2-saturated 1.0 M KOH media. The potential on Pt ring was fixed on 1.50 V vs. RHE, and polarization curve on GC disk was collected on a potential range from 0.2 to 0.8 V (vs. Hg/HgO) at 5 mV s<sup>-1</sup>. The FE was calculated as follows equation S1:

$$FE = \left| \frac{I_r n_d}{I_d n_r N_{CL}} \right|$$
(Equation S1)  
S5

where I<sub>r</sub> is the ring current, I<sub>d</sub> is the disk current, n<sub>d</sub> and n<sub>r</sub> are the electron transfer number of the reaction on disk (4OH<sup>-</sup>  $\rightarrow$  4e<sup>-</sup> + 2H<sub>2</sub>O + O<sub>2</sub>) and ring (2H<sub>2</sub>O + O<sub>2</sub> + 2e<sup>-</sup>  $\rightarrow$  2OH<sup>-</sup> + H<sub>2</sub>O<sub>2</sub>), respectively. Moreover, the N<sub>CL</sub> is the collect efficiency (N<sub>CL</sub> = 0.37).

### **1.5** Theoretical Calculations

The spin-polarized density functional theory (DFT) calculations were performed using Perdew-Burke-Ernzernhof (PBE) functional as implemented in the Vienna Ab-initio Simulation Package (VASP) code.<sup>[S2,S3]</sup> Projector augmented wave (PAW) pseudo-potentials was used to describe the mutual effect between atomic nucleus and valence electrons and increase the computation efficiency.<sup>[S4]</sup> A cut off energy of 400 eV and a  $3 \times 3 \times 1$  Monkhorst-Pack k-point were used for all slab models. The effective U values were applied to correct the strong electron-correlation of 3d transitional metals in three LDHs. The U values of Ni and Fe were set as 6.2 and 5.3 eV based on previously reported papers, respectively.<sup>[S5-S7]</sup> The convergence criterions of the electronic self-consistent iteration and maximum force on each atom were  $10^{-4}$  eV and 0.05 eV Å<sup>-1</sup>, respectively. A vacuum of at least 20 Å was adopted along z-axis.

# 2. Additional Data and Figures



Fig. S1. The photographic image of NiFeHf LDH, NiFe LDH, and NiHf LDH powders.



**Fig. S2.** Partial magnified PXRD patterns of NiFeHf LDH, NiFe LDH, and NiHf LDH powders.



Fig. S3. SEM images of (a, b) NiFeHf LDH, (c, d) NiFe LDH, and (e, f) NiHf LDH powders.



Fig. S4. HAADF-STEM images and corresponding elementary mappings of NiFeHf LDH

powders.



Fig. S5. XPS profiles of three LDH powders. (a) Survey and (b) High-resolution O 1s.



**Fig. S6.** Activity and mechanism of OER. (a) Polarization curves; (b) Tafel plots; (c)  $C_{dl}$  plots of NiFeHf LDH, NiFe LDH and NiHf LDH; The standard error bars of (d) Overpotential at a current density of 10 mA cm<sup>-2</sup>; (e) Tafel slope; (f)  $C_{dl}$  values of different catalysts.



**Fig. S7.** Chronopotentiometric stability test of the NiFeHf LDH during 8 h under a current density of 10 mA cm<sup>-2</sup>.



**Fig. S8.** LSV curves of all electrodes before and after *i*R-correction in 1.0 M KOH electrolyte. The correction level is 95%.



Fig. S9. Electrochemical impedance spectra (EIS) of three LDHs.



Fig. S10. (a) CV curves of NiFeHf LDH, NiFe LDH and NiHf LDH normalized by ECSA;

(b) Tafel plots obtained from the OER polarization curves in (a).



Fig. S11. Physical Characterization of NiFeHf LDH@NF electrode. (a) XRD patterns, (b)

SEM image, (c) EDS spectrum, and (d) corresponding elemental mappings.



Fig. S12. The standard deviation of  $\eta_{10}$ , Tafel slope, and C<sub>dl</sub> of the NiFeHf LDH@NF electrode.



Fig. S13. Characterization of mechanical stability of NiFeHf LDH@NF electrode. The

surface of 3D electrode remains unchanged before and after ultrasonication for 10 min.



Fig. S14. SEM images of NiFeHf LDH@NF electrode before and after the measurement of OER.



**Fig. S15.** Repeatability of OER indicators of all modified GC and NF electrodes. (a-c) NiFeHf LDH, (d-f) NiFe LDH, (g-i) NiHf LDH, and (j-l) NiFeHf LDH@NF.



Fig. S16. NiFeHf LDH@NF catalyst before and after the measurement of OER. (a) XRD

pattern. (b) TEM image, (c)HRTEM pattern, (d) HAADF image and mapping.



Fig. S17. XPS profiles of NiFeHf LDH@NF catalyst before and after the measurement of

OER. (a) Survey. High-resolution (b) Ni 2p, (c) Fe 2p, (d) Hf 4f, (e) C 1s and (f) O 1s.



**Fig. S18.** DFT + U calculations for the (001) plane of three LDHs. Proposed four-electron mechanism of the OER. (a) Ni sites, (b) Fe sites, and (c) Hf sites of NiFeHf LDH. (d) Ni sites and (e) Fe sites of NiFe LDH. (f) Ni sites and (g) Hf sites of NiHf LDH. \*Ni, \*Fe, and \*Hf refers to active sites;  $\Delta G$  represents Gibbs free energy.



**Fig. S19.** Gibbs free energy diagrams for the four-electron reaction steps of OER on (a) NiFeHf LDH, (b) NiFe LDH and (c) NiHf LDH.

 Table S1. Preparation conditions of three LDH catalysts. All autoclaves were heated at

 120 °C for 6 h.

Catalusts	Ni <sup>2+</sup>	Fe <sup>2+</sup>	$\mathrm{H}\mathrm{f}^{4+}$	Urea
Catalysts	(mM)	(mM)	(mM)	(mM)
NiFeHf LDH	30	10	5	225
NiFe LDH	30	15	/	225
NiHf LDH	30	/	15	225
NiFeHf LDH@NF	30	10	5	225

Catalusta	Elements/ %			
Catalysis	Ni	Fe	Hf	
NiFeHf LDH	64.88	24.88	10.24	
NiFe LDH	68.69	30.58	0.72	
NiHf LDH	65.87	1.98	32.16	

 Table S2. Elemental atomic percentage content summary of different catalysts.

 Table S3. EIS fitting parameters of three LDHs.

Parameter	NiFeHf LDH	NiFe LDH	NiHf LDH
$R_{ct}(\Omega)$	4.499	4.993	8.242
$\mathbf{R}_{s}(\Omega)$	3.864	3.996	3.878
CPE (F)	0.1851×10 <sup>-6</sup>	0.1726×10 <sup>-6</sup>	0.09054×10 <sup>-6</sup>

1	5			
Catalysts	j / mA cm <sup>-2</sup>	η /mV	Tafel slope /mV dec <sup>-1</sup>	Ref.
NiFeHf LDH/GC	10	276	111	This work
NiFeAl LDH/GC	10	300	50	<b>S</b> 8
NiFeCo LDH/GC	10	290	52	<b>S</b> 9
NiFeCr LDH/GC	10	280	131	<b>S</b> 10
NiFeAl LDH/GC	10	300	50	S11
NiFeHf LDH@NF	10	177	100	This work
NiFeCe LDH@NF	10	229	37.9	S12
NiFeAl LDH@NF	20	304	57	<b>S</b> 8
NiFeRu LDH@NF	10	246	56.6	S13
NiFeMo LDH@NF	10	200	30	S14
Ru-NiFe LDH@NF	10	230	50.2	S15
NiFeIr LDH@NF	10	200	/	S16
NiFe(II, III) LDH@NF	10	220	58	S17
Ni40Fe55W5 LDH@NF	10	224	41	S18

**Table S4.** The comparison of the OER activity and performance of NiFeHf LDH to and the reported trimetallic LDH catalysts in 1.0 M KOH media.

Notes: GC-glassy carbon electrode; NF-nickel foam;

/-the material was dropped and casted on the substrate;

@-the material *in situ* grown on the substrate.

Ni (221.6 nm)	Fe (259.9 nm)	Hf (232.2 nm)
0.0027	0.0006	0.0021
	0.0027	0.0027 0.0006

0.0033

0.0046

0.0104

 Table S5. ICP-OES data of Ni, Fe, Hf elements in alkaline media before and after the stability test.

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After OER

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