Electronic Supplementary Information

Adjusting the Electronic Structure by Ni Incorporation: a Generalized In Situ Electrochemical Strategy to Enhance Water Oxidation Activity of Oxyhydroxides

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1. Material synthesis

1.1. Chemicals. All chemicals are analytical grade and used as received without further purification. Ni foam (30 mm×5 mm×0.5 mm) is sonicated with acetone, 0.3 M HCl aqueous solution, and deionized water for several times, respectively, to remove organic molecules and oxide layer. Then, the Ni foam is dried in a vacuum oven for the following experiments.

1.2. Preparation of \beta-FeOOH nanoprisms. β -FeOOH nanoprisms are prepared according to the reported method with slight modifications.¹ For a typical synthesis, 1.350 g of FeCl₃·6H₂O is dissolved in 10 mL deionized water under stirring for 10 min, then the mixed solution is transferred to a 20 mL Taflon-lined stainless-steel autoclave

and maintained at 120 °C for 12 h. After the autoclave is cooled down naturally, the product is collected by centrifugation, washed by deionized water and ethanol for three times and finally dried in a vacuum oven at room temperature for 6 h.

1.3. Synthesis of Ni- β -FeOOH nanoprisms. The *in situ* electrochemical incorporations are carried out using a standard three-compartment cell consisting of a working electrode, a glassy carbon counter electrode and a Hg/HgO (1 M KOH) reference electrode. For a typical procedure, 2 mg of β -FeOOH catalysts are dispersed in a solution containing 1 mL ethanol and 40 μ L 5% Nafion solution by sonicating for 20 min. Then 250 μ L of the homogeneous catalyst ink is spread uniformly on a Ni foam (the area is controlled to 1 cm², the loading amount of ~0.5 mg cm⁻²), then dried at room temperature to be used as the working electrode. A typical cyclic voltammetry (CV) method is used to obtain Ni- β -FeOOH nanoprisms in a voltage range of 1.174~1.824 V vs. RHE with a scan rate of 0.1 mV/s in 1 M KOH at room temperature. After the process of CV scans, the obtained Ni- β -FeOOH electrode is washed by water and dried at room temperature. The catalyst for detailed characterization and discussion is obtained after 2000 CV scans.

1.4. Synthesis of γ **-FeOOH and Ni-** γ **-FeOOH nanosheets.** To synthesize γ **-**FeOOH porous nanosheets, inorganic–organic hybrid FeS-DETA nanosheets are refluxed with water at 100 °C. The precursor, named as FeS-DETA, is synthesized using a modified method reported by our group.² In a typical procedure, FeS-DETA suspension is stirred vigorously to be homogeneous. Then 0.8 mL of suspension and 11.1 mL of deionized water are added into a round-bottom flask with volume of 50 mL and sonicated for 5 min. After the mixture is refluxed at 100 °C for 1 h and aged for 4 h under continuous magnetic stirring, the brown precipitate is collected by centrifugation and washed with ethanol and water. The final product is dried in a vacuum oven at room temperature for 6 h. Ni- γ -FeOOH is obtained *via* the same process with that of Ni- β -FeOOH.

1.5. Synthesis of CoOOH and Ni-CoOOH nanosheets. CoOOH nanosheets are synthesized by a simple chemical precipitation used in a reported literature.³ 250 μ L of NaOH solution (1.0 M) was added to 1 mL of CoCl₂ solution (10 mM) and sonicated for 1 min. Then 50 μ L NaClO (0.9M) is added to the mixture and sonicated for 10 min. Subsequently, the mixed solution is adjusted to pH=7.3 by adding 1.0 M HCl solution under stirring. After centrifuging and washing three times with deionized water and dried in a vacuum oven, the brownish black CoOOH powder is fabricated. Ni-CoOOH can be obtained *via* the same process with that of Ni- β -FeOOH.

2. Characterization. The SEM images are taken with a Hitachi S-4800 scanning electron microscope (SEM, 3kV). Transmission electron microscopy (TEM), highermagnification transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopic (EDS), STEM-EDS elemental distribution mapping images and electron energy loss spectroscopy (EELS) elemental distribution images are obtained by JEOL-2100F system equipped with EDAX Genesis XM2 and GIF 863 Tridiem (Gatan). Powder X-ray diffraction (XRD) patterns are collected using a Bruker D8 Focus Diffraction System with a Cu K α source ($\lambda = 0.154178$ nm). X-ray photoelectron spectroscopy (XPS) measurements are conducted with a PHI-1600 X-ray photoelectron spectrometer equipped with Al K α radiation and all binding energies are referenced to the C 1s peak at 284.8 eV. Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x, USA) is used to determine the compositions of the products. Raman spectroscopy is tested using inVia reflex Raman microscope under an excitation of 532 nm laser light with the power of 20 mW. Auger depth profiling is tested on a PHI 710 Auger electron spectroscopy (AES) with a sputter rate of ~6 nm/30 s and the sampling interval is 30 s.

Samples of Ni- β -FeOOH for characterization except SEM and AES are treated in following steps: (1) The Ni- β -FeOOH powder separated from Ni- β -FeOOH/NF electrode by sonication is collected and dispersed in water. (2) AgNO₃ solution is added

into Ni- β -FeOOH and sonicated to remove trace amount of metal Ni, which may come from Ni foam during the sonication stripping, *via* a displacement reaction of Ni and Ag⁺. (3) Dimethylglyoxime is added into the supernatant to determinate Ni²⁺ and repeated the displacement reaction until Ni²⁺ could not be detected through the change of colour. (4) Ni- β -FeOOH is collected and washed with water for several times. Samples of Ni- β -FeOOH for SEM and AES are collected from Ni- β -FeOOH/NF electrode without adding Nafion solution in fabrication because the existence of Nafion will interfere the observation of surface morphology and depth analysis, and other steps are the same to the process mentioned above.

3. Electrochemical measurements. Electrochemical measurements are carried out using a standard three-compartment cell consisting of a working electrode, a glassy carbon counter electrode and a Hg/HgO (1 M KOH) reference electrode performed with a CHI 660D electrochemical workstation (CH Instruments, Austin, TX). A solution of 1 M KOH is employed as the electrolyte. For a typical procedure for fabricating the working electrode, 2 mg of catalysts are dispersed in a solution containing 1 mL ethanol and 40 μ L 5% Nafion solution by sonicating for 20 min. Then 250 μ L of the homogeneous catalyst ink is spread uniformly on a Ni foam and the geometric area is controlled to 1 cm² (loading amount: ~0.5 mg cm⁻²). The as-prepared working electrode is dried at room temperature. The electrochemical impedance spectroscopy (EIS) measurements are carried out in the same configuration of *E*=1.474 V from 100 kHz to 0.1 Hz. The Faradic efficiency is tested at 1.574 V and the oxygen is collected by a water-gas displacing method.

4. Theoretical calculations We only calculate data of pure tetragonal β -FeOOH and Ni- β -FeOOH nanoprism instead of nanoprisms on Ni foam as the setup of such composite is too difficult. To simplify the theoretical model, we neglect the effects of intrinsic tunnels and chloride ions on activity, and only consider the surface reaction on highly exposed {100} facets because chloride ions mainly promote the infiltration of

electrolyte and electron transfer.⁴ Since {100} surfaces of space group $I4/m^4$ are exposed with plenty of adsorption sites available for water oxidation reaction, we only calculate (100) surface to understand the origin of the promoted activity of Ni- β -FeOOH.

The calculations are carried out using density functional theory plus Hubbard U (DFT+U) with the Perdew-Burke-Ernzerbof (PBE) form of generalized gradient approximation functional (GGA).⁵ The Vienna ab-initio simulation package (VASP) is employed.^{6, 7} A supercell (1×4) is built, in which 8 Fe atoms are contained in the (001) surface (Fig. 1a). In the process of calculating band structure and the projected density of states (PDOS), the optimized structure of two single unit cells and a supercell (1×1×3) of tetragonal β -FeOOH is adopted to calculate pure β -FeOOH, Ni- β -FeOOH with the Ni/Fe atomic ratio of 0.09:1, and Ni- β -FeOOH with the Ni/Fe atomic ratio of 0.14:1, respectively.

To model the surface of Ni- β -FeOOH, Fe atoms is partially replaced by Ni atoms. The electrocatalyst is working under a potential in reality. To investigate the effects of the electric potential on the activity of OER, the free energy diagrams of OER are employed.⁸ In alkaline media, water oxidation is usually considered to contain the following processes:

$$* + OH^{-} \rightarrow * OH + e^{-} \tag{1}$$

$$* OH + OH^{-} \rightarrow * O + H_2O + e^{-}$$
 (2)

$$* + 0H^{-} \rightarrow * 00H + e^{-} \tag{3}$$

$$* 00H + 0H^{-} \rightarrow 0_{2} + H_{2}0 + e^{-}$$
 (4)

where * refers to the surface site of OER catalysts (Fig. S7a). Free energy change from initial states to final states of the reactions is calculated as follows:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + \Delta G_U + \Delta G_{pH}$$

where ΔE is the total energy change based on the DFT+U calculations, ΔZPE and ΔS is

the change in zero-point energy and in entropy, respectively, *T* is room temperature (298.15 K).⁸ ΔG =-*eU*, where *U* is the electrode potential with respect to standard hydrogen electrode, and *e* is the transferred charge. ΔG_{pH} = k_BT ln10×pH, where k_B is the Boltzmann constant, and pH=14 for alkaline medium according to the experimental conditions.

The ΔG_{*OOH} , ΔG_{*O} , and ΔG_{*OH} are calculated according to the following reactions (* denotes the free site on (100) surface of the catalyst).⁹

- $* + 2H_20 \rightarrow *00H + 1.5H_2$ (1)
- $* + H_2 0 \rightarrow * 0 + H_2 \tag{2}$
- $* + H_2 0 \rightarrow * 0H + 0.5H_2 \tag{3}$

To ensure the OER can be occurred on the (100) facets of the catalyst, all the elementary reactions of the OER must be positive free energy change. As the electrode potential increases from -0.83 to 0.4 V, the protonation reactions become less endothermic. There is a highest potential to keep all the elementary reactions endothermic and the potential is defined as the onset overpotential. Meanwhile the difference between the onset overpotential and 0.4 V (alkaline medium) is the overpotential.¹⁰



Fig. S1. Simulated structures of β -FeOOH. Fe atoms: grey, O atoms: red, and H atoms:

white.



Fig. S2 Morphology characterizations of β -FeOOH and Ni- β -FeOOH. a) Lowmagnification SEM image, b) TEM image, and c) EELS element mapping images of β -FeOOH nanoprisms. d) Low-magnification SEM image, e) TEM image, and f) XRD patterns of β -FeOOH and Ni incorporated β -FeOOH after different CV scans. The comparison of β -FeOOH and Ni- β -FeOOH indicate the rod-like morphology can be maintained well after the incorporation of Ni. Inset of a) shows the top view of nanoprisms are square (a=b), indicating the tetragonal morphology of β -FeOOH.



Fig. S3 a) EDS spectrum of Ni- β -FeOOH obtained by the CV scan method. b) EDS spectrum of samples obtained from the solution-chemical thermal treatment of β -FeOOH with nickel ions. The characteristic peak of Ni can be observed clearly in (a), but the content of Ni is below the detection limit of EDS analysis in (b).



Fig. S4 a) XPS spectra of the Ni 2p region of Ni- β -FeOOH. b) Raman spectra of β -FeOOH after different cycles of CV scans. In Fig. S4a, the intensity of satellite peaks are higher than that of main peaks of Ni 2p3/2 and Ni 2p1/2, because the Auger peaks of F originating from Nafion solution coincide with the satellite peaks of Ni 2p and contribute to the intensity. In Fig. S4b, the original Raman signals in the dotted box is enlarged and displayed on the right.



Fig. S5 The result of Faradic efficiency measurement of Ni- β -FeOOH, showing a Faradaic efficiency of ~100%.



Fig. S6 Stimulated band structures of β -FeOOH and Ni- β -FeOOH. a) Band structure of pure β -FeOOH. b) Band structure of Ni- β -FeOOH with Ni/Fe atomic ratio of 0.09:1. c) Band structure of Ni- β -FeOOH with Ni/Fe atomic ratio of 0.14:1.The simulated PDOS and band structure (Fig. S1b and Fig. S6b) suggest that β -FeOOH is a typical semiconductor with a band gap of ~2eV. With the incorporation of Ni into β -FeOOH, the band gap becomes more and more narrow.



Fig. S7 a) Proposed oxygen evolution reaction path with intermediates *OH, *O and *OOH presented by using the reaction on Ni-4f site of the (100) surface in Ni- β -FeOOH (with a Ni/Fe atomic ratio of 0.14:1) as an example. b-e) Standard free energy diagrams at different electrode overpotentials of Fe-4f site in β -FeOOH (b), Fe-5f site in β -FeOOH (c), Fe-4f site in Ni-4f incorporated β -FeOOH (Ni-4f- β -FeOOH) (d), and Ni-4f site in Ni-4f- β -FeOOH (e). Insets of (b-e) are optimized model structures of (100) facets, and the calculated sites are circled in black.



Fig. S8 a-c) Standard free energy diagrams for OER at different polarization potentials of Fe-4f site (a), Fe-5f site (b) and Ni-5f site (c) in Ni-5f- β -FeOOH (with a Ni/Fe atomic ratio of 0.14:1). Insets of (a-c) are optimized model structures of (100) facets, and the calculated sites are circled in black. d) OER activity volcano. Pink, red and blue diamonds are associated with the surface sites on (100) of β -FeOOH, Ni-4f- β -FeOOH and Ni-5f- β -FeOOH, respectively. The surface sites are named as M-xf, where M refers to the metallic element and xf refers to the coordination numbers according to the numbers of M-O bond.

Both Fe and Ni are possible to be the catalytic center for OER, so Ni-4f, Ni-5f, Fe-4f and Fe-5f sites in both β -FeOOH and Ni- β -FeOOH are all investigated, and the free energies of the intermediates in OER on Ni and Fe atoms for all the configurations are carried out (Fig. S7, S8 and Table S3). The trends of the onset overpotentials of surface sites in β -FeOOH and Ni- β -FeOOH follow a volcano-shaped curve (Fig. S7d), in which the lowest OER overpotential corresponds to Ni-4f of Ni-4f- β -FeOOH (0.34 V), and its Fe-4f also own a low potential of 0.59 V.



Fig. S9 a) LSV curves and b) EIS plots of γ -FeOOH after different CV scans (CVs).



Fig. S10 a) SEM image, b) TEM image, c) and XRD pattern of CoOOH. d) STEM-EDS mapping images of Co, O and Ni in Ni-CoOOH.



Fig. S11 a) XPS spectra of Co 2p region for CoOOH and Ni-CoOOH. b) LSV curves for OER of CoOOH and Ni-CoOOH. The overpotential of Ni-CoOOH at a current density of 10 mA cm⁻² is 369 mV, while that of CoOOH is 439mV. Scan rate: 10 mV s⁻¹.

Electrode materials	<i>j</i> /mA cm ⁻²	η/mV at j	Electrolyte	Referenc
				e
Ni-β-FeOOH	10	247	1 M KOH	This work
	100	289		
FeOOH/Co/FeOOH	20	250		Ref.11
NTAs/NF	100	298	I M NaOH	
NiFe-LDH nanosheets	10	302	1 M KOH	Ref.12
Co _{0.46} Fe _{0.54} OOH	0.3	>250	1 M KOH	Ref.13
Ni _{0.75} Fe _{0.25} OOH LDH	4	>250	1 M KOH	Ref.14
WFe-CoOOH/gold foam	10	191	1 M KOH	Ref.15

 Table S1. OER activity comparisons for some Fe-contained-oxyhydroxide

 electrocatalysts.

Table S2. OER activity comparisons for some Fe (Co, Ni)-based electrocatalysts.

Electrode materials	<i>j</i> /mA cm ⁻²	η/mV at j	Electrolyte	Reference
Ni-β-FeOOH	10	247	1 M KOH	This work
	100	289		
Fe ₆ Ni ₁₀ O _x	10	286	1 M KOH	Ref.16
NiCeO _x -Au	10	271	1 M NaOH	Ref.17
Ni _{0.75} V _{0.25} -LDH	27	350	1 M KOH	Ref.18
FeP-rGO (50:50)@CFP	10	260	1 M KOH	Ref.19
Ni ₃ N nanosheets/CC	10	256	1 M KOH	Ref.20
Ni ₃ FeN	10	280	1 M KOH	Ref.21
СоООН	10	300	1 M KOH	Ref.22
CP/CTs/Co-S	10	306	1 M KOH	Ref.23
NiFe-LDH/carbon	10	247	1 М КОН	Ref 24
nanotube		= : ;		

Table S3. Theoretical calculation results of Gibbs adsorption free energy values (eV) of key intermediates and onset overpotentials (V) at surface sites on β -FeOOH and Ni- β -FeOOH.

Surface sites		$\Delta G_{* m OH}$	ΔG_{*0}	ΔG_{*OOH}	η
<i>β</i> -FeOOH	Fe-4f	2.27	0.37	4.11	0.86
	Fe-5f	2.23	0.31	4.14	0.91
Ni-4f	Ni-4f	2.11	0.89	3.89	0.34
incorporated	Fe-4f	2.51	1.03	4.28	0.59
β-FeOOH	Fe-5f	5.25	0.49	3.95	N/A*
Ni-5f	Ni-5f	3.80	3.51	4.86	1.17
incorporated	Fe-4f	2.07	0.59	4.59	0.9
β-FeOOH	Fe-5f	3.43	3.41	4.16	1.22

*The theoretical onset overpotential of Fe-5f in Ni-4f incorporated β -FeOOH does not exist because the charging reaction of this site is difficult to occur.

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