Electronic Supplementary Information

Ligand-assisted capping growth of self-supporting ultrathin FeNi-LDH nanosheet arrays with atomically dispersed chromium atoms for efficient electrocatalytic water oxidation

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1. Experimental Section

1.1 Chemicals and Materials

 $Ni(NO_3)_2 \cdot 6H_2O$ (98%), FeCl₃ $\cdot 6H_2O$ (98%), N,N'-dimethylacetamide (DMA), and hydrochloric acid (HCl, ~37 wt%) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Stainless steel (304, 1000 mesh) were purchased from Anping Tangzheng Wire Mesh Co., Ltd. 2,5-dihydroxybenzenedicarboxylic acid (H₄DOBDC) was bought from Aladdin Reagent.

1.2 Synthesis of Electrocatalysts

Synthesis of Cr₁/FeNi-LDH-SS: Cr₁/FeNi-LDH-SS was fabricated by a facile ligand-assisted capping growth approach (LACGA) with stainless steel (SS) mesh as a semisacrificial template and H₄DOBDC as a capping agent. Typically, the commercial SS (304, 1000 mesh) with a size of $4.0 \times 2.5 \text{ cm}^2$ was firstly immersed in 2.0 M HCl with ultrasonic treatment to remove the surface oxide layer, followed by washing with distilled water and ethanol in sequence and dried in an oven at 60 °C. Then, H₄DOBDC (20.0 mg) and 2.0 M HCl (15.0 mL) were dissolved in DMA (15.0 mL) by magnetic stirring to form a homogeneous solution, to which the pre-treated SS was added. The mixture in a Teflon-lined stainless steel autoclave (50 mL) was maintained at 150 °C for 18 h. After naturally cooling down to room temperature, the obtained dark green Cr₁/FeNi-LDH-SS was washed with ethanol and distilled water for several times and dried at 60 °C. The as-prepared Cr₁/FeNi-LDH-SS was directly used as the working electrode for the subsequent electrochemical tests.

Synthesis of FeNi-LDH-SS: The fabrication process of NiFe-LDH-SS is similar to Cr₁/FeNi-LDH-SS, except that additional iron and nickel salts were added. Generally, H₄DOBDC (20.0 mg), Ni(NO₃)₂·6H₂O (218.4 mg) and FeCl₃·6H₂O (67.5 mg) were dissolved in 30.0 mL of DMA, and then the solution and pre-treated SS were transferred into a Teflon-lined stainless steel autoclave (50 mL), which was maintained at 150 °C for 18 h.

Synthesis of CrFeNi-LDH: The CrFeNiCr-LDH powder was synthesized following the similar procedures to that of NiFe-LDH-SS, except without using SS.

Preparation of CrFeNi-LDH/SS and RuO₂/SS electrodes: The CrFeNi-LDH/SS and RuO₂/SS electrodes were prepared as following: the CrFeNiCr-LDH or RuO₂ powder (5.0 mg) was dispersed

in the solution containing H₂O (0.7 mL), ethanol (0.2 mL), and 5 wt% Nafion solution (0.1 mL) with ultrasonic treatment for 1 h. Then, 0.1 mL of the suspension was dropped on a piece of SS (1.0 \times 1.0 cm²) and then dried at room temperature.

1.3 Physical characterizations

The powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Rikagu Miniflex 600 Benchtop X-ray diffraction instrument with Cu K α radiation. Scanning electron microscopy (SEM) characterization was performed on a JEOL JSM6700-F instrument. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the samples were obtained using a FEI Tecnai F20 instrument. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo Fischer ESCALAB 250Xi X-ray photoelectron spectrometer with monochromatic Al K α Radiation (E = 1486.2 eV), and the binding energies were obtained in a Bruker Dimension ICON atomic force microscope.

1.4 Electrochemical characterizations

All electrochemical measurements were carried out by using an electrochemical workstation (Autolab PGSTAT302N) in 1.0 M KOH in a conventional three-electrode system. All the asprepared electrodes $(1.0 \times 1.0 \text{ cm}^2)$ were directly used as working electrodes. Pt mesh and saturated Ag/AgCl electrode were used as counter and reference electrode, respectively. Polarization curves with 95% iR compensation were recorded at a scanning rate of 5 mV s⁻¹. All of the measured potentials were displayed versus reversible hydrogen electrode (RHE) through the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ pH}$. Tafel slopes were obtained from their corresponding polarization curves. Electrochemically active surface areas (ECSAs) were estimated based on electrochemical double-layer capacitances (*C*dl), which can be obtained by measuring CV curves at different scan rates in a nonFaradic region (0.2–0.3 V *vs*. Ag/AgCl). Electrochemical impedance spectroscopy (EIS) measurements were conducted in a frequency range from 0.1 to 10⁵ Hz at the AC amplitude of 5 mV.

1.5 Computational details

In our work, spin-polarized DFT calculations were performed as implemented in the Vienna ab initio simulation package (VASP).¹ The projector augmented wave (PAW) method was adopted to describe interactions between ions and electrons.² The generalized gradient approximation (GGA) in the form of Perdew, Burke, Ernzerhof (PBE) was used to describe electron exchange and correlation.³ The plane-wave basis set along with a kinetic cutoff energy was 400 eV. The Brillouin zones were sampled with $3 \times 3 \times 1$ Monkhorst-Pack meshes. The structures were fully relaxed until the maximum force on each atom was less than -0.02 eV/Å and 10^{-5} eV . A vacuum space of at least 15 Å was inserted along the z direction to avoid any interactions between the periodically repeated images. The Perdew–Burke–Ernzerh exchange correlation functional with the on-site Coulomb Repulsion U term was used, U=3 was chosen for Ni, Fe and Cr.⁴

The Gibbs free energy (ΔG) was defined as follow:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \tag{1}$$

 ΔE is the reaction energy from the density functional theory calculations. ΔE_{ZPE} and ΔS are the zero point energy difference and the entropy difference between the products and the reactants at room temperature, respectively.



Fig. S1 PXRD patterns of Cr_1 /FeNi-LDH-SS and FeNi-LDH-SS.



Fig. S2 Photographic images of (a) SS and (b) Cr₁/FeNi-LDH-SS.



Fig. S3 SEM images of (a, b) pristine SS and (c, d) Cr_1 /FeNi-LDH-SS at different magnifications.



Fig. S4 SEM images of Cr-doped FeNi-LDH-SS prepared with different amounts of the added ligand.



Fig. S5 The influence of the added ligand amounts on the OER performances of the Crdoped FeNi-LDH-SS. (a) LSV curves and (b) required overpotentials at the current density of 100 mA cm⁻² of the catalysts.



Fig. S6 SEM images of (a) FeNi-LDH-SS and (b) CrFeNi-LDH.



Fig. S7 Cr 2p XPS spectra of Cr₁/FeNi-LDH-SS.

As shown in Figure S7, there are a pair of peaks at 577.2 and 586.8 eV in Cr 2p XPS spectra, suggesting the dominance of Cr^{3+} in Cr_1 /FeNi-LDH-SS.



Fig. S8 LSV curves of the prepared electrodes in the reverse sweep direction.



Fig. S9 CV curves at different scan rates for (a) SS, (b) FeNi-LDH-SS, (c) CrFeNi-LDH/SS and (d) Cr₁/FeNi-LDH-SS.



Fig. S10 ECSA-normalized LSV curves of the as-prepared electrodes.

It is generally known that the values of ECSAs are proportional to those of C_{dl} . Therefore, we suppose that ECSAs = $\alpha * C_{dl}$ (α is a constant coefficient). As shown in Figure S10, Cr₁/FeNi-LDH-SS presents much higher ECSA-normalized OER activity as compared to CrFeNi-LDH/SS, FeNi-LDH-SS, and SS, demonstrating that the intrinsic OER activity of the active sites of Cr₁/FeNi-LDH-SS is much enhanced by the doping of atomically dispersed Cr³⁺ atoms.



Fig. S11 (a) SEM image of Cr₁/FeNi-LDH-SS after OER test; (b) Fe 2p, (c) Ni 2p and (d) Cr 2p XPS spectra of Cr₁/FeNi-LDH-SS before and after OER test.



Fig. S12 Top and side views of (a) FeNi-LDH and (b) Cr_1 /FeNi-LDH.

Table S1 Comparison of the OER performances of the recently reported FeNi-based
 electrocatalysts.

Catalysts	Electrolyte	Substrates	Overpotential (mV)	Reference
Cr ₁ /FeNi-LDH-SS	1.0 M KOH	SS	202@10 mA cm ⁻² 242@100 mA cm ⁻²	This work
NiFeCr LDH	1.0 M KOH	GCE Carbon paper	280@10 mA cm ⁻² 225@25 mA cm ⁻²	5
CS-NiFeCr	1.0 M KOH	Copper foil	200 mV@10 mA cm ⁻² 230 mV@50 mA cm ⁻²	6
NiFeV LDH	1.0 M KOH	Ni foam	192@10 mA cm ⁻² 195@20 mA cm ⁻²	7
w-Ni(OH) ₂	1.0 M KOH	GCE	237 mV@10 mA cm ⁻² 267 mV@80 mA cm ⁻²	8
CoFeW oxy-hydroxide	1.0 M KOH	GCE	$217@10 \text{ mA cm}^{-2}$	9
Ni:FeOOH/NGF	1.0 M KOH	N-doped graphite foam	214@10 mA cm ⁻²	10
CoFeMo (oxy)hydroxides	1.0 M KOH	GCE	$277@10 \text{ mA cm}^{-2}$	11
NiCr-LDH	1.0 M KOH	Ni foam	319@100 mA cm ⁻² 390@300 mA cm ⁻²	12
NiFe-LDH	1.0 M KOH	Graphite paper	250@10 mA cm ⁻²	13
ultrathin Ni-Fe LDH	1.0 M KOH	Ni foam	210@10 mA cm ⁻² 320@500mA cm ⁻²	14
FeOOH/NPC	1.0 M KOH	Ni foam	230 mV@100 mA cm ⁻²	15
NiFe LDH/NF	1.0 M NaOH	Ni foam	$240@10 \text{ mA cm}^{-2}$	16
NESS	1.0 M KOH	Stainless steel	$278@10 \text{ mA cm}^{-2}$	17
Porous monolayer NiFe LDH	1.0 M KOH	Graphite paper	230@10 mA cm ⁻²	18
FeOOH(Se)/IF	1.0 M KOH	Iron foam	287@10 mA cm ⁻² 364@100 mA cm ⁻²	19
NiFe LDH@NiCoP/NF	1.0 M KOH	Ni foam	$220@10 \text{ mA cm}^{-2}$	20
NiFe-LDH@NiCu	1.0 M KOH	GCE	218@10 mA cm ⁻²	21
FeOOH/CeO ₂	1.0 M NaOH	Ni foam	$230@10 \text{ mA cm}^{-2}$	22
δ-FeOOH	1.0 M KOH	Ni foam	265@10 mA cm ⁻²	23
CoMn LDH	1.0 M KOH	GCE	324@10 mA cm ⁻²	24
Ni ₃ Se ₄ @NiFe LDH	1.0 M KOH	Carbon Fiber Cloth	$223@10 \text{ mA cm}^{-2}$	25
Ni-Fe-OH@Ni ₃ S ₂ /NF	1.0 M KOH	Ni foam	$165@10 \text{ mA cm}^{-2}$ 240@100 mA cm $^{-2}$	26
CoAl LDH nanosheets	1.0 M KOH	3D graphene network	$252@10 \text{ mA cm}^{-2}$	27
NiFe(OH) _x /FeS/IF	1.0 M KOH	Iron foam	$245@50 \text{ mA cm}^{-2}$	28
NiCeO _x H _y	1.0 M KOH	Graphite	177@10 mA cm ⁻²	29
Ni@NiFe LDH	1.0 M KOH	Ni foam	218@10 mA cm ⁻²	30

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