Supplemental Information

One-step synthesis of wire-in-plate nanostructured materials made of

CoFe‑LDH nanoplates coupled with Co(OH)$_2$ nanowires grown on Ni foam for

high-efficiency oxygen evolution reaction

Experimental

Materials

Cobalt nitrate hexahydrate (Sinopharm Chemical Reagent Co., Ltd.), Iron(Ⅱ)sulfate heptahydrate (Sinopharm Chemical Reagent Co., Ltd.), ammonium fluoride (Sinopharm Chemical Reagent Co., Ltd.), urea (Aladdin), ethanol (Sinopharm Chemical Reagent Co., Ltd.), Ruthenium (IV) oxide (Adamas-beta) and Nafion dispersion (5 wt%, Alfa Aesar) were used in this work as received without further purification from commercial sources.

Synthesis of CoFe LDH with different molar ratios of Co and Fe on Ni foam substrate (CoxFey-LDH/NF)

The Co_xFe_y/NF nanoarrays with x/y=4/0, 4/1, 4/2, 4/3 and 4/4 on Ni foam were synthesized by a facile hydrothermal reaction (x and y present the amount of added Co^{2+} and Fe^{2+}, respectively). Prior to the synthesis, a piece of Ni foam (3.5×6.5cm) was placed into the solution of HCl and deionized water (Volume ratio 1:3) with ultrasonic treatment for 30 min to remove surface oil stains and oxide layer, following by washing the NF till pH=7. In a typical procedure (Co_4Fe_2-LDH/NF), Co(NO$_3$)$_2$ · 6H$_2$O(1.1640

g, 4mmol), $FeSO_4 \cdot 7H_2O$(0.5560 g, 2mmol), urea(0.7205 g, 12mmol), NH_4F(0.3704 g, 10mmol) were dissolved in 80 mL deionized water with vigorous stirring until the solution is clear and transparent (about 20 min). The resulting solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave with a piece of clean nickel foam immersed into the reaction solution almost vertically. The autoclave was sealed and heated at 120 °C for 12 h, and then allowed to cool to room temperature. The obtained material was washed three times with deionized water in ultrasound (10s each), and then dried in a vacuum oven at 60 °C for 12 h. LDHs with the other Co:Fe ratios were synthesized using the same procedure with different added amount of Co and Fe.

For comparison, a benchmark RuO_2 catalyst on Ni foam was fabricated by the following steps: 280 μL ethanol, 20 μL naphthol, 70 μL deionized water and 50 mg RuO_2 were mixed to prepare dispersion, then add the prepared dispersion to the NF (the mass added to the electrode is determined according to the loading mass).

Material characterizations

The morphologies, energy dispersion spectra (EDS) and elemental mapping of the samples were collected by a scanning electron microscope (FE-SEM, JSM-7500, Japan), transmission electron microscope (FE-TEM,G2F20, USA) and scanning transmission electron microscopy (STEM, Tecnai G2F30). The phase structures of the materials were performed by X-ray powder diffraction (XRD, Smart Lab, Riga ku with Cu Kα radiation) and XPS datas were collected on an X-ray photoelectron spectroscopy (XPS, PHI 5000).

Electrochemical measurements

Electrochemical measurements were performed with a workstation (CHI660E, Shanghai, China) in a typical three-electrode configuration consisting of a carbon rod (the counter electrode), a saturated Hg/HgO (the reference electrode) and the active material (the working electrode) in 1 M KOH solution. The linear sweep voltammetry (LSV) polarization curves were collected at a scan rate of 2mV s^{-1}. The measured potentials vs. Hg/HgO were converted to the reversible hydrogen electrode (RHE) scale experimentally. The measured potentials vs. Hg/HgO were converted to the reversible hydrogen electrode (RHE) scale experimentally. The Hg/HgO reference electrode was calibrated according to the method published by Y. Liang and co-workers.[1] All the potential values measured were calibrated by using the following equation: E(RHE)=E(Hg/HgO) + 0.919 V. The calibration was conducted in the high purity hydrogen saturated electrolyte with a Pt wire as the working electrode. CVs were run at a scan rate of 1 mV s^{-1}. The overpotential (η) was calculated by η (V) = E(RHE) - 1.23 V. Tafel slope was obtained with corresponding LSV according to the equation: η= b • log J + a (η is the overpotential; b is the Tafel slope; J is the current density; and a is the overpotential at current density of 1 mA cm^{-2}).

Scheme:

Scheme S1. Schematic representation of the fabrication procedure for Co_4Fe_2-LDHs/Co(OH)$_2$-NWs with wire-in-plate structure via a simple one-step hydrothermal method

Figures:

Element	Weight percentage	Atomic percentage
C	8.38	16.33
O	44.02	64.43
Fe	15.03	6.30
Co	32.58	12.94
Total:	100.00	100.00
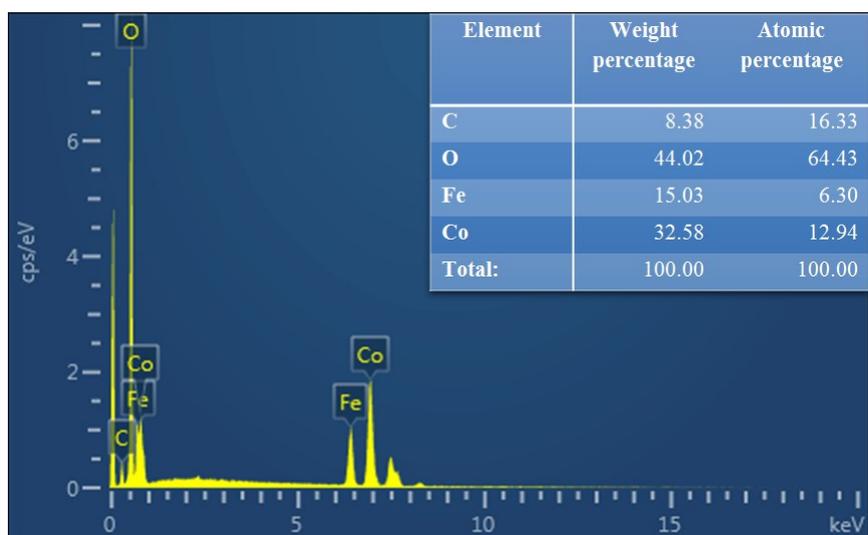
Fig. S1 Typical energy-dispersive X-ray spectroscopy (EDS) for Co_4Fe_2-LDHs/Co(OH)$_2$-NWs
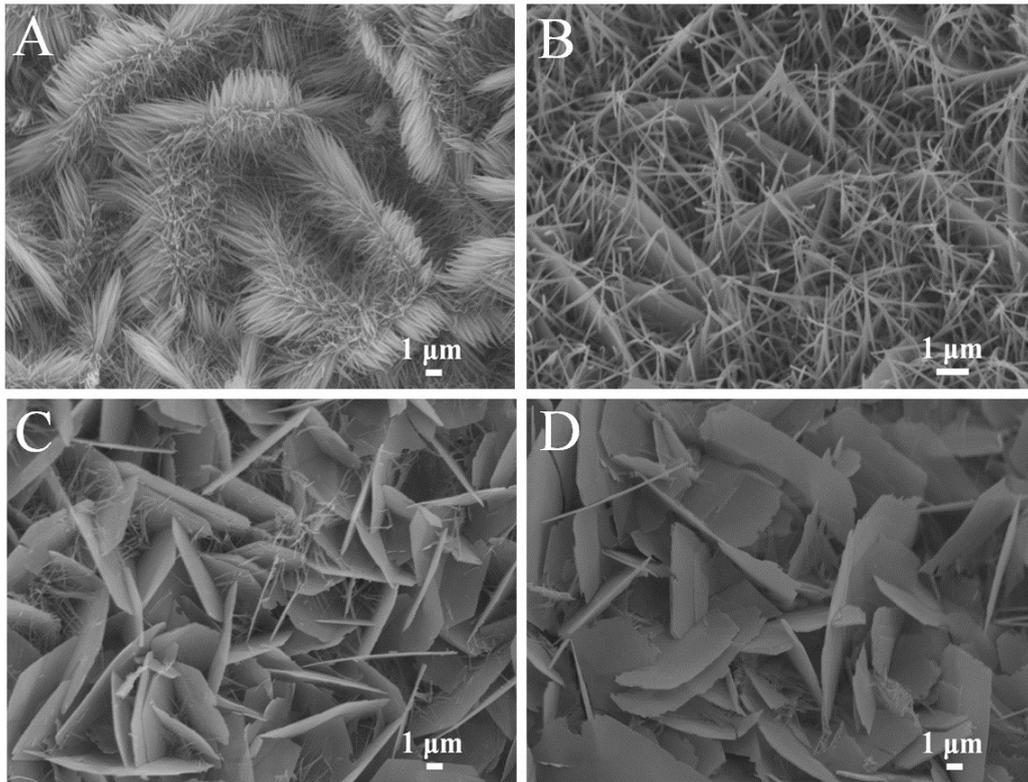
Fig. S2 (A) SEM image of $Co(OH)_2$/NF; (B-D) SEM images of Co_4Fe_1-LDHs/$Co(OH)_2$-NWs, Co_4Fe_3-LDHs/$Co(OH)_2$-NWs and Co_4Fe_4-LDHs/$Co(OH)_2$-NWs, respectively.
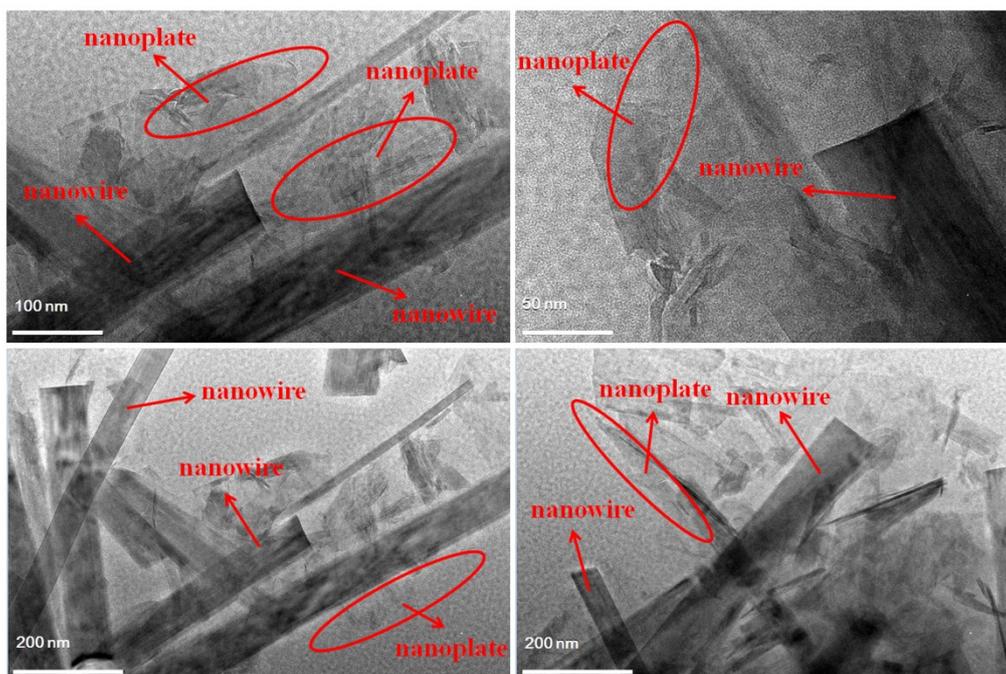
Fig. S3 TEM images of different scales of Co_4Fe_2-LDHs/$Co(OH)_2$-NWs
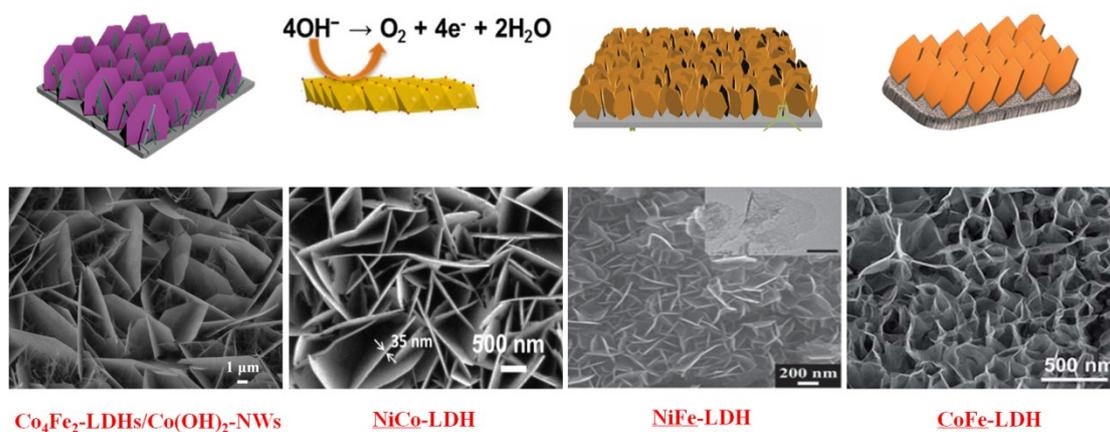
Fig. S4 comparison of traditional NiCo-LDH[2], NiFe-LDH[3], CoFe-LDH[4] and the as-fabricated Co_4Fe_2-LDHs/$Co(OH)_2$-NWs from the schematic diagrams and SEM images
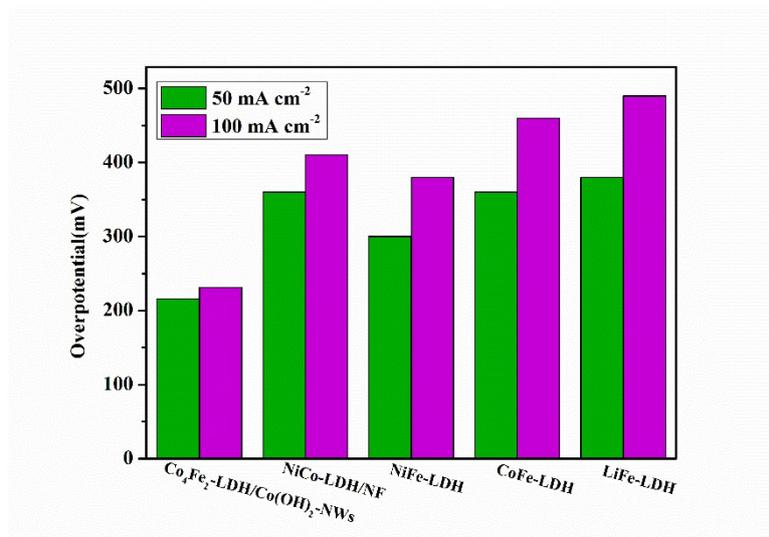
Fig. S5 comparison of traditional NiFe-LDH[4], CoFe-LDH[4], LiFe-LDH[4], NiCo-LDH/NF [5] and the as-fabricated Co_4Fe_2-LDHs/$Co(OH)_2$-NWs of overpotentials (at 50 and 100 mA cm^{-2})

Table S1. Comparison of the catalytic OER performance between our Co_4Fe_2-LDHs/Co(OH)$_2$-NWs and other various reported earth-abundant electrocatalysts in 1 M KOH.

Catalyst	Support	η@10 mA cm^{-2}	η@100 mA cm^{-2}	Stability	Ref.
Co_4Fe_2-LDHs/Co(OH)$_2$-NWs	Ni foam	-	225	40h at 1.849 V(vs. RHE)	This work
5.0%Ce-NiFe-LDH/CNT	CNT	~227	-	30000s at 10 mA cm^{-2}	S6
Cu(OH)$_2$@CCHH NW/CF	macroporous copper foam	120*	290	20h at η=260 mV	S7
Ni$_{0.67}$Fe$_{0.33}$/C	-	210	260	28h at 40 mA cm^{-2}	S8
NiFe-LDH/Cu	Cu foam	199	281	48h at 10 and 100 mA cm^{-2}	S9
CuNi(OH)$_x$	Cu foil	280	323*	24h at 1.55 V(vs. RHE)	S10
NiCo-UMOFNs	Cu foam	189	-	200h at η=250 mV	S11
NiCo-NiCoO$_2$@NC	-	318	400*	12h at η= 320 mV	S12
Ni$_{0.7}$Fe$_{0.3}$S$_2$	Ni foam	198	287	50000s at 10 mA cm^{-2}	S13
MnO$_2$/NiCo$_2$O$_4$/NF	Ni foam	340	425*	-	S14
MoP/Ni$_2$P/NF	Ni foam	-	380	12h at η= 330 mV	S15
MnCo$_2$S$_4$	Ti mesh	-	350*	100h at 20 and 50 mA cm^{-2}	S16

Water-plasma-enabled exfoliated CoFe LDHs	-	232	-	40000s at 1.47 V(vs. RHE)	S17
Co-B@CoO/Ti	Ti mesh	286	310*	20h at 50 mA cm^{-2}	S18

* The value is calculated from the curves shown in the literature.

Table S2. Comparison of the catalytic OER performance between our Co$_4$Fe$_2$-LDHs/Co(OH)$_2$-NWs and other traditional LDH-based electrocatalysts in 1 M KOH.

Catalyst	Support	η@50 mA cm^{-2}	η@100 mA cm^{-2}	Stability	Ref.
Co$_4$Fe$_2$-LDHs/Co(OH)$_2$-NWs	Ni foam	216	231	40h at 1.849 V(vs. RHE)	This work
NiCo-LDH/NF	Ni foam	~360	~410	20h at 40 mA cm^{-2}	S5
NiFe-LDH	Ni foam	~300	380	10h at 10 mA cm^{-2}	S4
CoFe-LDH	Ni foam	~360	460	10h at 10 mA cm^{-2}	S4
LiFe-LDH	Ni foam	~380	490	10h at 10 mA cm^{-2}	S4
Ni$_{0.67}$Fe$_{0.33}$/C	-	~245	260	28h at 40 mA cm^{-2}	S8
NiFe-LDH/Cu	Cu foam	~250	281	48h at 10 and 100 mA cm^{-2}	S9
FeNi-rGO LDH	Ni foam	~228	-	80h at 5, 10 and 20 mA cm^{-2}	S19
water-plasma exfoliated CoFe LDH nanosheets	Ni foam	~250	~265	40000s at 1.47 V(vs. RHE)	S17

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