

## Supplementary Information for

# **Accelerating Oxygen Evolution Electrocatalysis of Two-dimensional NiFe Layered Double Hydroxide Nanosheets via Space Confined Amorphization**

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## EXPERIMENTAL SECTION

**Synthesis of the NiFe layered double hydroxide (NiFe-LDH) electrocatalyst.** The NiFe-LDH electrocatalysts were synthesized using a hydrothermal method. In a standard synthesis, 440 mg  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 88 mg  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 480 mg urea and 120 mg  $\text{NH}_4\text{F}$  were dissolved in 32 mL of ultrapure water (HHitech, Master-S15Q) and then stirred for 40 min to form a uniform solution. The solution was transferred to a stainless Teflon-lined autoclave and heated in a muffle furnace at 120 °C for 6 h, and the heating rate is around 5 °C min<sup>-1</sup>. The obtained product was then cooled to room temperature, and washed three times with deionized water and once with ethanol. Finally, the samples were dried in vacuum at 60 °C overnight for further characterizations.

**Synthesis of the space-confined amorphous NiFe-LDH (SCA-NiFe-LDH) electrocatalyst.** To synthesize the space-confined amorphous NiFe-LDH electrocatalysts, 10 mg NiFe-LDH was dispersed into 10 mL of NaOH solution (5 M). The solution was then heated to 90 °C in 10 min and kept for 1 h in an oil bath to obtain the SCA-NiFe-LDH-1. After cooling to room temperature, the product was washed three times with deionized water and once with ethanol. and finally dried in vacuum at 60 °C overnight for further characterizations. The synthesis for SCA-NiFe-LDH-0.5 and SCA-NiFe-LDH-2 were similar to the SCA-NiFe-LDH-1, but the heating time changed to 0.5 h and 2 h, respectively.

**Characterization Methods.** High-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and tomography images were measured on a Cs-corrected FEI Titan 80/300 kV TEM/STEM microscope at ORNL. Powder X-ray diffraction (XRD) patterns were recorded by using an X-ray diffractometer (Smart Lab (3), Rigaku) operated at 3 kW. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos Ultra DLD spectrometer equipped with monochromatic Al K radiation. The binding-energy scales were calibrated using the C 1s peak at 284.6 eV, resulting from C contamination. Morphologies of the samples were examined with the transmission electron microscope (TEM, JEOL H-7000). Raman measurements were performed in backscattering geometry at room temperature using a

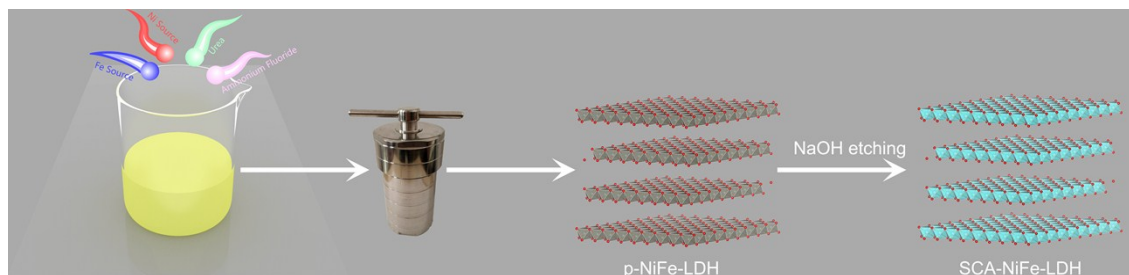
confocal Raman spectroscopy set up (NTEGRANTMDT) using a 532 nm laser.

**Electrochemical OER performance test.** All the electrochemical OER performance tests were measured in the O<sub>2</sub>-saturated 1 M KOH aqueous solution by using a standard three-electrode system, consisting of platinum wire, Ag/AgCl and glassy carbon as count electrode, reference electrode, and work electrode, respectively. All the potential in the text were recorded relative to the reversible hydrogen electrode (vs. RHE), without exception. To obtain the catalytic ink, 4 mg catalysts and 2 mg carbon black were added to 1 mL solution of water and ethanol (water: ethanol = 3:1 in volume), then sonicated for 30 min to form a uniform solution. 5  $\mu$ L ink was dropped in glassy carbon electrode ( $\phi$  = 3 mm) and dried at room temperature. The line sweep voltammetry (LSV) were obtained at a scan rate of 5 mV s<sup>-1</sup> with 95% *iR*-compensation. And the potential *E* was calculated using the equation  $E = E_{\text{measured}} - 0.95 \times iR$ , in which,  $E_{\text{measured}}$  is the potential obtained by electrocatalytic test vs. RHE, *i* is current, and the *R* is the Ohmic drop caused by impedance. The chronoamperometry and cyclic voltammetry (CV) were obtained without consideration of the *iR*-compensation. The electrochemical impedance spectroscopy (EIS) was obtained at 1.5 V (vs. RHE) from 1000 kHz to 0.1 Hz with an amplitude of 5 mV. The double-layer capacitance (*C*<sub>dl</sub>) was measured at the non-Faradaic potential range of 1.13 -1.18 V (vs. RHE) with different scan rates. The electrochemically active surface area was estimated by the equation:  $A_{\text{ECSA}} = C_{\text{dl}} / (40 \mu\text{F cm}^{-2} \text{ per cm}^{-2}_{\text{ECSA}})$

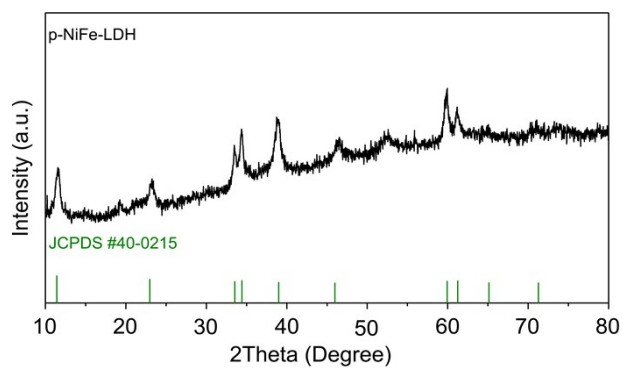
**Turnover Frequency (TOF) Calculation.** Turnover frequency (TOF) was calculated according to the equation:

$$TOF = \frac{j \times A}{4 \times F \times n}$$

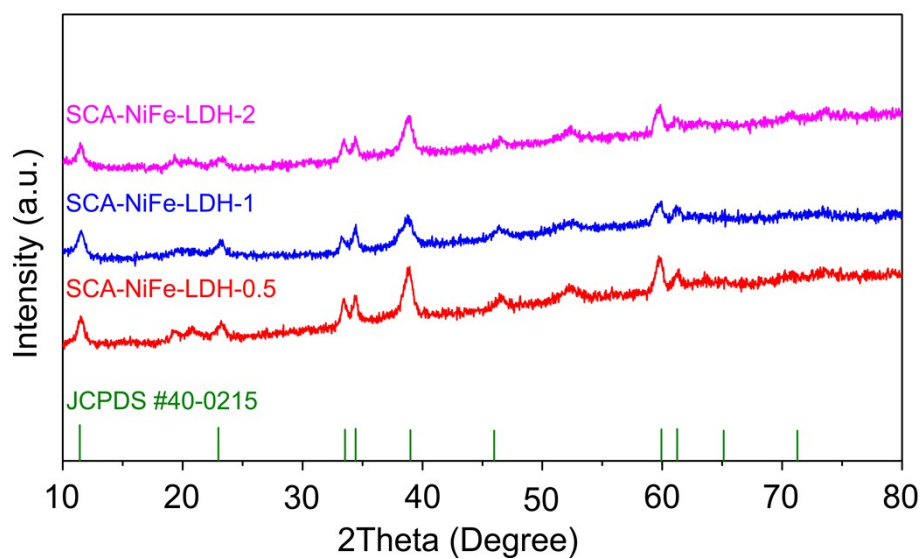
*A* is the area of glassy carbon, *j* is the current density at a given overpotential, 4 is the electron transfer for per mole of O<sub>2</sub>, *F* is the Faraday constant, *n* is the number of moles of the Fe atoms on the electrode. The Fe content was obtained from ICP-MS results.



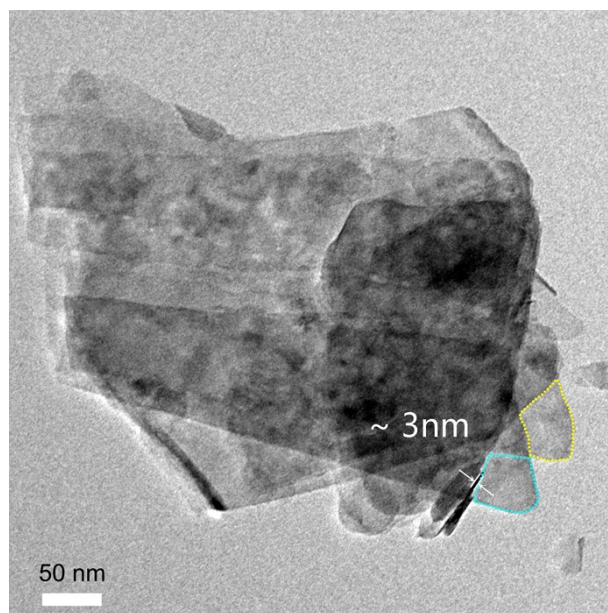
**Supplementary Figure S1.** Schematic illustration of the preparation process of the SCA-NiFe-LDH.



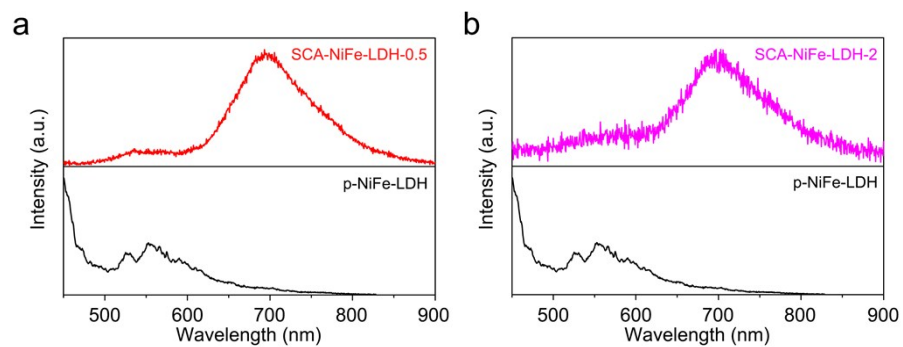
**Supplementary Figure S2.** XRD pattern of the pristine NiFe-LDH (p-NiFe-LDH).



**Supplementary Figure S3.** XRD patterns of the space-confined amorphous NiFe-LDH (SCA-NiFe-LDH) under different treatment durations.

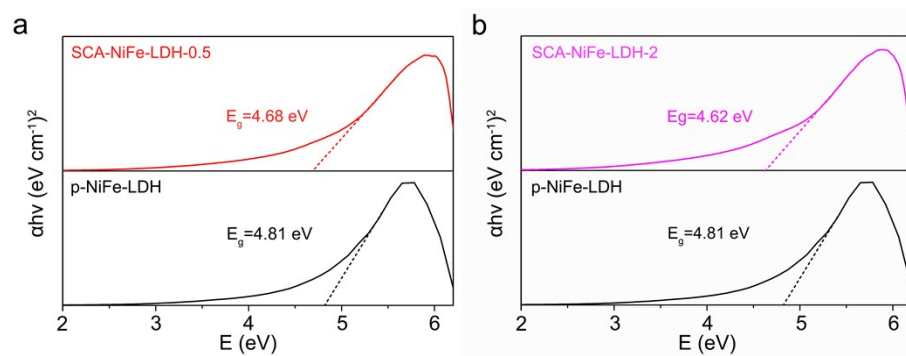


**Supplementary Figure S4.** Low-magnification TEM images of the SCA-NiFe-LDH-1.

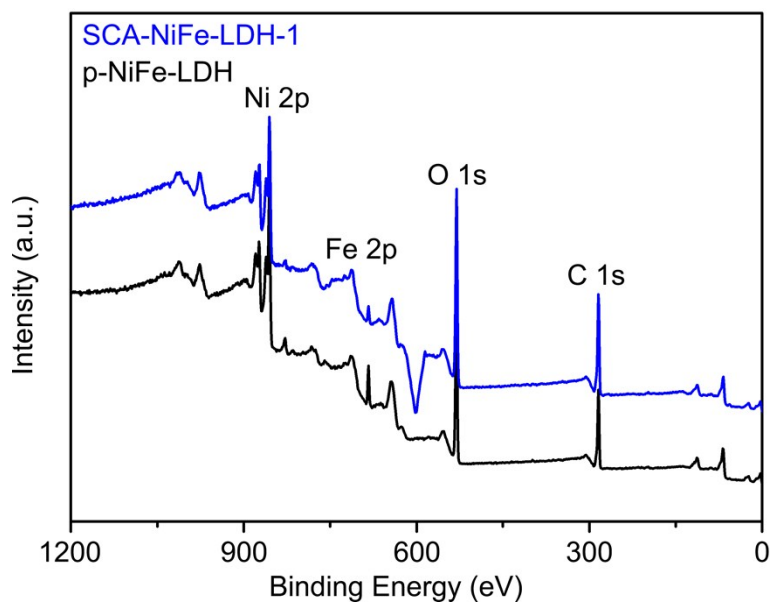


**Supplementary Figure S5.** PL spectra for the SCA-NiFe-LDH-0.5 and SCA-NiFe-LDH-2.

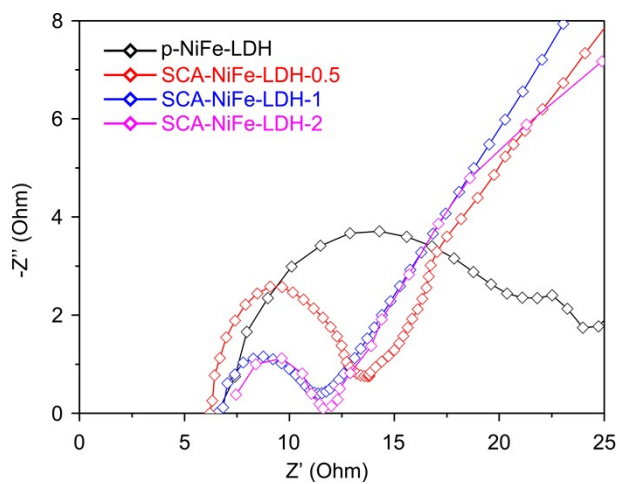




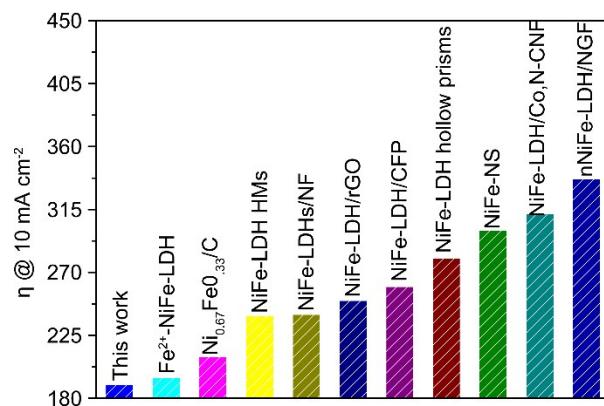
**Supplementary Figure S6.** UV-vis spectra for the SCA-NiFe-LDH-0.5 and SCA-NiFe-LDH-2.



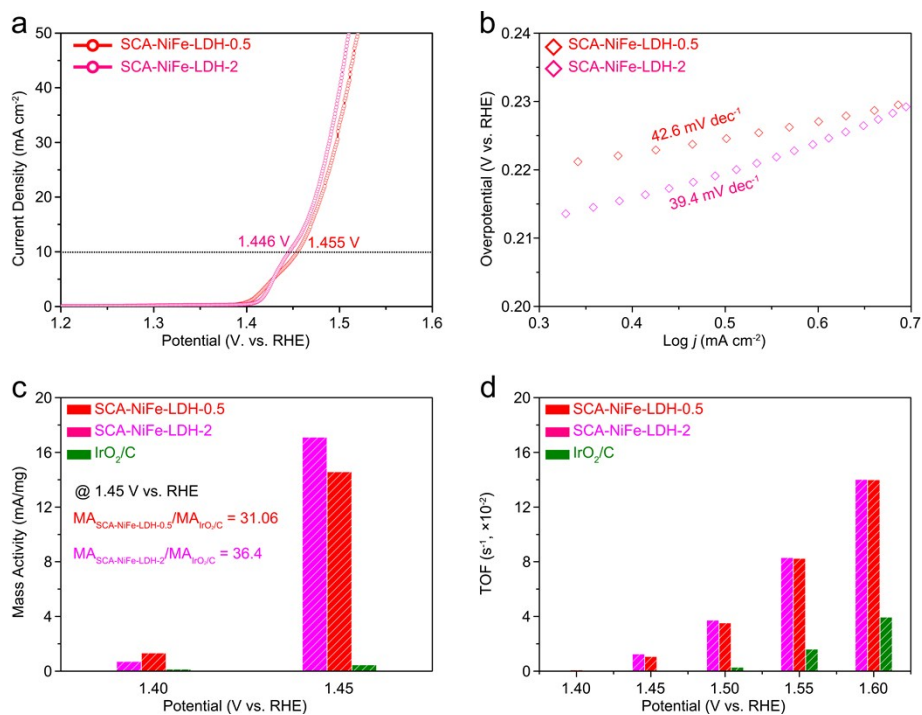
**Supplementary Figure S7.** XPS survey spectra and SCA-NiFe-LDH-1 and p-NiFe-LDH.



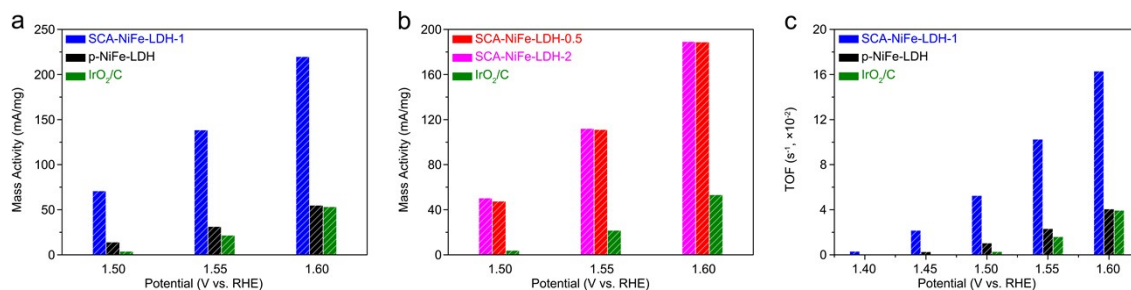
**Supplementary Figure S8.** EIS patterns of p-NiFe-LDH, SCA-NiFe-LDH-1, SCA-NiFe-LDH-0.5, and SCA-NiFe LDH-2.



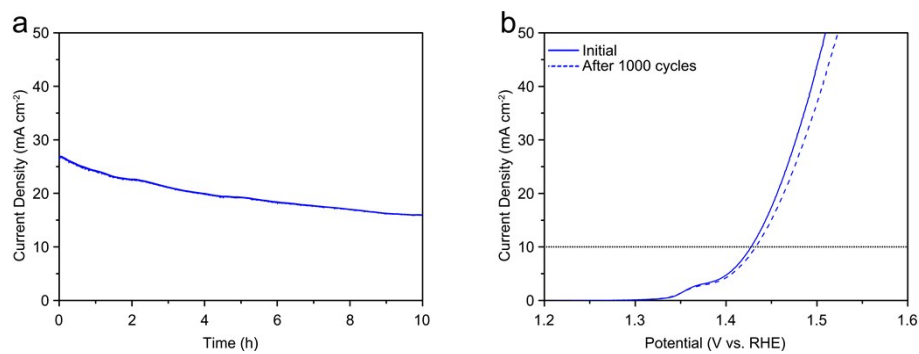
**Supplementary Figure S9.** Comparison of the overpotentials at the current density of 10 mA cm<sup>-2</sup> for different NiFe-LDH based catalysts.



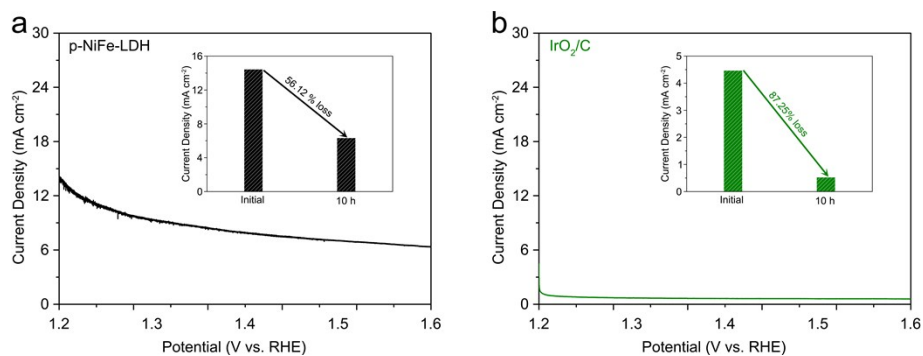
**Supplementary Figure S10.** (a) LSV curves, (b) Tafel plots, (c) mass activity and (d) Turnover frequency (TOF) at different overpotentials of SCA-NiFe-LDH -0.5 and SCA-NiFe-LDH -2.



**Supplementary Figure S11.** (a-b) Mass activity of different electrocatalysts under the potentials of 1.50, 1.55 and 1.6 V vs. RHE. (c) TOF of the SCA-NiFe-LDH-1, p-NiFe-LDH, and IrO<sub>2</sub>/C under different potentials.

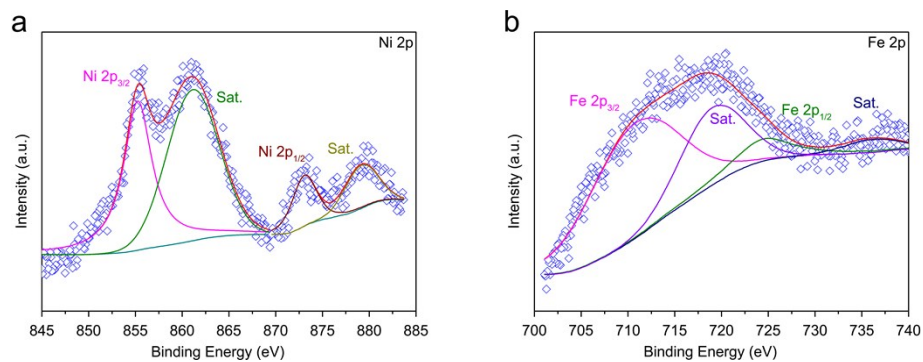


**Supplementary Figure S12.** Stability test of SCA-NiFe-LDH-1. (a) Chronopotentiometry curve under a constant potential of 1.46 V (vs. RHE). (b) LSV curves before and after 1000 CV cycles.

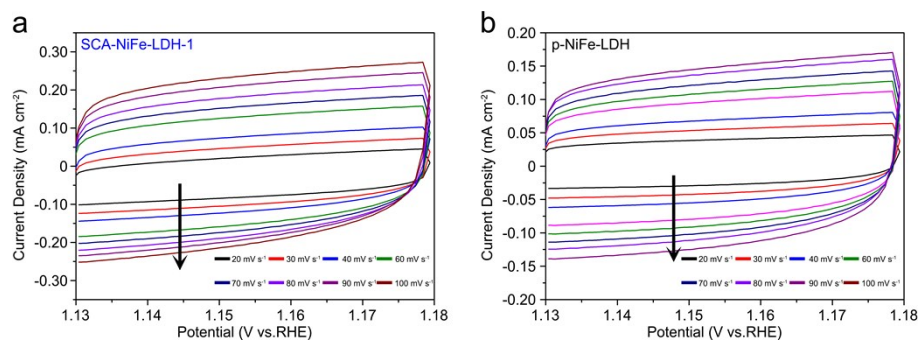


**Supplementary Figure S13.** Chronopotentiometry curves under a constant potential 1.46 V for p-NiFe-LDH (a) and IrO<sub>2</sub>/C (b) and the current loss after continuous electrocatalytic reaction after 10 h (inset).

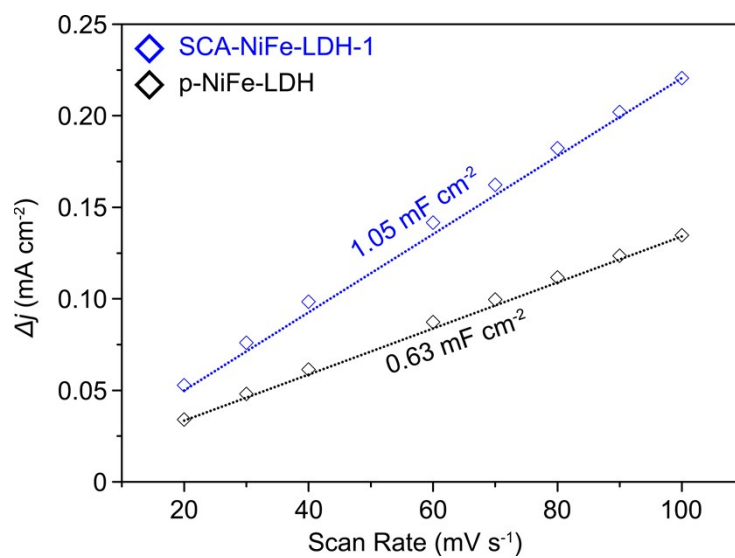




**Supplementary Figure S14.** XPS patterns of the SCA-NiFe-LDH-1 after the stability test. (a) Ni 2p. (b) Fe 2p.



**Supplementary Figure S15.** Cyclic voltammetry (CV) curves at different scan rates ( $\text{mV s}^{-1}$ ) and SCA-NiFe-LDH-1 and p-NiFe-LDH.



**Supplementary Figure S16.** Capacitive  $\Delta j$  as a function of the scan rate for SCA-NiFe-LDH-1 and p-NiFe-LDH.

**Table 1.** Comparison of NiFe-LDH based electrocatalysts.

Catalysts	Electrolyte	Current Density (mA cm <sup>-2</sup> )	Overpotential (mV)	Ref.
NiFe-NS	1.0 M KOH	10	300	1
nNiFe LDH/NGF	0.1 M KOH	10	337	2
NiFe-LDH/rGO	1.0 M KOH	10	250	3
NiFe-LDH/Co, N-CNF	0.1 M KOH	10	312	4
Ni-Fe LDH hollow prisms	1.0 M KOH	10	280	5
NiFe-LDH HMs	1.0 M KOH	10	239	6
NiFe-LDH @ NiCu	1.0 M KOH	10	218	7
Ni <sub>0.66</sub> Fe <sub>0.33</sub> /C	1.0 M KOH	10	210	8
Fe <sup>2+</sup> -NiFe LDH	1.0 M KOH	10	195	9
This work	1.0 M KOH	10	190	-

**Supplementary Reference:**

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