Supporting Information

Fluorine-Anion Confined in Nickel-Based Catalysts for Greatly Increasing Oxygen Evolution Activity

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S1. Experimental Section

Synthesis of the F-Ni foam: All of the chemicals were of analytical grade and used without further purification. F-Ni foam was prepared as follows. In a typical procedure, the Nickel foam (1.5 cm × 2 cm) was cleaned using a 3 M HCl solution in an ultrasonic bath for 20 min to remove nickel oxides on the surface, and then sonicated with deionized acetone, water and ethanol for some times in sequence. Subsequently, 1 g NH_4F and the dry Nickel foam were placed on the upstream and downstream of the tube furnace under N_2 atmosphere. The samples was heating to 350 ℃, 500 ℃ and 600 ℃ at 5 ℃/min and maintained at this temperature for 1 h for F-Ni-350℃, F-Ni-500℃ and F-Ni-600℃. Another series of F-Ni foam samples were prepared under the same calcination conditions using different amount of NH_4F (0.5 g, 1.0 g, 1.5 g and 2.0 g).

Synthesis of the F-NiAl LDH-NF: Typically, one piece of nickel foam was put into 35 mL of mixed salt solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (6 mmol); $Al(NO_3)_3 \cdot 9H_2O$ (2 mmol) and urea (20 mmol) under vigorous stirring for 20 min. And next, above solution was transfer into a 40 mL stainless steel autoclave with a Teflon lining. The autoclave was then placed in a preheated oven, followed by hydrothermal treatment at 180 °C for 18 h. The NiAl LDH-NF precursor was collected and washed by deionized water and ethanol for several times. Next, 1 mmol NH_4F powder was mixed with NiAl LDH-NF precursor, and placed on the tube furnace under N_2 atmosphere. The temperature was heated to 400 ℃ at 5 ℃/min and maintained at this temperature for 1 h. After that, the resulting sample was taken out and washed by water and ethanol for several times. After drying, the as-prepared samples was directly used as working electrode to perform the OER activation process. After 200 times CV cycling test in 1 M KOH solution, the F modified NiAl LDH-NF catalyst was successfully synthesized.

Structural Characterization: The phase compositions of the catalysts were characterized by X-ray diffraction (XRD) on a DX-2700 diffractometer (Dandong Haoyuan Instrument Co. Ltd. China). The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) mapping analyses were executed on a COXEM EM-30 Plus. X-Ray photoelectron spectroscopy (XPS) was performed on a PHI5300 with Mg Kα radiation. The microstructures, morphology and element analysis were carried out by transmission electron microscopy (TEM) on a JEOL JEM-2001 electron microscope.

Electrochemical Measurements: Electrochemical measurements were performed in a three electrode system on an electrochemical workstation (CHI660E) by using a saturated calomel electrode (SCE) as the reference electrode, Pt foil as the counter electrode, and the F-Ni foam and F-NiAl LDH-NF as the working electrode. OER performances were measured through performing Cyclic voltammetry (CV, scan rate of 5 mV/s) in 1.0 M KOH solution. All of the measured potential (vs. SCE) were converted to the potentials against the reversible hydrogen electrode (RHE). The electrochemical impedance spectroscopies (EIS) of the catalysts were carried out by applying an AC voltage with a 5 mV amplitude in the frequency range from 100 kHz to 0.1 Hz.

S2. Ni 2p XPS for bare Ni foam

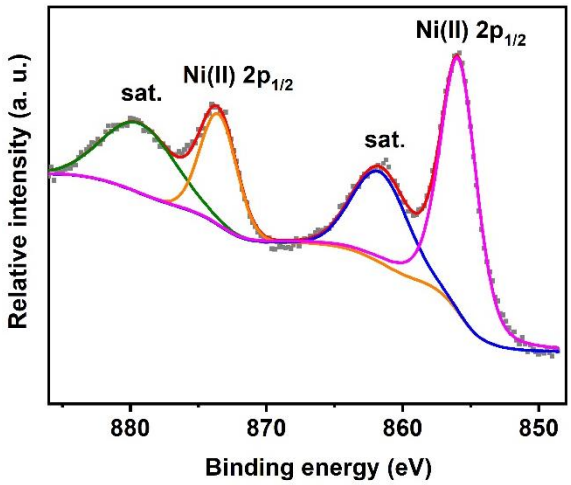

Figure S2 The Ni 2p XPS image of bare Ni foam.

S3. O 1s XPS image of bare Ni foam

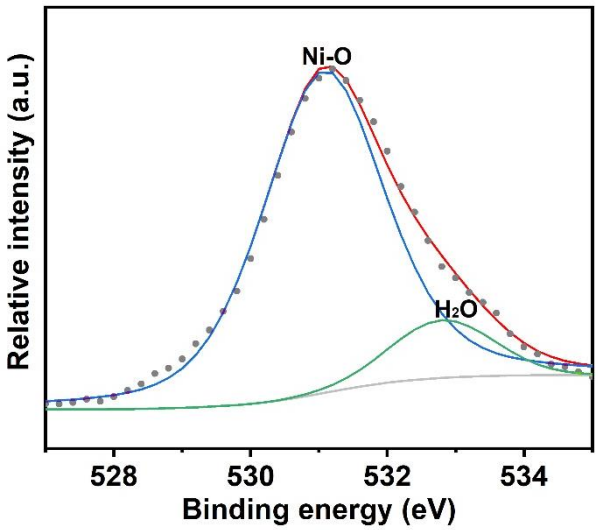

Figure S3 O 1s XPS image of bare Ni foam, in which two separated peaks can be ascribed to Ni-O bond caused by surface oxidation and adsorbed H_2O.

S4. The corresponding elemental mapping images of F-Ni foam.

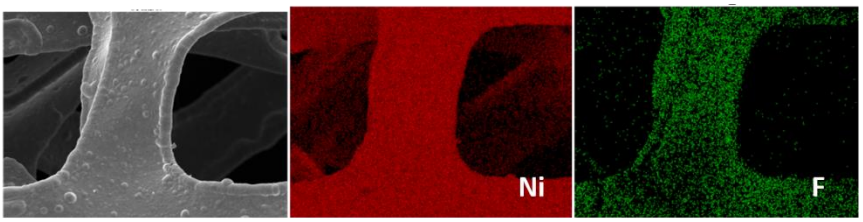

Figure S4 The elemental mapping images of F-Ni foam.

S5. XPS survey spectra of series products

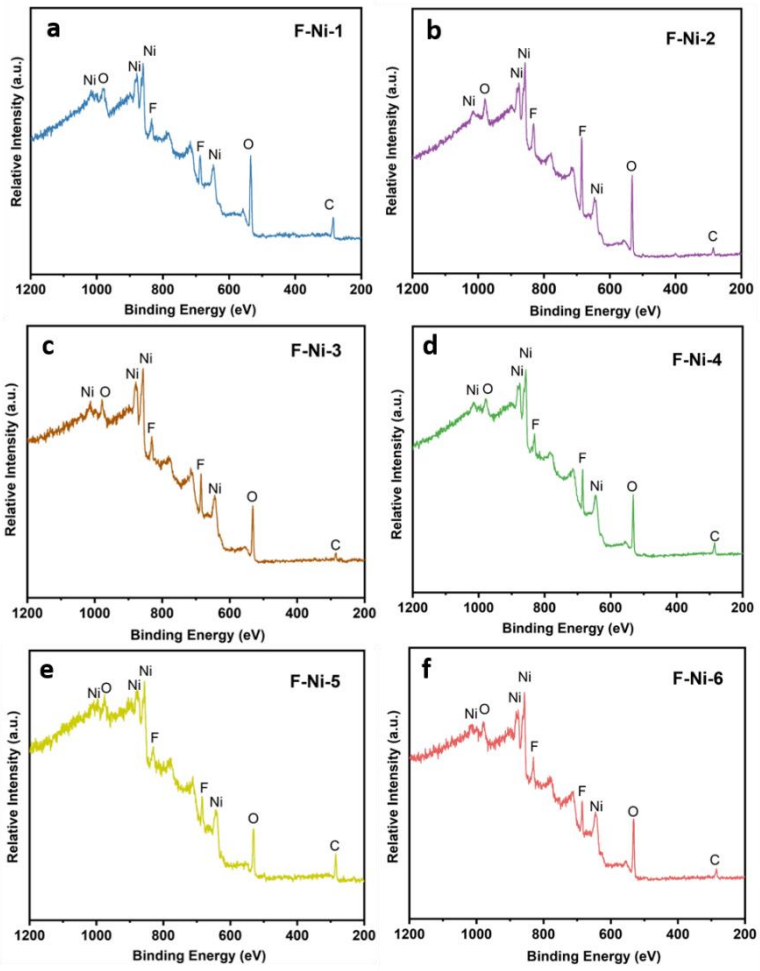

Figure S5 XPS survey spectra of F-Ni-1, F-Ni-2, F-Ni-3, F-Ni-4, F-Ni-5 and F-Ni-6.

Table S1 the content of incorporated F in the series of products calculated by XPS.

Sample	Condition	Content of F (%)
F-Ni-1	500 °C, 0.5 g NH_4	11.78
F-Ni-2	500 °C, 1.0 g NH_4	21.93
F-Ni-3	500 °C, 1.5 g NH_4	18.85
F-Ni-4	500 °C, 2.0 g NH_4	17.62
F-Ni-5	350 °C, 1.0 g NH_4	16.26
F-Ni-6	600 °C, 1.0 g NH_4	14.07

S6. XRD pattern for F-doped Ni foam with different temperature

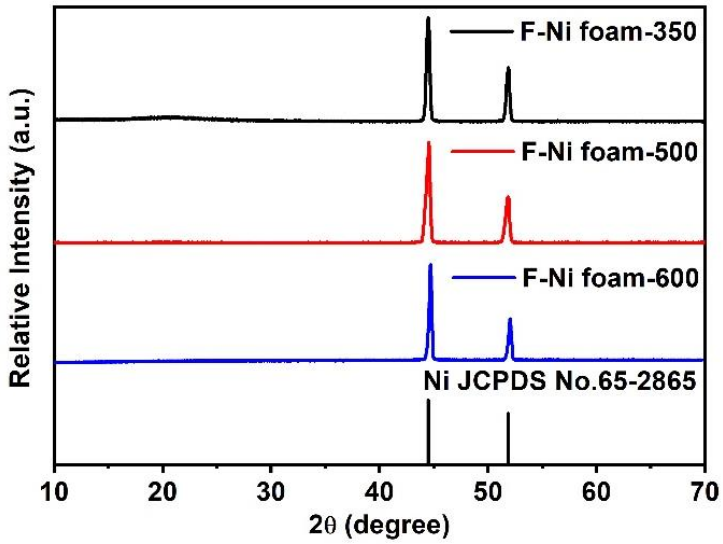

Figure S6 XRD pattern for F-doped Ni foam with different temperature of 350 °C, 500 °C and 600 °C.

S7. The Nyquist plots of series F-Ni samples

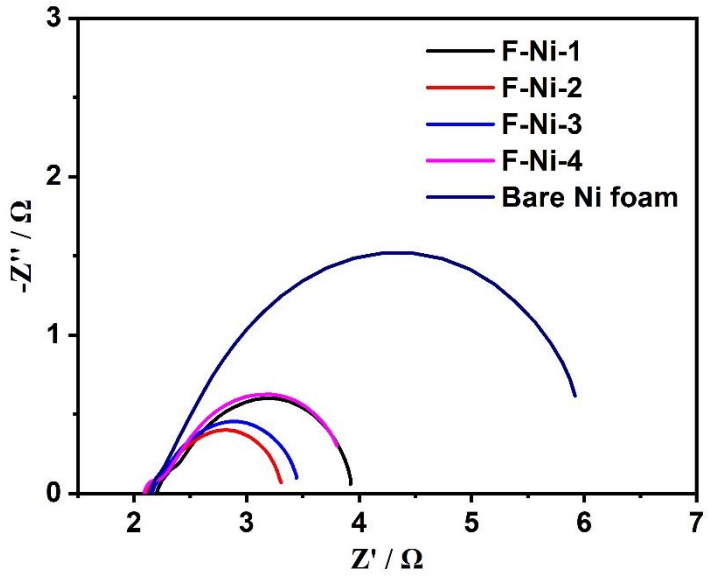

Figure S7 Nyquist plots for bare Ni foam, F-Ni-1, F-Ni-2, F-Ni-3 and F-Ni-4.

S8. The stability test of F-Ni foam

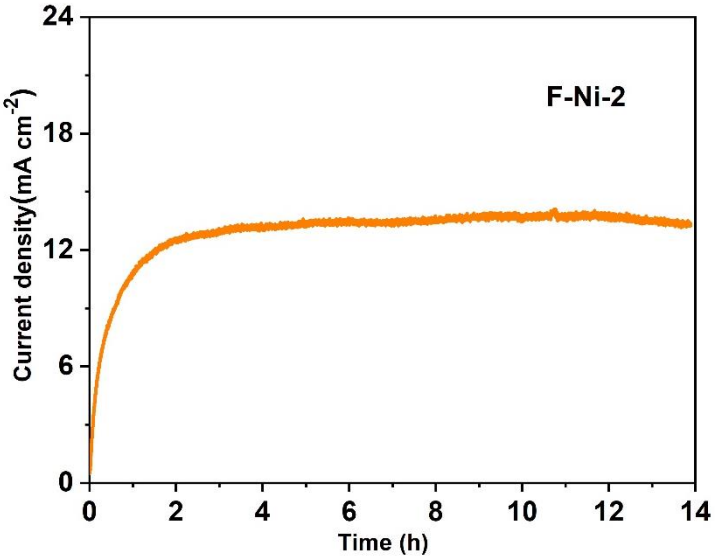

Figure S8 Chronoamperometric response of F-Ni foam at the applied potential of 1.6 V vs. RHE.

S9. OER catalytic performance of F-Ni samples with fluorination temperature variation.

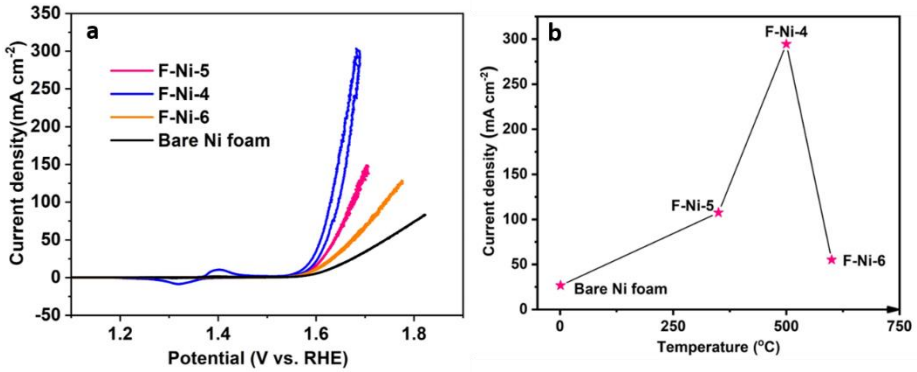

Figure S9 (a) iR-corrected polarization curves in 1M KOH. (b) the comparison current density at the same overpotential of 450mV for different F-Ni foam samples.

S10. Tafel slopes for F doped Ni foam with different fluorination temperature

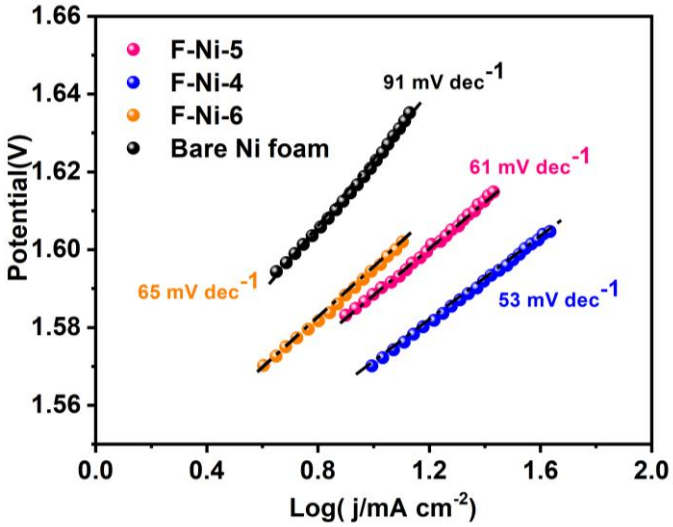

Figure S10 Tafel slopes for bare Ni foam, F-Ni-4, F-Ni-5 and F-Ni-6.

S11. The Nyquist plots of F doped Ni foam with different fluorination temperature

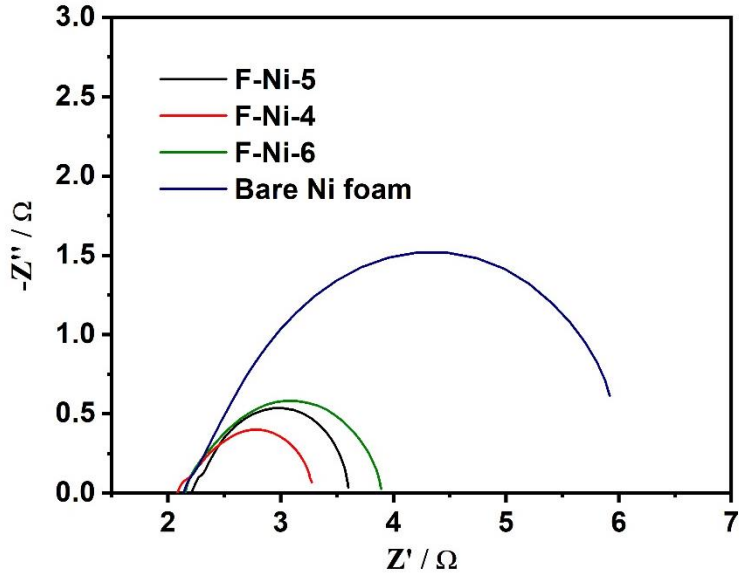

Figure S11 Nyquist plots for bare Ni foam, F-Ni-4, F-Ni-5 and F-Ni-6.

S12. Capacitance measurements and active surface area for bare Ni foam.

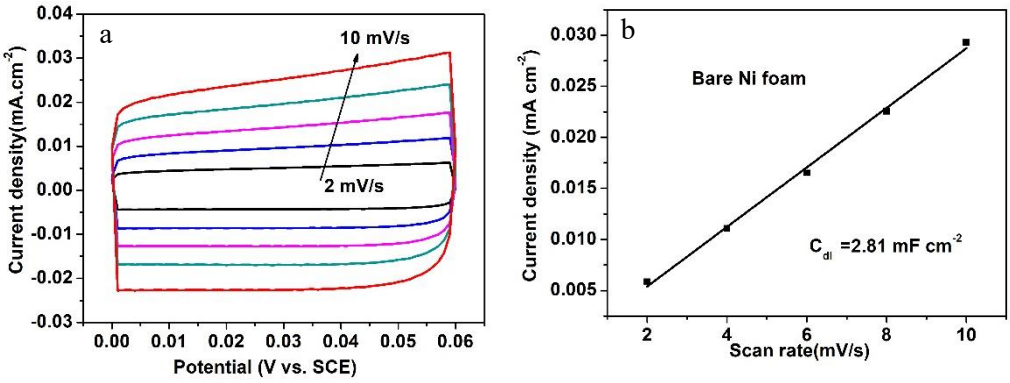

Figure S12 Cyclic voltammograms (CVs) of bare Ni foam measured at different scan rates from 2 to 10 mV s^{-1}. (b) Plot of the current density bare Ni foam at 0.05 V vs the scan rate.

S13. Capacitance measurements and active surface area for F-Ni foam.

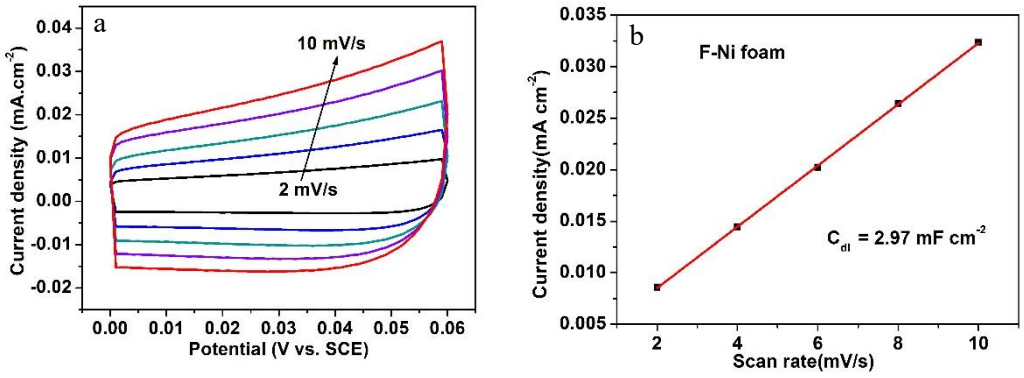

Figure S13 Cyclic voltammograms (CVs) of F-Ni foam measured at different scan rates from 2 to 10 mV s^{-1}. (b) Plot of the current density F-Ni foam at 0.05 V vs the scan rate.

S14. Comparison of XRD pattern for F-Ni foam before and after OER process

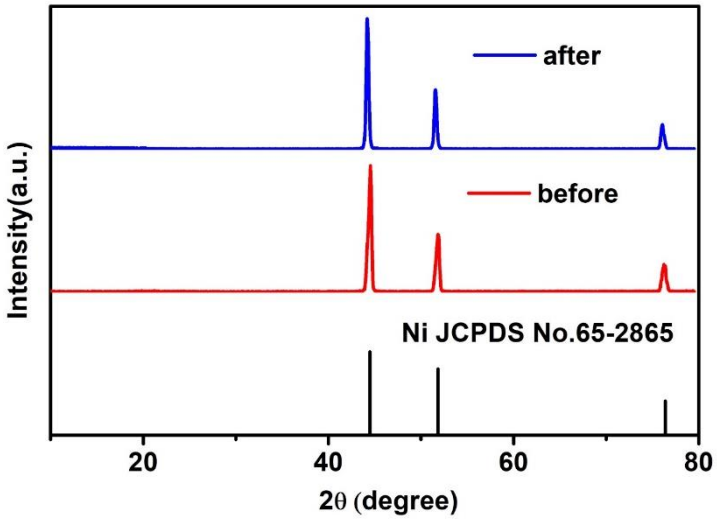

Figure S14 The XRD pattern for F-Ni foam before and after OER test.

S15. Ni XPS spectrum of F-Ni foam sample after OER catalytic test.

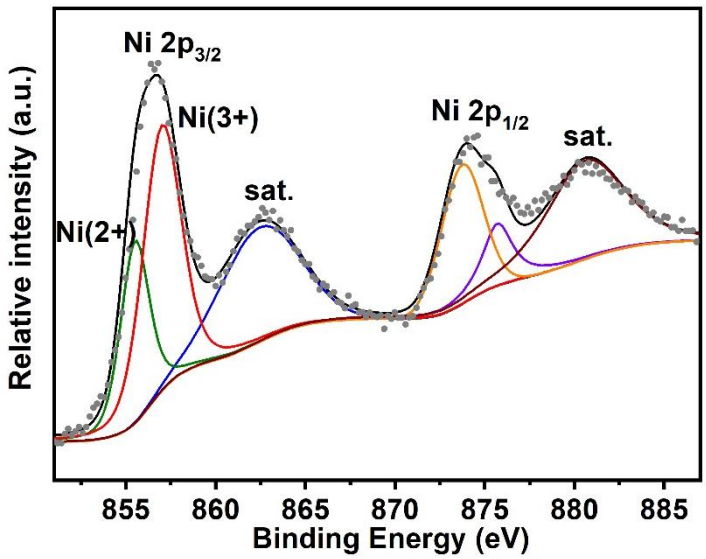

Figure S15 Ni 2p XPS spectra of F-Ni-2 after OER catalytic performance test.

S16. The activated process of F-Ni foam

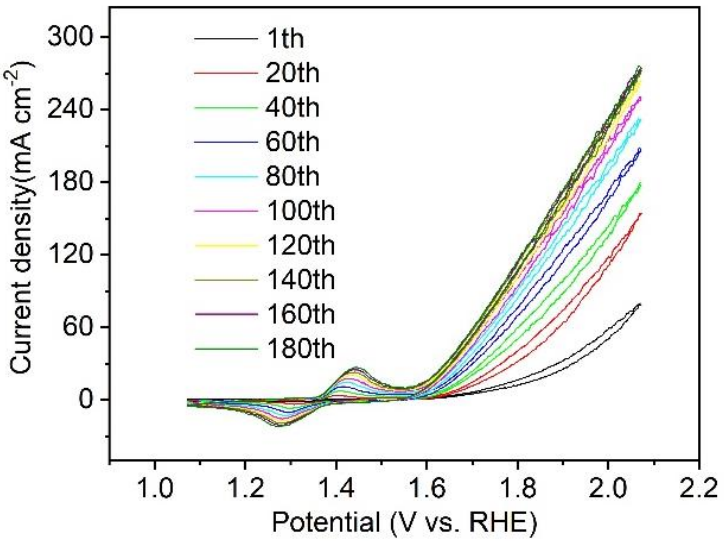

Figure S16 The polarization curves for OER activated process of 180 CV cycles for F-Ni foam

S17. O 1s XPS spectrum of F-Ni foam sample during activated process

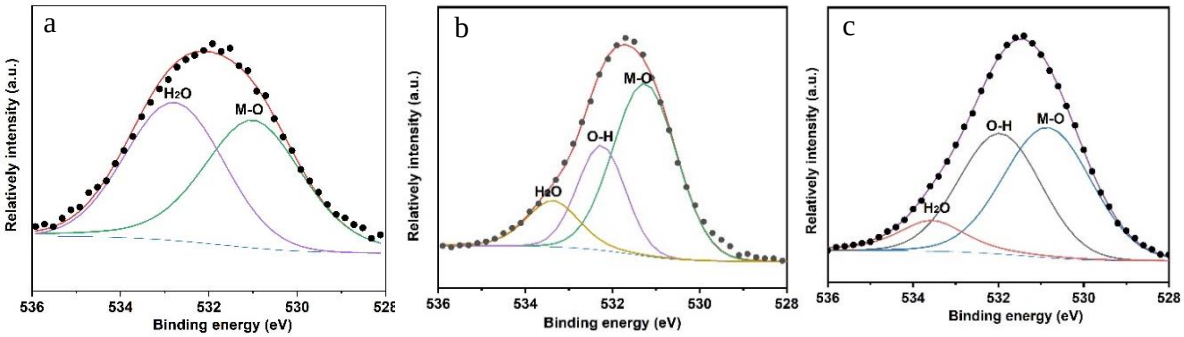

Figure S17 O 1s XPS spectrum of F-Ni foam sample after (a) 0^{th}, (b) 60^{th} and (c) 180^{th} CV.

S18. EDS spectrum of F-NiAl LDH nanosheet

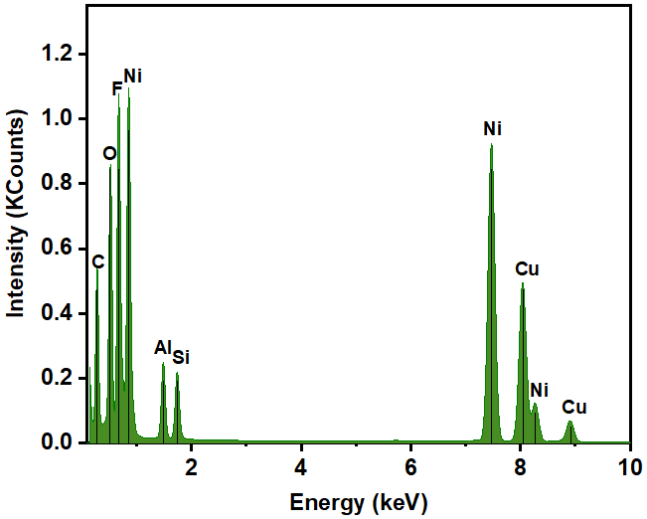

Figure S18 EDS spectrum of F-NiAl LDH nanosheet.

S19. The elemental mapping image of F-NiAl LDH nanosheet

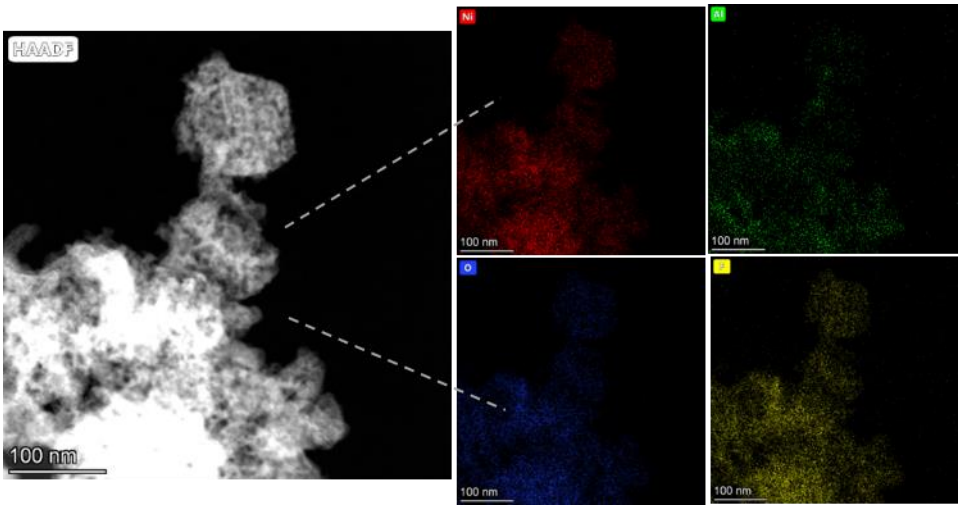

Figure S19 The elemental mapping image of F-NiAl LDH nanosheet.

Table S2 Comparison of OER activity of our catalysts with other Ni-based catalysts

Catalyst	Current density ($mA\ cm^{-2}$)	Overpotential (mV)	References
F-Ni-2	10	330	This work
F-NiAl LDH-NF	10	250	This work
F-NHO	10	280	*Chem. Commun., 2019, 55, 3406*
NiFe-OH-F-SR	10	181	*Nano Lett., 2019, 19, 530–537*
Ni–Fe–Se cages	10	240	*Adv. Mater. 2017, 29, 1703870*
$Ni_2Co_2O_4$	10	380	*J. Am. Chem. Soc. 2018, 140, 13644*
Ni–Co–S	10	350	*Adv. Funct. Mater. 2019, 29, 1807031*
Ni–Co–P HNBs	10	390	*Energy Environ. Sci. 2018, 11, 872*
Ni/Mo_xC	10	328	*ACS Appl. Mater. Interfaces 2018, 10, 35025−35038*
Ni–P nanoplate	10	300	*Energy Environ. Sci., 2016, 9, 1246*