Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

In-situ Growth of Ultrathin Ni-Fe LDHs Nanosheets for High Performance Oxygen Evolution Reaction

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Experimental section:

1、Fabrication of u-$Ni_{70}Fe_{30}$ LDHs/CF Electrodes.

The u-$Ni_{70}Fe_{30}$ LDHs were in-situ electrodeposited on a-CF with the mass loading of 0.19 mg cm^{-2}. For the synthesis of u-$Ni_{70}Fe_{30}$ LDHs/CF samples, the collected u-$Ni_{70}Fe_{30}$ LDHs powders were drop-casted onto CF. Specifically, 9.1 mg u-$Ni_{70}Fe_{30}$ LDHs were dispersed into a 5 mL mixture solution (2 mL water, 300 μL 5% Nafion solution, and 2.7 mL ethanol), after being sonicated for 30 min, a homogeneous catalyst ink was obtained, and then 50 μL catalyst ink was loaded on the surface of CF (surface area: 1.92 cm^2) for 4 times (2 times for each side of the CF). Consequently, the overall catalysts loading amounts of u-$Ni_{70}Fe_{30}$ LDHs/CF samples are 0.19 mg cm^{-2}, which is consistent with the mass loading of u-$Ni_{70}Fe_{30}$ LDHs/a-CF.

2、Estimation of electrochemically active surface areas (A_{echem})

Based on previous reports,[1, 2] cyclic voltammetry (CV) could be carried out in neutral media to probe the electrochemical double layer capacitance of various samples at non-Faradaic overpotentials as the means for estimating the A_{echem} of samples. Accordingly, a series of CV measurements were performed at various scan rates (4 mV s^{-1}, 8 mV s^{-1}, 12mV s^{-1}, 16 mV s^{-1}, etc.) in 0.1 to 0.2 V vs. RHE range, and the sweep segments of the measurements were set to 10 to ensure consistency. By plotting the difference in current density (J) between the anodic and cathodic sweeps (J_{anodic} - $J_{cathodic}$) at 0.15 V vs. RHE against the scan rate, a linear trend was observed. The slope of the fitting line is found to be equal-to-twice the geometric double layer capacitance (C_{dl}), which is proportional to the A_{echem} of the materials. Therefore, the A_{echem} of different samples can be compared with one another based on their C_{dl} values. However, it should be noted that this comparison makes sense only when the measurement of materials are carried out under same condition.

3、Measurements of electrochemical impedance spectroscopy (EIS)

EIS were performed under operating conditions (i.e., at a cathodic bias that drives rapid hydrogen evolution) according to the literature.[2] In our work, the initial electric potential was set as 1.5 V vs. RHE for direct comparison. A sinusoidal voltage with amplitude of 5 mV and scanning frequency values ranging from 100 kHz to 0.01 Hz were applied to carry out the measurements.

4、Determination of Faradaic efficiency

The Faradic efficiency of a catalyst in OER is defined as the ratio of the amount of O_2, respectively, evolved during the experiments to the amount of O_2 expected based on theoretical considerations.[2] For example, to measure the Faradic efficiency of OER, we carried out the following experiment. We collected the evolved O_2 gas by water drainage method, and then calculated the moles of O_2 generated from the reaction with an ideal gas law. The purity of the generated gas was confirmed by gas chromatography (GC) analysis. As for the theoretical value, we assumed that 100% current efficiency occurs during the reaction, which means only the OER process takes place at the working electrode. We can then calculate the theoretical amount of O_2 evolved by applying the Faraday law, which states that the passage of 96485.4 C charge causes 1 equivalent of reaction.

5、Physical methods

Determination of the loading amount of ultrathin-thin $Ni_{70}Fe_{30}$ LDHs (u-$Ni_{70}Fe_{30}$ LDHs) grown on the copper foil (CF) substrate, denoted m(d-$NiC_{0.2}$NS), was carried out as follows. (1) After synthesis of u-$Ni_{70}Fe_{30}$ LDHs/a-CF electrode, mass of u-$Ni_{70}Fe_{30}$ LDHs film grown on the a-CF equals the weight increment of CF (x mg), which can be directly obtained by comparing the weight of a-CF before and after the synthesis of electrode. As a result, the m(u-$Ni_{70}Fe_{30}$ LDHs) of u-$Ni_{70}Fe_{30}$ LDHs/a-CF electrode equals the x mg of weight increment divide geometric area of electrode ($A_{electrode}$), m(u-$Ni_{70}Fe_{30}$ LDHs) = x / $A_{electrode}$, with the value of 1.03 mg/cm^2.

To determine the mole ratio of Ni and Fe in the u-$Ni_{70}Fe_{30}$ LDHs of u-$Ni_{70}Fe_{30}$ LDHs/a-CF, the ICP-OES elemental analyses were performed on a Perkin Elmer (Optima-4300DV) ICP spectrometer. Using the ICP-OES elemental analyses, the total mole content of Ni and Fe was measured, which enabled us to estimate the mole content of Ni and Fe in the u-$Ni_{70}Fe_{30}$ LDHs/a-CF.

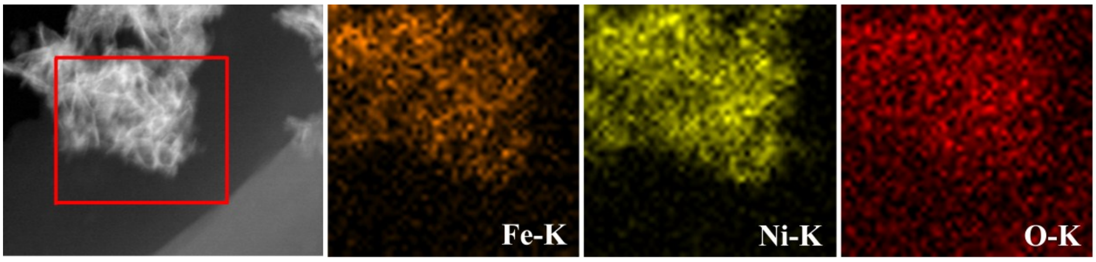

Figure S1. Elemental mappings of u-$Ni_{70}Fe_{30}$ LDHs, Fe (orange), Ni (yellow) O (red).

Elemental analysis revealed that Ni and Fe were distributed uniformly throughout the entire nanosheets.

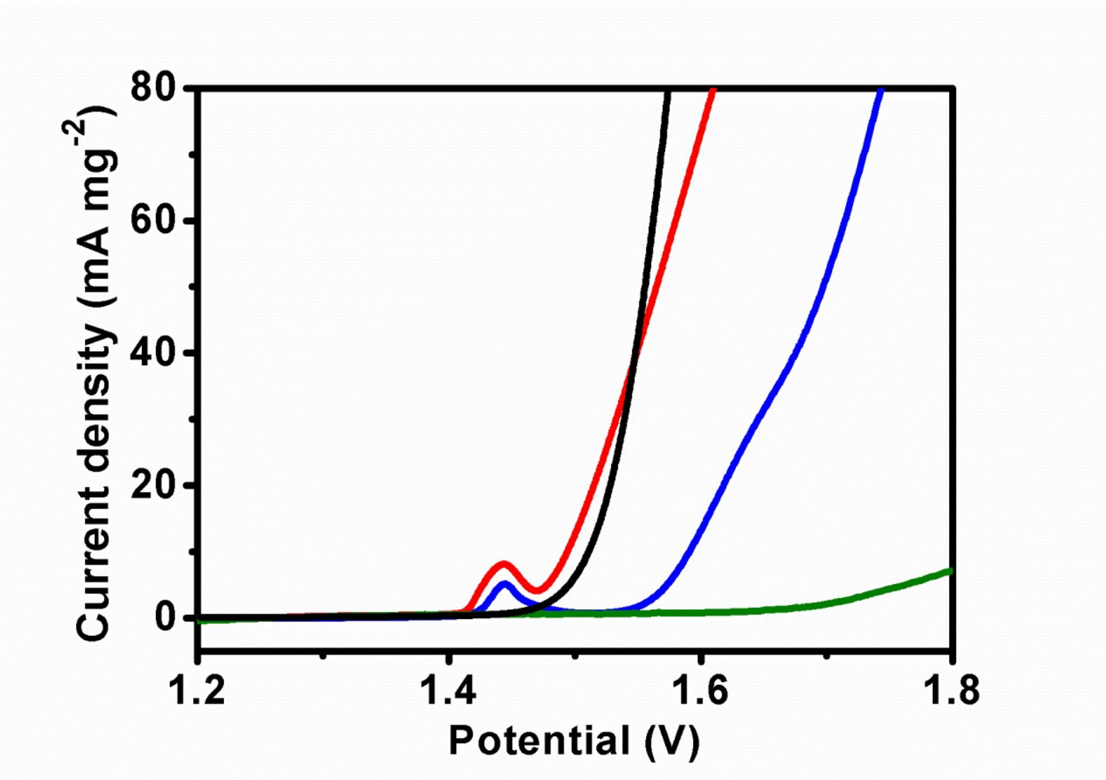

Figure S2. The OER LSV curves of mass activity for u-$Ni_{70}Fe_{30}$ LDHs/a-CF, a-CF, u-$Ni_{70}Fe_{30}$/CF, and RuO_2/a-CF. u-$Ni_{70}Fe_{30}$ LDHs/a-CF exhibits a remarkably electrocatalytic mass activity, which is slightly lower than that of RuO_2/a-CF a higher potential and higher than that of RuO_2/a-CF a lower potential for OER. Based on the these results, we can conclude that u-$Ni_{70}Fe_{30}$ LDHs/a-CF is a versatile and efficient electrocatalyst for OER.

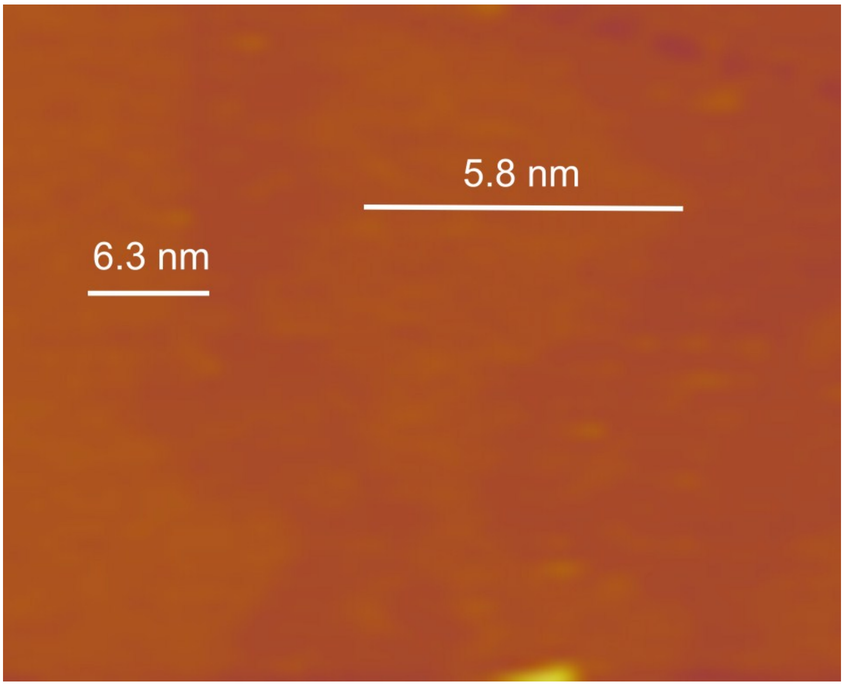

Figure S3. (a) AFM images of as-synthesized s-(-8)-30%.

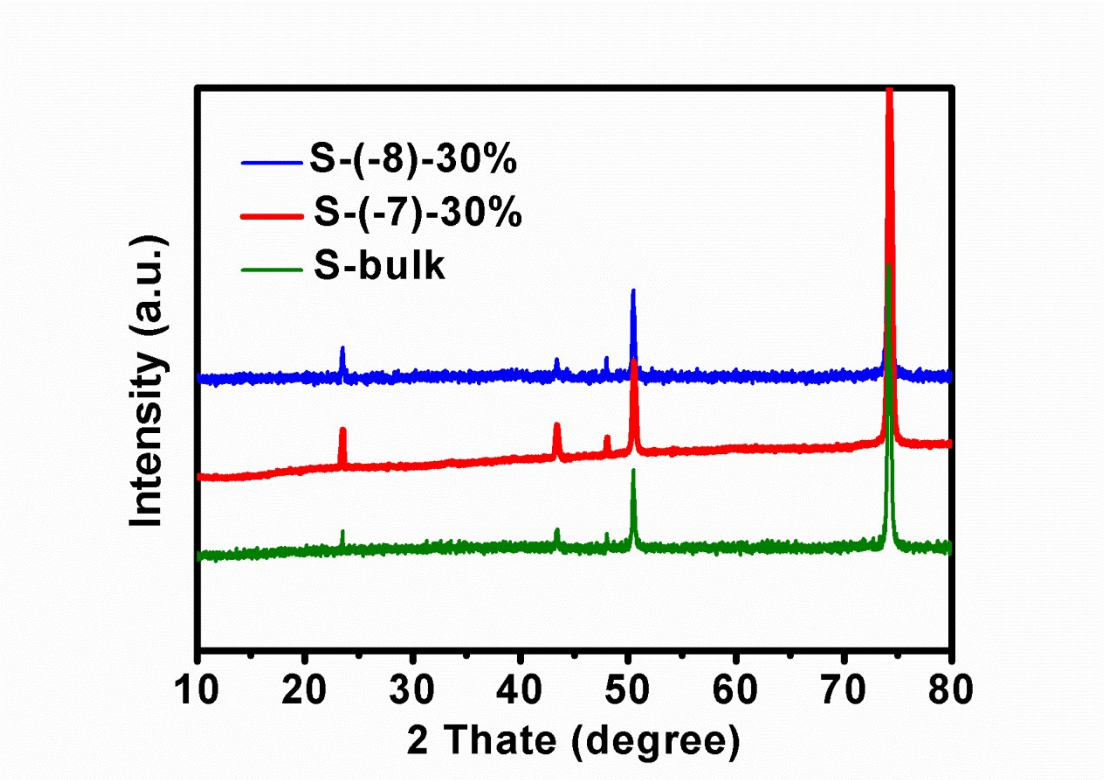

Figure S4. XRD spectras of as-synthsized s-(-7)-30%, s-(-8)-30%, and s-bulk.

Table S1. The ICP-OES measured value of Ni : Fe mole ratio for s-(-7)-0%, s-(-7)-10%, s-(-7)-20%, s-(-7)-30% (u-$Ni_{70}Fe_{30}$ LDHs/a-CF), and s-(-7)-40%, respectively.

Sample	**Molar ratio (Ni : Fe)**
s-(-7)-0%	100 :0
s-(-7)-10%	89.2 :10.8
s-(-7)-20%	77.3 : 22.7
s-(-7)-30%	72.5 : 27.5
s-(-7)-40%	63.1 : 36.9

Table S2. Comparison of the electrocatalytic performance of u-$Ni_{70}Fe_{30}$ LDHs/a-CF versus OER electrocatalysts reported recently.

Catalyst	**Electrolyte Solution**	**Current density (j)**	**Overpotential at the corresponding j**	**Stability**	**Reference**
u-$Ni_{70}Fe_{30}$ LDHs/a-CF	1 M KOH	10 mA/cm^2	260 mV	50 h	This work
$NiCo_2O_4$	1 M KOH	10 mA/cm^2	~300 mV	45 h	[3]
CoOOH	1 M KOH	10 mA/cm^2	300 mV	13 h	[4]
Ni–Co oxide	1 M NaOH	10 mA/cm^2	325 mV	5.6 h	[5]
$CoFe_2O_4$/PANI-MWCNT	1 M KOH	10 mA/cm^2	314 mV	40 h	[6]
NiCo-LDH	1M KOH	10 mA/cm^2	367 mV	6 h	[7]
NiO-$NiFe_2O_4$/rGO	1M KOH	10 mA/cm^2	296 mV	_	[8]
$Ni_{0.5}Fe_{0.5}O_x$	0.1M KOH	10 mA/cm^2	584 mV	_	[9]
$NiFe_2O_4$/α-$Ni(OH)_2$	0.1M NaOH	10 mA/cm^2	340 mV	15 h	[10]
$NiFe_2O_4$	1M KOH	10 mA/cm^2	342 mV	2 h	[11]
NiFe-LDH/G/Ni foam	0.1M KOH	10 mA/cm^2	325 mV	-	[12]
nNiFe LDH/NGF	0.1M KOH	10 mA/cm^2	337 mV	-	[13]
NiFe-LDHs assembled 3D microspheres	0.1M KOH	Oneset potential	435 mV	10000 s	[14]
NiFe LDH/RGO	1M KOH	10 mA/cm^2	245 mV	-	[15]

Table S3. The ICP-OES measured value of Ni : Fe mole ratio for s-(-5)-30%, s-(-6)-

10%, s-(-7)-20%, s-(-8)-30%, and s-bulk, respectively.

Sample	Molar ratio (Ni : Fe)
s-(-5)-30%	73.1 :26.9
s-(-6)-30%	70.1 : 29.9
s-(-7)-30%	72.5 : 27.5
s-(-8)-30%	71.7 : 28.3
s-bulk	71.8 : 28.2

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