Supporting information

1D/2D core-shell structure Ni-Mo-S@NiFe LDH grown on nickel foam: a bifunctional electrocatalyst for efficient oxygen evolution and urea oxidation reactions

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1. Experimental part

1.1. Materials and chemicals

The nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O), ammonium molybdate tetrahydrate ((NH$_4$)$_2$MoO$_4$·4H$_2$O) and nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) are purchased from Shanghai Macklin Biochemical Co., Ltd. Thioacetamide (TAA), ethanol (CH$_3$CH$_2$OH), ferric nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) and urea (CO(NH$_2$)$_2$) are purchased from Sinopharm Chemical Reagent Co. Ltd, China. potassium hydroxide (KOH) and hydrochloric acid (HCl) are provided by Aladdin. All chemical reagents are used directly without further purification.

1.2. Synthesis of NiMoO$_4$·xH$_2$O/NF

First, a piece of NF (1.5×3 cm^2) is ultrasonically cleaned with 1M HCl, ethanol and deionized water for 10 minutes each to remove impurities. Then, 0.25 g of Ni(CH$_3$COO)$_2$·4H$_2$O and 0.2 g of (NH$_4$)$_2$MoO$_4$·4H$_2$O are dispersed in 30 mL of deionized water and mixed uniformly for 30 min. Next, the above solution is poured into 50 mL Teflon-lined autoclave containing the treated NF, then hydrothermal treatment at 180 °C for 10 h. Finally, NiMoO$_4$·xH$_2$O/NF is washed by deionized water and ethanol, and dried under vacuum at 60 °C for 12 h.

1.3. Synthesis of Ni-Mo-S/NF

First, 0.4 g of thioacetamide (TAA) is dispersed into 15 mL of ethanol solution and stirred uniformly for 15 min. Subsequently, the NiMoO$_4$·xH$_2$O/NF synthesized in the first step is immersed in the solution with hydrothermal treatment at 150 °C for 6 h. Afterwards, the NF is washed several times with ethanol, and then dried under vacuum at 60°C overnight to obtain Ni-Mo-S/NF.

1.4. Synthesis of Ni-Mo-S@NiFe LDH/NF

First, 0.103 g of Fe(NO$_3$)$_3$·9H$_2$O, 0.218 g of Ni(NO$_3$)$_2$ and 0.075 g of urea are dispersed in 15 mL of deionized water and stirred uniformly for 30 min. Then, the solution is transferred into a Teflon-lined autoclave with Ni-Mo-S/NF, and reacted at 120 °C for 10 h. In contrast, We also directly prepared NiFe LDH samples in the absence of Ni-Mo-S/NF.

1.5. Synthesis of Pt/C/NF and RuO$_2$ /NF electrodes

10 mg of catalyst (commercial Pt/C or RuO$_2$) is added to a solution containing 980 μL of

ethanol and 20 µL of 5% Nafion solution. The ink solution is then sonicated for 30 min to obtain a uniformly dispersed ink solution[1]. Subsequently, 200 µL of ink solution is dropped onto NF (1×1 cm^2) and dried with hot air.

2.Characterization

The structure and composition of the samples are analyzed via X'Pert PRO X-ray diffractometer（XRD）with Cu Kα radiation (λ=1.5406 Å). Scanning electron microscope images (SEM) are taken on a ZEISS Sigma 300. High-resolution morphology and elemental diffraction analysis of the samples are performed using transmission electron microscopy (TEM) of FEI Talos-F200S. The chemical valence states of the samples are investigated by Thermo Fisher ESCALAB 250Xi X-ray Photoelectron Spectrometer (XPS) with Al Kα radiation. Then, the obtained XPS spectra are calibrated by the binding energy of the C 1s peak (284.8 eV).

3.Electrochemical test

All electrochemical measurements are performed in a three-electrode system on an electrochemical station (CHI660E) at room temperature. NF supported catalyst ($1*1.5$ cm^{-2}), graphite rod and saturated Ag/AgCl (the internal liquid is saturated KCl) are used as working electrode, counter electrode and reference electrode, respectively. Before OER and UOR tests, all samples are cycled at 5 mV s^{-1} for 50 cycles in 1.0 M KOH solution to stabilize the current. Electrochemical impedance spectroscopy (EIS) is collected at frequencies from 100 kHz to 0.01 kHz. All potentials measurements are converted to the RHE based on the following formula : E_{RHE} = $E_{Ag/AgCl}$ + 0.197 + 0.059×pH^2. Linear sweep voltammetry (LSV) polarization curves of OER and UOR are obtained in 1.0 mol L^{-1} KOH with or without urea at 5 mV s^{-1}, with 80% iR compensation. And the Tafel slope is calculated according to the following equation: η = $b \log j$ + a (b is the Tafel slope (mV dec^{-1}), the j is the current density (mA cm^{-2}))[3]. The ECSA values are measured through cyclic voltammetry (CV) in the selected non-faradaic range. And, the ECSA of the electrocatalyst is according to the following equation: ECSA = C_{dl}/C_s (C_{dl} is the double-layer capacitance, C_s is the specific capacitance of the material per unit area under identical electrolyte conditions, The general value of C_s is 40 µF cm^{-2})[4].

Ni-Mo-S/NF (OER):

$$A^{Ni-Mo-S}_{ECSA} = \frac{5.14\ mF.cm^{-2}}{40\ \mu F.cm^{-2} per\ cm^{2}_{ECSA}} = 128.5\ cm^{2}_{ECSA}$$

NiFe LDH/NF (OER):

$$A^{NiFe\ LDH}_{ECSA} = \frac{6.45\ mF.cm^{-2}}{40\ \mu F.cm^{-2} per\ cm^{2}_{ECSA}} = 161.25\ cm^{2}_{ECSA}$$

Ni-Mo-S@NiFe LDH/NF (OER):

$$A^{Ni-Mo-S@NiFe\ LDH}_{ECSA} = \frac{6.74\ mF.cm^{-2}}{40\ \mu F.cm^{-2} per\ cm^{2}_{ECSA}} = 168.5\ cm^{2}_{ECSA}$$

Stability tests are performed with chronopotentiometry. The overall water splitting and urea electrolysis system is performed using Ni-Mo-S@NiFe LDH/NF as anode and Ni-Mo-S/NF as cathode in a two-electrode configuration in 1.0 mol L^{-1} KOH with or without urea.
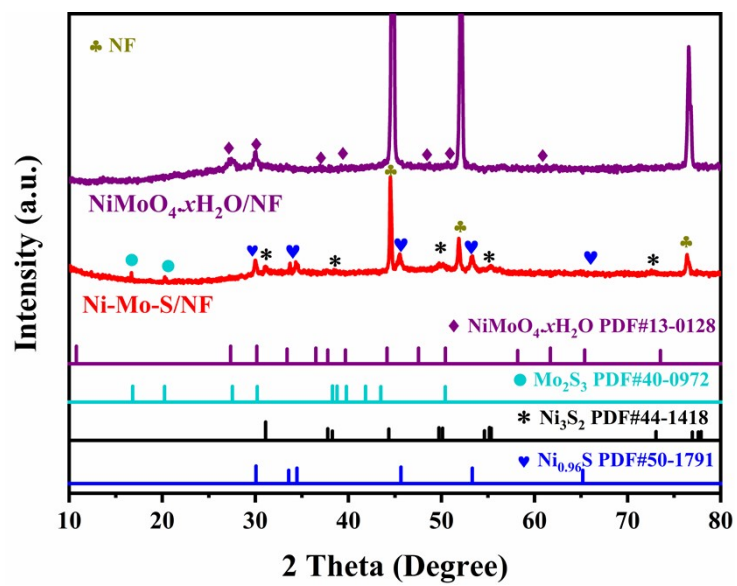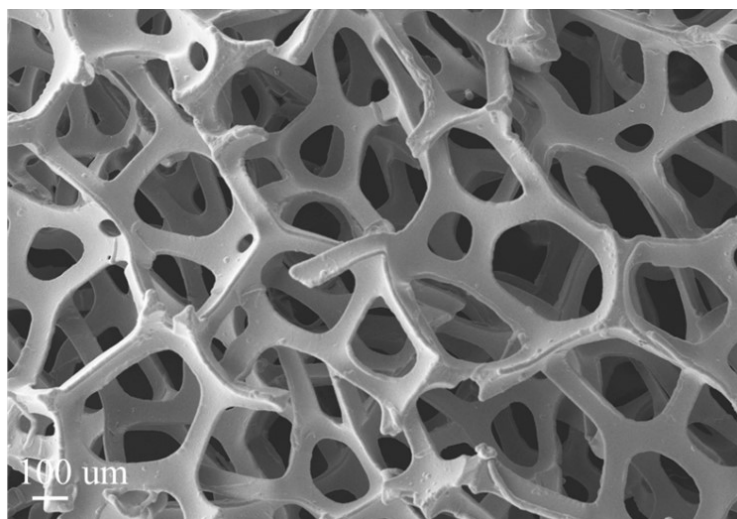
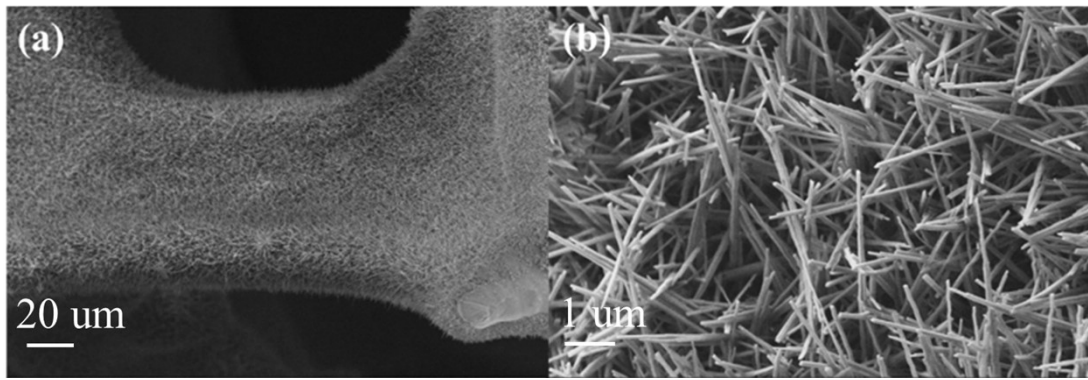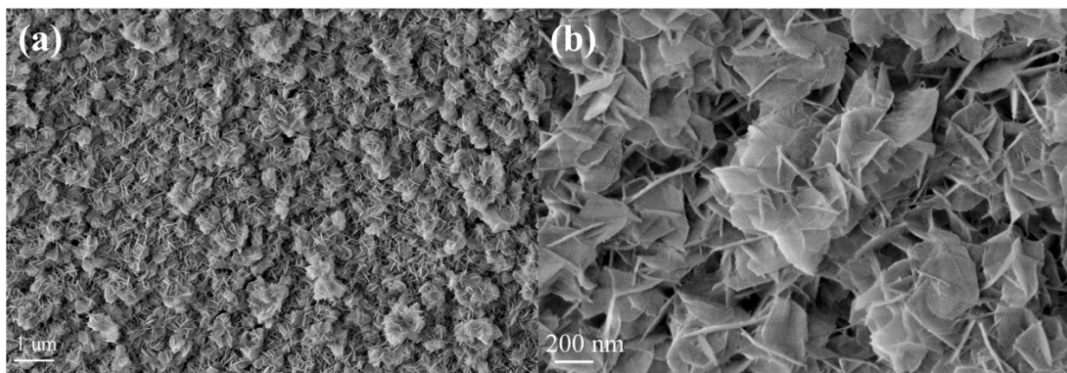**Fig.S1** XRD pattern of Ni-Mo-S/NF and NiMoO$_4$·xH$_2$O/NF.

Fig.S2 SEM image of NF.

Fig.S3 SEM image of NiMoO$_4$·xH$_2$O/NF.

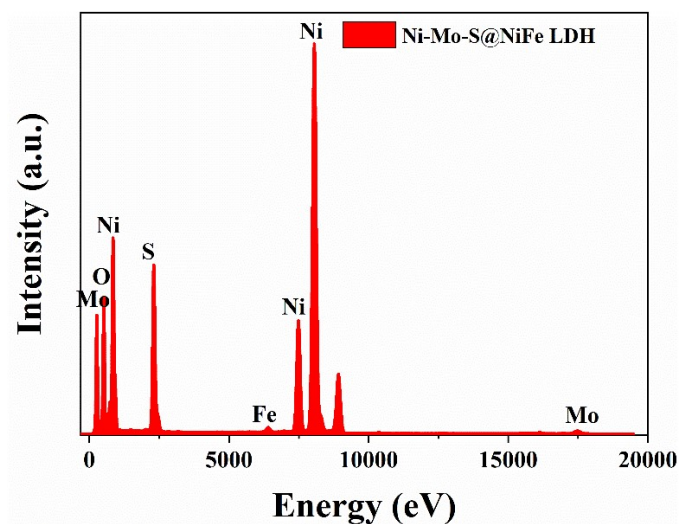**Fig.S4** SEM image of NiFe LDH/NF.

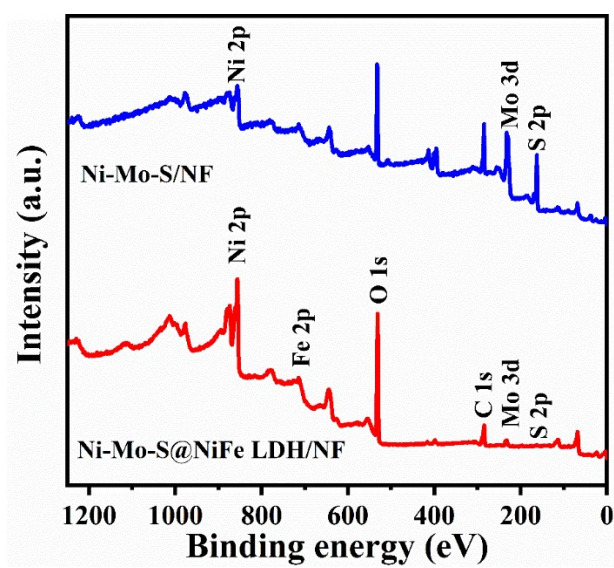**Fig.S5** EDS spectrum of Ni-Mo-S@NiFe LDH/NF.

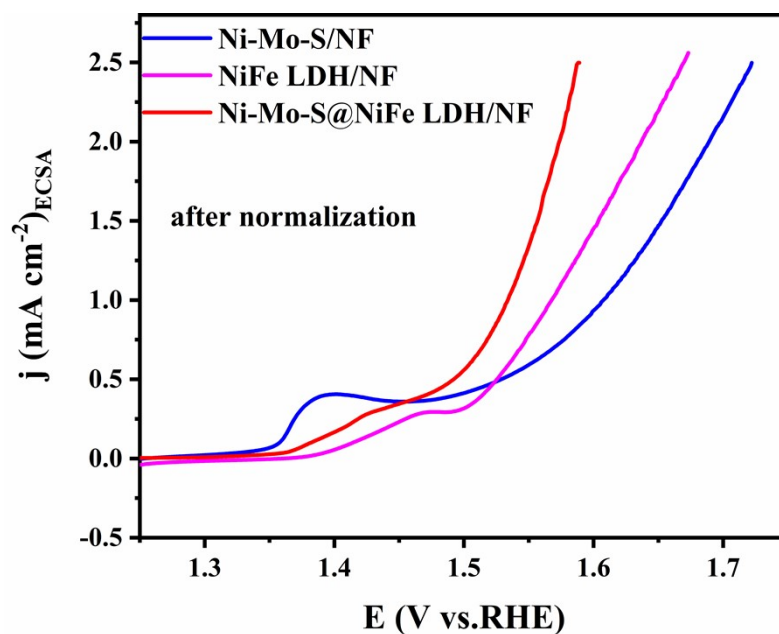**Fig.S6** Survey XPS of Ni-Mo-S@NiFe LDH/NF and Ni-Mo-S/NF.

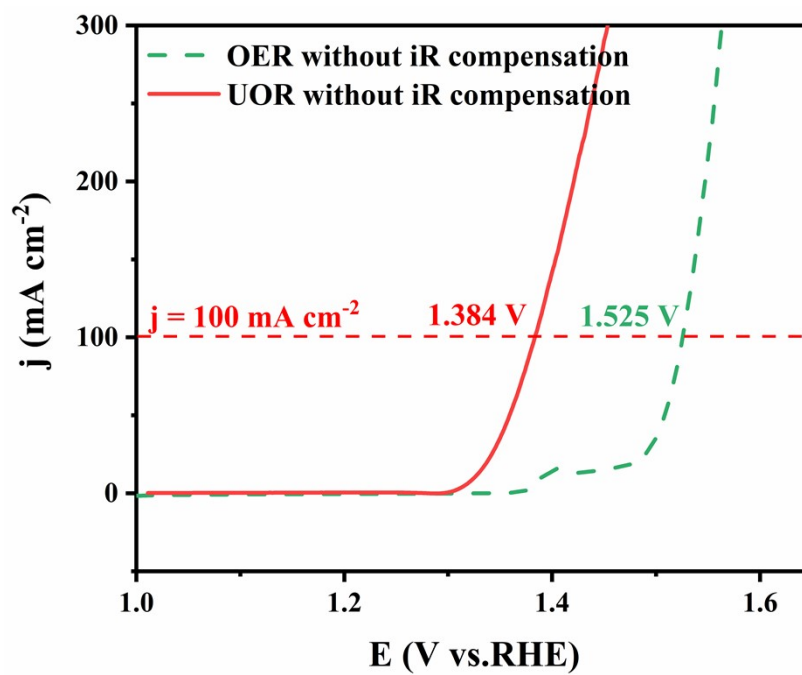**Fig.S7** The ECSA-normalized current vs. voltage curves of the catalyst.

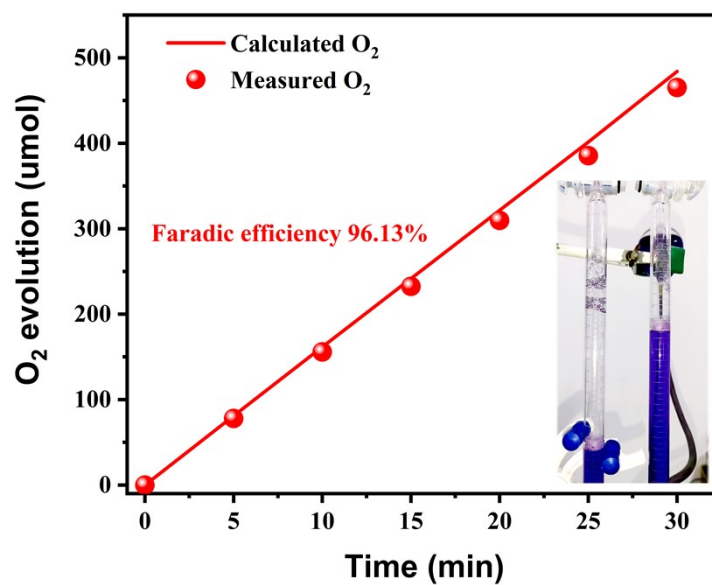**Fig.S8** LSV curves of Ni-Mo-S@NiFe LDH/NF without iR compensation.

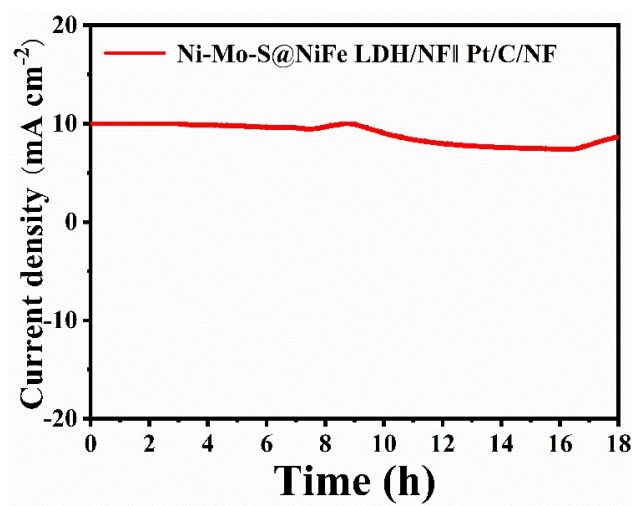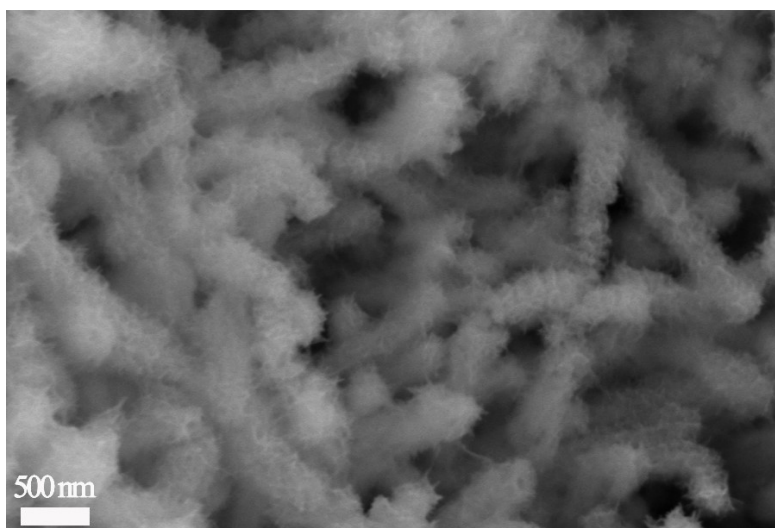**Fig.S9** Faradaic efficiency of Ni-Mo-S@NiFe LDH/NF at 100 mA cm^{-2}.

Fig.S10 Long-term stability test of overall water splitting.

Fig.S11 SEM images of Ni-Mo-S@NiFe LDH/NF after stability test.

Catalysts	Overpotential 100 mA/cm^2	Reference
Ni-Mo-S@NiFe LDH/NF	274	This work
V-Ni$_3$S$_2$@NiFe LDH/NF	286	J. Mater. Chem. A, 2019[5]
MoNi/NiMoOx @ NiFe LDH/NF	278	Electrochimica Acta, 2021 [6]
NiCo$_2$S$_4$@Co$_1$Ni$_4$-LDH/NF	337	J Alloy Compd, 2020[7]
NiCo$_2$(SOH)$_x$/NF	349	ACS Catalysis, 2017[8]
FeCo-LDH/PANI	323	Int J Hydrogen Energ, 2020
NiFeVP/NF	360	J. Mater. Chem. A, 2021[9]
FeOOH/NiFe LDH/NF	237	Electrochimica Acta, 2023[10]
FeNi-Mo$_2$C/CF	280	Chem Eng J, 2022[11]
Ni(OH)$_2$/NiCo$_2$O$_4$	305	Int J Hydrogen Energ, 2020[12]
VO$_x$/Ni$_3$S$_2$@NF	358	J Mater Chem A, 2019[13]
Co/CoMoN/NF	303	Advanced Science,2022 [14]

Table.S1 Comparison of the OER activity of several recently highly active catalysts.

Catalysts	Overpotential 10 mA/cm^2	Reference
Ni-Mo-S@NiFe LDH/NF	1.318	This work
Ni(OH)S	1.34	Applied Catalysis B, 2022[15]
NiS/MoS$_2$/CC	1.36	Chem Eng J, 2022[16]
W-NiS$_2$/MoO$_2$@CC	1.3	Chem Eng J, 2022[17]
Fe$_3$O$_4$/NF	1.38	J Colloid Interface Sci, 2022[18]
Fe-Ni$_3$S$_2$@FeNi$_3$-8	1.40	Chem Eng J, 2020[19]
FeCoCuNiZn-LDH/CC	1.326	J Colloid Interface Sci, 2023[20]
CoFe$_{0.75}$Mn$_{0.25}$-LDH/NF	1.367	J Alloy Compd, 2022[21]
MoP@NiCo LDH/NF	1.392	J. Mater. Chem. A, 2021[22]

Table.S2 Comparison of the UOR activity of several recently highly active catalysts.

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