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Supplementary Information for

Amorphous NiFe layered double hydroxide nanosheets decorated on 3D nickel phosphide nanoarrays: a hierarchical core-shell electrocatalyst for efficient oxygen evolution

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Experimental Section

Chemicals. Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2\cdot6H_2O$, 98%, Sigma-Aldrich), iron(II) sulfate heptahydrate ($FeSO_4\cdot7H_2O$, ≥99.95%, Sigma-Aldrich), nafion 117 solution (5%, Sigma-Aldrich), iridium oxide powder (IrO_2, 99%, Alfa Aesar), potassium hydroxide (KOH, 50% w/v, Alfa Aesar), red phosphorous powder (P, ≥ 97%, Sigma-Aldrich), potassium hydroxide (KOH, 50% w/v, Alfa Aesar), and Ni foam (thickness: 1.6 mm) were used as received. Deionized water (resistivity: 18.3 MΩ·cm) was used for the preparation of all aqueous solutions.

Synthesis of Ni_5P_4/NiP_2 foam. The Ni_5P_4/NiP_2 microosheet arrays catalyst was synthesized by direct phosphorization of the commercial Ni foam in a tube furnace according to previous reports.[1, 2] The precursor phosphorus powder (100 mg) was placed at the upstream during the phosphorization, and a small piece of Ni foam (~ 1 cm^2) was placed at the middle (~ 14 cm apart from the P source) of tube furnace in a direction perpendicular to the argon (Ar) gas flow. The temperature was raised at a constant rate of 15 ^oC min^{-1} to 500 ^oC and kept at 500 ^oC for 1 hour for the growth. Then the sample was taken out after the furnace was automatically turned off and naturally cooled down to room temperature under Ar atmosphere.

Fabrication of Ni_5P_4/NiP_2/NiFe LDH electrode. The 3D core-shell Ni_5P_4/NiP_2/NiFe LDH electrode was synthesized by growing NiFe LDH nanosheets on the as-prepared Ni_5P_4/NiP_2 foam via our previous electrodeposition method,[3] which was carried out in a three-electrode configuration by using as-prepared Ni_5P_4/NiP_2 foam, Pt net and saturated calomel electrode (SCE) as the working, counter and reference electrode, respectively. The electrolyte was prepared by dissolving $Ni(NO_3)_2\cdot6H_2O$ (0.15 M) and $FeSO_4\cdot7H_2O$ (0.15 M) in 100 mL water with a continuous Ar flow. The applied potential was -1.0 V vs. SCE, and different electrodeposition time with 30, 60, 75, and 90 s were used to control the amount of the NiFe LDH, which were labeled with

Ni_5P_4/NiP_2/NiFe LDH-30, Ni_5P_4/NiP_2/NiFe LDH-60, Ni_5P_4/NiP_2/NiFe LDH-75, and Ni_5P_4/NiP_2/NiFe LDH-90, respectively. The loading mass of NiFe LDH for the four samples are 1.1, 1.9, 2.4, and 3.0 mg cm^{-2}, respectively. The samples were then washed with deionized water and dried in air. For comparison, pure NiFe LDH was prepared on Ni foam by the same method for 75 s.

Preparation of IrO_2 electrode on Ni foam. To prepare the IrO_2 electrode, 40 mg IrO_2 and 60 µL Nafion, 540 µL ethanol and 400 µL deionized water were ultrasonicated for 30 min to obtain a homogeneous dispersion. Then, the dispersion was coated onto a Ni foam, which was then dried in air overnight at room temperature. The loading of IrO_2 catalyst on Ni foam is ~ 2 mg cm^{-2}, just the same with that of NiFe LDH on Ni_5P_4/NiP_2 foam.

Materials characterization. The morphology and crystal structure of the samples were investigated with scanning electron microscopy (SEM, LEO 1525) and transmission electron microscope (TEM, JEOL 2010F) coupled with energy dispersive X-ray (EDX) spectroscopy. The phase composition of the samples was characterized by X-ray diffraction (PANalytical X'pert PRO diffractometer with a Cu Ka radiation source). X-ray photoelecton spectroscopy (XPS) (PHI Quantera XPS) was conducted using a PHI Quantera SXM Scanning X-ray Microprobe.

Electrochemical Tests. All electrochemical tests were carried out at room temperature on an electrochemical station (Bio-logic SP 150) in a typical three-electrode system with the prepared samples as the working electrode, a Pt net (graphite foil for HER) as the counter electrode, and a standard Hg/HgO electrode as the reference. The OER activity was assessed using linear sweep voltammetry (LSV) with a sweep rate of 2 mV s^{-1} and chronopotentiometry at constant current densities of 10, 100, and 200 mA cm^{-2} in O_2-saturated 1 M KOH solution. The HER tests were conducted in Ar-saturated 1 M KOH solution with a sweep rate of 2 mV s^{-1}. Cyclic voltammetry

(CV) curves were collected at different scan rates in the potentials from 1.025 V to 1.125 V vs RHE to estimate the double-layer capacitance. Electrochemical impedance spectroscopy (EIS) was measured at an overpotential of 250 mV from 0.1 Hz to 100 KHz with an amplitude of 10 mV. The overall water splitting performance was evaluated in 1 M KOH using a two-electrode configuration, and the polarization curve was recorded at a scan rate of 2 mV s^{-1}. All the measured potentials vs. Hg/HgO were converted to RHE by the Nernst equation ($E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.0591$ pH + 0.098). All the curves were reported with iR compensation.

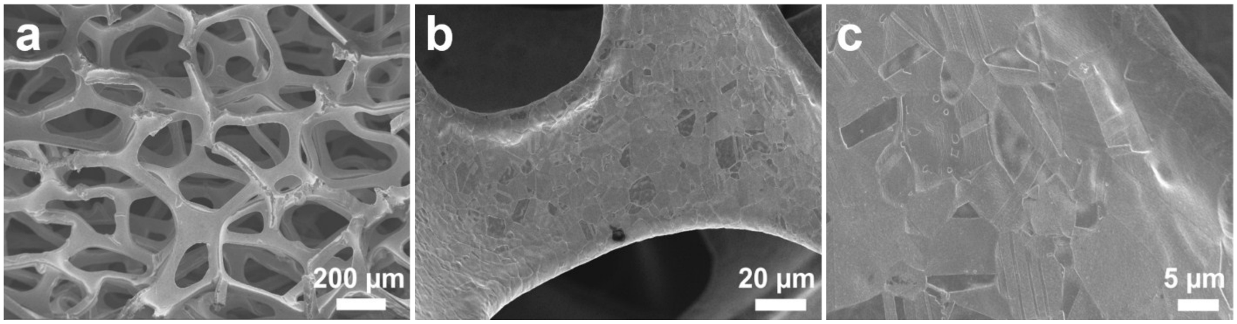


Fig. S1 SEM images of the commercial Ni foam.

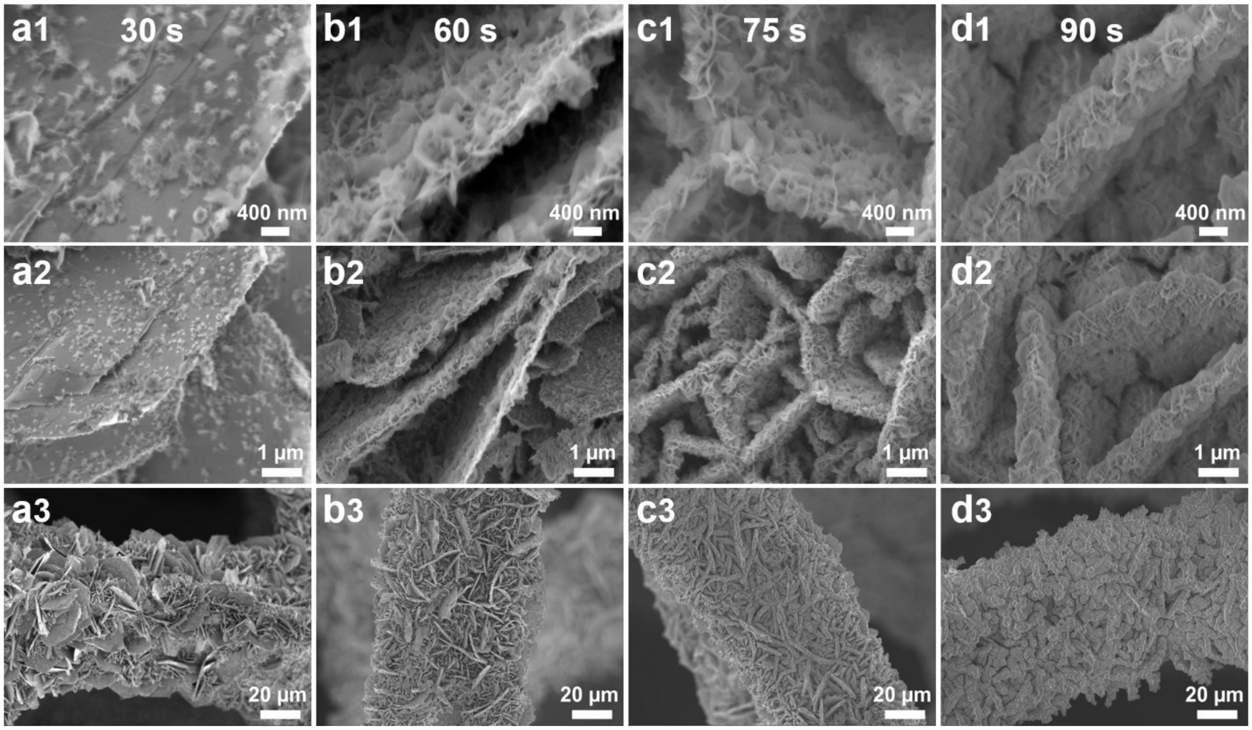


Fig. S2 SEM images of Ni_5P_4/NiP_2/NiFe LDH samples prepared under different electrodeposition time of NiFe LDH. (a1-a3) 30 s; (b1-b3) 60 s; (c1-c3) 75 s; (d1-d3) 90 s.

The NiFe LDH nanosheets grew very fast on the Ni_5P_4/NiP_2 foam via electrodepostion method. For 30 s sample, we can observe that there were scattered NiFe LDH nanosheets attached on the Ni_5P_4/NiP_2 microsheets. After another 30 s, the nanosheets were fully decorated with the edges of microsheets exposing outside. For the 75 s sample, all the Ni_5P_4/NiP_2 microsheets were uniformly decorated NiFe LDH nanosheets, and the large interspace between the neighboring arrays was totally preserved. For the 90 s sample, the thickness of the hybrid microsheets was much improved, and some NiFe LDH nanosheets even blocked the interspace.

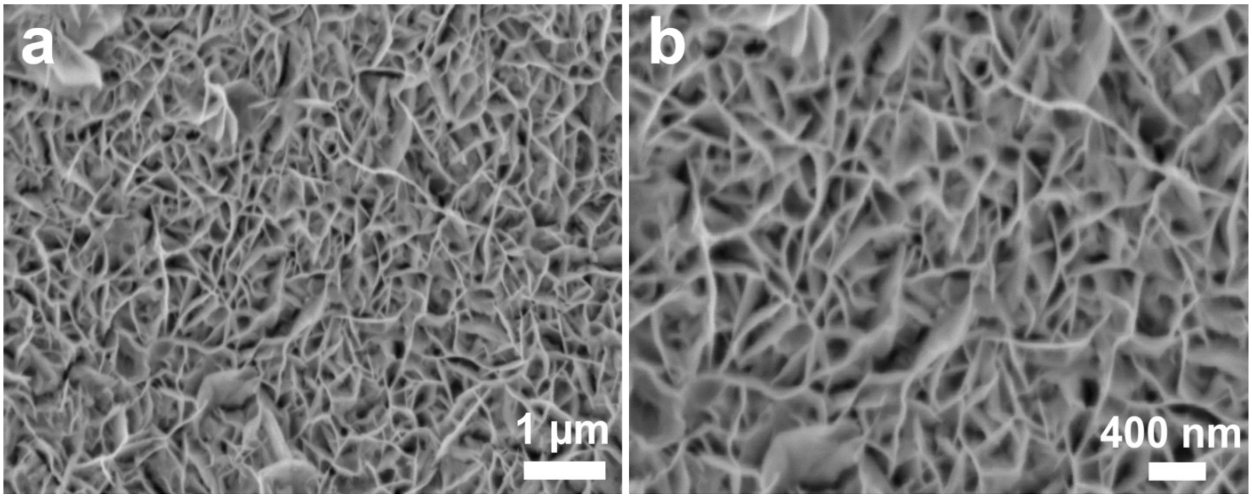


Fig. S3 SEM images of pure NiFe LDH on Ni foam.

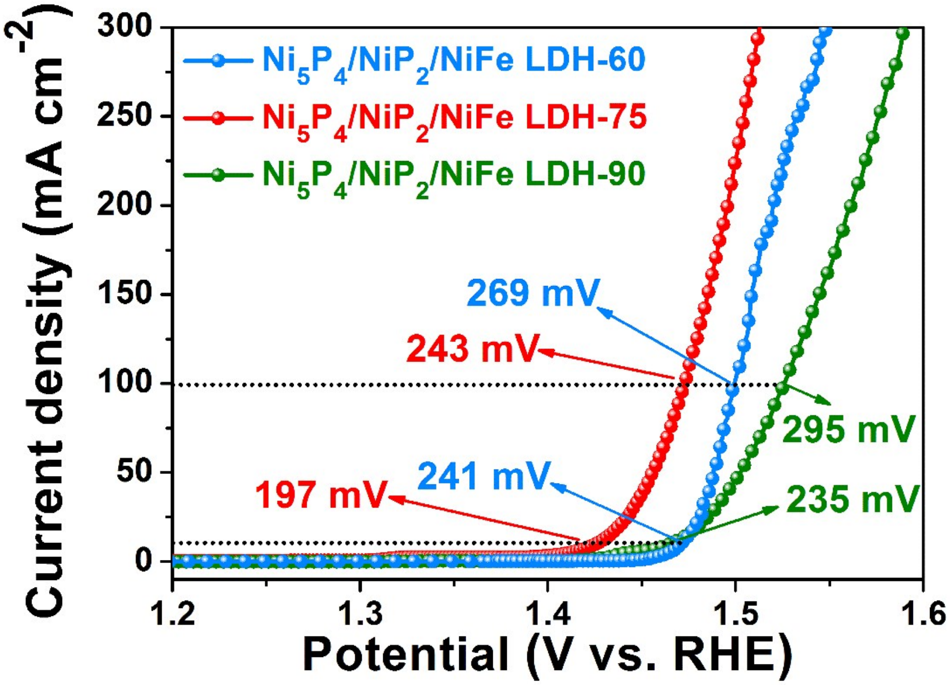


Fig. S4 OER polarization curves of Ni_5P_4/NiP_2/NiFe LDH electrodes with different electrodeposition time of NiFe LDH.

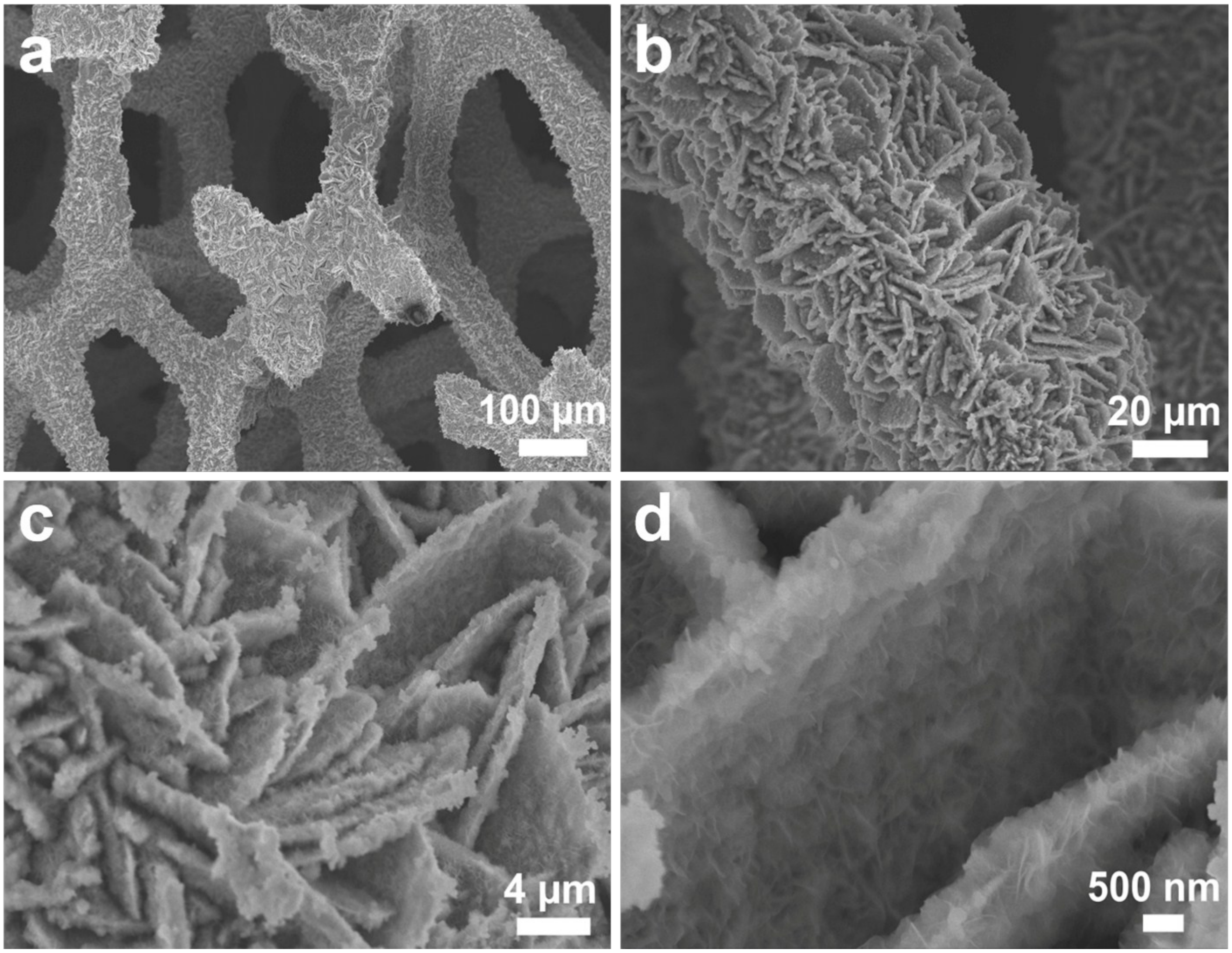


Fig. S5 SEM images of Ni_5P_4/NiP_2/NiFe LDH after long-term stability tests.

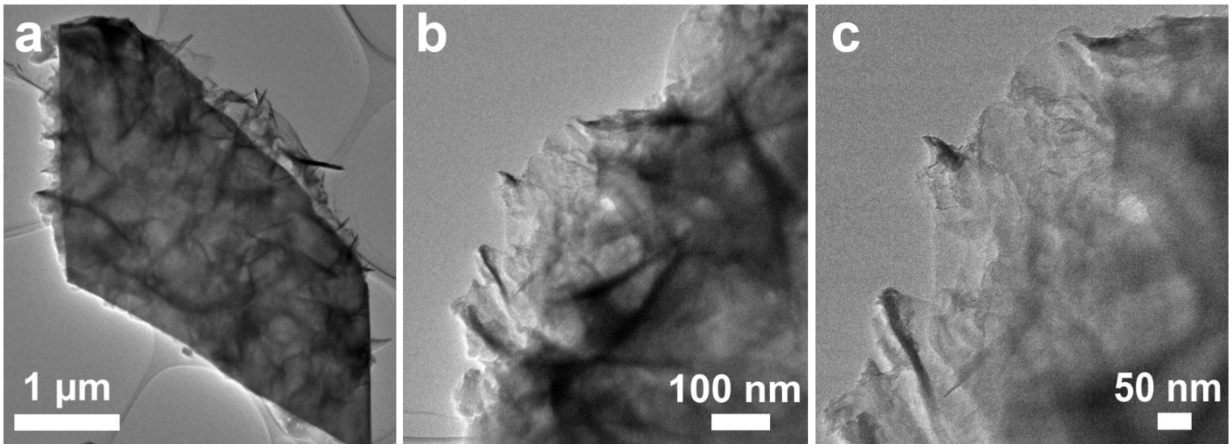


Fig. S6 TEM images of Ni_5P_4/NiP_2/NiFe LDH after long-term stability tests.

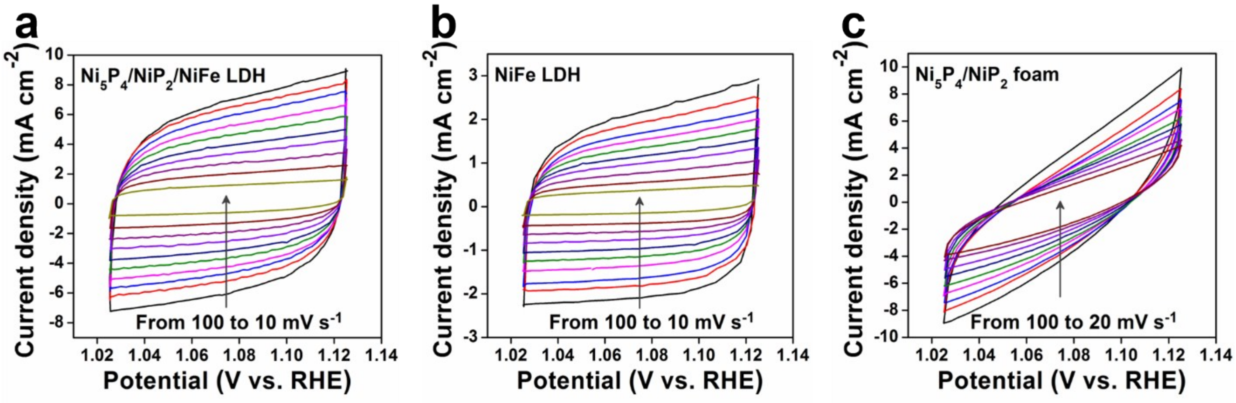
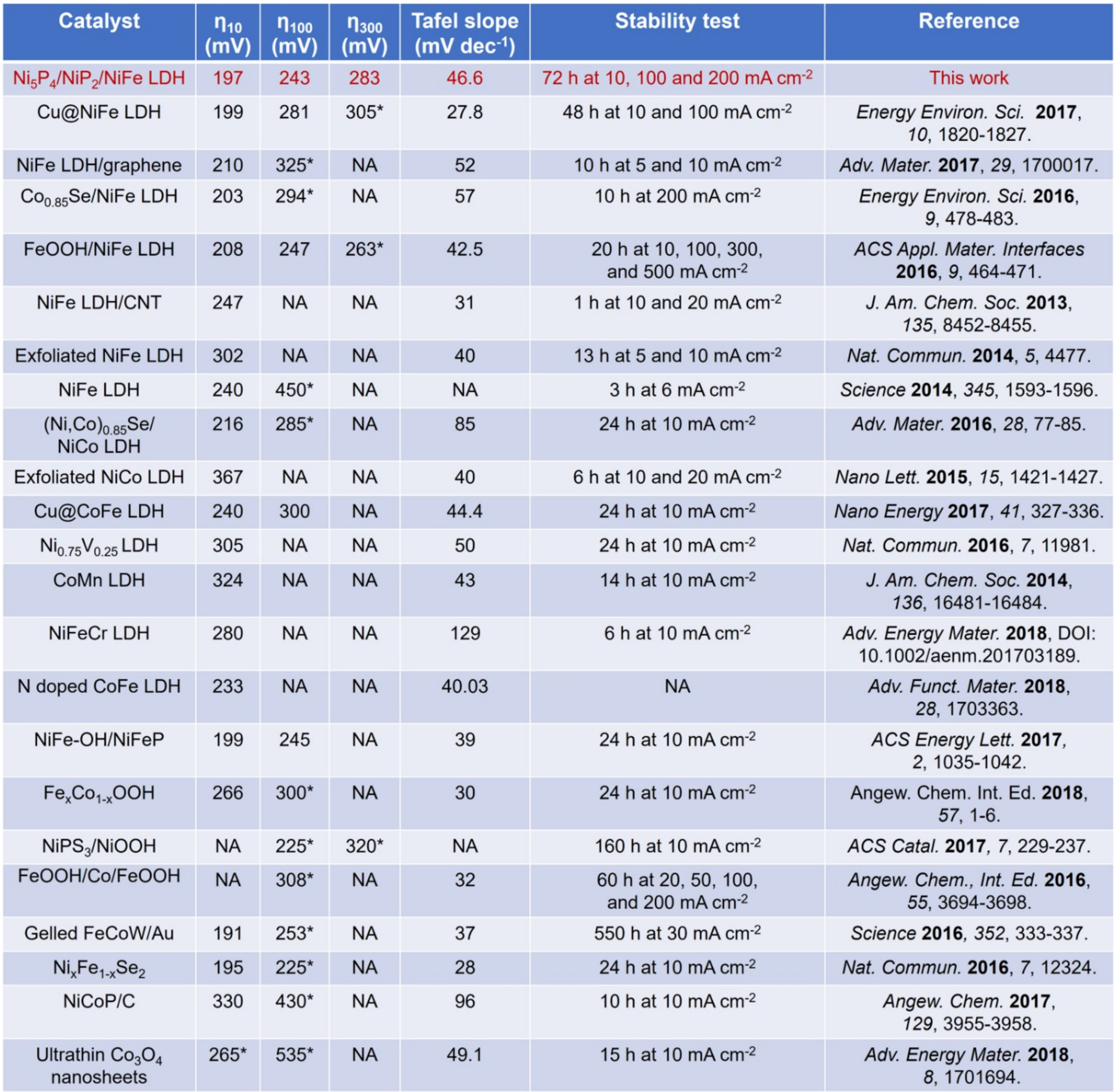


Fig. S7 Cyclic voltammograms of (a) Ni_5P_4/NiP_2/NiFe LDH, and (b) pure NiFe LDH at scan rates ranging from 10 mV s^{-1} to 100 mV s^{-1}, (c) $Ni_{2(1-x)}Mo_{2x}P$ at scan rates ranging from 20 mV s^{-1} to 100 mV s^{-1} with an interval point of 10 mV s^{-1}. The scanning potential range is from 1.025 V to 1.125 V vs RHE.

Table S1. Comparison of the OER performance for the Ni_5P_4/NiP_2/NiFe LDH catalyst with other reported OER electrocatalysts in 1 M alkaline media (KOH or NaOH). Here η_{10}, η_{100}, and η_{300} correspond to the overpotentials at current densities of 10, 100, and 300 mA cm^{-2}, respectively.



Catalyst	η_{10} (mV)	η_{100} (mV)	η_{300} (mV)	Tafel slope (mV dec^{-1})	Stability test	Reference
Ni_5P_4/NiP_2/NiFe LDH	197	243	283	46.6	72 h at 10, 100 and 200 mA cm^{-2}	This work
Cu@NiFe LDH	199	281	305*	27.8	48 h at 10 and 100 mA cm^{-2}	*Energy Environ. Sci.* **2017**, *10*, 1820-1827.
NiFe LDH/graphene	210	325*	NA	52	10 h at 5 and 10 mA cm^{-2}	*Adv. Mater.* **2017**, *29*, 1700017.
$Co_{0.85}Se$/NiFe LDH	203	294*	NA	57	10 h at 200 mA cm^{-2}	*Energy Environ. Sci.* **2016**, *9*, 478-483.
FeOOH/NiFe LDH	208	247	263*	42.5	20 h at 10, 100, 300, and 500 mA cm^{-2}	*ACS Appl. Mater. Interfaces* **2016**, *9*, 464-471.
NiFe LDH/CNT	247	NA	NA	31	1 h at 10 and 20 mA cm^{-2}	*J. Am. Chem. Soc.* **2013**, *135*, 8452-8455.
Exfoliated NiFe LDH	302	NA	NA	40	13 h at 5 and 10 mA cm^{-2}	*Nat. Commun.* **2014**, *5*, 4477.
NiFe LDH	240	450*	NA	NA	3 h at 6 mA cm^{-2}	*Science* **2014**, *345*, 1593-1596.
$(Ni,Co)_{0.85}Se$/ NiCo LDH	216	285*	NA	85	24 h at 10 mA cm^{-2}	*Adv. Mater.* **2016**, *28*, 77-85.
Exfoliated NiCo LDH	367	NA	NA	40	6 h at 10 and 20 mA cm^{-2}	*Nano Lett.* **2015**, *15*, 1421-1427.
Cu@CoFe LDH	240	300	NA	44.4	24 h at 10 mA cm^{-2}	*Nano Energy* **2017**, *41*, 327-336.
$Ni_{0.75}V_{0.25}$ LDH	305	NA	NA	50	24 h at 10 mA cm^{-2}	*Nat. Commun.* **2016**, *7*, 11981.
CoMn LDH	324	NA	NA	43	14 h at 10 mA cm^{-2}	*J. Am. Chem. Soc.* **2014**, *136*, 16481-16484.
NiFeCr LDH	280	NA	NA	129	6 h at 10 mA cm^{-2}	*Adv. Energy Mater.* **2018**, DOI: 10.1002/aenm.201703189.
N doped CoFe LDH	233	NA	NA	40.03	NA	*Adv. Funct. Mater.* **2018**, *28*, 1703363.
NiFe-OH/NiFeP	199	245	NA	39	24 h at 10 mA cm^{-2}	*ACS Energy Lett.* **2017**, *2*, 1035-1042.
$Fe_xCo_{1-x}OOH$	266	300*	NA	30	24 h at 10 mA cm^{-2}	Angew. Chem. Int. Ed. **2018**, *57*, 1-6.
$NiPS_3$/NiOOH	NA	225*	320*	NA	160 h at 10 mA cm^{-2}	*ACS Catal.* **2017**, *7*, 229-237.
FeOOH/Co/FeOOH	NA	308*	NA	32	60 h at 20, 50, 100, and 200 mA cm^{-2}	*Angew. Chem., Int. Ed.* **2016**, *55*, 3694-3698.
Gelled FeCoW/Au	191	253*	NA	37	550 h at 30 mA cm^{-2}	*Science* **2016**, *352*, 333-337.
$Ni_xFe_{1-x}Se_2$	195	225*	NA	28	24 h at 10 mA cm^{-2}	*Nat. Commun.* **2016**, *7*, 12324.
NiCoP/C	330	430*	NA	96	10 h at 10 mA cm^{-2}	*Angew. Chem.* **2017**, *129*, 3955-3958.
Ultrathin Co_3O_4 nanosheets	265*	535*	NA	49.1	15 h at 10 mA cm^{-2}	*Adv. Energy Mater.* **2018**, *8*, 1701694.

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

References

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(3) L. Yu, H. Zhou, J. Sun, F. Qin, F. Yu, J. Bao, Y. Yu, S. Chen and Z. Ren, *Energy Environ. Sci.*, 2017, **10**, 1820-1827.