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Supporting Information

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Defect-Rich Heterogeneous MoS_2/NiS_2 Nanosheets Electrocatalysts for Efficient Overall Water Splitting

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1. Experimental Section

Fabrication of MoS_2/NiS_2 nanosheets: The commercial carbon cloth was treated with concentrated HNO_3,ethanol and deionized water several times, according to previous research.[1] Firstly, 10 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 1.43 mmol $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 20 mmol hexamethylenetetramine were dissolved in 80 mL distilled water and stirred for 2 h. Then, the mixed solution with a piece of carbon cloth (2×5 cm^2) was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated to 150 ^oC for 12 h. The obtained Ni-Mo precursors were washed by distilled water and ethanol several times, and dried at 80 ℃ overnight. Secondly, sublimed sulfur and a piece of carbon cloth with Ni-Mo precursors were put at the upstream and downstream side of the tube furnace, then the furnace was heated to 400 ^oC for 1h with a ramp rate of 5 ^oC under Ar atmosphere to obtain MoS_2/NiS_2**.** To obtain different samples, various amounts of sublimed sulfur (50, 100, 200 and 400 mg) was used. For comparison, pure NiS_2 nansheets were synthesized by similar processes without Mo source, and the amount of sublimed sulfur is 200 mg. For comparison, Ni-Mo precursors were annealed in 400 ^oC for 2h in air to obtain $NiMoO_4$ samples.

Sample characterization

SEM (Helios Nanolab 600i), TEM (Tecnai G2 F30) and XRD (D8 Advance) were applied to investigate the nanostructure, morphology and crystalline phases of obtained samples. XPS (Thermo Fisher) and Raman (InVia-Reflex) were used to investigate the surface states. The Nitrogen adsorption/desorption isotherms were conducted at 77 K.

Electrochemical measurements

All electrochemical performances were measured in the electrochemical workstation

(CHI 760E and PARSTAT 4000A). The OER and HER properties were measured in a three-electrode system, using obtained samples, Hg/HgO and carbon rod as working electrode, reference electrode and counter electrode, respectively. All the potential was converted to RHE. The polarization curves were measured at 2 mV s^{-1}, and were compensated with iR-correction. Before OER and HER tests, all samples were cycled at 10 mV s^{-1} until the stability of cyclic voltammetry (CV), then the data were collected. The overall water splitting was tested in the two-electrode system. The reference electrodes of Pt/C (20 wt%) and RuO_2 were also prepared on carbon cloth, and the prepared method was according to previously reported researches.[2,3]

Reference

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2. Z. Zhang, X. Ma and J. Tang, *J. Mater. Chem. A* 2018, **6**, 12361.

3. Z. Wang, H. Liu, R. Ge, X. Ren, J. Ren, D. Yang, L. Zhang and X. Sun, *ACS Catal.* 2018, **8**, 2236.

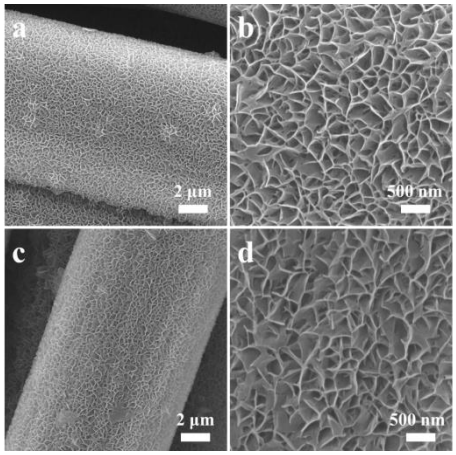

Fig. S1 SEM images of (a,b) NiMo-precursor and (c,d) $NiMoO_4$.

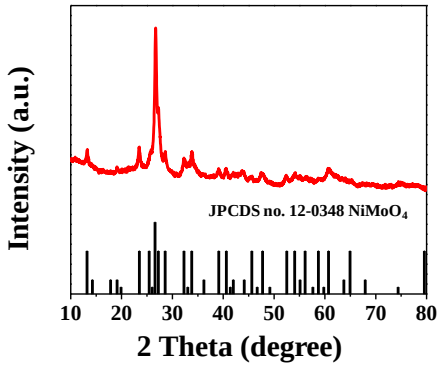

Fig. S2 XRD pattern of $NiMoO_4$ scratched from the carbon cloth.

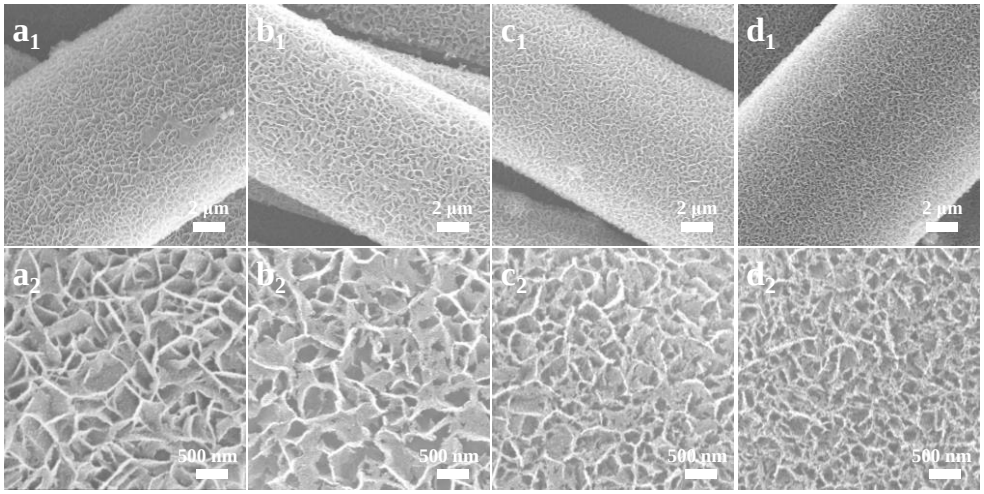

Fig. S3 SEM images of (a) MoS_2/NiS_2-1, (b) MoS_2/NiS_2-2, (c) MoS_2/NiS_2-3 and (d) MoS_2/NiS_2-4.

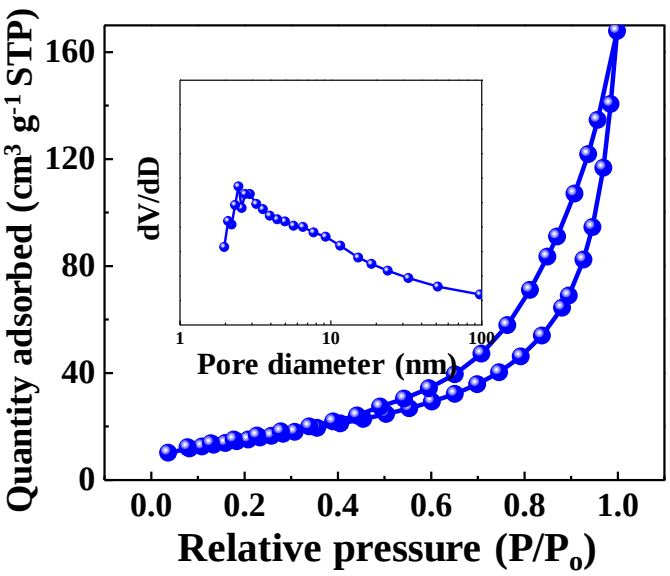

Fig. S4 The N_2 adsorption/desorption isotherm of MoS_2/NiS_2-3, and the inset is the corresponding pore size distribution

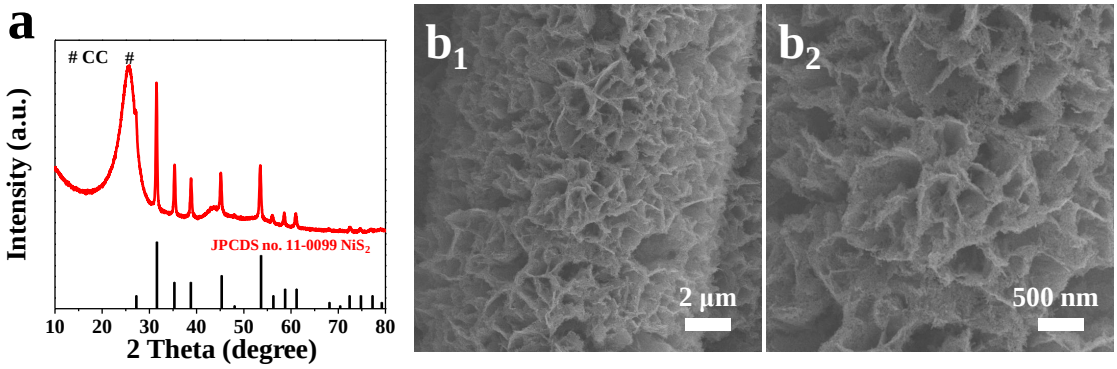

Fig. S5 (a) XRD pattern and (b) SEM images of pure NiS_2 nanosheets on carbon cloth.

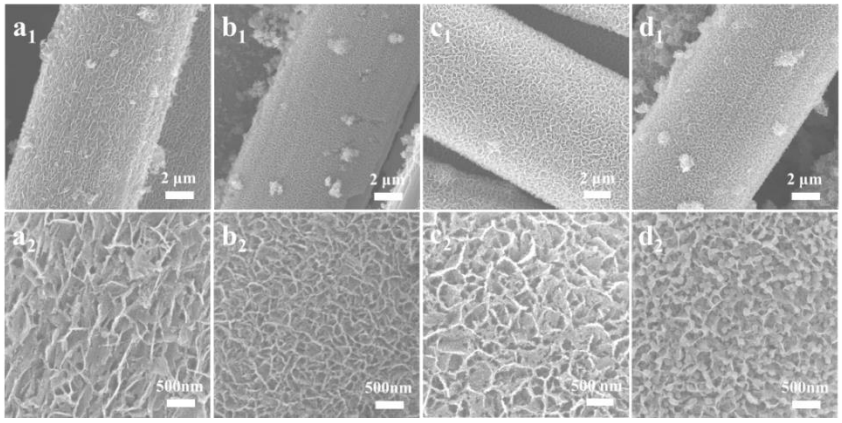

Fig. S6 SEM images of (a) MoS_2/NiS_2-300, (b) MoS_2/NiS_2-350, (c) MoS_2/NiS_2-400 and (d) MoS_2/NiS_2-500.

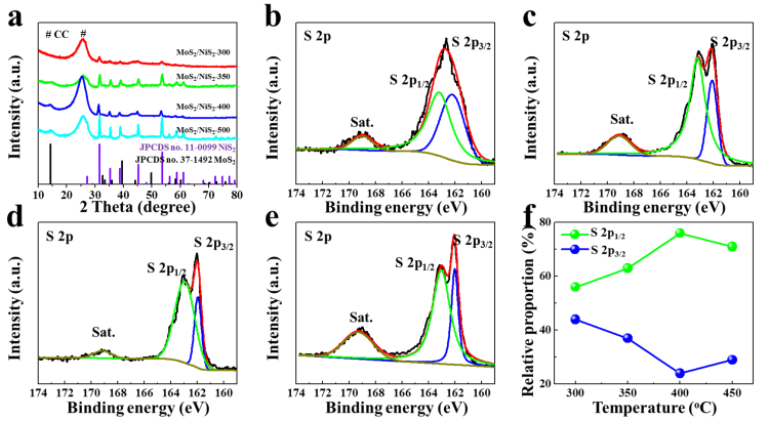

Fig. S7 (a) XRD patterns of obtained samples under different vulcanization temperature. S 2p spectra of samples obtained by different vulcanization temperatures: (b) 300 ^oC, (c) 350 ^oC, (d) 400 ^oC and (e) 500 ^oC. (f) The relative proportion of S $2p_{1/2}$ and S $2p_{3/2}$ of obtained samples under different vulcanization temperature.

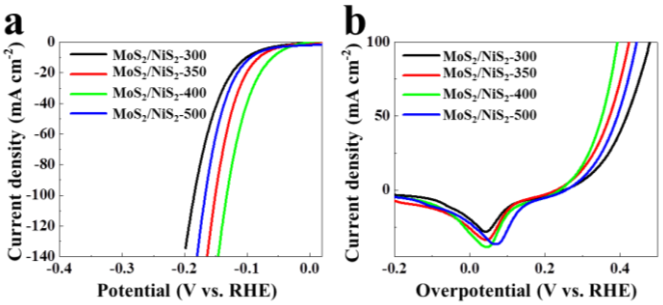

Fig. S8 Polarization curves of MoS_2/NiS_2 obtained at different temperatures for (a) HER and (b) OER.

As for defects, we prepared different samples by simply changing the annealing temperature (300, 350, 400 and 500 ^{o}C, denoted as MoS_2/NiS_2-300, 350, 400, 500), and the sublimed sulfur was fixed at 200 mg. As shown in **Fig. S6**, all samples maintain the nanosheet morphologies. As shown in **Fig. S7a**, all diffraction peaks except for the peak of carbon cloth could be well indexed to NiS_2 and MoS_2. To investigate the sulfur defects, we perform XPS analysis in **Fig. S7b-7f**. For S 2p in each sample, the peak at the lower binding energy is S $2p_{3/2}$ core level from metal-sulfur bonds,[1,2] while S $2p_{1/2}$ at the higher binding corresponds to the sulfur with low coordination that is generally related to sulfur vacancies.[3,4] Accordingly, the S $2p_{1/2}$/S $2p_{3/2}$ surface ratio of obtained samples is shown in **Fig. S7f**. It can be found that the more intensity of S $2p_{1/2}$ and less intensity of S $2p_{3/2}$ are observed, suggesting forming more sulfur defects. When the the annealing temperature reaches 400 ^{o}C, the S $2p_{1/2}$/S $2p_{3/2}$ surface ratio is largest, suggesting the richest sulfur defects in obtained samples. We also tested the HER and OER performances of these obtained samples in **Fig. S8**. The LSV polarization curves show that MoS_2/NiS_2-400 exhibit an admirable alkaline HER and OER performances, which is much better than thoes of other counterparts. These results demonstrate that, to some extent, sulfur defects could provide rich active sites and accelerate electron/mass transfer, resulting in improved catalytic performances.

Reference

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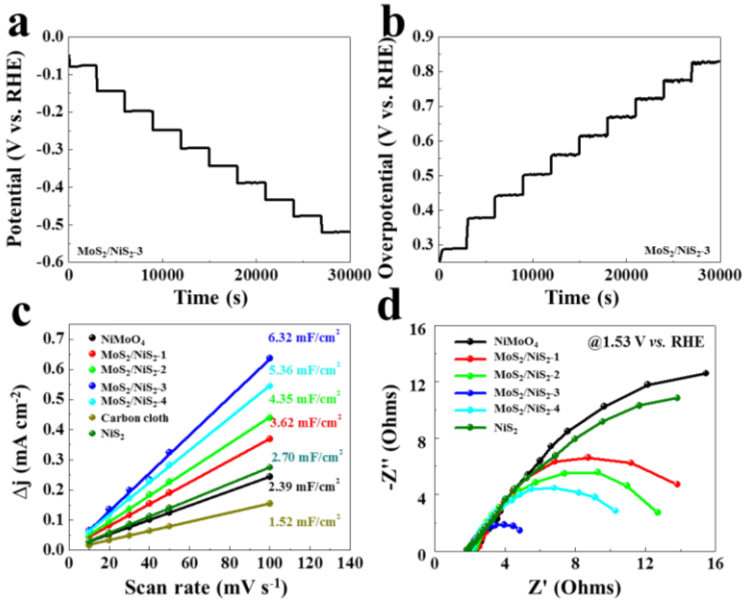

Fig. S9 The chronopotentiometric curves of MoS_2/NiS_2-3 from 10 to 190 mA cm^{-2} with an increment of 20 mA cm^{-2} every 3000 s in (a) HER and (b) OER tests (without iR-correction). (c) The current density against scan rate of obtained samples. (d) The Nyquist plots of obtained samples at 1.53 V vs. RHE.

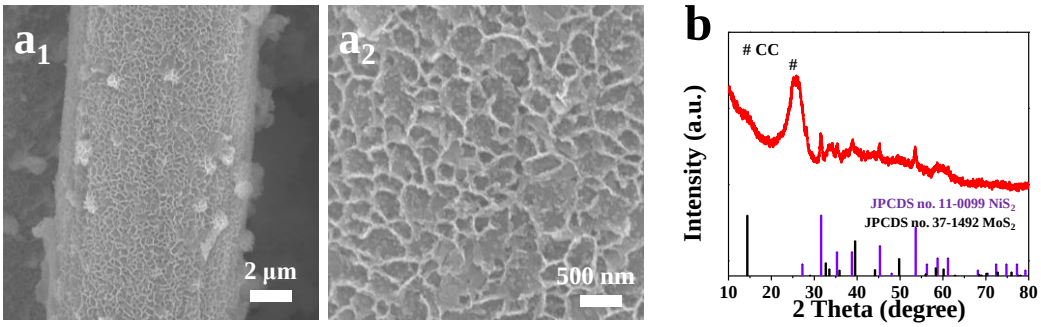

Fig. S10 SEM images and XRD pattern of MoS_2/NiS_2-3 after long-term HER tests.

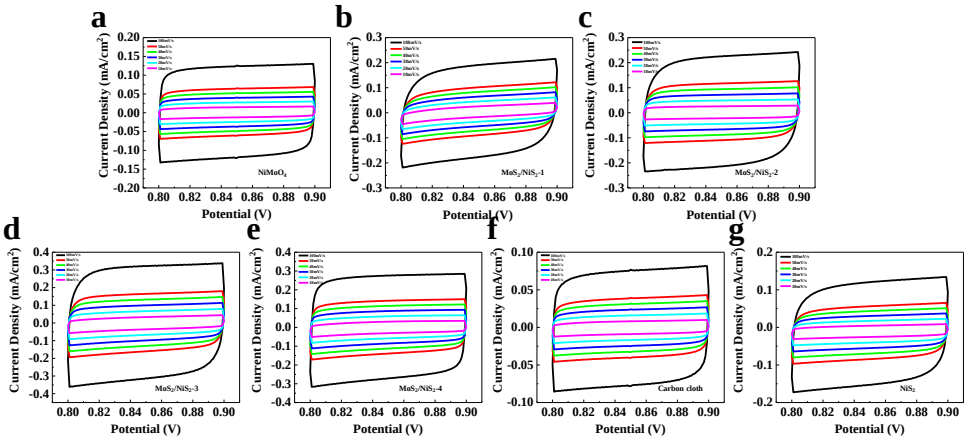

Fig. S11 CV curves of obtained samples in the window of 0.80-0.90 V vs. RHE.

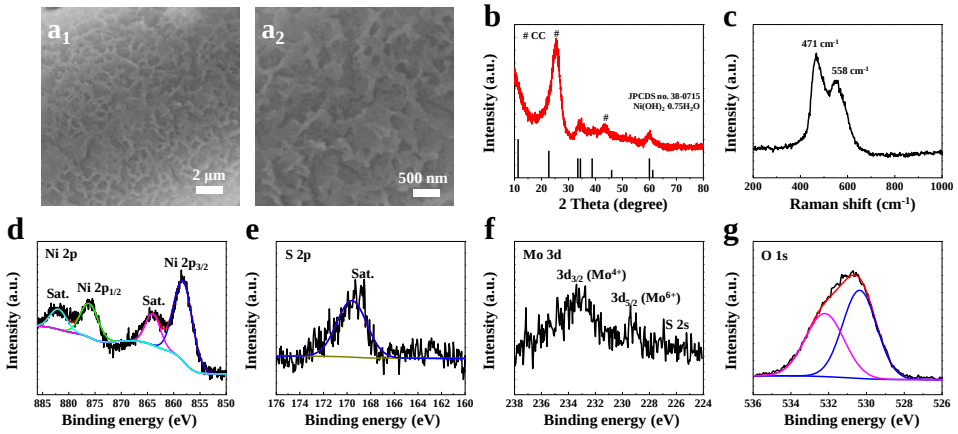

Fig. S12 (a) SEM images, (b) XRD, (c) Raman spectrum and XPS (d) Ni 2p, (e) S 2p, (f) Mo 3d, (g) O 1s spectra of MoS_2/NiS_2-3 after long-term OER tests.

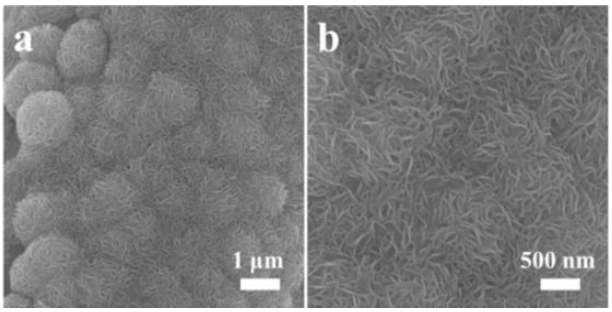

Fig. S13 SEM images of MoS_2 on carbon cloth.

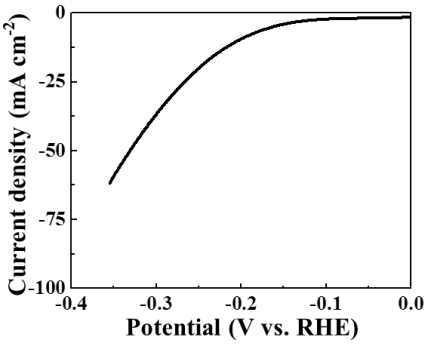

Fig. S14 Polarization curves of MoS for HER.

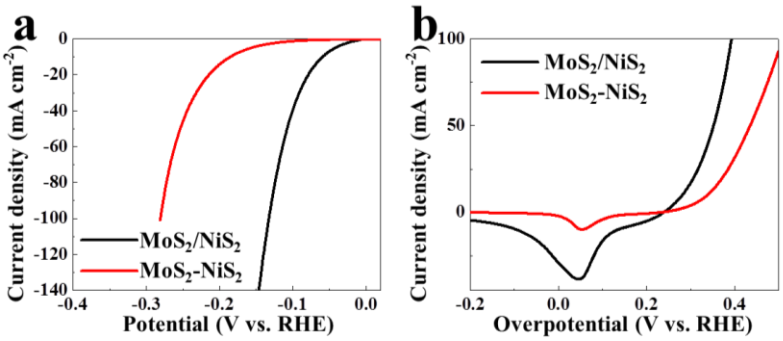

Fig. S15 Polarization curves of MoS_2-NiS_2 and MoS_2/NiS_2 for (a) HER and (b) OER.

We also synthesized pure MoS_2 nanosheets on carbon cloth.[1] Then, we scratched the MoS_2 and NiS_2 powders from the carbon cloth, then mechanically mixed MoS_2 and NiS_2 with the atomic ratio of Mo:Ni =1:1 (denoted as MoS_2-NiS_2). The mechanically mixed MoS_2-NiS_2 powders with mass loading of 1.1 mg cm^{-2} were also prepared on carbon cloth. Finally, we compared the HER and OER performances of MoS_2-NiS_2 and MoS_2/NiS_2. As shown in **Fig. S15**, it can be found that MoS_2/NiS_2 shows much better HER and OER performances than that of mechanically mixed MoS_2-NiS_2 sample. Consequently, these results further demonstrate the effect of the interface, which could enrich the active sites and promote the electronic transfer, and thus boost the sluggish water splitting efficiency.

Reference:

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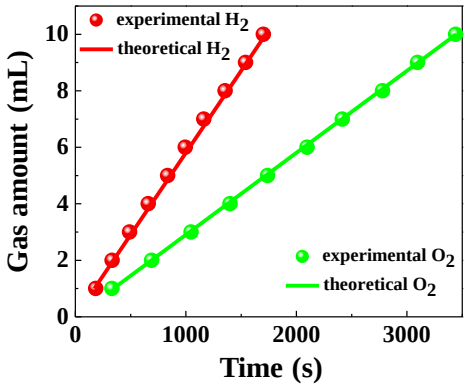

Fig. S16 The theoretical and experimental gas amounts in different time for overall water splitting of optimal MoS_2/NiS_2 nanosheets.

Table S1 Comparison of HER performances for MoS_2/NiS_2 nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
MoS_2/NiS_2	Carbon cloth	62, 108, 131 at 10, 50, 100 mA cm^{-2}	50.1	**This work**
CoP nanowire by oxygen plasma engraving	Carbon cloth	180 at 100 mA cm^{-2}	42.8	*Adv. Mater.* 2018, **30**, 1703322.
Cobalt Selenide	Co foil	268 at 100 mA cm^{-2}	61.4	*Adv. Energy Mater.* 2018, **8**, 1801926.
Ni_2P/Fe_2P	Ti foil	121, ~210 at 10, 100 mA cm^{-2}	67	*Adv. Energy Mater.* 2018, **8**, 1800484
Ni_2P-Ni_3S_2	Ni foam	80, ~175 at 10, 100 mA cm^{-2}	65	*Nano Energy* 2018, **51**, 26.
$Co_5Mo_{1.0}P$ nanoshets	Ni foam	173, 300 at 10, 100 mA cm^{-2}	190.1	*Nano Energy* 2018, **45**, 448.
Partially oxidized Ni nanoparticles	Carbon nanofibers	262, 295, 343, 371 at 10, 20, 50, 80 mA cm^{-2}	97.42	*Nano Energy* 2018, **51**, 286
Co-Ni_3N	Carbon cloth	194 at 10 mA cm^{-2}	156.0	*Adv. Mater.* 2018, **30**, 1705516
$CoNiPS_3$/C nanosheets	Glass carbon	136 at 30 mA cm^{-2}	60	*Adv. Mater.* 2018, **28**, 1805075
Mo-doped Ni_3S_2 nano-rods	Ni foam	180 at 100 mA cm^{-2}	72.9	*J. Mater. Chem. A* 2017, **5**, 1595.
N-Ni_3S_2	Ni foam	110, ~240 at 10, 100 mA cm^{-2}	-	*Adv. Mater.* 2017, **29**, 1701584.
$SrCo_{0.85}Fe_{0.1}P_{0.05}O_{3-\delta}$ nanofilm	Ni foam	110 at 10 mA cm^{-2}	94	*Adv. Mater.* 2018, **30**, 1804333
NC/CuCo/CuCoOx nanowires arrays	Ni foam	112, 190 at 10, 100 mA cm^{-2}	55	*Adv. Funct. Mater.* 2018, **28**, 1704447
TiO_2@Co_9S_8 core-branch arrays	Ni foam	139, ~190 at 10, 50 mA cm^{-2}	65	*Adv. Sci*. 2018, **5**, 1700772
Fe-Ni@NC-CNTs	Glassy carbon dish	202 at 10 mA cm^{-2}	113.7	*Angew. Chem.* 2018, **130**, 9059
Fe doped Ni_3S_2	Ni foam	47, 232 at10, 100 mA cm^{-2}	95	*ACS Catal.* 2018, **8**, 5431.

1. If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.

Table S2 Comparison of OER performances for MoS_2/NiS_2 nanosheets with previsoulsy reported electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential (mV)	Tafel slope (mV dec^{-1})	Ref.
MoS_2/NiS_2	Carbon cloth	278, 352, 393 at 10, 50, 100 mA cm^{-2}	91.7	**This work**
$NiCo_2P_2$/graphene quantum dot	Ti mesh	400 at 100 mA cm^{-2}	65.9	*Nano Energy* 2018, **48**, 284.
Partially oxidized Ni nanoparticles	Carbon nanofibers	420, 470, 560, 630 at 10, 20, 40, 60 mA cm^{-2}	113.1	*Nano Energy* 2018, **51**, 286
Co-Ni_3N	Carbon cloth	307 at 10 mA cm^{-2}	57.0	*Adv. Mater.* 2018, **30**, 1705516
$CoNiPS_3$/C nanosheets	Glass carbon electrodes	262 at 30 mA cm^{-2}	56.0	*Adv. Mater.* 2018, **28**, 1805075
CoS_2 nanotube	Carbon cloth	276 at 10 mA cm^{-2}	81	*Nanoscale Horiz.* 2017, **2**, 342--348
$SrCo_{0.85}Fe_{0.1}P_{0.05}O_{3-\delta}$ nanofilm	Ni foam	310 at 10 mA cm^{-2}	55	*Adv. Mater.* 2018, **30**, 1804333
NiO@Ni/WS_2	Carbon cloth	380 at 50 mA cm^{-2}	108.9	*ACS Cent. Sci.* 2018, **4**, 112.
Fe_2O_3-CoP	Indium tin oxide	302 at 10 mA cm^{-2}	-	*J. Mater. Chem. A*, 2018, **6**, 4783.
Mo-CoOOH	Carbon cloth	305, 365 at 10, 100 mA cm^{-2}	56	*Nano Energy* 2018, **48**, 73.
Fe-Ni@NC-CNTs	Glassy carbon dish	274 at 10 mA cm^{-2}	45.5	*Angew. Chem.* 2018, **130**, 9059
Mo-NiOOH	Ni foam	390 at 100 mA cm^{-2}	68	*Int. J. Hydrogen Energy* 2018, **43**, 12140.
NiCoP cone shaped nanowire	Ni foam	370 at 100 mA cm^{-2}	116	*J. Mater. Chem. A* 2017, **5**, 14828.
Co_3O_4-N-C frameworks	Glassy carbon	324 at 10 mA cm^{-2}	69	*Nano Energy* 2018, **48**, 600
Ni_3S_2@MoS_2/FeOOH	Ni foam	260 at 10 mA cm^{-2}	49	*Appl. Catal. B* 2019, **244**, 1004.
$Fe_{0.09}Co_{0.13}$-$NiSe_2$ nanosheets	Carbon cloth	251 at 10 mA cm^{-2}	63	*Adv. Mater.* 2018, 30, 1802121

1.If not metioned specifically, all overpotentials were corrected with iR compensation. 2. If not metioned specifically, all electrocatalysts are directly synthesized on conductive substrates.