Supporting Information

Construction of Hierarchical Yolk-Shell Nanospheres Organized by Ultrafine Janus Subunits for Efficient Overall Water Splitting

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Materials: PAA ($M_W \approx 1800$) was purchased from Sigma-Aldrich (USA). Nickel chloride hexahydrate ($NiCl_2.4H_2O$, 98.0%), Isopropyl alcohol (IPA), aqueous ammonia solution ($NH_3 \cdot H_2O$), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and S powders were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd and used without further purification. Deionized water was used in all experiments.

Synthesis of $Ni(OH)_2$/Mo-PAA NSs： In a 250 mL conical flask, a PAA aqueous solution (0.2 g mL^{-1}, 400 μL), $NH_3 \cdot H_2O$ (2 mol L^{-1}, 400 μL) and 150 mg $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were added in deionized water (50 mL) and ultrasonically dispersed for 30 min. After that, IPA (200 mL) was dripped to the flask under magnetic stirring to form a suspension. Subsequently, 90 mg $NiCl_2 \cdot 4H_2O$ was added into the suspension under magnetic stirring for more than 1 h to obtain the $Ni(OH)_2$/Mo-PAA NSs. The obtained $Ni(OH)_2$/Mo-PAA NSs were centrifuged and dried at 50 °C for 24 h for further experiment.

Synthesis of $NiMoO_4$ NSs: The highly dispersed Ni-Mo/PAA-NH_4 NSs were annealed from room temperature to 500 °C at a heating rate of 2 °C min^{-1} and then maintained at 500 °C for 3 h in a furnace under the air to obtain the $NiMoO_4$ NSs.

Synthesis of NiS_2/MoS_2 NSs: The as-synthesized $NiMoO_4$ NSs and S powders were put at two independent porcelain-boats with 500 mg S and 50 mg $NiMoO_4$ at the upstream and downstream side of the furnace, respectively, then the furnace was allowed to anneal at 350 °C for 1 h with a ramp rate of 2 °C min^{-1} under argon atmosphere to obtain the NiS_2/MoS_2 NSs.

Synthesis of NiS_2 Nanoparticls: The procedure to fabricate NiS_2 nanoparticls are almost the same with NiS_2/MoS_2 NSs, except the addition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

Synthesis of MoS_2 Nanosheets: 0.3 mmol $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 12 mmol CHN_2S were mixed into 70 mL distilled water and stirred for 20 min, then the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h to obtain the MoS_2 nanosheets.

Characterization: Transmission electron micrographs (TEM) were taken by JEOLJEM-2100F transmission electron microscope under a 200 kV accelerating voltage. High-resolution TEM (HRTEM) characterizations were recorded by a TECNAI G2 F20 transmission electron microscope under 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were obtained by using an XL30 ESEM-FEG field-emission scanning electron microscope (FEI Co.). X-ray diffraction (XRD) patterns were obtained on a D8 Focus diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was performed with an ECSALAB 250 by using non-monochromated Al Kα radiation. N_2 adsorption-desorption measurements were measured using an intelligent gravimetric analyser Autosorb-iQ (Quantachrome).

Electrochemical Tests: 5 mg of the prepared catalysts powder and 10 μL of Nafion (5 wt %) were added in 1 mL of 4/1(v/v) water/ethanol solution, which was a sonication treatment for 30 min to get homogeneous inks. Then, 5 μL of the mixed solution was drop-cast onto a glassy carbon electrode (GCE) with a diameter of 3 mm for the electrochemical measurements. All electrochemical experiments were performed in a three-electrode system at room temperature using a CHI760E electrochemical workstation. Catalyst-modified GCE, graphite rod, a saturated calomel electrode (SCE, 0.241V vs. RHE) were used as the working electrode, counter electrode and reference electrode, respectively. LSV curves were measured deaerated with nitrogen with a scan rate of 5 mV s^{-1} in 1 M KOH aqueous solution at 25 °C prior to the HER and overall water splitting measurements. And the 1 M KOH aqueous

solution was purged with O_2 prior to the OER test. The catalysts were activated using 20 CV scans with a scan rate of 100 mV s^{-1} before recording the electrochemical performance.

All plots displayed were calibrated to a (RHE) based on the equation ($E_{RHE} = E_{SCE} + 0.059$ pH + 0.241) and corrected against the iR compensation. EIS was carried out in potentiostatic mode from 0.1 to 10^5 Hz with AC voltage amplitude of 10 mV. In order to explore the changes in morphology and structure for NiS_2/MoS_2 NSs after the stability test, we fabricated the electrode by loading NiS_2/MoS_2 NSs on commercial carbon cloth (1 cm × 1 cm, mass loading: 3 mg cm^{-2}).

The ECSA was calculated through performing the capacitive current associated with double-layer charging from the scan-rate dependence of CVs. The CVs measurements were taken in non-faradic potential window with different scan rate. The C_{dl} of the samples were estimated by plotting the $\Delta J = J_a - J_c$ against the CV scan rate, The linear slope of curves is equivalent to twice of the double-layer capacitance C_{dl}, and the C_{dl} is proportional to the ECSA.

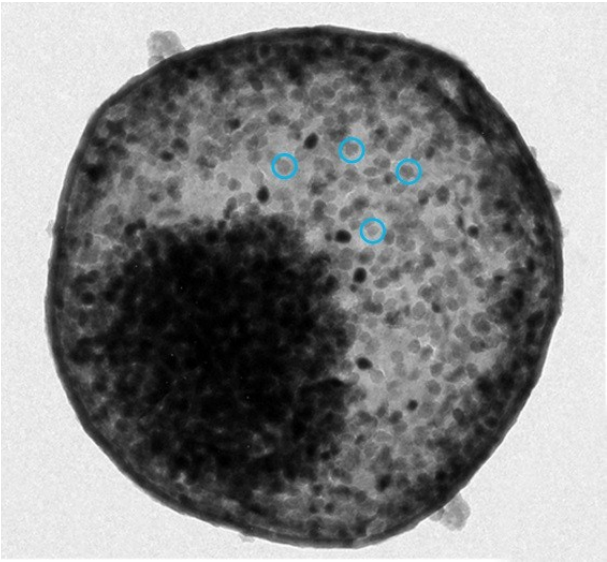

Fig. S1. TEM image of a single $NiMoO_4$ yolk-shell NS.

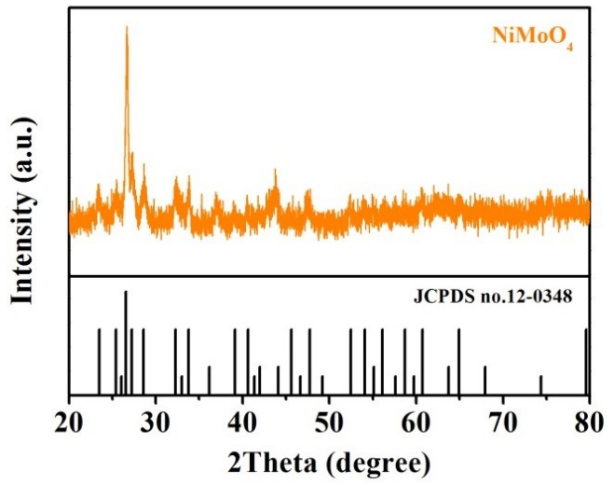

Fig. S2. XRD pattern of the $NiMoO_4$ yolk-shell NSs.

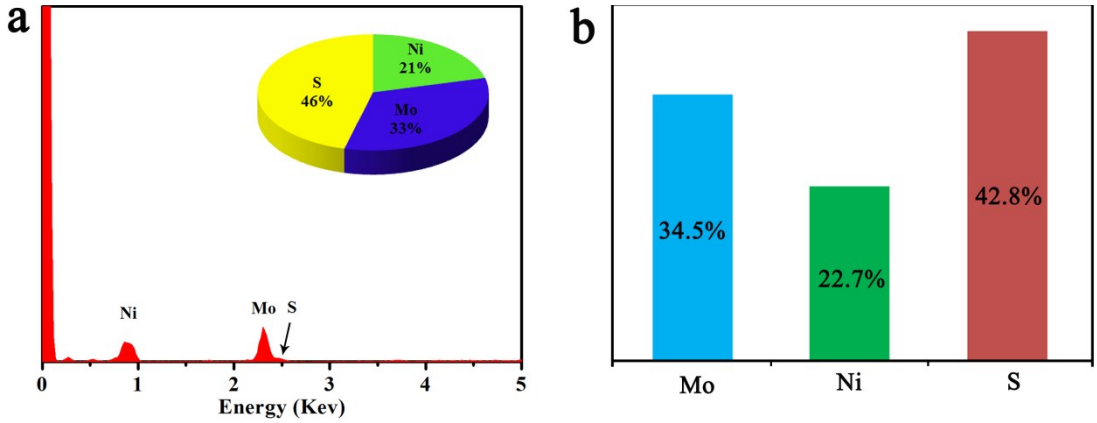

Fig. S3. (a) Energy dispersive X-ray spectrum of NiS_2/MoS_2 yolk-shell NSs. The inset shows the atomic (Ni, Mo and S) contents of NiS_2/MoS_2 yolk-shell NSs. (b) ICP-AES results of NiS_2/MoS_2 yolk-shell NSs.

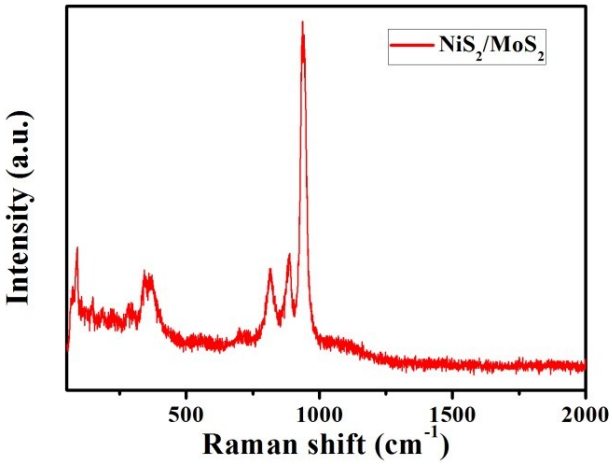

Fig. S4. Raman spectrum of the NiS_2/MoS_2 yolk-shell NSs.

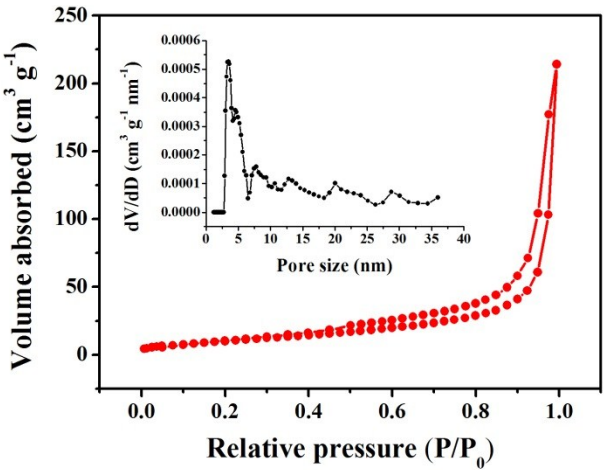

Fig. S5. N_2 adsorption-desorption isotherms and pore size distribution (inset) of NiS_2/MoS_2 yolk-shell NSs.

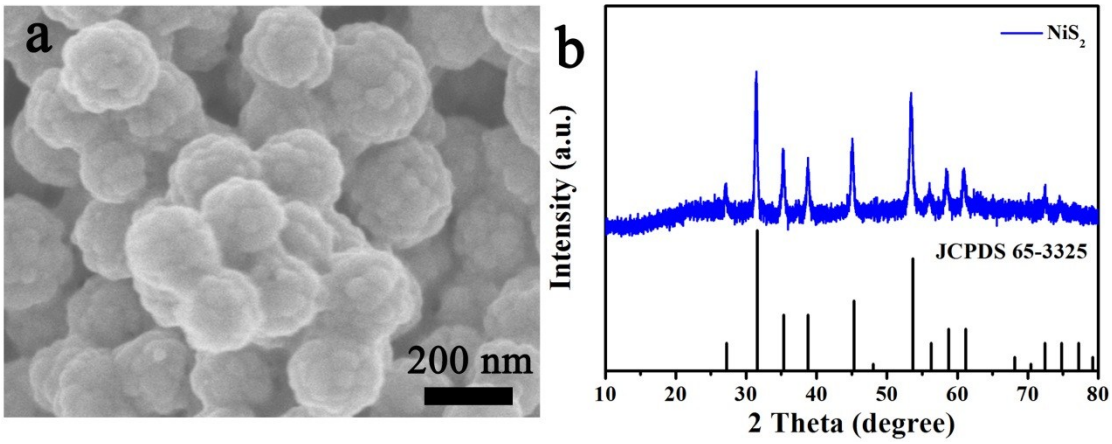

Fig. S6. (a) SEM image, (b) XRD pattern of NiS_2 nanoparticles.

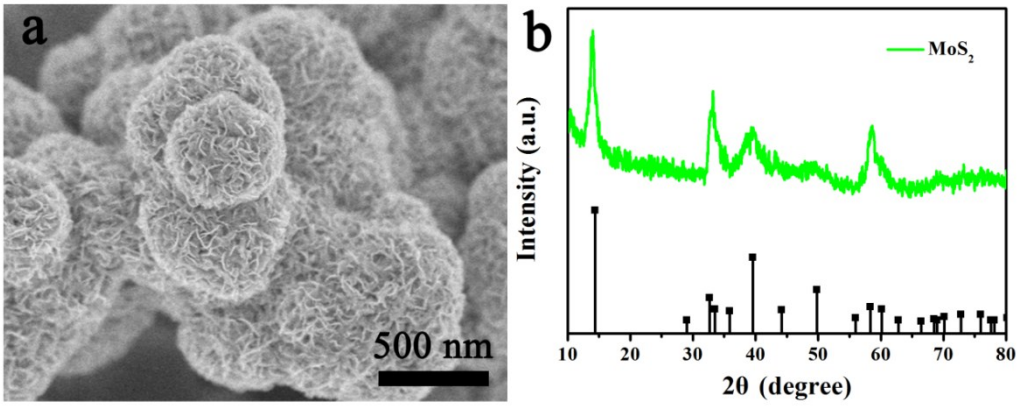

Fig. S7. (a) SEM image, (b) XRD pattern of MoS_2 nanosheets.

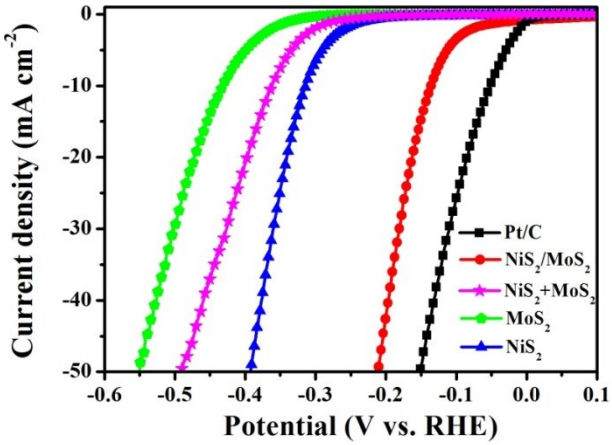

Fig. S8. Polarization curves of NiS_2/MoS_2, NiS_2 + MoS_2, MoS_2, NiS_2 and Pt/C electrodes at a scan rate of 5 mV s^{-1} for the HER in 1.0 M KOH.

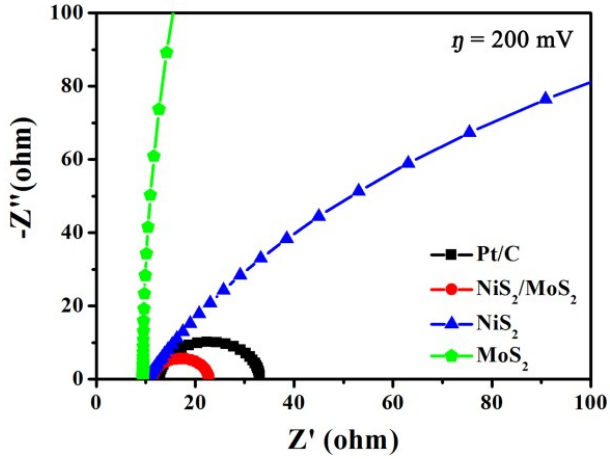

Fig. S9. Nyquist plots of EIS of NiS_2/MoS_2, MoS_2, NiS_2 and Pt/C obtained in 1 M KOH aqueous solutions at an overpotential of 200 mV.

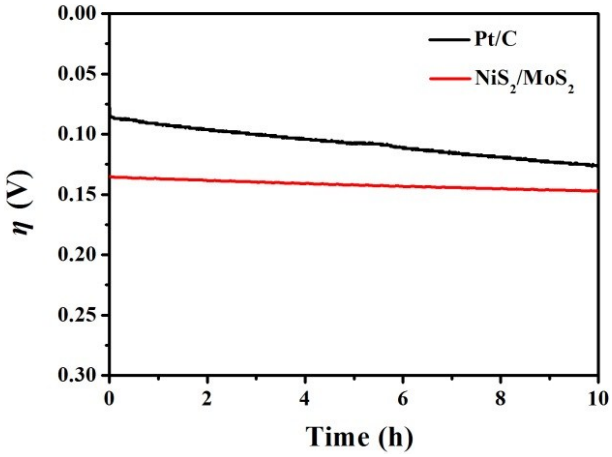

Fig. S10. Time-dependent overpotential of NiS_2/MoS_2 yolk-shell NSs electrode and commercial Pt/C with a constant current density of 10 mA cm^{-2} in 1.0 M KOH.

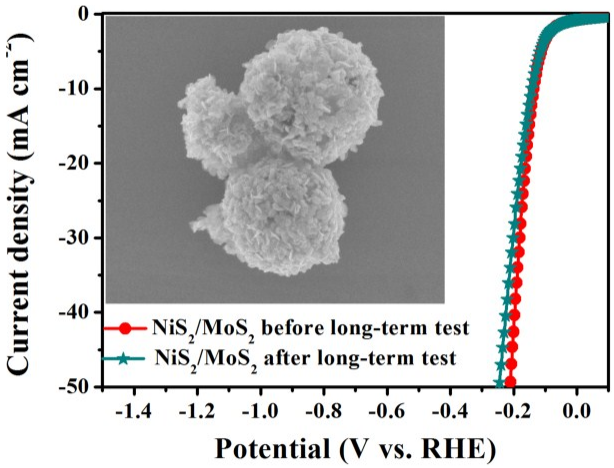

Fig. S11. Polarization curves of NiS_2/MoS_2 yolk-shell NSs before and after long-term HER tests in 1.0 M KOH, inset: the corresponding SEM image after long-term HER tests.

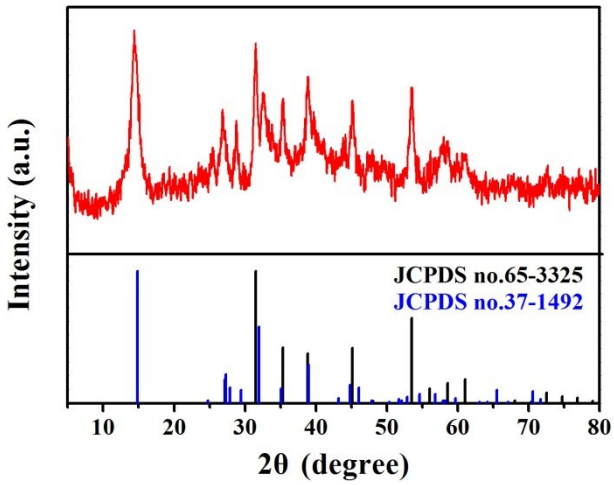

Fig. S12. The XRD pattern of NiS_2/MoS_2 yolk-shell NSs after HER test.

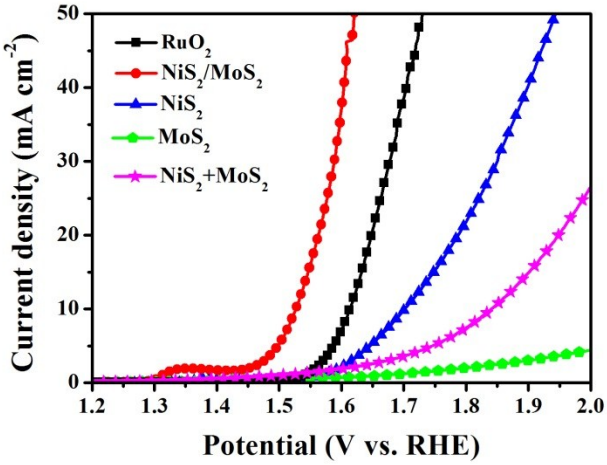

Fig. S13. Polarization curves of NiS_2/MoS_2, NiS_2 + MoS_2, MoS_2, NiS_2 and RuO_2 electrodes at a scan rate of 5 mV s^{-1} for the OER in 1.0 M KOH.

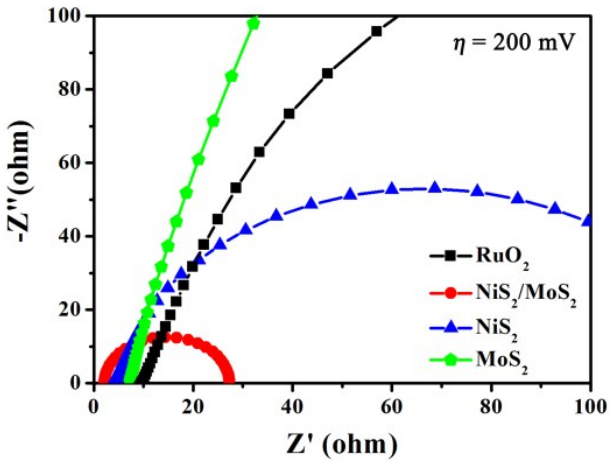

Fig. S14. EIS Nyquist plot of different electrodes recorded at the same applied voltage (1.43 V *vs*. RHE).

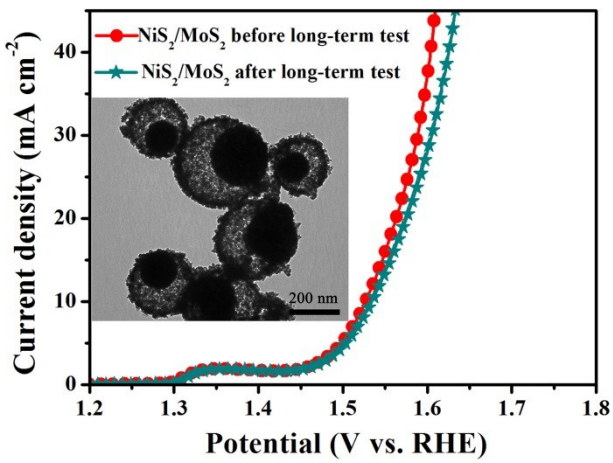

Fig. S15. Polarization curves of NiS_2/MoS_2 yolk-shell NSs before and after long-term OER test in 1.0 M KOH, inset: the corresponding TEM image after long-term HER test.

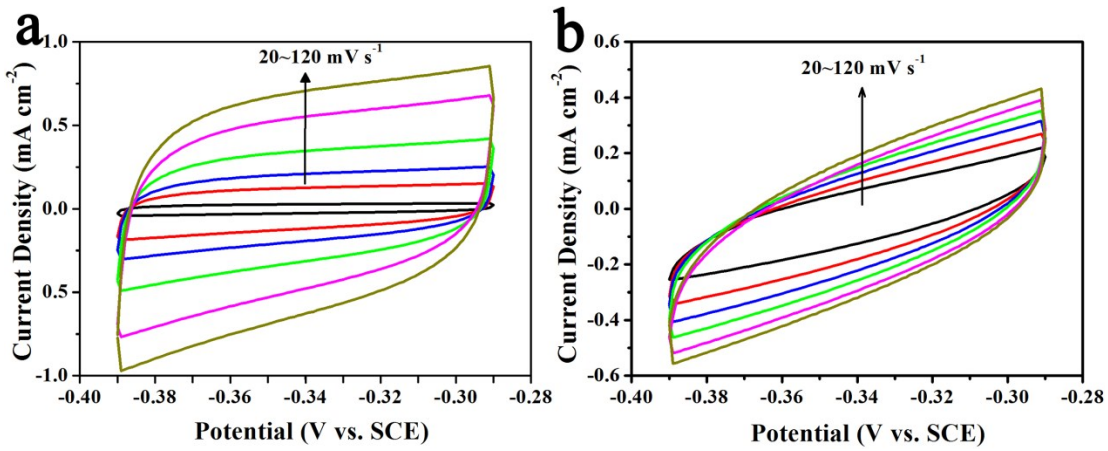

Fig. S16. CVs curves of (a) NiS_2 nanoparticles and (b) MoS_2 nanosheets in 1 M KOH.

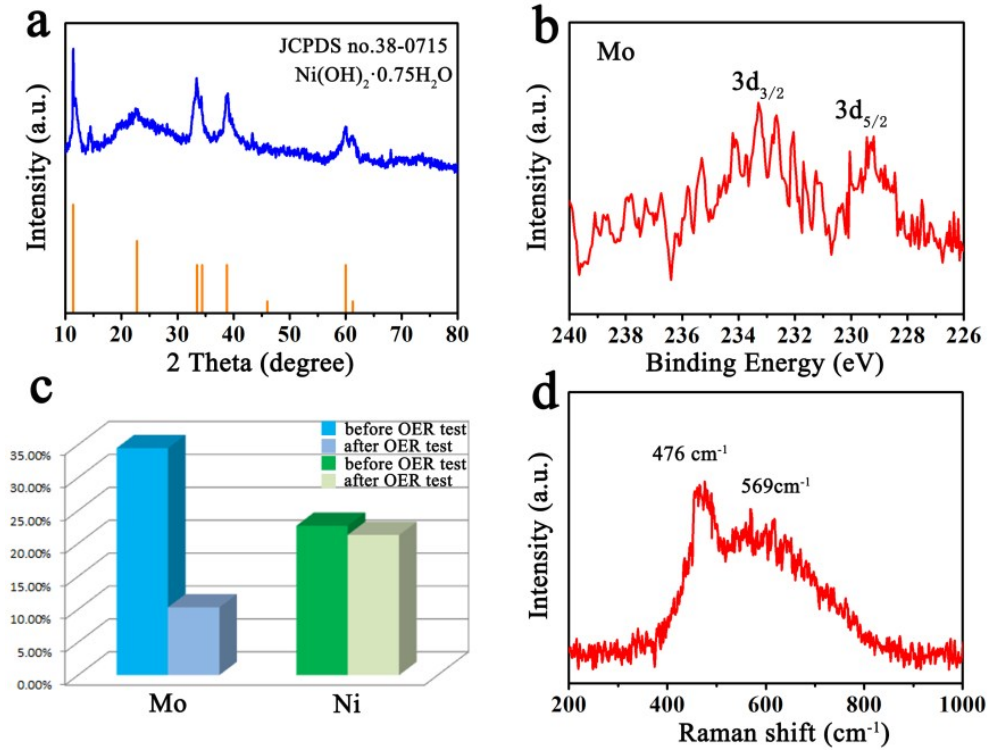

Fig. S17. (a) XRD, (b) XPS spectrum of Mo 3d, (c) ICP-AES results and (d) Raman spectrum of NiS_2/MoS_2 yolk-shell NSs after long-term OER tests.

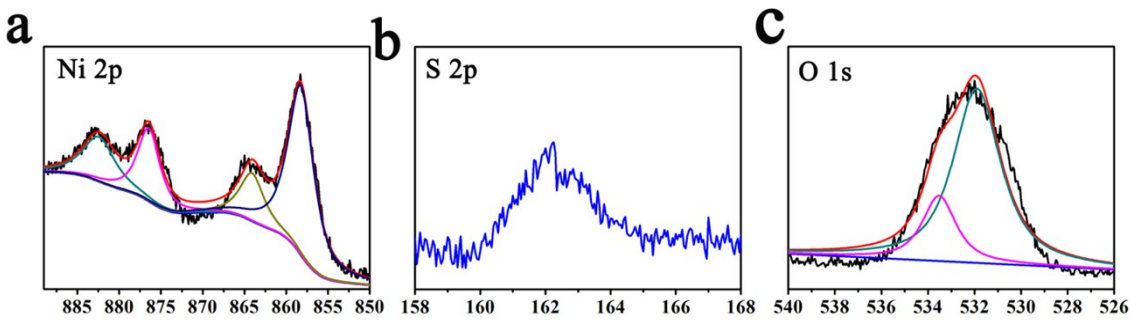

Fig. S18. XPS (a) Ni 2p, (b) S 2p, (c) O 1s spectra of NiS_2/MoS_2 yolk-shell NSs after long-term OER tests.

Table S1. Comparison of the HER performance of NiS_2/MoS_2 yolk-shell NSs with other electrocatalysts

Catalysts	η_{10} (mV)	Tafel slope (mV·dec^{-1})	Electrolytes	Refs.
NiS_2/MoS_2 NSs	135	82	1 M KOH	this work
Ni@NC-800	205	160	1 M KOH	*Adv. Mater.* **2017**, 29, 1605957
$Ni/Ni_2P/Mo_2C$@C	183	66	1 M KOH	*J. Mater. Chem. A* **2018**, 6, 5789
Co phosphide/phosphate	430	—	1 M KOH	*Adv. Mater.* **2015**, 27, 3175
NiFe LDHNS@DG10	300	110	1 M KOH	*Adv. Mater.* **2017**, 29, 1700017
$Ni_{1.5}Fe_{0.5}P$	282	125	1 M KOH	*Nano Energy* **2017**, 34, 472
$Ni_{12}P_5$	270	—	1 M KOH	*ACS Catal.* **2017**, 7, 103
c-$CoSe_2$/CC	190	85	1 M KOH	*Adv. Mater.* **2016**, 28, 7527
$NiMo_3S_4$	252	98	0.1 M KOH	*Angew. Chem. Int. Ed.* **2016**, 55, 1–6
ONPPGC/ OCC	446	154	1 M KOH	*Energy Environ. Sci.* **2016**, 9, 1210−1214
$Ni_{1-x}Fe_x$/NC	230	111	1 M KOH	*ACS Catal.* **2016**, 6, 580–588
$NiCo_2S_4$@NiFe LDH/NF	200	101	1 M KOH	*ACS Appl. Mater. Interfaces.* **2017**, 9 15364
Co-NRCNTs	370	—	1 M KOH	*Angew. Chem. Int. Ed.*

				2014, 53, 4372

Table S2. Comparison of the OER performance of NiS_2/MoS_2 NSs with other electrocatalysts

Catalysts	η_{10} (mV)	Tafel slope (mV·dec^{-1})	Electrolytes	Refs.
NiS_2/MoS_2 NSs	293	102.3	1 M KOH	this work
Ni/Mo_2C-PC	368	—	1 M KOH	*Chem. Sci.* **2017**, 8, 968
NiCo LDH	367	183	1 M KOH	*Nano Lett.* **2015**, 15, 1421
$Co_3O_4/NiCo_2O_4$	340	88	1 M KOH	*J. Am. Chem. Soc.* **2015**, 137, 5590
NiFe LDHNS@DG10	300	110	1 M KOH	*Adv. Mater.* **2017**, 29, 1700017
CoO/NG	340	71	1 M KOH	*Energy Environ. Sci.* **2014**, 7, 609
NiCo(OH)x	410	109	1 M KOH	*Adv. Energy Mater.* **2015**, 5, 1401880
c-$CoSe_2$/CC	190	85	1 M KOH	*Adv. Mater.* **2016**, 28, 7527
$NiMoP_2$	330	90.6	1 M KOH	*J. Mater. Chem. A* **2017**, 5, 7191