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Dimensional construction and morphological tuning of heterogeneous MoS_2/NiS electrocatalysts for efficient overall water splitting

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Experimental section

Materials

All the reagents in the experiment were analytical grade and used without any further treatment. N-hexane, n-pentanol and ethanol were purchased from Real&Lead Chemical Co., Ltd. Molybdic acid, thiurea, potassium hydroxide, CTAB and AOT were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Preparation of MoS_2/NiS heterogeneous catalysts

A simple solvethermal reaction followed by sulfurization annealing process is adopted for the synthesis of MoS_2/NiS catalysts. At first, 15 mL n-hexane and 1 mL n-pentanol were mixed with ultrapure water to form the solvent solution. For MoS_2/NiS NCs, 90 mg molybdic acid, 0.4 g CTAB and 0.2 g AOT were dissolved in the mixed solvent solution under continuous stirring. A piece of cleaned nickel foam (1 cm × 2 cm) and the mixed solution were together transferred to a 40 mL Teflon-lined autoclave and heated at 150 °C for 2 h. The nickel foam was washed with ethanol after reaction and dried in a vacuum oven. MoS_2/NiS NCs was obtained by the surfurization of as-prepared nickel foam at 450 °C in N_2 with thiurea as sulfur source. Same procedure was used to prepare MoS_2/NiS AGs with only addition of AOT and MoS_2/NiS NWs with only addition of CTAB. A cleaned nickel foam was directly treated by the same surfurization process without solvothermal reaction to obtain NiS for comparison

Material characterization

X-ray powders diffraction (XRD) was carried out by a PANalytical X'Pert Pro (Cu K_α radiation, λ=1.54056 Å). The morphology of samples was studied by scanning electron microscopy (SEM) (Hitachi S4800, Japan) with an energy dispersive spectroscopy detector (EDS). Transmission electron microscopy (TEM) was performed on JEM 3100 (JEOL, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analyses were conducted with a Physical Electronics PHI5802 instrument using X-rays magnesium anode (monochromatic K_α X-rays at 1253.6 eV) as the source. Nitrogen adsorption was conducted at 77 K using a BEL-mini instrument (BEL Inc., Japan), the specific surface area was obtained by Brunauer-Emmett-Teller (BET) analyses of the adsorption/desorption isotherm.

Electrochemical measurement

All the electrochemical measurements were performed on CHI660E (Shanghai Chenhua, China) electrochemical workstation in a three electrodes system. The as-prepared foam-like catalysts cast with Nafion solution (5%) were directly served as working electrode with graphite rod (φ=6 mm) as counter electrode and Hg/HgO as reference electrode. Linear sweep voltammetry (LSV) was measured for both HER and OER at a scan rate of 2 mV s^{-1} in 1 M KOH to evaluate the catalytic activity. Cyclic voltammogram (CV) scanning from 0.1 to 0.2 V vs. RHE was conducted to evaluate the electrochemical active surface areas of the catalyst. Chronopotentiometry was performed at a constant current density of 10 mA cm^{-2} for HER and 15 mA cm^{-2} for OER in 1 M KOH solution. Electrochemical impedance spectroscopy (EIS) was measured at an overpotential of 150 mV for HER and 300 mV for OER from 0.1 Hz to 100 kHz with an amplitude of 5 mV. The overall water splitting performance was evaluated in a two-electrode configuration, and the LSV curve was recorded at a scan rate of 2 mV s^{-1}. The electrolyte should be bubbled using N_2 for 0.5 h before all electrochemical test. All the potentials were transformed to potentials vs RHE based on equation E (vs. RHE) = E (vs. Hg/HgO) + 0.0977 + 0.05916 × pH. Only the LSV and Tafel curves were reported with IR compensation.

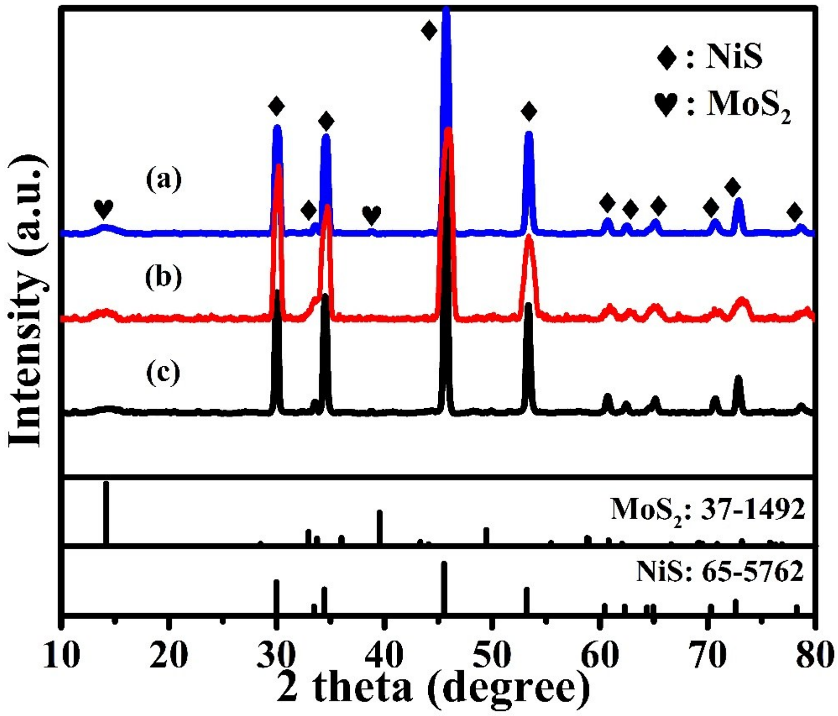


Fig. S1 XRD patterns of (a) MoS_2/NiS NCs, (b) MoS_2/NiS NWs, (c) MoS_2/NiS AGs.

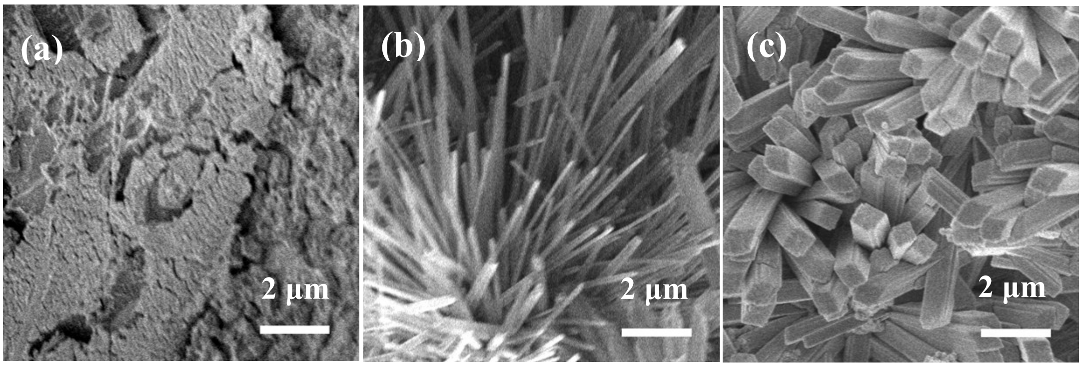


Fig. S2 SEM images of precursors (a) MoS_2/NiS AGs, (b) MoS_2/NiS NWs, (c) MoS_2/NiS NCs.

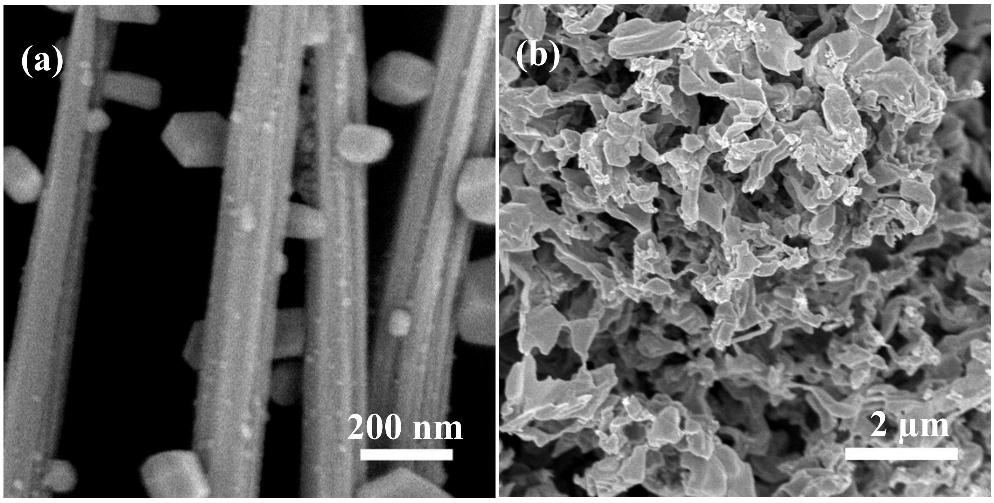


Fig. S3 SEM images of (a) MoS_2/NiS NWs, (b) MoS_2/NiS AGs.

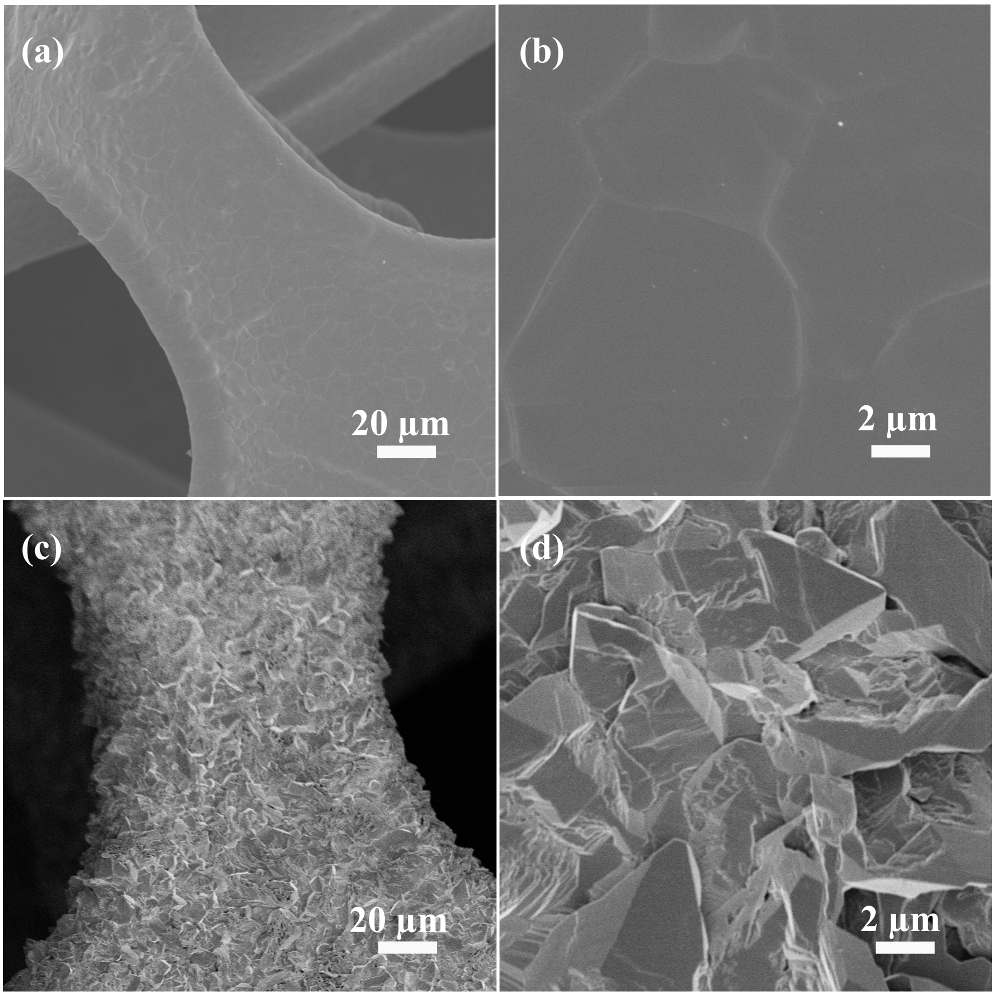


Fig. S4 SEM images of (a, b) bare Ni foam and (c, d) bare NiS foam.

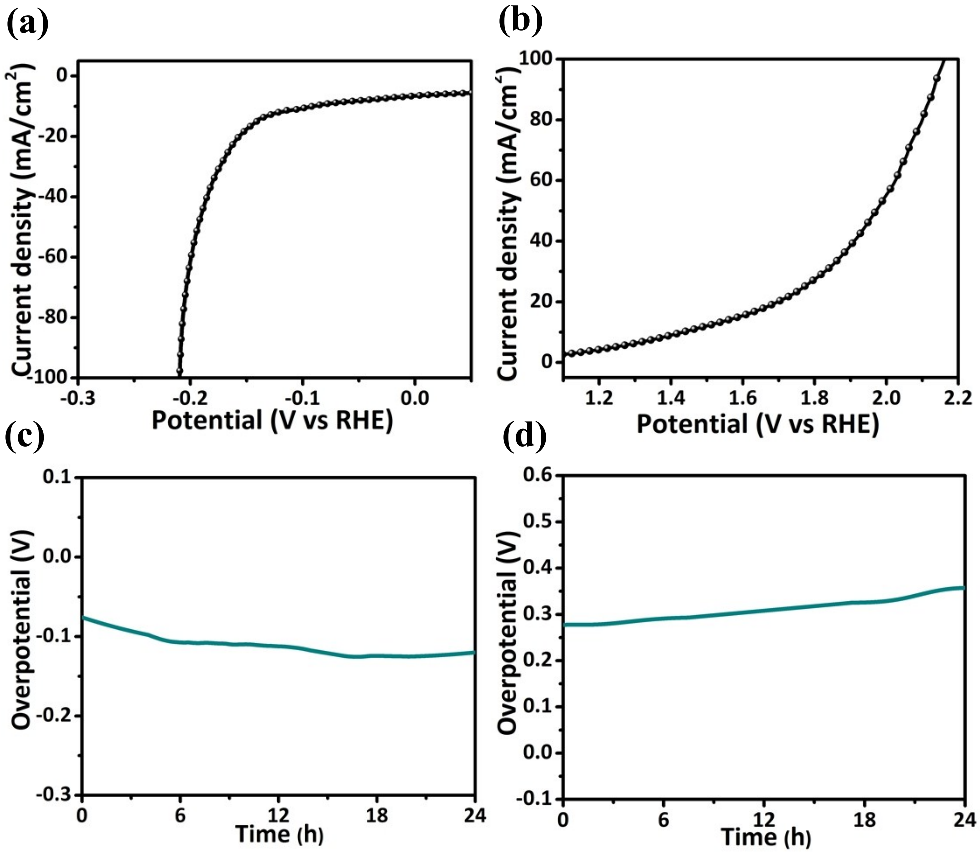


Fig. S5 (a) HER and (b) OER performance of MoS_2/NiS NCs in 0.5 M H_2SO_4. Chronopotentiometric curve at a current density of 10 mA cm^{-2} for (c) HER (d) OER in 0.5 M H_2SO_4 without IR correction.

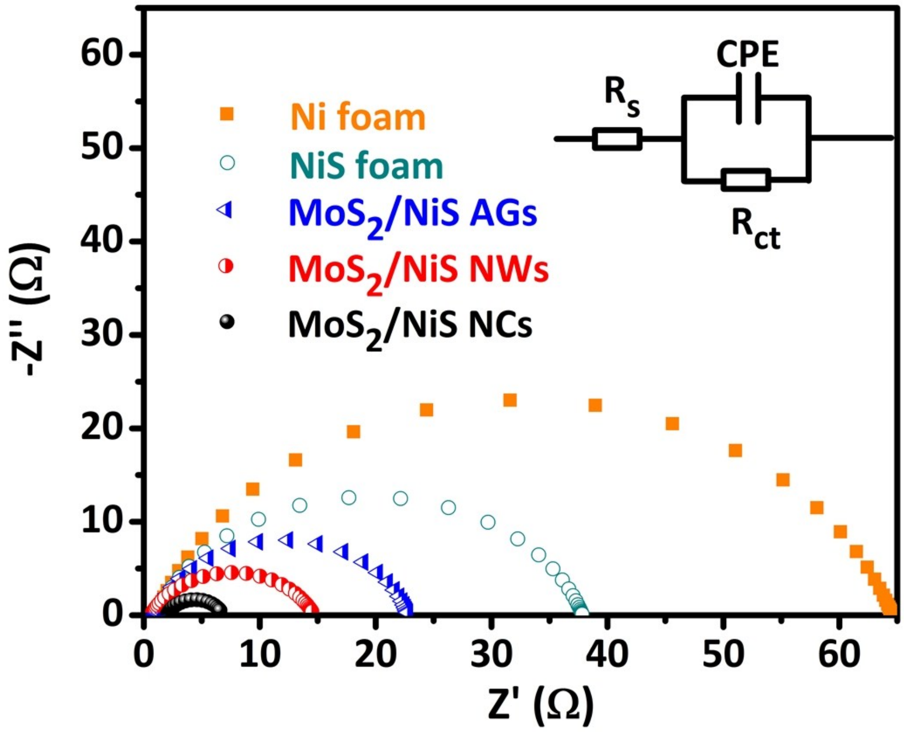


Fig. S6 HER Nyquist plots of MoS_2/NiS NCs, MoS_2/NiS NWs, MoS_2/NiS AGs, NiS foam and Ni foam under 150 mV (versus 0 V) overpotential.

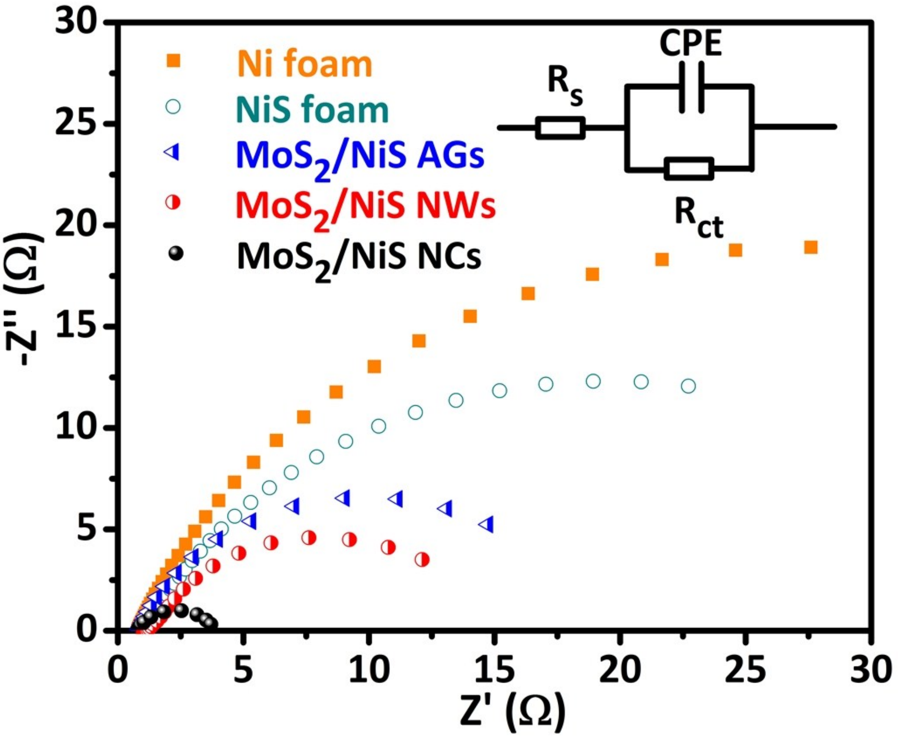


Fig. S7 OER Nyquist plots of MoS_2/NiS NCs, MoS_2/NiS NWs, MoS_2/NiS AGs, NiS foam and Ni foam under 300 mV (versus 1.23 V) overpotential.

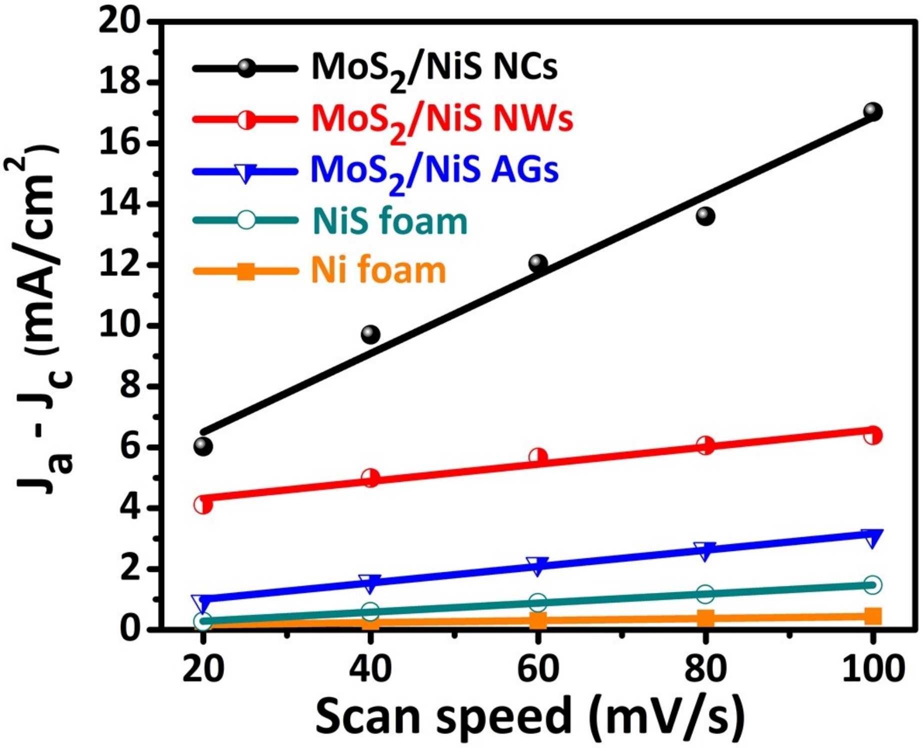


Fig. S8 Estimation of Cdl at 150 mV vs RHE obtained from the cyclic voltammogram.

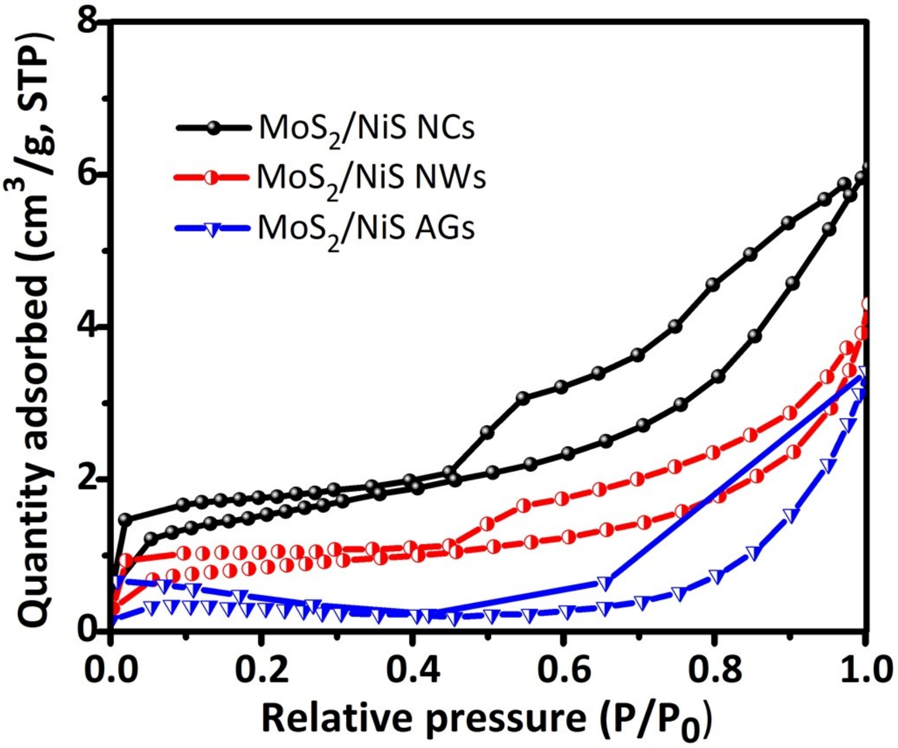
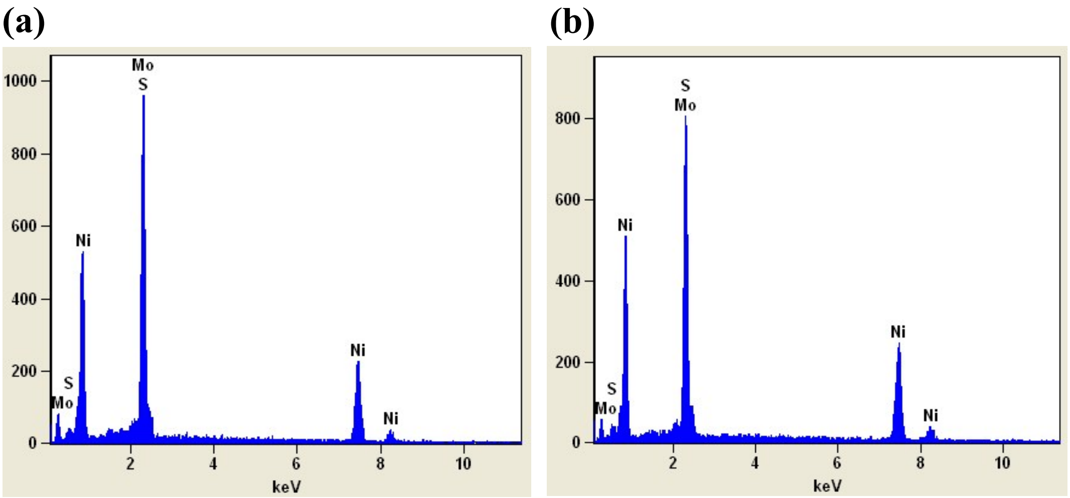
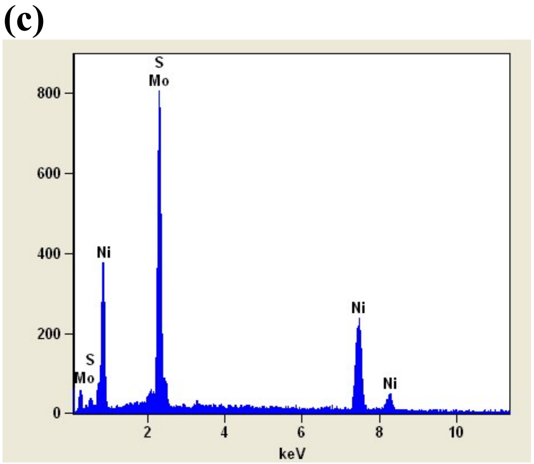


Fig. S9 Nitrogen adsorption-desorption isotherms of MoS$_2$/NiS NCs, MoS$_2$/NiS NWs, MoS$_2$/NiS AGs.





(d)

Samples	Mo/Ni radio
MoS_2/NiS NCs	0.100
MoS_2/NiS NWs	0.093
MoS_2/NiS AGs	0.071

Fig. S10 EDS analysis of (a) MoS_2/NiS AGs, (b) MoS_2/NiS NWs, (c) MoS_2/NiS NCs. (d) Mo/Ni radio of as-prepared samples.

Table S1. Comparison of the electrocatalytic performance and stability for transition metals sulfides-based electrocatalysts.

Catalyst	Current Density (*j*)		Overpotential at Corresponding *j*	Cell Voltage	Stability test	Ref
$NiCo_2S_4$ nanowires on Ni foam	10 mA cm^{-2}	HER	210 mV		50 h	1
	15 mA cm^{-2}	OER	~320 mV		50 h (~20mA cm^{-2})	
	10 mA cm^{-2}	OWS		1.63 V	50 h	
NiS sheres on Ni foam	20 mA cm^{-2}	HER	158 mV		20 h	2
	50 mA cm^{-2}	OER	335 mV		20 h (~20mA cm^{-2})	
	10 mA cm^{-2}	OWS		1.64 V	30 h (~13mA cm^{-2})	
Interface Engineered MoS_2/Ni_3S_2	10 mA cm^{-2}	HER	110 mV		10 h	3
	15 mA cm^{-2}	OER	~240 mV		10 h	
	10 mA cm^{-2}	OWS		1.56 V	10 h	
$Ni_xCo_{3-x}S_4$ / Ni_3S_2 sheets on Ni foam	10 mA cm^{-2}	HER	136 mV		50 h	4
	15 mA cm^{-2}	OER	~275 mV		30 h	
	10 mA cm^{-2}	OWS		1.53 V	200 h	
MoS_2/Ni_3S_2 nanorods	10 mA cm^{-2}	HER	98 mV		48 h	5
	15 mA cm^{-2}	OER	~270 mV		48 h	
	10 mA cm^{-2}	OWS		1.50 V	48 h	
V-doped NiS_2	10 mA cm^{-2}	HER	110 mV		20 h	6
	15 mA cm^{-2}	OER	~200 mV		20 h	
	10 mA cm^{-2}	OWS		~ 1.60 V	20 h	
WS_2/ Co_9S_8	20 mA cm^{-2}	HER	138 mV			7
	15 mA cm^{-2}	OER	~265 mV			
	10 mA cm^{-2}	OWS		1.65 V	24 h	
N-doped Ni_3S_2 on Ni foam	10 mA cm^{-2}	HER	110 mV		10 h	8
	100 mA cm^{-2}	OER	330 mV		10000s (~50 mA cm^{-2})	
	10 mA cm^{-2}	OWS		1.48 V	10 h (~85 mA cm^{-2})	
MoS_2/NiS NCs	**10 mA cm^{-2}**	**HER**	**92 mV**		**80h**	**This work**
	15 mA cm^{-2}	**OER**	**272 mV**		**80h**	
	10 mA cm^{-2}	**OWS**		**1.61V**	**45h (~15 mA cm^{-2})**	

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