Supporting Information

Tailorable Surface Sulfur Chemistry of Mesoporous Ni_3S_2 Particles for Efficient Oxygen Evolution

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Part I: Experimental Section

1.1 Synthesis of the sulfur-engineered Ni_3S_2 electrocatalyst

Prior to use, nickel foams (0.5 cm × 0.6 cm × 0.3 mm) were immersed in 3 M HCl for 15 min to clean the surface. The sulfur-engineered Ni_3S_2 electrocatalyst was prepared by a low temperature hydrothermal method. Typically, 0.3 g of L-Cysteine was put into 20 mL of deionized water with strong stirring for 15 min to form a homogenous solution. Subsequently, the solution was then transferred in a 25 mL Teflon-lined autoclave. And then, the nickel foam was put into the autoclave, which was sealed and heated to 160 ^oC for 2 h. After cooled down to room temperature, the sample was washed with deionized water and absolute ethanol for three times. Finally, the sulfur-engineered Ni_3S_2 electrocatalyst was obtained after dried at 60 ^oC for 6 h in vacuum. For comparison, the pristine Ni_3S_2 and O-Ni_3S_2 electrocatalysts were prepared by the similar strategy except for finely adjusting reaction temperature to 165 ^oC and 170 ^oC, respectively. The mass loadings of the S-Ni_3S_2, Ni_3S_2 and O-Ni_3S_2 are 11.2, 19.3 and 9.0 mg cm^{-2}, respectively.

1.2 Synthesis of the RuO_2 electrocatalyst

The RuO_2 powder was supported on the Ni foam to test OER performances. Typically, 5 mg of RuO_2 powder (Adamas Reagent Co., Ltd.), 950 mL of isopropanol and 50 mL of 5 wt% Nafion solution were mixed by 30 min sonication to obtain well-dispersed ink. After that, the resulting ink was dropped onto the Ni foam with a mass loading of 11.2 mg cm^{-2}.

1.3 Characterization

The scanning electron microscope (SEM) images were taken from Hitachi, S-4800 at an accelerating voltage of 15.0 kV. The transmission electron microscope (TEM)

images were taken from JEOL, JEM-2100F with an X-ray energy-dispersive spectrometer (EDS) at an accelerating voltage of 200.0 kV. The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 diffractometer with Cu Kα radiation at a scan rate of 1° min^{-1}. X-ray photoelectron spectroscopy (XPS) spectra were recorded by an ESCALAB 250Xi X-ray photoelectron spectrometer at pass energy of 40 eV with an Al Kα X-ray source. Elemental analysis of sulfur content was performed on an Agilent 7700 Inductively coupled plasma (ICP) mass spectrometer. The samples were directly conducted by the scanning electron microscopy and X-ray powder diffractometer, were dispersed in absolute ethanol for transmission electron microscopy analysis, and were grinded to powder for X-ray photoelectron spectrometer measurement.

1.4 Electrochemical Measurements

The OER performances were measured by a CHI660E electrochemical workstation (Chenhua, Shanghai). All electrochemical measurements were performed in a standard three-electrode system comprising of a saturated Ag/AgCl reference electrode, a graphite counter electrode and a 30 mL 1.0 M KOH electrolyte. The electrocatalysts supported on nickel foam were directly applied as working electrode. The measured potential was calibrated to reversible hydrogen electrode (RHE) potential according to the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.1976 + 0.0591 \times pH$$

Before OER test, O_2-saturated condition was achieved by purging with O_2 for 30 min, which was kept during whole test process. Linear sweep voltammetry technique was applied to

record OER polarization curves at a sweep rate of 1 mV s^{-1}. Chronopotentiometry was applied to measure the stability of electrocatalysts at constant current densities of 10, 50 and 100 mA cm^{-2}. Electrochemical impedance spectroscopy (EIS) was performed at 1.56 V *vs.* RHE in a wide frequency ranging (10 kHz - 100 mHz) with a current voltage amplitude of 5 mV. The presented data was compensated with 95% *iR* correction, and ohmic resistance was estimated from the EIS results at a phase angle of 0° in high frequency. Electrochemically active surface area (ECSA) was calculated by the following equation:

$$ECSA = \frac{C_{DL}}{C_s}$$

where C_{DL} is the double layer capacitance, C_S is the specific capacitance. The specific capacitance of Ni is 25 μF cm^{-2} in alkaline media. Turnover frequency (TOF) was estimated from the following equation:

$$TOF = \frac{J \times A}{2 \times F \times \mathrm{n}}$$

where J is the current density in the OER polarization curves, A is the geometric area of electrode, F is the Faraday constant (C mol^{-1}), and n is the mole number of active sites on the electrode.

Part II: Supporting Figures

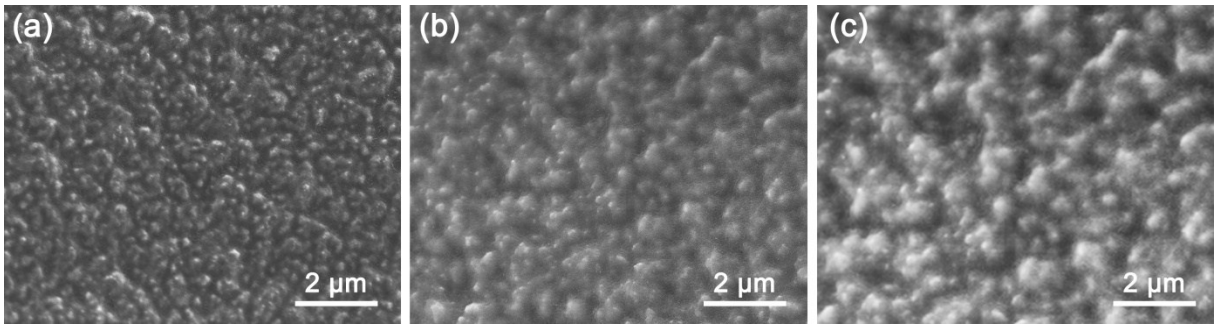

Fig. S1 SEM images of (a) the S-Ni_3S_2, (b) the pristine Ni_3S_2 and (c) the O-Ni_3S_2 electrocatalysts.

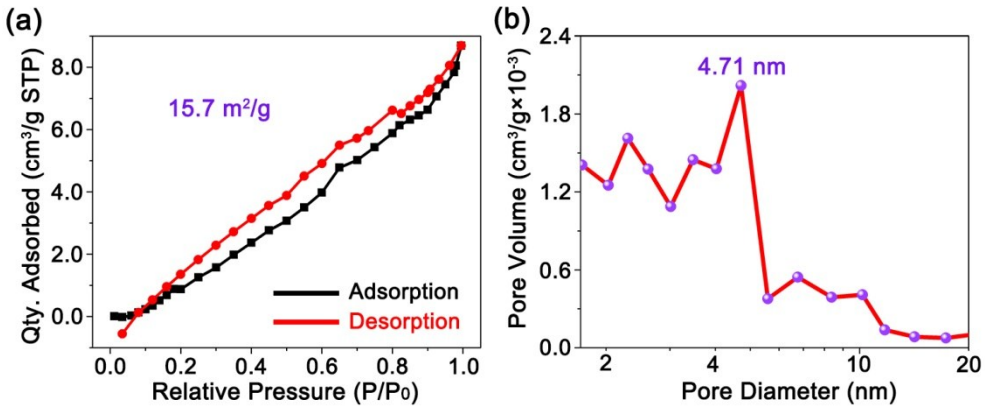

Fig. S2 (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore-size distribution curve of S-Ni_3S_2.

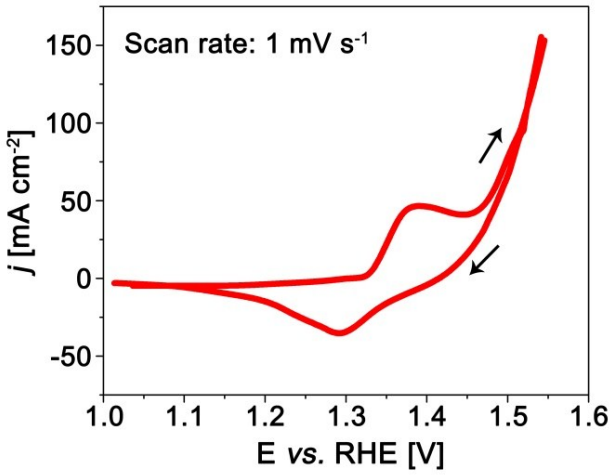

Fig. S3 Cyclic voltammetric curve of the S-Ni_3S_2 electrocatalyst.

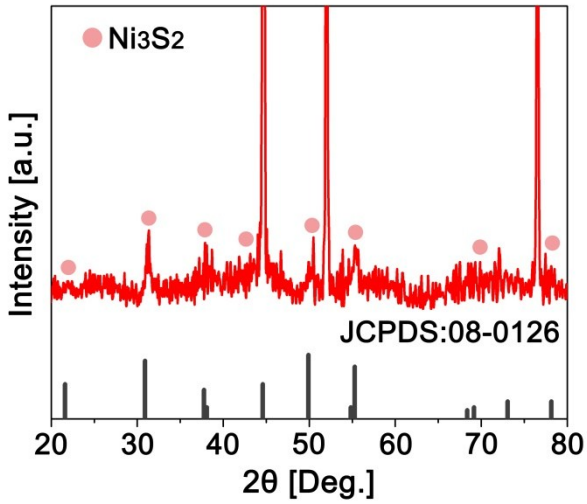

Fig. S4 XRD pattern of the S-Ni_3S_2 electrocatalyst after OER.

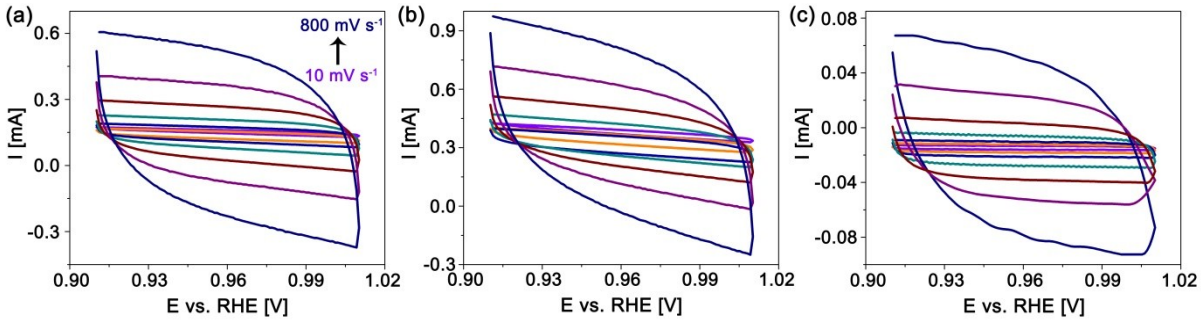

Fig. S5 Cyclic voltammogram curves of (a) the S-Ni_3S_2, (b) the pristine Ni_3S_2 and (c) the O-Ni_3S_2 electrocatalysts in the non-faradic potential range at different sweep rates.

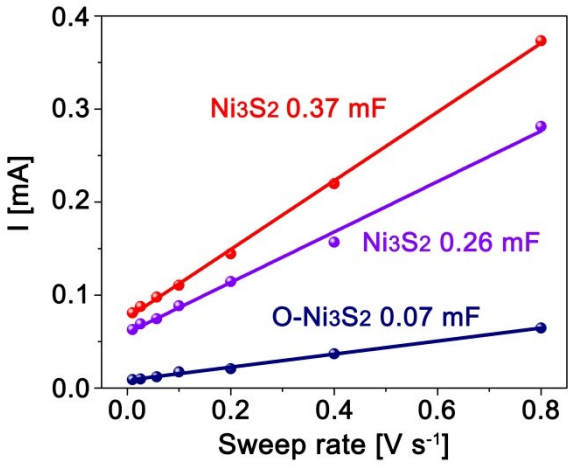

Fig. S6 Capacitive currents as a function of sweep rate of the S-Ni_3S_2, the pristine Ni_3S_2 and the O-Ni_3S_2 electrocatalysts measured at 0.96 V *vs.* RHE. The double-layer capacitances are calculated from the slope of the linear fitting to the data.

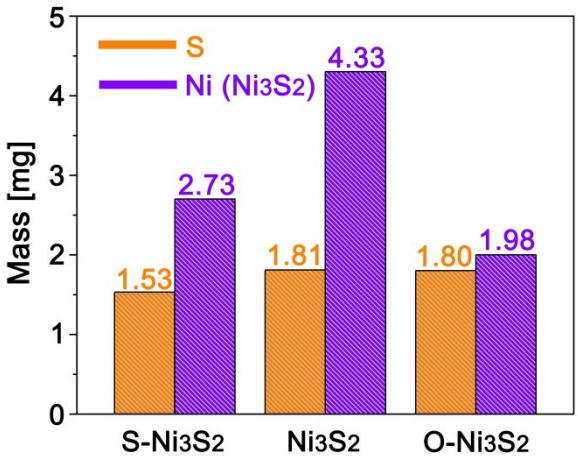

Fig. S7 Total S content and the corresponding Ni content in the S-Ni_3S_2, the pristine Ni_3S_2 and the O-Ni_3S_2 electrocatalysts. The total S content in S-Ni_3S_2, Ni_3S_2 and O-Ni_3S_2 samples are based on ICP-MS results and the percentages of S-Ni are estimated according to the peak areas of XPS S_{2p} spectra. As a result, the Ni content in Ni_3S_2 is calculated as follows:

$$m_S = m_{total} \times wt_{S-Ni} \quad (1)$$

$$m_{Ni} = \frac{m_S}{M_S} \times \frac{3}{2} \times M_{Ni} \quad (2)$$

where m_S is the S content in Ni_3S_2, m_{total} is the total S content based on ICP-MS results, $wt_{S\text{-}Ni}$ is the percentage of S-Ni according to the peak areas of XPS S_{2p} spectra, m_{Ni} is the Ni content in Ni_3S_2, M_S and M_{Ni} are the molar mass of S and Ni, respectively.

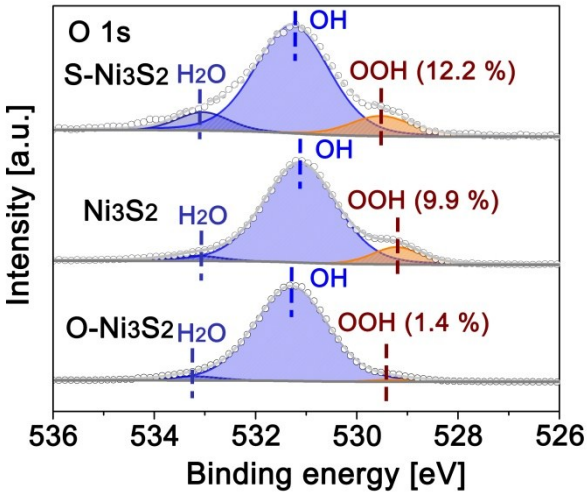

Fig. S8 XPS spectra of O 1s region after OER of the S-Ni_3S_2, the pristine Ni_3S_2 and the O-Ni_3S_2 electrocatalysts.

Part III: Supporting Table

Table S1 Comparison of OER performances of various Ni_3S_2 electrocatalysts.

Catalyst	Measurement	Loading (mg cm^{-2})	J (mA cm^{-2})	η (mV)	Tafel slope (mV dec^{-1})	Ref.
Ni_3S_2 nanorods	Ni foam 1.0 M KOH	37.0	10 100	237 > 400	159	10
Fe-doped Ni_3S_2 nanosheet array	Ni foam 1.0 M KOH	6.0	10	214	42	11
Ni_3S_2-NGQDs	Ni foam 1.0 M KOH	8.0	10 100	216 390	95	12
NCDs/Ni_3S_2	Ni foam 1.0 M KOH	4.2	10 100	270	67	13
3D hierarchical Ni_3S_2 superstructure	Ni foam 1.0 M KOH	\	100	320	59	15
Ni_3S_2 nanosheet arrays	Ni foam 1.0 M KOH	1.6	10	245	\	16
N-Ni_3S_2 electrocatalys	Ni foam 1.0 M KOH	\	100	330	70	22
Zn-doped Ni_3S_2 nanosheet array	Ni foam 1.0 M KOH	2.3	100	330	74	24
Sulfur-engineered Ni_3S_2	**Ni foam 1.0 M KOH**	**11.2**	**10 100**	**213 286**	**45**	**This work**