

Supporting Information

Surface covalent sulfur enriching Ni active sites of Ni₃S₂ nanoparticles for efficient oxygen evolution

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Part I Experimental Section

1.1 Synthesis of the Ni₃S₂ nanoparticles

Prior to use, commercial NF in size of 6 mm × 5 mm × 0.3 mm was soaked in 3 M HCl under ultrasound to wash the surface impurities. In a typical synthesis, a piece of fresh NF and 4 mg of sulfur powder were enfolded by aluminum foil, in which the surface of NF was fully covered by the powder. Then, the sealed foil was put into a 2-ml vial and transferred into a glove box filled with Ar atmosphere. After that, the vial was heated to 200 °C for 20 min and subsequently cooled down to room temperature followed by washing treatment using CS₂, ethanol and deionized water to remove the residual. After dried at 60 °C for 12 h, the sample labeled as Ni₃S₂-200 was collected for structural characterization and performance evaluation. For reference, the melting temperature was altered to 180 °C and 220 °C, respectively, to obtain the Ni₃S₂-180 and Ni₃S₂-220 samples without varying other conditions.

1.2 Characterization

The crystalline structure of the resulting samples was investigated by powder X-ray diffraction (XRD, Rigaku D/Max 2550, Cu K α radiation) at a scan rate of 1° min⁻¹. Morphological information was collected by field-emission scanning electron microscopy (FESEM, Hitachi, S-4800) with an X-ray energy dispersive spectrometer (EDS) and transmission electron microscopy (TEM, JEOL-2100F) at an accelerating voltage of 200 kV. Surface chemical information was recorded using an ESCALAB 250Xi X-ray photoelectron spectrometer (XPS) at a pass energy of 40 eV with an Al K α X-ray source. The surface sulfur content of the resulting samples was characterized by an Agilent 7700 inductive couple plasma mass spectrometer (ICP-MS).

1.3 Electrochemical Measurements

OER performances were assessed by CHI 760E electrochemical workstation connected with a typical three-electrode configuration, in which graphite, saturated Ag/AgCl and resulting sample were applied as a counter electrode, reference electrode and self-supported working electrode, respectively, in 1 M KOH aqueous electrolyte. To prepare RuO₂ electrode for comparison, 5 mg of RuO₂ powder, 0.42 mL of distilled water, 0.5 mL of ethanol and 80 μ L of

5 wt% Nafion solution were mixed by sufficient sonication to obtain a well-dispersed ink. Subsequently, the ink was coated onto NF with a mass loading of 2.0 mg cm⁻². All the data was compensated with 95% *iR* drop and calibrated to reversible hydrogen electrode (RHE) based on the following equation:

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

OER polarization curves were recorded by linear sweep voltammetry (LSV) technique at a scan rate of 5 mV s⁻¹. Tafel slopes (*b*) were calculated by fitting the Tafel plots:

$$\eta = b \log(j) + a$$

where η is the overpotential, and j is the corresponding current density. Electrochemical impedance spectroscopy (EIS) was tested by an Autolab PGSTAT302N electrochemical workstation in the frequency from 0.01 Hz to 100 kHz at the potential of 1.52 V. Catalytic stability was evaluated using chronopotentiometry (CP) at a current density of 100 mA cm⁻². Electrochemically active surface area (ECSA) was calculated according to the following equation:

$$ECSA = C_{DL} / C_S$$

where C_{DL} is the electrochemical double layer capacitance, C_S is the specific capacitance. The C_{DL} was measured by a cyclic voltammetry (CV) method at non-Faradic potential of 5 to 200 mV s⁻¹. The specific capacitance of Ni is 25 μ F cm⁻² in alkaline media. Turnover frequency (TOF) was estimated by the following equation:

$$TOF = (J \times A) / (4 \times n \times F)$$

where J is the current density obtained from polarization curves, A is the geometric area of the electrode, F is the Faraday constant (96485 C mol⁻¹), and n is the mole number of active sites of the electrode.

Part II Supporting Figures

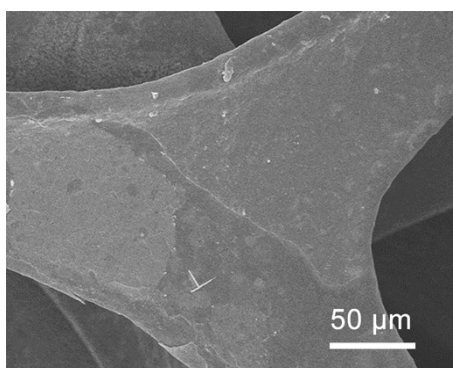


Fig. S1 Low-magnification SEM image of the Ni₃S₂-200 sample.

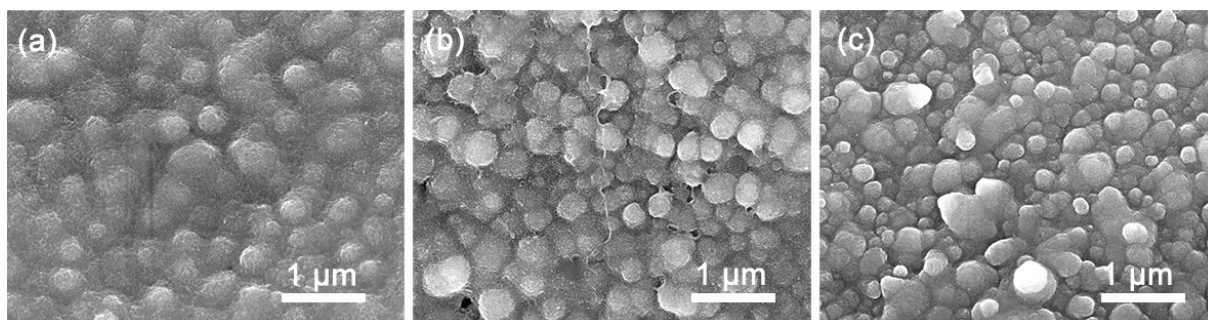


Fig. S2 SEM images of the (a) Ni₃S₂-180, (b) Ni₃S₂-200 and (c) Ni₃S₂-220 samples.

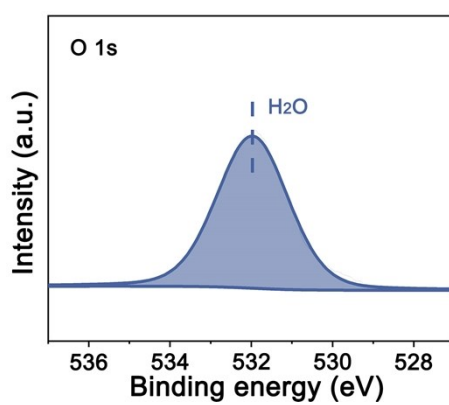


Fig. S3 XPS spectrum of O 1s for the Ni₃S₂-200 sample.

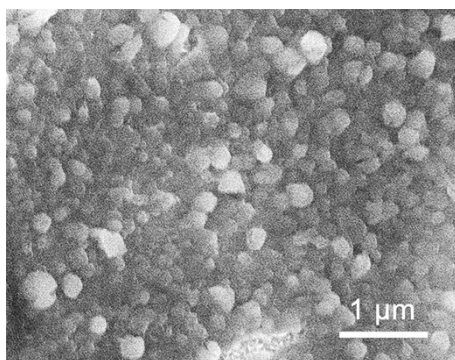


Fig. S4 SEM image of the Ni₃S₂-200 sample after OER.

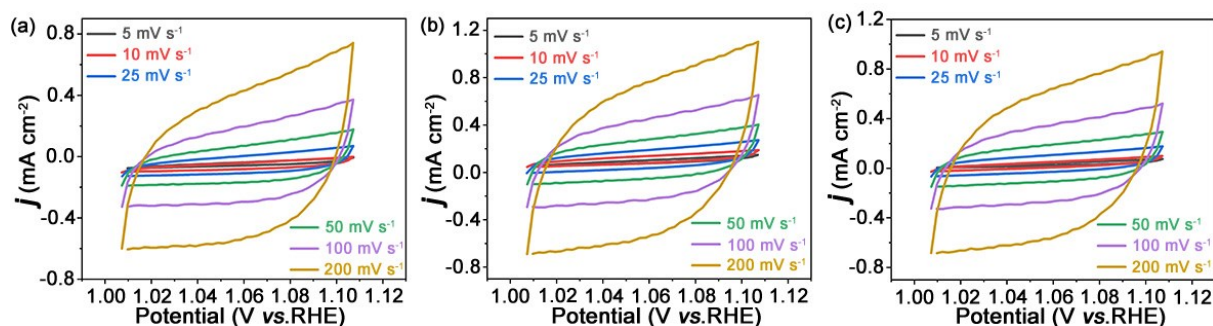


Fig. S5 Cyclic voltammogram curves of the (a) Ni₃S₂-180, (b) Ni₃S₂-200 and (c) Ni₃S₂-220 samples in non-faradic potential range at different sweep rates.

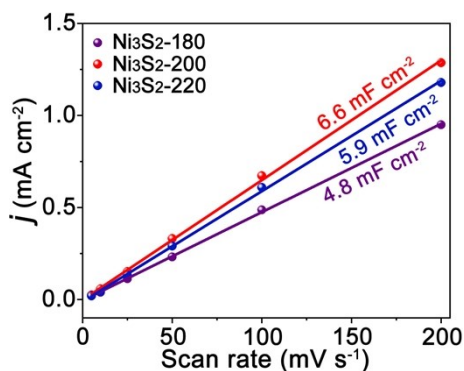


Fig. S6 Double-layer capacitances of the Ni₃S₂-180, Ni₃S₂-200 and Ni₃S₂-220 samples.

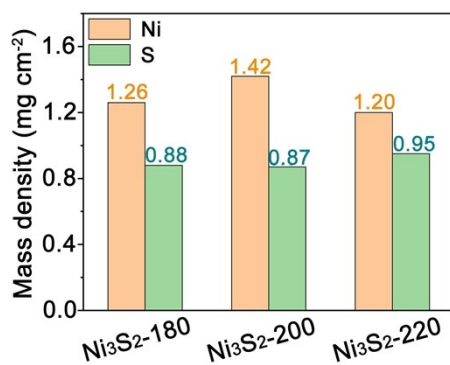


Fig. S7 Mass densities of Ni and S elements in the Ni₃S₂ samples. S content is based on ICP-MS results, whilst Ni content is estimated from the following formula:

$$m_{\text{Ni}} = m_{\text{S}} \times M_{\text{Ni}} / (M_{\text{S}} \times R_{\text{S/Ni}})$$

Where $R_{\text{S/Ni}}$ is the ratio of atomic S and Ni based on XPS data as shown in **Table S3**, and M_{S} and M_{Ni} are the molecular mass of S and Ni, respectively.

Part III Supporting Tables

Table S1 OER performance Comparison of the reported Ni₃S₂ electrocatalysts in 1 M KOH.

Electrocatalysts	<i>J</i> (mA cm ⁻²)	<i>η</i> (mV)	Tafel slope (mV dec ⁻¹)	Reference
Ni ₃ S ₂ @Co(OH) ₂	100	440	90.7	S1
Ni ₃ S ₂ @NF	100	293	60.5	S2
Fe-Ni ₃ S ₂ NS	10	295	71	S3
Ni ₃ S ₂ P	100	420	224	S4
Ni ₃ S ₂ @N-C	10	271	99	S5
Ni ₃ S ₂ -CeO ₂ /NF	100	370	146	S6
Mo-Ni ₃ S ₂ NS	10	260	85	S7
Ni₃S₂-200	10 100	242 290	40	This work

Table S2 Geometric values of the electronic elements extracted from the electrical equivalent circuit model.

Electrocatalysts	R _s (Ω)	R _{ct} (Ω)	C _{dl} (mF)
Ni ₃ S ₂ -180	8.635	28.098	0.715
Ni ₃ S ₂ -200	10.0913	21.767	0.742
Ni ₃ S ₂ -220	10.185	25.879	0.755

R_s is related to the series resistance. R_{ct} denotes the charge transfer resistance. C_{dl} is the constant phase angle element, representing the double layer capacitance.

Table S3 Comparisons of Ni, S content in the Ni₃S₂ electrocatalysts based on XPS results.

Electrocatalysts	Ni content (Atomic%)	S content (Atomic%)
Ni ₃ S ₂ -180	15.29	19.71
Ni ₃ S ₂ -200	13.68	15.48
Ni ₃ S ₂ -220	12.81	18.55

References

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