Supporting Information

Tailorable Surface Sulfur Chemistry of Mesoporous Ni₃S₂ Particles for Efficient Oxygen Evolution

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Part I: Experimental Section

1.1 Synthesis of the sulfur-engineered Ni$_3$S$_2$ 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$_3$S$_2$ 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 °C 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$_3$S$_2$ electrocatalyst was obtained after dried at 60 °C for 6 h in vacuum. For comparison, the pristine Ni$_3$S$_2$ and O-Ni$_3$S$_2$ electrocatalysts were prepared by the similar strategy except for finely adjusting reaction temperature to 165 °C and 170 °C, respectively. The mass loadings of the S-Ni$_3$S$_2$, Ni$_3$S$_2$ and O-Ni$_3$S$_2$ 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:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.1976 + 0.0591 \times pH \]

Before OER test, O₂-saturated condition was achieved by purging with O₂ 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 \(\mu\)F cm\(^{-2}\) in alkaline media. Turnover frequency (TOF) was estimated from the following equation:

\[
TOF = \frac{J \times A}{2 \times F \times n}
\]

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$_3$S$_2$, (b) the pristine Ni$_3$S$_2$ and (c) the O-Ni$_3$S$_2$ electrocatalysts.

Fig. S2 (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore-size distribution curve of S-Ni$_3$S$_2$. 
**Fig. S3** Cyclic voltammetric curve of the S-Ni$_3$S$_2$ electrocatalyst.

**Fig. S4** XRD pattern of the S-Ni$_3$S$_2$ electrocatalyst after OER.
**Fig. S5** Cyclic voltammogram curves of (a) the S-Ni$_3$S$_2$, (b) the pristine Ni$_3$S$_2$ and (c) the O-Ni$_3$S$_2$ 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$_3$S$_2$, the pristine Ni$_3$S$_2$ and the O-Ni$_3$S$_2$ 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$_3$S$_2$, the pristine Ni$_3$S$_2$ and the O-Ni$_3$S$_2$ electrocatalysts. The total S content in S-Ni$_3$S$_2$, Ni$_3$S$_2$ and O-Ni$_3$S$_2$ 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$_3$S$_2$ is calculated as follows:

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

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

where $m_S$ is the S content in Ni$_3$S$_2$, $m_{total}$ is the total S content based on ICP-MS results, $wt_{S-Ni}$ is the percentage of S-Ni according to the peak areas of XPS S$_{2p}$ spectra, $m_{Ni}$ is the Ni content in Ni$_3$S$_2$, $M_S$ 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$_3$S$_2$, the pristine Ni$_3$S$_2$ and the O-Ni$_3$S$_2$ electrocatalysts.
## Part III: Supporting Table

### Table S1 Comparison of OER performances of various Ni$_3$S$_2$ electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Measurement</th>
<th>Loading (mg cm$^{-2}$)</th>
<th>$J$ (mA cm$^{-2}$)</th>
<th>$\eta$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>Ni$_3$S$_2$ nanorods</td>
<td>Ni foam 1.0 M KOH</td>
<td>37.0</td>
<td>10 100</td>
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<td>216 390</td>
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<td>NCDs/Ni$_3$S$_2$</td>
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<tr>
<td>3D hierarchical Ni$_3$S$_2$ superstructure</td>
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<td>45</td>
<td>This work</td>
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</tbody>
</table>

Note: The Tafel slope is given in mV dec$^{-1}$.