

## Electronic Supplementary Information

### *Experimental Section*

**Materials:** Ni foam was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd., S powder was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All the reagents in our experiment were used as received. The water used throughout all experiments was purified through a Millipore system.

**Preparation of NiS/Ni foam:** A piece of Ni foam was soaked in 2.0 M HCl for 10 minutes to remove the NiO on the surface, then washed with ethanol and deionized water, respectively, and dried at room temperature. To prepare NiS/Ni foam, a piece of Ni foam (0.5 mm in thickness) and S powder were put at two separate positions in two porcelain boats with S powder at the upstream side of the furnace. Subsequently, the sample was heated at 350 °C with a heating rate of 8 °C min<sup>-1</sup> under Ar atmosphere, and then naturally cooled to ambient temperature under Ar. In this process, the reaction time, the amount of S powder and temperature are three key factors, since the Ni foam is fragile and this reaction is actually an incomplete reaction. The sample was collected and washed with water and ethanol several times and then dried at 60 °C for 2 h.

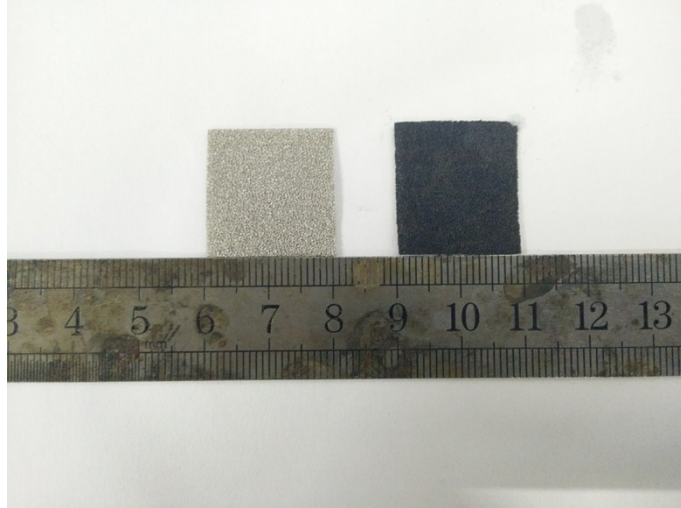
**Preparation of Pt/C and RuO<sub>2</sub> loaded electrodes:** RuO<sub>2</sub> catalyst was prepared according to reported method. In brief, 0.01 mol of RuCl<sub>3</sub>•3H<sub>2</sub>O was dissolved in 100 mL deionized water and heated under air atmosphere at 100 °C for 10 min, followed by the addition of 1 mL KOH solution (1.0 M). The reaction mixture was

maintained at this temperature under stirring for 45 min. After that, the solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with deionized water to remove the remaining chlorides. The resulting Ru-hydroxide was dried for 5 h at 80 °C and then calcined in air at 300 °C for 3 h to obtain RuO<sub>2</sub>. To prepare Pt/C and RuO<sub>2</sub> loaded electrodes, 20 mg Pt/C or RuO<sub>2</sub> and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30 min sonication to form an ink finally. Then the catalyst ink was coated on Ni foam with the same loading with NiS/Ni foam.

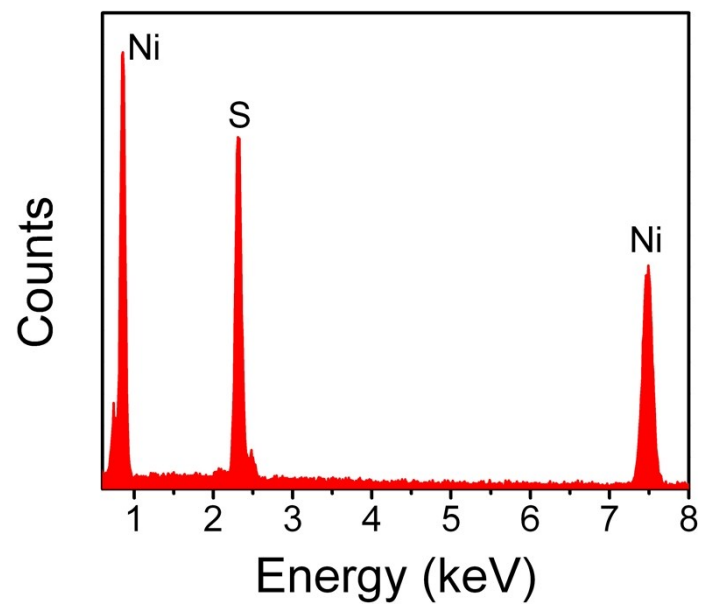
**Characterizations:** XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å). SEM measurements and energy-dispersive X-ray (EDX) spectra were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Raman spectra were collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.) at ambient conditions.

**Electrochemical measurements:** Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system in an aqueous KOH electrolyte (1.0 M) using NiS/Ni foam as the working electrode, a graphite plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All currents presented are corrected against the ohmic potential drop. All potentials measured were calibrated to RHE using the following equation:  $E$  (RHE) =  $E$  (SCE) + 1.068. Onset

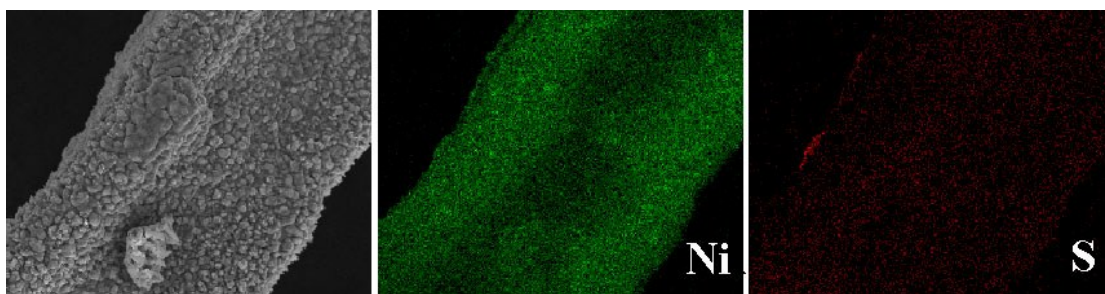
was determined by the start point of Tafel slope. The mass of NiS microspheres film grown on the Ni foam was calculated as following: the weight increment ( $x$  mg) of Ni foam can be directly weighted after the synthesis of NiS on Ni foam.  $m_{\text{NiS}} = x \text{ mg} \times (M_{\text{NiS}}/M_{\text{S}}) = x \text{ mg} \times (91/32) = 2.84x \text{ mg}$ , where  $M$  is the molecular or atomic weight. For NiS electrode, the loading mass of NiS is about  $43 \text{ mg cm}^{-2}$ .



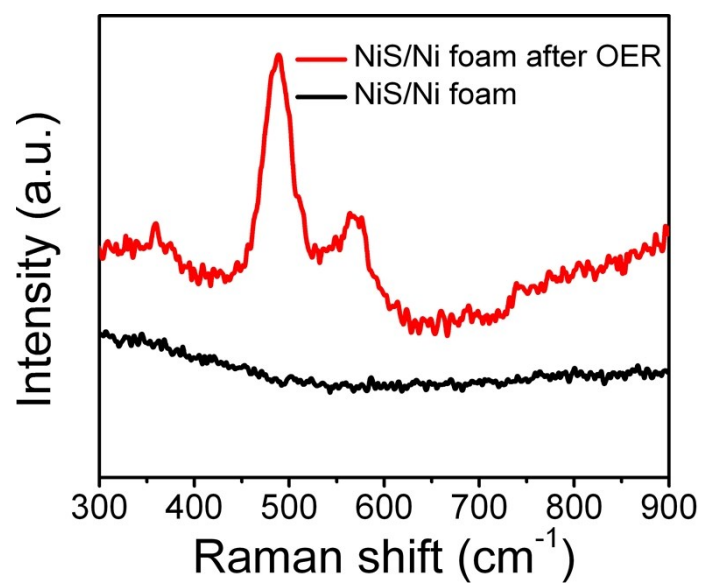
**Figure S1.** Optical photograph of bare Ni foam (left) and NiS/Ni foam (right).



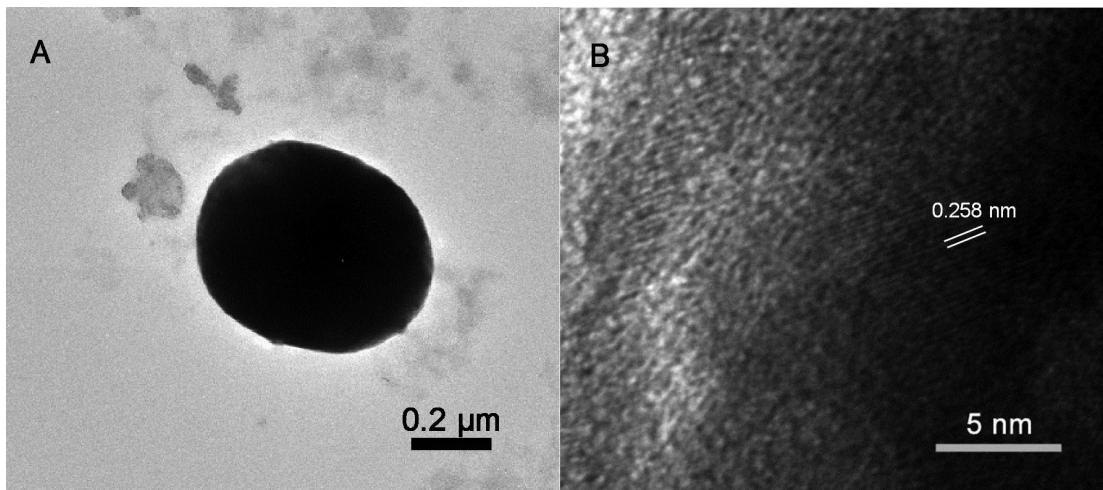
**Figure S2.** EDX spectrum of NiS/Ni foam.



**Figure S3.** EDX elemental mapping of Ni and S for the NiS/Ni foam.

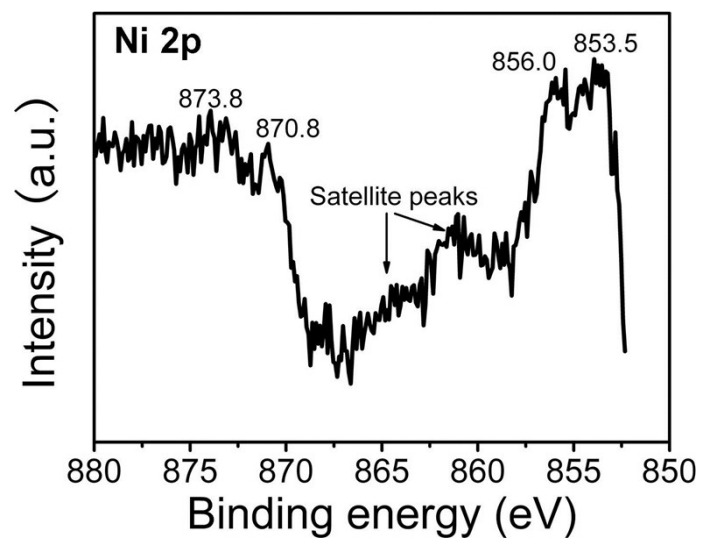


**Figure S4.** Raman spectrum of NiS/Ni foam.

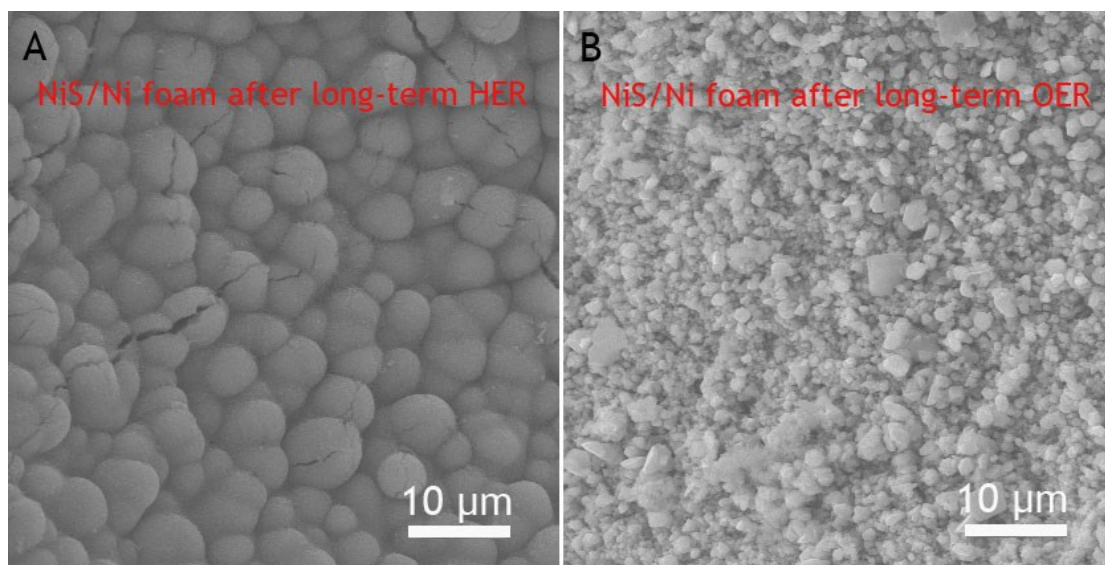


**Figure S5.** TEM and HRTEM images of NiS.

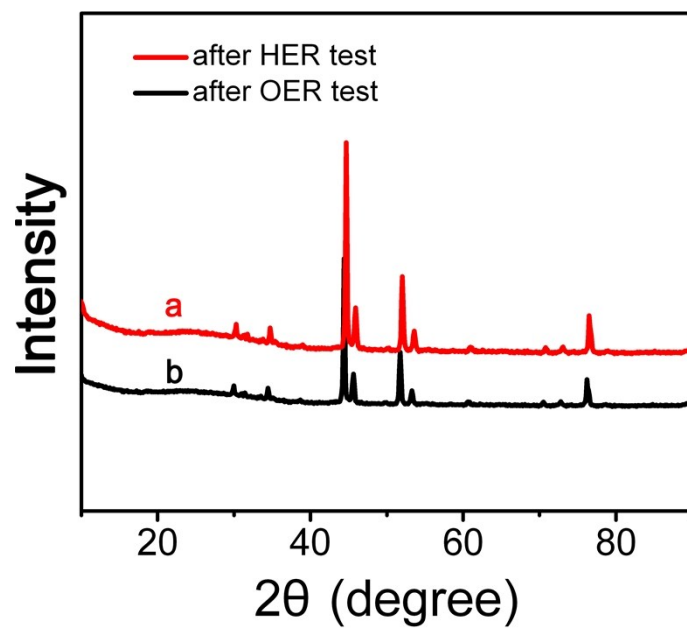




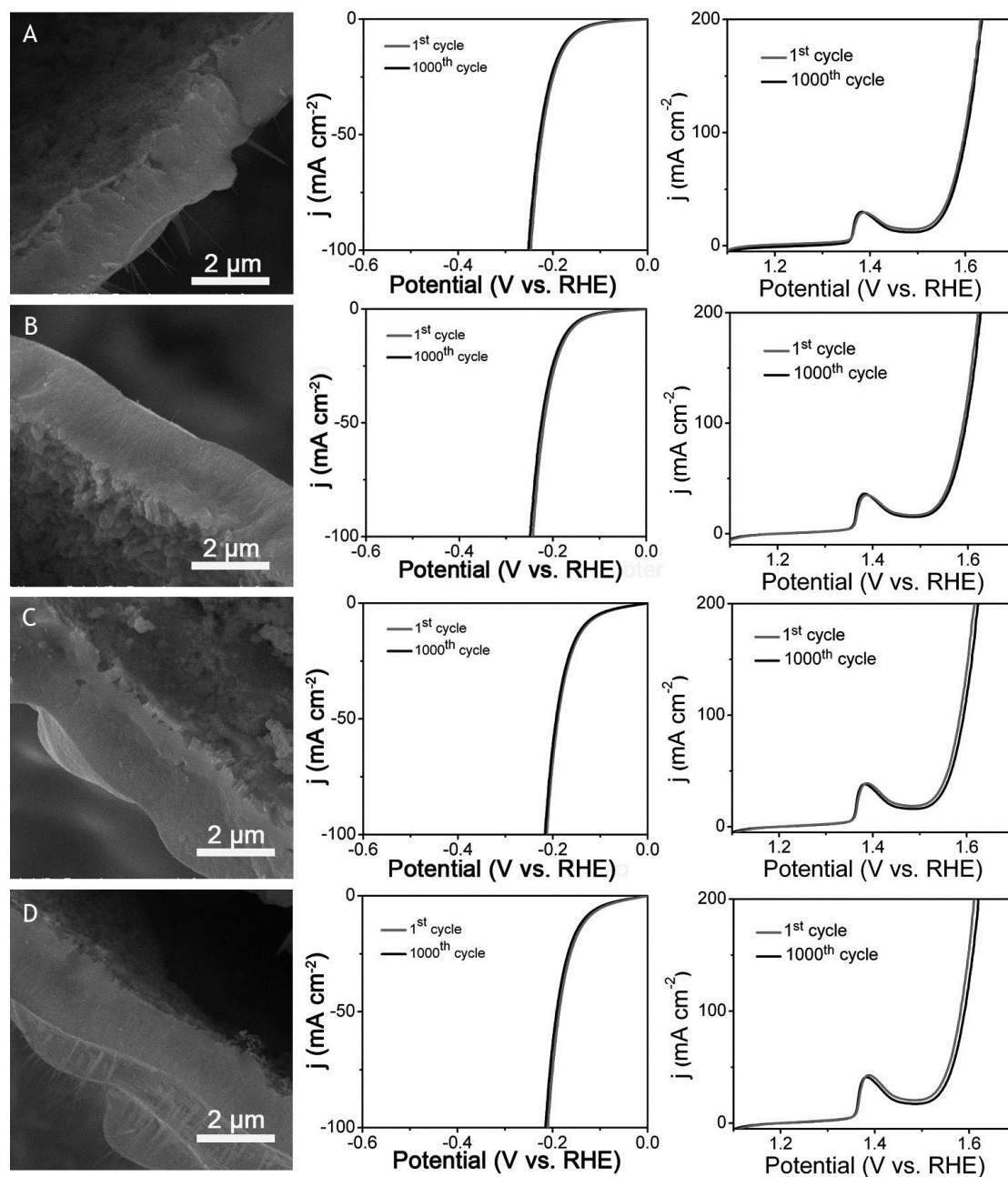
**Figure S6.** High-resolution XPS spectrum in the Ni 2p region for NiS.



**Figure S7.** The morphologies of NiS/Ni foam after long-term HER and OER tests.



**Figure S8.** XRD patterns of NiS/Ni foam after HER and OER tests.



**Figure S9.** Influence of the NiS thickness (From top to down: 200, 300, 500 and 600 mg S powder) on the catalytic performances and stability.