

Supporting Information for

Facile Electrodeposition of Amorphous Nickel/Nickel Sulfide Composite Films for High-efficiency Hydrogen Evolution Reaction

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Experimental section

Preparation of Samples. All the chemical reagents are analytical grade and used without any further purification. The electrochemical experiments are performed with a three-electrode system. A piece of cleaned nickel foam with a size of $1.0 \times 1.0 \text{ cm}^2$ is used as the working electrode, a graphite rod is employed as the counter electrode, and an Ag/AgCl electrode is adopted as the reference electrode. To deposit nickel/nickel sulfide on the Ni foam, a 75 mL electrolyte solution containing 0.05 mol/L NiCl_2 , 0.10 mol/L $\text{CS}(\text{NH}_2)_2$, and 0.15 mol/L NH_4F is prepared. The electrodeposition process is carried out with two continuous steps, namely, the first step of a small current density at $0.50 \text{ mA} \cdot \text{cm}^{-2}$ for 90 min and the second step with a large current density at $10 \text{ mA} \cdot \text{cm}^{-2}$ for 75 min, respectively. The obtained nickel/nickel sulfide composite sample labelled as Sample 1 is washed several times with deionized water, and then dried naturally in air. Meanwhile, the nickel/nickel sulfide composite samples labelled as Sample 2 and Sample 3 are also synthesized by the same method with adding 0.10 mol/L and 0.20 mol/L $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ into the electrolyte. In addition, Sample 1', Sample 2' and Sample 3' are also prepared on carbon cloth by the same experimental condition with adding 0 mol/L, 0.10 mol/L and 0.20 mol/L, respectively.

Material Characterization. The phase formation is identified using X-ray diffraction (XRD, D8 Advance, Bruker, Cu $\text{K}\alpha$ radiation). The composition is tested using

Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Agilent 5110). Morphology of the catalysts is observed by a scanning electron microscope (SEM, Nova NanoSEM 450, FEI Company). The X-ray photoelectron spectroscopy (XPS, PHI5000VersaProbe equipped with a monochromatic Al $\text{K}\alpha$ source, ULVAC-PHI) analyses are carried out to investigate the elemental composition and chemical states of the active materials grown on NF. The transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns are obtained from JEM 2100, JEOL.

Electrochemical Measurements. Electrochemical measurements are performed by an electrochemical workstation on CHI 760E (Shanghai Chenhua Instrument Cvbeo., Ltd.) in a standard three-electrode system. The as-prepared samples on NF are used as working electrodes without further treatments in the alkaline medium of 1.0 M KOH solution. Graphite electrode and a saturated Ag/AgCl electrode are used as counter and reference electrodes, respectively. Linear sweep voltammetry (LSV) is performed at the scan rate of $2 \text{ mV}\cdot\text{s}^{-1}$ for HER. The double layer capacitance (C_{dl}) is evaluated by cyclic voltammogram (CV) curves with the scanning rates from 10 to $80 \text{ mV}\cdot\text{s}^{-1}$ and from the slope of the plots of capacitive current versus scan rate. Electrochemical impedance spectroscopy (EIS) is carried out at 0 V vs. reversible hydrogen electrode (RHE) with a frequency range of 10^{-2} to 10^5 Hz with AC signal amplitude of 5 mV. Equivalent circuit for fitting EIS data is achieved with Zview software. The current density is normalized to

geometric area of the electrodes. Measured potentials vs. Ag/AgCl (saturated solution) are converted to RHE according to the Nernst equation (Eq. 1).

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{ pH} \quad (1)$$

The stability test of sample is performed by taking 5000 CV cycles at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ from -1.0 to -1.6 V vs. Ag/AgCl, and then again LSV is measured with the same condition as the initial one. The stability is also performed by the chronopotentiometry measurements at a fixed current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ for 20 h.

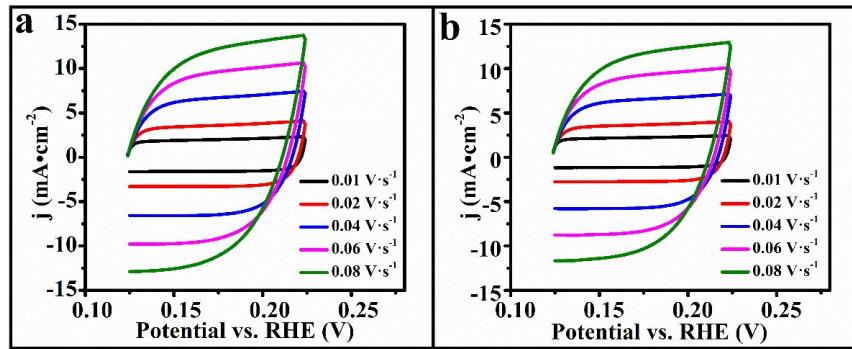


Figure S1. CV plots by different scan rates of prepared samples. (a) Sample 1, (b) Sample 2.

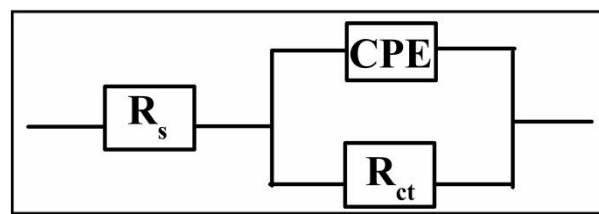


Figure S2. The equivalent circuit of resistances of Nyquist plots.

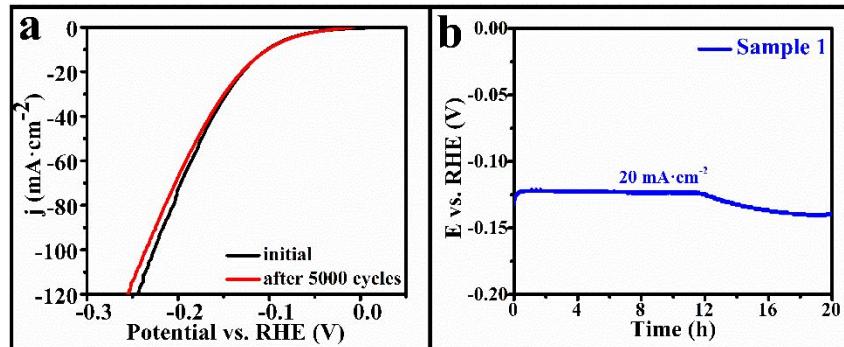


Figure S3. Stability test of Sample 1. (a) linear sweep voltammetry curves of Sample 1 before and after cyclic voltammogram scanning for 5000 cycles, (b) Stability test of Sample 2 at $20 \text{ mA}\cdot\text{cm}^{-2}$ for 20 h.

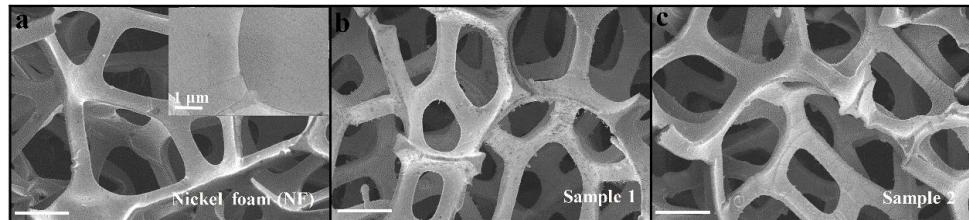


Figure S4. Morphology of samples. SEM images of (a) bare NF, (b) Sample 1, (c) Sample 2. Scale bar is 200 μ m.

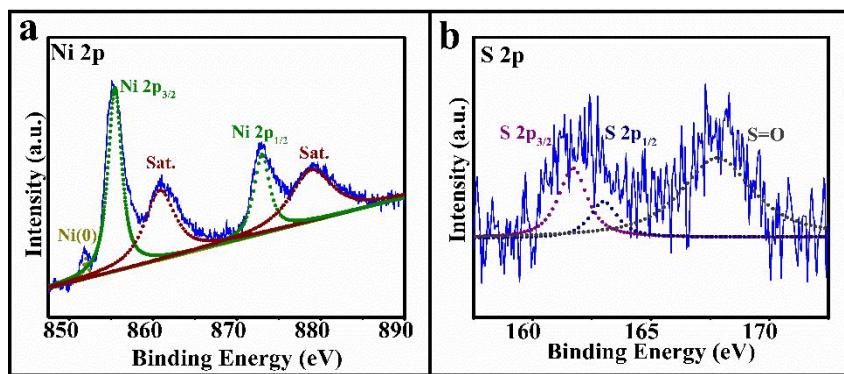


Figure S5. Surface state of Sample 1 after stability test. High-resolution XPS spectra of (a) Ni 2p, (b) S 2p.

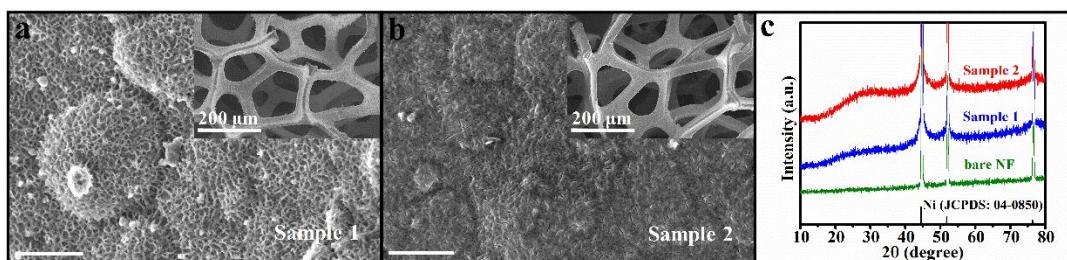


Figure S6. Morphology and crystal structure of samples after stability test. SEM images after stability testing of (a) Sample 1, (b) Sample 2, (c) XRD patterns of all samples after stability testing. Scale bar is 1 μ m.

Table S1. The molar ratio of as-prepared samples.

| Samples | Ni : S (Molar ratio) |
|----------|----------------------|
| Sample 1 | 2.46: 1 |
| Sample 2 | 3.09: 1 |
| Sample 3 | 3.60: 1 |