Supporting Information

An efficient Ni_3S_2-Ni electrode constructed by one-step powder metallurgy approach for hydrogen evolution reaction

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Supplementary Pictures and Table

Experimental section

1. Materials and Synthesis of Ni_3S_2-Ni-X-Y electrode. Commercial Ni powder and nano S powder are used directly without further treatment. First, 2 g Ni powder and 20 mg nano S powder were mixed together. Second, the mixed Ni and S were pressed to form a cylinder with a diameter of 20 mm. As illustrated in **Figure S1**, the mixed Ni powder and S powder were firstly loaded into a home-made stainless steel mold. The mold was then placed on the working table of the hydraulic press, and the powder was pressed by applying pressure to the mold. Finally, a small round piece was obtained after disassembly of the mold. Finally, a Ni_3S_2-Ni-500-20 electrode (500 represent the sintering temperature, 20 represent the S content) was obtained after the one-step powder metallurgy of cylinder at 500 ^oC for 1 h under vacuum. Other electrodes sintered at other temperatures of 400, 600 and 700 ^oC were labeled as Ni_3S_2-Ni-400-20, Ni_3S_2-Ni-600-20 and Ni_3S_2-Ni-700-20. When the Ni was fixed at 2 g, the Ni_3S_2-Ni-500-Y electrodes with other different S content were labeled as Ni_3S_2-Ni-500-10, Ni_3S_2-Ni-500-40 and Ni_3S_2-Ni-500-60, where S content was 10, 40 and 60 mg, respectively.

2. Characterization. The phase and the surface chemical states of the electrodes were determined by X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The morphology of the electrodes was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Electrochemical characterization. The electrochemical performances were tested in 1.0 M KOH electrolyte with a standard three-electrode system using the Biologic VSP electrochemical workstation. The prepared self-supporting electrode was used directly as working electrode, graphite-rod was used as counter electrode and Hg/HgO electrode was used as reference electrode. The HER catalytic activity of Ni_3S_2-Ni was obtained by linear sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1}. All measured potentials were calibrated to RHE using the following equation:

$E_{vs\ RHE} = E_{vs\ Hg/HgO} + E^{\theta}_{Hg/HgO} + 0.059 \times pH$, ($E^{\theta}_{Hg/HgO} = 0.098$ V, pH = 14).

Nyquist plots were measured at the frequency range of 1.0 MHz to 10 mHz. Chronoamperometry (CA) measurements were appied under different current densities of 100, 200, 300 and 400 mA cm^{-2} for 24 h to verify the stability of the Ni_3S_2-Ni-500 -20 electrode. Long-term stability with three-electrodes system was tested under a current density of 260 mA cm^{-2}.

Table S1. A list of preparation conditions of Ni_3S_2-Ni-X-Y electrodes

Electrode	Ni (mg)	S (mg)	Temperature (°C)	Time (h)
Ni_3S_2-Ni-500-10	2000	10	500	1
Ni_3S_2-Ni-500-20	2000	20	500	1
Ni_3S_2-Ni-500-40	2000	40	500	1
Ni_3S_2-Ni-500-60	2000	60	500	1
Ni_3S_2-Ni-400-20	2000	20	400	1
Ni_3S_2-Ni-600-20	2000	20	600	1
Ni_3S_2-Ni-700-20	2000	20	700	1
Ni_3S_2-Ni-500-20-1.5h	2000	20	500	1.5
Ni_3S_2-Ni-500-20-2h	2000	20	500	2

Table S2. Comparison of electrochemical performance of different catalysts

	Current density (mA cm^{-2})	Overpotential (mV)	Electrolyte	Ref.
RCFP/NF	100	191	1M KOH	42
Fe-doped Ni_3S_2	100	254	1M KOH	36
Co-NiOOH/Ni_3S_2@NF	100	203	alkaline medium	43
F，P-Fe_3O_4/IF	100	179.5	1M KOH	44
Mo-NiS/Ni_3S_2-0.08S	100	230	1M KOH	32
Ni_3S_2-Ni	100	157.8	1M KOH	This work

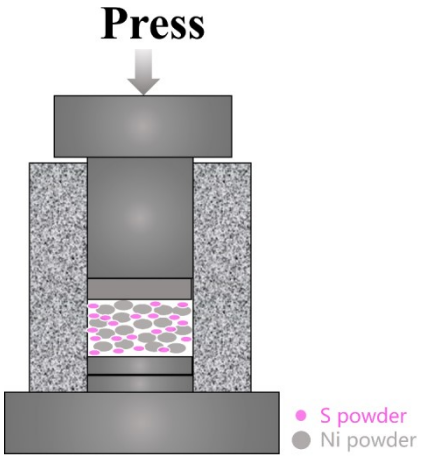

Figure S1. The schematic diagram of pressing process.

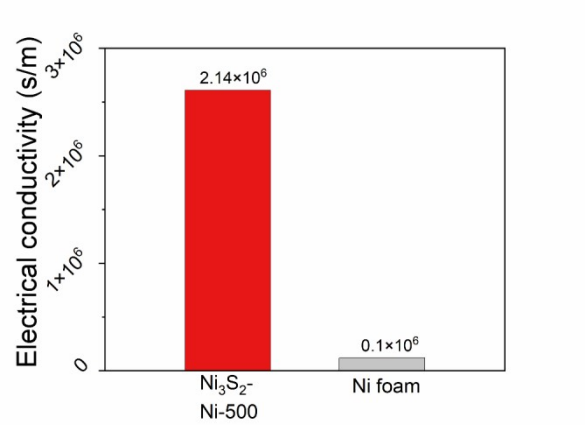

Figure S2. The comparison of the electrical conductivity of different electrodes

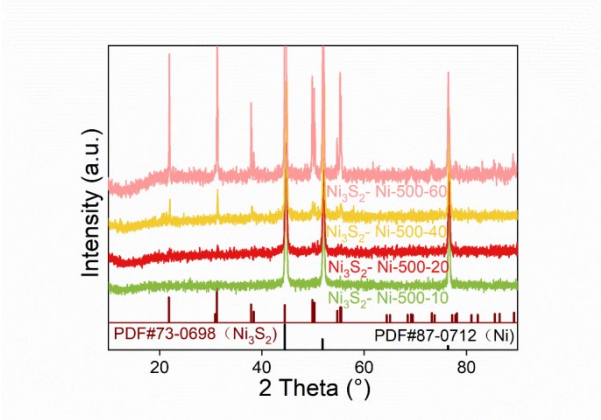

Figure S3. XRD patterns of Ni_3S_2-Ni-500-Y electrodes.

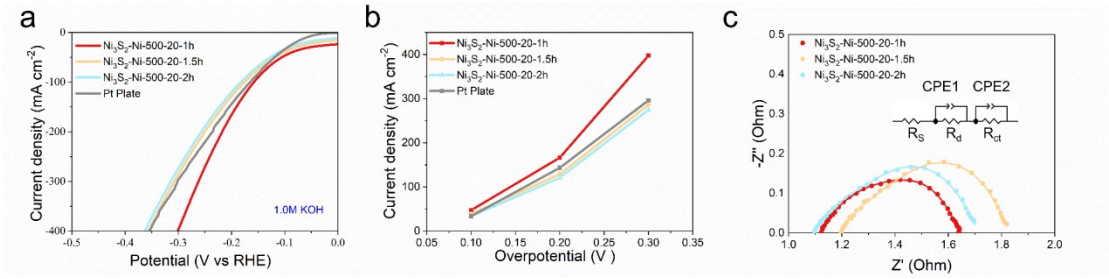

Figure S4. (a) HER polarization curves of Ni_3S_2-Ni-500-20-1h, Ni_3S_2-Ni-500-20-1.5h, Ni_3S_2-Ni-500-20-2h, and Pt plate electrodes. (b) Comparison of the current density of Ni_3S_2-Ni-500-20-1h, Ni_3S_2-Ni-500-20-1.5h, Ni_3S_2-Ni-500-20-2h, and Pt plate electrodes under the same overpotential. (c) EIS of Ni_3S_2-Ni-500-20-1h, Ni_3S_2-Ni-500-20-1.5h and Ni_3S_2-Ni-500-20-2h electrodes.