Electronic Supplementary Material (ESI) for Energy & Environmental Science

[Electronic Supplementary Information]

Ni_3S_2 Nanorods/Ni Foam Composite Electrode with Low Overpotential for Electrocatalytic Oxygen Evolution

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Experimental section

Growth of Ni_3S_2/Ni hybrid structure: Ni_3S_2 nanorods on Ni foam, referred to as Ni_3S_2/Ni, were prepared by a simple one-step hydrothermal process. A piece of Ni foam was wrapped by Teflon tape with exposure area of ~1 cm^2, and immersed into a Teflon-lined stainless steel autoclave containing a 20 mL aqueous solution of 320 mg thioacetamide (TAA, C_2H_5NS). Then, the autoclave was sealed for hydrothermal reaction at 180 ^oC for 2, 4 and 6 h to obtain the Ni_3S_2/Ni with different morphologies, *e.g.* nanoparticles, short nanorods and long nanorods, respectively. After the autoclave was cooled down to room temperature, the samples were rinsed with copious distilled water and then dried in an electric oven at 60 ^oC for 12 h.

Characterization: Field emission scanning electron microscopy (FESEM, Model JSM-7600F, JEOL Ltd., Tokyo, Japan) was used to characterize the morphologies and size of the synthesized samples. Transmission electron microscopy (TEM) images were carried out with a JOEL JEM 2100F microscope. X-ray powder diffraction (XRD) patterns of the samples were recorded on a Bruke D8 Advance powder X-ray diffractometer with Cu Kα (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250.

The detailed electrochemical measurement

Electrochemical measurements were performed on an electrochemical workstation (CHI 760C, CH Instruments Inc., Shanghai) using a three-electrode mode

in 0.1 M KOH aqueous solution (pH = ~13). The reference electrode and counter electrode were Ag/AgCl electrode (saturated KCl) and platinum wire, respectively. The Ni_3S_2/Ni electrodes were directly used as the anodes for electrochemical characterizations. The mass of Ni_3S_2 nanorods 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 Ni_3S_2 on Ni foam. $m_{Ni3S2} = x\ mg \times (M_{Ni3S2}/2M_S) = x\ mg \times (240/64) = 3.75x\ mg$, where M is the molecular weight or atomic weight. For Ni_3S_2/Ni electrode obtained by 4 h, the loading mass of Ni_3S_2 is about 37 mg/cm^2. Prior to the experiments, the Ni_3S_2/Ni electrodes were sealed on all edges except for the working surface area (~0.25 cm^2) with epoxy resin. The current densities were evaluated in terms of the geometric surface area of the Ni_3S_2/Ni electrodes.

Polarization curves: Before the electrochemical measurement, the electrolyte (0.1 M KOH) was degassed by bubbling oxygen for 30 min. The polarization curves were obtained by sweeping the potential from 0 to 0.8 V (vs. Ag/AgCl) with a sweep rate of 5 mV/s. Reverse scans were operated by CV in a potential range of 0 to 0.6 V at a constant scan rate of 10 mV/s.

For comparison on Ni foam electrodes, working electrodes comprised of 0.5 cm × 0.5 cm pieces of nickel foam loaded with 20 wt% Pt/C (37 mg/cm^2). 9.3 mg of 20 wt% Pt/C was dispersed in 10 mL distilled water and 20 μl Nafion solution (5 wt%, Sigma-Aldrich) with 30 min sonication treatment followed by deposition of this solution on Ni foam electrode, and final evaporation of the water.

For comparison on GC electrodes, all samples including Ni_3S_2, Fe_2O_3, Co_3O_4, MnO_2 and 20 wt% Pt/C, were loaded on GC electrode for electrochemical measurement. Ni_3S_2 nanorods were obtained from Ni_3S_2/Ni by sonication treatment. Except for Ni_3S_2, all above reference samples were purchased from Sigma-Aldrich Co. LLC. In short, 4 mg of catalyst powder was dispersed in 1 ml of 4:1 (v/v) water/ethanol mixed solvent with 10 μl Nafion solution, then the mixture was ultrasonicated for 30 min. Next, 4 μl of the above solution was transferred onto the GC disk, leading to the catalyst loading ~0.22 mg/cm^2. Finally, the as-prepared catalyst film was dried at room temperature.

The thermodynamic potential for $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ in 0.1 M KOH (pH =13):

$E°(OH^-/O_2) = 1.228 - 0.0591 \times 13$

$= 0.46$ V (vs. SHE)

$= 0.46 - 0.197 = 0.263$ V (vs. Ag/AgCl)

Results of polarization studies were compensated by η (V) = V_{appl} - 0.263, where η is the corrected overpotential, V_{appl} is the applied potential, and 0.263 is the theoretical onset potential of oxygen evolution (vs. Ag/AgCl).

Stability test: The accelerated stability tests were performed in O_2-saturated 0.1 M KOH at room temperature, which was tested by cyclic voltammetry (CV) between 0 and 0.6 V (vs. Ag/AgCl) at a sweep rate of 100 mV/s for given number of cycles. Amperometic current-time curves of electrodes were performed at 0.5 V and 0.6 V

(vs. Ag/AgCl), respectively.

Oxygen production test: The oxygen production of Ni_3S_2/Ni electrode was applied with potential at +0.5 V. The methylene blue was used to qualitatively detect dissolved oxygen in 0.1 M KOH aqueous solution. The color of electrolyte would change from transparent (oxygen-free) to blue (oxygen). The gas production rate from Ni_3S_2/Ni electrode was quantificationally measured by gas chromatography (GC-2060F, LuNan Analytical Instrument, LTD, China).

Supplementary Figures

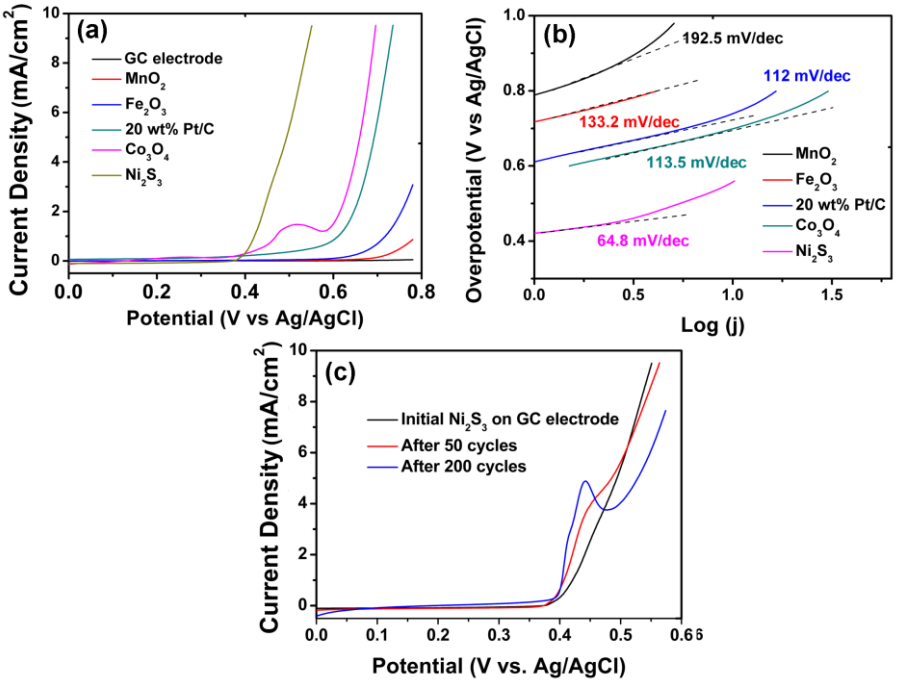

Fig. S1 (a) Polarization curves for OER on bare GC electrode and modified GC electrodes with the Ni_3S_2 nanorods, 20 wt % Pt/C, MnO_2, Fe_2O_3, and Co_3O_4, respectively. (b) Tafel plot (overpotential versus log current) derived from a). (c) OER polarization curves for Ni_3S_2 nanorods loaded on GC electrode before and after 50, 200 cycles of accelerated stability test, respectively.

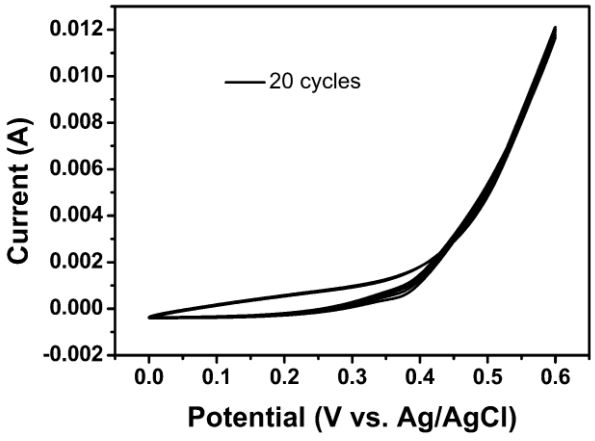

Fig. S2 Cyclic voltammograms of Ni_3S_2/Ni electrode in a potential range of 0 to 0.6 V at a constant scan rate of 10 mV/s.

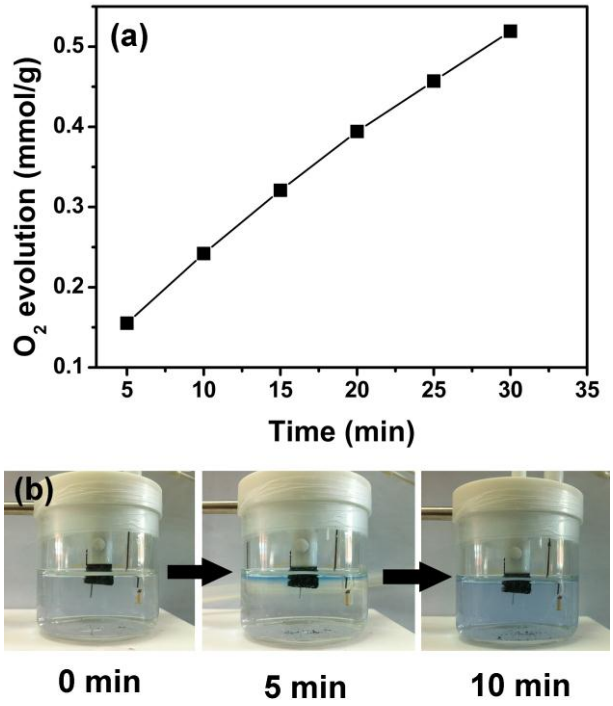

Fig. S3 (a) The oxygen production activity of Ni_3S_2/Ni electrode with applied potential at +0.5 V. (b) The bubbles formed on the Ni_3S_2/Ni electrode and the color change of electrolyte.

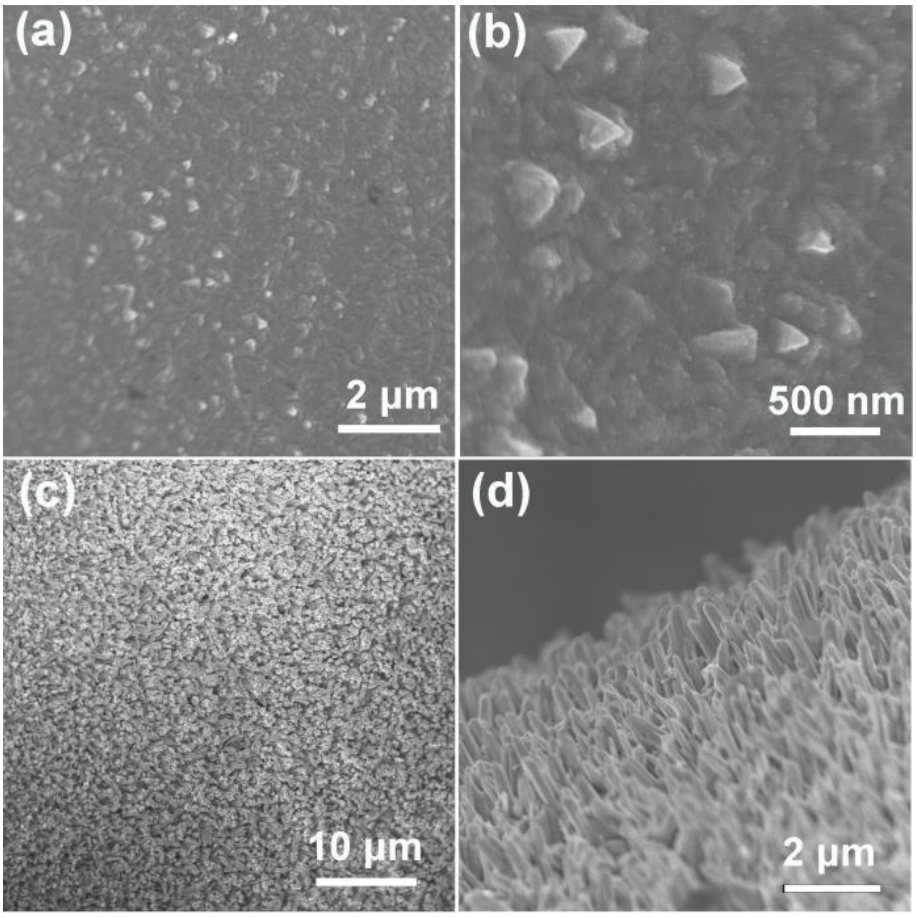

Fig. S4 SEM images of the Ni_3S_2/Ni obtained by different hydrothermal reaction time: (a, b) 2 h and (c, d) 6 h.

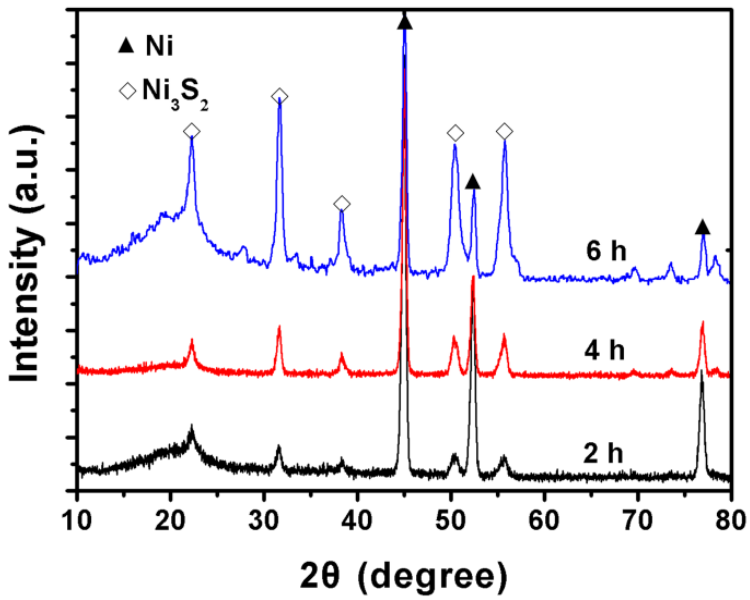

Fig. S5 XRD result of the Ni_3S_2/Ni obtained by different hydrothermal reaction time.

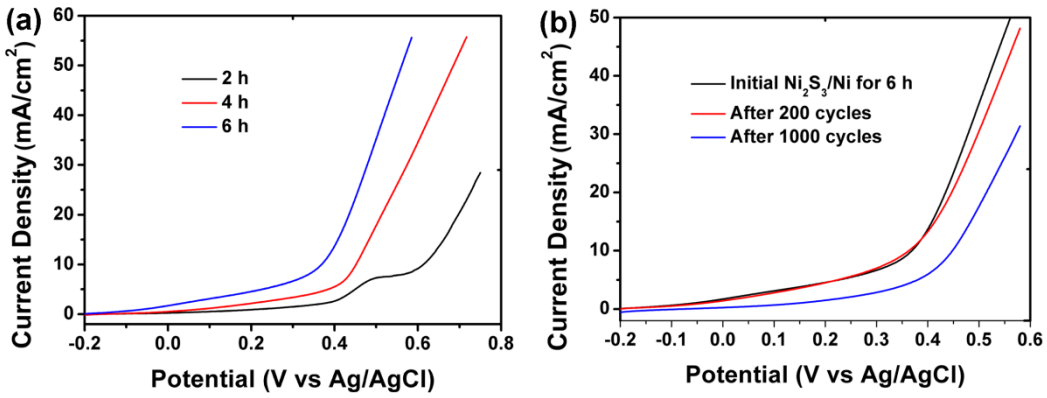

Fig. S6 (a) OER polarization curves of the Ni_3S_2/Ni electrodes obtained by different hydrothermal reaction time. (b) OER polarization curves of Ni_3S_2/Ni electrodes (6 h) before and after the different cycles of accelerated stability test.

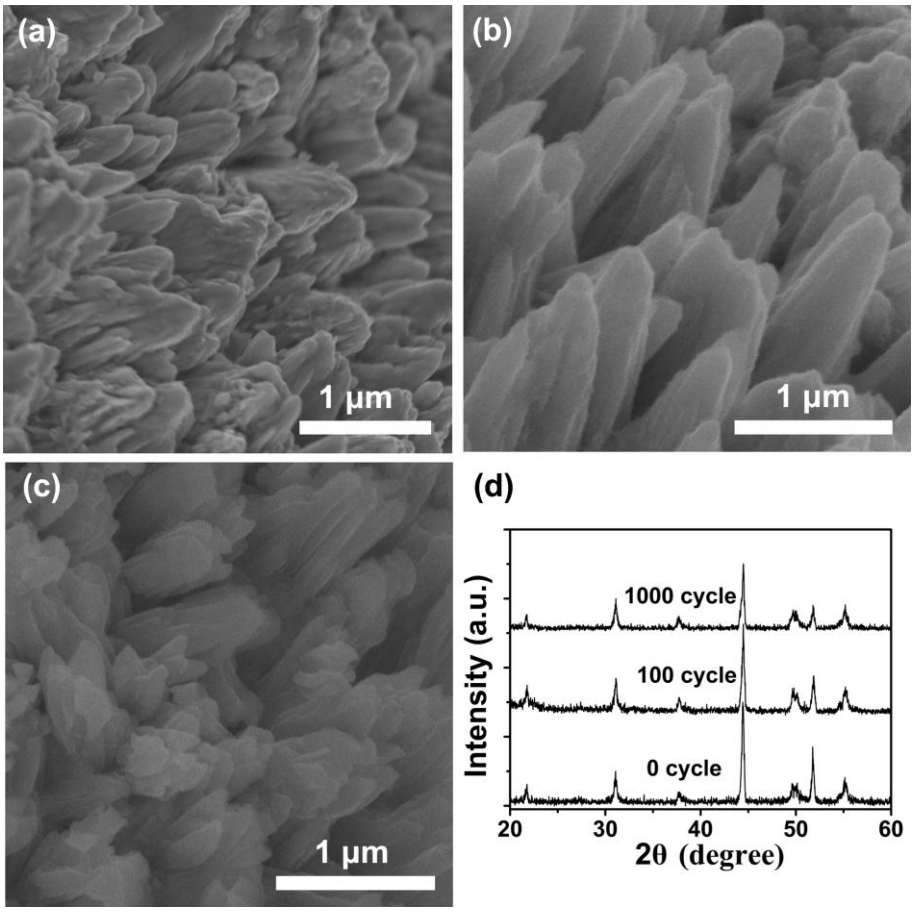

Fig. S7 SEM images of the Ni_3S_2 nanorods/Ni foam composite electrodes: (a) before

catalytic reaction, (b) after 100 cycles and (c) after 1000 cycles of catalytic reaction, (d) XRD results of the corresponding composite electrodes.