

Supplementary Materials for

Electrocatalytic water splitting with unprecedentedly low overpotentials by nickel sulfide nanowires stuffed into carbon nitride scabbards

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Materials and Methods

Materials.

The Nickel Foam (NF, 1.6 x 100 x 110 mm, Nilaco Co) was purchased, and cleaned by sonication in dilute HCl, distilled water, and acetone for 5 min each, and finally dried at 70 °C overnight before use. Millipore water (18 M Ω cm) was used for all the experiments. All solvents and reagents of the purest grade were used as received.

Preparation of a control NiS_x electrode.

The control NiS_x electrode was prepared in the same manner using sulfur powder (4.0 g) instead of CH₄N₂S and characterized by XRD, SEM, and EDS (Fig. S5).

Preparation of a control IrO_x electrode.

10 mg of commercially-available IrO_x (Sigma-Aldrich) was dispersed into water/isopropanol (0.6/0.35 ml) and then 50 μ l of Nafion (Nafion 117 solution, Sigma-Aldrich) was added into the solution. The mixture was sonicated for 2 h to form a uniform ink, which was then dropwise cast onto the NF electrode with a mass loading of 1.0 mg cm⁻². The prepared electrodes were dried at 70° for 1 h before measurement.

Preparation of a Pt-coated electrode.

H₂PtCl₆ was added in 10 ml of MeOH / MeIm solvents (3:1, volume ratio) to give a yellow precursor solution (20 mM). The solution was sonicated for at least 2 h before use. The NF electrode (1.0 x 2.0 cm) was soaked into the precursor solution for 30 s and dried to form a Pt layer on the NF surface. The layer was calcined under air from room temperature to 200 °C at 5.8 °C min⁻¹ and maintained for 2 h, followed by raising the temperature to 450 °C at 8.3 °C min⁻¹ and maintained for 2 h to form the Pt-coated NF electrode. The formed film was washed thoroughly with deionized water, and then dried at 70 °C for at least 2 h.

Structural characterization.

X-ray diffraction patterns (XRD) were collected by Rigaku (MiniFlex 600) using monochromated Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation. The XRD patterns were recorded from 5 to 70 degree in 2θ at a step size of 0.02 degree and a scan rate of 0.25 degree min⁻¹. The surface morphology was observed by a scanning electron microscope (SEM; JEOL JSM-6500F) operated at 15 KV accelerating voltage and 15 mm working distance. The energy dispersive X-ray spectroscopic (EDS) data were taken using an electron probe microanalysis (JEOL JED-

2300) operated at an accelerating voltage of 10 kV. The transmission electron microscopic (TEM) and scanning transmission electron microscopic (STEM) images were recorded by JEOL JEM-2100F with a EDS spectrometer (EX-24200M1G2T), operated at 200 kV. X-ray photoelectron spectra (XPS) were obtained using a Ulvac Phi 5000 Versa Probe CU X-ray photoelectron spectrometer. The photoelectrons emitted by a monochromated Al K α (1486.6 eV; 350 W) radiation were collected with path energy of 23.5 eV through a hemispherical analyzer. The pressure in the analyzing chamber was below 1×10^{-9} Torr during the measurements. All spectra in XPS were calibrated to C 1s = 284.8 eV.

Table S1. Comparison in OER performances of the present NiS_x/C₃N₄ anode with the state-of-the-art OER anodes with the excellent $\eta_{O_2}^{10}$ values less than 200 mV ^{a)}.

Anodes	Current collector	Γ / mg cm⁻²	Fabrication method	Medium	$\eta_{O_2}^{10}$/ mV	Tafel slope / mV dec⁻¹	Ref.
NiS _x /C ₃ N ₄	NF	NA	Gas-solid reaction	1.0 M KOH	32	48	This work
Ni(OH) ₂ NR ^{b)}	carbon cloth	1.9	Electrochemical oxidation of NiS ₂	1.0 M KOH	162	72	(24)
FeNiWO _x	NF	43.2	Dipping, calc. 450 °C	1.0 M KOH	167	49	(23)
Fe ²⁺ -NiFe LDH ^{c)}	NF	3.0	Drop casting with Nafion	1.0 M KOH	195	NA	(22)
NiFeCu metal/oxide	NF	10.2	Electrodeposition	1.0 M KOH	180	33	(18)
FeCoWO(OH)	Au/NF	0.39	Drop casting with Nafion	1.0 M KOH	191	NA	(19)
NiCo ₂ S ₄ /NiFe LDH ^{d)}	NF	NA	Hydrothermal	1.0 M KOH	195	46.3	(21)
Fe _{0.2} Ni _{0.8} Se ₂ -derived oxide	NF	NA	Hydrothermal	1.0 M KOH	195	28	(20)
Cr ⁶⁺ /N-G ^{e)}	NF	1.0	Drop casting with Nafion	1.0 M KOH	197	NA	(17)

^{a)} “NA” expresses “not available”, ^{b)} NR = nanoribbon ^{d)} LDH = Layered double hydroxide, ^{e)} N-G nitrogen-doped graphene.

Figs. S1-S16

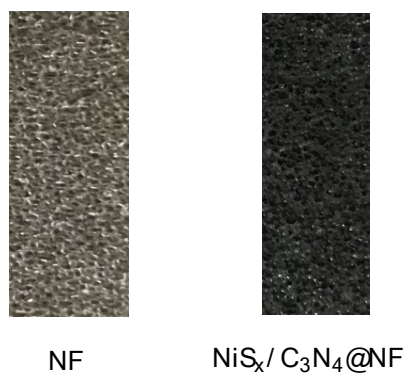
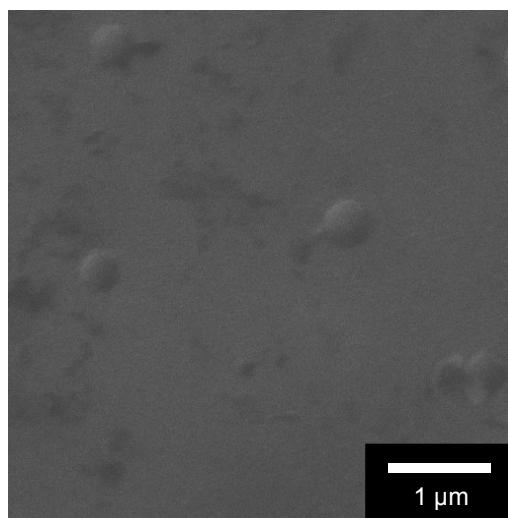


Fig. S1. Photos of NF and $\text{NiS}_x/\text{C}_3\text{N}_4$ on NF.



□□ **Fig. S2.** Top view SEM image of the bare NF surface.

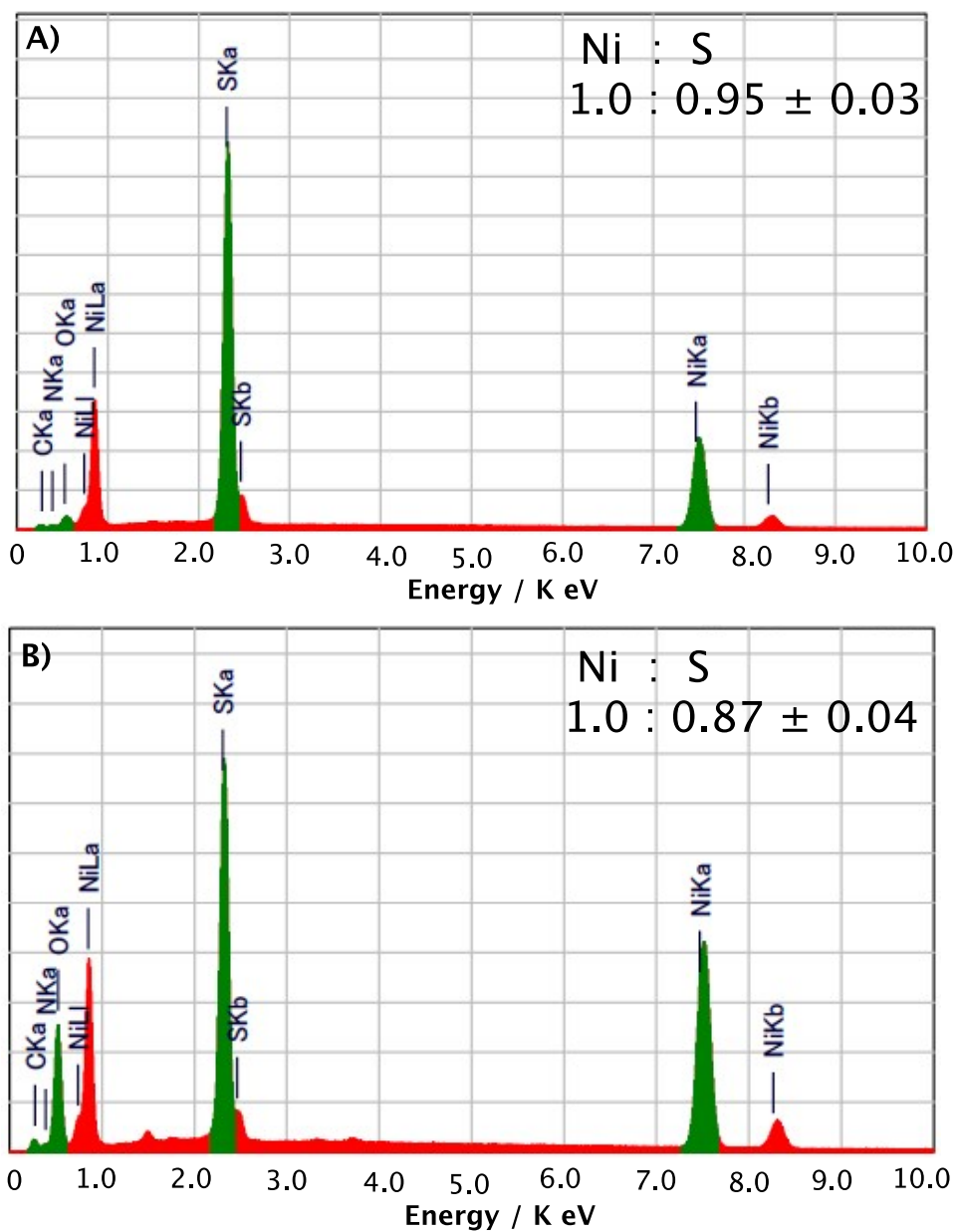


Fig. S3. EDS spectra of the NiS_x/C₃N₄ on NF (A) before and (B) after electrolysis under galvanostatic conditions at 10 mA cm⁻² for 5 h.

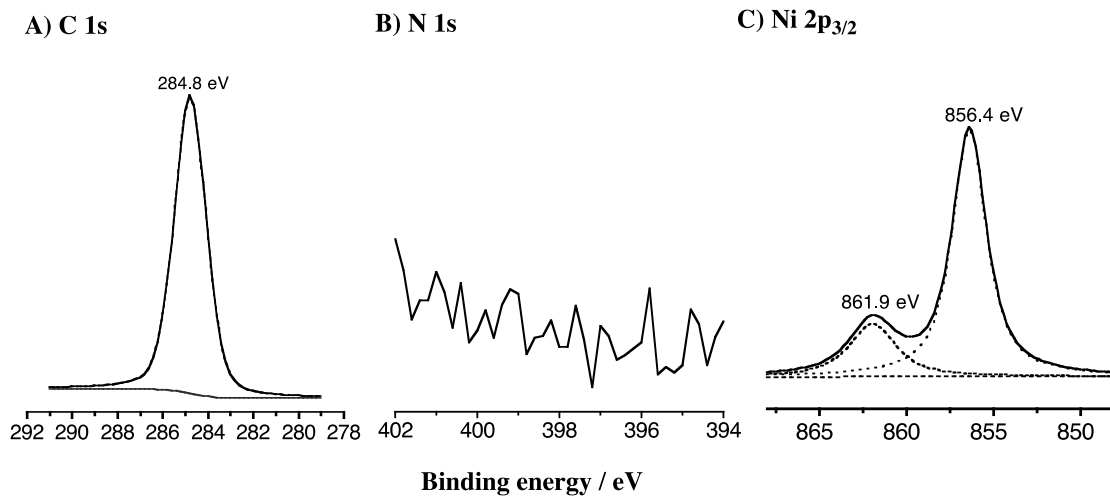


Fig. S4. X-ray photoelectron spectroscopy (XPS) spectra of the NF electrode in (A) C 1s, (B) N 1s, and (C) Ni 2p_{3/2} regions.

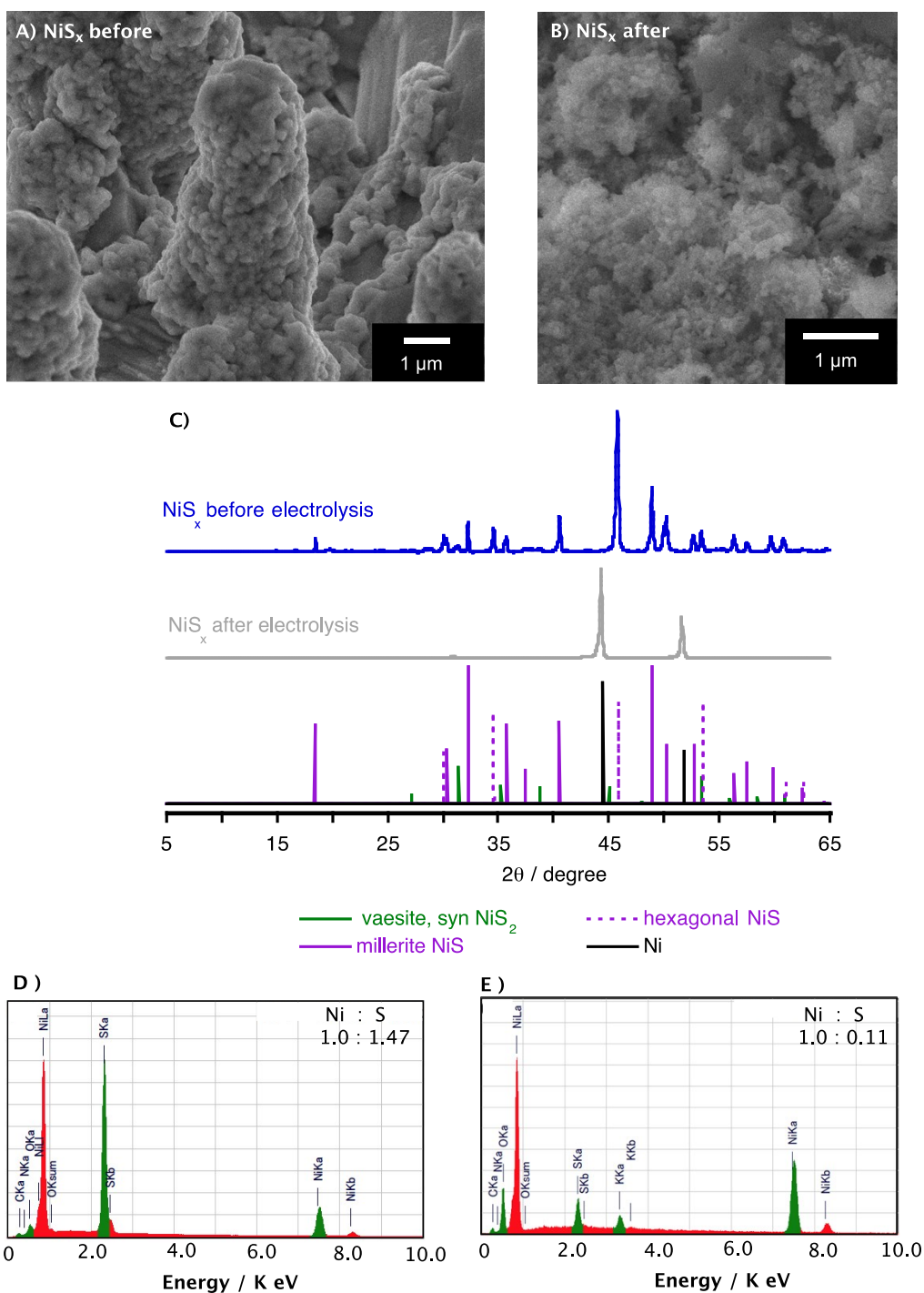


Fig. S5. Characterization of the control NiS_x electrode before and after 5h chronopotentiometry at 10 mA cm^{-2} . SEM images (A) before and (B) after electrolysis. (C) XRD patterns before (blue) and after (grey) electrolysis and pdf data of the assigned compounds. Ni: 01-070-0989, millerite NiS: 03-065-2117, hexagonal nickel sulfide NiS: 75-0613 and vaesite, syn NiS_2 : pdf 01-089-7142. EDS data (D) before and (E) after electrolysis.

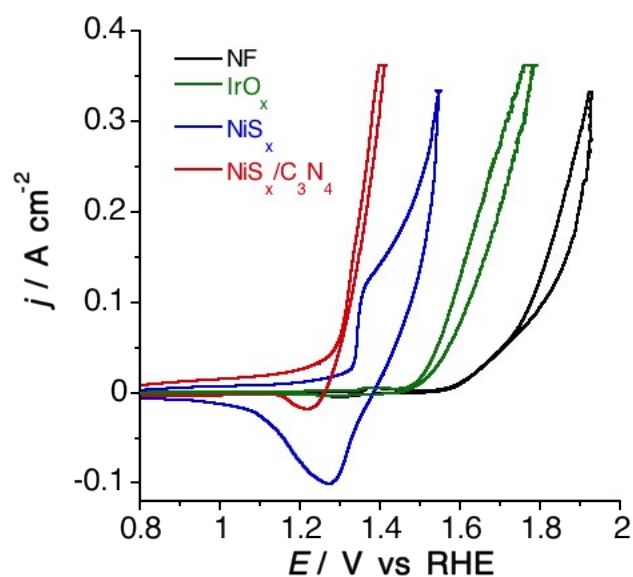


Fig. S6. CVs (iR corrected) of $\text{NiS}_x/\text{C}_3\text{N}_4$, NiS_x , IrO_x on the NF electrode (1.0 cm^2 of geometric area) in 1.0 M KOH solutions (pH 14.0) at 10 mV s^{-1} of a scan rate. The used electrodes are indicated by different colors in the figure.

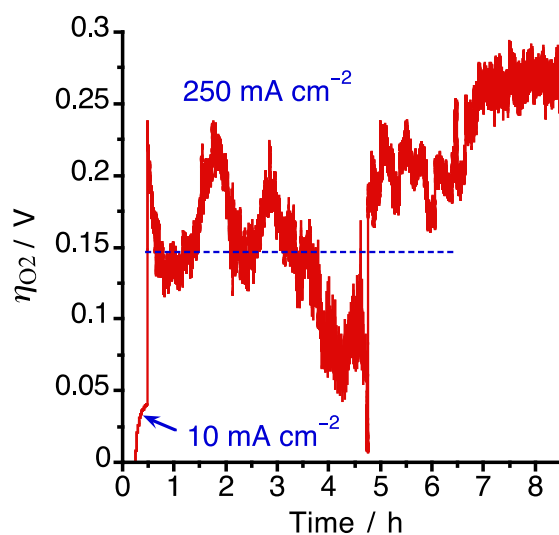


Fig. S7. Chronopotentiogram in OER at the current density of 10 mA cm^{-2} and then switched to 250 mA cm^{-2} after 30 min for the $\text{NiS}_x/\text{C}_3\text{N}_4$ electrode.

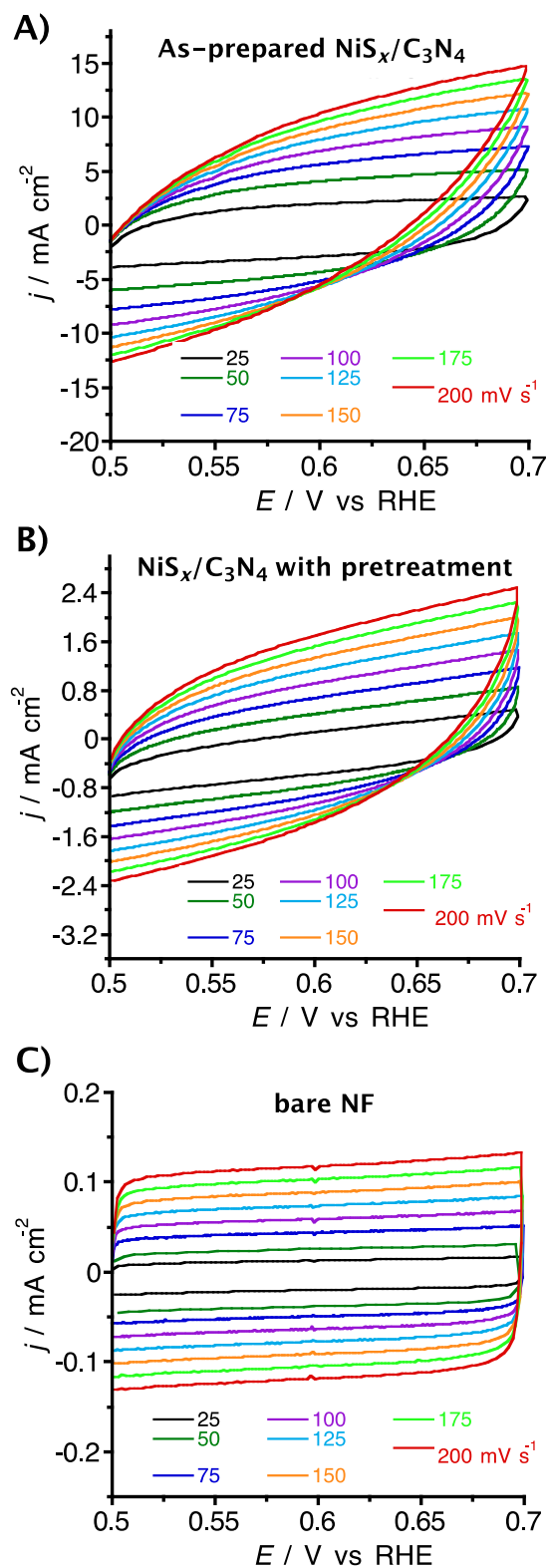


Fig. S8. CVs of (A) the as-prepared $\text{NiS}_x/\text{C}_3\text{N}_4$ electrode, (B) one with the pretreatment of anodic polarization for 30 min at 10 mA cm^{-2} in 1.0 M KOH , (C) the bare NF electrode in 1.0 M KOH solutions (pH 14.0) in the potential range of $0.5\text{-}0.7 \text{ V vs RHE}$ at different scan rates (v) of $25\text{-}200 \text{ mV s}^{-1}$. The v values are indicated by different colors in respective figures.

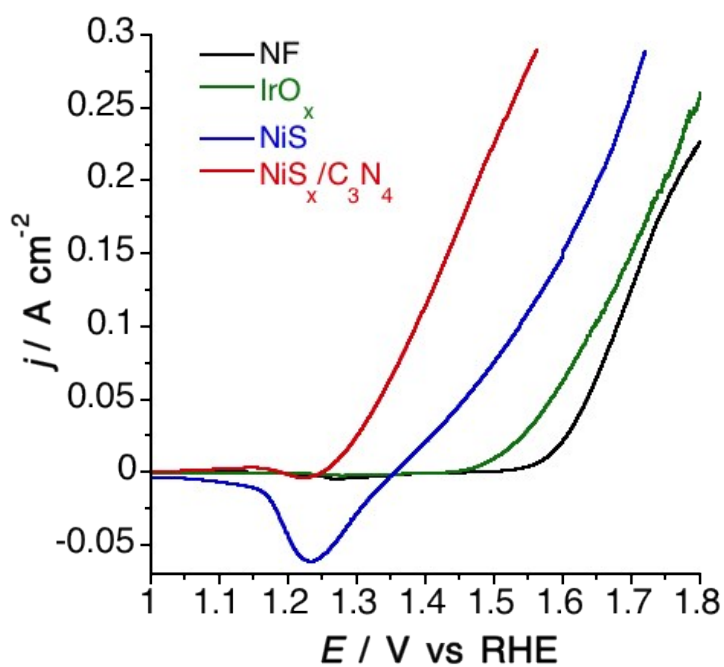


Fig. S9. LSVs without iR corrections of $\text{NiS}_x/\text{C}_3\text{N}_4$, NiS_x , IrO_x on the NF electrode (1.0 cm^2 of geometric area) in 1.0 M KOH solutions (pH 14.0) at 5 mV s^{-1} of a scan rate in a negative scan direction. The used electrodes are indicated by different colors in the figure.

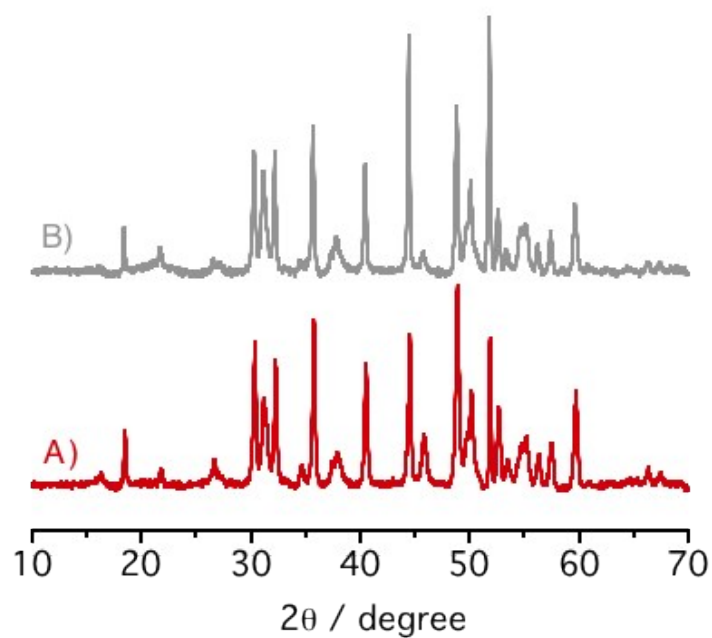


Fig. S10. XRD patterns of the $\text{NiS}_x/\text{C}_3\text{N}_4$ on NF (A) before and (B) after electrolysis at 10 mA cm^{-2} for 5 h.

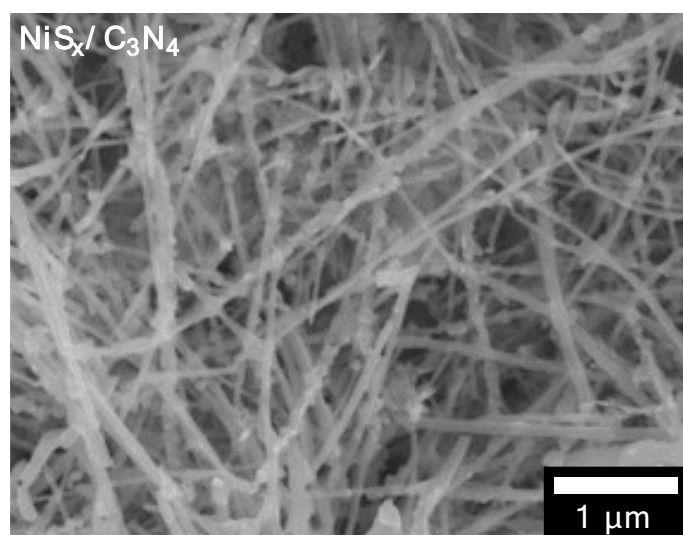


Fig. S11. SEM images (top view) of the $\text{NiS}_x/\text{C}_3\text{N}_4$ surface of NF after electrolysis at 10 mA cm^{-2} for 5 h.

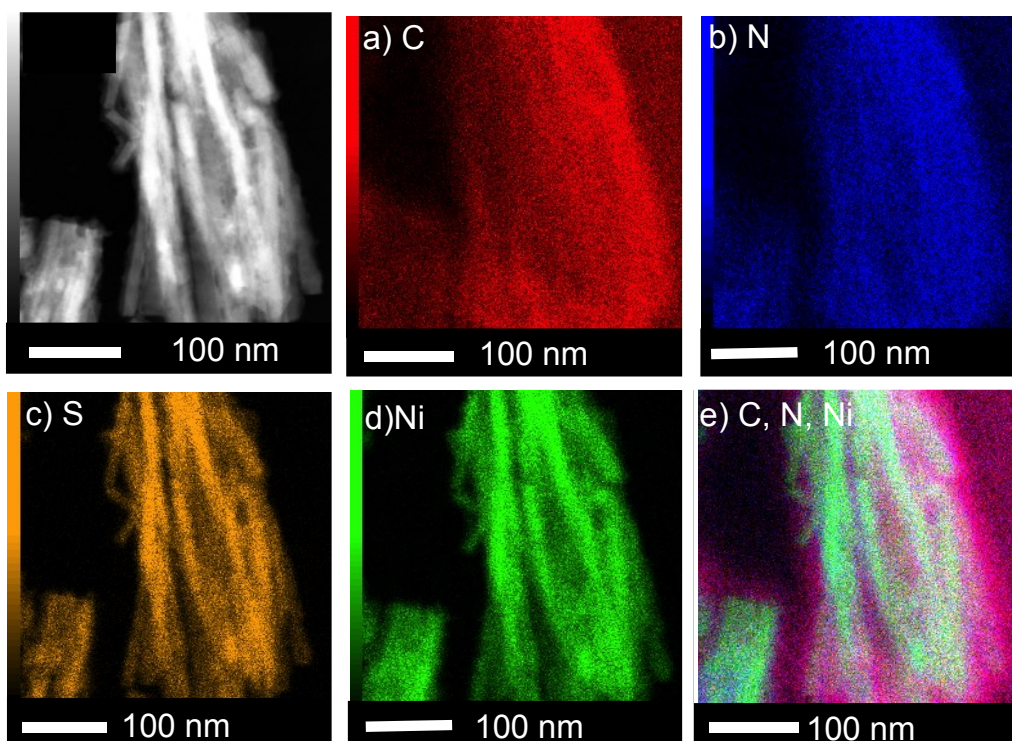


Fig. S12. STEM image of $\text{NiS}_x/\text{C}_3\text{N}_4$ with EDS-elemental mapping of (a) C, (b) N, (c) S, (d) Ni, and (e) overlapped image of elements C (red), N (blue), and Ni (green) after electrolysis at 10 mA cm^{-2} for 5 h.

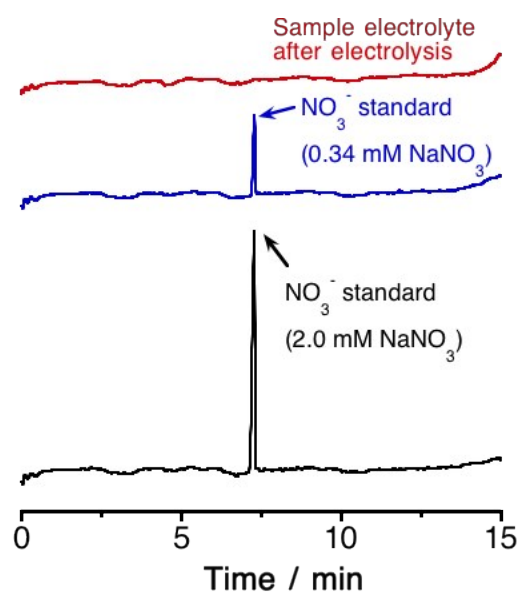


Fig. S13. Capillary electrophoresis chromatograms of the electrolyte solution after the 5 h electrolysis using the $\text{NiS}_x/\text{C}_3\text{N}_4$ electrode (red) and the NO_3^- standard solutions with different concentrations of 0.34 (blue) and 2.0 mM (black).

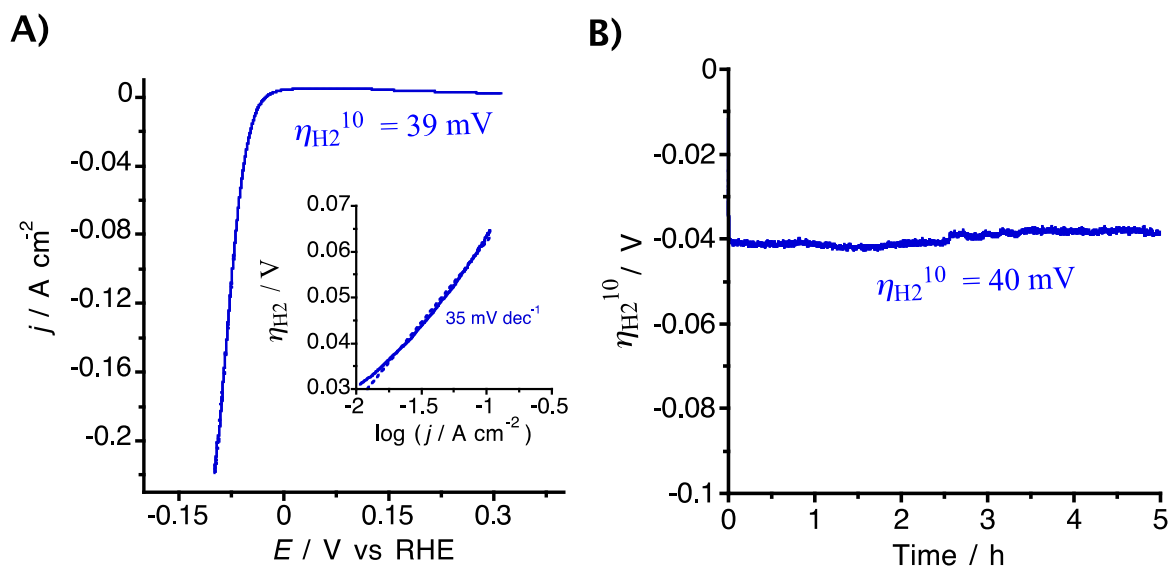


Fig. S14. HER performance. (A) LSV of the Pt-coated NF cathode (1.0 cm^2 of geometric area) as measured at 5 mV s^{-1} of a scan rate in a positive scan direction. The inset shows Tafel plot (solid line) and slope (dashed line) obtained from the LSV. (B) Chronopotentiogram in HER at a current density of -10 mA cm^{-2} using the Pt-coated NF cathode. The electrochemical data were measured in 1.0 M KOH solutions (pH 14.0) and have iR corrections.

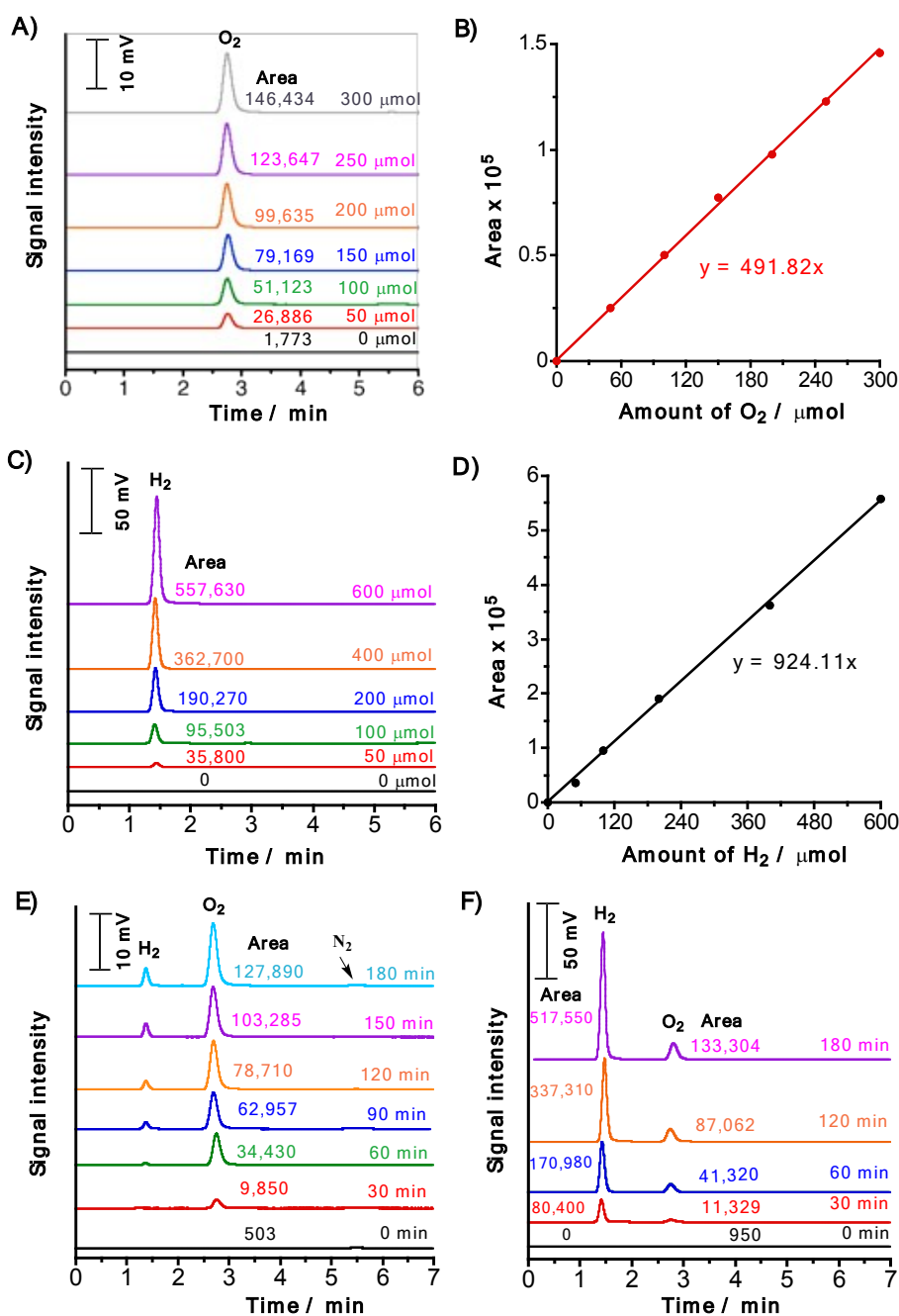


Fig. S15. Gas chromatograph (A and C) with different known amounts and calibration curves (B and D) for O₂ (A and B) and H₂ (C and D) derived from the peak area and the amounts of used gases, respectively. (E) Gas chromatographic data for the anodic compartment equipped with NiS_x/C₃N₄ (1.0 cm² of geometric area) during the electrolysis at 10 mA cm⁻² in a 1.0 M KOH solution (pH 14.0). The signals of H₂ are caused by H₂ evolved and diffused from the cathodic compartment. The very small signals of N₂ were detected, meaning negligible air contamination during the electrolysis. (F) Gas chromatographic data for one compartment cell equipped with the NiS_x/C₃N₄ anode and the Pt-coated NF cathode during the electrolysis at 10 mA cm⁻² in a 1.0 M KOH solution (pH 14.0).

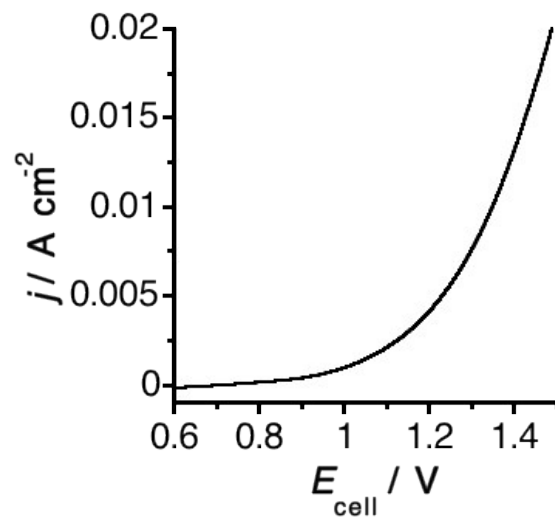


Fig. S16. LSV (without iR correction) of the water spitting (WS) cell (two electrode system) equipped with the $\text{NiS}_x/\text{C}_3\text{N}_4$ anode (1.0 cm^2) and the Pt-coated NF cathode (1.0 cm^2) at 5 mV s^{-1} of a scan rate in a negative scan direction after electrolysis for 5 h.