Supplementary Material

Construction of Core-Shell Ni-Co(OH)F@NiCo$_2$S$_4$ Nanorods for Highly-Efficient Hydrazine-assisted Hydrogen Evolution

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Experimental section

1. Materials

Cobalt nitrate hexahydrate ($Co(NO_3)\cdot6H_2O$) and hydrazine hydrate aqueous solution (80%) were purchased from Fuchen (Tianjin) Chemical Reagent Co. Urea ($CO(NH_2)_2$), ammonium fluoride (NH_4F) and ammonium fluoride (KOH) were purchased from Sinopharm Group Chemical Reagent Co. Nickel foam was purchased from Kunshan Shengshijing New Material Co. Carbon cloth was purchased from Suzhou Shengeruo Technology Co. Usually, nickel foam and carbon cloth was cleaned by ultrasonication in DIW/HCl=1 solution for 5 min before use.

2. Preparation of Ni-Co(OH)F

The Ni-Co(OH)F precursor was prepared through a hydrothermal process. Specifically, 1.0 mmol $Co(NO_3)_2\cdot6H_2O$, 10.0 mmol $CO(NH_2)_2$ and 4.0 mmol NH_4F were dispersed in 40 mL deionized water (DIW). After stirring for 15 minutes, the mixture solution was transferred to a 100-mL Teflon-lined stainless autoclave. After that, the nickel foam (2 cm × 4 cm) was added into the autoclave. Then, the autoclave was sealed, and subsequently heated at 120 °C for 20 h. Finally, the Ni-Co(OH)F precursor was taken out, and washed by DIW for several times, and dried in oven (80 °C in air) for 12 h.

3. Preparation of Ni-Co(OH)F@NiCo$_2$S$_4$

1 cm×2 cm Ni-Co(OH)F precursor and 0.3 g sublimated sulfur were both set in a porcelain boat. The Ni-Co(OH)F precursor was put at upstream position of a tube furnace. Under Ar atmosphere, the tube oven was gradually (2 ℃ min^{-1}) heated to 350 ℃, and kept for 2 h. Finally, the Ni-Co(OH)F@NiCo$_2$S$_4$ sample was obtained.

4. Preparation of NiCo$_2$S$_4$

1 cm×2 cm Ni-Co(OH)F precursor and 0.6 g sublimated sulfur were both set in a porcelain boat. The Ni-Co(OH)F precursor was put at upstream position of a tube furnace. The tube oven was heated to 350 °C (2 °C min^{-1}), and kept for 2 h under Ar atmosphere. Finally, the NiCo$_2$S$_4$ sample was obtained.

5. Preparation of Co(OH)F@CoS$_2$ reference sample

The Co(OH)F precursor was prepared through a hydrothermal process. Specifically, 1.0 mmol Co(NO$_3$)·6H$_2$O, 10.0 mmol CO(NH$_2$)$_2$ and 4.0 mmol NH$_4$F were dispersed in 40 mL DIW. After stirring for 15 minutes, the mixture solution was transferred to a 100-mL Teflon-lined stainless autoclave. After that, the carbon cloth (2 cm × 4 cm) was added into the autoclave. Then, the autoclave was sealed, and subsequently heated at 120 °C for 20 h. Finally, the Co(OH)F precursor was taken out, and washed by DIW for several times, and dried in oven (80 °C in air) for 12 h. 1 cm×2 cm Co(OH)F precursor and 0.3 g sublimated sulfur were both set in a porcelain boat. The Co(OH)F precursor was put at upstream position of a tube furnace. Under Ar atmosphere, the tube oven was gradually (2 °C min^{-1}) heated to 350 °C, and kept for 2 h. Finally, the reference sample Co(OH)F@CoS$_2$ was obtained.

5. Material Characterization

The X-ray diffraction (XRD) pattern was obtained from a Bruker D8 Advance X-ray diffractometer with Cu K$_\alpha$ (λ = 1.5418 Å) radiation (40 kV, 40 mA), and all samples were directly exposed to air. The surface morphology of the samples was observed by scanning electron microscopy (SEM) technique on a Hitachi S-4800 microscope. The microstructure and chemical composition of the samples were taken on a JEOL JEM-2100F transmission electron microscopy (TEM) and additional energy dispersive spectrometer (EDS) with an acceleration voltage of 200 kV. Surface valence states were characterized by X-ray photoelectron

spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). The H_2 pulse chemical adsorption was measured on a Xianquan TP-5080 adsorption analyzer with a TCD detector. Specifically, 50 mg sample was placed in a quartz tube and degassed at 150 °C for 1 h under Ar atmosphere (30 ml min^{-1}). Then, the sample was cooled down to 50 °C. After the baseline was stabilized, pulse adsorption experiments were carried out by using a mixture of 1 vol.% H_2/Ar. The number of cycles was 20.

6. Electrochemical test

The test system. All electrochemical tests were performed on CHI 660e electrochemical workstation at room temperature. In three-electrode system, the nickel foam with electrocatalysts, Hg/HgO and graphite rod (0.6 cm diameter) were used as the work electrode, reference electrode and counter electrode, respectively. The potentials were calculated by the equation: E (RHE) = E (Hg/HgO) + 0.094 V + 0.059 × pH. All experiments were implemented 1.0 M KOH solution, 1.0 M KOH + X M N_2H_4 (X=0.1, 0.3, 0.5, 1.0) solution or 0.1 M H_2SO_4 solution.

The electrode preparation. 5 mg Pt/C (20%, Johnson Matthey) was dispersed in a solution containing 50 μL Nafion and 450 μL ethanol to form a homogeneous catalyst ink. 100 μL ink was dropped onto the clean nickel foam substrate (1 cm^{-2}), and then the nickel foam was dried in oven (60 °C in air) for 12 hours. The mass loading of Pt/C (20%, Johnson Matthey) was set at 1 mg cm^{-2}. The Ni-Co(OH)F, Ni-Co(OH)F@NiCo$_2$S$_4$, NiCo$_2$S$_4$ and Co(OH)F@CoS$_2$ supported on the nickel foam/carbon cloth substrate were directly used as the work electrode. Effective electrode area (nickel foam/carbon cloth substrate) was set at 1 cm^{-2} (1 cm × 1 cm).

The test methods. Linear sweep voltammetry (LSV) was measured by 5 mV s^{-1} for the polarization curves. The electrochemical surface-active area (ECSA) was tested *via* the cyclic voltammetry (CV), scan rates were 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s^{-1}. The double-layer capacitance (C_{dl}) was calculated out

according to ECSA CV curves. Electrochemical impedance spectroscopy (EIS) was obtained at the frequency range between 0.01 Hz and 100 KHz. The drainage method was used in Faradaic efficiency measurements. Chronopotentiometry was implemented under the potential of 97 mV and 0.25 V (vs. RHE) to test the HER and cell stability, respectively.
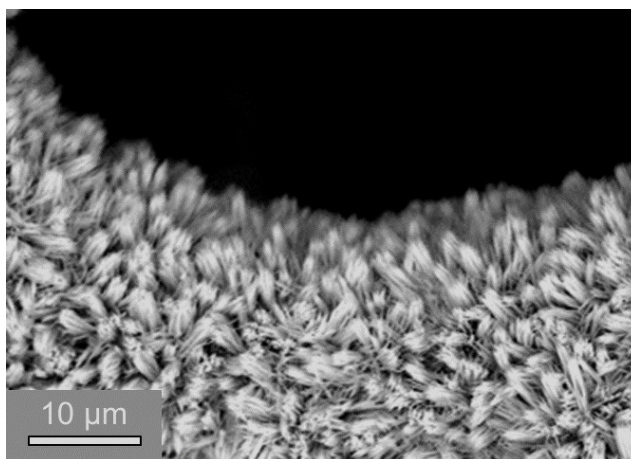
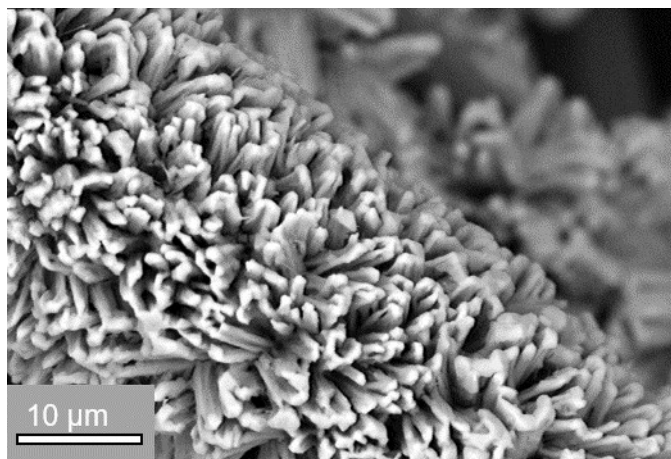**Figure S1.** SEM image of Ni-Co(OH)F nanorods on Ni foam.
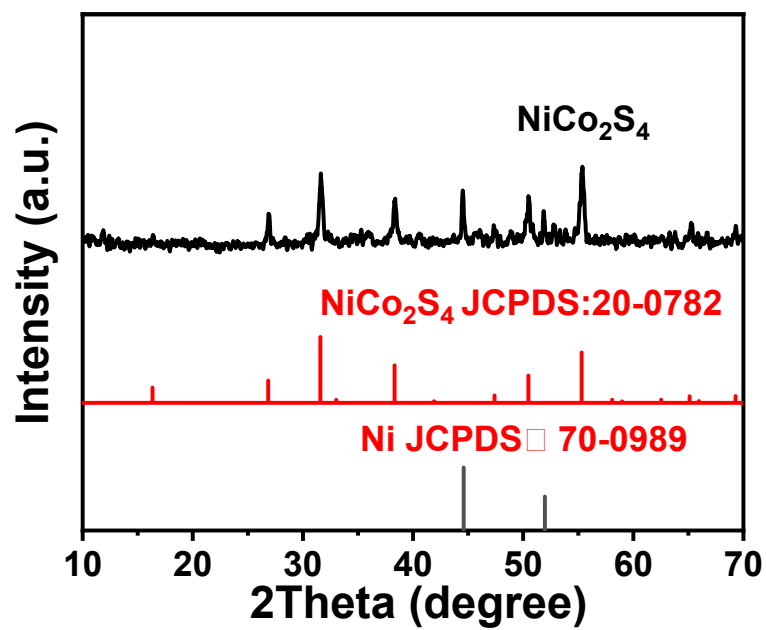
Figure S2. SEM image of Co(OH)F@Co$_2$S reference sample.

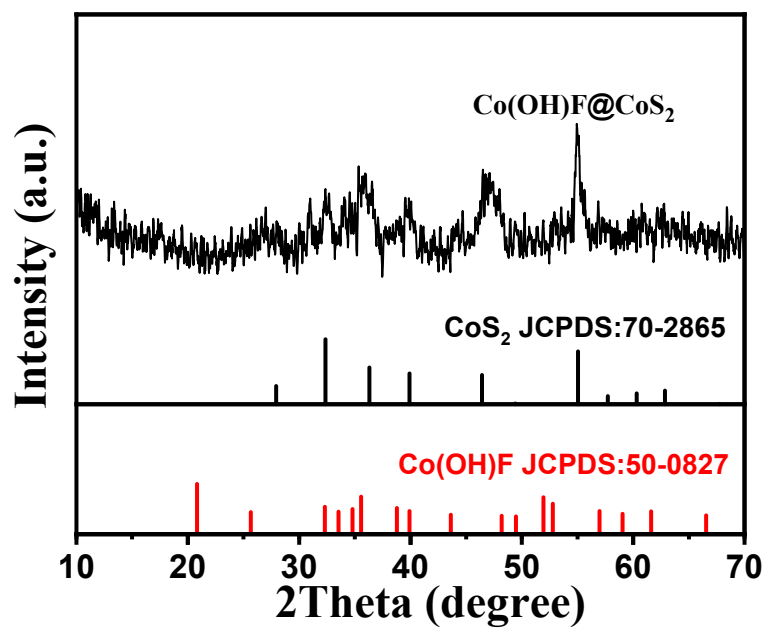**Figure S3.** XRD pattern of $NiCo_2S_4$ reference sample.

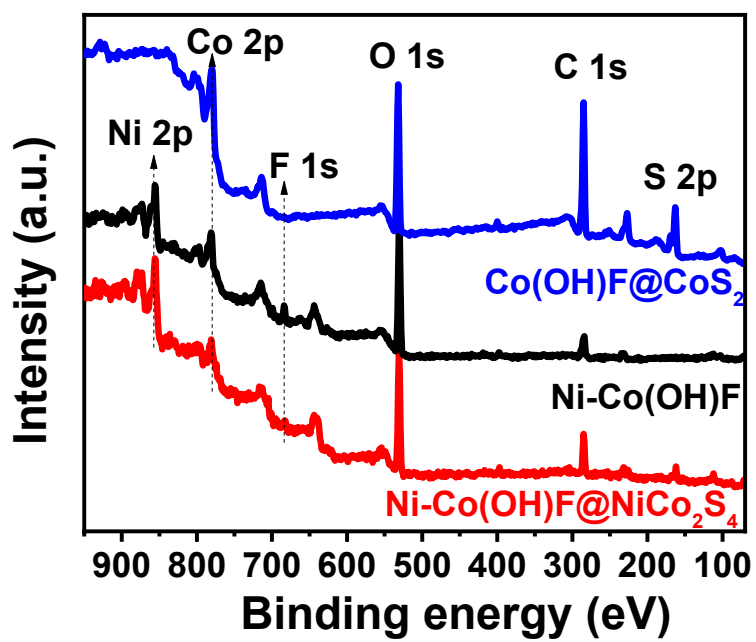**Figure S4.** XRD pattern of Co(OH)F@CoS$_2$ reference sample.

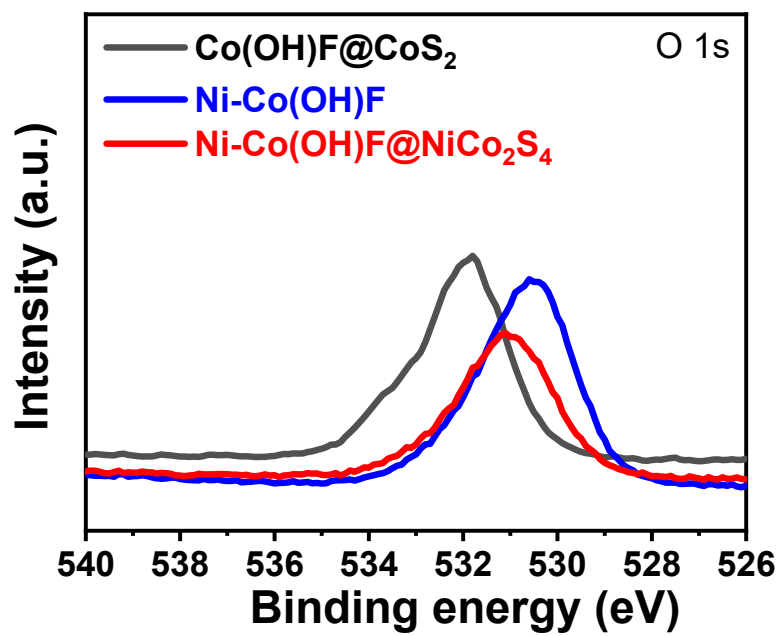**Figure S5.** XPS survey spectra for Ni-Co(OH)F@NiCo$_2$S$_4$, Ni-Co(OH)F and Co(OH)F@CoS$_2$.

Figure S6. The O 1s spectra for Co(OH)F@CoS$_2$, Ni-Co(OH)F and Ni-Co(OH)F@NiCo$_2$S$_4$.
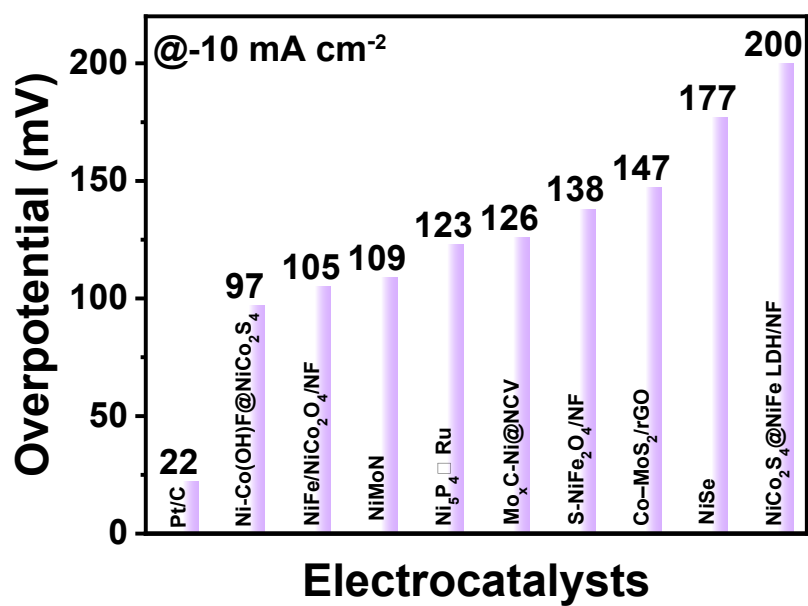
Figure S7. Overpotential comparison (@-10 mA cm^{-2}) of recent reported electrocatalysts.
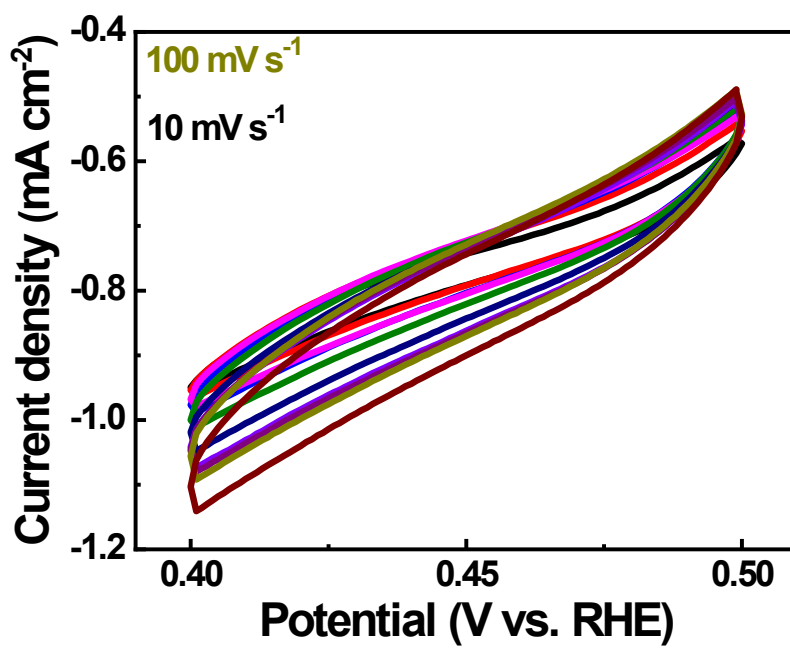
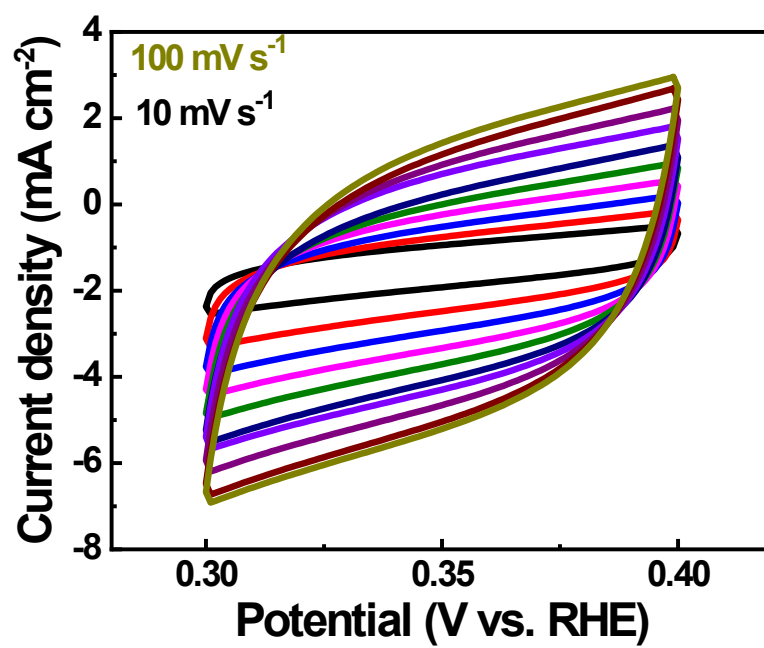**Figure S8.** CV curves of Ni-Co(OH)F at different scanning rates.

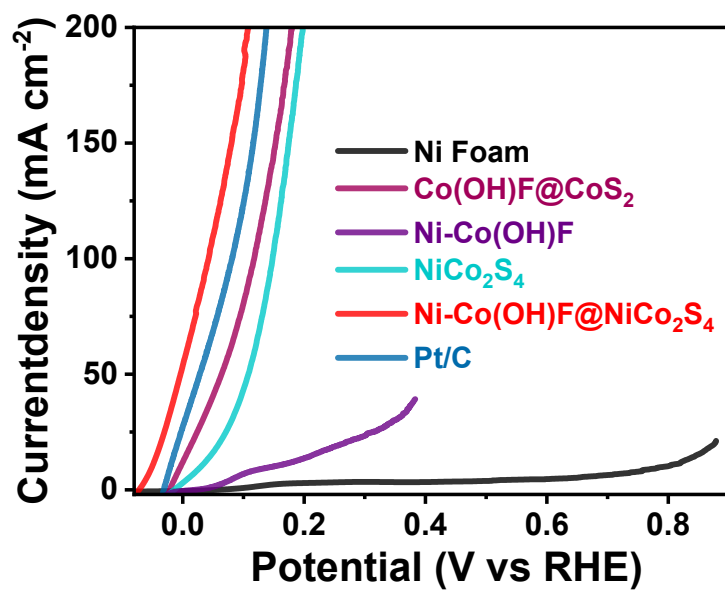**Figure S9.** CV curves of Ni-Co(OH)F@NiCo$_2$S$_4$ at different scanning rates.

Figure S10. Hydrazine oxidation reaction activity analysis: *iR*-corrected LSV curves of Co(OH)F@CoS$_2$,

Ni-Co(OH)F, NiCo$_2$S$_4$, Ni-Co(OH)F@NiCo$_2$S$_4$, Ni Foam and Pt/C in 1.0 M KOH containing 1.5 M

hydrazine.

Table S1. The HER activities of Ni/Co-involved electrocatalysts.

Catalyst	Potential (mV) at 10 mA cm^{-2}	Tafel slope (mV/decade)	Refs.
Ni-Co(OH)F@NiCo$_2$S$_4$	97	58	This work
Ni$_5$P$_4$-Ru	123	56.7	Adv. Mater. 2020, 32, 1906972
Mo$_x$C-Ni@NCV	126	97	J. Am. Chem. Soc. 2015, 137, 15753–15759
NiMoN	109	95	Adv. Energy Mater.2016, 6, 1600221
NiSe	177	58.2	Adv. Energy Mater. 2018, 8, 1702704
Co–MoS$_2$/rGO	147	49.5	Int. J. Hydrogen Energy 2020, 45, 9583–9591
NiSe	177	58.2	Adv. Energy Mater. 2018, 8, 1702704
NiCo$_2$S$_4$@NiFe LDH/NF	200	101.1	ACS Appl. Mater. Interfaces 2017, 9, 15364-15372
NiFe/NiCo$_2$O$_4$/NF	105	88	Adv. Funct. Mater. 2016, 26, 3515-3523
S-NiFe$_2$O$_4$/NF	138	61.3	Nano Energy 2017, 40, 264-273
Co$_{6.25}$Fe$_{18.75}$Ni$_{75}$O$_x$/NF	84	53.6	J. Mater. Chem. A 2018, 6, 167-178

Table S2. The HzOR activities of Ni/Co-involved electrocatalysts.

Catalyst	Electrolyte	J (mA cm^{-2})	Potential (mV)	Refs.
Ni-Co(OH)F@NiCo$_2$S$_4$	1.0 M KOH+ 1.0 M N$_2$H$_4$	10	30	This work
NiCo/NiCo$_2$S$_4$@NiCo/NF	1.0 M KOH	10	294	Electrochim. Acta 2018, 265, 19-31
Ni$_3$S$_2$/NF	1.0 M KOH	10	295	Nanoscale. 2019, 11, 2355-2365
CoP/Co-20	1.0 M KOH+ 0.5 M N$_2$H$_4$	10	-69	J. Phys. Chem. Lett. 2021, 12, 4849-4856
Co$_3$Ta/C	3.0 M KOH+ 0.5 M N$_2$H$_4$	10	-39	Nat. Commun. 2019, 10, 4514
CoS$_2$	1.0 M KOH+ 0.1 M N$_2$H$_4$	100	205	Nat. Commun. 2018, 9, 4365