

Supporting information

CoS₂ needle arrays induced local pseudo-acidic environment for alkaline hydrogen evolution

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Experimental section

Materials: Cobaltous nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium fluoride (NH_4F), and urea ($\text{CO}(\text{NH}_2)_2$) were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20wt% Pt) was bought from Sigma-Aldrich Chemical Reagent Co., Ltd. Carbon cloth was purchased from Suzhou Siner Technology Co., Ltd. and cleaned by sequential sonication in acetone, ultrapure water, and ethanol several times. All the chemicals in the experiments were analytical grade and used without further treatments. Deionized water was purified through a Millipore system.

Preparation of $\text{Co}(\text{OH})\text{F}@$ carbon cloth

The carbon cloth substrate (1 cm \times 2 cm) was cleaned sequentially in acetone, ethanol, and water, each for 20 min through sonication treatment. During in-situ growth, 8 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 16 mmol of $\text{CO}(\text{NH}_2)_2$, and 16 mmol of NH_4F were dissolved in 40 mL of deionized water under vigorous stirring. Afterward, the cleaned carbon cloth was immersed into the solution, and transferred into a Teflon-lined stainless-steel autoclave, and then maintained at 120 °C for 6 h in an electric oven. The carbon cloth with precursor $\text{Co}(\text{OH})\text{F}$ was washed by deionized water and ethanol several times, and then dried at 60 °C for 12 h.

Preparation of CoS_2 NAs@C and DNs@C

To synthesize the CoS_2 NAs@C sample, a piece of $\text{Co}(\text{OH})\text{F}@$ C was placed near to the sulfur powder in a porcelain boat, with sulfur powder at the upstream side of the tube furnace. Subsequently, the furnace was heated to 400 °C at 2 °C min^{-1} under a flowing Ar atmosphere and maintained for 2 h, and then program-cooled to ambient temperature.

The synthesis process of the CoS_2 DNs@C electrode was similar to that of the CoS_2 NAs@C electrode, with changing the ratio of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$. Specially, 0.8 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 16 mmol of $\text{CO}(\text{NH}_2)_2$, and 16 mmol of NH_4F were dissolved in 40 mL of deionized water to prepared the precursor.

Preparation of Pt/C@C

The commercial Pt/C powders were dispersed into mixed solutions containing water, ethanol, and Nafion. The obtained inks were then drop-cast onto carbon cloth to prepare Pt/C@C. The mass loading of Pt on carbon cloth was about 2 mg cm⁻².

Characterization: Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Discover diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were made on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 10 keV. Transmission electron microscope (TEM) images were taken on a Tecnai G2 F20 electron microscope (FEI, Tokyo, American) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Thermo Scientific K-Alpha X-ray photoelectron spectrometer using Al as the exciting source.

Electrochemical measurement: All electrochemical properties of as-prepared electrodes were tested in 1.0 M KOH electrolyte using a CHI 6009E electrochemical workstation in a three-electrode system. The NAs@C, DNs@C, Pt/C and carbon cloth electrodes were directly used as the working electrode, while a carbon rod and an Ag/AgCl served as the counter and reference electrode, respectively. LSV measurements were obtained at a sweep rate of 5 mV s⁻¹, and CV was conducted at various scan rates in the potential range of $-0.6 \sim 0 \text{ V (vs. RHE)}$ from 20 to 100 mV s⁻¹ to evaluate C_{dl} of electrode. CV for stability testing was performed at a scanning rate of 100 mV s⁻¹ for 1000 cycles from $-0.6 \sim 0 \text{ V (vs. RHE)}$. Long-term durability was calculated by chronopotentiometry at fixed potentials for 21 h. Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of 10⁵ to 0.1 Hz at an AC amplitude of 10 mV. All potentials mentioned in this work were calibrated with respect to the RHE by the equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + E_0(\text{Ag/AgCl}) + 0.059 \times \text{pH (V)}$.

Finite-element simulations (COMSOL Multiphysics simulations): The LEF and OH^- concentration around the electrodes within the vicinity of the electrodes was simulated using the COMSOL multiphysics finite-element-based solver. Electric field E was computed as the opposite gradient of the electric potential V as follows: $E = -\nabla V$. The electric conductivity of the CoS_2 electrode was taken to be $3.2 \times 10^6 \text{ S m}^{-1}$. The electrolyte conductivity was assumed to be 166.6 S m^{-1} . The ‘Electrostatics’ and the ‘Transport of diluted species’ modules were combined to solve the potassium ion density. The diffusion coefficients D of the bicarbonate ion in water was taken to be $7.02 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. In the diffusion layer, there are cations and anions diffusing freely in the electrolyte, forming concentration gradients towards and away from the electrode surface.

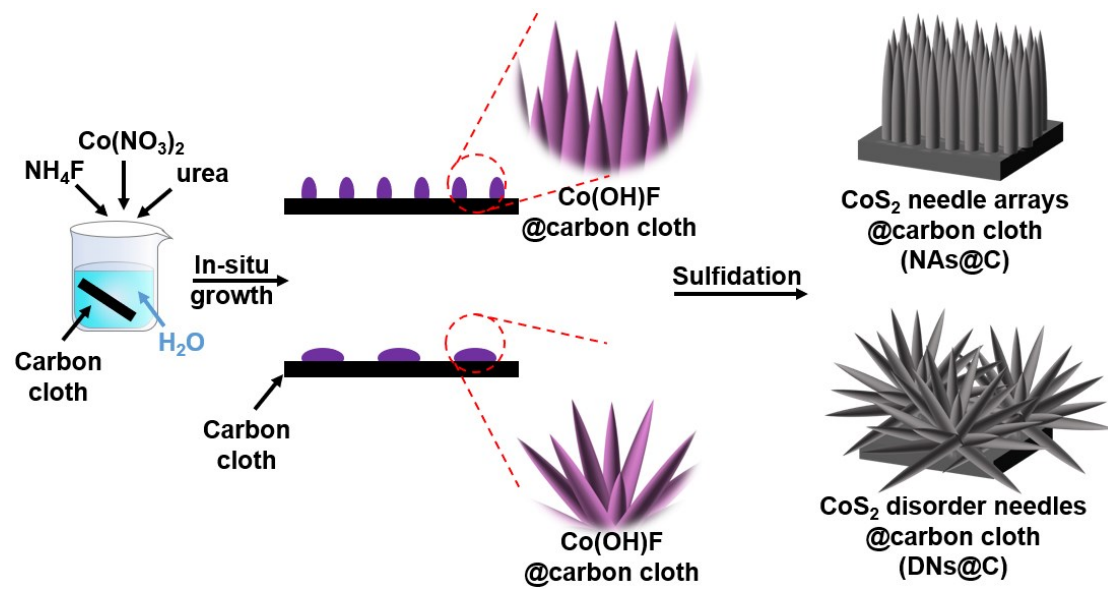


Fig. S1 Schematic description of the fabrication process of NAs@C and DNAs@C.

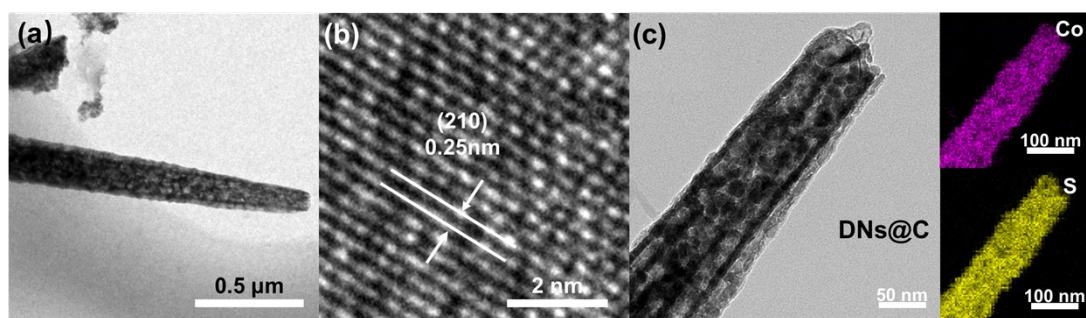


Fig. S2 (a) TEM image of DNs@C. (b) HRTEM image of DNs@C. (c) The corresponding EDX mapping images of DNs@C.

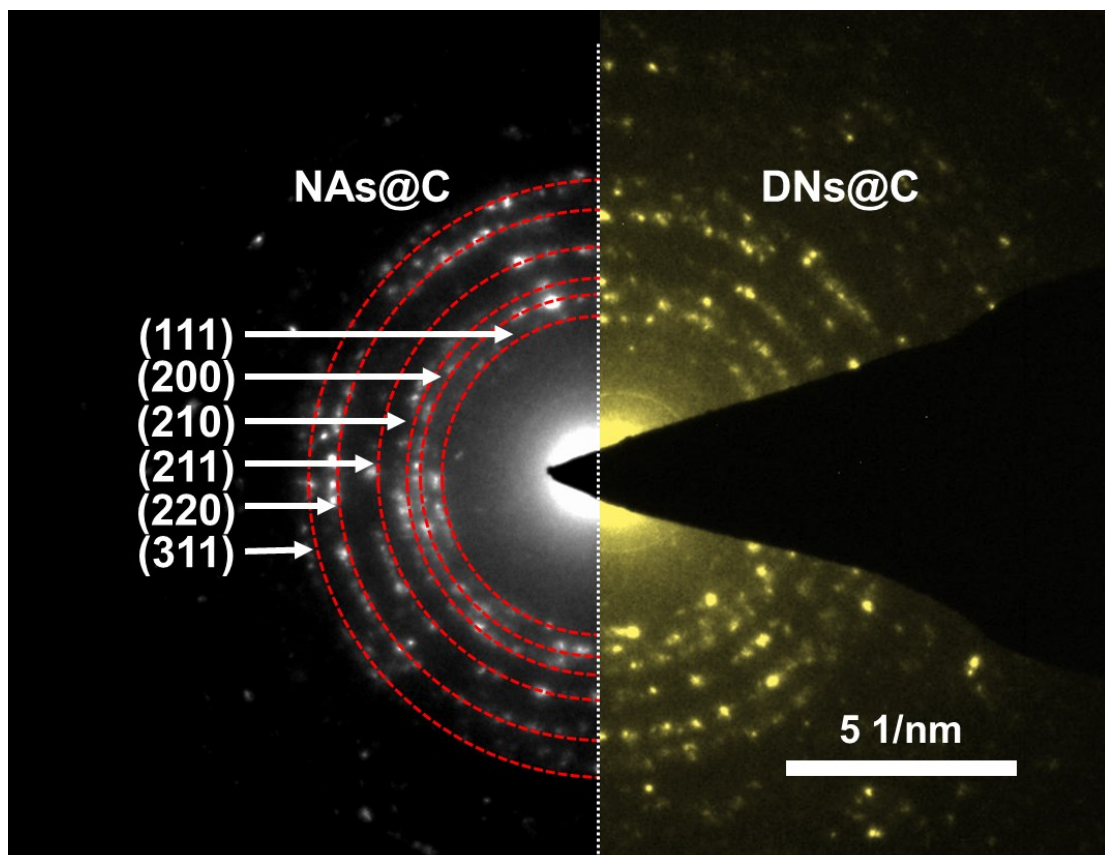


Fig. S3 The selected area electron diffraction (SAED) pattern of NAs@C and DNs@C.

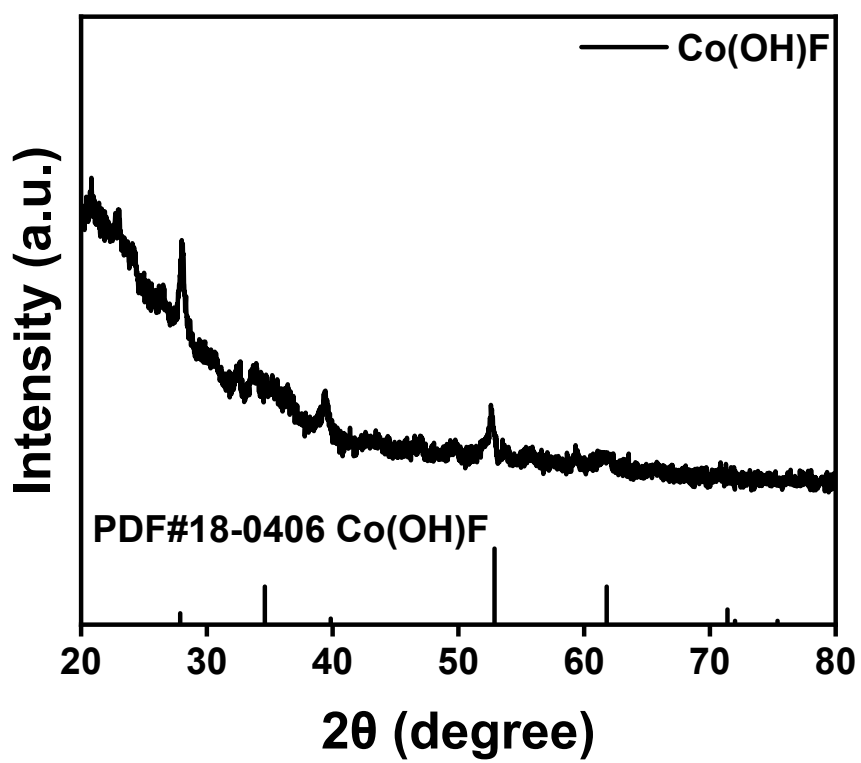


Fig. S4 The XRD pattern of the precursor Co(OH)F@C.

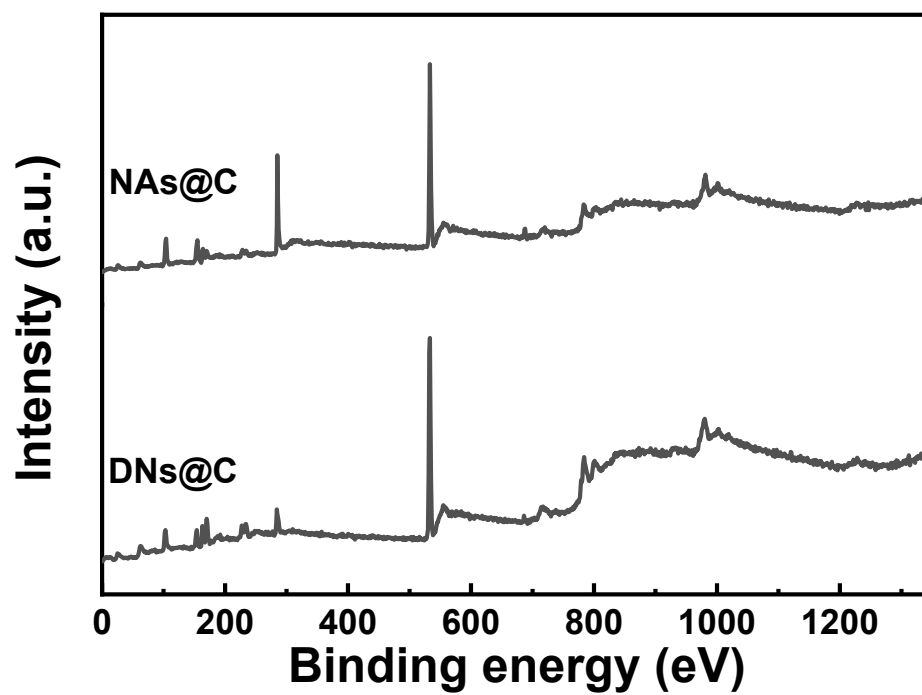


Fig. S5 The XPS survey spectra of NAs@C and DNs@C.

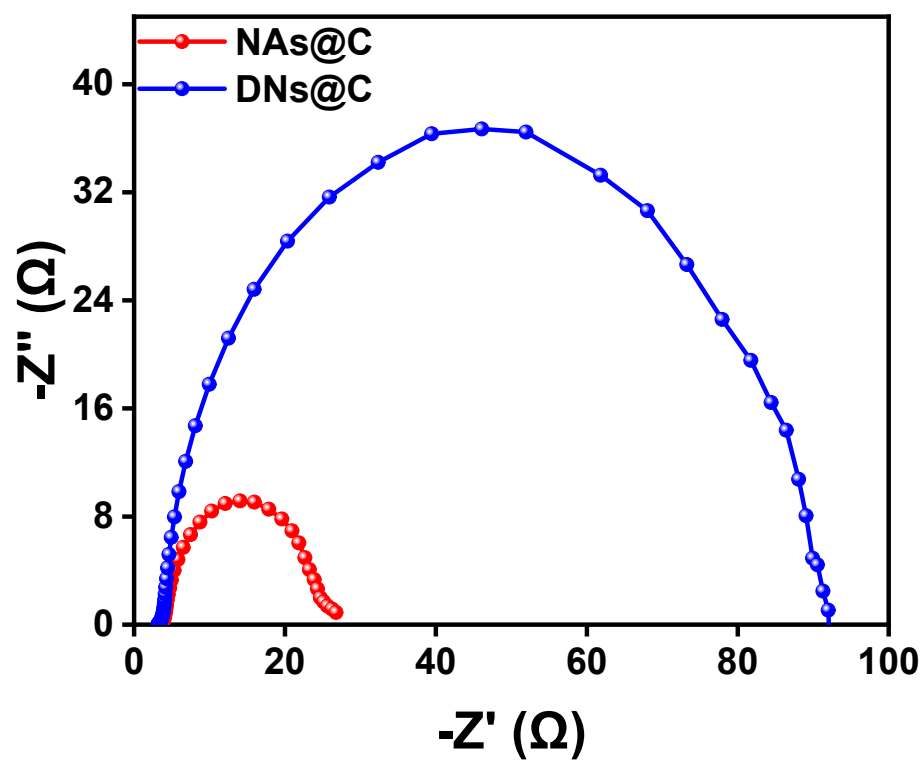


Fig. S6 The Nyquist plots of NAs@C and DNs@C obtained at OCP.

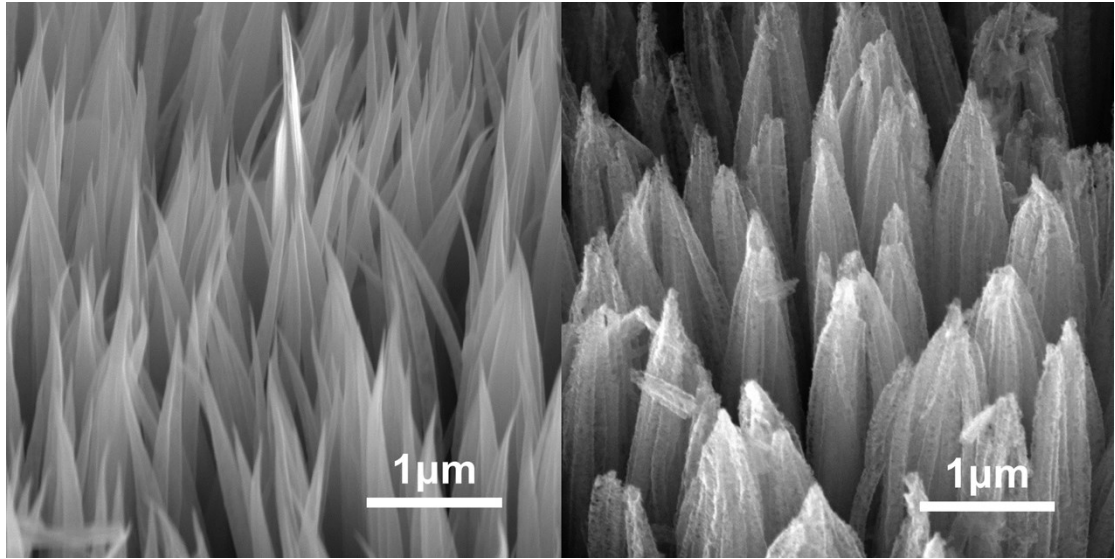


Fig. S7 The SEM images of NAs@C before and after continuous tests at the same potential of -0.13 V vs. RHE.

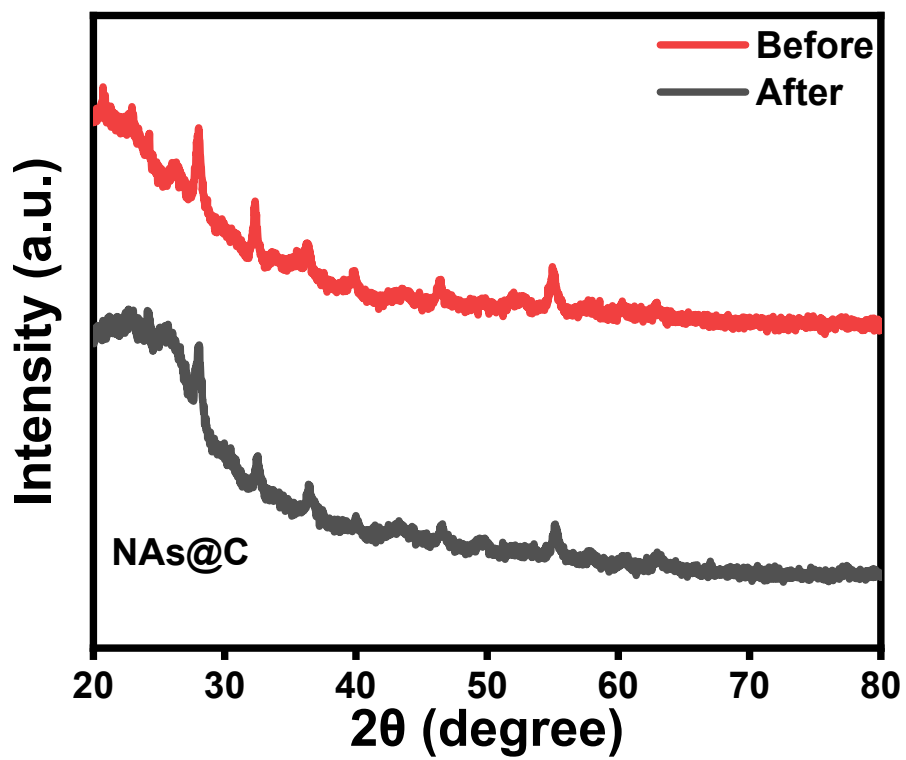


Fig. S8 The XRD patterns of NAs@C before and after continuous tests at the same potential of -0.13 V vs. RHE.

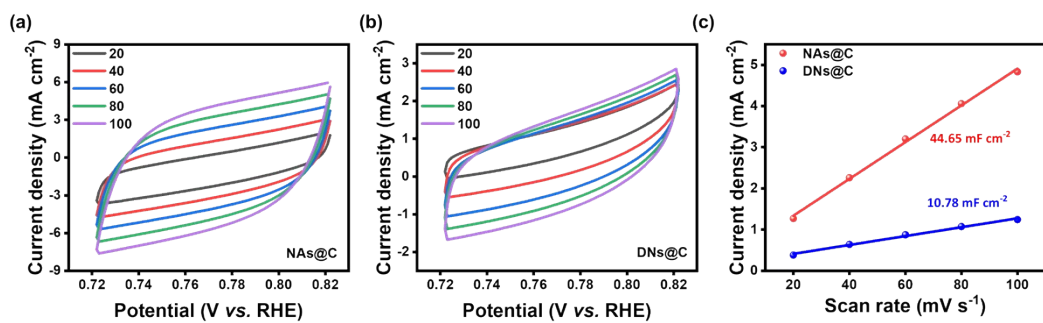


Fig. S9 CVs of (a) NAs@C and (b) DNAs@C at various scan rates (20, 40, 60, 80, 100 mV s⁻¹). (c) Differences ($\Delta j = (j_a - j_b)/2$) in current density at 0.76 V vs. RHE plotted against scan rate.

Table S1 The HER activity of the NAs@C compared with other recently reported Co-based catalysts in the alkaline (1M KOH) medium.

Catalysts	η (mV)	Tafel slopes (mV dec ⁻¹)	References
NAs@C	121	59.87	This work
CoNiP-4	138	65	Nanoscale 2019, 11(44), 21259-21265
Co-MoS ₂ / Mo ₂ CT _x	112	158	Nanoscale 2019, 11(22), 10992-11000.
CoMoOS	123	86	Nanoscale 2019, 11(8), 3500-3505.
Co _{0.75} Ni _{0.25} Se/NF	106	74	Nanoscale 2019, 11(16), 7959-7966.
Co _{0.2} -VOOH	130	30.8	Nanoscale 2019, 11(39), 18238-18245.
Co/Mo ₂ C@NC-800	121	166.85	J. Colloid Interface Sci. 2021, 583, 614-625
S-CoO _x /NF	136	80	Nano Energy 2020, 71, 104652
O-doped Co ₂ P/CuO NWs/CF	101	74.4	Appl. Catal. B 2020, 261, 118268
Co@Co ₃ O ₄ / FeNS-RG	130	69	Electrochim. Acta 2019, 323, 134821
Co ₉ S ₈	173	78	Appl. Catal. B 2019, 254, 186-193
Co-SCN/RGO	150	94	ACS Sustainable Chem. Eng. 2019, 7(18), 15373-15384
CoP S	103	58	Appl. Catal. B 2019, 251, 213-219
CoS _x @MoS ₂	239	103	ACS Sustainable Chem. Eng. 2018, 6(10), 12961-12968
S,N-CNTs/CoS ₂ @Co	112	104.9	Sci. Bull. 2018, 63(17), 1130-1140
Co-Mo compounds	169	63	ACS Appl. Energy Mater. 2018, 1(11), 5822-5829
S:CoP particle	175	82	Nano Energy 2018, 53, 286-295