

Electronic Supplementary Material (ESI)
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Efficient hydrogen production by saline water electrolysis at high current densities without the interfering chlorine evolution

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Experimental procedures

Preparation of the Co-Ni-P/CP electrodes:

The carbon paper (CP, FuelCellStore) was firstly treated in a mixed solution of sulfuric acid and nitric acid (v (98% H₂SO₄):v (70% HNO₃):v (H₂O) = 1:1:1) at 60 °C for 6 h under vigorous magnetic stirring, in order to make the surface hydrophilic and to introduce the nucleation sites for the growth of cobalt-nickel-carbonate-hydroxide precursor NWs. The precursor solution was prepared by dissolving 10 mmol urea, 5 mmol NH₄F, 2 mmol Co(NO₃)₂·6H₂O and 2 mmol Ni(NO₃)₂·6H₂O in 30 ml deionized (DI) water under continuous magnetic stirring until a homogeneous, transparent solution was obtained (typically for 30 min), according to a previous report.¹ Afterwards, the solution was transferred into a Teflon-lined stainless steel autoclave reactor, and a piece of acid-treated CP (4 × 3 cm²) was completely submerged in the precursor solution. Subsequently, the reactor was sealed and heated up to 120 °C, and maintained at this temperature for 6 h. After the autoclave reactor was cooled down to room temperature, the CP was taken out and thoroughly rinsed several times with DI water and then dried under vacuum at 70°C.

The Co-Ni-P/CP electrode was obtained by phosphorization of the precursor electrode using NaH₂PO₂ as the source of phosphorus at 300°C. Specifically, the CP coated with precursor NWs was loaded in a ceramic boat and 1.0 g of NaH₂PO₂ powders was placed 2 cm away from the CP at the upstream side. Subsequently, the furnace was purged with high-purity N₂ (99.999%) for 1 h to remove air, heated to 300 °C at a ramping rate of 5 °C min⁻¹ and held at this temperature for 2 h. Finally, the furnace was naturally cooled down to room temperature. The mass loading of Co-Ni-P NWs on the CP electrode is around 6 mg cm⁻².

Materials Characterization:

The morphology of Co-Ni-P/CP electrode was characterized by scanning electron microscopy (SEM, FEI Quanta 650 FEG microscope equipped with an INCA 350 spectrometer) and transmission electron microscopy (TEM, FEI ChemiSTEM 80-200, probe corrected). The X-ray diffraction (XRD) experiment was conducted on an X'Pert PRO diffractometer (PANalytical) set at 45 kV and 40 mA, using Cu K_{α} radiation ($\lambda = 1.541874 \text{ \AA}$) and a PIXcel detector. Data were collected with the Bragg–Brentano configuration in the 2θ range of $20 - 80^{\circ}$ at a scan speed of $0.011^{\circ} \text{ s}^{-1}$. X-ray photoelectron spectroscopy (XPS) characterization was carried out on an ESCALAB 250Xi instrument with the monochromated Al K_{α} (1486.6 eV) X-ray source.

Electrocatalytic tests:

All electrochemical measurements of the Co-Ni-P/CP electrode was performed in a three-electrode configuration at room temperature using a Biologic VMP3 potentiostat/galvanostat. The as-synthesized Co-Ni-P/CP electrode, a saturated calomel electrode (SCE), and a graphite rod were employed as the working, reference, and counter electrodes, respectively. The SCE reference was calibrated before each measurement in the H_2 -saturated 0.5 M H_2SO_4 solution using a clean Pt wire as the working electrode. All potentials in this study were converted to the reversible hydrogen electrode (RHE) scale according to the following equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \times \text{pH} + 0.244 \quad (\text{S1})$$

The HER, OER and HzOR measurements were carried out in the simulated seawater containing 1.0 M KOH + 0.5 M NaCl. For HzOR tests, different concentrations of hydrazine were dissolved in the electrolyte. The linear scan voltammetry (LSV) was performed at a scan rate of 5 mV s^{-1} . An iR -correction (85%) was applied to compensate

for the voltage drop between the reference and working electrodes, which was measured by the single-point high-frequency impedance test. The electrochemical impedance spectroscopy (EIS) measurements were conducted at -0.110 V vs. RHE for the HER, -0.057 V vs. RHE for the HzOR and 1.550 V for OER in the frequency range of $10^5 - 0.01$ Hz with a 10 mV sinusoidal perturbation. The stability of the Co-Ni-P/CP electrode was assessed using chronopotentiometry (CP) at a constant current density of 500 mA cm^{-2} for the OER, HzOR, OSWE and HzOR + HER, and -500 mA cm^{-2} for the HER. Moreover, the stability of the Co-Ni-P/CP pair toward HzOR + HER at 1000 mA cm^{-2} was also assessed.

Supplementary figures:

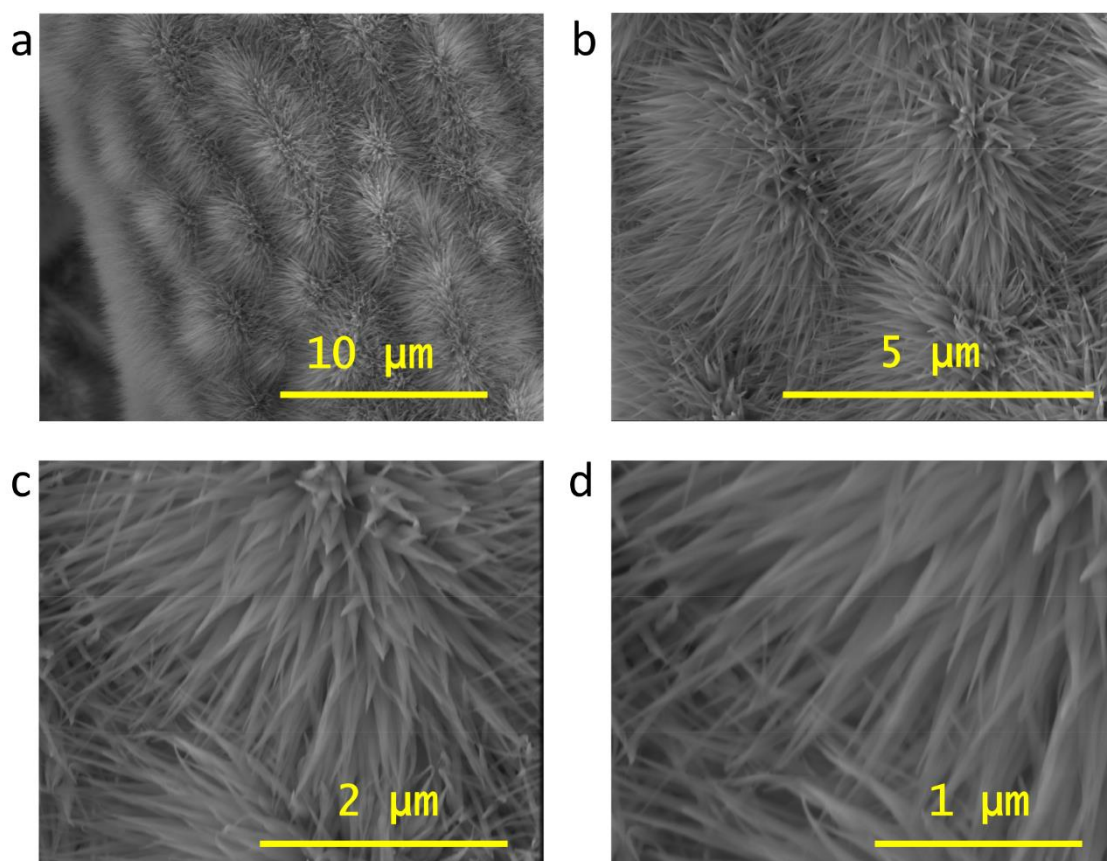


Fig. S1 (a, b) Low-magnification and (c, d) high-magnification SEM images showing the morphology of the as-prepared cobalt-nickel-carbonate-hydroxide precursor ($\text{CoNi}(\text{CO}_3)(\text{OH})_2$) nanowires on carbon paper.

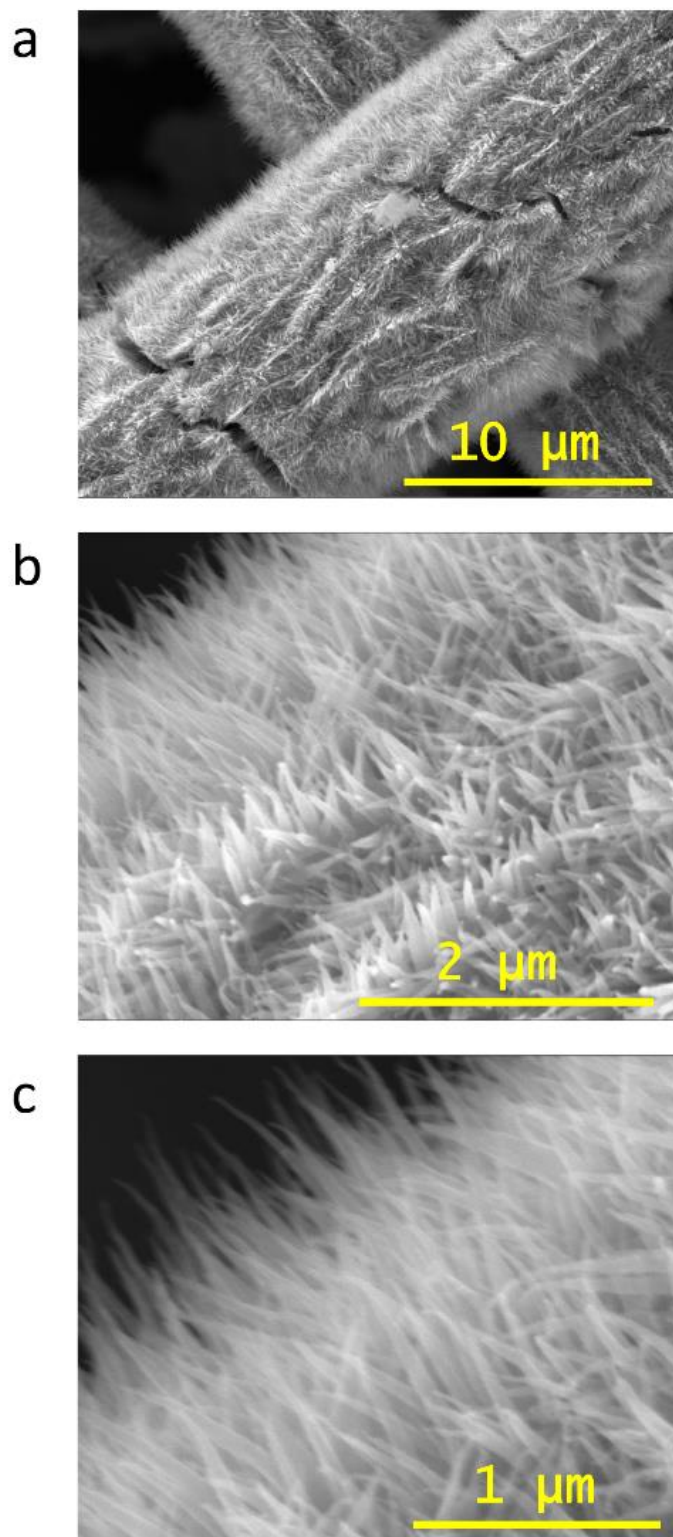


Fig. S2 (a) Low- and (b, c) high-magnification SEM images showing the morphology of the as-prepared Co-Ni-P/CP electrode.

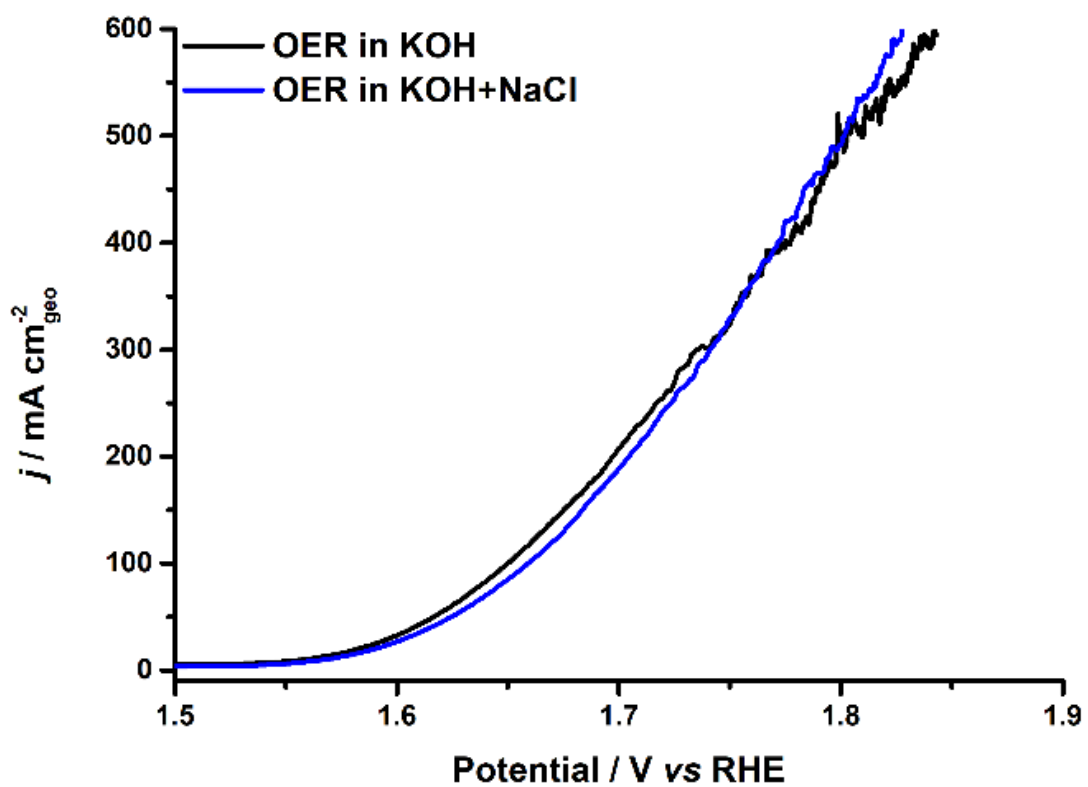


Fig. S3 LSV curves showing the electrocatalytic activity of the Co-Ni-P/CP in 1.0 M KOH and 1.0 M KOH + 0.5 M NaCl solutions (zoomed view of **Fig. 3a** in the main text).

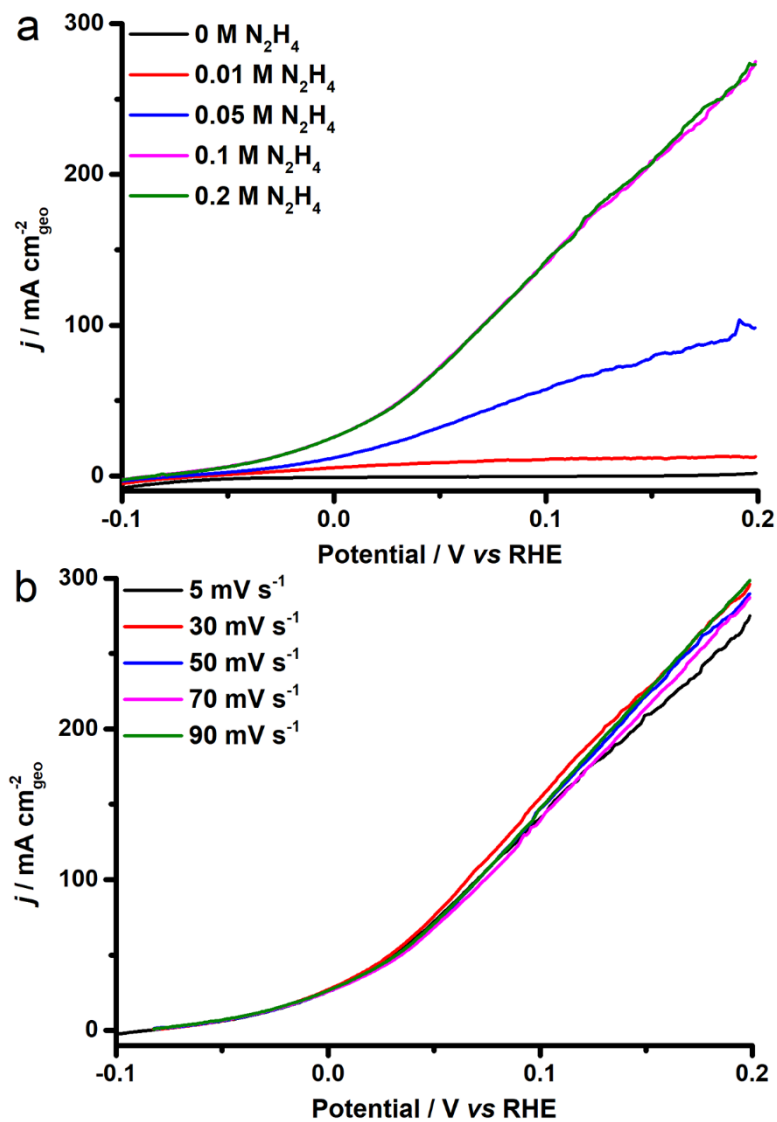


Fig. S4 (a) LSV curves of the Co-Ni-P/CP electrode recorded in the $1.0 \text{ M KOH} + 0.5 \text{ M NaCl}$ electrolytes with different concentrations of hydrazine. (b) LSV curves of the Co-Ni-P/CP electrode recorded in $1.0 \text{ M KOH} + 0.5 \text{ M NaCl} + 0.1 \text{ M N}_2\text{H}_4$ at different scan rates.

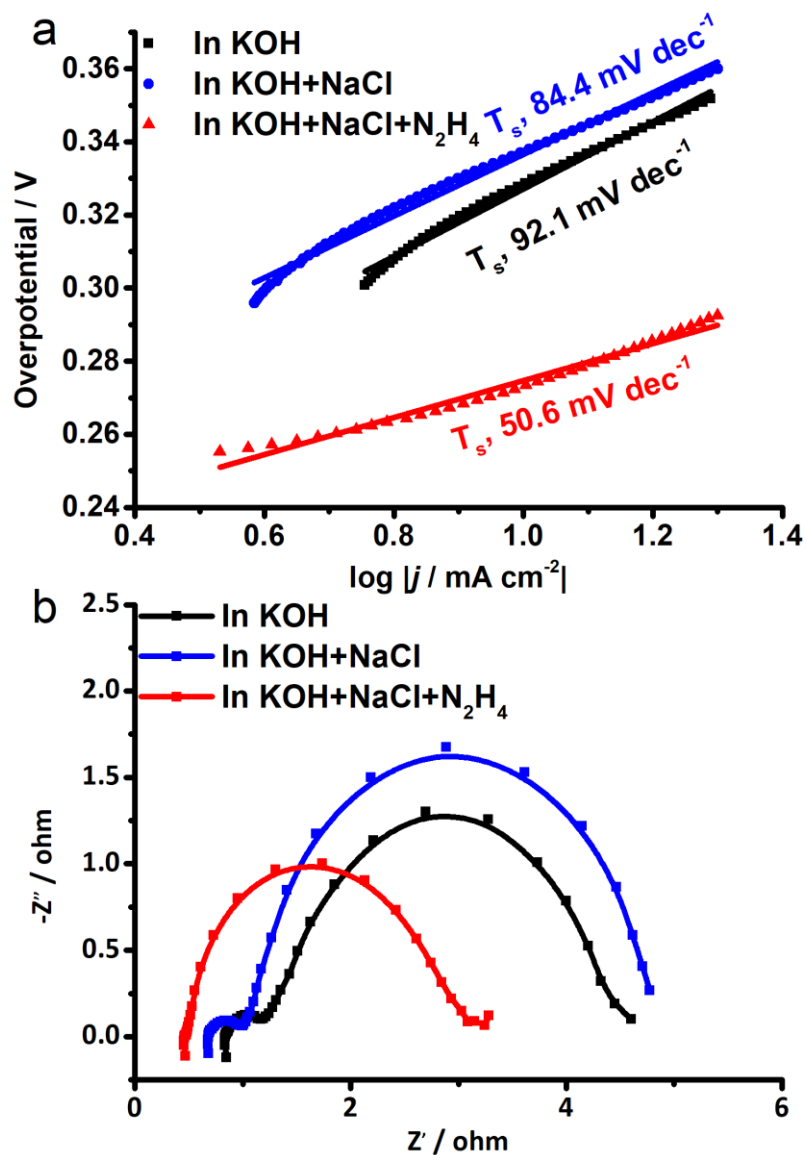


Fig. S5 (a) Tafel plots and (b) Nyquist plots of the Co-Ni-P/CP electrode measured at -0.057 V vs. RHE toward the HzOR and 1.550 V vs. RHE toward the OER.

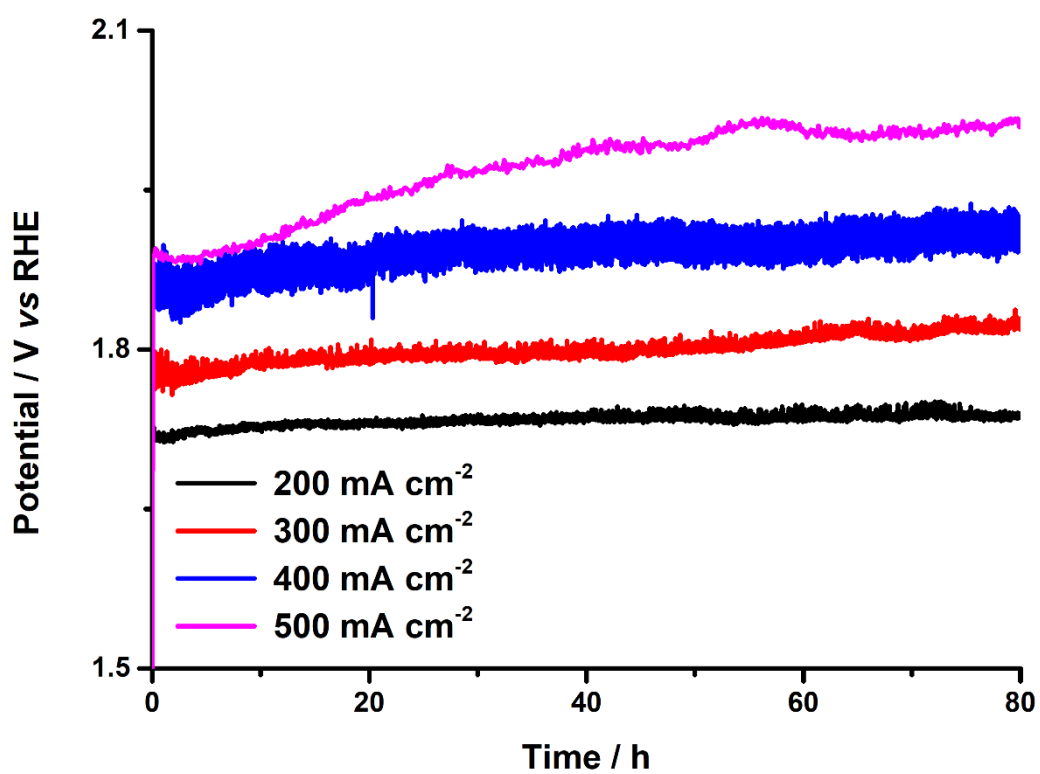


Fig. S6 Chronopotentiometric curves of the Co-Ni-P/CP electrode recorded in 1.0 M KOH + 0.5 M NaCl electrolyte at different current densities.

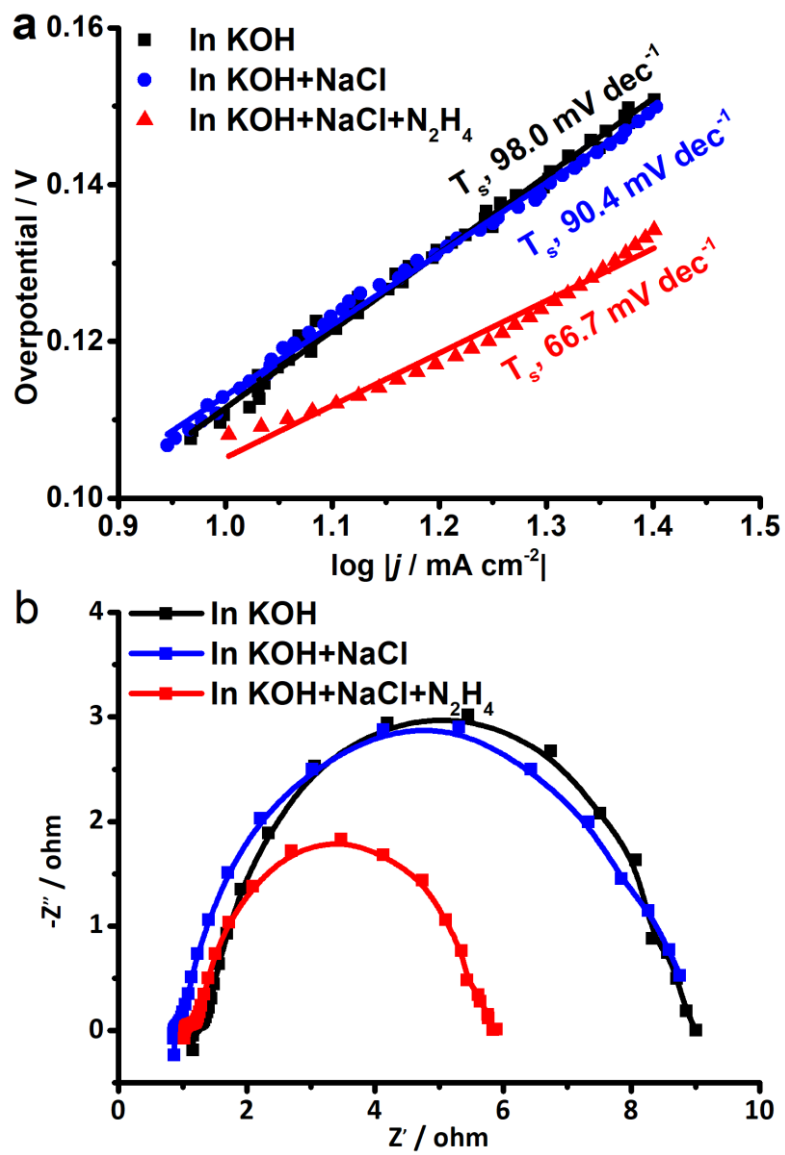


Fig. S7 (a) Tafel plots and (b) Nyquist plots of the Co-Ni-P/CP electrode measured at -0.110 V vs. RHE toward the HER.

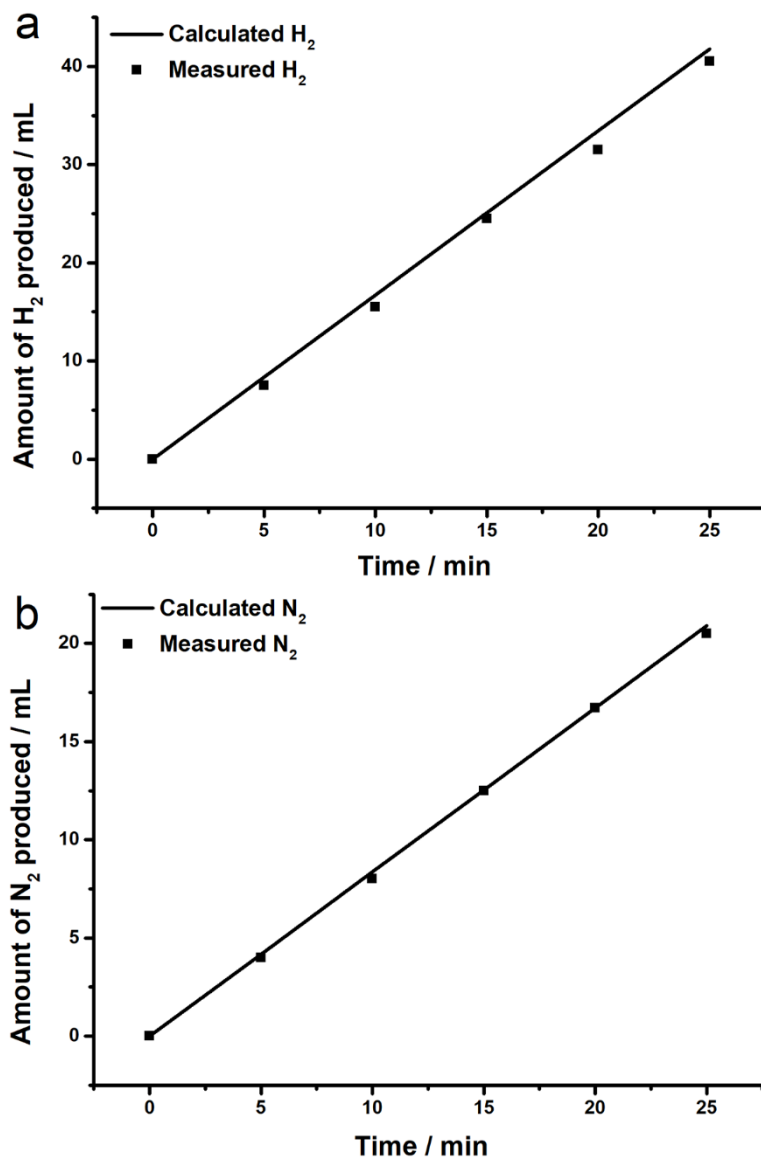


Fig. S8 The volume of (a) H₂ gas and (b) N₂ gas theoretically evolved (solid line) and experimentally measured (scattered data points) for the HzOR + HER at the current density of 500 mA cm⁻².

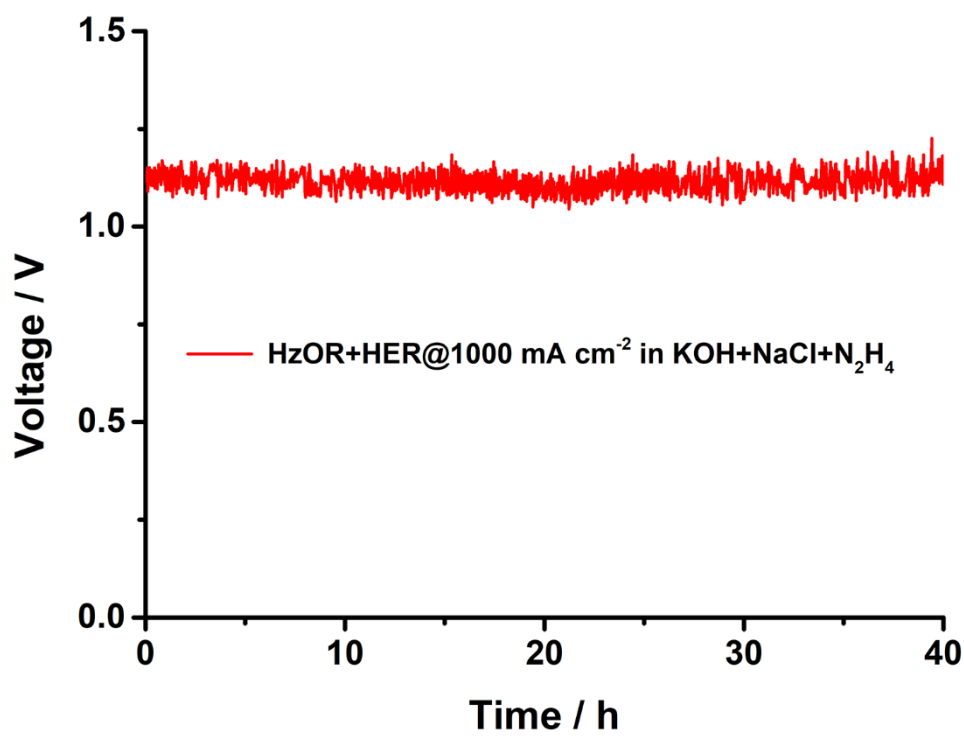


Fig. S9 Chronopotentiometric curve of the HzOR + HER recorded at a constant current density of 1000 mA cm^{-2} in $1.0 \text{ M KOH} + 0.5 \text{ M NaCl} + 0.1 \text{ M N}_2\text{H}_4$.

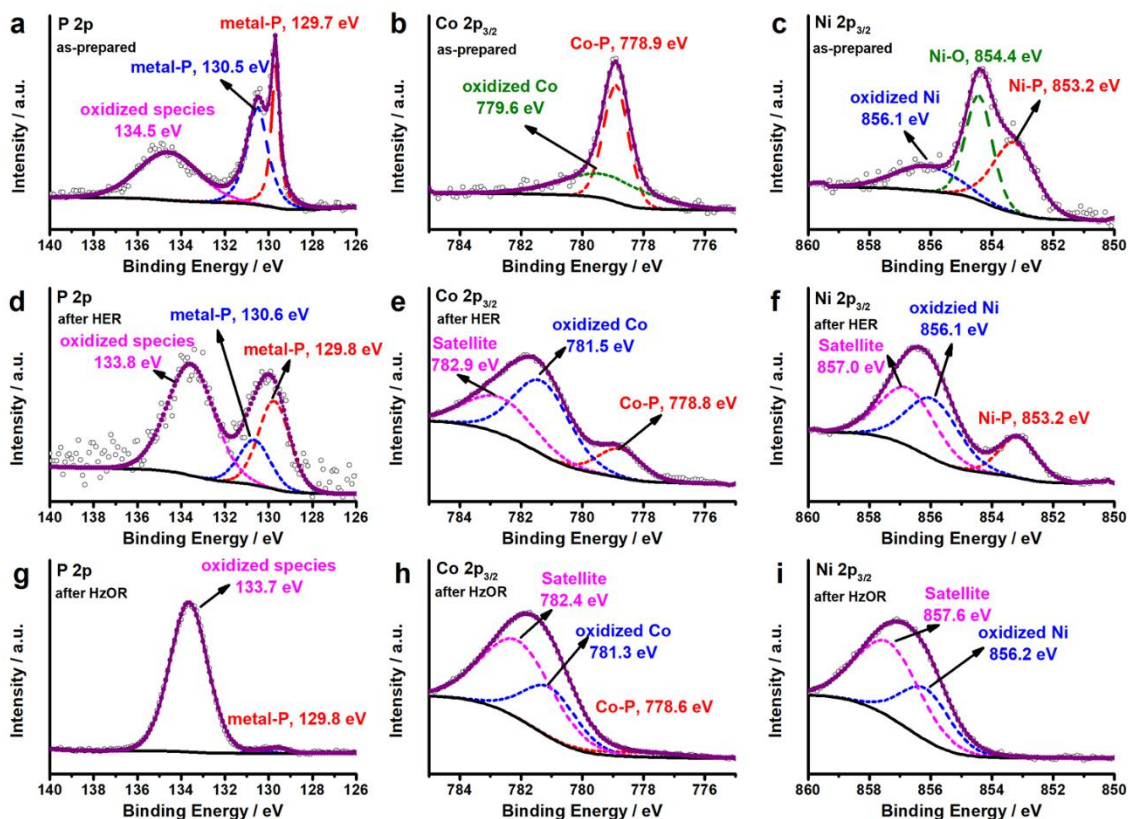


Fig. S10 High-resolution (a, d, g) P 2p, (b, e, h) Co 2p_{3/2}, and (c, f, i) Ni 2p_{3/2} XPS spectra of the Co-Ni-P/CP electrode (a-c) before and after the (d-f) HER and (g-i) HzOR at 500 mA cm⁻² for 80 h in 1.0 M KOH + 0.5 M NaCl + 0.1 M N₂H₄ in the two-electrode configuration.

Table S1. The comparison of hydrazine electrolysis performance for the Co-Ni-P/CP electrode reported in this work with that of electrocatalysts/catalytic electrodes recently reported in the literature.

Catalysts	Electrolyte	Cell voltage (V)	j (mA cm ⁻²)	Stability	Reference
Co-Ni-P/CP	1 M KOH + 0.5 M NaCl + 0.1 M N ₂ H ₄	0.216	100	500 mA cm ⁻²	This work
		0.533	500	² @80 h, 1000	
		1.116	1000	mA cm ⁻² @40 h	
NiCo-MoNi ₄	1 M KOH+ 0.1 M N ₂ H ₄	0.315	100	0.1 V for 10 h	<i>Chem. Eng. J.</i> , 2021, 414 , 128818.
Cu ₁ Ni ₂ -N	1 M KOH + 0.5 M N ₂ H ₄	0.24	10	10 mA cm ⁻² @75 h	<i>Adv. Energy Mater.</i> , 2019, 9 , 1900390.
CoSe ₂	1 M KOH + 0.5 M N ₂ H ₄	0.164	10	10 mA cm ⁻² @14 h	<i>Angew. Chem. Int. Ed.</i> , 2018, 57 , 7649-7653.
CoP	1 M KOH + 0.1 M N ₂ H ₄	0.2	10	0.1 V for 20 h	<i>ChemElectroChem</i> , 2017, 4 , 481-484.
CoS ₂	1 M KOH + 0.1 M N ₂ H ₄	0.81	100	25 mA cm ⁻² @5.6 h	<i>New J. Chem.</i> , 2017, 41 , 4754-4757.
Ni(Cu)	1 M KOH + 0.5 M N ₂ H ₄	0.41	100	100 mA cm ⁻² @10 h	<i>ACS Sustain. Chem. Eng.</i> , 2018, 6 , 12746-12754.
Cu ₃ P	1 M KOH + 0.5 M N ₂ H ₄	0.72	100	10 mA cm ⁻² @3 h	<i>Inorg. Chem. Front.</i> , 2017, 4 , 420-423.
CoSe	1 M KOH + 0.5 M N ₂ H ₄	0.5	50	40 mA cm ⁻² @10 h	<i>J. Power Sources</i> , 2018, 401 , 238-244.
Ni ₃ S ₂	1 M KOH + 0.2 M N ₂ H ₄	0.867	100	20 mA cm ⁻² @11 h	<i>J. Mater. Chem. A</i> , 2018, 6 , 19201-19209.
Rh-C-N	1 M KOH + 0.5 M N ₂ H ₄	0.2	20	20 mA cm ⁻² @3 h	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11 , 35039-35049.

References

1. I. Amorim, J. Xu, N. Zhang, D. Xiong, S. M. Thalluri, R. Thomas, J. P. S. Sousa, A. Araújo, H. Li and L. Liu, *Catal. Today*, 2020, **358**, 196-202.