

Supplementary Information

**Organic ligand promoting the electrocatalytic activity of cobalt oxide for
hydrogen evolution reaction**

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Experimental section

Chemicals. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99.9 %) and NaOH (99.99 %) were bought from Alfa Aesar. 2,2'-dipyridylamine (Hdap) was purchased from Tokyo Chemical Industry. Methanol solvent was bought from Duksan. Sodium sulfate (Na_2SO_4 , >99.0%) was purchased from Fluka. Platinum on carbon (40 wt. % Pt/C, Pt on an activated carbon support) and Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water, contains 15-20% water) were bought from Sigma-Aldrich. All chemicals were used directly without further purification. Ultrapure water (18.2 M Ω) used in the experiments was supplied by a Millipore System (Direct-Q® 3).

Electrode Preparation. The electrodeposition was carried out with a standard three-electrode electrochemical cell containing glassy carbon disk (surface area: 0.0707 cm²), a graphite rod (L 100 mm, diam. 3 mm) and a saturated calomel electrode (SCE) as the working, auxiliary and reference electrodes, respectively. The electrolyte solution of Co_3O_4 -dpa-C was prepared; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.024 g, 0.1 mmol), Hdpa (0.017g, 0.1 mmol) and NaOH (0.004g, 0.1 mmol) were first dissolved in 5 mL methanol and then the solution after the addition of Na_2SO_4 (14.204 g, 0.1 mol) was added water to 100 mL. Similarly, the preparation of Co_3O_4 -C electrolyte solution was followed above the procedure without Hdpa. The Co_3O_4 -C and Co_3O_4 -dpa-C films were prepared through controlled potential electrolysis at -1.644 V vs SCE with violently stirring until the constant current ($\sim 240 \text{ mA cm}^{-2}$) for 24 h at ambient temperature. After deposition, the films by careful rinse with water were directly used for electrochemistry tests. 40 wt.% Pt-C (20 mg) was dispersed in a 5 mL mixture solution containing 0.5 mL 5% Nafion solution and 4.5 mL methanol, followed by sonication for 30 min to obtain a homogeneous catalyst ink. The catalyst ink was

loaded on the surfaces of the glassy carbon disk electrode to achieve 2.8 mg cm^{-2} .

Physical characterization. Powder X-ray diffraction (pXRD) data were obtained using a Bruker D8 X-ray Powder Diffractometer with a Cu K- α radiation source in the range $2\theta = 5\text{-}80^\circ$. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectra (EDX) were obtained with a JSM 7000F microscope (JEOL) equipped with an Oxford EDX system. X-ray photoelectron spectroscopy (XPS) spectra were collected on a ULVAC-PHI XPS spectrometer equipped with a monochromatized 1486.6 eV Al K α X-ray line source directed 45° with respect to the sample surface. The spectra were registered at a base pressure of $<5 \times 10^{-10}$ torr. Low-resolution survey scans were acquired with a 100 μm spot size between the binding energies of 1-1100 eV. High-resolution scans with a resolution of 0.1 eV were collected between 280-292 (for C), 392-408 (for N), 525-540 (for O) and 770-810 (for Co) eV. IR and ATR-IR spectra were recorded on a ALPHA FT-IR spectrometer and ALPHA Eco ATR with ZnSe crystal, respectively. NMR spectra were recorded on a Varian Unity Inova 500 spectrometer.

ESI-MS and ICP-MS experiments. Co_3O_4 -dpa-C film on the glassy carbon electrode was scraped in 10 mL methanol solution containing a magnetic stirring bar. The solution was sonicated for 1 h and then stirred for overnight. The clarified part of solution was collected for electrospray ionization mass spectrometer (ESI-MS) and inductively coupled plasma-mass spectrometry (ICP-MS) experiments. Coldspray ionization time-of-flight mass (CSI-TOF MS) spectral data were collected on a JMS-T100LP4G (JEOL) mass spectrometer equipped with the CSI source. Typical measurement conditions are as follows: needle voltage: 0 kV, orifice 1 voltage: 100 V, ring lens voltage: 10 V, spray temperature: 0°C . ICP-MS was performed on a Agilent

7500ce. Dry samples were dissolved in concentrated HNO_3 .

Electrochemical measurements. All electrochemical experiments were performed with a CH Instrument 621b potentiostat. Fundamental electrochemical testing was carried out, consisting of samples as the working electrode, a graphite rod (L 100 mm, diam. 3 mm) auxiliary electrode and a saturated calomel electrode (SCE) reference electrode. All potentials reported in this paper were converted from vs SCE to vs reversible hydrogen electrode (RHE). $\text{RHE} = \text{SCE} + 0.244 + 0.059 \times \text{pH}$. In all experiments, the iR compensation was performed by CHI model 621b software. The linear sweep voltammetry (LSV) curves were obtained in 1.0 M $\text{NaOH}_{(\text{aq})}$ at a scan rate of 2 mV/s. Tafel slopes were calculated using the Polarization curves by plotting overpotential against $\log(\text{current density})$. Controlled potential electrolysis (CPE) experiments were conducted in 1.0 M $\text{NaOH}_{(\text{aq})}$ stirred constantly. The auxiliary electrode in CPE cell was separated from the solution of the working electrode by a medium-porosity sintered-glass frit. The electrochemically active surface area (ECSA) was evaluated in terms of double-layer capacitance. Cyclic voltammogram (CV) scans were conducted in static solution by sweeping the potential from the more positive to negative potential and back at 8 different scan rates: 2, 4, 8, 12, 16, 20, 40 and 80 mV s^{-1} . This range is typically a 0.1 V potential window centered on the open-circuit potential (OCP) of the system. The capacitance was determined from the tenth cyclic voltammetry curve of each scan rate. The electrochemical double-layer capacitance, C_{DL} , as given by $i_c = \nu C_{\text{DL}}$ (i_c : current density from CV, ν : scan rate). The specific capacitance for a flat surface is generally found to be in the range of 20-60 mF cm^{-2} . We used a value of 40 mF cm^{-2} in the following calculations of the electrochemical active surface area. The electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 0.1 Hz to 100 kHz with

an amplitude of 5 mV at an overpotential of 270 mV. The curve fitting was performed by Zview2 software.

Determinations of Faradaic Efficiency and TOF. Quantification of the produced H₂ gas was performed by gas chromatography (SRI 8610C) equipped with a molecular sieves (MS-13x) column and helium ionization detector (HID). Helium was used as the carrier gas. Calibration curves were built by the injection of the known amounts of pure H₂. The amounts of H₂ dissolved in the solution were corrected by the Henry's law ($K_H = 7.8 \times 10^{-4}$ mol/atm·L for H₂).

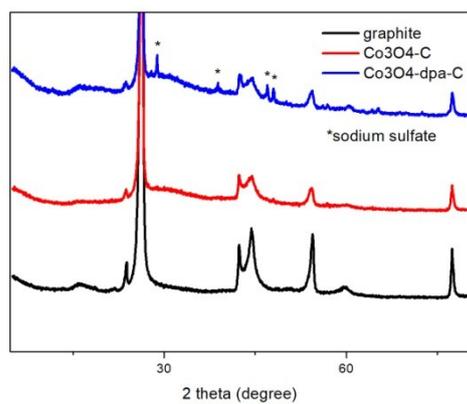
Faradaic efficiency (%) = [Charge (CPE)/2/96485]×100%/[Volume (H₂ gas of GC detection)/24.5]

TON = [Charge (CPE)/2/96485]×[Faradaic efficiency (%)]/[number of catalyst (mol)]

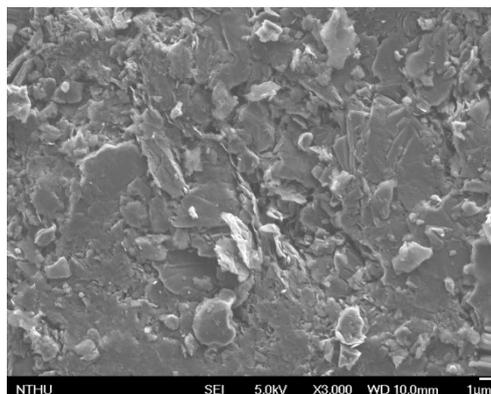
The number of catalyst was determined from ICP analysis.

TOF = [TON]/[time of CPE] (s⁻¹)

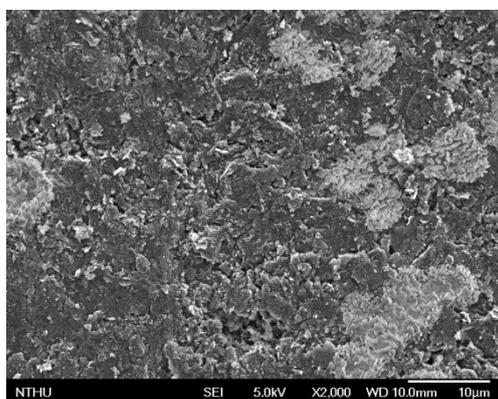
a.



b.



c.



d.

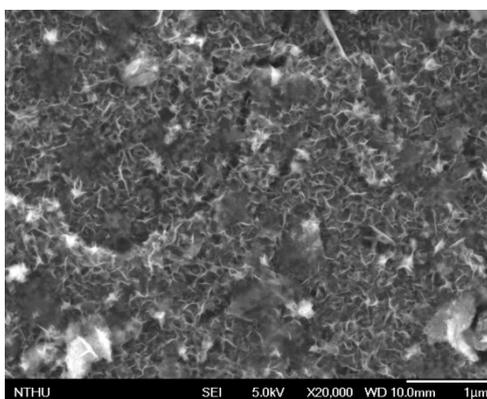


Figure S1. (a) The magnified X-ray diffraction patterns of fresh graphite, Co₃O₄-C and Co₃O₄-dpa-C. The stars are the diffraction peaks of residual sodium sulfate. SEM images of (b) fresh graphite plate and (c,d) Co₃O₄-C.

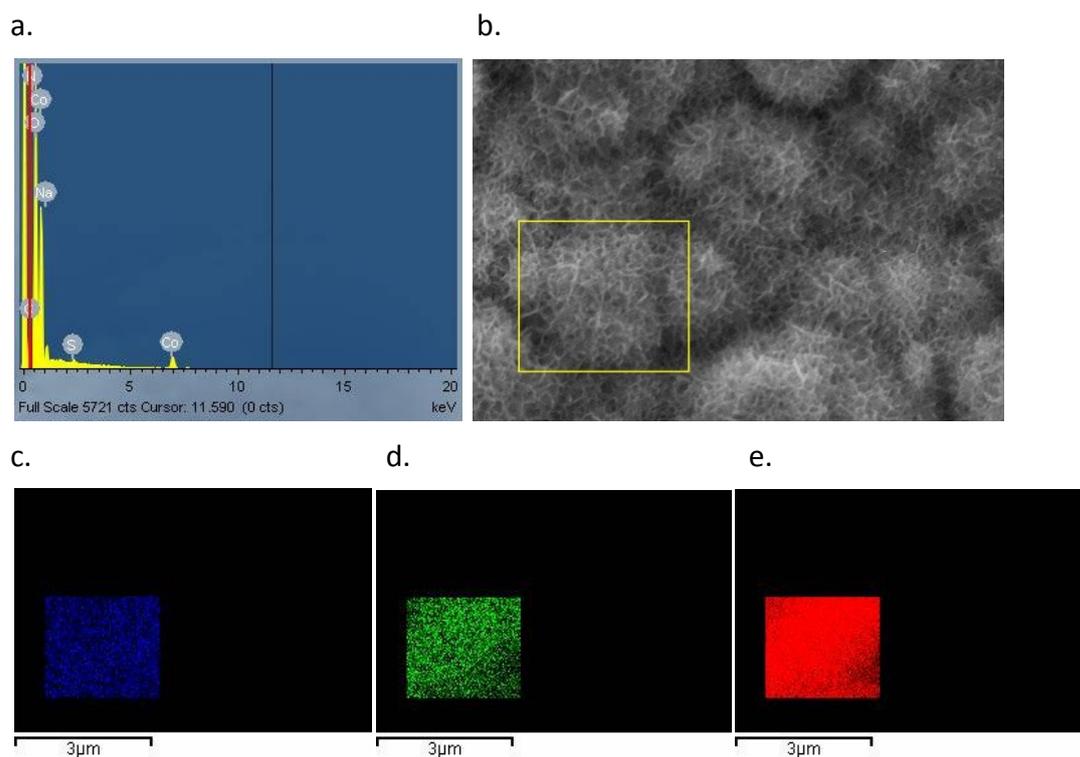


Figure S2. (a) EDX spectrum and (b-e) SEM-EDX elemental maps (Co, N and O elements are shown as blue, green and red, respectively) of Co_3O_4 -dpa-C.

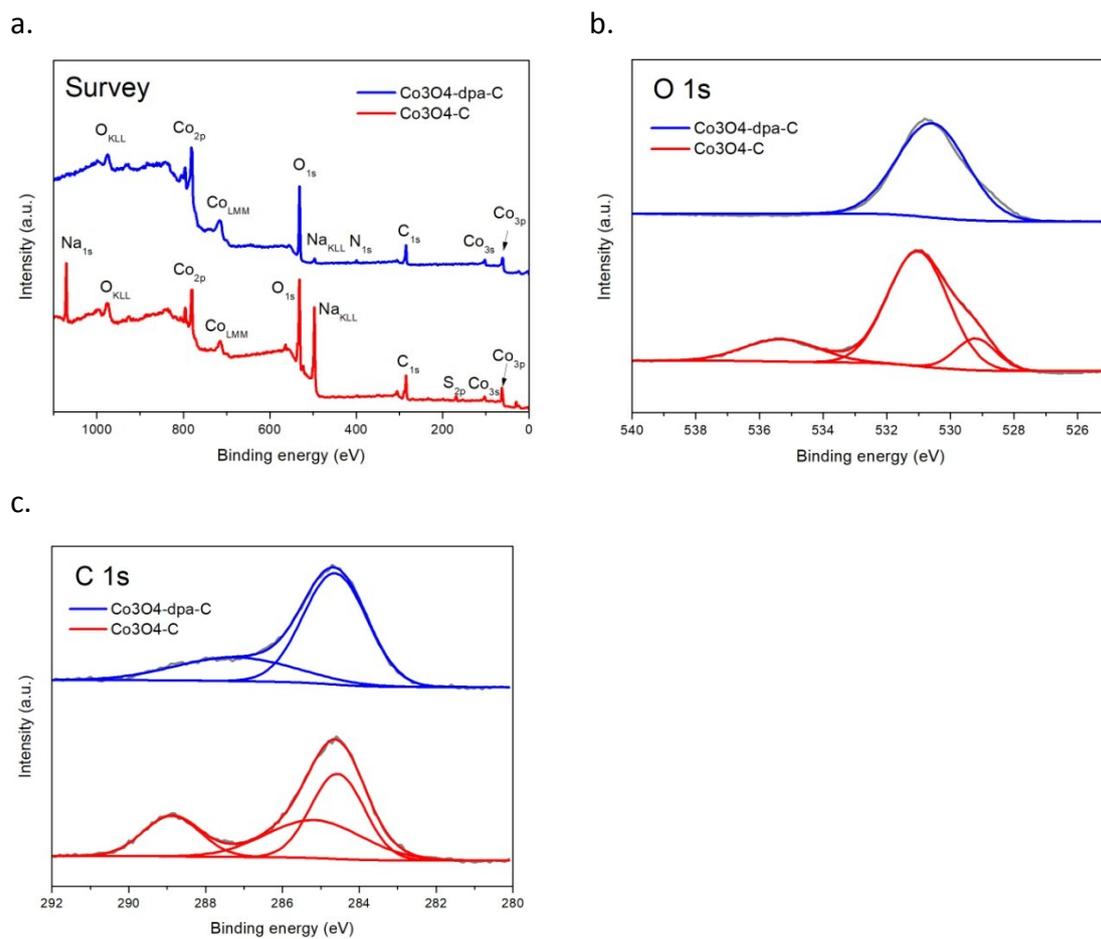


Figure S3. (a) Survey, (b) O 1s and (c) C 1s XPS spectra of Co_3O_4 -dpa-C and Co_3O_4 -C.

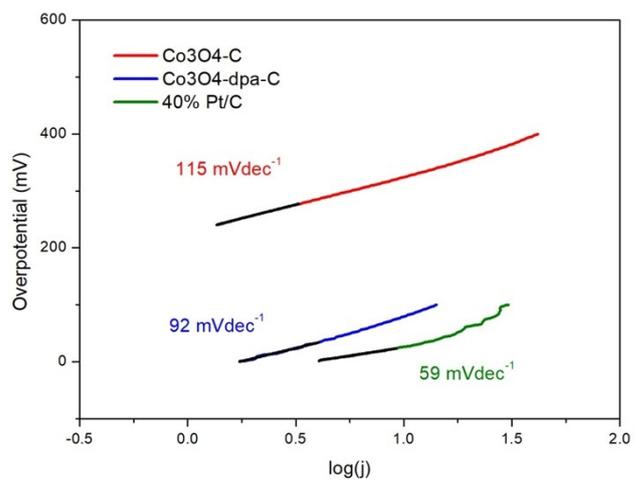


Figure S4. The corresponding Tafel plots of Co₃O₄-C (red), Co₃O₄-dpa-C (blue) and 40% Pt/C electrodes (green) in 1.0 M NaOH_(aq) (scan rate 2 mVs⁻¹).

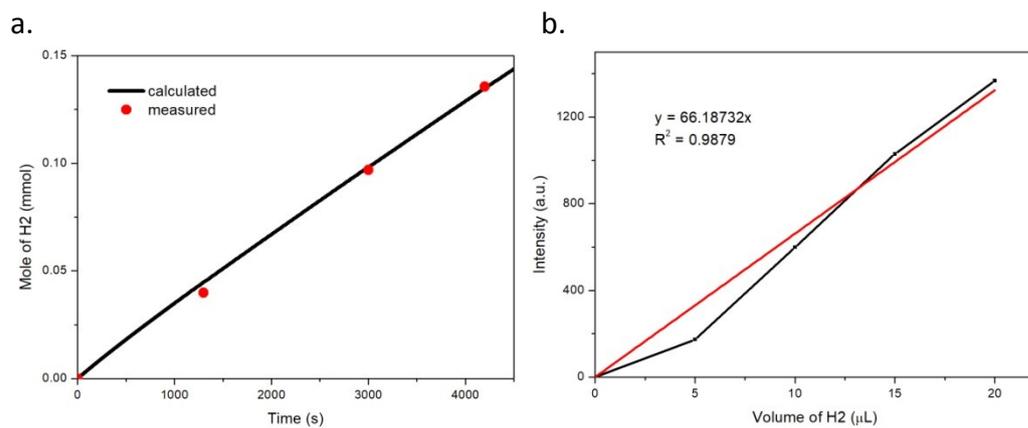


Figure S5. (a) The amount of H₂ gas obtained by theoretical calculation (red) and experimental measurements (black) versus time for the controlled potential electrolysis of 1.0 M NaOH_(aq) employing Co₃O₄-dpa-C as working electrode at applied overpotential of 270 mV. (b) The calibration curve of H₂.

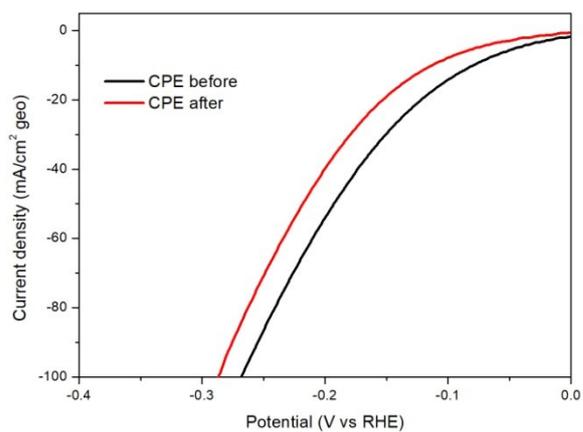


Figure S6. LSV curves of the Co_3O_4 -dpa-C before and after CPE for 45 h in 1.0 M $\text{NaOH}_{(\text{aq})}$ at an applied overpotential of 270 mV (scan rate 2 mVs^{-1}).

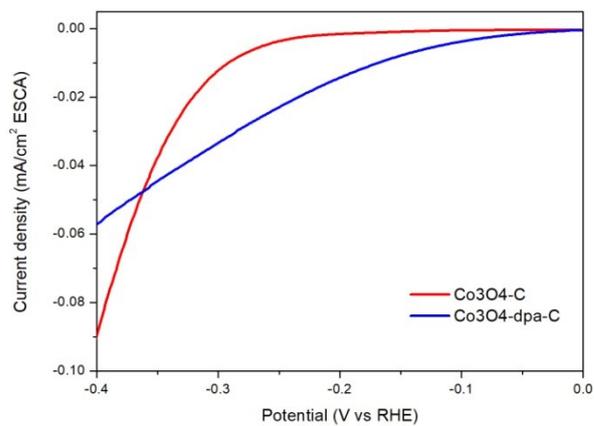


Figure S7. The LSV curves from Fig. 2a normalized to the electrochemical active surface area (ECSA).

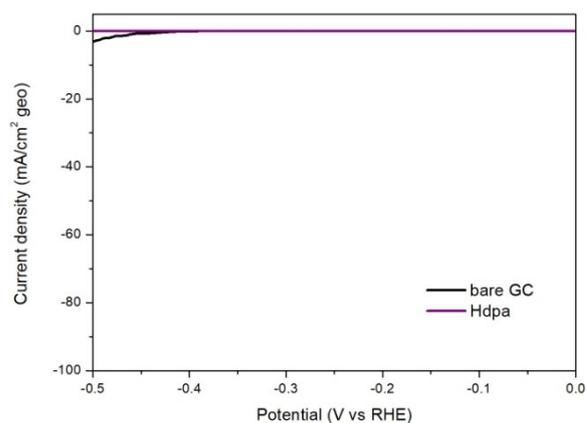
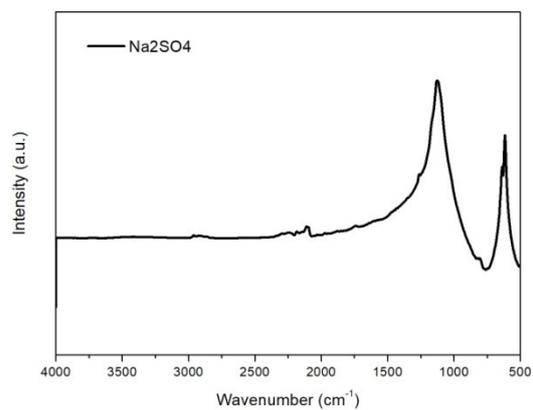


Figure S8. LSV curves of glassy carbon (black) and Hdpa (purple) electrodes in 1.0 M NaOH_(aq) (scan rate 2 mVs⁻¹). Hdpa electrode was prepared by homogeneously depositing 0.2 mg of Hdpa in methanol solution onto the glassy carbon electrode

a.



b.

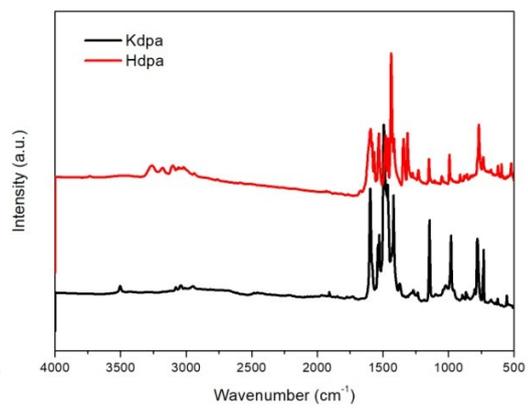


Figure S9. IR spectra of (a) Na₂SO₄, (b) Kdpa and Hdpa (in KBr).

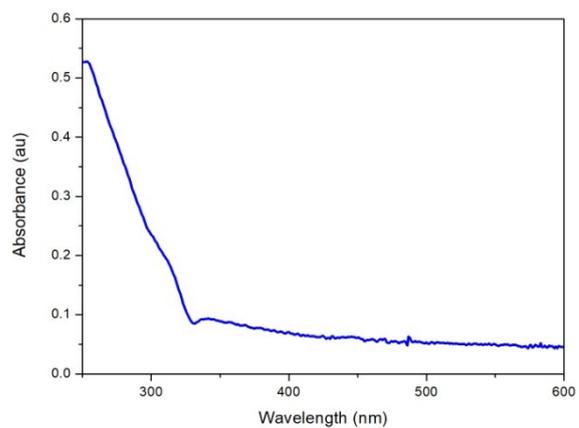


Figure S10. UV-vis spectrum of the extracting Co₃O₄-dpa-C in methanol solution.

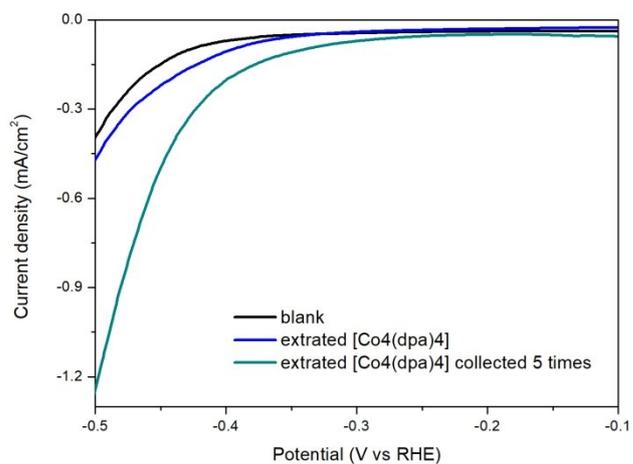


Figure S11. LSV curves of blank (black), the extracted [Co₄(dpa)₄]-cores (blue) and the extracted [Co₄(dpa)₄]-cores collected 5 times (dark cyan) in 1.0 M NaOH H₂O-methanol solution (volume ratio = 19:1) (scan rate 2 mV s⁻¹).

Table S1. Selected the non-precious HER catalysts in alkaline condition.

Catalysts	η_{10} (mV)	Tafel (mV/dec)	Condition	Electrode ^a	References
Carbon-based electrodes:					
Co ₃ O ₄ -dpa-C	53	92	1 M NaOH	GC	This work
Ni-C-N NSs	30.8		1M KOH	GC	J. Am. Chem. Soc., 2016, 14546.
MoP/SNG	49	54	1 M KOH	GC	ACS Catal., 2017, 3030.
WC/W ₂ C	56	59	1 M KOH	GC	J. Mater. Chem. A, 2018, 15395.
Mo ₂ C@NC	60		1 M KOH	GC	Angew. Chem. Int. Ed., 2015, 10752.
CuNDs/Ni ₃ S ₂	60	76.2	1 M KOH	CF	J. Am. Chem. Soc., 2018, 610.
Co ₃ S ₄ PNS _{vac}	63	58	1 M KOH	GC	ACS Catal., 2018, 8077.
MoSe ₂ /MO _x	64		1 M KOH	GC	Adv. Energy Mater., 2018, 1801764.
Ni(OH) ₂ @Ni	68	97	1 M KOH	CC	J. Mater. Chem. A, 2017, 7744.
Ni ₃ N@CQDs	69	108	1 M KOH	GC	ACS Nano, 2018, 4148.
MoP-NC	69	52	1 M KOH	CC	Adv. Funct. Mater., 2018, 1801527.
MoC	77	50	1 M KOH	GC	J. Mater. Chem. A, 2016, 6006.
Ni/WC	77	68.6	1 M KOH	GC	Energy Environ. Sci., 2018, 2114.
Mo ₃ P/Mo	78	43	1 M KOH	GC	Angew. Chem. Int. Ed., 2018, 14139.
CoMnP@C	81	55.53	pH = 14	GC	Energy Environ. Sci., 2017, 788.
Zn _{0.3} Co _{2.7} S ₄	85		1 M KOH	GC	J. Am. Chem. Soc., 2016, 1359.
NiFeO _x	88	150	1 M KOH	CFP	Nat. Commun., 2015, 7261.
Ni-MoS ₂	98	60	1 M KOH	CC	Energy Environ. Sci., 2016, 2789.
NiO/Ni-CNT	<100	82	1 M KOH	RDE	Nat. Commun., 2014, 4695.
TiO ₂ /Co	106	62	1 M KOH	CF	Angew. Chem. Int. Ed., 2017, 2960.
CoP/NC	129	58	1 M KOH	GC	ACS Catal., 2017, 3824.
MoNC ₂	132	90	0.1 M KOH	GC	Angew. Chem. Int. Ed., 2017, 16086.
MoB/g-C ₃ N ₄	133	46	1 M KOH	GC	Angew. Chem. Int. Ed., 2018, 496.
MoC _x	151	59	1 M KOH	GC	Nat. Commun., 2015, 6512.
CoMoS _x	~158 (5)		0.1M KOH	GC	Nat. Mater., 2016, 197.
Fe/FeO _x	160	93	1 M NaOH	GC	Dalton Trans., 2018, 7128.
Co-NRCNT	160 (1)		1 M KOH	GC	Angew. Chem. Int. Ed., 2014, 4372.
CoN _x /C	170	75	1 M KOH	GC	Nat. Commun., 2015, 7992.
α -Mo ₂ C	176		1 M KOH	GC	J. Mater. Chem. A, 2015, 8361.
Co ₂ P/WC@NC	180	90	1 M KOH	GC	ChemSusChem, 2018, 1082.
c-CoSe ₂	190	85	1 M KOH	CC	Adv. Mater., 2016, 7527.
NiS ₂ /MoS ₂	204	65	1 M KOH	GC	ACS Catal., 2017, 6179.
NiMo ₃ S ₄	257	98	0.1M KOH	GC	Angew. Chem. Int. Ed., 2016, 15240.

Non-carbon-based electrodes: <i>(continue)</i>					
MoNi ₄	15	30	1 M KOH	NF	Nat. Commun., 2017, 15437.
MoNi/CoMoO ₃	18	35	1M KOH	NF	J. Mater. Chem. A, 2018, 15558.
Co-Co ₂ Mo ₃ O ₈	25	33	1 M KOH	NF	ACS Catal., 2018, 5062.
Porous-MoO ₂	27	41	1 M KOH	NF	Adv. Mater., 2016, 3785.
NiCoP	32	37	1 M KOH	NF	Nano Lett., 2016, 7718.
N-NiCo ₂ S ₄ NWs	41	37	1 M KOH	NF	Nat. Commun., 2018, 1425.
WO ₂ HN	48	43	1 M KOH	NF	J. Mater. Chem. A, 2017, 9655.
Ni ₅ P ₄	49	98	1 M NaOH	Ti	Energy Environ. Sci., 2015, 1027.
Ni ₃ N _{1-x}	55	54	1M KOH	NF	Adv. Sci., 2018, 1800406.
Cu ₉₅ Ti ₅	60	110	0.1 M KOH		Nat. Commun., 2015, 6567.
(Co _{1-x} Fe _x) ₂ P	64	45	1 M KOH		Energy Environ. Sci., 2016, 2257.
Ni ₂ P	69	118	1 M NaOH	Ti	Energy Environ. Sci., 2015, 1027.
CoMnP	76	52	1 M KOH	Ti	ACS Catal., 2017, 98.
Fe-CoP	78	92	1M KOH	NF	Adv. Sci., 2018, 1800949.
Ni ₂ P/CeO ₂	84 (20)	87	1 M KOH	Ti mesh	Inorg. Chem., 2018, 548.
Co(OH) ₂ @PA	90	91.6	1 M NaOH	NF	Adv. Mater., 2015, 7051.
meso-FeS ₂	96	78	0.1 M KOH	NF	J. Am. Chem. Soc., 2017, 13604.
N-NiO	100	112.58	1 M KOH	NF	ChemSusChem, 2018, 1020.
Vc-FeP	108	62	1 M KOH	Ti	ChemSusChem, 2017, 1509.
Co/Co ₃ O ₄	129 (20)	44	1 M KOH	NF	Nano Lett., 2015, 6015.

^a GC: glassy carbon, CC: carbon cloth, RDE: rotating disk electrode, CFP: carbon fiber paper, CF: carbon fiber, NF: nickel foam.

Table S2. TOF values of Co₃O₄-dpa-C and other catalysts.

Catalysts	TOF (s ⁻¹)	η (mV)	Condition	electrode	References
Co ₃ O ₄ -dpa-C	0.95	270	1M NaOH	GC	This work
CoO NR	0.41	100	1M KOH	CFP	Nat. Commun., 2017, 1509.
Fe-CoP	0.069	200	1M KOH	NF	Adv. Sci., 2018, 1800949.
CFeCoP	0.0024	100	1M NaOH	GP ^a	ACS Appl. Energy Mater, 2018, 5298.
MoNi/CoMoO ₃	0.56	100	1M KOH	NF	J. Mater. Chem. A, 2018, 15558.
NiCoP	8.93	100	1M KOH	NF	Nano Lett., 2016, 7718.
Ni-C-N NSs	8.52	200	1M KOH	GC	J. Am. Chem. Soc., 2016, 14546.
Ni ₅ P ₄	0.79	100	1 M NaOH	Ti	Energy Environ. Sci., 2015, 1027.
	2.9	200			
Ni ₂ P	0.004	100	1 M NaOH	Ti	Energy Environ. Sci., 2015, 1027.
	0.014	200			
NiMo	0.2	100	2M KOH	Ti mesh	ACS Catal., 2013, 166.
Ni-MoS ₂	0.32	150	1M KOH	CC	Energy Environ. Sci., 2016, 2789.
MoNC ₂	0.148	50	0.1M KOH	GC	Angew. Chem. Int. Ed., 2017, 16086.
	0.465	100			
	1.46	150			
α -Mo ₂ C	0.5	176	1M KOH	GC	J. Mater. Chem. A, 2015, 8361.
	0.9	200			
	2.5	250			

^aGP: graphite plates.