CoO_x-carbon nanotubes hybrids integrated on carbon cloth as a new generation of 3D porous hydrogen evolution promoter

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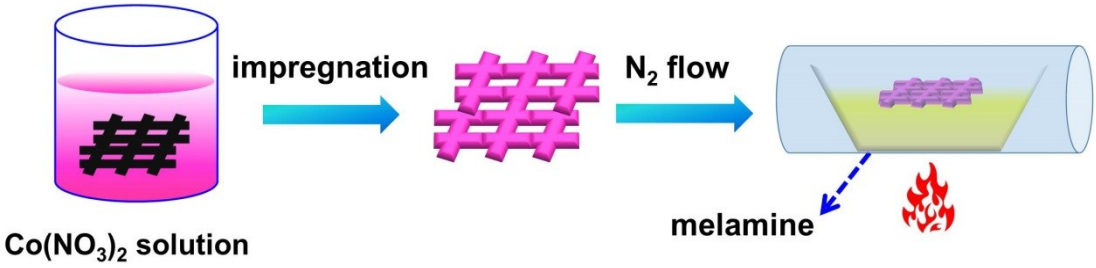
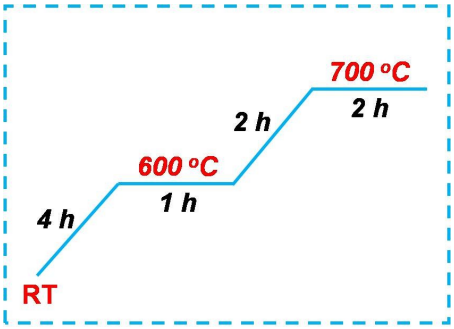


Scheme S1. Schematic diagram for the preparation of 3D porous electrode.



Scheme S2. Calcination program for the preparation of 3D porous electrode.

$H_2O + e^- \rightarrow H^* + OH^-$ (1) Volmer (120 mV dec^{-1})

$H_2O + e^- + H^* \rightarrow H_2 + OH^-$ (2) Heyrovsky (40 mV dec^{-1})

$H^* + H^* \rightarrow H_2$ (3) Tafel (30 mV dec^{-1})

Scheme S3. Hydrogen evolution reaction mechanism in alkaline media.

Table S1. Textural properties of the catalysts.

catalyst	BET surface area (m^2/g)	total pore volume (cm^3/g)	pore size (nm)	percentage of micropore volume (%)
CoO_x-CNT-CC	88	0.07	5.02	48.5
CoO_x-CC	119	0.06	2.88	98.4
M-CC	109	0.06	3.21	70.1
CC-700	324	0.17	2.68	88.2
CC	1	--	--	--

Table S2. Summary of the BET surface area of the recently reported solid-state catalysts.

Catalyst	BET surface area (m^2/g)	Reference
CoO_x-CNT-CC	88	This work
CoP/CC	5.64	*Nano Energy*, 2015, 15, 634
Mo-W-P/CC	25	*Energy. Environ. Sci.* 2016, 9, 1468
CoP/CC	36.5	*J. Am. Chem. Soc.* 2014, 136, 7587
WP_2 NWs/CC	23.04	*Nanoscale*, 2016, 8, 19779
MoP-HS@CC	48.98	*RSC Adv.*, 2016, 6, 68568
Co-HNP/CC	38	*Angew. Chem. Int. Ed.*, 2016, 55, 6724
CoP_3 NAs/CFP	21.4	*J. Mater. Chem. A*, 2016, 4, 14539
NiP_2 NS/CC	21.9	*Nanoscale*, 2014, 6, 13440
GCNF@MoS_2	19.4	*Electrochimica Acta* 2016, 219, 604

Table S3. Electrochemical parameters of the catalysts.

catalyst	electric conductivity (κ / Ω^{-1} m^{-1})	η^a	TS[b]	C_{dl}[c]	ECD[d]
CoO_x-CNT-CC	1250	99	101	1155	2.29
CoO_x-CC	400	193	155	427	0.96
M-CC	625	--	--	162	--
CC-700	588	--	--	349	--
CC	526	--	--	--	--

[a] η (mV) represents the overpotential was calculated at 20 mA cm^{-2}.
[b] TS (mV dec^{-1}) represents Tafel slope.
[c] C_{dl} (mF/cm^2) represented electrochemical double layer capacitances.
[d] ECD (mA cm^{-2}) represents exchange current density.

Table S4. Summary of the recently reported solid-state catalysts for HER in basic electrolytes.

Catalyst	η-j[a]	j[b]	Electrolyte solution	Reference
CoO_x-CNT-CC	99-20 190-100	374	1 M KOH	This work
CoO_x@CN	232-10	28	1 M KOH	*J. Am. Chem. Soc.* **2015**, 137, 2688
FeP NAs/CC	218-10	20	1 M KOH	*ACS Catal.* **2014**, *4*, 4065
Co-NRCNTs	370-10	4	1 M KOH	*Angew. Chem. Int. Ed.* **2014**, 53, 4372
$Co(OH)_2$@PANI on Ni foam	90-10	180	1 M NaOH	*Adv. Mater*. **2015**, 27, 7051
$CoSe_2$/CC	190-10	28	1 M KOH	*Adv. Mater.* **2016**, 28, 7527
NiP_2 NS/CC	270-100	120	1 M KOH	*Nanoscale* **2014**, *6*, 13440
Co@NG	220-10	60	1 M KOH	*Adv. Funct. Mater.* **2016**, 26, 4397
CP/CTs/Co-S	190-10	50	1 M KOH	*ACS Nano* **2016**, *10*, 2342
WP NAs/CC	271-100	140	1 M KOH	*ACS Appl. Mater. Interfaces* **2014**, 6, 21874
NiCoFe/NF	160-10	85	0.1 M KOH	*J. Mater. Chem. A.* **2016**, 4, 7245
CoMn-S@NiO/CC	232-100	200	1 M KOH	*ACS Catal.* **2016**, *6*, 2797
Co_3O_4 NCs/CFP	350-16.5	8	1 M KOH	*Chem. Commun.*, **2015**, 51, 8066
CoP/CC	209-10	42	1 M KOH	*J. Am. Chem. Soc.* **2014**, 136, 7587
Co-NCNT/CC	180-10	100	1 M KOH	*ChemSusChem* **2015**, 8, 1850
Co_9S_8@C	250-10	30	1 M KOH	*ACS Appl. Mater. Interfaces* 2015, 7, 980
Fe-CoP/Ti	78-10	--	1 M KOH	*Adv. Mater.* **2017**, *29*, 1602441

Co-NCNT/CC	180-10	100	1 M KOH	*ChemSusChem* **2015**, 8, 1850
NiS_2 NA/CC	149-10	~150	1 M KOH	*Electrochim. Acta* **2015**, 153, 508
Zn-Co-S/TM	238-20	50	1 M KOH	*Electrochim. Acta* **2016**, 190, 360

[a] η (mV) represents overpotential at current density of j (mA cm^{-2}).
[b] j represents the current density, which was calculated at -0.3 V.

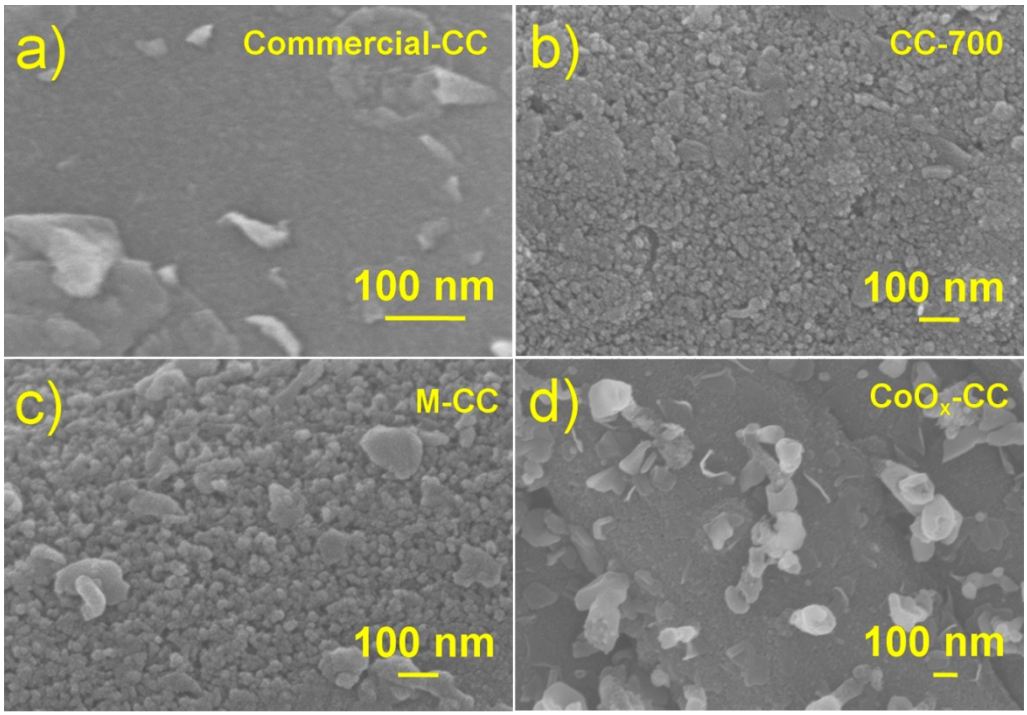


Fig. S1 SEM images of commercial CC a), CC-700 b), M-CC c), CoO_x-CC d).

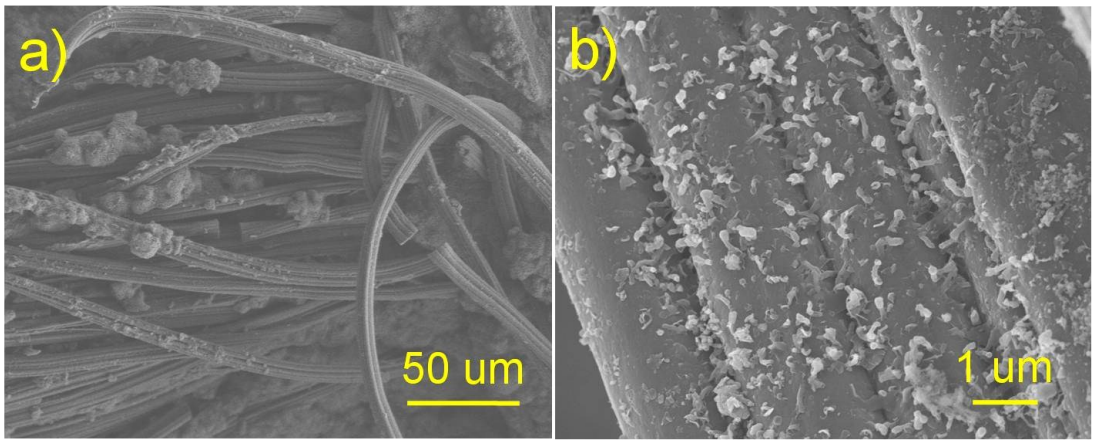


Fig. S2 a) SEM images of CoO_x-CNT-CC at low magnifications; b) The enlarged SEM images of CoO_x-CNT-CC.

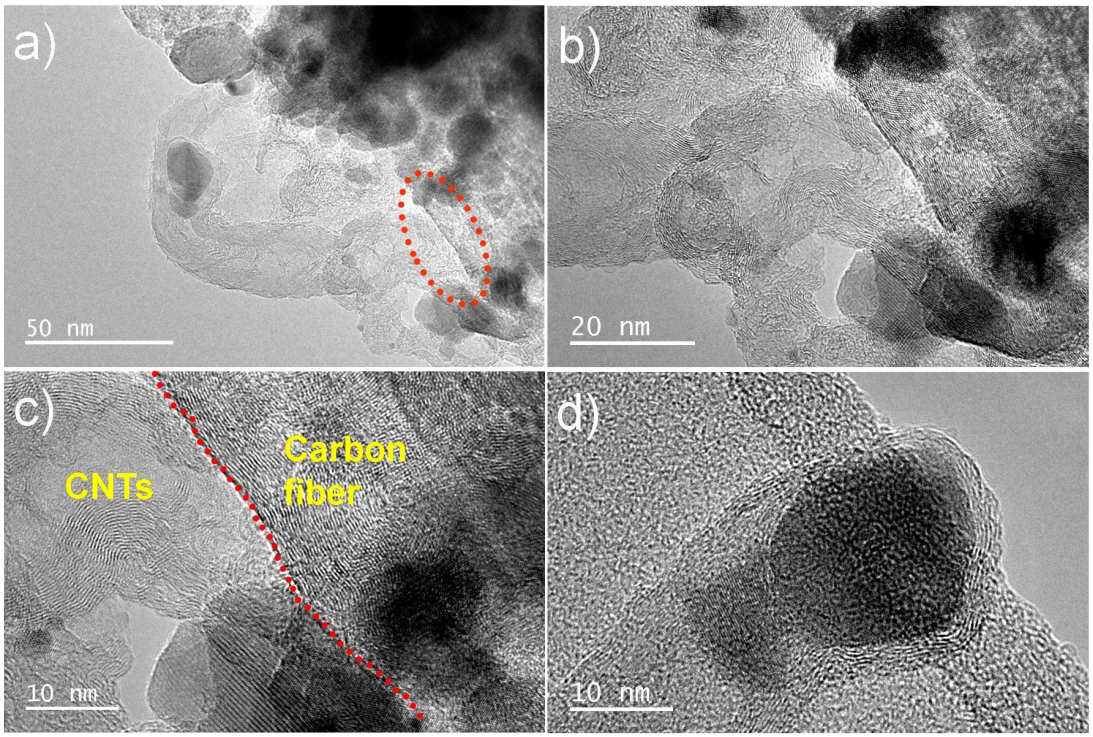


Fig. S3 a, b, c, d) TEM images of CoO_x-CNT-CC with different magnifications. The red dotted line in c represents the contact surface of CNTs and carbon fiber.

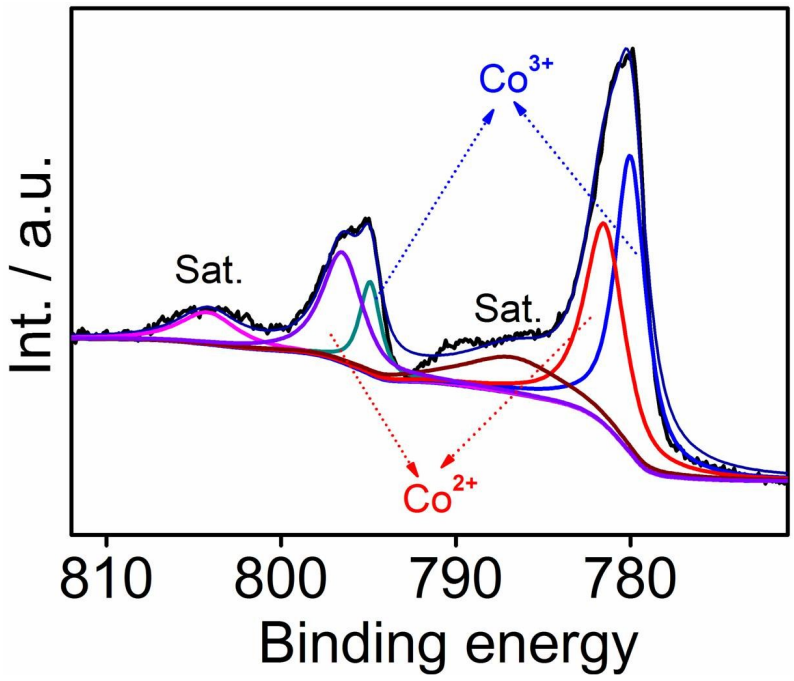


Fig. S4 Co2p XPS of CoO_x-CNT-CC.

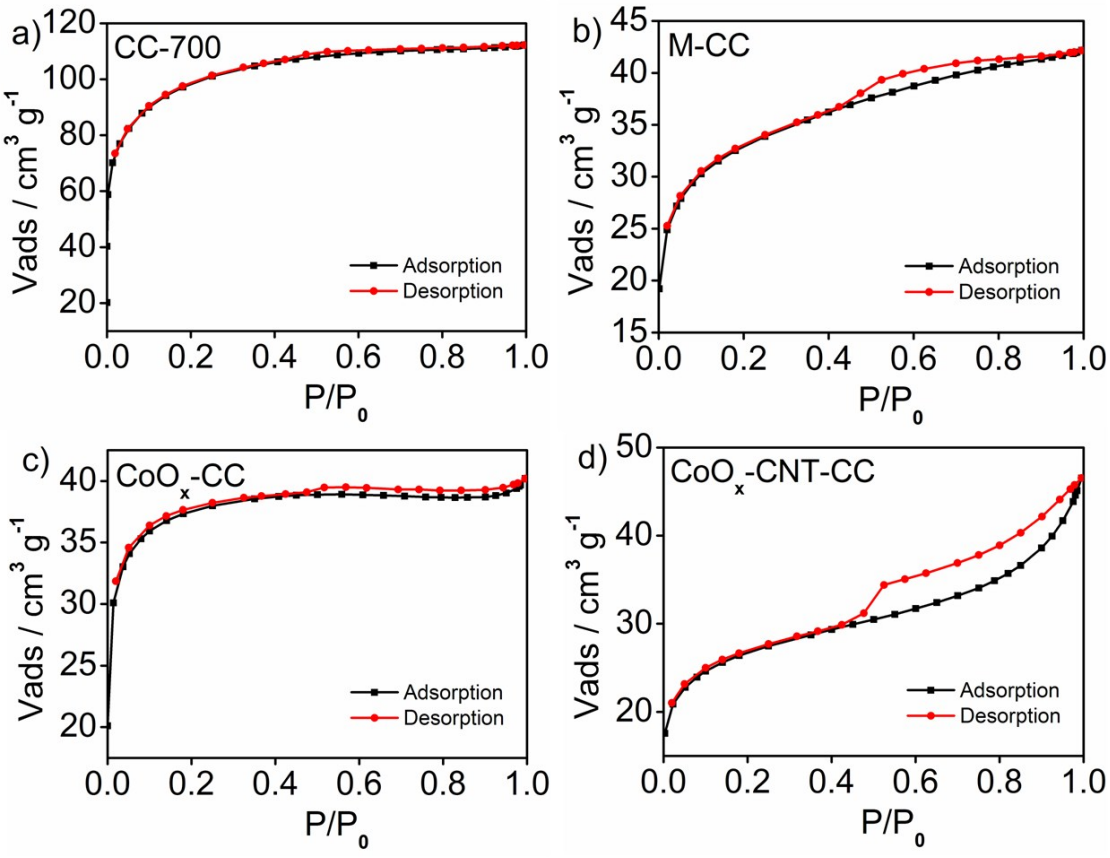


Fig. S5 N_2 adsorption-desorption isotherms of CC-700 a), M-CC b), CoO_x-CC c), CoO_x-CNT-CC d).

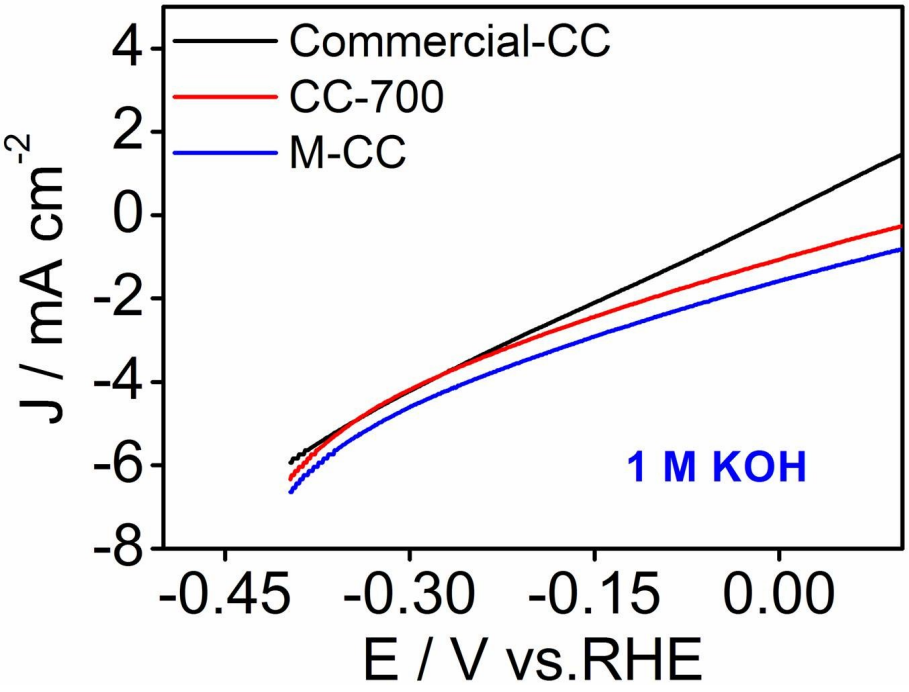


Fig. S6 The enlarged Polarization curves of Fig. 2a.

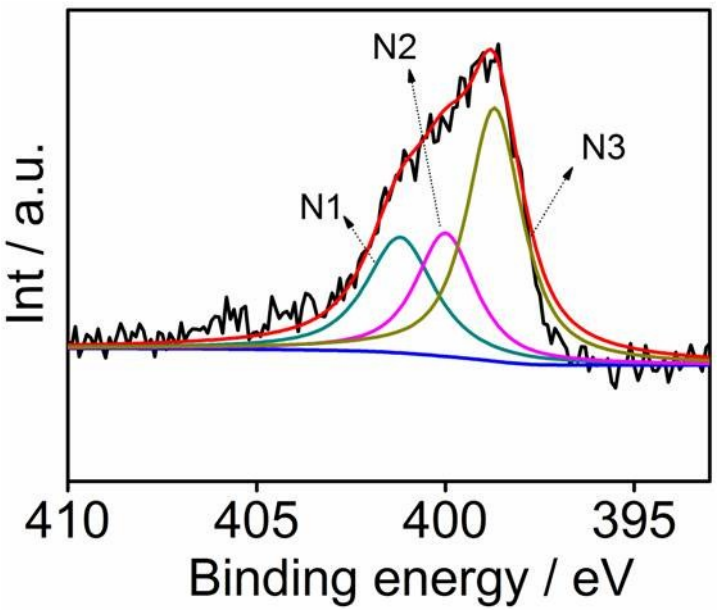


Fig. S7 High-resolution N 1s XPS spectra of CoO_x-CNT-CC, N1 (graphitic quaternary N, ~401.1 eV), N2 (pyrrole N, ~400.0 eV), and N3 (pyridine N, ~398.5 eV). The content of N1, N2 and N3 is 27%, 25% and 48%, respectively.

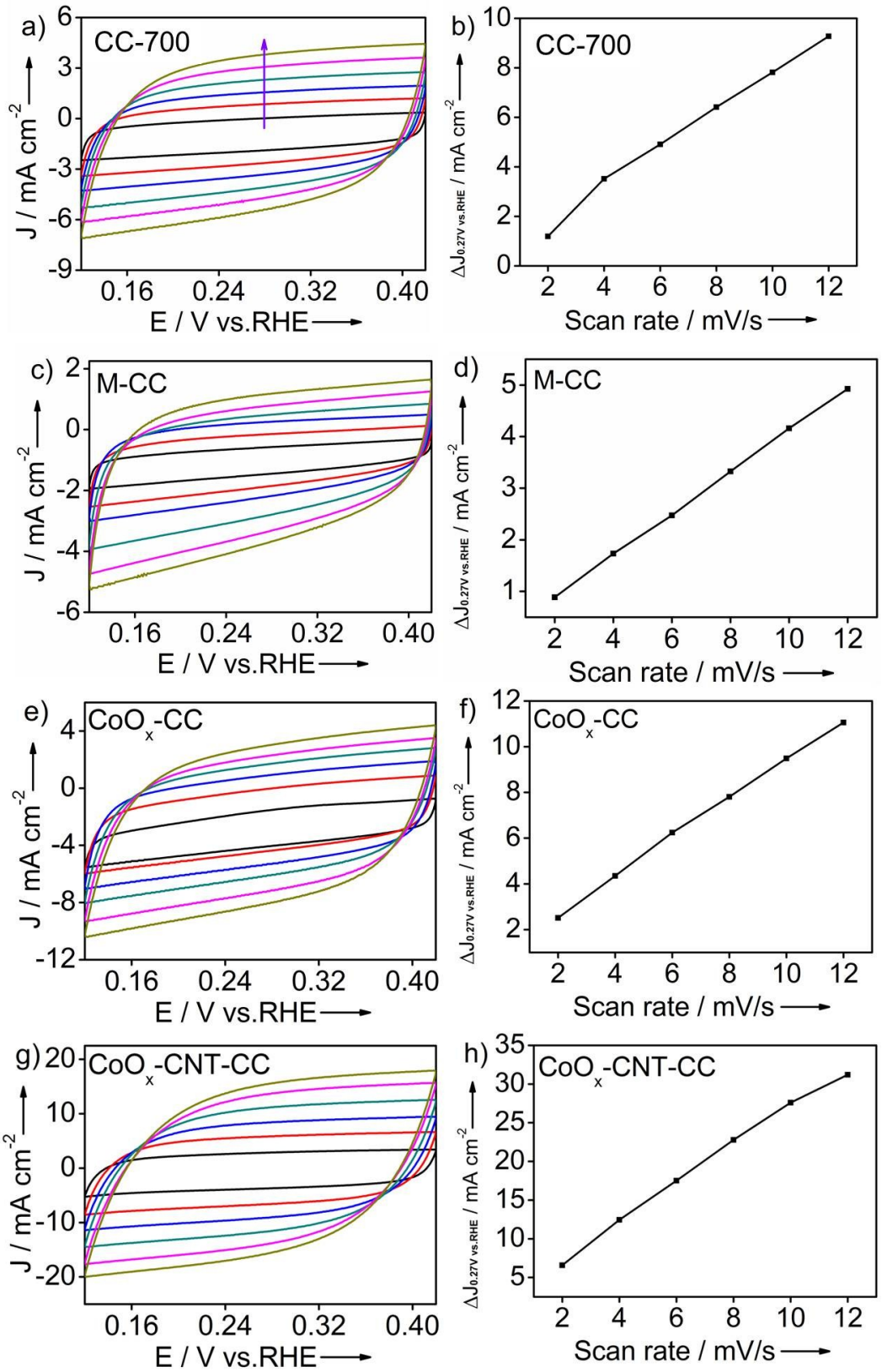


Fig. S8 a, c, e, g) Cyclic voltammetry curves of CC-700, M-CC, CoO_x-CC and CoO_x-CNT-CC, respectively, at different scan rates. The purple arrow indicates the scan rate from 2 mV to 12 mV. b, d, f, h) The differences in current density variation

(ΔJ=Ja-Jc) at an overpotential of 0.27 V plotted against scan rate fitted to a linear regression enables the estimation of C_{dl}, where the slope is twice C_{dl}.

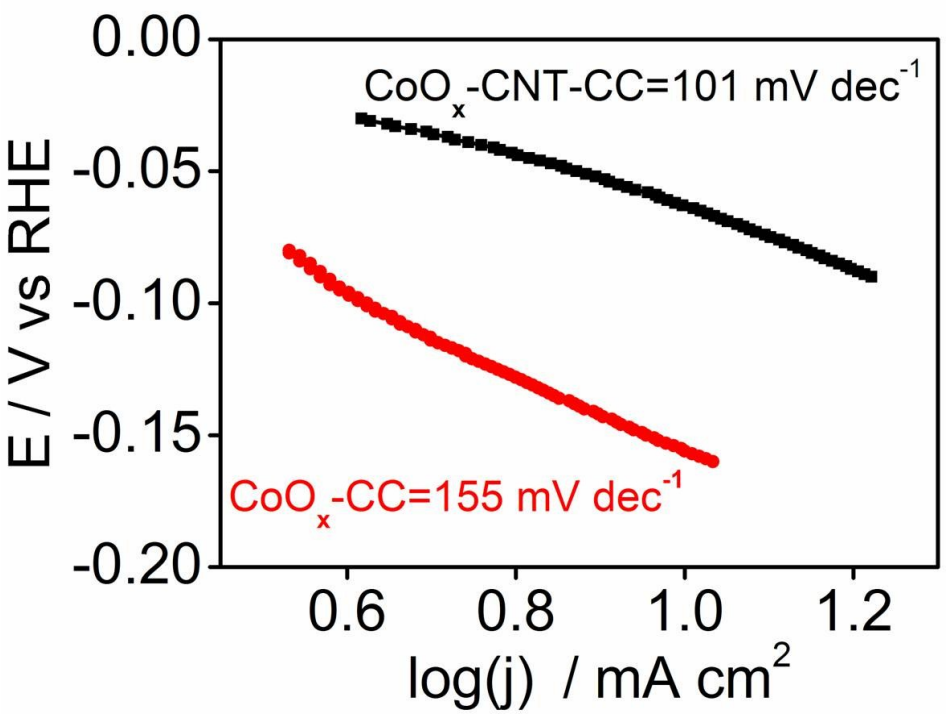


Fig. S9 Tafel curves of CoO_x-CNT-CC and CoO_x-CC.

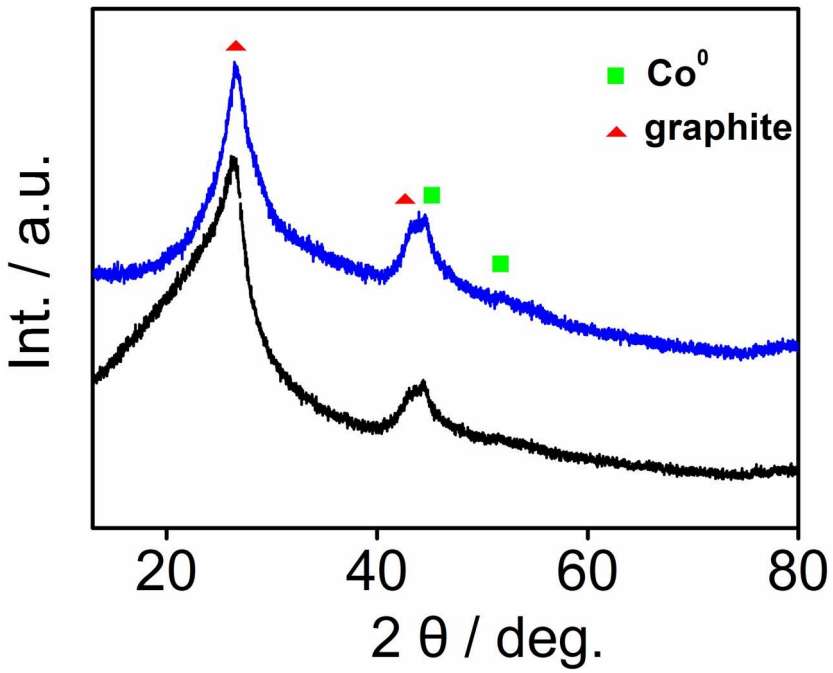


Fig. S10 The black line represents the XRD pattern of the CoO_x-CNT-CC-HER-acid. The blue line represents the XRD pattern of the electrode that CoO_x-CNT-CC-HER-acid after HER test.

As shown in Fig. S10, even CoO_x-CNT-CC-HER-acid was further tested, it appeared the characteristic peaks of metallic cobalt, suggesting that metallic cobalt is extremely stable in our system.

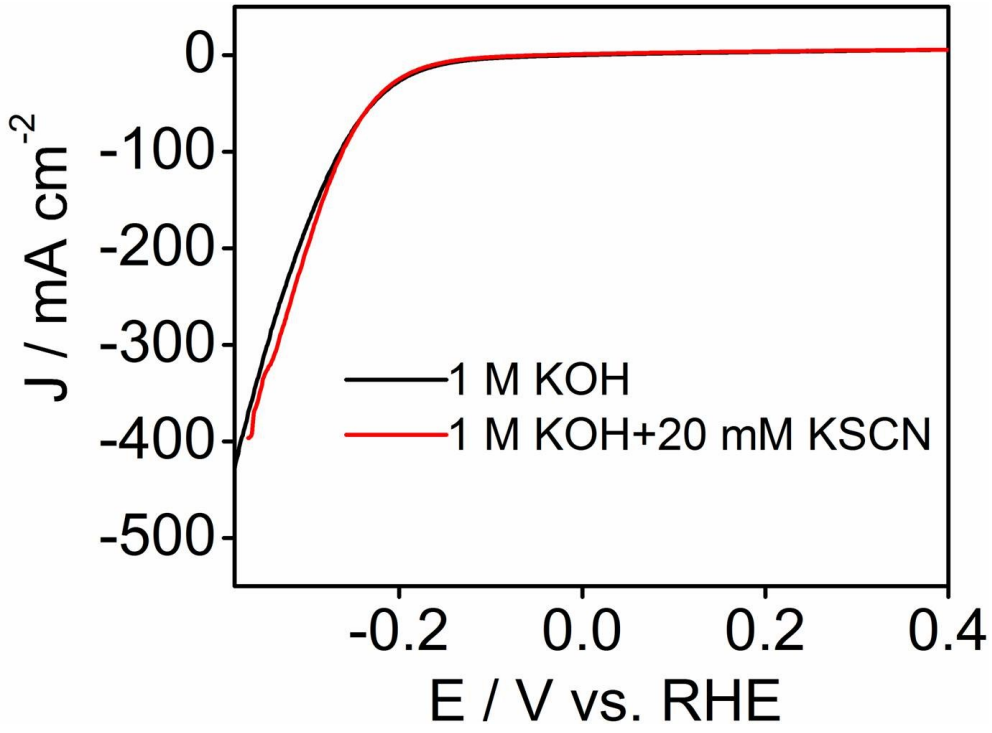


Fig. S11 Polarization curves of CoO_x-CNT-CC-HER-acid in 1 M KOH and 1 M KOH+20 mM KSCN.

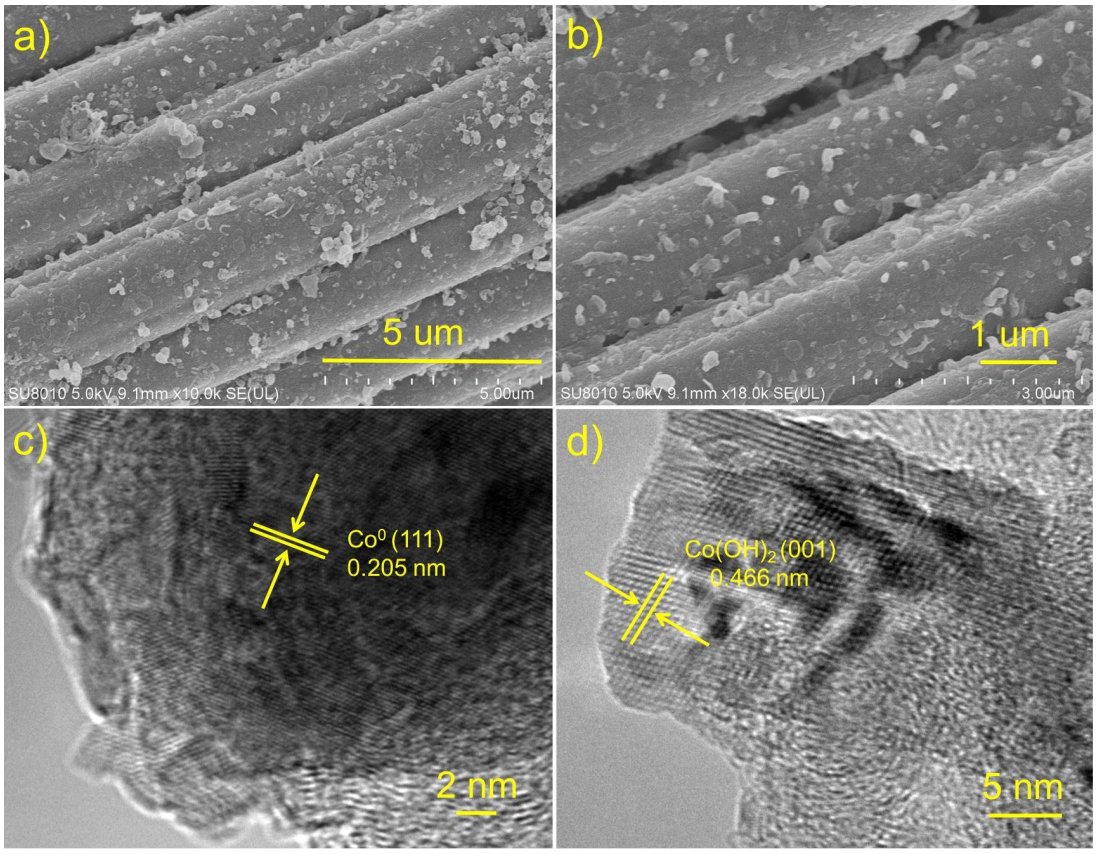


Fig. S12 a, b) SEM images of CoO_x-CNT-CC after long-term HER test. c, d) HRTEM images of CoO_x-CNT-CC after long-term HER test.

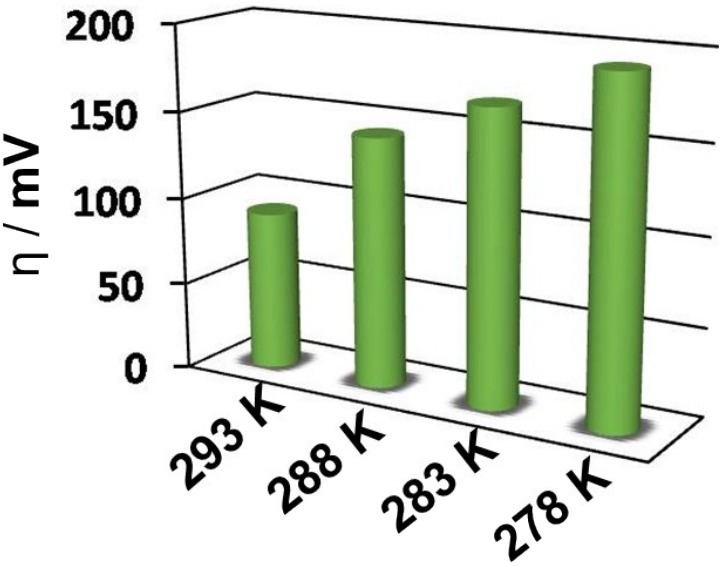


Fig. S13 Overpotential (η) of CoO_x-CNT-CC tested under different temperature. η was calculated at 10 mA cm^{-2}.