Simultaneous Hydrogen and Oxygen Evolution Reactions using Free-Standing Nitrogen-Doped-Carbon-Co/CoO_x Nanofiber Electrodes Decorated with Palladium Nanoparticles

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Supplementary Materials

Table S1. Crystallite size (based on the XRD data), elemental composition (AAS analysis), and I_D/I_G value (based on the Raman spectra) of the free-standing electrodes under study.

Sample	**Crystallite size (nm)**	**Elemental Composition**		**I_D/I_G value**
		Carbon (wt%)	Cobalt (wt%)	
N-CNF	Non	100	0.0	1.13
N-C-Co10	32.0±0.4	86	14	1.01
N-C-Co20	35.1±0.3	75	25	0.92

Table S2. Results of the XPS elemental analysis of the prepared N-C-Co20 and N-C-Co20-Pd100 electrodes

Elemental analysis	N-C-Co20	N-C-Co20-Pd100
	Atomic Mass %	Atomic Conc.%
C	95.1	87.7
O	2.7	2.0
N	1.4	1.0
Co	0.8	0.9
Pd	0.0	8.4

Table S3. Results of the XPS analysis and fitting parameters for the Pd 3d peak of the C-Co20-Pd100 electrode

Pd 3d peak	Binding Energy (eV)	FWHM (eV)	Atomic Concentration (%)
Pd 3d 5/2 (0)	335.1	1.1	44.3
Pd 3d 3/2 (0)	340.5	1.1	29.3
Pd 3d 5/2 (+II)	336.3	1.8	15.7

Pd 3d 3/2 (+II)	341.6	1.8	10.4

Table S4. Mean surface area (BET method), and mean pore diameter and volume (BJH method).

Electrodes	Surface area (cm^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
N-CNF	6.7	13.8	0.0143
N-C-Co10	114.1	3.8	0.0927
N-C-Co20	239.7	5.6	0.0439
N-C-Co10-Pd100	86.2	4.3	0.0715
N-C-Co10-Pd200	76.6	6.1	0.0385
N-C-Co20-Pd100	150.4	8.1	0.0830
N-C-Co20-Pd200	113.2	4.4	0.0671

Table S5. Electrocatalytic data of the indicated electrodes (based on the LSV, CSV, and EIS measurements during HER and OER). Standard deviation was calculated from at least three measurements.

Electrodes		$\eta^{@}$ 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	j_0 (mA cm^{-2})	C_{dl} (mF cm^{-2})	ECSA (cm^2)	R_{ct}* (Ohm)
N-CNF	HER	498 ± 0.04	333 ±0.16	0.56 ±0.017	--	--	22
	OER	537 ± 0.015	540 ± 0.2	0.48 ± 0.01			72
N-C-Co10	HER	364 ± 0.013	119 ±0.09	0.57 ±0.17	39	975	12
	OER	460 ± 0.02	508 ± 0.07	0.49 ± 0.02			69
N-C-Co20	HER	312 ± 0.06	74 ±0.08	0.78 ±0.016	20	500	11.2
	OER	418 ± 0.031	416 ± 0.09	0.50 ± 0.09			60
N-C-Pd100	HER	296 ± 0.024	73 ±0.05	1.13 ±0.12	15	375	7.2

	OER	380 ± 0.054	412 ± 0.07	0.53 ± 0.11			55
N-C-Co10-Pd200	HER	167± 0.06	63± 0.015	1.43± 0.05	31	775	4
	OER	366 ± 0.052	412± 0.07	0.53± 0.07			39
N-C-Co20-Pd200	HER	155± 0.025	55± 0.01	1.47± 0.04	24	600	2.4
	OER	290 ± 0.034	399± 0.05	0.549± 0.02			21
N-C-Co10-Pd100	HER	148 ± 0.042	39 ±0.04	1.5 ±0.09	30	750	2.5
	OER	270± 0.012	316 ± 0.02	0.62 ± 0.04			24
N-C-Co20-Pd100	HER	100± 0.03	33± 0.01	1.8± 0.08	70	1750	1.2
	OER	160 ± 0.041	113± 0.03	1.22± 0.06			12.5
Pt sheet	HER	50±0.08	36±0.05	1.65±0.03	--	--	--
IrO_2 sheet	OER	210±0.01	156±0.04	0.95±0.07	--	--	--

Table S6. HER activity with free-standing N-CNF-Co/CoOx-Pd electrodes in comparison work from literature.

Electrode	**Support**	**η@j =10 mA cm^{-2} (mV) HER**	**Tafel slope (mVdec^{-1}) HER**	**Ref**
CNFs-Au-Cu	Free-standing	83	70	[8]
CNFs-Cu	Free-standing	200	152	[9]
CNFs-Ni	Free-standing	300	105	[17]
CNFs-Ni-Pd	Free-standing	55	57	[67]
CNFs-Ni-Pt	Conductive glass	47	31	[75]
CNF-Ni/NiO-Pt	Free-standing	63	72	[51]

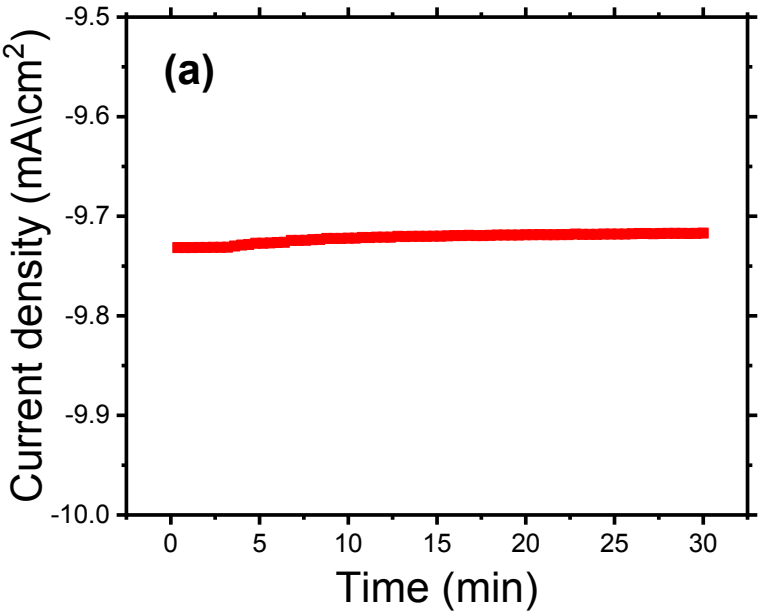
This work	Free-standing	62	35	--

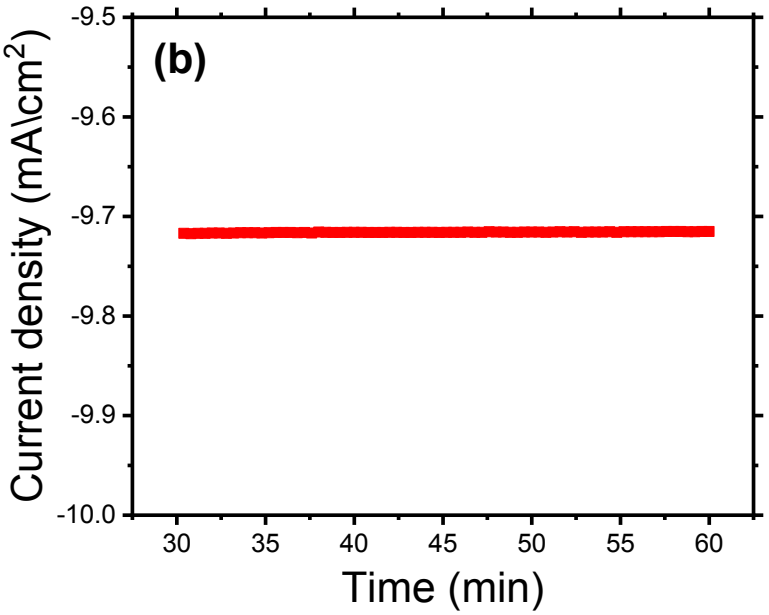
Hydrogen characterization and Faradic efficiency measurements:

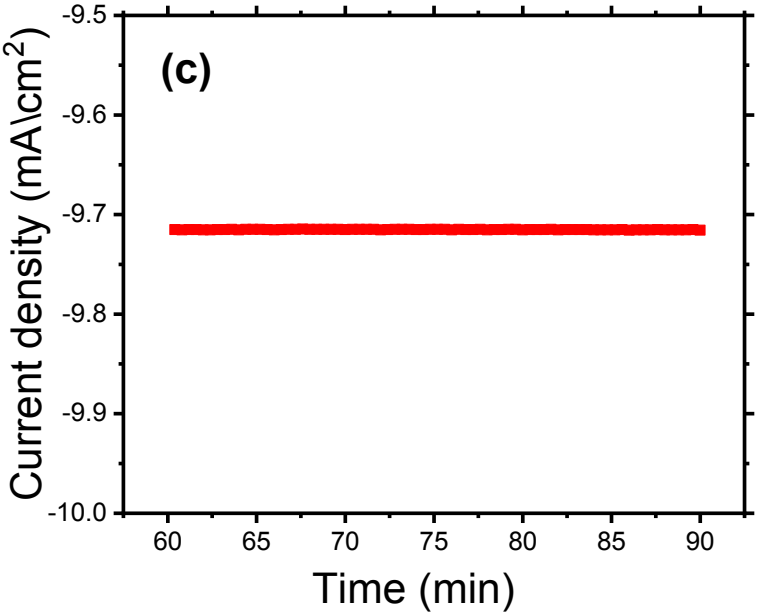
Hydrogen evolution was monitored by gas chromatography of a Clarus-400, PerkinElmer system equipped with a thermal conductivity detector TCD. Ultra-high purity helium gas was used as the carrier gas for hydrogen detection. Chronoamperometry measurements have been performed at 65 mV for the desired duration time of 30 min as illustrated in Figure (S1). The samples were collected from the dead volume of the cell using a lock-in syringe and injected into the GC system under identical conditions. Faradaic efficiency (FE) measurements were calculated using the following equation:

FE (%) = [(moles of H_2 (measured by GC)) / (j (mA/cm^2) x t(S) / nF)] * 100

where n=2 is the number of electrons required for HER reaction, F is the Faraday constant.




(b)
Current density (mA\cm^2)
-9.5
-9.6
-9.7
-9.8
-9.9
-10.0
30
35
40
45
50
55
60
Time (min)


(c)
Current density (mA\cm^2)
-9.5
-9.6
-9.7
-9.8
-9.9
-10.0
60
65
70
75
80
85
90
Time (min)

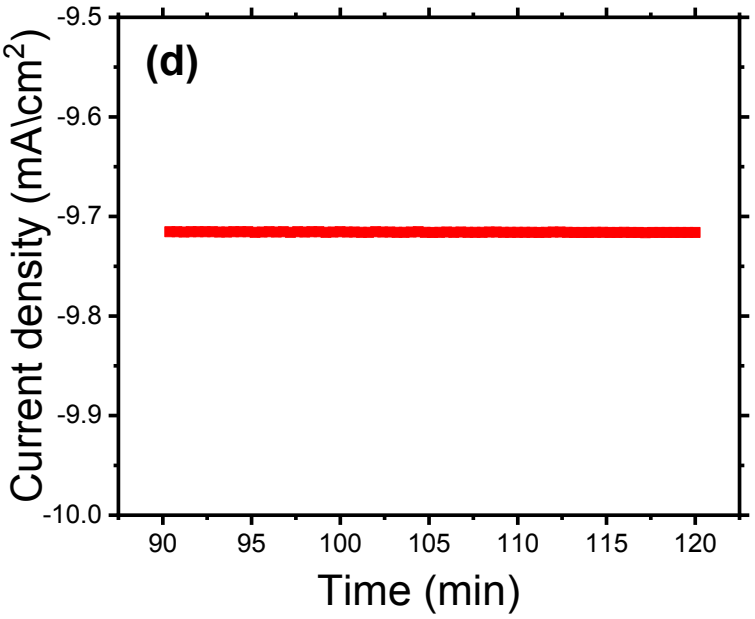


Figure S1. Current-time (i-t) curves of the N-C-Co-Pd100 obtained from chronoamperometry tests for FE measurements at different time intervals: (a) 30 min; (b) 60 min; (c) 90 min; (d) 120 min.