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Supporting Information

Facile one-pot synthesis of nitrogen-doped mesoporous carbon architecture with cobalt oxides encapsulated in graphitic layers as a robust bicatalyst for oxygen reduction and evolution reactions

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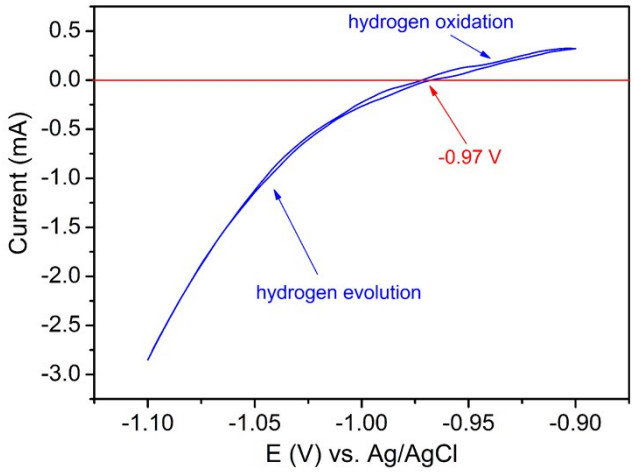
Calibration of Ag/AgCl/saturated KCl reference electrode and conversion to RHE

The calibration of Ag/AgCl/saturated KCl reference electrode was performed in a standard three-electrode system with polished Pt wires as the working and counter electrodes, and Ag/AgCl/saturated KCl as the reference electrode. Before tests, the electrolyte (0.1 M KOH, pH=13) was pre-purged with high purity H_2 for at least 20 min to ensure H_2 saturation. CVs were run at a scan rate of 1 mV s^{-1}, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions.[1]



In 0.1 M KOH, the average potential of zero current points is -0.97 V, so E (RHE) = E (Ag/AgCl) + 0.97 V.

Table S1. The I_D/I_G ratios of Co-N/C 750, 800 and 850, respectively.

Samples	I_D/I_G
Co-N/C 750	1.08
Co-N/C 800	1.01
Co-N/C 850	0.98

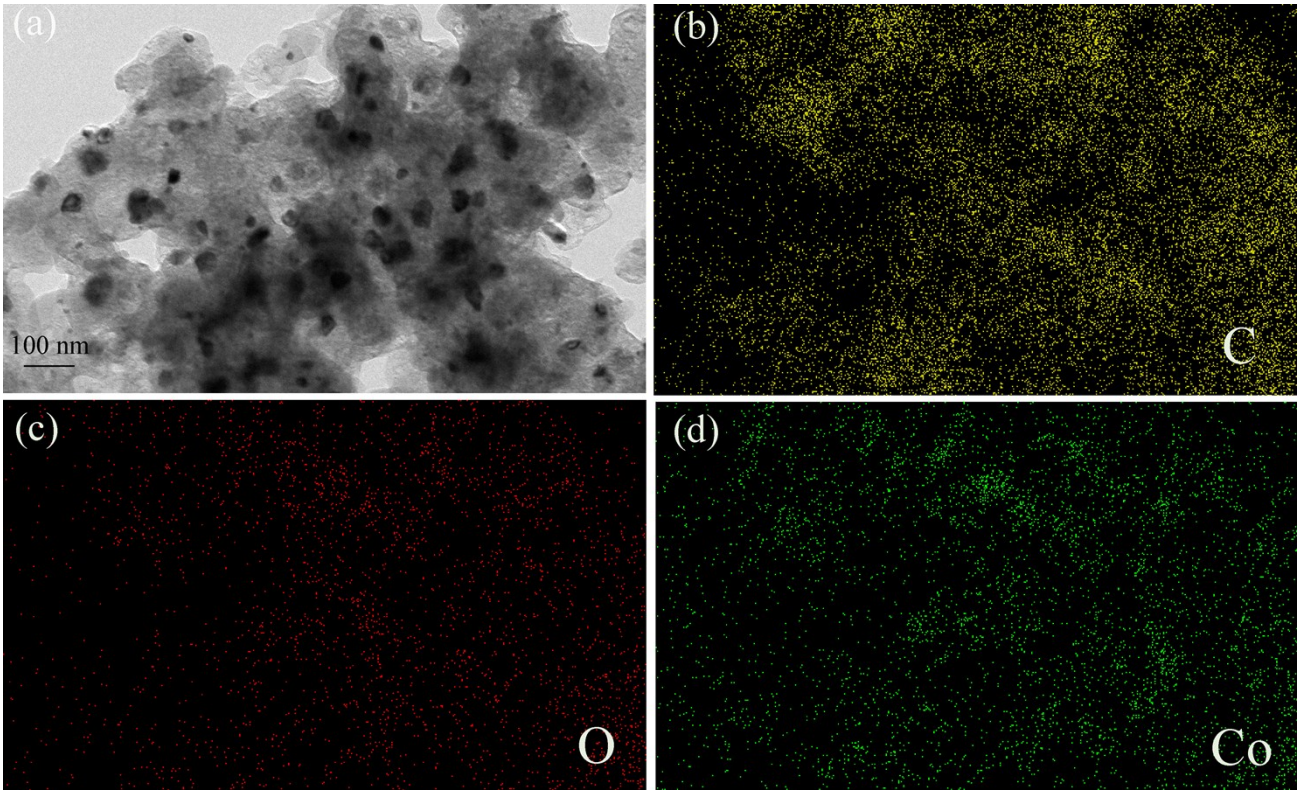


Figure S1. (a) TEM image and (b) corresponding EDS elemental mappings of C, O and Co elements for Co-N/C 800.

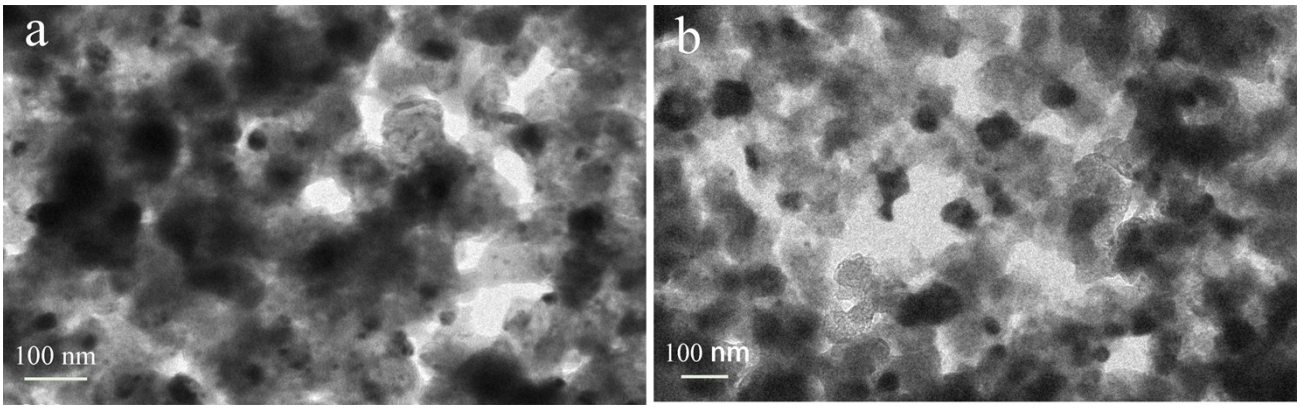


Figure S2. TEM images of (a) Co-N/C 750 and (b) Co-N/C 850.

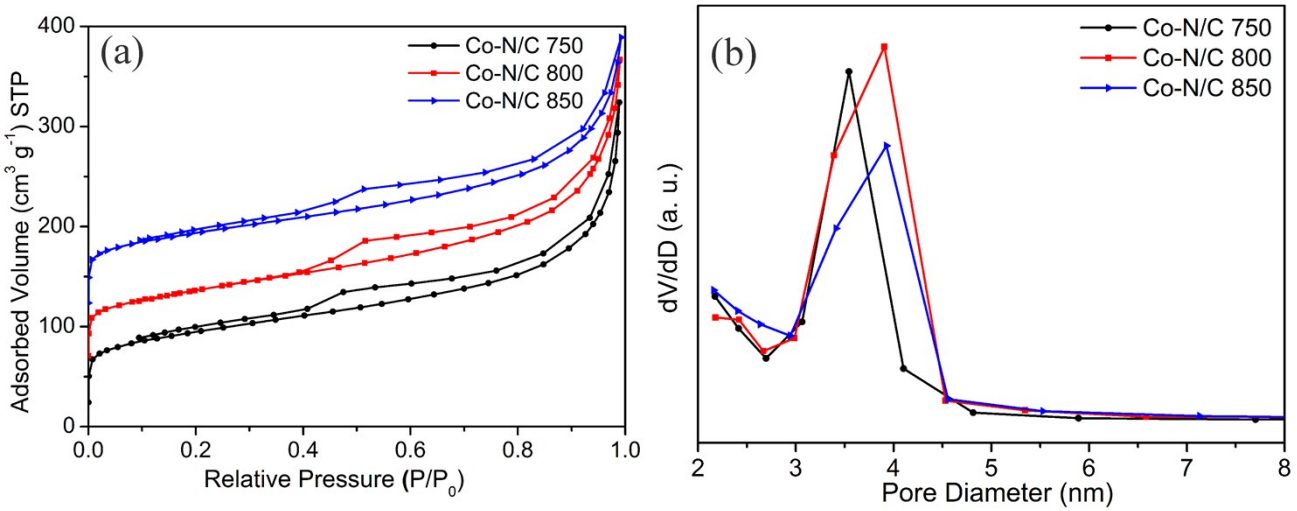


Figure S3. (a) N_2 adsorption/desorption isotherms and (b) corresponding pore size distribution curves of Co-N/C 750, Co-N/C 800 and Co-N/C 850, respectively.

Table S2. Physicochemical properties and average particle sizes of Co-N/C 750, 800, and 850.

Samples	surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
Co-N/C 750	305	0.50	3.54
Co-N/C 800	312	0.49	3.87
Co-N/C 850	324	0.45	3.91

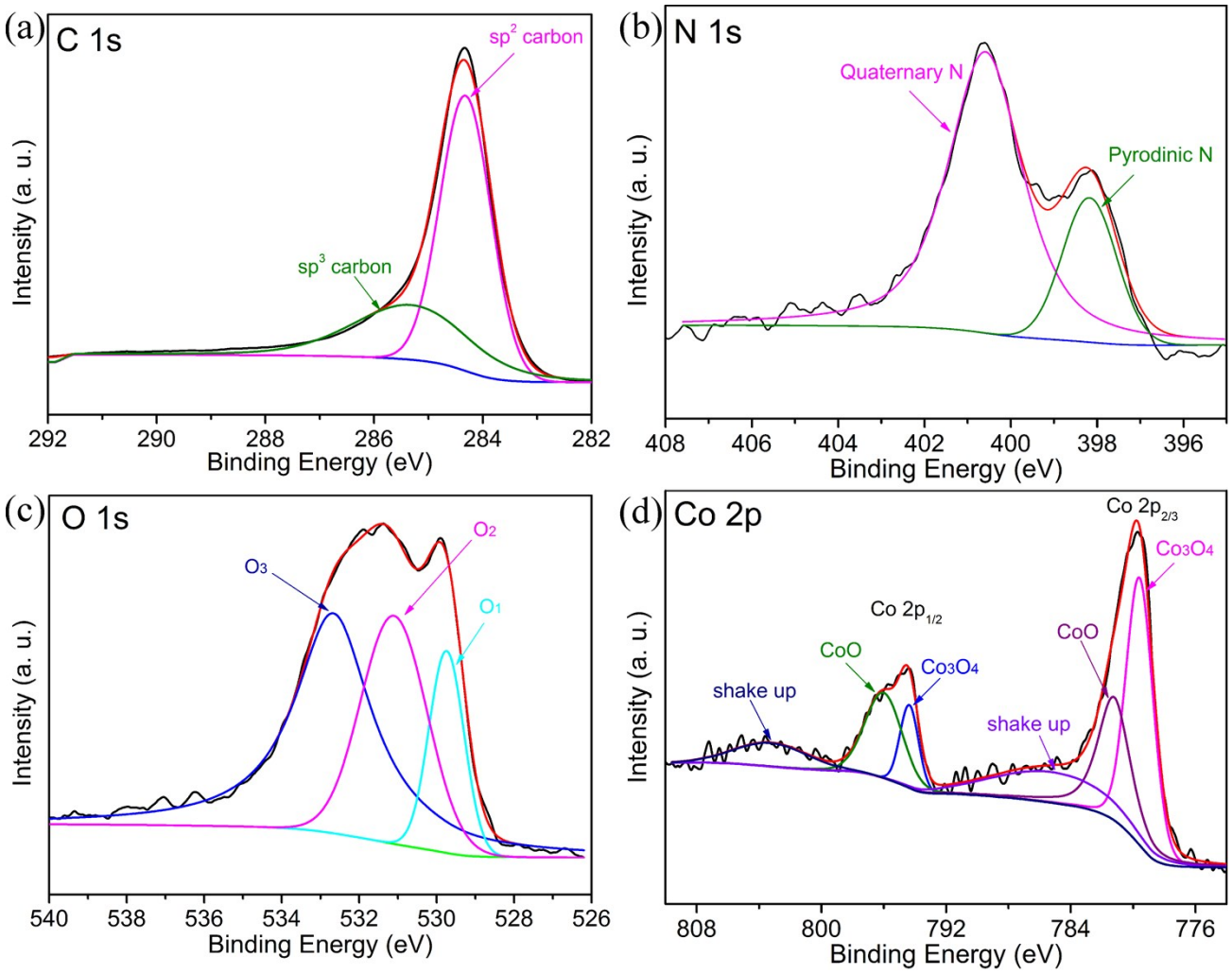


Figure S4. High-resolution XPS patterns of (a) C 1s, (b) N 1s, (c) O 1s and (d) Co 2p of Co-N/C 750.

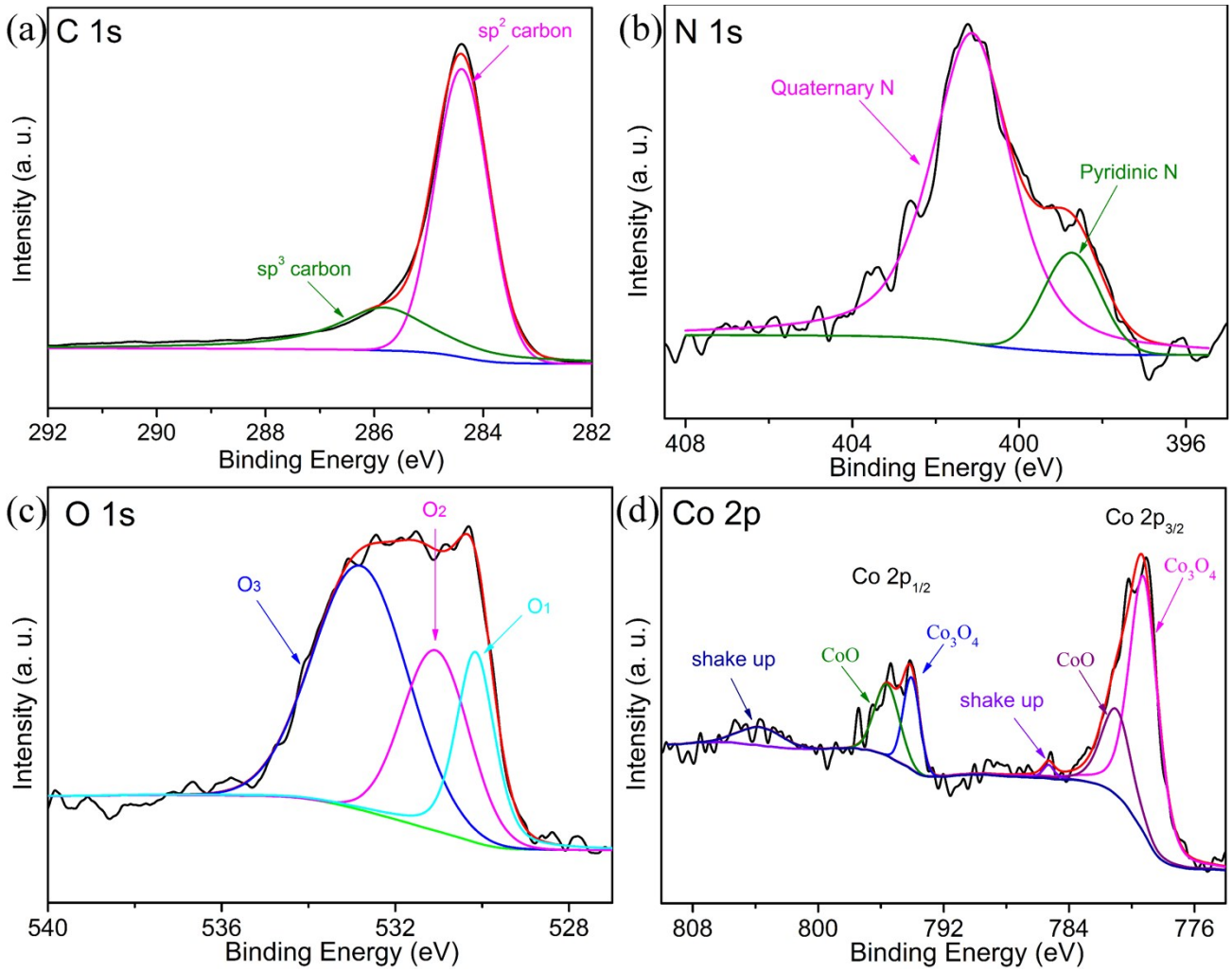


Figure S5. High-resolution XPS profiles of (a) C 1s, (b) N 1s, (c) O 1s and (d) Co 2p of Co-N/C 850.

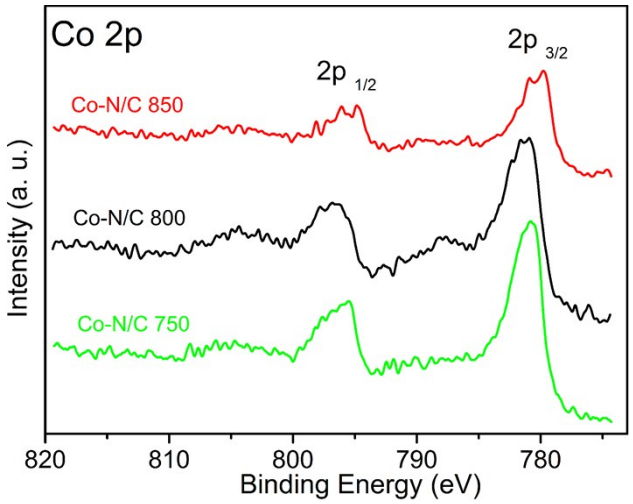


Figure S6. XPS Co 2p spectra of Co-N/C catalysts pyrolyzed at different temperatures.

Table S3. Elemental composition of the near-surface region of Co-N/C 750, 800 and 850 examined by XPS.

Samples	C (at. %)	N (at. %)	Ratio (Quaternary N/ Pyridinic N)	O (at. %)	Ratio (N+O)/ C (%)	Co (at. %)	Ratio (Co_3O_4/ CoO)
Co-N/C 750	90.56	2.64	3.50	5.77	9.3	1.03	1.10
Co-N/C 800	90.63	2.27	4.29	5.92	9.0	1.17	1.99
Co-N/C 850	92.98	2.04	5.59	4.08	6.6	0.9	2.14

Table S4. Elemental contents of Co-N/C 750, 800 and 850 tested by elemental analysis (EL).

Samples	C (wt. %)	H (wt. %)	N (wt. %)
Co-N/C 750	70.90	0.42	1.63
Co-N/C 800	76.67	0.33	1.27
Co-N/C 850	66.54	0.27	1.14

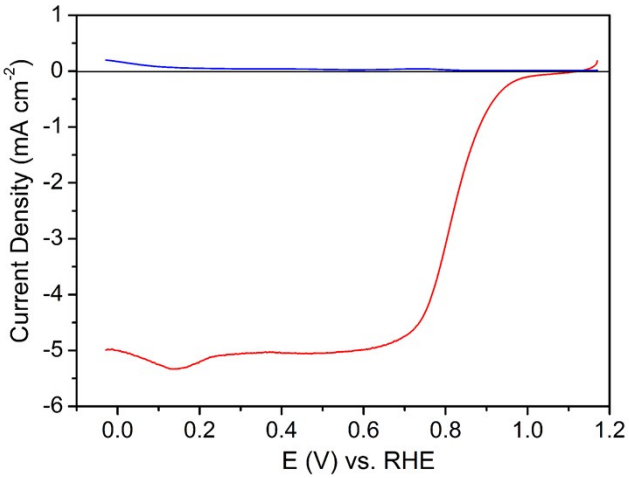


Figure S7. Electrochemical activity of commercial 20 wt. % Pt/C catalyst tested on RRDE technique in O_2-purged 0.1 M KOH at 1600 rpm.

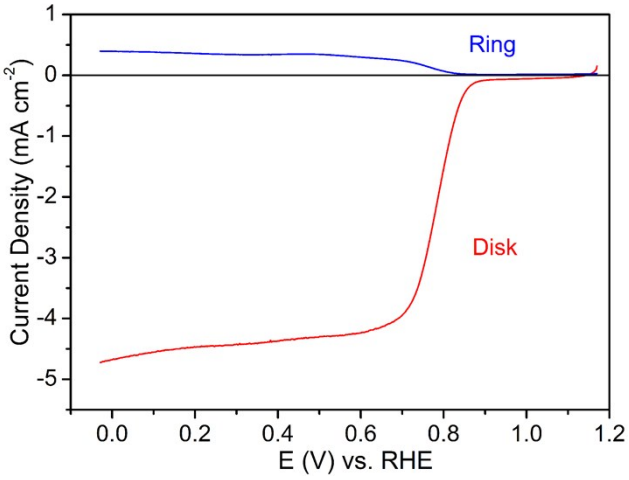


Figure S8. Electrochemical activity of Co-N/C 750 examined by RRDE technique in O_2-saturated 0.1 M KOH aqueous solution at 1600 rpm.

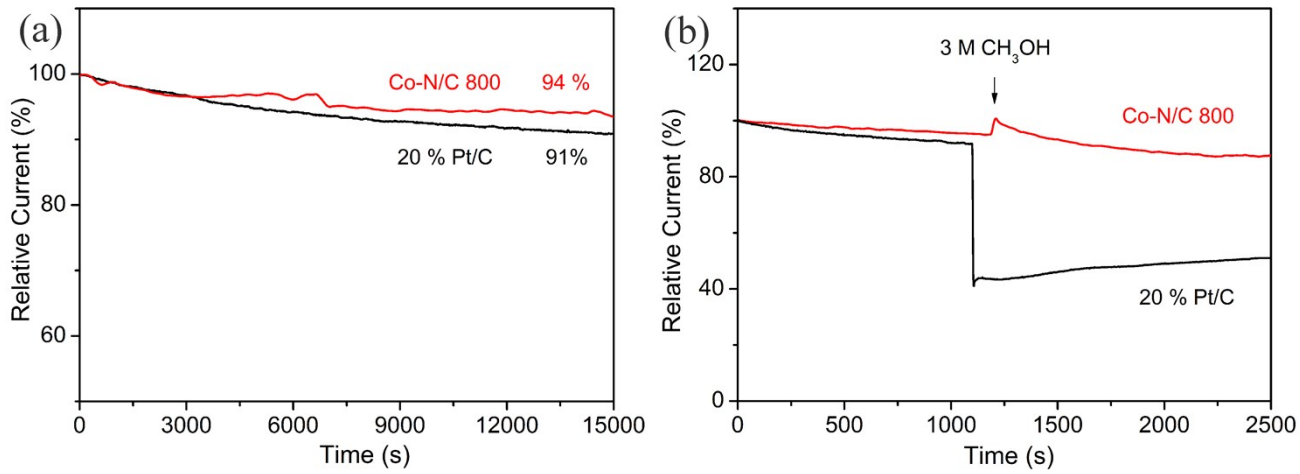


Figure S9. Long-term stability for ORR and methanol crossover resistance test of Co-N/C 800 by chronoamperometry at +0.57 V (vs. RHE) in comparison with commercial 20 wt. % Pt/C in O_2-saturated 0.1 M KOH electrolyte under 1600 rpm.

Table S5. The bifunctional activities of various catalysts for oxygen electrode reactions.

Catalysts	E_{OER} at I = 10 mA cm^{-2} (V)	E_{ORR} at I = -3 mA cm^{-2} (V)	Oxygen electrode activity ΔE (V)	Catalyst loading (mg cm^{-2})	Electrolyte	References
Co-N/C 800	1.74	0.78	0.96	0.24	0.1 M KOH	This work
20 wt.% Pt/C	2.08	0.85	1.23	0.24	0.1 M KOH	This work
IrO_2	1.71	0.29	1.42	0.24	0.1 M KOH	This work
RuO_2	1.64	0.29	1.35	0.24	0.1 M KOH	This work
Co@Co_3O_4/NC-1	1.65	0.80	0.85	0.21	0.1 M KOH	[2]
Co/N-C-800	1.599	0.74	0.859	0.25	0.1 M KOH	[3]
macro/meso-NC-NH_3+Co_3O_4 microtrepangs	1.72	0.82	0.90	0.255	0.1 M KOH	[4]
meso-Co_3O_4-35	1.64	0.61	1.03	0.1	0.1 M KOH	[5]
LDO/CNT	1.64	0.65	0.99	0.25	0.1 M KOH	[6]

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