

# Supporting Information

## A Cobalt-Iron Double-Atom Catalyst for the Oxygen Evolution Reaction

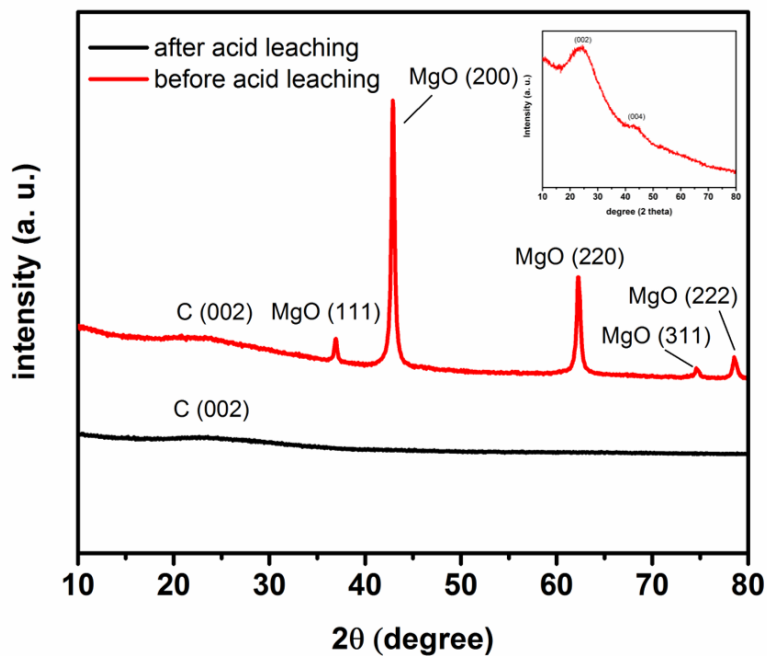
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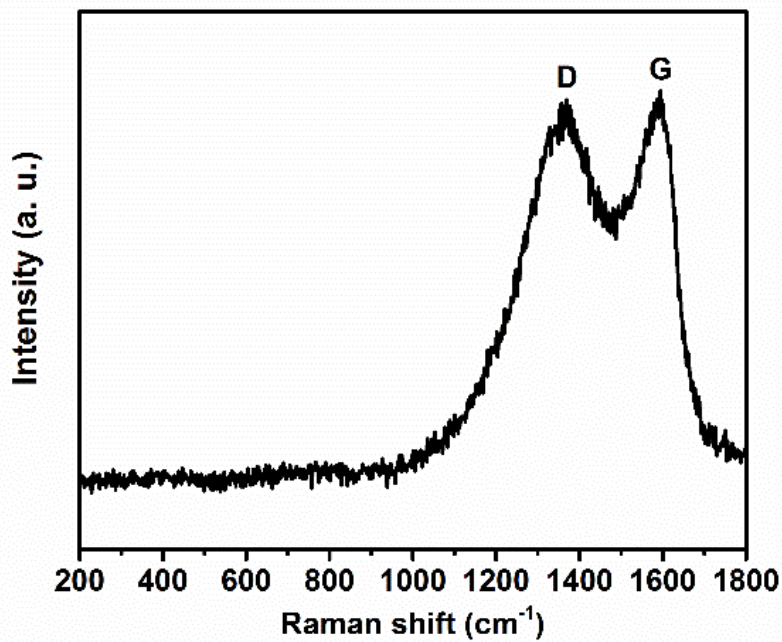
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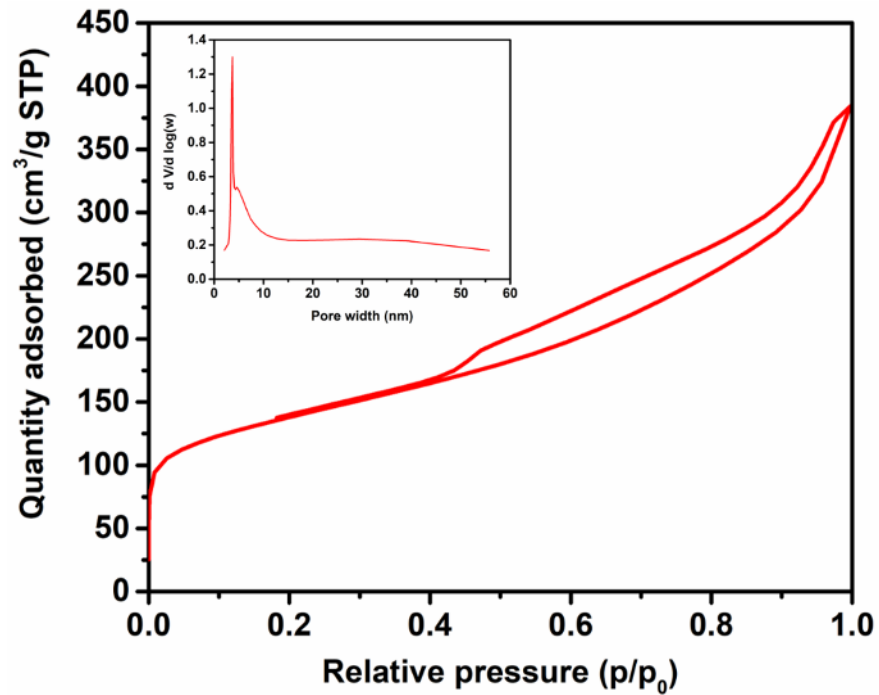
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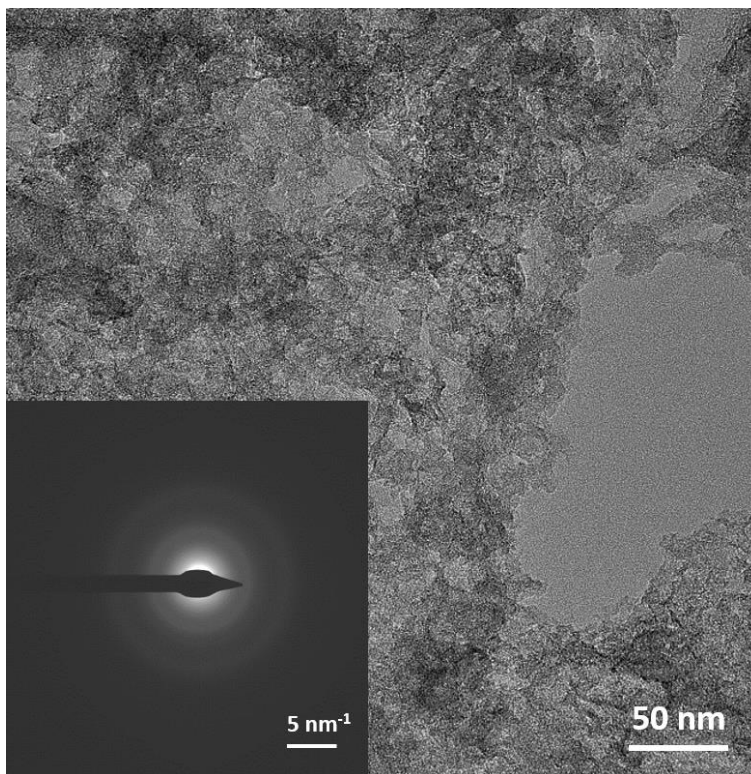
**Figure S1.** XRD of the as-prepared material and the material after acid leaching (Co-N-C). The inset is the magnified XRD pattern of the Co-N-C after acid leaching.



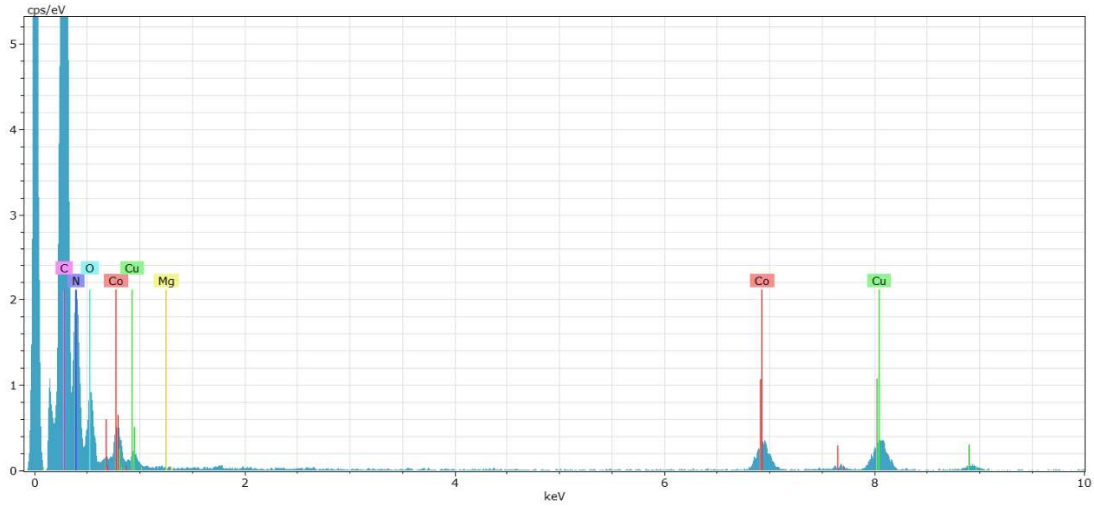
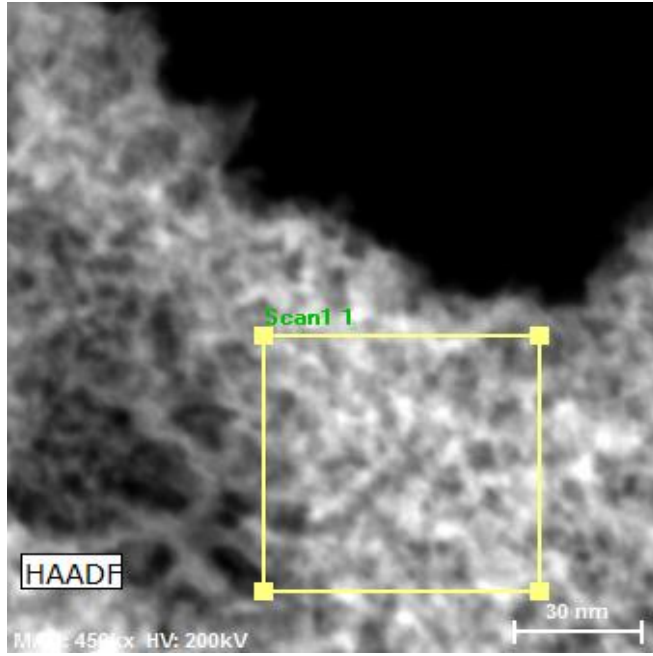
**Figure S2.** The Raman spectrum of Co-N-C calcinated at 700 °C.



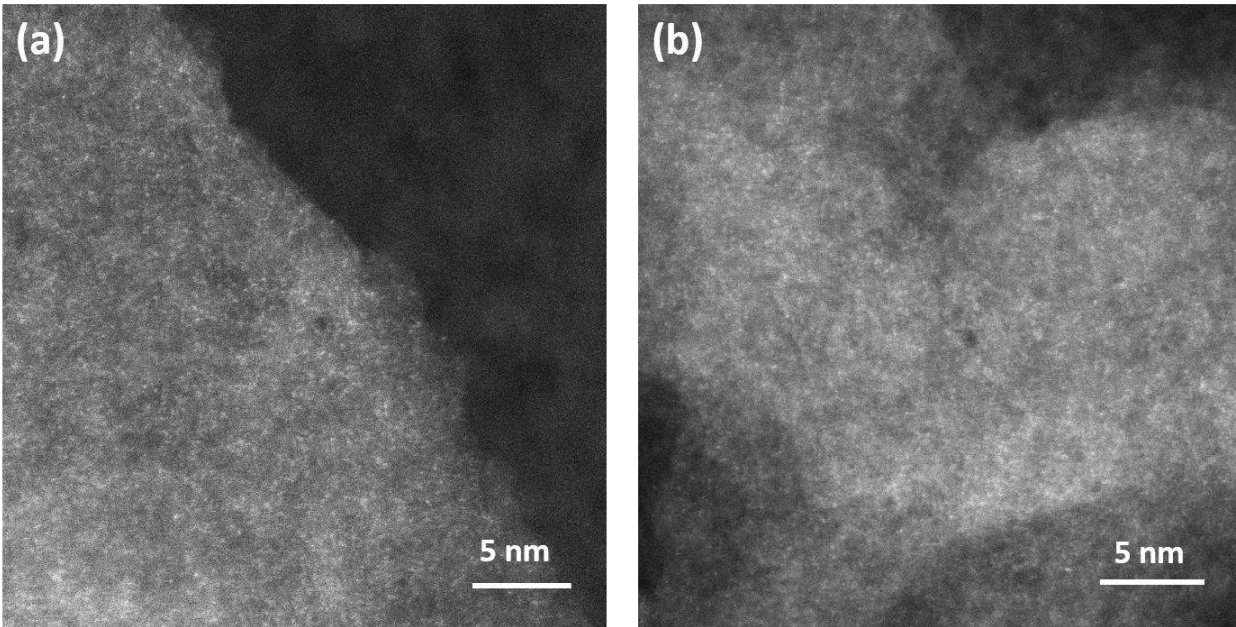
**Figure S3.** N<sub>2</sub> adsorption-desorption isotherms curve of Co-N-C. Inset is the curve of pore size distribution.



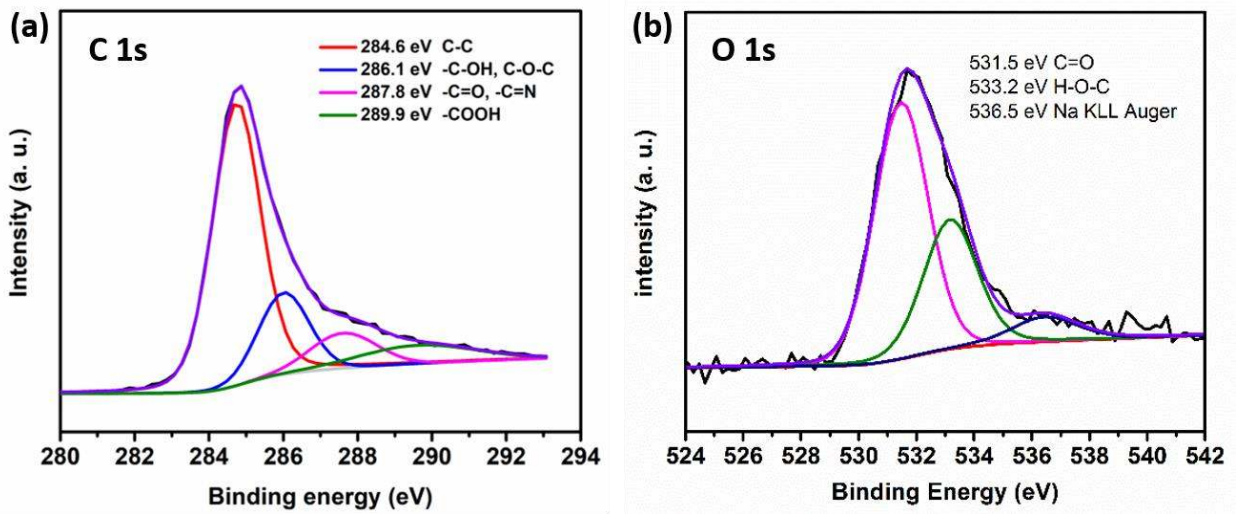
**Figure S4.** TEM image of Co-N-C; inset: the corresponding SAED pattern.



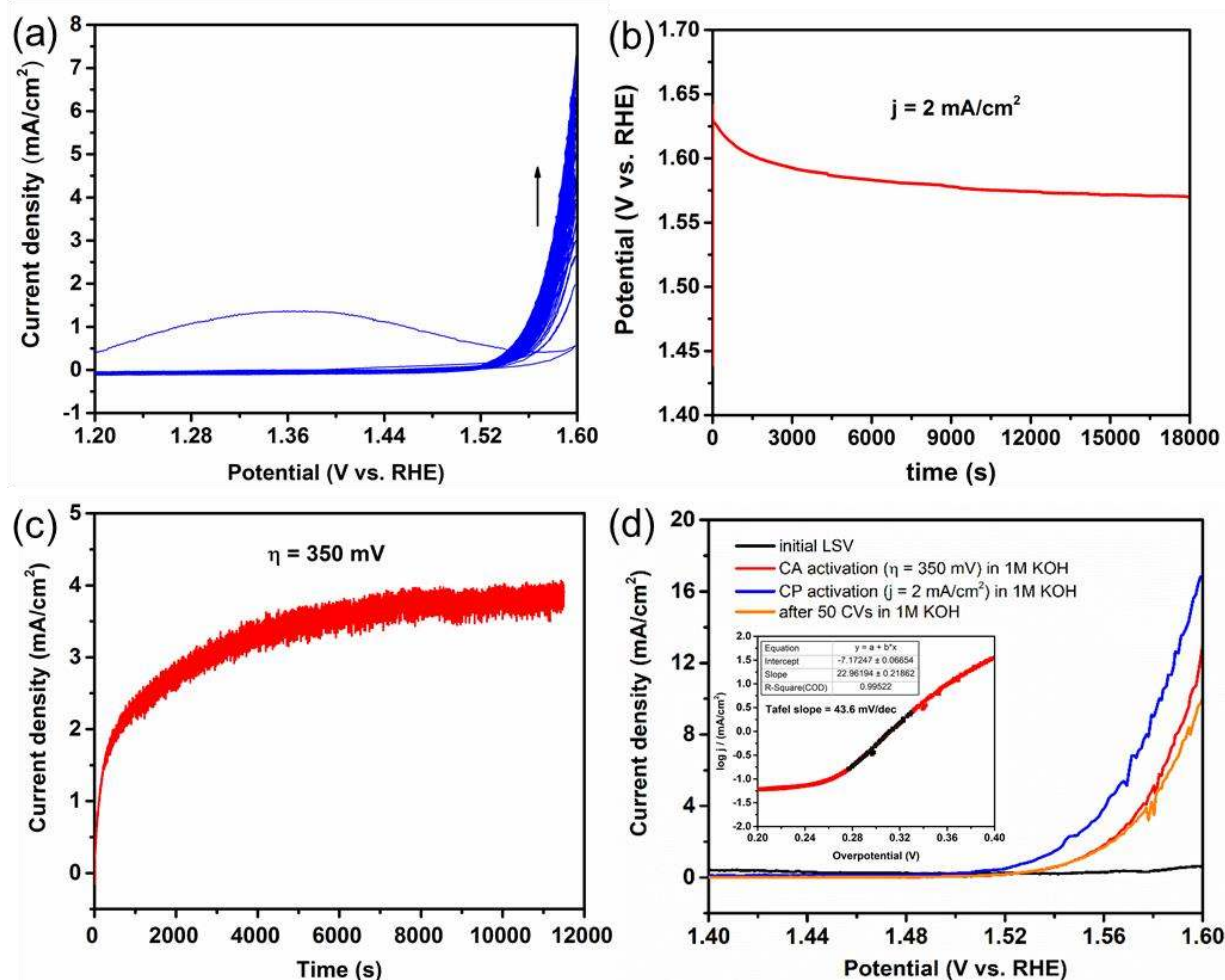
**Figure S5.** HAADF-STEM image of Co-N-C and the corresponding EDX spectrum from the indicated region. The Cu signals came from the Cu grid on which the sample was casted.



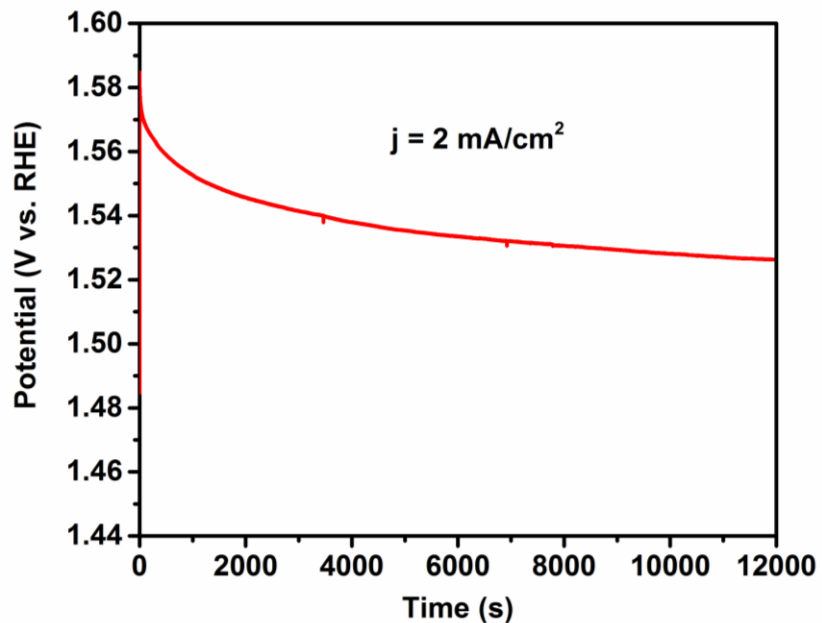
**Figure S6.** Additional spherical aberration-corrected HAADF-STEM images of Co-N-C.



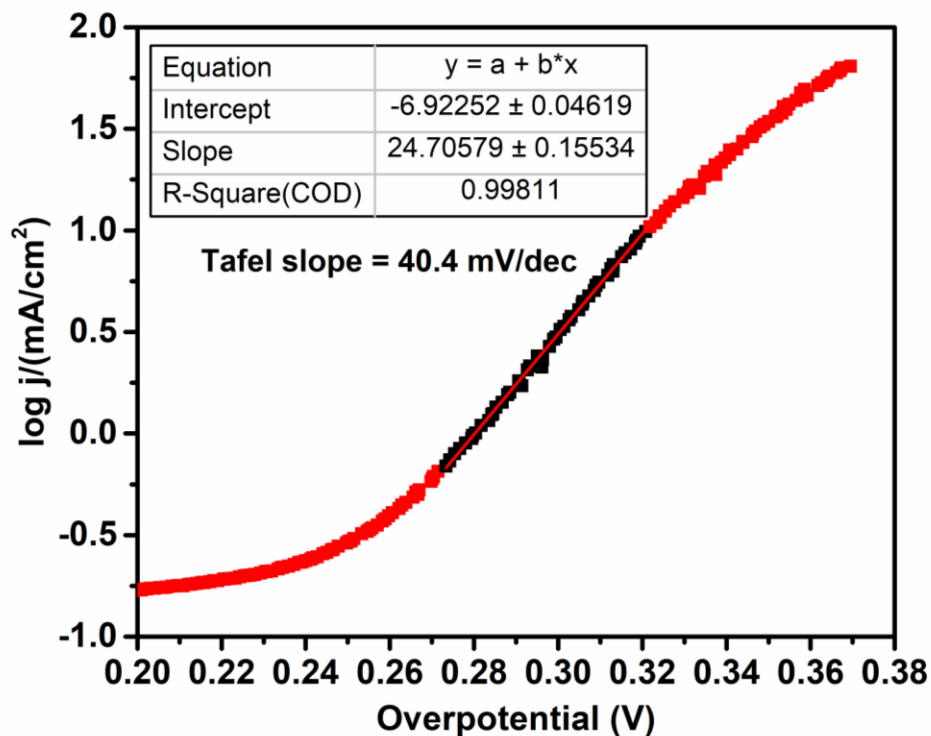
**Figure S7.** High resolution XPS of Co-N-C: (a) C 1s and (b) O 1s region.



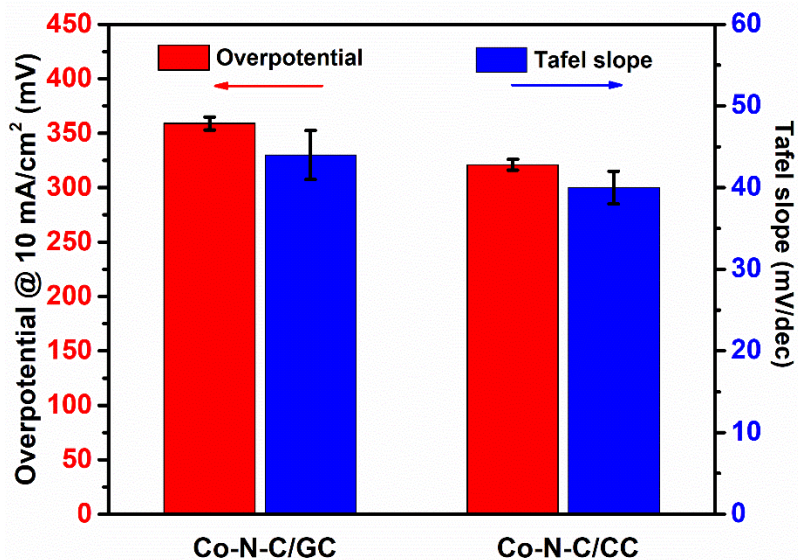
**Figure S8.** (a) Multiple CVs, (b) constant current activation process, and (c) constant potential activation process of Co-N-C. (d) Polarization curves of Co-N-C after activation. Inset: Tafel plot derived from polarization curve of Co-N-C activated by chronopotential method (blue line), the Tafel slope is 44 mV/dec. All the measurements were performed on a GC electrode.



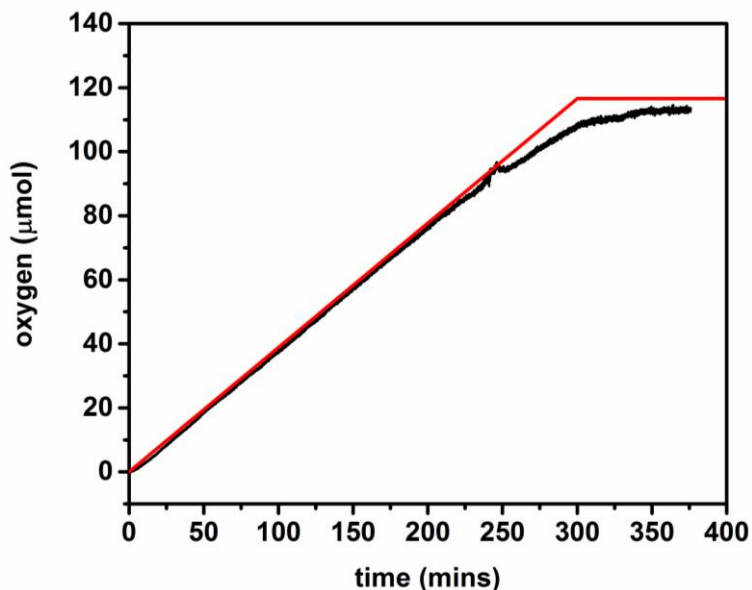
**Figure S9.** Constant current activation process of Co-N-C on a carbon-cloth electrode.



**Figure S10.** Tafel plot of Co-N-C on a carbon-cloth electrode after activation, the Tafel slope is 40 mV/dec.

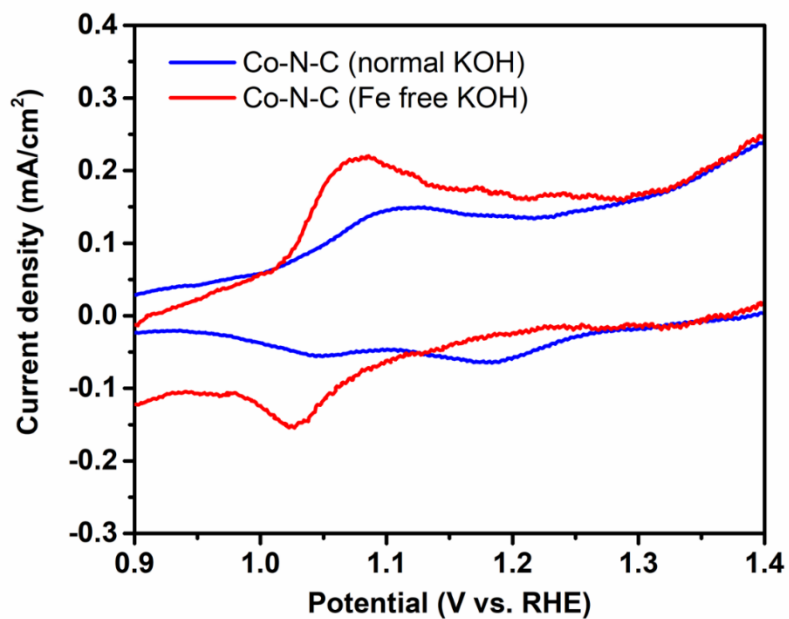


**Figure. S11.** Comparison of overpotential at the current density of 10 mA/cm<sup>2</sup> and Tafel slope for the activated Co-N-C modified on different electrode. GC = glassy carbon, CC = carbon-cloth.

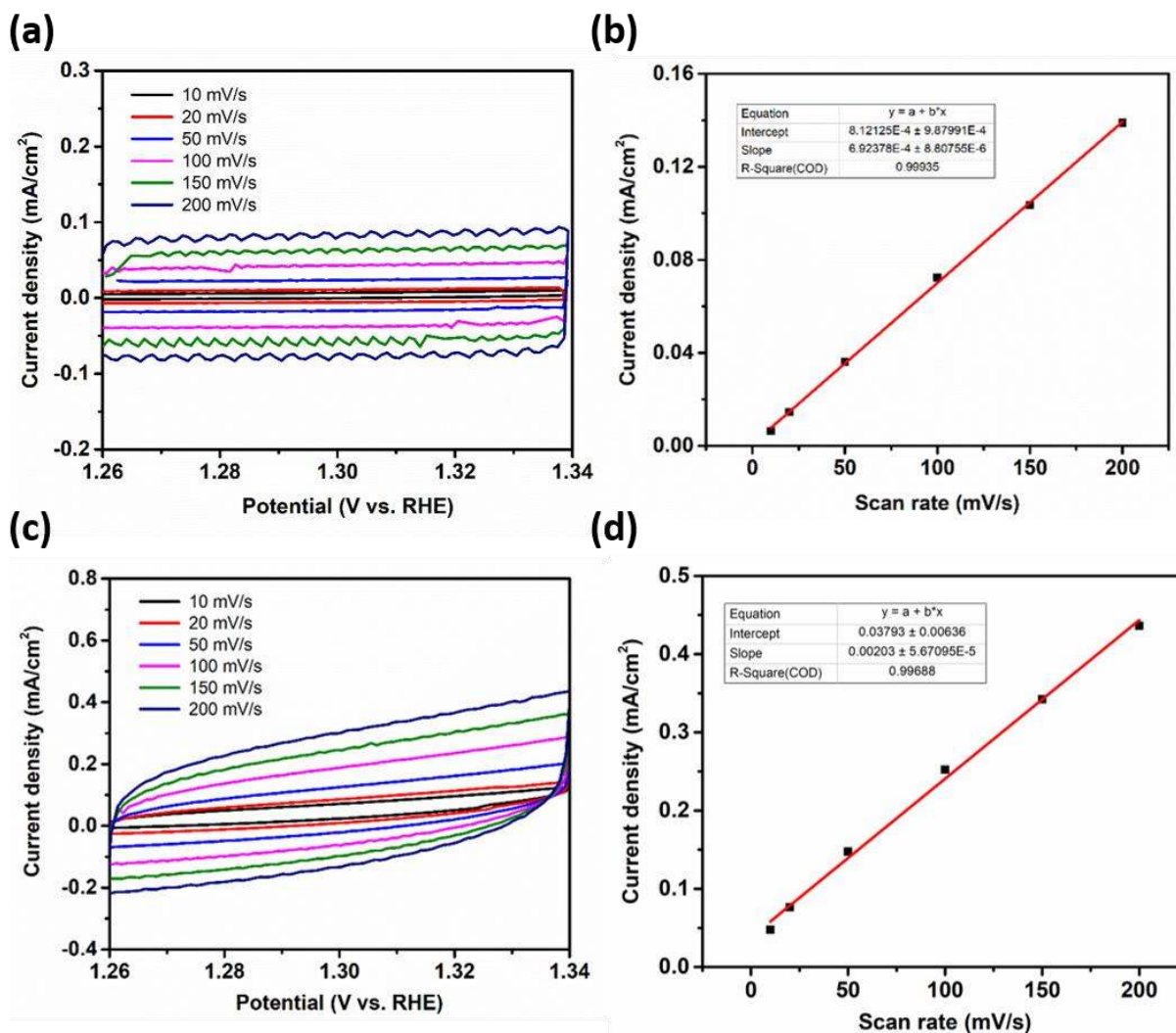


**Figure S12.** Oxygen evolution curve (black) of the activated Co-N-C (the red curve is the theoretical oxygen evolution curve assumed 100% Faradaic efficiency).

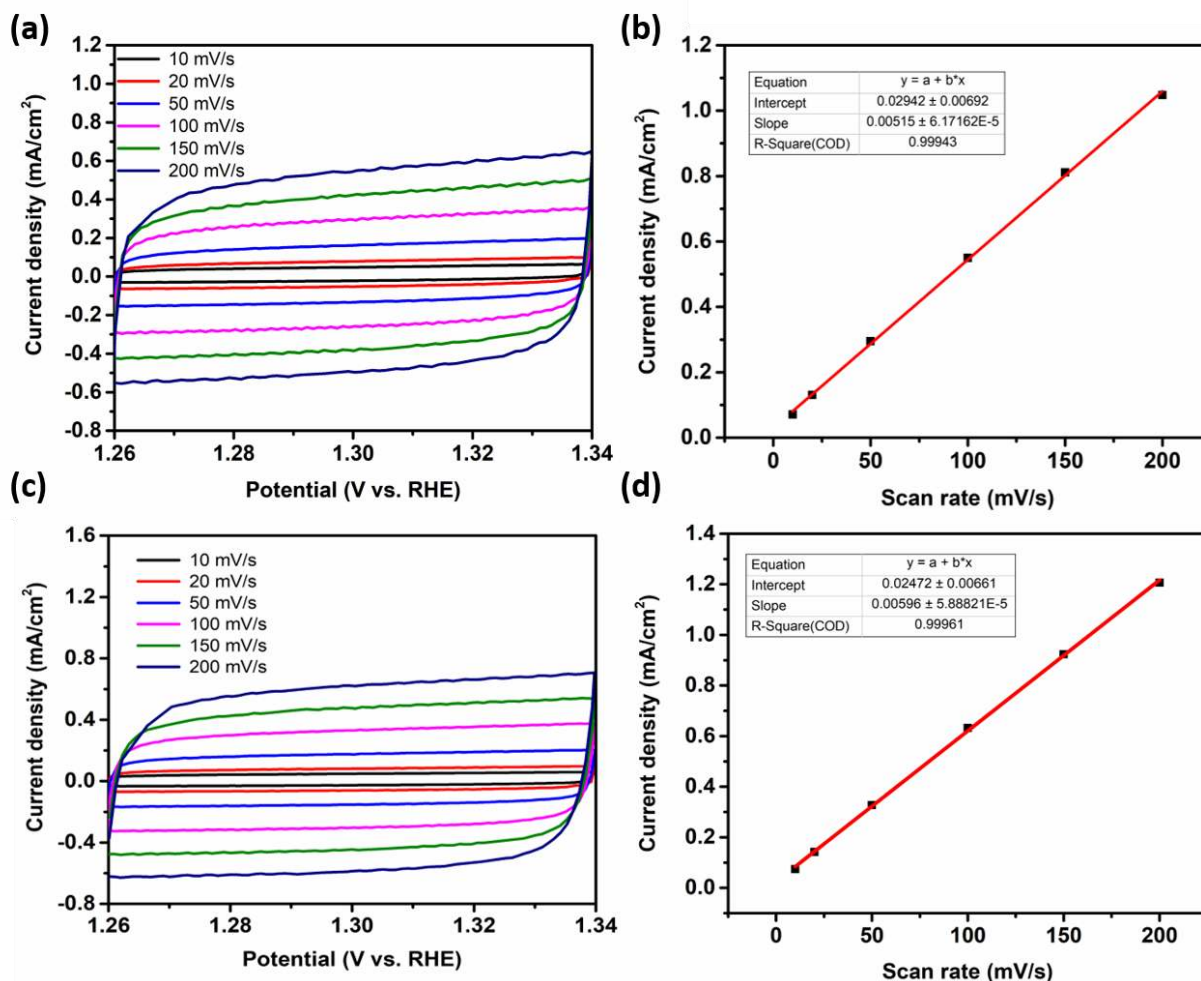




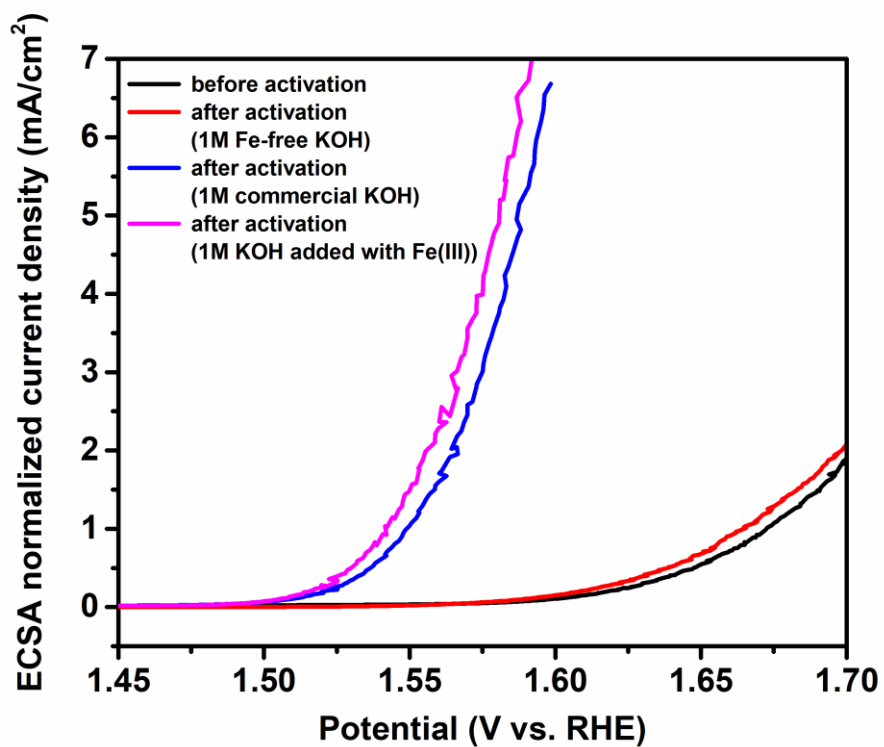
**Figure S13.** The CVs of Co-N-C after activated in normal KOH (Co-Fe-N-C, blue), Ni(OH)<sub>2</sub> treated KOH (Fe free, red).



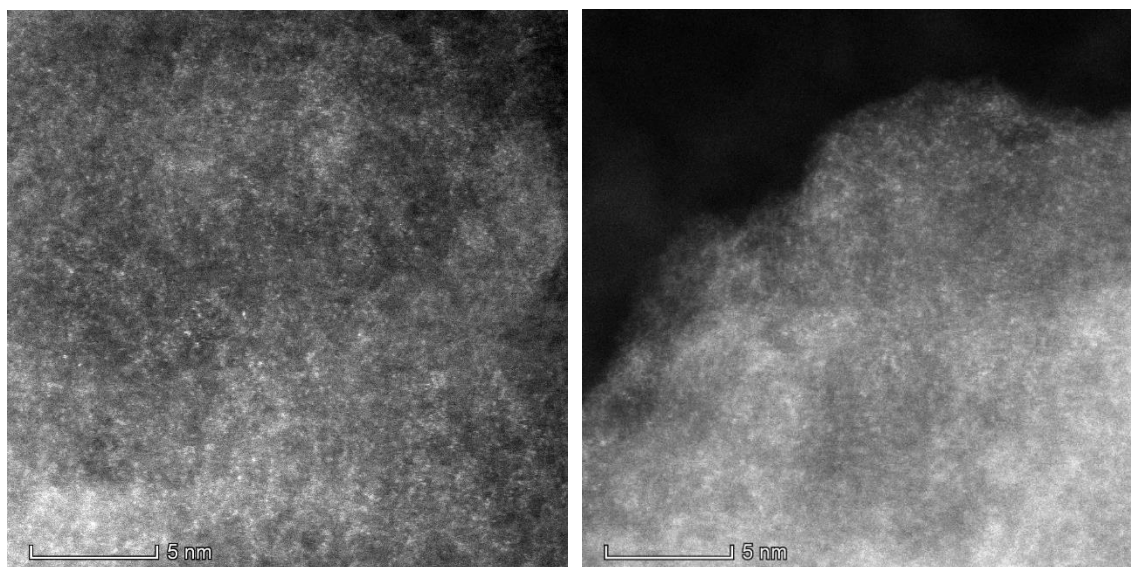
**Figure S14.** Measurements of double-layer capacitance of blank carbon-cloth electrode (CC) (a, b) and pristine Co-N-C on CC electrode (Co-N-C/CC) in Fe-free KOH (c, d). CVs from 1.26-1.34 V at different scan rates are shown for blank CC (a) and pristine Co-N-C/CC (c). The differences of current densities between charging and discharging process were plotted versus the scan rate for blank CC electrode (b) and pristine Co-N-C/CC (d). The calculated double-layer capacitance of blank CC and pristine Co-N-C/CC is  $0.311 \pm 0.082$  and  $1.04 \pm 0.18$  mF/cm<sup>2</sup>, respectively. Therefore the ECSA of the pristine Co-N-C is  $3.34 \pm 0.42$  cm<sup>2</sup>. The measurements were conducted on four different samples for each electrode.



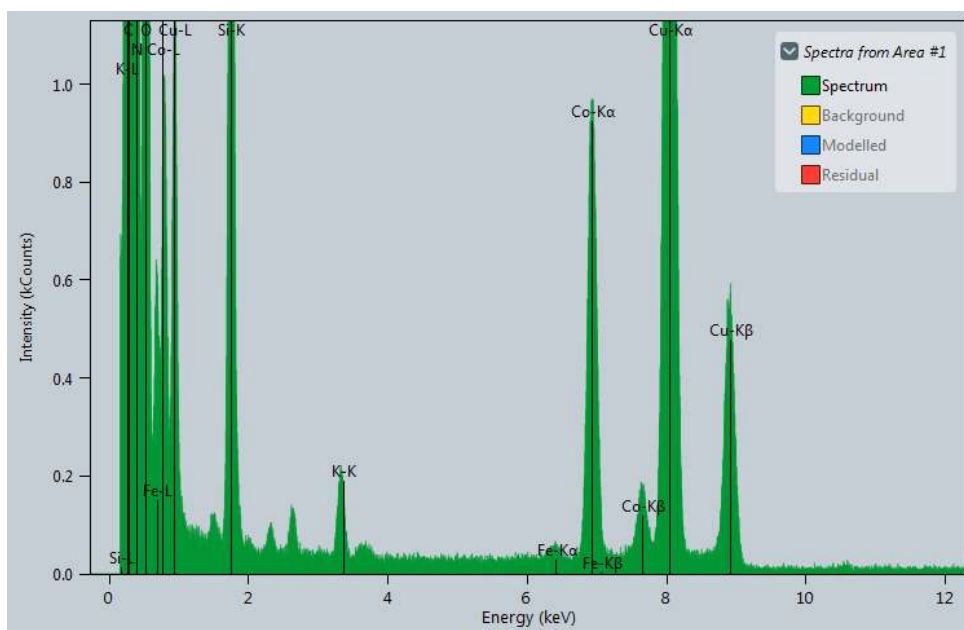
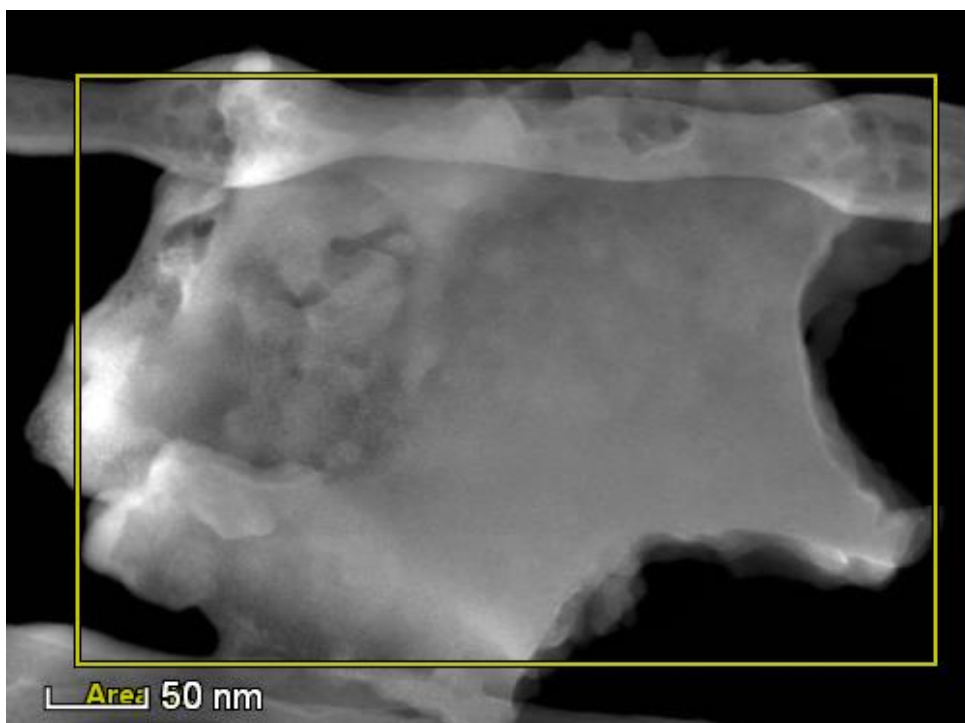
**Figure S15.** Measurements of double-layer capacitance of Co-N-C activated in Fe-free KOH (a, b) and Co-Fe-N-C (c, d) on CC electrodes. CVs from 1.26-1.34 V at different scan rate are shown for Co-N-C activated in Fe-free KOH (a) and Co-Fe-N-C (c). The differences of current densities between charging and discharging process were plotted versus the scan rate for Co-N-C activated in Fe-free KOH (b) and Co-Fe-N-C (d). The calculated double-layer capacitance of Co-N-C activated in Fe-free KOH and Co-Fe-N-C is  $2.60 \pm 0.27$  and  $3.20 \pm 0.47$  mF/cm<sup>2</sup>, respectively. Therefore the ECSA of the Co-N-C activated in Fe-free KOH and the Co-Fe-N-C is  $8.36 \pm 1.84$  and  $10.29 \pm 1.11$  cm<sup>2</sup>, respectively. The measurements were conducted on four different samples for each electrode.



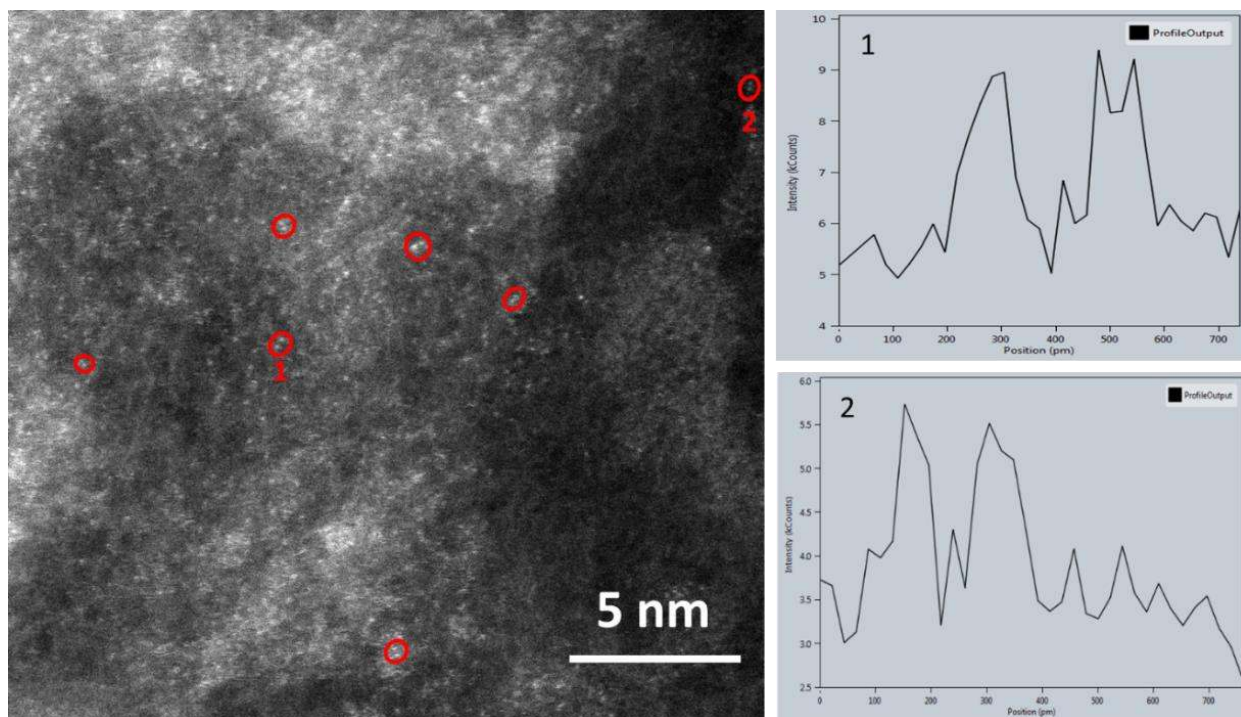
**Figure S16.** ECSA-normalized activity of pristine Co-N-C (black), Co-N-C activated in Fe-free KOH (red), in normal KOH (blue) and Fe(III)-added KOH (pink).



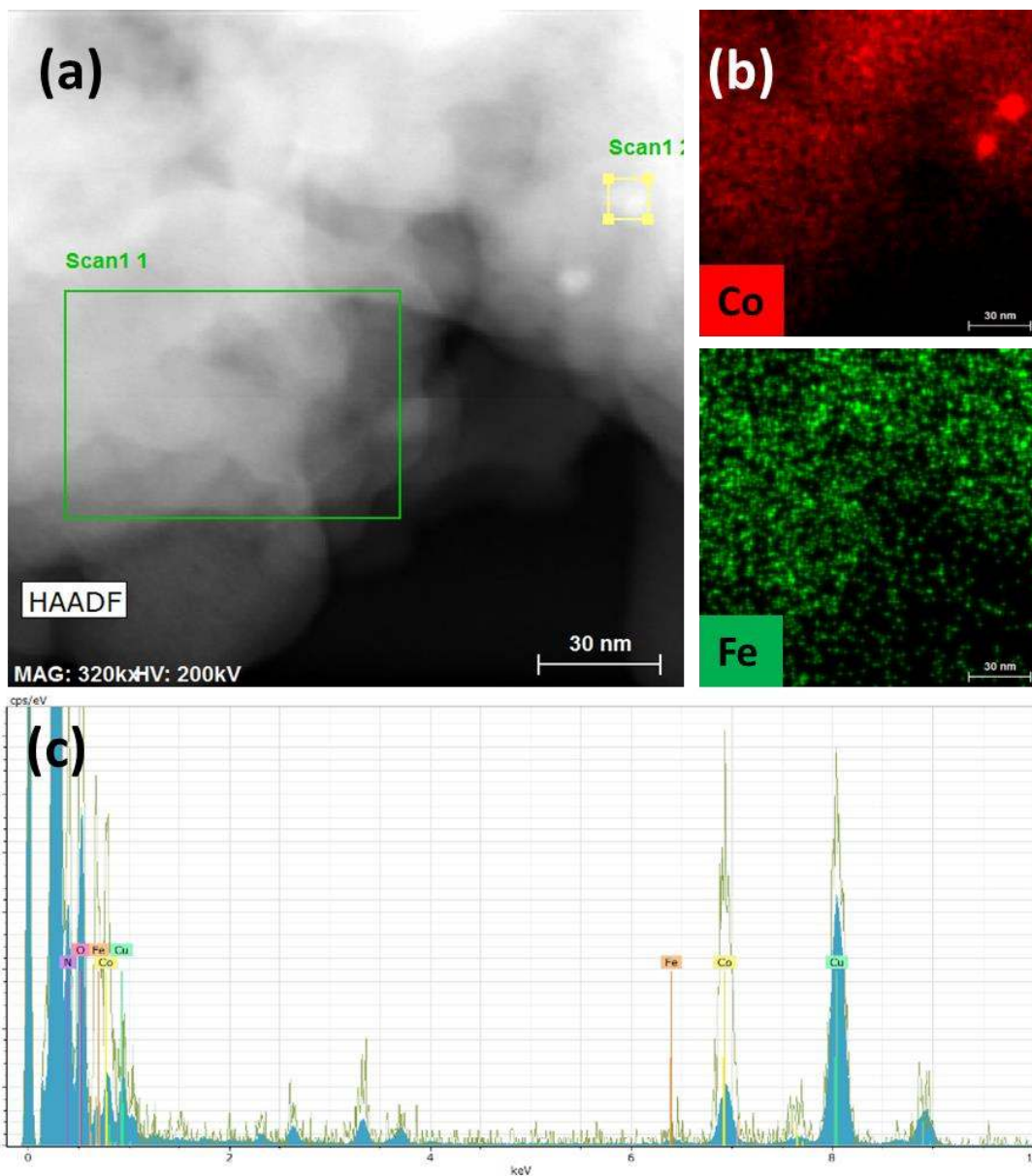
**Figure S17.** Additional aberration-corrected HAADF-STEM images of Co-Fe-N-C.



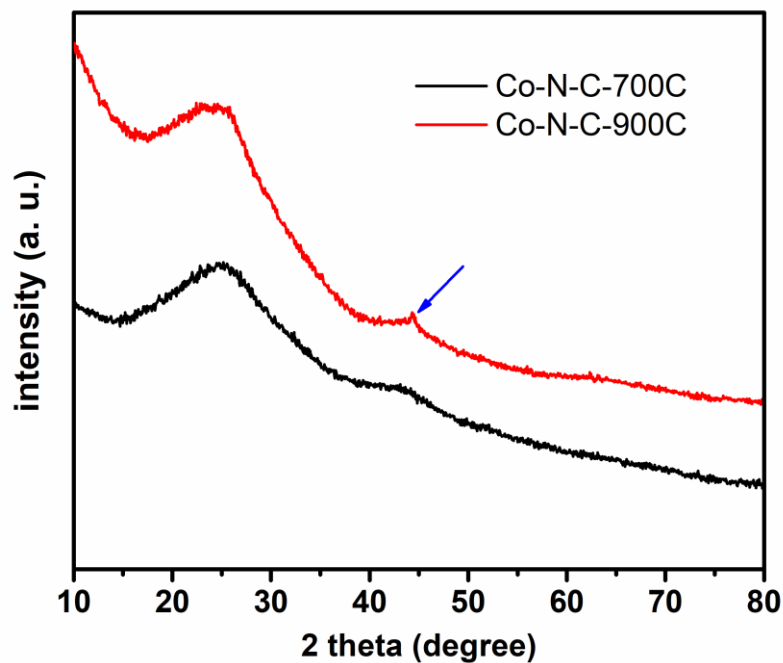
**Figure S18.** Upper: HAADF-STEM image of Co-Fe-N-C (Fig. 3c in main text) and bottom: EDX spectrum of indicated region in the HAADF-STEM image. The Cu signals came from the Cu grid on which the sample was casted.



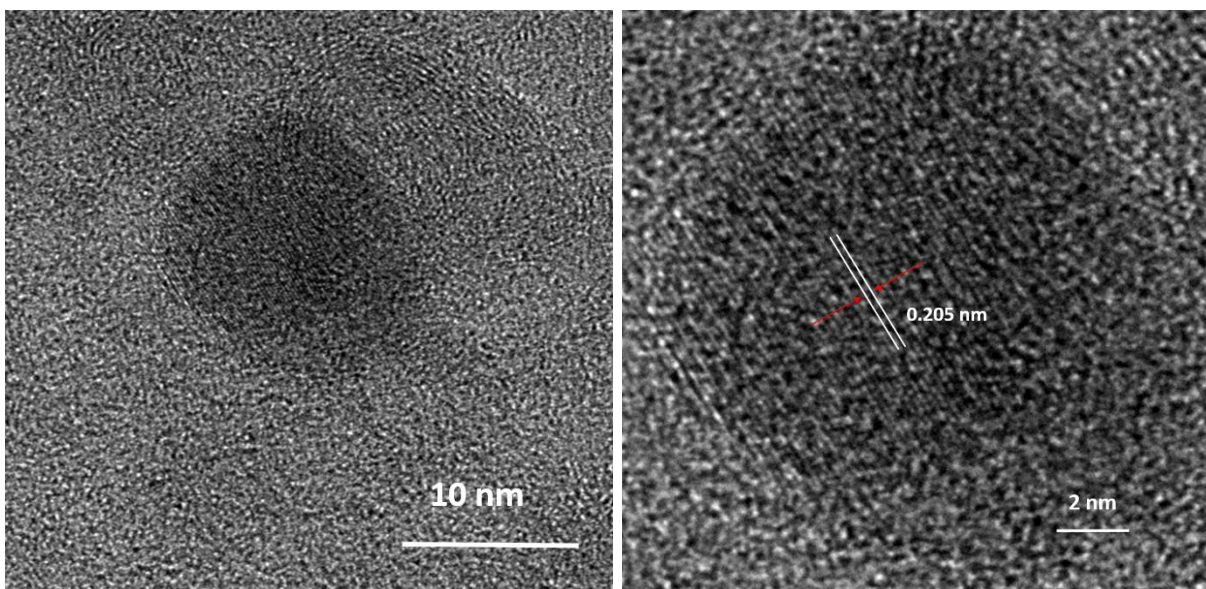
**Figure S19.** Analysis of a typical aberration-corrected HAADF-STEM image of Co-Fe-N-C (Fig. 3b in the maintext). Some closely-located atom pairs are marked with red circles. The intensity profiles (e.g., for 1 and 2) indicate that they are possibly Co-Fe dimers. (The HAADF intensity of each atom would be very similar because of their neighboring atomic numbers.)



**Figure S20.** (a) HAADF-STEM image, (b) elemental EDXS mapping and (c) EDX spectra of Co-Fe-N-C from an area that contained nanoparticles. The spectra showed that the content of Co is higher for the region containing a nanoparticle (1-2) but the content of Fe is similar to the area without nanoparticles (1-1). The Cu signals came from the Cu grid on which the sample was casted.

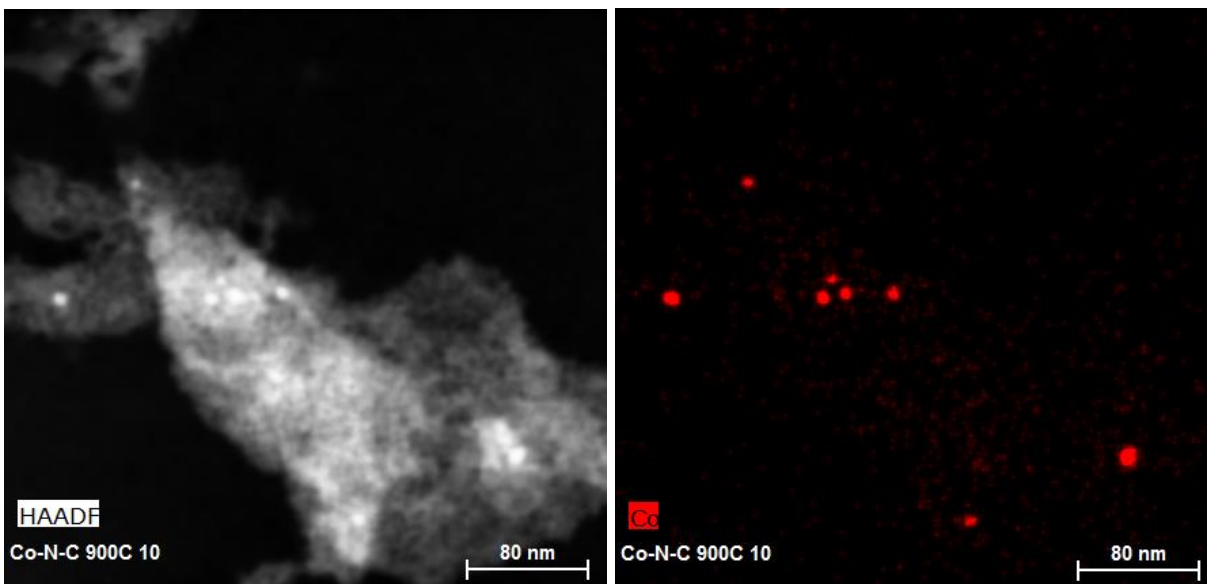


**Figure S21.** XRD of Co-N-C calcinated at different temperatures. The blue arrow indicated the diffraction peak of (111) facet of metallic Co (Reference code: 00-015-0806).

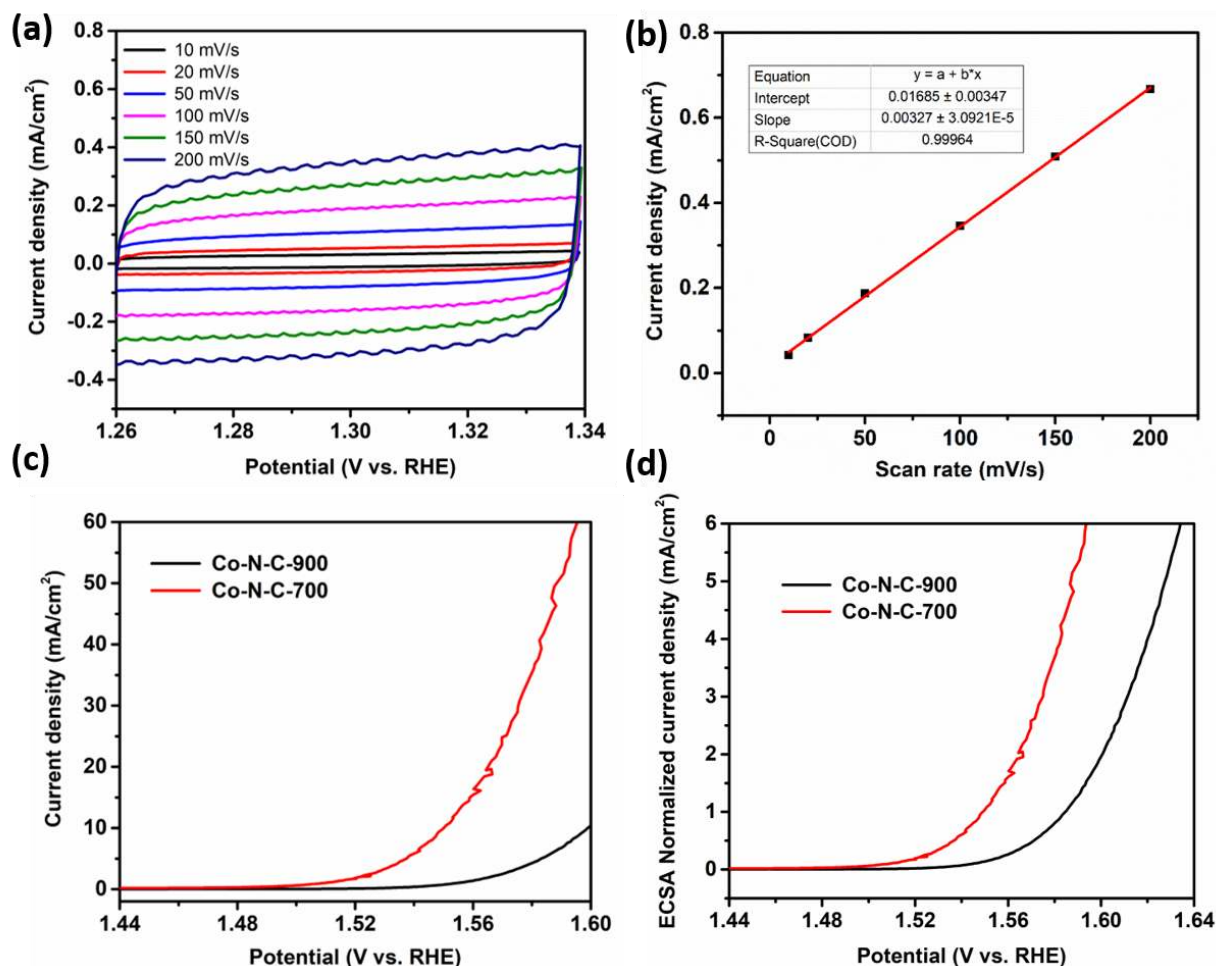


**Figure S22.** HR-TEM image of Co-N-C-900C. The marked distance of the lattice fringes corresponds to (111) planes of metallic Co (Reference code: 00-015-0806).

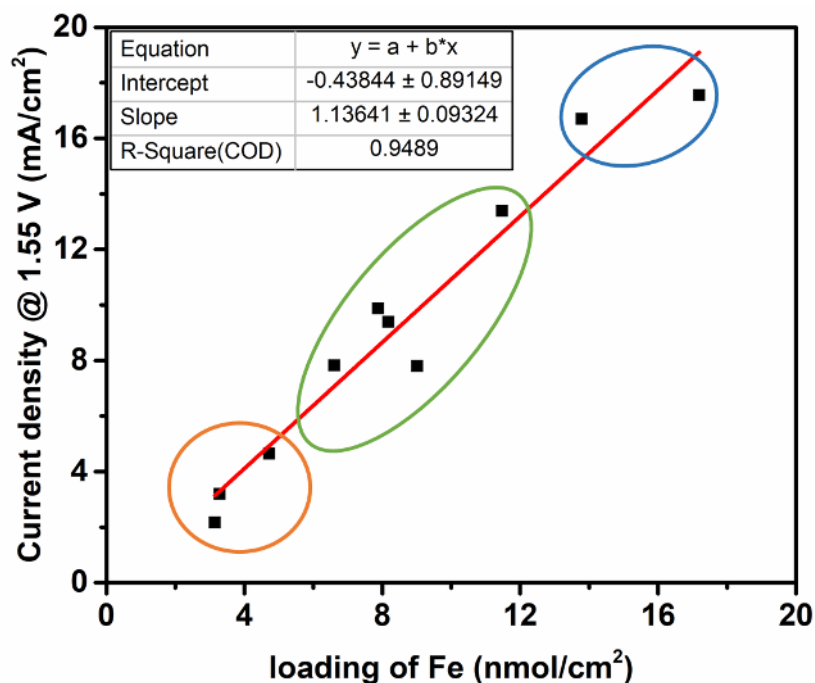




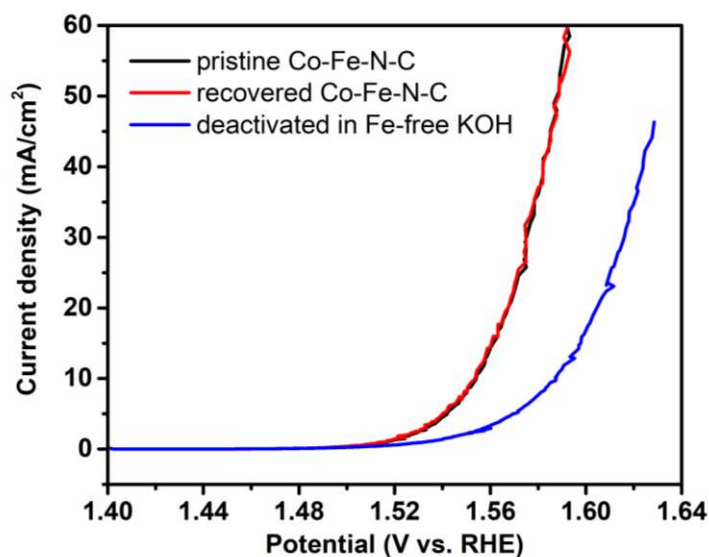
**Figure S23.** HAADF STEM images and the corresponding EDXS mapping of Co for Co-N-C-900.



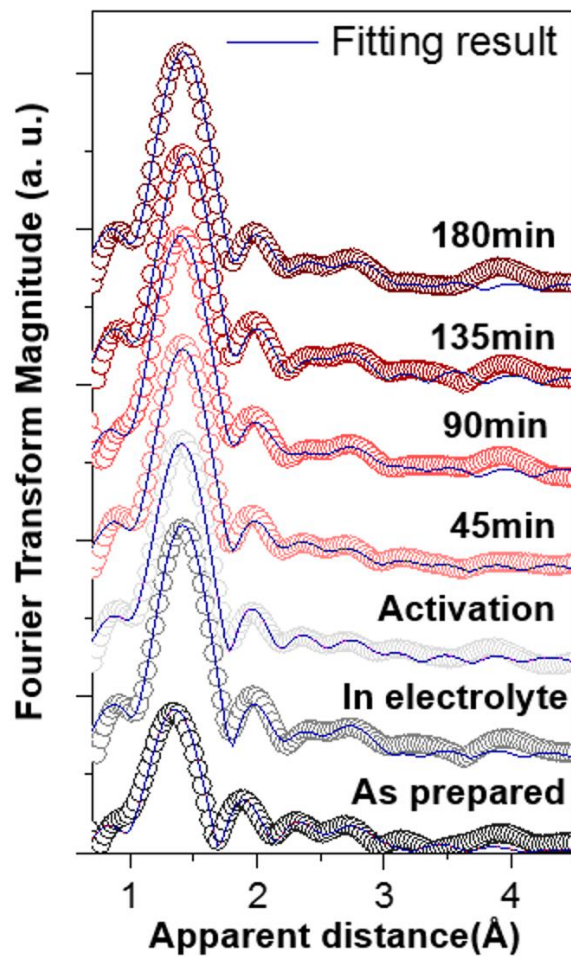
**Figure S24.** (a, b) Measurements of double-layer capacitance of Co-N-C-900 after activation in normal KOH. (a) CVs from 1.26-1.34 V at different scan rates; (b) The differences of current densities between charging and discharging process were plotted versus the scan rates. The calculated double-layer capacitance of activated Co-N-C-900 is  $1.65 \pm 0.14$  mF/cm<sup>2</sup>. Therefore the ECSA of the activated Co-N-C-900 is  $5.30 \pm 1.30$  cm<sup>2</sup>. The measurements were conducted on four different samples (c) LSVs and (d) ECSA-normalized LSVs of Co-N-C calcinated at different temperature after activation in normal KOH.



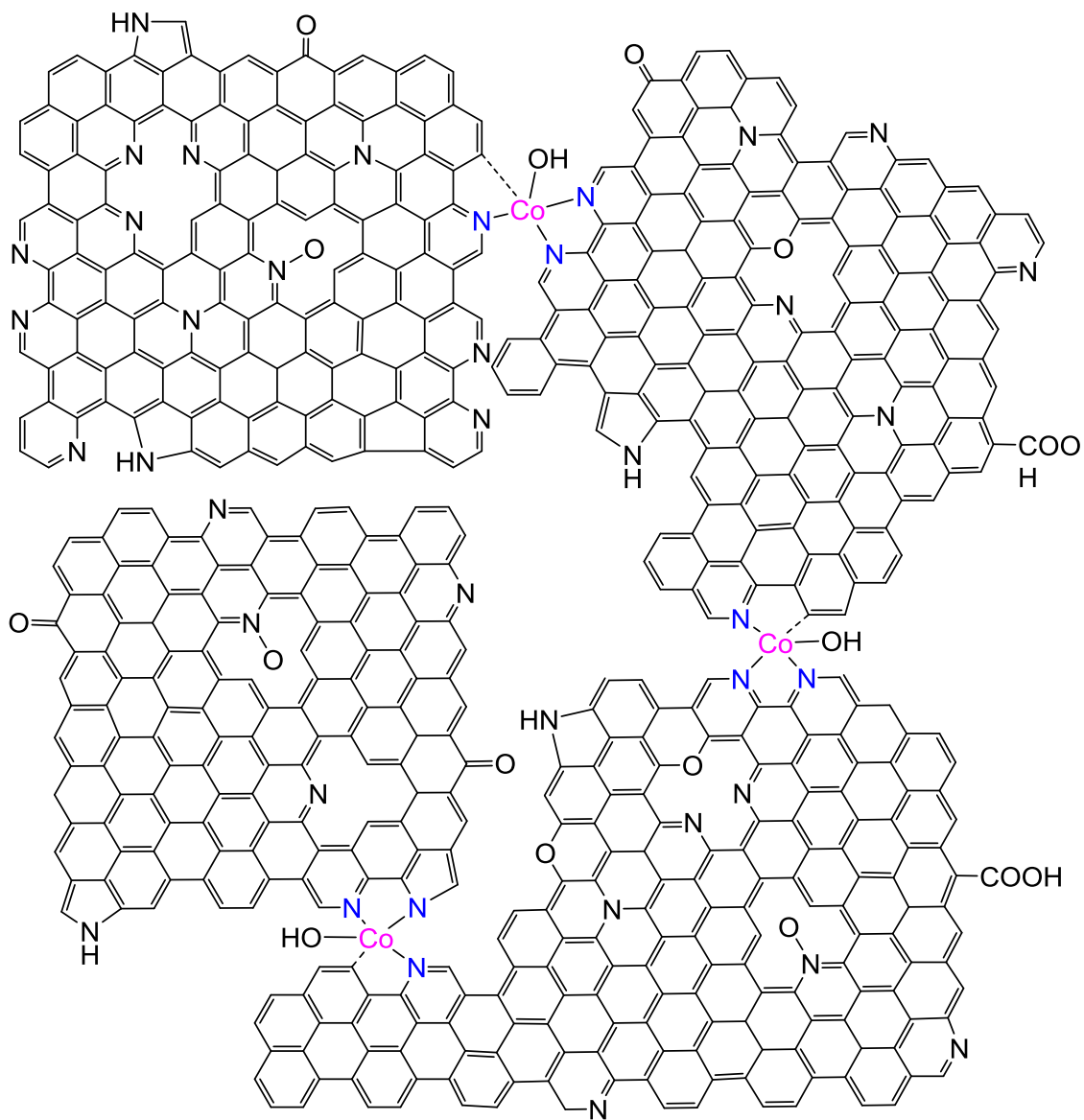
**Figure S25.** The current density at 1.55 V vs. RHE for the catalysts with different Fe loadings. The circles with different colors pointed the samples activated in different electrolyte. Orange: activated in 1M KOH for 2h. Green: activated in 1M KOH until stabilized performance. Blue: activated in 1M KOH added with 10 ppm  $\text{Fe}^{3+}$  until stabilized performance.



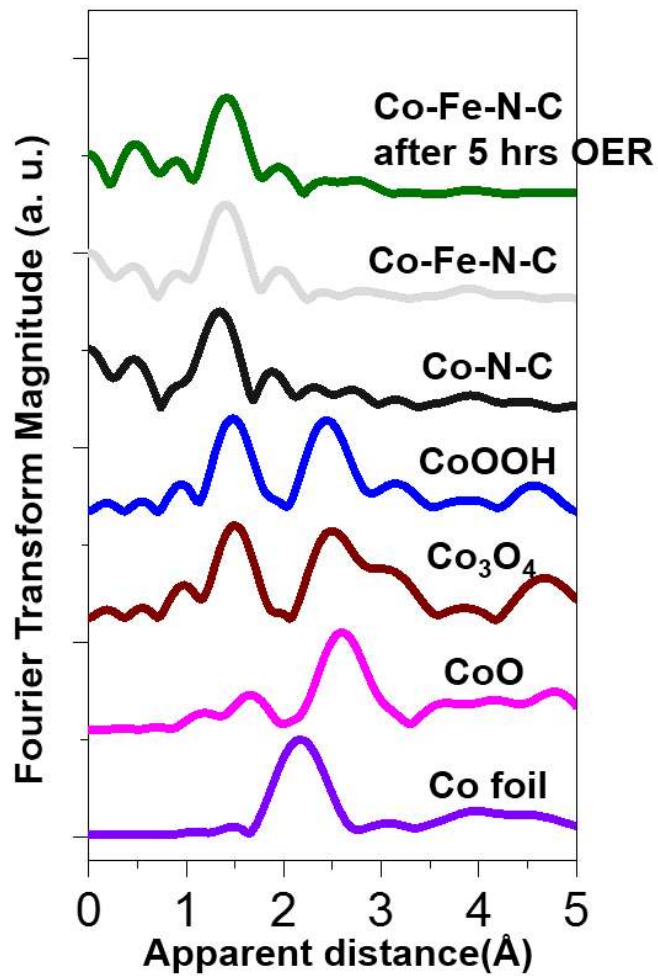
**Figure S26.** LSVs of Co-Fe-N-C before and after electrolysis in 1M Fe free KOH for 2h. The activity can be recovered by re-activating the catalyst in fresh 1M KOH.



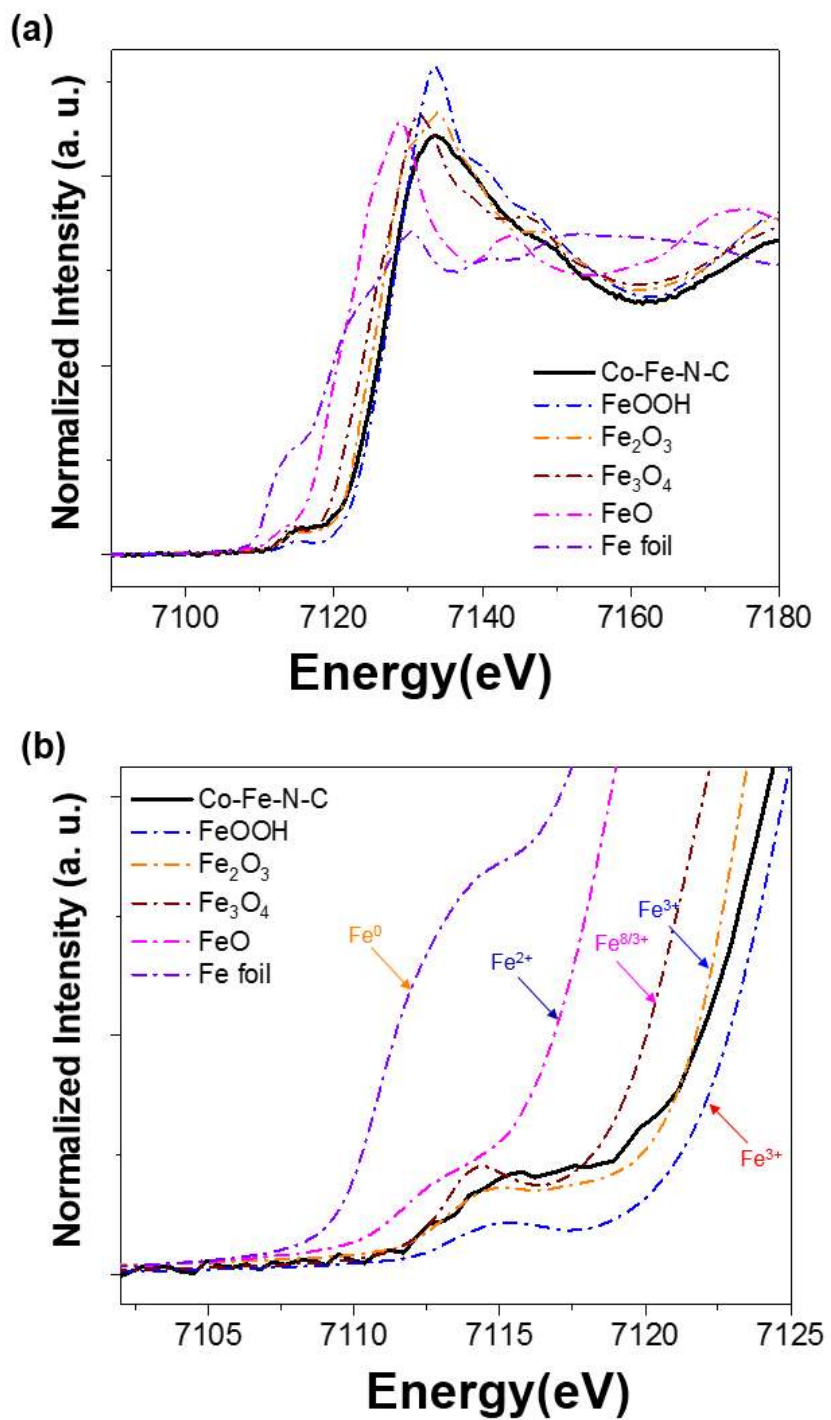
**Figure S27.** EXAFS r-space spectra of operando Co K-edge for Co-Fe-N-C sample (experimental data; color circle) and the corresponding fitting (red line). Fitting structural parameters are gathered in Table 1 and S3.



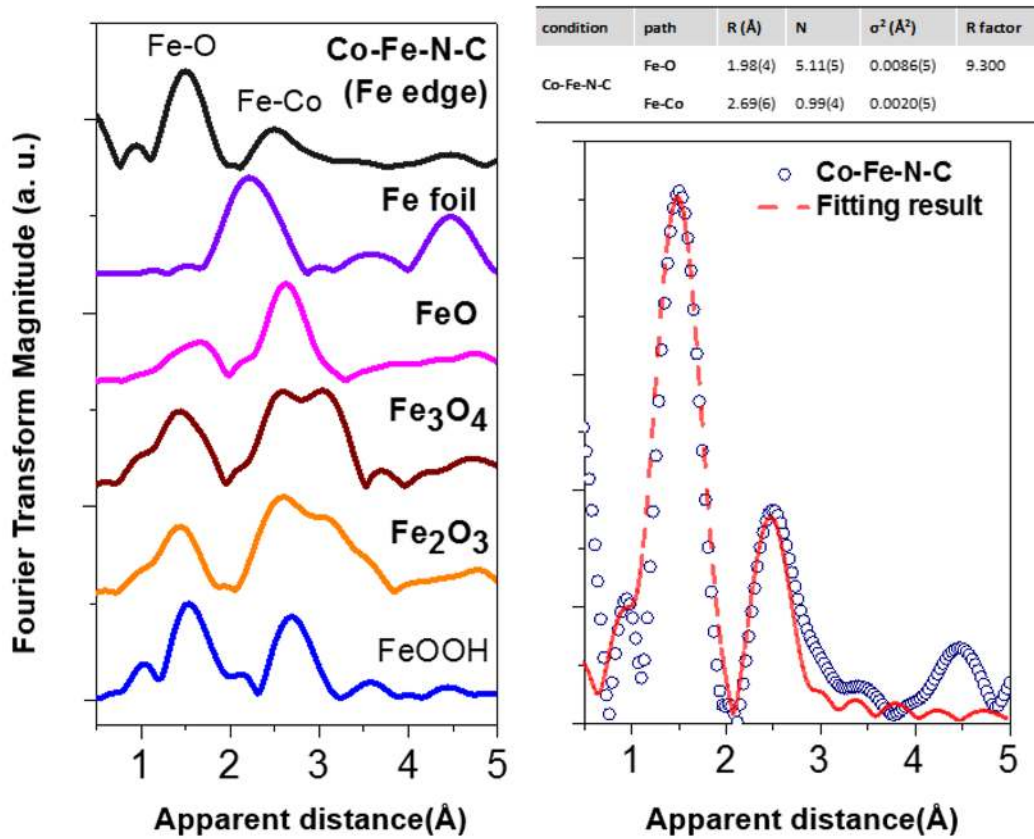
**Figure S28.** The proposed, indicative structure of the Co-N-C sample taking account of the results from the XAS study.



**Figure S29.** Fourier transform Co K-edge EXAFS spectra of as-prepared Co-N-C, Co-Fe-N-C (after activation) and Co-Fe-N-C after OER for 5 hours in comparison with Co reference samples.

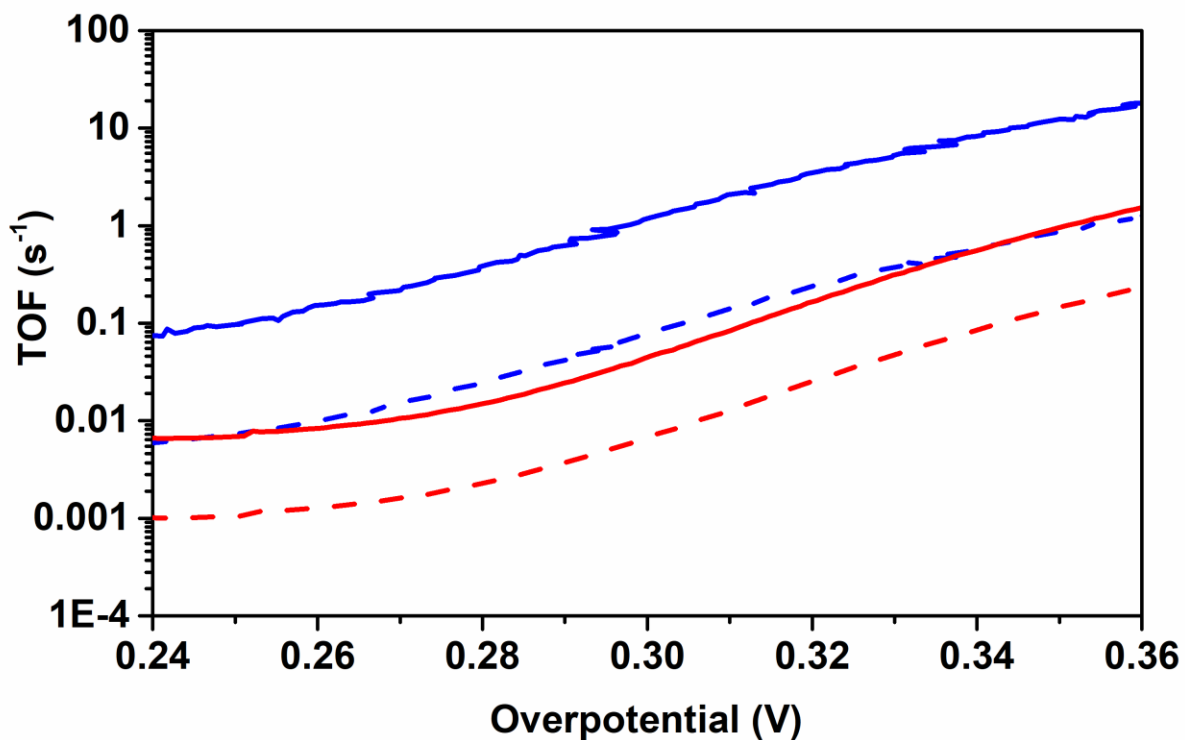


**Figure S30.** (a) XANES spectra of Fe K-edge for Co-Fe-N-C (after activation) and references including iron oxides and foil. (b) Magnified XANES for the transition from 1s to 4p.



**Figure S31.** EXAFS spectra of Fe K-edge for Co-Fe-N-C (after activation) and references including iron oxides and foil. EXAFS r-space spectra of Fe K-edge for Co-Fe-N-C sample (experimental data; color circle) and the corresponding fitting (red line). Fitting structural parameters are gathered in Table.





**Figure S32.** Potential-dependent TOFs of Co-Fe-N-C (blue curve) and activated Co-N-C-900 (in normal KOH, red curve). The solid lines are based on the loadings of dimetric Co-Fe sites and the dashed lines are based on the loadings of total metals (Co+Fe). The former represents the true activity while the latter is an indicative TOF.

**Table S1.** The performance of the activated Co-N-C (Co-Fe-N-C) modified on different electrode.

Type of the electrode	Overpotential @ 10 mA/cm <sup>2</sup> (mV)	Tafel Slope (mV/dec)
Glassy carbon	360 ± 8	44 ± 3
Carbon-cloth	321 ± 5	40 ± 2

**Table S2.** The performance of Co-N-C before and after activation in different KOH (1M).

	Overpotential @ 10 mA/cm <sup>2</sup> (mV)	Tafel Slope (mV/dec)
Before activation	495±19	72±4
Activated in Fe-free KOH	443±15	58±4
Activated in normal KOH	321±5	40±2
Activated in KOH with Fe (10 ppm)	309±4	37±2

**Table S3.** Structural parameters of Co-N-C and Co-Fe-N-C extracted from operando Co K-edge EXAFS refinement for as-prepared Co-N-C and after activation as well as under OER for various duration.

condition	path	R (Å)	N	$\sigma^2$ (Å <sup>2</sup> )	R factor
As-prepared	Co-C	1.59(6)	1.09(4)	0.0096(8)	9.901
	Co-N	1.87(4)	3.35(7)	0.0087(4)	
	Co-O	2.19(4)	0.74(6)	0.0040(9)	
	Co-C1	2.90(5)	3.41(9)	0.0099(8)	
	Co-C2	3.19(4)	4.00(11)	0.0094(9)	
	Co-Fe	-	-	-	
In electrolyte	Co-C	1.37(8)	0.41(5)	0.0089(9)	3.926
	Co-N	1.63(4)	1.52(5)	0.0097(4)	
	Co-O	1.87(4)	3.19(4)	0.0054(4)	
	Co-C1	2.79(6)	2.30(5)	0.0073(9)	
	Co-C2	3.33(5)	2.19(8)	0.0076(5)	
	Co-Fe	-	-	-	
Activation	Co-C	1.43(6)	0.46(6)	0.0093(5)	3.191
	Co-N	1.64(4)	1.51(6)	0.0092(4)	
	Co-O	1.83(6)	3.31(5)	0.0061(4)	
	Co-C1	2.83(5)	2.21(7)	0.0074(8)	
	Co-C2	3.41(7)	2.10(8)	0.0084(9)	
	Co-Fe	2.51(4)	0.25(5)	0.0099(7)	
45 min	Co-C	1.46(4)	0.47(4)	0.0095(6)	2.883

	<b>Co-N</b>	<b>1.65(5)</b>	<b>1.51(6)</b>	0.0083(8)	
	<b>Co-O</b>	<b>1.84(4)</b>	<b>3.43(8)</b>	0.0064(4)	
	<b>Co-C1</b>	2.83(6)	2.27(6)	0.0091(9)	
	<b>Co-C2</b>	3.41(7)	2.17(8)	0.0097(9)	
	<b>Co-Fe</b>	2.61(5)	0.25(4)	0.0084(4)	
<b>90 min</b>	<b>Co-C</b>	<b>1.45(6)</b>	<b>0.43(4)</b>	0.0026(6)	4.034
	<b>Co-N</b>	<b>1.67(5)</b>	<b>1.53(4)</b>	0.0061(7)	
	<b>Co-O</b>	<b>1.87(4)</b>	<b>3.42(5)</b>	0.0050(4)	
	<b>Co-C1</b>	2.83(6)	2.28(6)	0.0053(7)	
	<b>Co-C2</b>	3.41(7)	2.15(7)	0.0046(9)	
	<b>Co-Fe</b>	2.63(7)	0.26(6)	0.0096(6)	
<b>135 min</b>	<b>Co-C</b>	<b>1.49(4)</b>	<b>0.45(1)</b>	0.0033(7)	4.015
	<b>Co-N</b>	<b>1.66(4)</b>	<b>1.54(6)</b>	0.0024(5)	
	<b>Co-O</b>	<b>1.85(5)</b>	<b>3.47(6)</b>	0.0053(4)	
	<b>Co-C1</b>	2.83(4)	2.24(6)	0.0038(6)	
	<b>Co-C2</b>	3.40(7)	2.17(8)	0.0073(9)	
	<b>Co-Fe</b>	2.63(5)	0.26(4)	0.0061(5)	
<b>180 min</b>	<b>Co-C</b>	<b>1.41(6)</b>	<b>0.45(4)</b>	0.0093(7)	3.043
	<b>Co-N</b>	<b>1.69(5)</b>	<b>1.54(4)</b>	0.0095(4)	
	<b>Co-O</b>	<b>1.86(4)</b>	<b>3.23(6)</b>	0.0048(4)	
	<b>Co-C1</b>	2.89(4)	2.14(5)	0.0083(7)	
	<b>Co-C2</b>	3.35(8)	2.10(8)	0.0066(9)	
	<b>Co-Fe</b>	2.71(4)	0.27(5)	0.0097(6)	

**Table S4.** Comparison of OER activity of Co-Fe-N-C with other OER catalysts based on nanomaterials based on 1<sup>st</sup> transition metals.

Catalysts	Electrolyte	Overpotential (mV) @ 10 mA/cm <sup>2</sup>	Tafel slope (mV/dec)	TOF (s <sup>-1</sup> ) /overpotential (mV)	Reference
Co-N-C activated*	1 M KOH	321	40	12/350	<b>This work.</b>
CoOOH nanosheet	1 M KOH	300	38	0.09/340	1
Fe adsorbed CoO <sub>x</sub>	1 M KOH	309	28	1.6/350	2
CoAl LDH-graphene	1 M KOH	252	36	1.14/350	3
FeO <sub>x</sub> clusters on Ni foam	1M KOH	215	34	0.82/270	4
NiFe LDH-rGO	1 M KOH	207	39	0.99/300	5
NiFe LDH-CNT	1 M KOH	245	31	0.56/300	6
NiFeO <sub>x</sub>	1 M KOH	297	37	1.9/300	7
Exfoliated NiFe LDH	1 M KOH	301	40	0.11/300	8
Plasma-assisted Exfoliated CoFe LDH	1 M KOH	267	38	4.78/300	9

\* In a KOH adding with 10 ppm Fe(III), the overpotential is 309 mV (@10 mA/cm<sup>2</sup>) while the Tafel slope is 37 mV/dec.

**Table S5.** Comparison of OER activity of Co-Fe-N-C with other single-atom catalysts and the catalysts based on sub-nano clusters.

Catalysts	Electrolyte	Overpotential (mV) @ 10 mA/cm <sup>2</sup>	Tafel slope (mV/dec)	TOF (s <sup>-1</sup> ) /overpotential (mV)	Reference
Co-N-C activated*	1 M KOH	321	40	12/350	<b>This work.</b>
Co-g-C <sub>3</sub> N <sub>4</sub> -CNT	1 M KOH	370	62	-	10
Co-N,S-graphene	1 M KOH	370	62	0.27/350	11
Plasma treated ZIF-67	1 M KOH	319	70	0.082/320	12
Plasma treated ZIF-67	1 M KOH	310	54	0.462/300	13
Fe-N,S-CNT	1 M KOH	370	82	-	14
Ni <sub>4</sub> (PET) <sub>8</sub>	0.1 M KOH	330	38	-	15
Ni <sub>6</sub> (PET) <sub>12</sub>	0.1 M KOH	430	69	10/470	16
Ni-NHGF	1M KOH	331	63	0.72/300	17
Mn-GO	1 M KOH	337	55	-	18

\* In a KOH adding with 10 ppm Fe(III), the overpotential is 309 mV (@10 mA/cm<sup>2</sup>) while the Tafel slope is 37 mV/dec.

## References

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