

Supplementary Information

Anchoring Co/2-methylimidazole complex on ion exchange resin and its transformation to Co/N doped carbon as an electrocatalyst for ORR

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Experimental Section

1 Preparation of precursors

In a typical synthesis of Co/N/Amb, the 2 g Amberlyst[®] 15 hydrogen form (Amb) was grinded into powder firstly and then added into deionized water (30 g). The Co(NO₃)₂·6H₂O (14.7 mM) dissolved in deionized water (10 g) was added into the above solution containing Amberlyst under stirring drop by drop to perform the ion exchange. After filtration and drying, the three fourth of the obtained precursor (Co/Amb) was added into 679 mM of 2-methylimidazole (2-MeIm) methanol solution (40 ml). The resulting material (Co/N/Amb) was washed by methanol to remove excess 2-MeIm and dried for several hours. As a comparison, we also prepared the Co/Amb with high content of Co by using the concentration of Co²⁺ solution to 235 mM.

2 Preparation of ORR electrocatalysts

The obtained Amb, Co/Amb and Co/N/Amb were placed in a ceramic boat, respectively. Then the composites were heated under N₂ atmosphere at 800 °C for 3 h at a heating rate of 13 °C·min⁻¹ to obtain C(Amb), Co/C and Co/N/C. Further activation treatment was carried out under CO₂ atmosphere to prepare the catalyst donated as act-Co/N/C.

3 Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on the PANalytical X'Pert PRO X-ray diffractometer with Cu-Kα radiation. Transmission electron microscopy (TEM) images were recorded on Hitachi H800. The specific surface area determination, pore size analysis was performed by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, respectively. The energy dispersive X-ray spectroscopy (EDX) for the determination of cobalt content were performed on JEOL JCM-6000PLUS. X-ray photo electron spectroscopic (XPS) analysis was carried out on a JPS-9000MX spectrometer (JEOL) with Mg Kα source radiation (10 kV, 10 mA) as the energy source.

4 Electrochemical measurements

The electrochemical measurements were carried out on a VersaSTAT 3 Potentiostat. Electrochemical characterization of the synthesized catalysts was performed in a rotating ring-disk electrode apparatus as the working electrode; a Pt coil electrode is the counter electrode and a Hg/ Hg₂(Cl)₂ acted as the reference electrode. The potentials were normalized to the reversible hydrogen electrode (RHE) referred to the Nernst equation:

$$E_{RHE} = E_{Hg/Hg_2(Cl)_2} + 1.0083$$

The electrocatalysts (8.8 mg) were dispersed ultrasonically in a 1ml solvent with 0.1ml Nafion, 0.1ml isopropanol and 0.8ml deionized water. The electrocatalytic activity of the catalyst was measured in an O₂

saturated 0.1 M KOH solution as the electrolyte. The Linear sweep voltammetry (LSV) tests were measured at a sweep rate of $10\text{mV}\cdot\text{s}^{-1}$ under different rotating rates (400, 800, 1200, 1600 and 2000 rpm). The electron transfer number (n) per oxygen molecule at different potentials during the oxygen reduction reaction (ORR) was calculated from the Koutecky-Levich (K-L) equation:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{nFkC_0} + \frac{1}{0.62nFC_0D_0^{\frac{2}{3}}\nu^{\frac{-1}{6}}\omega^{\frac{1}{2}}}$$

where J is the current density, J_L and J_K are the diffusion and kinetic-limiting current densities, ν is the kinematic viscosity of the solution ($0.01\text{ cm}^2\cdot\text{s}^{-1}$), n represents the number of electrons transferred per oxygen molecule, F represents the Faraday constant ($96485\text{ C}\cdot\text{mol}^{-1}$), k is the electron transfer rate constant, C_0 is the O_2 concentration in the bulk of electrolyte ($1.2\times 10^{-6}\text{mol}\cdot\text{cm}^{-3}$), D_0 is the diffusion coefficient of O_2 in the electrolyte ($1.8\times 10^{-5}\text{ cm}^2\cdot\text{s}^{-1}$), and ω is the rotation rate ($\text{rad}\cdot\text{s}^{-1}$).

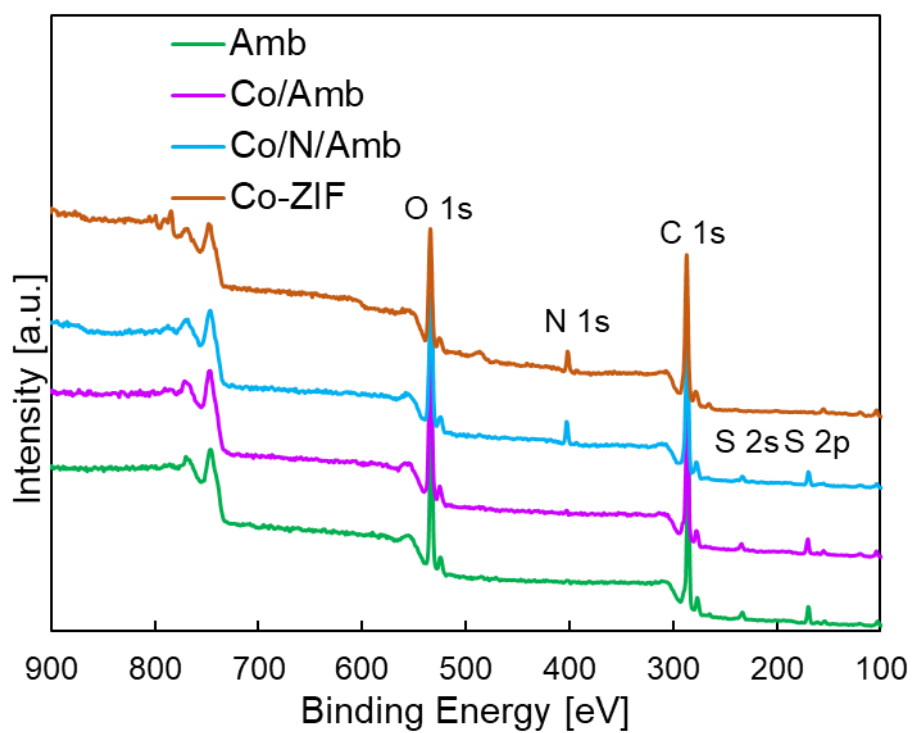


Figure S1. Wide-ranged XPS spectrum of the precursors and ZIF-67.

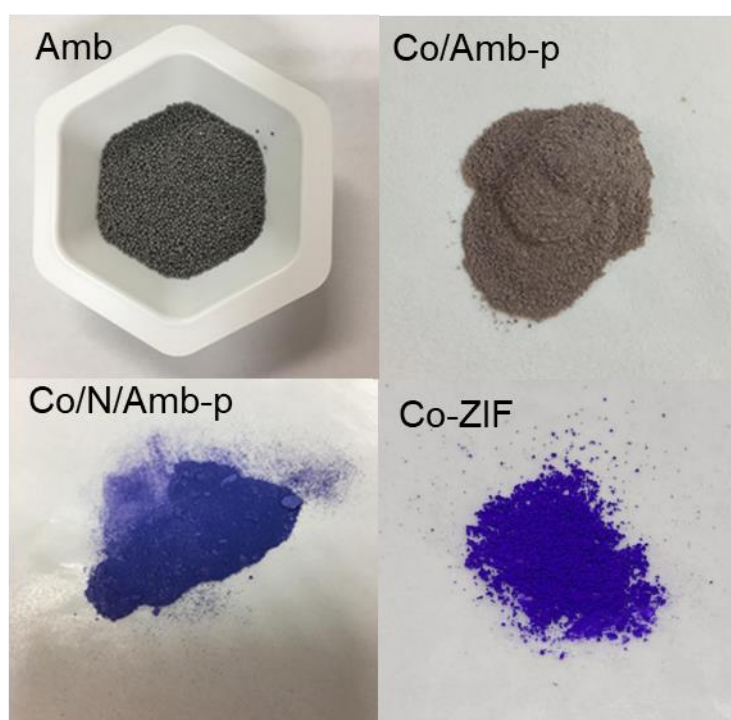
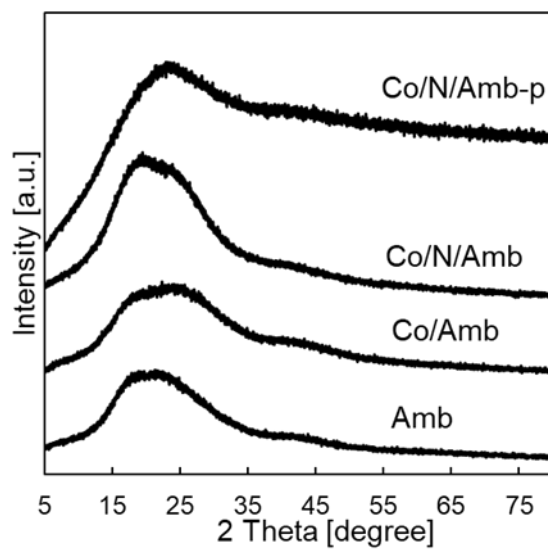
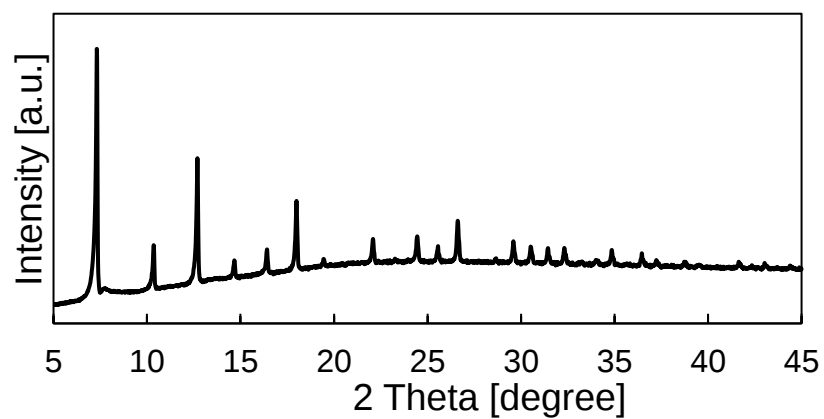


Figure S2. Pictures of the precursors.

(a)



(b)



(c)

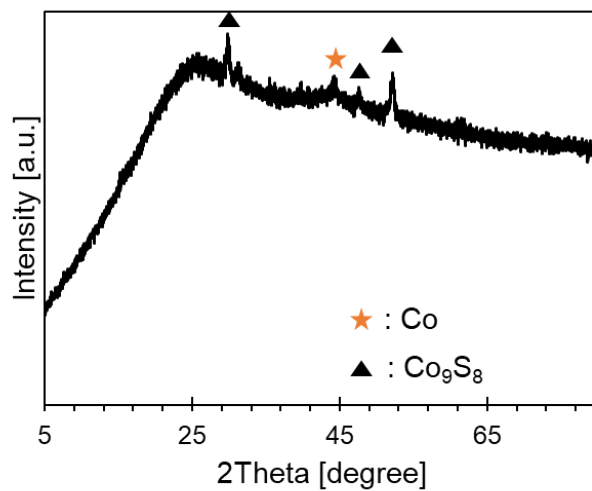


Figure S3. XRD patterns of (a) the precursors and (b) ZIF-67 (c) carbonized Co/N/C with excess of Co.

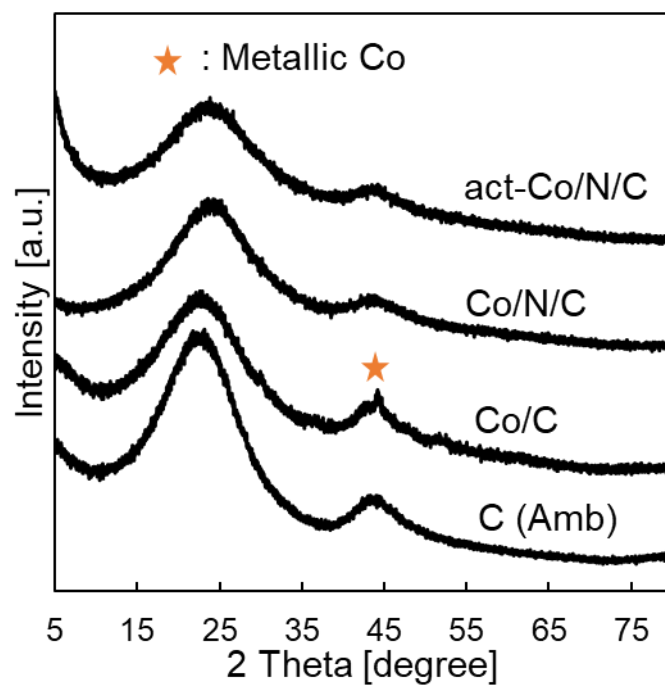


Figure S4. XRD patterns of the carbonized samples.

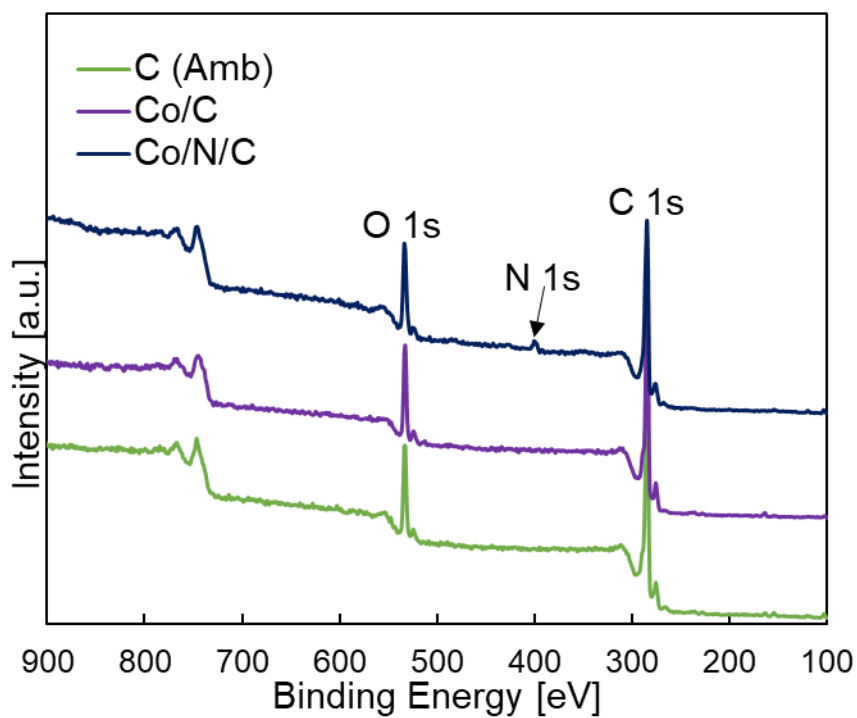


Figure S5. Wide ranged XPS spectrum of C(Amb), Co/C, Co/N/C, and act-Co/N/C.

(a)

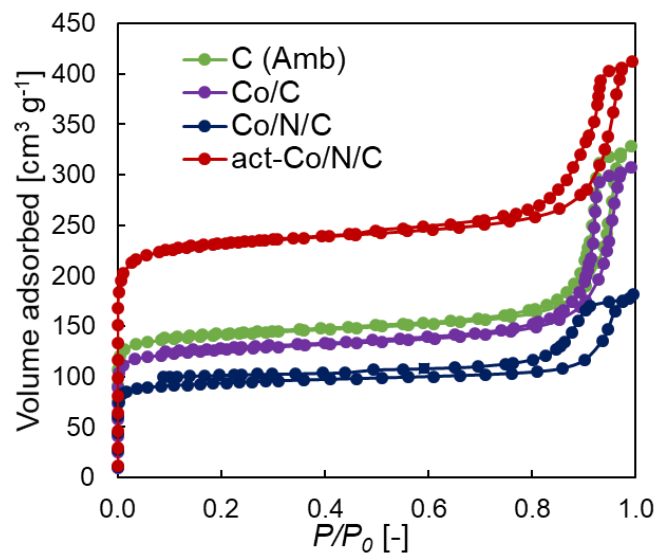


Figure S6. (a) N₂ sorption isotherms of the carbonized samples.

(b)

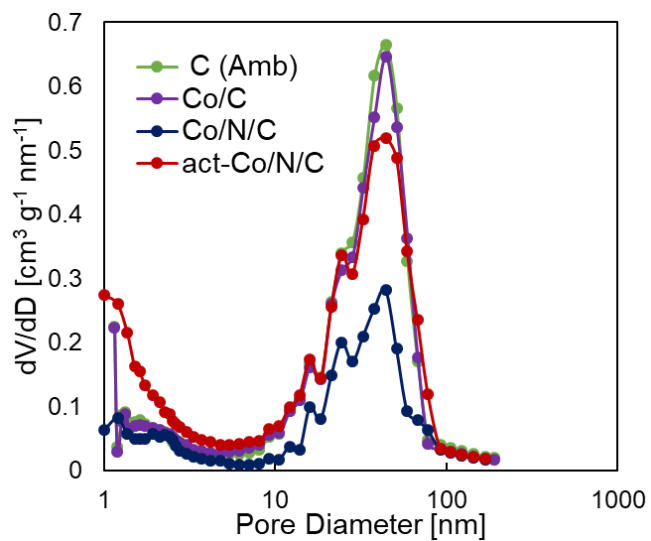
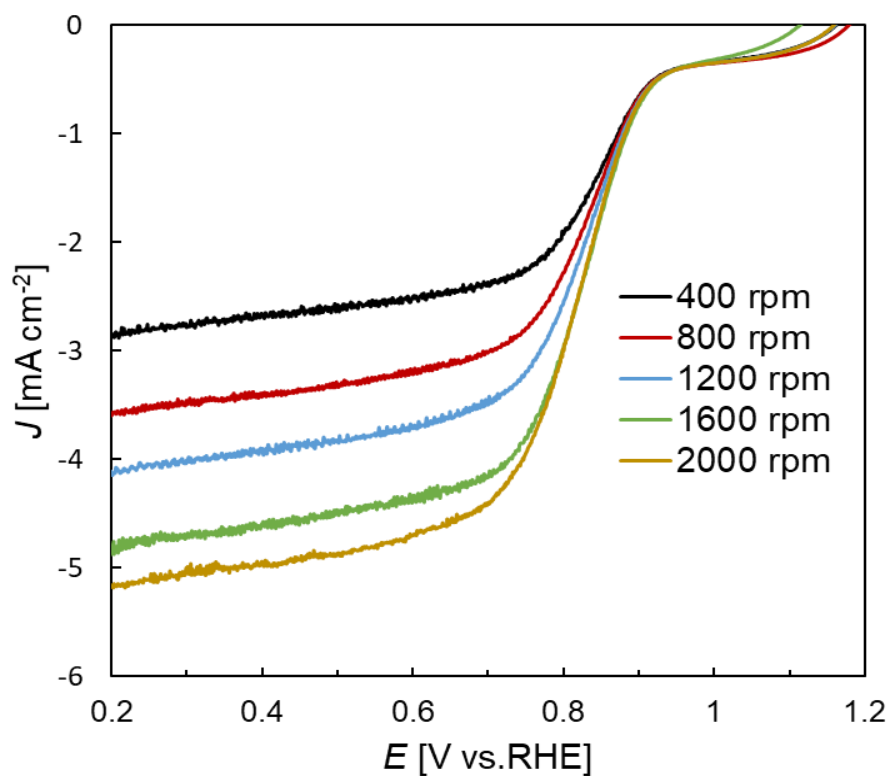


Figure S6. (b) Pore size distribution of the carbonized samples.

Table 1. BET surface of the carbonized samples

Samples	S_{BET} (m ² g ⁻¹)	V_{total} (cm ³ g ⁻¹)
C (Amb)	345	0.51
Co/C	310	0.47
Co/N/C	204	0.37
act-Co/N/C	562	0.64

(a)



(b)

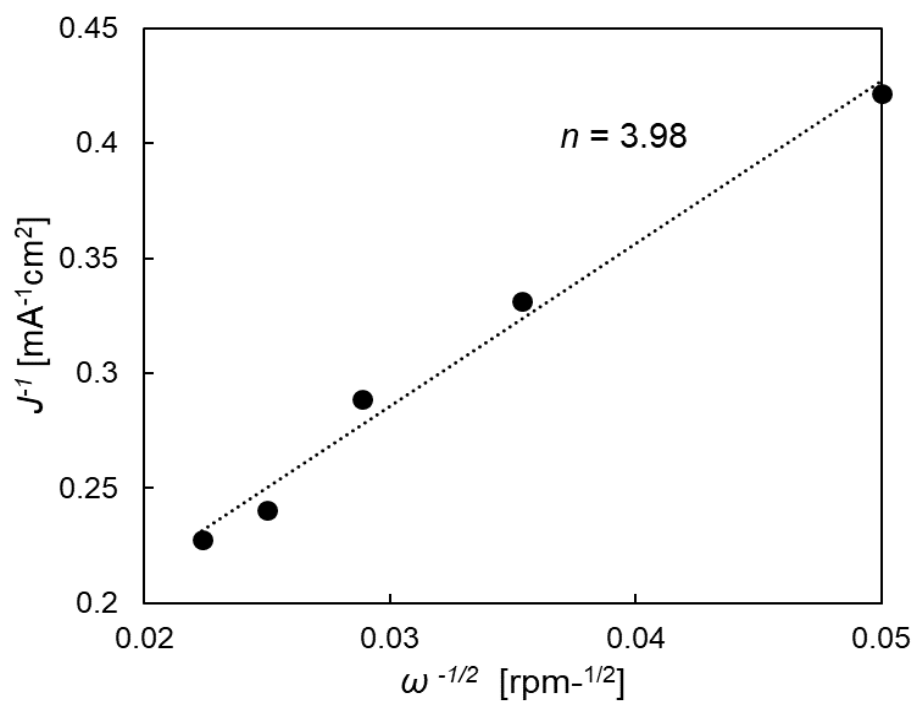
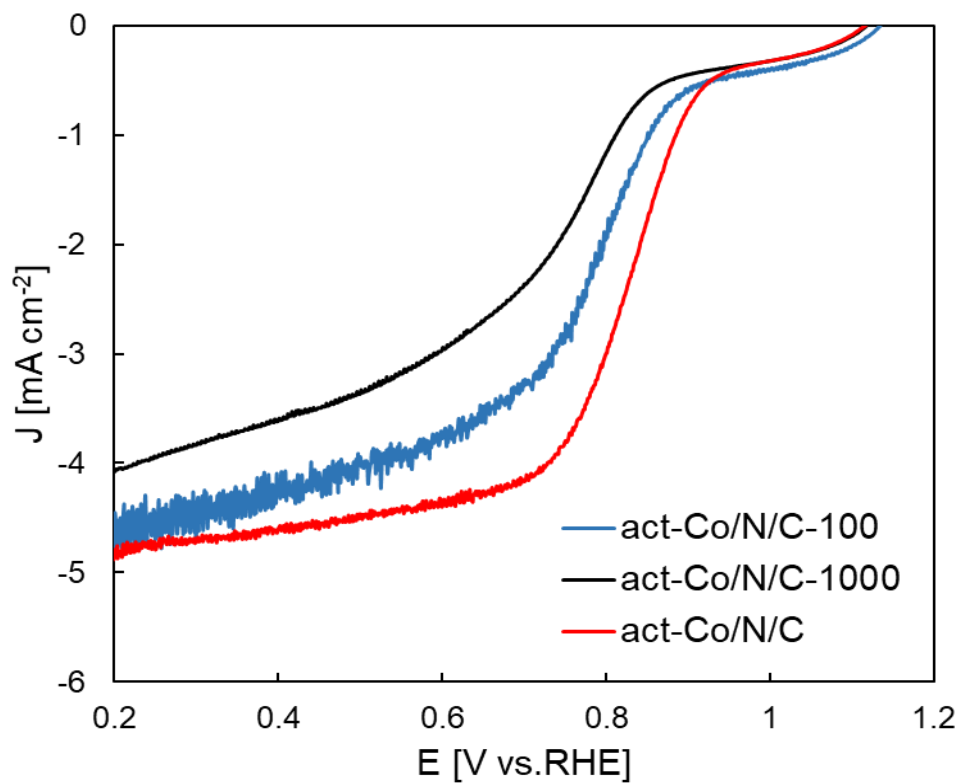


Figure S7. (a) LSV curves of act-Co/N/C in O₂ saturated 0.1M KOH at various rotation speeds, (b) Koutecky-Levich (K-L) plot.

(a)



(b)

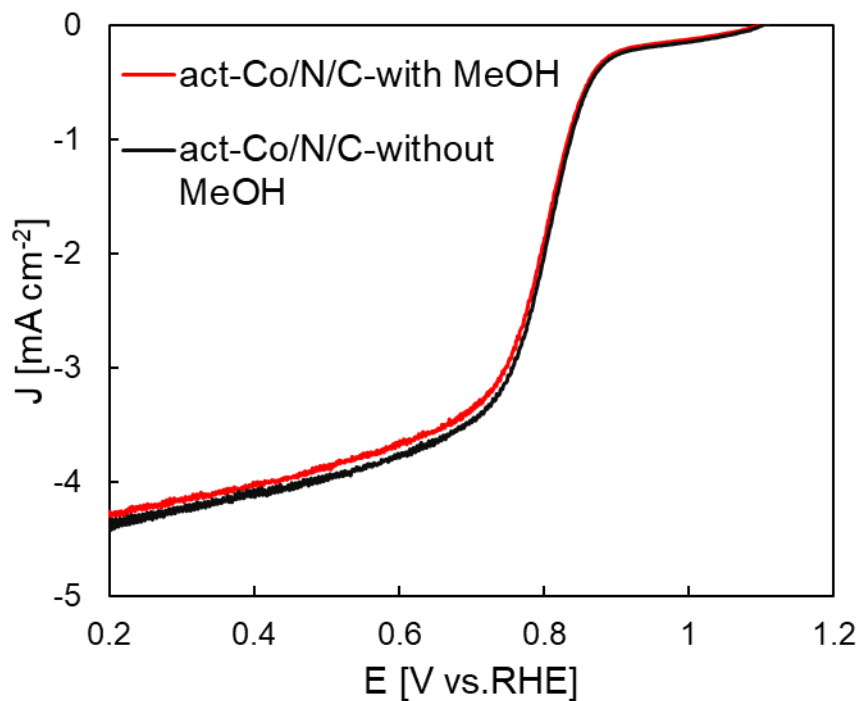


Figure S8. (a) ORR polarization curves before and after 100 cycles and 1000 cycles, (b) ORR polarization curves of act-Co/N/C in O_2 -saturated 0.1 M KOH with 3 M CH_3OH , 10 mV/s, and 1600 rpm.

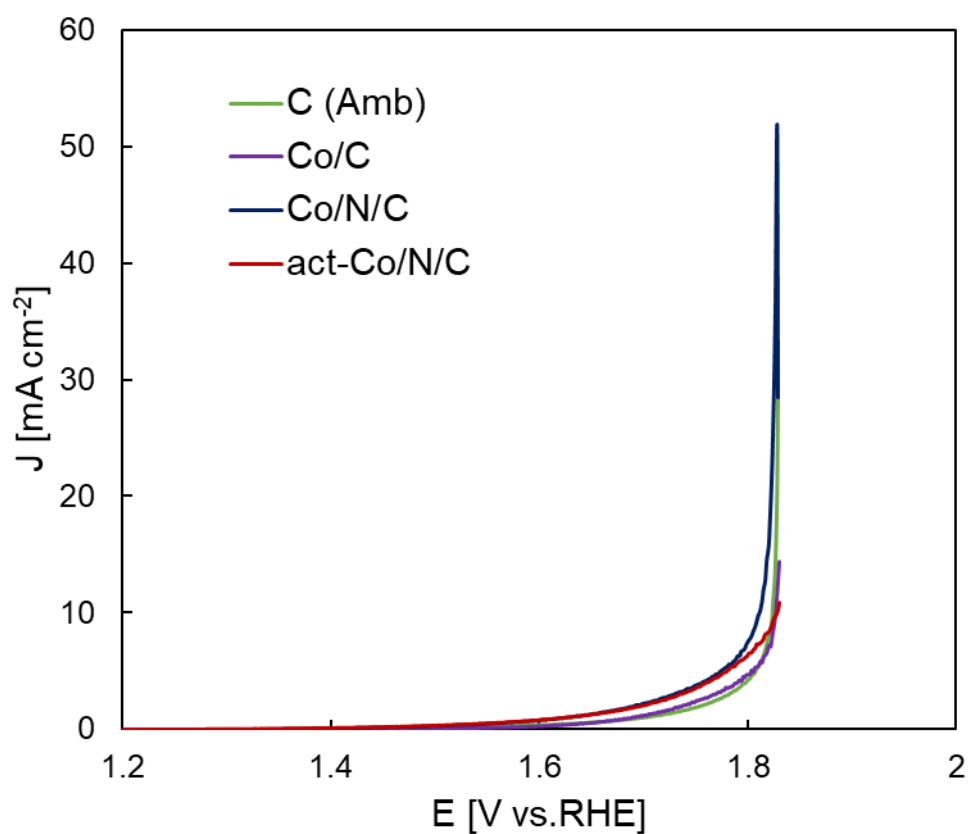


Figure S9. OER polarization curves of C (Amb), Co/C, Co/N/C, act-Co/N/C acquired in 0.1 M KOH aqueous electrolyte with a scan rate of 10 mV/s.

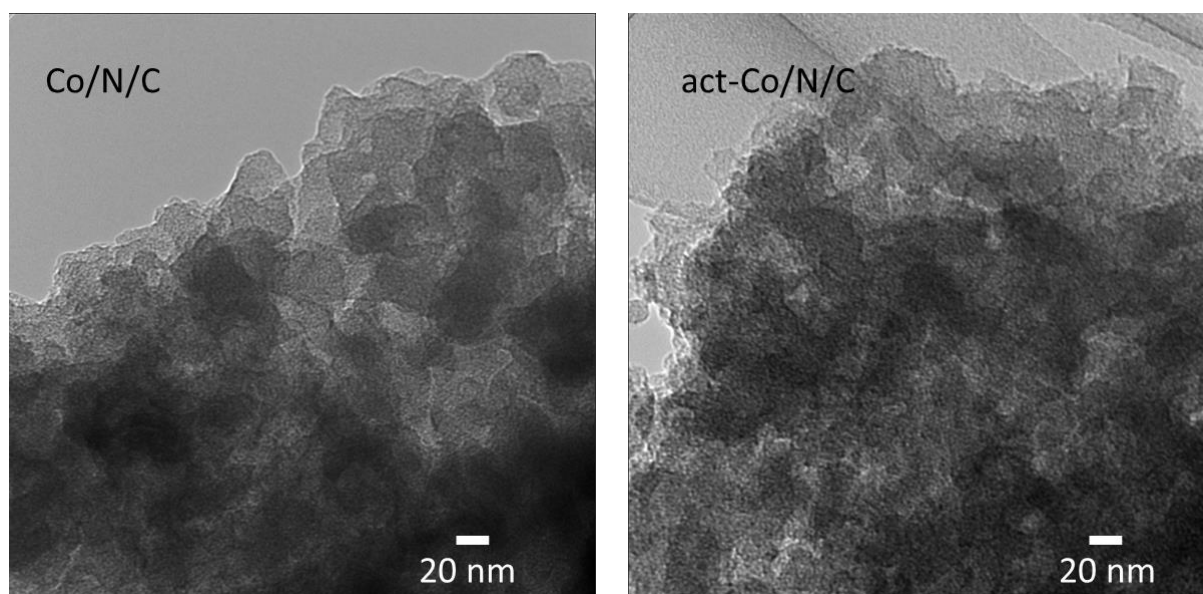


Figure S10. TEM images of Co/N/C and act-Co/N/C.

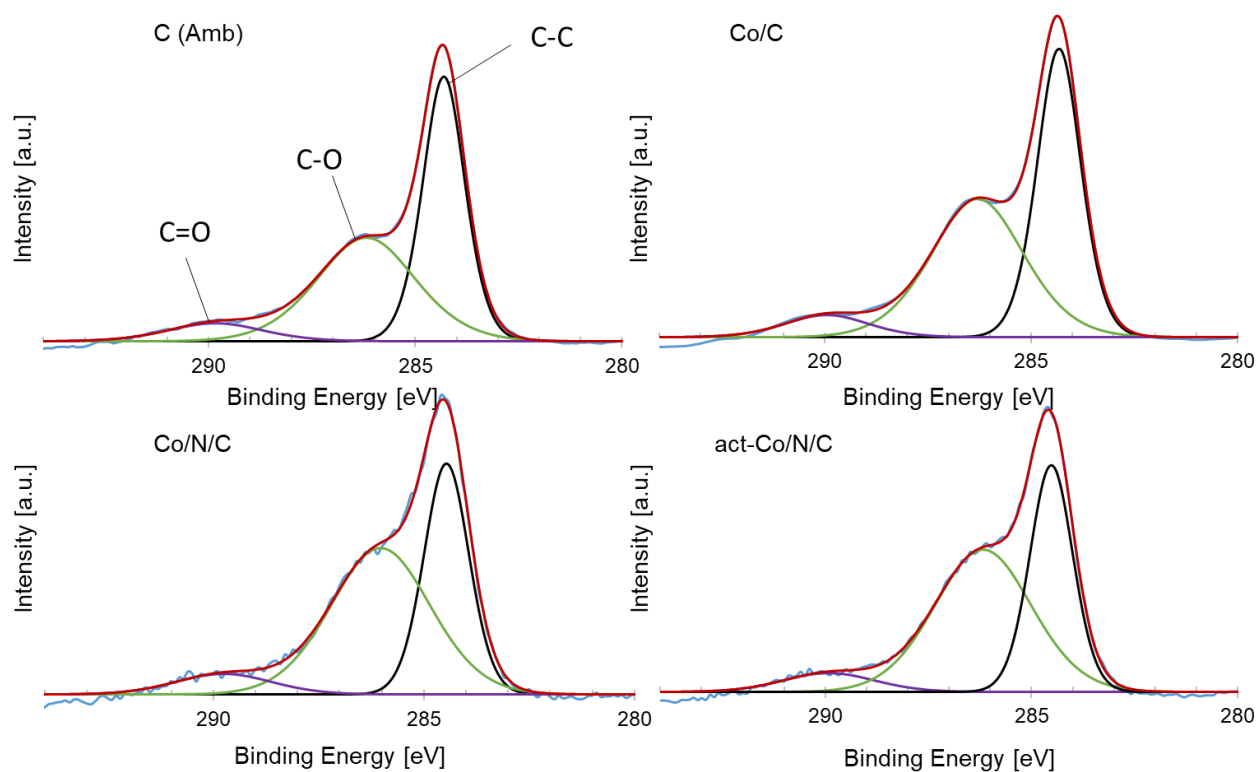


Figure S11. XPS spectra and relative peak deconvolutions relative to carbon 1s.

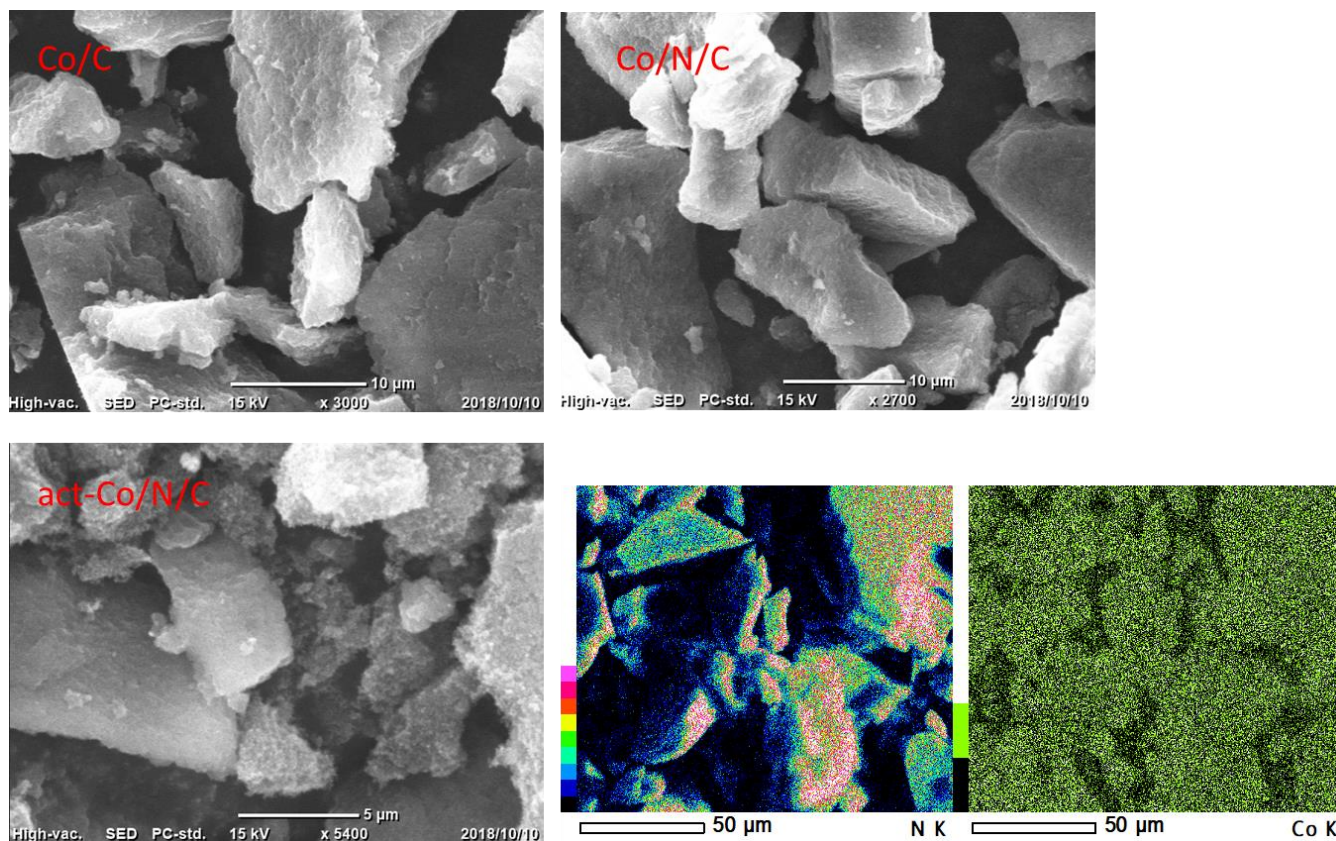


Figure S12. SEM images and elements mapping of Co/N/C.

(a)

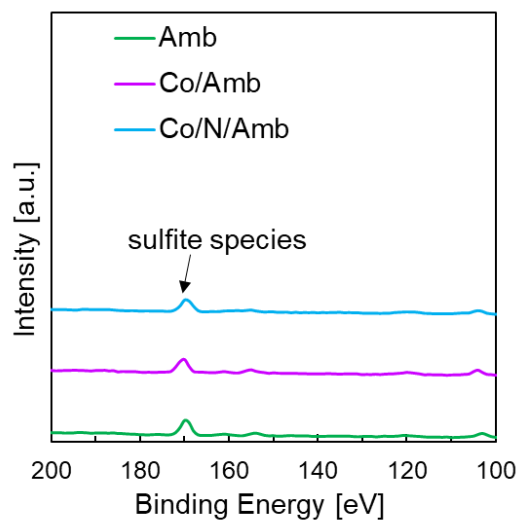


Figure S13. (a) XPS spectrum of the precursors.

(b)

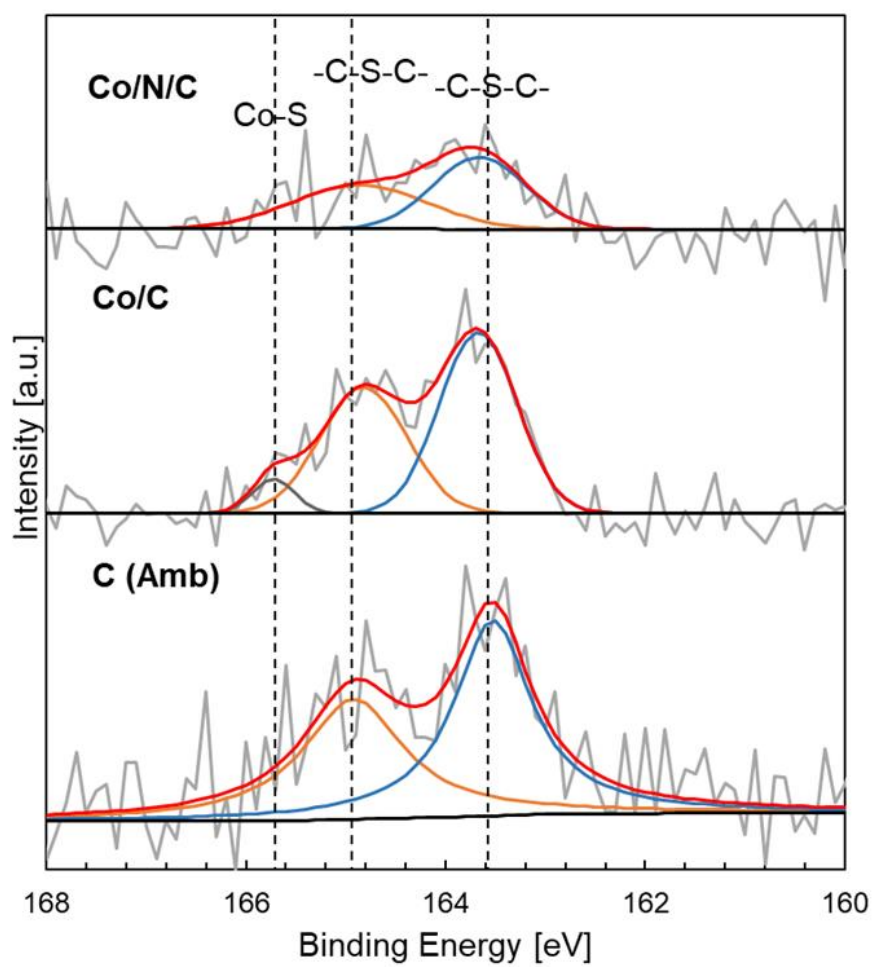


Figure S13. (b) XPS spectrum of the carbonized samples.