Supplementary Information

Cobalt-carbon nanofibers as an efficient support-free catalyst for oxygen reduction reaction with a systematic study of active site formation

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1. IR spectra

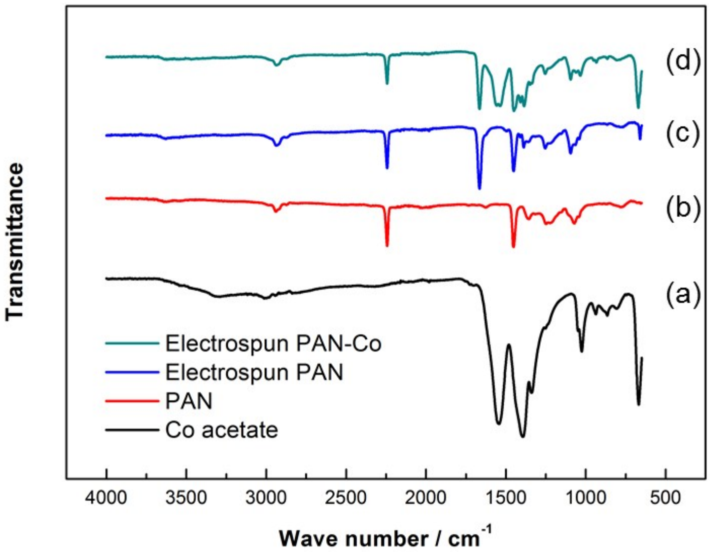

Figure S1. IR spectra of (a) cobalt(II) acetate, (b) PAN, (c) PAN nanofiber, and (d) Co -PAN nanofiber in the region 4000 ~ 400 cm^{-1}

Figure S1 shows the IR spectra of precursors for electrospinning solution (cobalt acetate, PAN) and electrospun nanofibers (PAN nanofiber, Co-PAN nanofiber). Figure. S1 (a) presents the spectrum of cobalt (II) acetate. The absorption band around 1560 cm^{-1} and 1385 cm^{-1} assigned to the stretching of C-O (ν_{as}(C-O) 1582 cm^{-1}, ν_s(C-O) 1442 cm^{-1}) and bending of CH_3 (δ_{as}($CH_3$1406cm^{-1}), δ_{as}(CH_3) 1340 cm^{-1}) respectively in the acetate unit. Figure. S1(b) presents the spectrum of PAN. The absorption band at 2243 cm^{-1} is assigned to the C≡N stretching of acrylonitrile unit in the polymer chain. The assignments of other absorption bands are given as follows: 2929 cm^{-1} (ν_{as}(CH_2)), 1454 cm^{-1} (ν_s(CH_2)). Electrospun PAN nanofiber shows almost same IR spectra with PAN additional absorption band at 1660 cm^{-1} assigned to conjugated alkenyl (C=C) stretch. This absorption band might be due to disprotonation in the PAN polymer chain during the electrospinning. The IR spectrum of electrospun Co-PAN nanofiber has well corresponding absorption band of both cobalt acetate and electrospun PAN nanofiber as shown in Figure S1(d). There is no additional or disappeared peak compared with the IR spectra of cobalt acetate and electrospun PAN nanofiber.

2. RRDE experiments

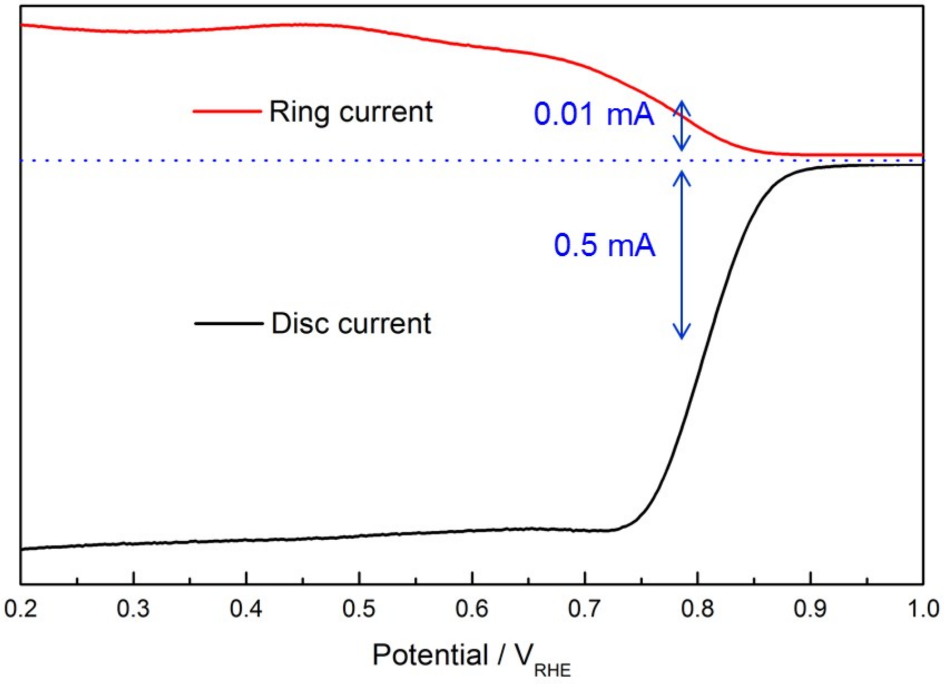

Figure S2. Ring current and disc current of 32.2 wt. % Co-CNF catalyst in O_2-saturated 0.1 M KOH solution at 1600 rpm.

The electron transfer number (n) and H_2O_2 yield of catalysts was evaluated based on followed equations.

$$H_2O_2 \text{ yield} = 200 \times \frac{I_r / N}{I_d + I_r / N} \qquad \text{Equation S1}$$

$$\text{Electron transfer number (n)} = 4 \times \frac{I_d}{I_d + I_r / N} \qquad \text{Equation S2}$$

I_d and I_r are measured disc and ring current respectively. N is the ring current collection efficiency, which is 0.37 in this study.

3. Rotating-disk voltammograms

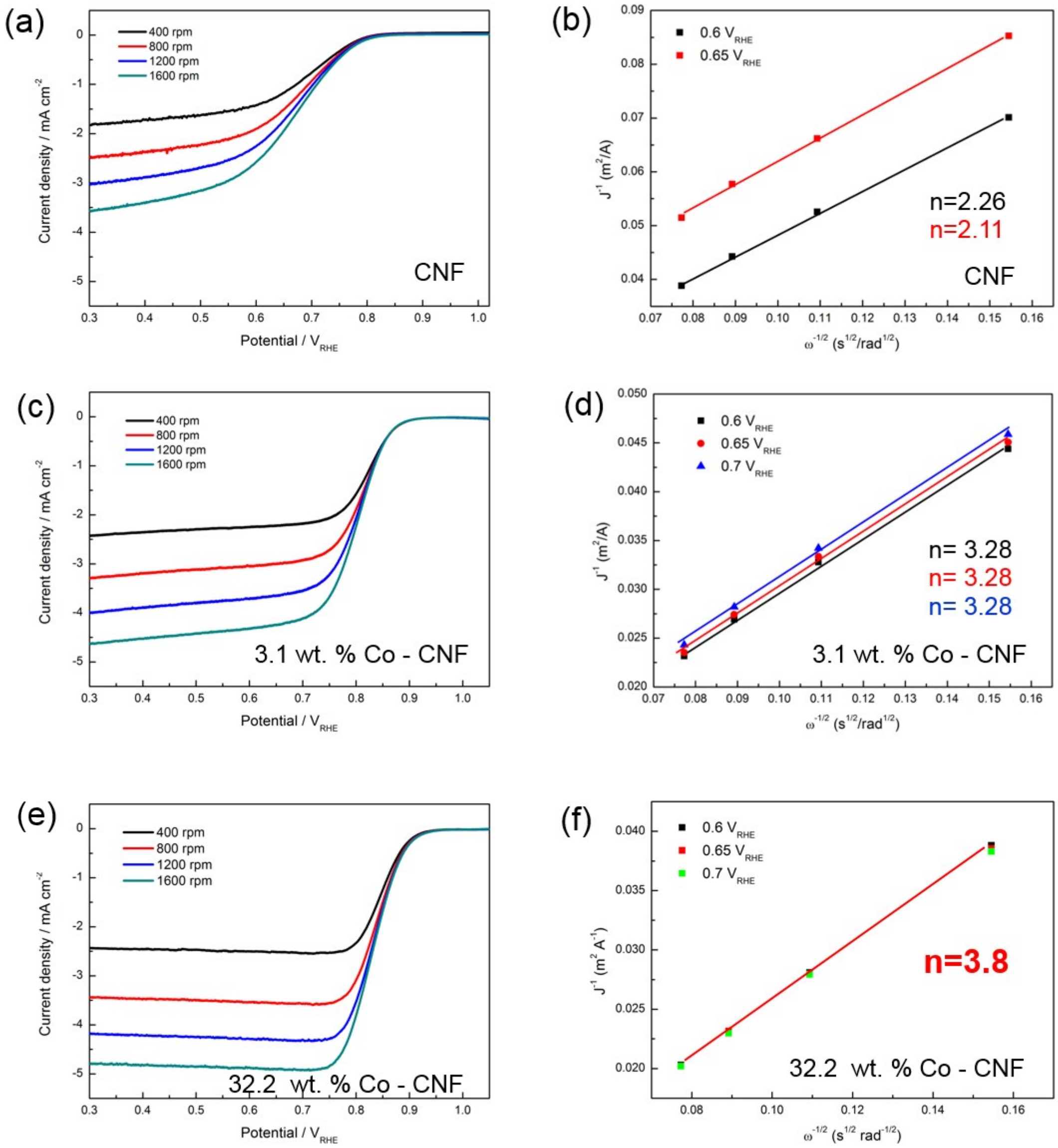

Figure S3. Rotating-disk voltammograms in O_2-saturated 0.1 M KOH at a sweep rate of 5 mV/s at different rotation rates, and the corresponding Koutecky–Levich plots at different potentials of (a) and (b) CNF, (c) and (d) 3.1 wt. % Co-CNF, and (e) and (f) 32.2 wt. % Co-CNF catalysts.

Koutecky-Levich plot express linear relationship between j^{-1} and $\omega^{-1/2}$. j is the Levich current density for the electrode reaction of a reactive species by a diffusion-controlled process, and ω is the rotating speed of the electrode. Koutecky-Levich plots were achieved from Levich equation as below.

$$I_L = 0.62\, n\, F\, A\, D^{\frac{2}{3}}\, e^{\frac{1}{2}}\, v^{\frac{-1}{6}}\, C$$

I_L = Levich current

n = electron transfer number per mole of a reactive species

F = Faraday constant

A = electrode area

ω = rotating speed

D = diffusion coefficient of the reactive species (1.9 x 10^{-5} cm^2 s^{-1} in 0.1 M KOH solution)

v = viscosity of water (0.01 cm^2 s^{-1} in 0.1 M KOH solution)

C = concentration of the reactive species (1.2 x 10^{-6} mol cm^{-3} in 0.1 M KOH solution)

4. XPS Co 2p analysis

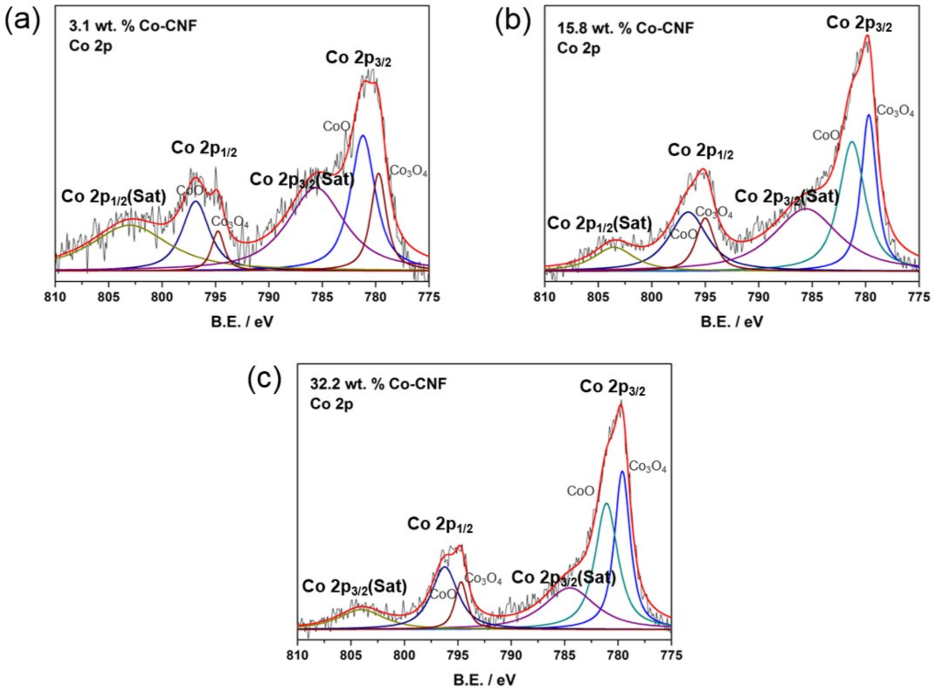

Figure S4. XPS Co 2p peaks of (a) 3.1 wt. % Co-CNF, (b) 15.8 wt. % Co-CNF and (c) 32.2 wt. % Co-CNF catalysts.

All the samples clearly exhibit $2p_{3/2}$ and $2p_{1/2}$ peaks, each of which is composed of two components from CoO and Co_3O_4, respectively: $2p_{3/2}$ and Co $2p_{1/2}$ peaks of CoO is at about 781.2 and 796.4 eV; [1] $2p_{3/2}$ and Co $2p_{1/2}$ peaks of Co_3O_4 is at about 779.8 and 794.6 eV. [2] The peaks at about 785.6 and 803.5 eV can be assigned to $2p_{3/2}$ (sat) and $2p_{1/2}$ (sat) peaks.

These results show that Co-CNF catalysts include CoO and Co_3O_4, as demonstrated by XRD pattern and Raman spectra (Fig. 3) in the manuscript and are well coincident with a previous report.[3]

[1] J. Am. Chem. Soc., 1991, 113, 855

[2] Surf. Interface Anal., 1990, 15, 265

3 J. Mater. Chem., 2010, 20, 4875