Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Atomic Layer Deposition of Co_3O_4 Nanocrystals on N-Doped Electrospun Carbon Nanofibers for Oxygen Reduction and Oxygen Evolution Reactions

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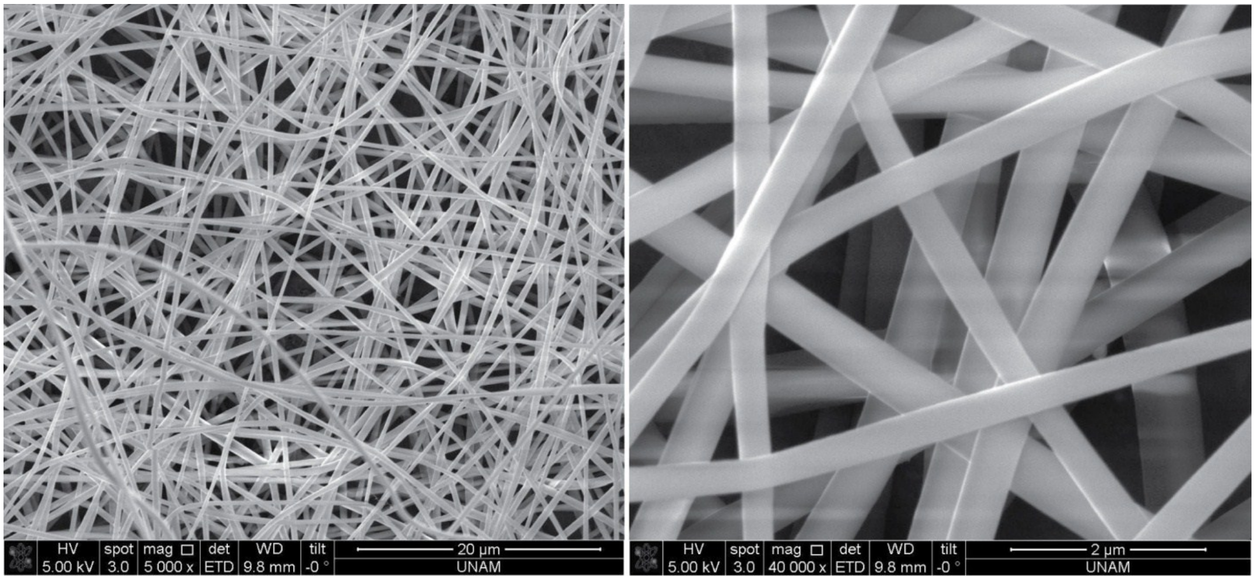

Figure S1. SEM images of electrospun PAN nanofibers

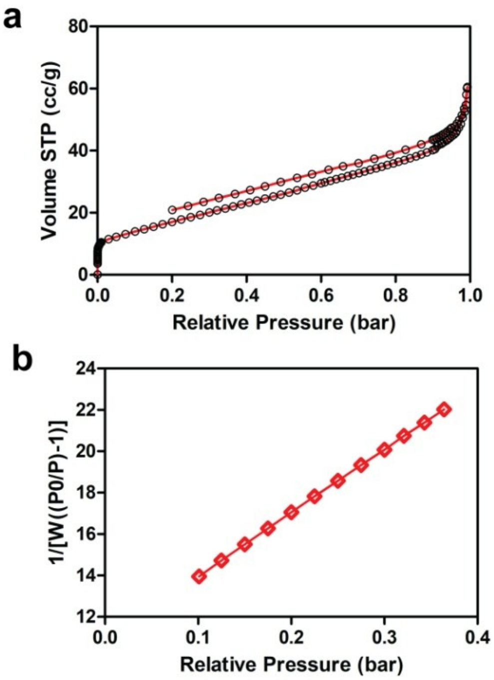

Figure S2. N_2 adsorption isotherm (a) and BET plot (b) for nCNF

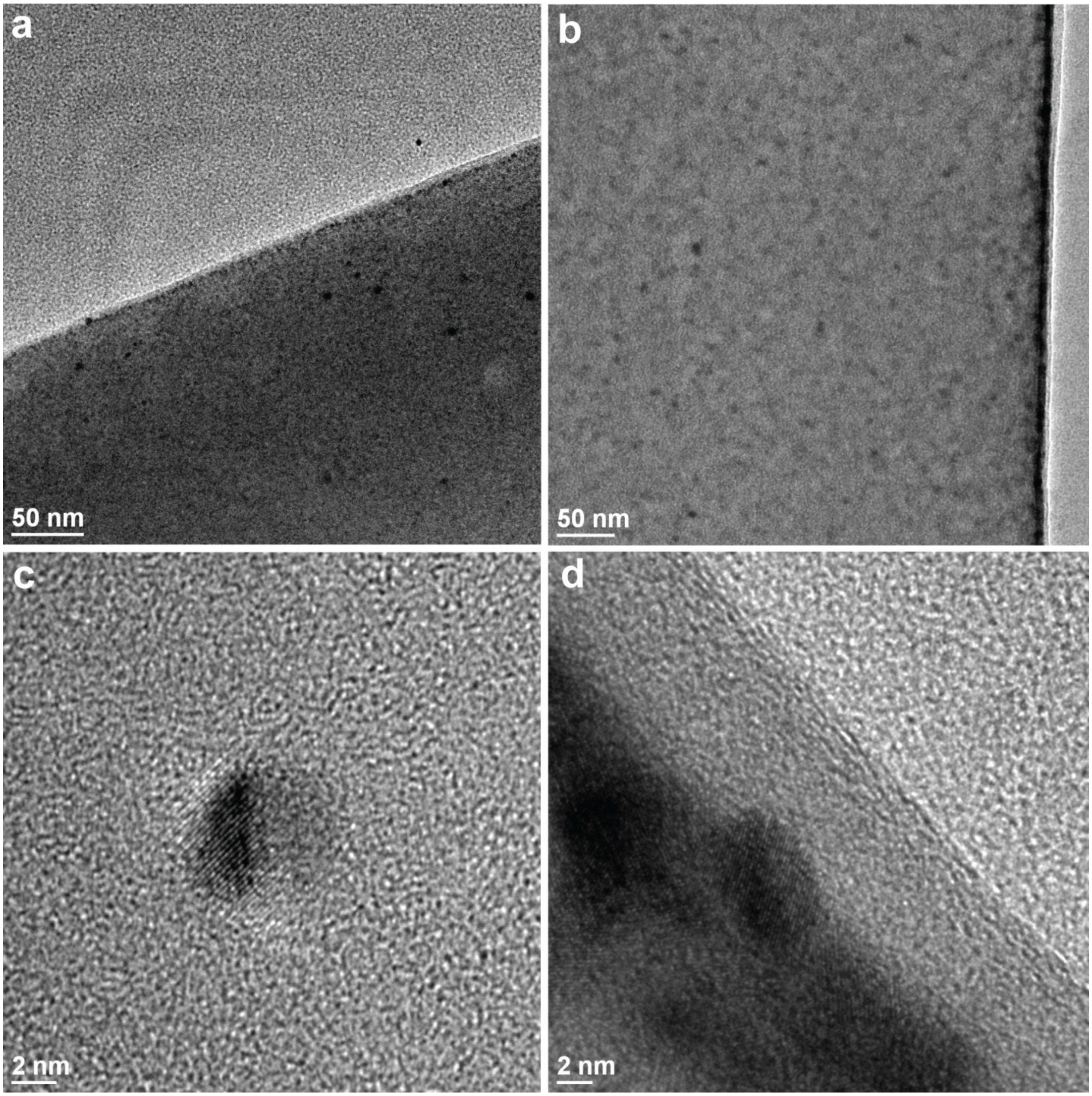

Figure S3. TEM imges of Co50@nCNF (a), Co150@nCNF (b) and HRTEM images of Co50@nCNF (c) and Co150@nCNF (d)

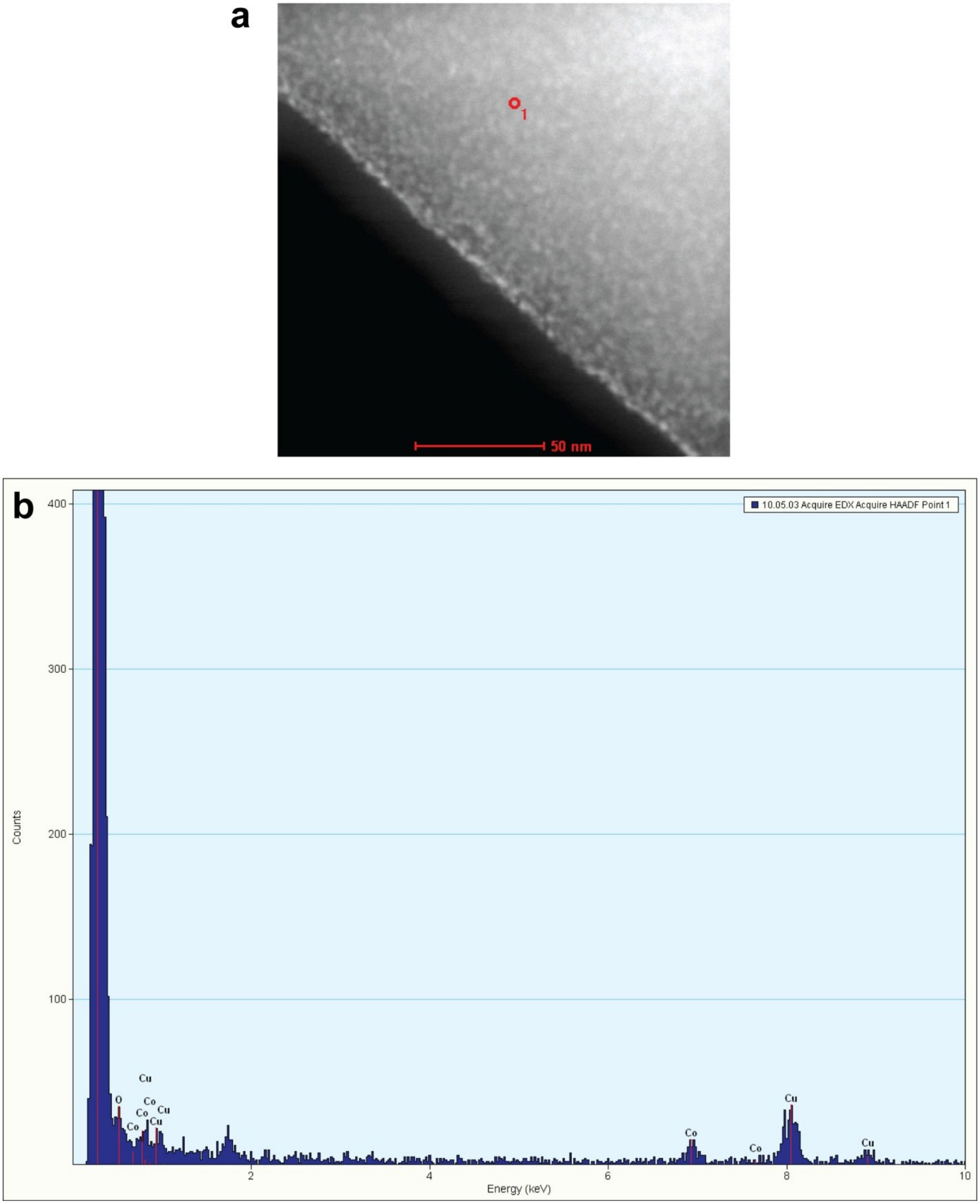

Figure S4. STEM image (a) and EDS spectrum (b) of Co100@nCNF

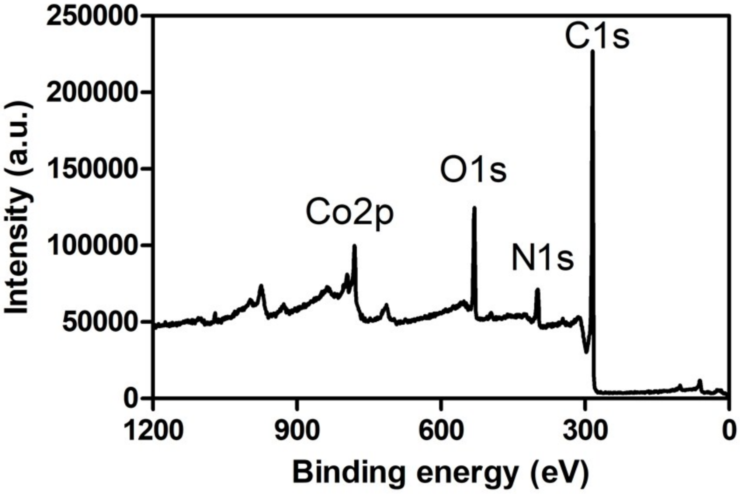

Figure S5. Survey XPS spectrum of Co100@nCNF

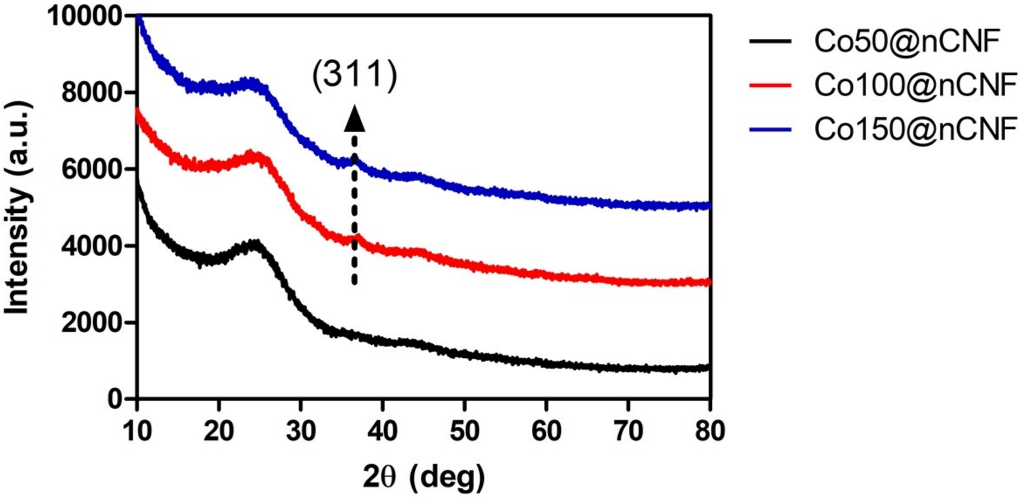

Figure S6. XRD spectra of the electrocatalysts

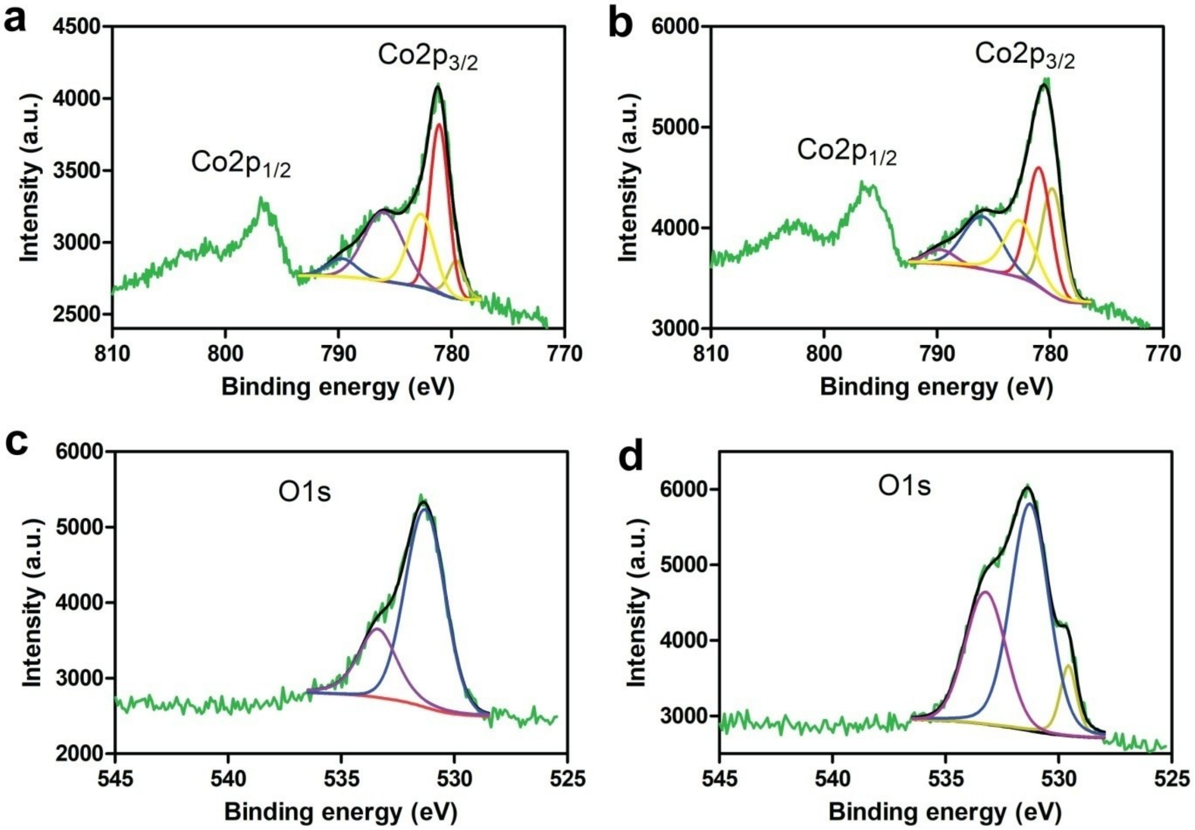

Figure S7. Gaussian deconvolution of Co2p for Co50@nCNF (a) and Co150@nCNF (b) samples. Gaussian deconvolution of O1s for the Co50@nCNF (c) and Co150@nCNF (d) samples.

Electrochemical Caculations

All experiments were performed at room temperature at the Biologic SP-150 potentiostat with the standard three−electrode electrochemical cell. The catalyst modified glassy carbon electrode (GC, 3 mm diameter, 0.07068 cm^2 of geometric surface area), Pt spiral wire and Ag|AgCl|KCl$_{(sat.)}$ were used as working, counter and reference electrodes, respectively. The ORR, OER and HER were performed in 20 ml 0.1 M KOH solution where prior to each measurement the electrolyte solution was saturated with either N_2 or O_2 gas (99.999% of purity) for 45 min. Rotating disk electrode (RDE) linear sweep voltammetry (LSV) technique was to determine ORR mechanism and kinetics. The Nernst equation (SE1) used to convert all the potentials measured vs. Ag|AgCl|KCl$_{(sat.)}$ to the reversible hydrogen electrode (RHE) [1]:

$E_{\mathrm{RHE}} = E_{\mathrm{Ag|AgCl|KCl(sat.)}} + 0.059\ \mathrm{pH} + E^{\mathrm{o}}_{\mathrm{Ag|AgCl|KCl(sat.)}}$ (SE1)

Where E_{RHE} is potential estimated vs. RHE, $E_{\mathrm{Ag|AgCl|KCl(sat.)}}$ is measured potential vs. Ag|AgCl|KCl$_{\mathrm{(sat.)}}$ electrode and $E^{\mathrm{o}}_{\mathrm{Ag|AgCl|KCl(sat.)}}$ is the standard electrochemical potential of the Ag|AgCl|KCl$_{\mathrm{(sat.)}}$ electrode i.e. 0.197 V.

The electrocatalyst slurries were prepared by mixing 8 mg catalyst (nCNF, Co50@nCNF, Co100@nCNF, Co150@nCNF, and PtC) in the 500 µL of DI water, 100 µL of ethanol and 40 µL of 5 wt% Nafion solution followed by vortex for 10 min. The GC surface was cleaned with aqueous slurries of consecutively finer alumina powder (1 µm down to 0.06 µm) with the help of a polishing microcloth. To remove the alumina, the electrode was ultrasonically cleaned in the 18 MΩ Millipore water followed by ethanol for 10 min, individually. To fabricate nCNF, CoOx50@nCNF, CoOx100@nCNF, CoOx150@nCNF, PtC modified GC, 4 µL electrocatalyst slurry was drop casted on cleaned GC, individually. Then prepared electrodes were dried in an oven at 60° C for 30 min prior to electrochemical measurements. All the calculations were measured based on the geometric surface area unless specified.

ORR calculations

An electrocatalytic activity of ORR obtained at nCNF, Co50@nCNF, Co100@nCNF, Co150@nCNF and PtC samples were analyzed with RDE measurements from 100 to 1600 rpm with the scan rate of 10 mV s^{-1}. This RDE data was used for the Koutecky–Levich plots at the steady state currents were shown in Fig. and . The number of electrons involved in the ORR per oxygen molecule was determined from the slope using Koutechy-Levich equitation [2]:

$1/j = 1/j_k + 1/j_L = 1/j_k + 1/(B\omega^{1/2})$ (SE2)

where $B = 0.62nFCD^{2/3}v^{-1/6}$, j_k is the kinetic current density, j is the measured current density, j_L is the Levich current density, n is the number of electrons transferred per oxygen molecule, F is the Faraday constant i.e. 96,485 C mol^{-1}, C is the dissolved oxygen concentration in the solution (1.26 x 10^{-6}mol cm^{-3}), v is the kinematic viscosity of the solution (1.009 x 10^{-2} cm^{2}s^{-1}), D is the diffusion coefficient of oxygen (2.1 x 10^{-5} cm^2 s^{-1}) and ω is the rotation rate (rad s^{-1}) [2]. Assuming a four-electron reaction and the known geometric electrode surface area, the theoretical slope B is 2.5 cm^2 rad$^{1/2}$ mA^{-1} s$^{-1/2}$.

To find out kinetics of ORR at these catalysts, the kinetic current density was calculated from equation (SE3) and used to estimate Tafel slope (Fig. and). Based on the slope and constant obtained from the straight line of log j_k vs. potential were used to estimate Tafel slope and the exchange current density, respectively.

$$j_k = (j \times j_L)/(j_L - j) \qquad \text{(SE3)}$$

OER TOF Calculations

The rate of electron delivered per surface metal atom per second or the rate of product molecules evolved per surface metal atom was determined from turn over frequency (TOF) based on eq (SE4):

$$\mathrm{TOF} = I / (4 \text{ x } F \text{ x } m) \qquad \text{(SE4)}$$

Where I is the measured current in Amperes, F is Faraday constant and m is the number of moles of the active catalyst. Moles were estimated based on the ICPMS data and molar mass of Co oxides. It was assumed that all of the materials in the catalysts are catalytically active for the OER [3].

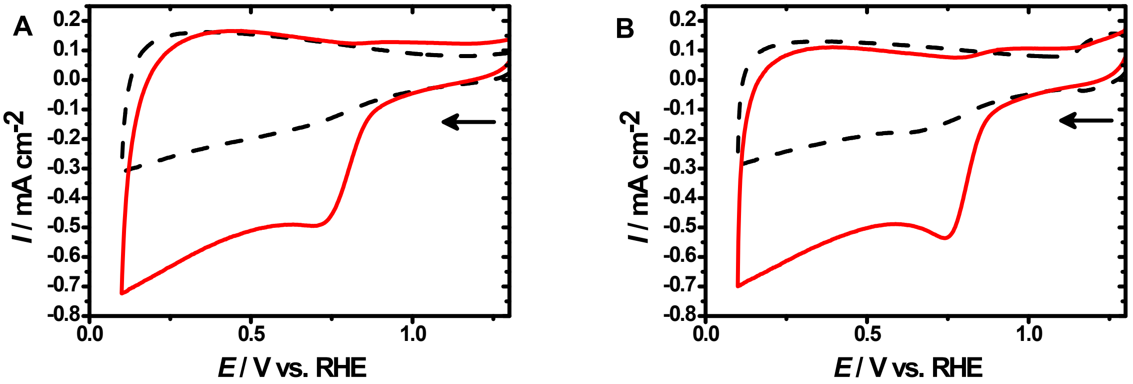

Figure S8. CVs of oxygen reduction obtained at the Co50@nCNF (A) and Co150@nCNF (B) in N_2 (dotted black lines) and O_2-saturated (solid red lines) 0.1 M KOH solution at a scan rate of 10 mV s^{-1}

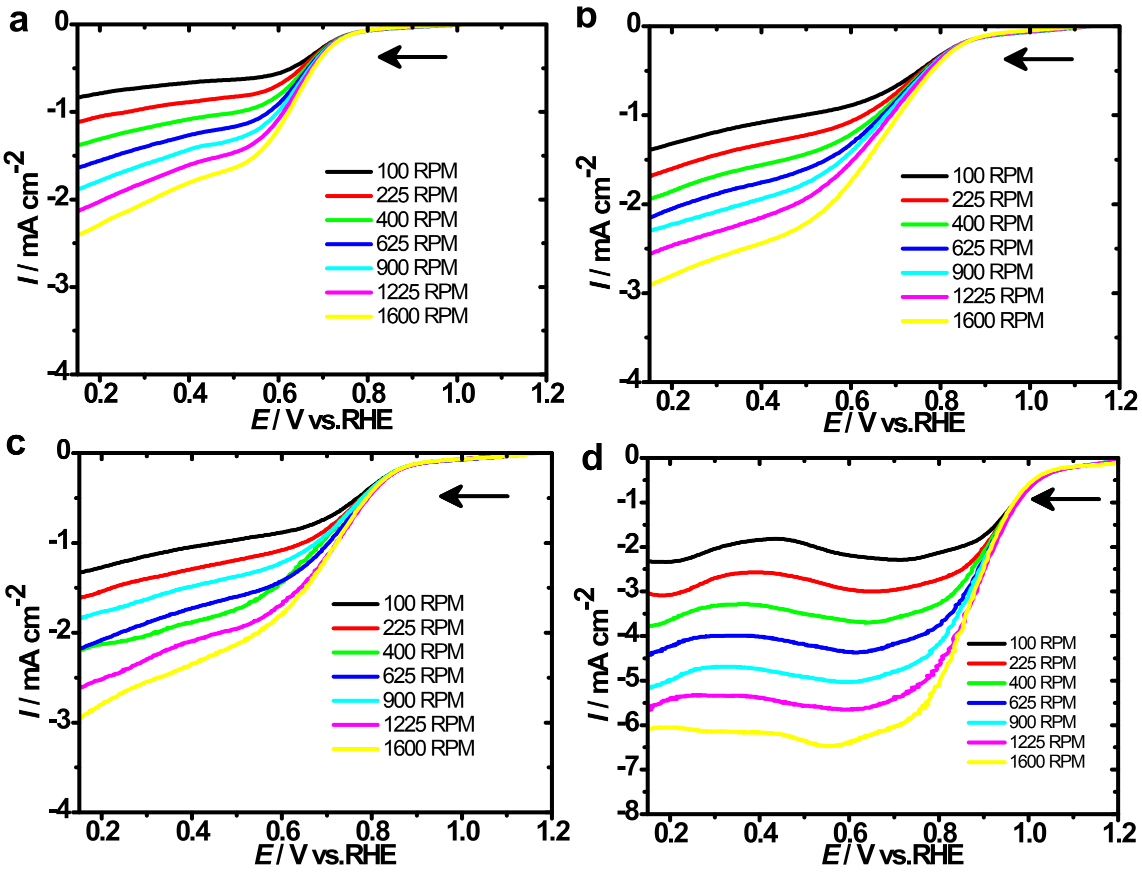

Figure S9. RDE measurements at the nCNF (a), Co50@nCNF (b), Co150@nCNF (c) and PtC (d) from 100 to 1600 rpm under O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1}.

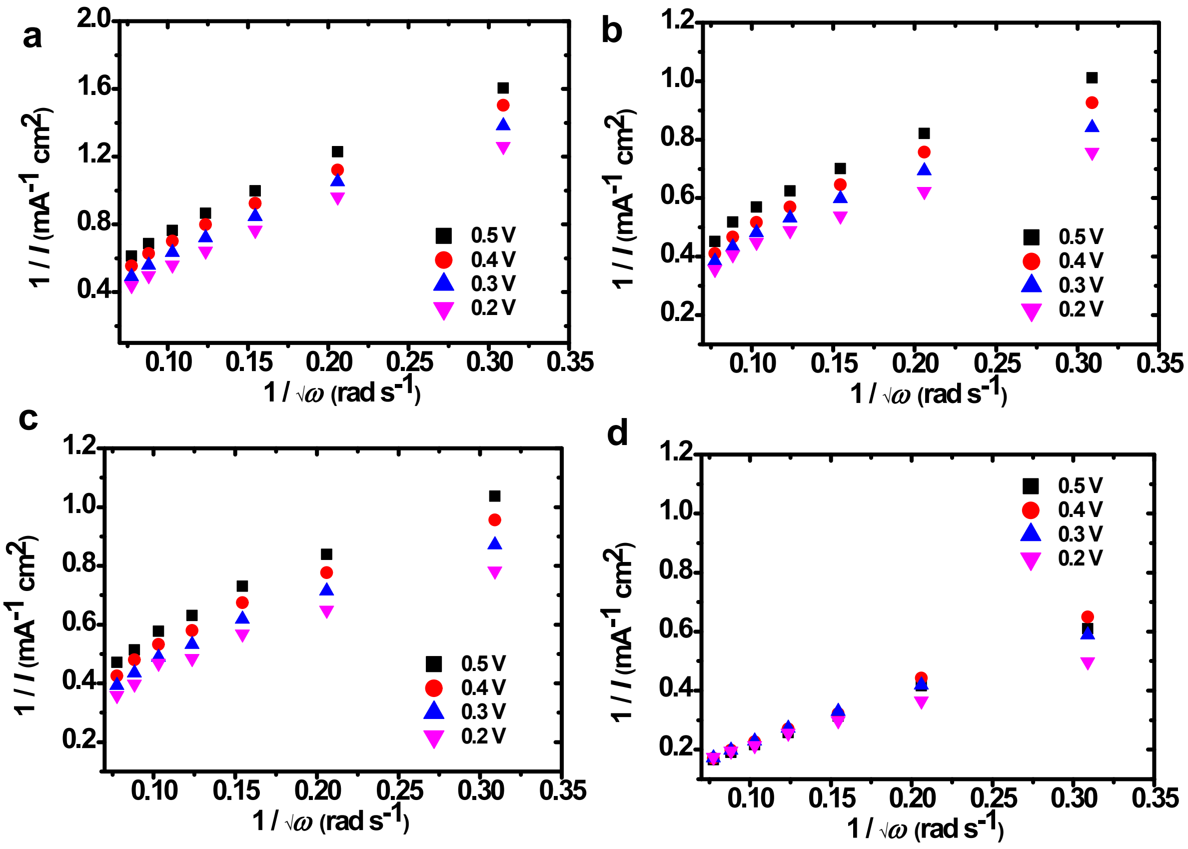

Figure S10. The Koutecky–Levich plot at 0.5, 0.4, 0.3, 0.2 V vs. RHE at the nCNF (a), Co50@nCNF (b), Co150@nCNF (c) and PtC (d) (data used from the Figure S9).

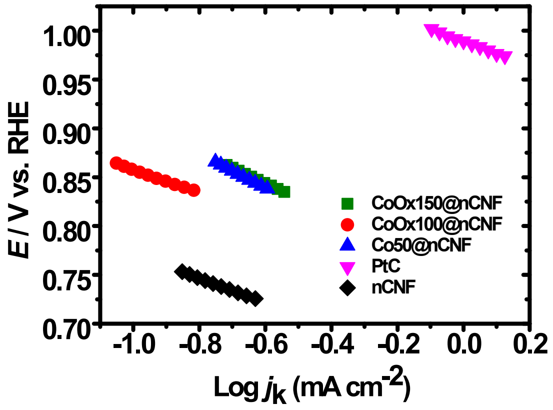

Figure S11. The Tafel plot obtained at the nCNF (a), Co50@nCNF (b), Co150@nCNF (c) and PtC (d) for the ORR (data used from the Figure S9).

Table S1. The bifunctional catalytic activity of Co100@nCNF catalyst for ORR and OER

Catalyst	ORR $E_{1/2}$ mV vs. RHE	OER η @ 10 mA cm^{-2} / V	Reference
Co100@nCNF	700*	1.78*	This work
Co-N/G-600	764*	1.724*	4
Co3O4/N-GAs	870	1.66	5
Co@Co3O4/NC-1	800	1.65	6
Co3O4/NPC	740*	1.63*	7
Co3O4/N-GAs	870	1.66	5

*Converted potential vs. RHE

References

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