

Electronic Supplementary Information

Cobalt and nitrogen co-doped porous carbon/carbon nanotubes hybrid carbon frameworks anchored with nickel nanoparticles as a high-performance electrocatalyst for oxygen reduction reaction

Yan Wu ^a, Liya Ge ^a, Andrei Veksha ^a, Grzegorz Lisak ^{a,b,*}

^a Residues and Resource Reclamation Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Clean Tech One, Singapore 637141, Singapore

^b School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

* Corresponding author at: a Residues and Resource Reclamation Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Clean Tech One, Singapore 637141, Singapore

E-mail addresses: g.lisak@ntu.edu.sg (G. Lisak).

Experimental Details

Synthesis of ZIF-67 nanocubes: In a typical synthesis, 2 mL of aqueous solution containing 58 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mg of cetyltrimethylammonium bromide (CTAB) is rapidly injected into 14 mL of aqueous solution with 908 mg of 2-methylimidazole and vigorously stirred at room temperature for 20 min. Then, the precipitate was collected by repeatedly washing with ethanol for at least 6 times before vacuum drying at room temperature overnight.

Synthesis of pristine Co/N-doped porous carbon/carbon nanotubes (Co-NC): The ZIF-67 powder was annealed at 900°C for 2 h with a heating rate of 2 °C/min under a N_2 flow, and cooled down to room temperature naturally. During this process, the organic ligand was carbonized to form porous N-doped graphitic carbon, while the Co^{2+} ions were reduced to Co metals by the derived carbon.

Synthesis of acid-treated Co/N-doped porous carbon/carbon nanotubes (Co-NC): 20 mg of the as prepared pristine Co/N-doped porous carbon/carbon nanotubes was added to 100 mL of 4 M HCl solution. After sonication for 5 min, the mixture was strongly stirred at room temperature for 12 h, washed by ethanol three times (9000 rpm, 10 min), and dried at 70 °C in a vacuum.

Synthesis of NiPc@Co-NC (Ni/Co-NC): 60 mg as-obtained Co-NC was dispersed in 60 mL DMF with the assistance of ultrasonication for 30 min. Then 6 mg of Nickel Phthalocyanine (NiPc) was added to the suspension and followed by ultrasonication for 1 h. The suspension was then stirred at room temperature for 24 h. Subsequently, Ni/Co-NC was collected by centrifugation and washed with DMF for 2 times and ethanol for 2 times, respectively. The

obtained precipitate was dried at 70 °C overnight and then annealed at 900 °C for 1 h with a heating rate of 5 °C/min under a N₂ atmosphere to obtain the final product.

Materials characterization. Transmission electron microscope (TEM) images were obtained using the JEOL 2010 HR & UHR (Japan) operated at an accelerating voltage of 100 kV. The freshly prepared sample was dispersed by ultrasound before characterization. Scanning electron microscope (SEM) images were obtained using the JEOL JSM 6700F (Japan) in different magnifications at an accelerating voltage of 15 kV. The powder X-ray diffraction (XRD) patterns were recorded using Bruker AXS D8 Advance diffractometer operating with the Cu-K α source to investigate the crystal structure of the samples. The X-ray photoelectron spectroscopy (XPS) measurements were conducted with an Axis Ultra DLD spectrometer (Kratos Analytical Ltd., England) with monochromatized Al K α X-ray source ($h\nu = 1486.6$ eV). The Raman spectra were provided by a micro Raman spectrometer (Raman, Renishaw InVia) with 532 nm laser excitation. The Brunauer-Emmett-Teller (Micromeritics 3Flex BET) was used to determine the specific surface area and pore-size distribution of the samples. The NLDFT (Non-Linear Density Functional Theory) equilibrium model was used to calculate pore size distribution and total pore volume. The contents of the Co and Ni were detected with an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 8300, MA, US) after dissolving the samples with a mixture of HCl and HNO₃ (3/1 v/v).

Electrochemical measurements. The electrochemical measurements were conducted in a three-electrode configuration on an electrochemical workstation CHI 660E (CHI Instruments) at room temperature. The catalyst coated on glassy carbon rotating disk electrode (diameter 5 mm) was used as a working electrode. A platinum plate and Ag/AgCl electrode with

saturated KCl solution were employed as the counter and reference electrodes, respectively. All potentials were calculated with respect to the reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{\text{RHE}} = E_{(\text{Ag}/\text{AgCl})} + 0.0591 \times \text{pH} + 0.197 \text{ V}$, at 25 °C). To prepare the working electrode, 5 mg of catalysts and 15 μL of 5 wt% Nafion solutions were dispersed in 1 mL of 3:1 v/v water/isopropanol mixed solvent under sonication to form a homogeneous ink. For ORR test, 10 μL of the catalyst ink was dropped onto the surface of the glass carbon rotating disk electrode and dried at room temperature under air to produce a uniform film with a catalyst loading of 0.25 mg/cm^2 . Commercial 20 wt.% Pt on Vulcan carbon black (Pt/C, Premetek) was used as a reference.

Before each experiment, the working electrode was continuously cycled at least 40 times between 0 and 1.0 V at a scan rate of 100 mV/s until a stable CV was recorded. Rotating disk electrode (RDE) experiments were conducted in O_2 -saturated electrolyte at a scan rate of 5 mV/s and different rotation speeds (400-2025 rpm) controlled by Pine Modulated Speed Rotator (MSR). The electrolyte was saturated with O_2 before each experiment and a gentle flow of O_2 was maintained during the measurement. The electron transfer number (n) during oxygen reduction reaction was calculated at various electrode potential according to the Koutecky-Levich equation,

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.62nFC_0(D_0)^{2/3} \nu^{-1/6}$$

$$J_K = nFKC_0$$

$$J_L = 0.62nFC_0(D_0)^{2/3} \nu^{-1/6} \omega^{1/2}$$

where J represents the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity ($\omega = 2\pi N$, N is the linear rotation speed), n is the overall transferred electron number in oxygen reduction reaction, F is the Faraday

constant ($F = 96485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$) in 0.1 M KOH electrolyte, D_0 is the O_2 diffusion coefficient in 0.1 M KOH electrolyte ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant.

To detect H_2O_2 yield, rotating ring-disk electrode (RRDE) measurements were conducted with the disk electrode at a scan rate of 5 mV/s. The ring potential was set to 1.5 V in 0.1 M KOH to oxidize H_2O_2 transferred from glass carbon disk electrode. The H_2O_2 yield and electron transfer number (n) were calculated by following equations:

$$H_2O_2(\%) = \frac{200 \times I_r}{N \times I_d + I_r}$$

$$n = \frac{4 \times I_d}{I_d + I_r/N}$$

where I_r is ring current, N ($= 0.37$) is ring current collection efficiency, I_d is disk current, and n is electron transfer number, respectively.

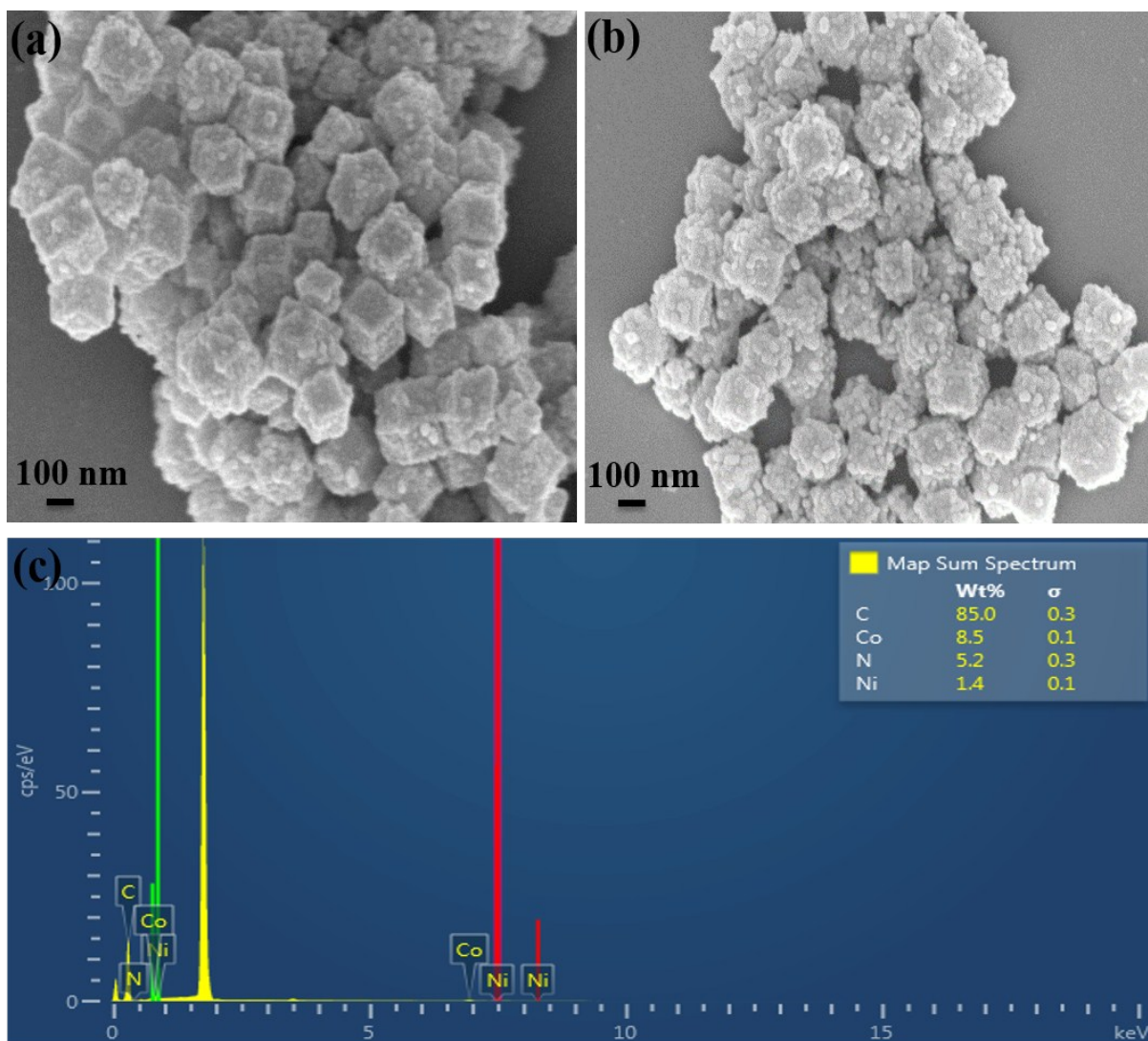


Fig. S1. SEM images of Co-NC (a) and Ni/Co-NC (b), EDS images of Ni/Co-NC(c).

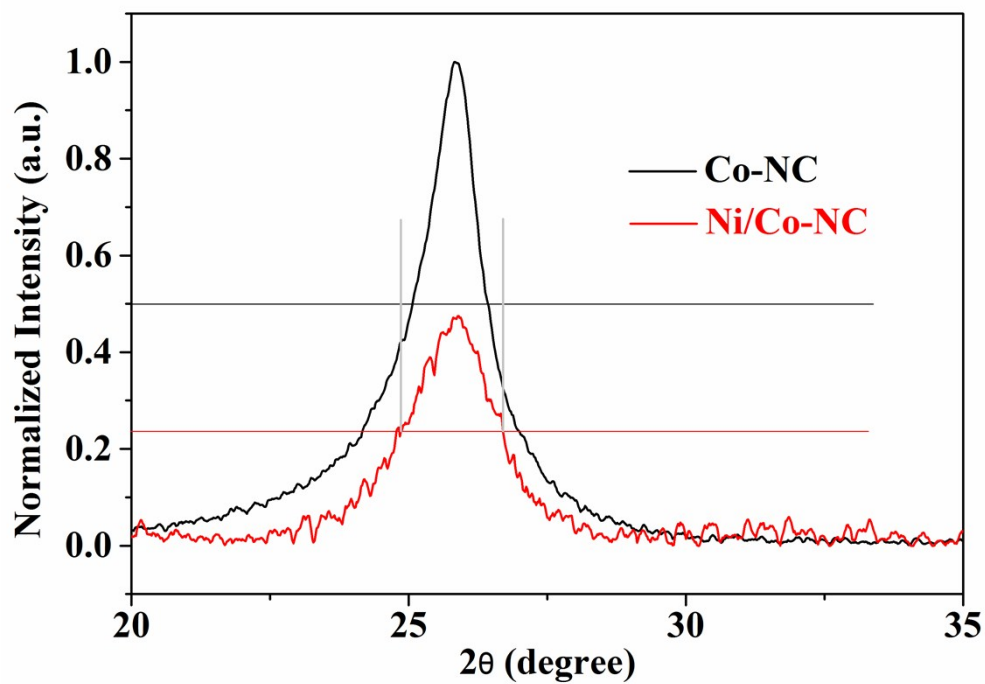


Fig.S2 The XRD of Co-NC and Ni/Co-NC samples

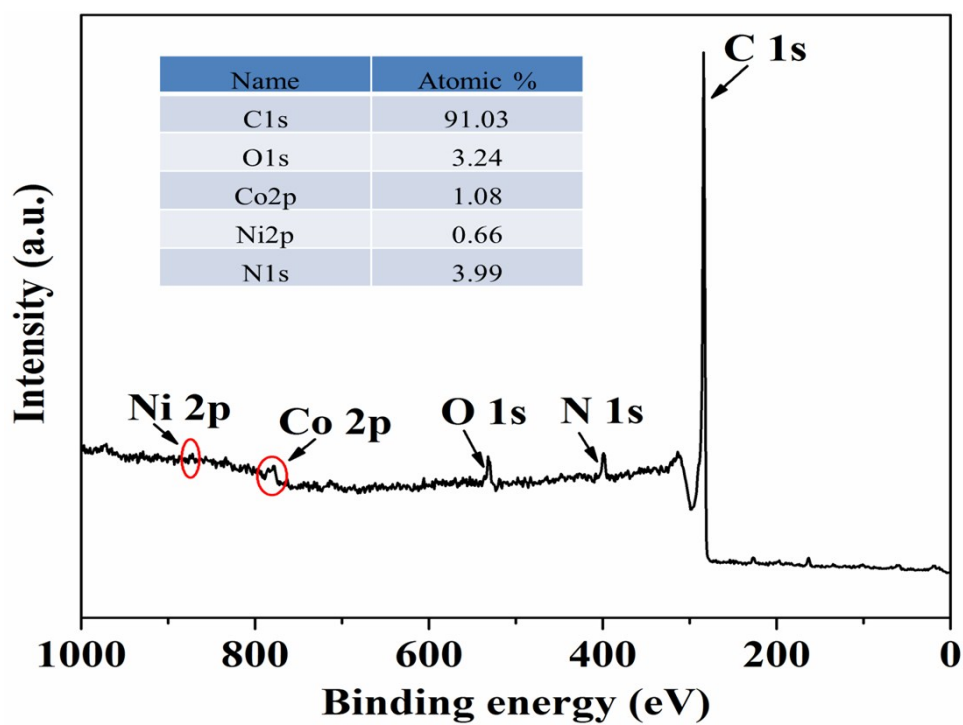


Fig. S3. The total spectrum of the Ni/Co-NC

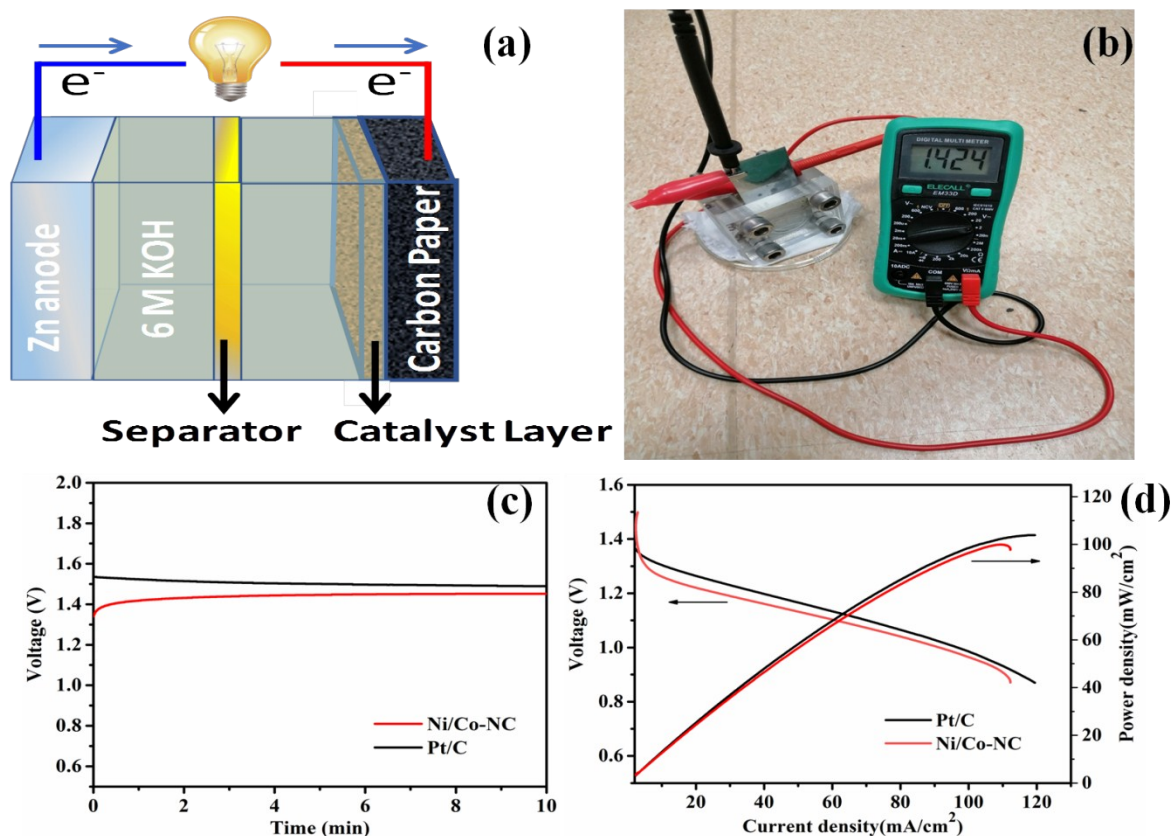


Figure S4. (a) The scheme of the as-assembled two-electrode rechargeable Zn–air batteries; (b) digital image of the as-assembled zinc-air battery to display open-circuit voltage; (c) open circuit voltage curves of Ni/Co-NC and commercial Pt/C catalysts; (d) battery discharge polarization and corresponding power density curves of zinc-air battery using Ni/Co-NC and commercial Pt/C catalysts as cathode.

Table S1 Comparison of the electrocatalytic ORR activity of Ni/Co-NC with other representative non-noble-metal ORR electrocatalysts recently reported in the literatures.

Catalyst	Electrolyte	Loading (mg/cm)	$E_{1/2}$ (V vs. RHE)	Reference
Ni/Co-NC	0.1 M KOH	0.25	0.869	This work
Co-N/CNFs	0.1 M KOH	0.1	0.82	ACS Catal. 2017, 7, 6864-6871.
Fe ₃ C@N-CNT	0.1 M KOH	0.25	0.85	Energy Environ. Sci. 2016, 9,

				3092-3096.
S,N-Fe/N/CCNT	0.1 M KOH	0.6	0.85	Angew. Chem. Int. Ed. 2017, 56, 610.
Mn/C-NO	0.1 M KOH	0.3	0.86	Adv. Mater. 2018, 1801732.
Fe@Aza-PON	0.1 M KOH	N.A.	0.839	J. Am. Chem. Soc. 2018, 140, 1737-1742.
cal-CoZIF-VXC72-H	0.1 M KOH	0.4	0.86	Adv. Mater. 2017, 1701354.
Zn-N-C-1	0.1 M KOH	0.08	0.873	Angew. Chem. Int. Ed. 2019, 58, 7035-7039.
C-MOF-C2-900	0.1 M KOH	N.A.	0.82	Adv. Mater. 2018, 30, 1705431.
CCNTs-Co-800	0.1 M KOH	0.198	0.84	Angew. Chem. Int. Ed. 2018, 57, 13187-13191.
Al and N codoped graphene	0.1 M KOH	0.15	0.86	ACS Catal. 2019, 9, 610-619.
Fe/N/S-PCNT	0.1 M KOH	0.1	0.84	J. Mater. Chem. A, 2019, 7, 1607-1615.
Co-SAs@NC	0.1 M KOH	0.612	0.82	Angew. Chem. Int. Ed. 2019, 58, 5359-5364.
Fe NS-PC-800	0.1 M KOH	N. A.	0.85	Chem. Commun., 2018, 54, 12974-12977.
Co ₃ (PO ₄) ₂ C-N- HA/rGO	0.1 M KOH	0.25	0.837	Energy Environ. Sci., 2016, 9, 2563-2570.