# **Supporting Information**

# Aqueous alkaline pH stable halide perovskite ((PEA)<sub>2</sub>CoCl<sub>4</sub>) for oxygen reaction electrocatalysis

Pranjit Barman,<sup>a</sup> Vijay Kumar,<sup>b</sup> Kotaro Takeyasu,<sup>c</sup> and Santosh K. Singh\*<sup>a</sup>

<sup>a</sup>Electrochemical Energy Research Laboratory, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence (SNIoE) Dadri, Uttar Pradesh, India-201314. E-mail: <u>santoshk.singh@snu.edu</u>.

<sup>b</sup>Center for Informatics, School of Natural Sciences, Shiv Nadar Institution of Eminence (SNIoE) Dadri, Uttar Pradesh -201314, India. and Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122001, Haryana, India.

<sup>c</sup>Institute of Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.

# **1. Experimental Section**

#### **1.1. Chemicals and reagents:**

Graphite powder, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), potassium permanganate (KMnO<sub>4</sub>), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), cobalt(II)chloride hexahydrate (CoCl<sub>2</sub>.6H<sub>2</sub>O<sub>5</sub>), 2-phenylethylamine (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>), hydrochloric acid (HCl), potassium hydroxide (KOH), zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>) were purchased from Sigma Aldrich and used without any further purification. The organic solvents such as ethanol, acetone, and isopropyl alcohol were procured from Fischer Scientific.

#### 1.2. Synthesis of graphene oxide (GO) and N-doped reduced graphene oxide (NrGO):

Improved Hummer's method was used to synthesize GO.<sup>1</sup> In brief, a mortar and pestle were used to thoroughly mix 3 g of graphite powder with 18 g of KMnO<sub>4</sub>, keeping the ratio at 1:6. In an ice-cooled water bath, the mixed powder was gradually added to a solution of  $H_3PO_4$ : $H_2SO_4$  (1:9). Following the complete addition of the mixture, the resultant solution was stirred (550 rpm) for 24 hours at 60 °C. After the completion of the reaction, the reaction mixture was carefully collected and gradually added to the water containing 3%  $H_2O_2$ . The light-yellow solution was repeatedly centrifuged at 12,000 rpm and then thoroughly washed with water. Subsequently, 30% HCl was added to the solution to remove unreacted metal impurities. After several times washing with DI water, graphene oxide sheets were obtained after washing with ethanol and acetone and then dried at room temperature. The GO obtained sheets were collected and ground well to make powder by using a mortar pestle.

The NrGO was synthesized by calcining the obtained graphene oxide under an ammonia environment at 900  $^{0}$ C for 3 hrs. in a tubular furnace with a heating rate of 10  $^{0}$ C/min.<sup>2</sup>

**1.3.** Synthesis of (PEA)<sub>2</sub>CoCl<sub>4</sub> perovskite (PCo) and NrGO coated (PEA)<sub>2</sub>CoCl<sub>4</sub> perovskite (NPCo): PCo single crystal has grown by solubilizing the metal and organic precursors at 120 °C and then cooling down to promote the precipitation.<sup>3</sup> In brief, the phenylethylammonium chloride (PEACl) crystal was synthesized first by adding 252  $\mu$ l of 2-phenylethylamine into a solution of 164  $\mu$ l of HCl and 3 ml of ethanol. A 1 mmol of obtained PEACl and 0.5 mmol of CoCl<sub>2</sub>.6H<sub>2</sub>O were mixed well, and the solution was stirred at 120 °C for 30 min and then transferred to room temperature to allow the growth of single

crystals. The single crystals were washed several times with diethyl ether and dried for further analysis.

In situ synthesis of NrGO coated (PEA)<sub>2</sub>CoCl<sub>4</sub> perovskite obtained by first NrGO dispersed homogeneously in DMF solution. DMF is used because of its high solvating ability, effectively dissolves perovskite precursors, and facilitates the nucleation and growth of well-ordered perovskite. Then, 1 mmol of PEACl and 0.5 mmol of CoCl<sub>2</sub>.6H<sub>2</sub>O as a metal precursor were mixed with 100  $\mu$ l of HCl solution and slowly added to the dispersed NrGO solution. The final solution was stirred at 120 <sup>o</sup>C for 1 h. The solid powder was obtained after filtering the solution and washed several times with diethyl ether.

#### **1.4.** Characterization techniques

Powder X-ray diffraction (XRD) analysis was done using a Rigaku SmartLab 3 kW with Cu-K $\alpha$  source ( $\lambda = 1.54$  Å) at 40 kV and 200 mA at the scan rate of 5°/min to acquire the crystal phases. Infrared spectroscopy was performed by using Nicolet<sup>™</sup> iS50 FTIR spectrometer. The Raman spectroscopy was carried out with a Horiba Jouen Raman spectrometer (STR500 Airix microscope using a 532 nm laser at a power of 3 mW. Ultraviolet spectroscopy (UV) was performed using a Shimadzu spectrophotometer (UV vis 3700) at a resolution of 0.1 nm. Photoluminescence (PL) spectroscopy used a cryostat (JANIS CS204SE-FMX-1AL). The surface chemical states and compositions of all the materials were investigated by X-ray photoelectron spectroscopy (ESCALAB-250Xi model equipped with Al-Ka monochromatic X-ray source (20 mA, 15 kV) operated under ultrahigh vacuum (7 x 10-9 mbar) at room temperature with the spot size of 650  $\mu$ m). All the XPS data were analyzed using CASAXPS software. The reference C1s signal at 284.8 eV was used to correct all the reported binding energies. Thermogravimetric analysis (TGA) was performed by using a built-in gas controller (TGA2 SF/1100) fitted with an XP1U TGA balance (ultra-microbalance) under a 50 ml min<sup>-1</sup> flow rate of air and zero nitrogen in the temperature range of 35–800 °C at a heating rate of 10 °C min<sup>-1</sup>. The morphology of the prepared materials was analyzed using scanning electron microscopy (SEM) equipped with energy-dispersive X-ray (EDX) analysis. SEM and EDAX were performed using the Jeol JSM-7610Plus model instrument with an electron acceleration voltage detector of 15 kV. Moreover, the transmission electron microscopy analysis was conducted using a Technai instrument with an electron gum power of 20 kV. The obtained TEM images were further analyzed using Gatan Digital Micrograph software. Oxford MFP-3D origin, Asylum research AFM Instrument in the tapping mode with the applied potential of 600 mV was

used for AFM analysis of the materials. Four probe conductivity measurements were carried out by the Ossila four-point probe system(T2001A3). All the electrochemical analyses were conducted using an SP-300/240 model of biologic potentiostat and an ALS-3A RRDE setup. The Brunauer–Emmett–Teller (BET) surface area is measured by using Microtrac (MRB) and Belsorp Max G instruments.

#### 1.5. Analysis of Single Crystal X-ray Measurements

A very good quality single crystal was taken for data collection under a polarizable microscope. The high-resolution X-ray diffraction data was collected using a Bruker D8 Venture diffractometer using monochromatic Cu  $K\alpha$  radiation ( $\lambda = 1.54178$  Å) at 100K using an Oxford Cryostream device. The crystal-to-detector distance was set to 50 mm. Unit cell parameters measurements, data integration, scaling, and crystal absorption corrections were performed with Bruker *APEX4* suite. The crystal structure refinement was done in the program package *OLEX2*,<sup>4</sup> and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations based on *F*2 with *SHELXL*-2018.<sup>5</sup> MERCURY<sup>6</sup> program was used for structural analysis and preparation of molecular and crystal structure drawings.<sup>6</sup> All the details of crystal data collection and data refinement are given in **Table S1**.

#### 1.6. Stability test of PCo

For the stability of PCo in KOH solution, the crystals are first dispersed in KOH solution and water, respectively. The crystals are dispersed in the KOH solution, where PCo got degraded in water after some time. The dispersity and color of PCo in KOH solution indicate that PCo is s not as degraded as in water solution, as shown in **Figure S2**. Further, to characterize whether the structure degradation happens or not, the KOH solution containing PCo must be filtered and dried properly. Since the single crystals were not recovered, the single-crystal XRD data could not be collected. However, IR, Powder XRD, UV and PL indicate the structural integrity of PCo after recovery from the KOH solution.

#### 2.0 Electrochemical Measurement

#### 2.1. Working electrode preparation

The working electrode was prepared by coating the catalyst slurry on the polished glassy carbon electrode. The amount of NPCo for the coating on the glassy carbon electrode was  $1.01 \text{ mg cm}^{-2}$ . In the controls, Pt/C and RuO<sub>2</sub> catalysts coated electrodes were constructed similarly with a mass loading of 0.5 mg cm<sup>-2</sup>. Typically, catalyst slurry was prepared by

dispersing 5 mg of material in 960  $\mu$ l IPA solution and adding 40  $\mu$ L Nafion® solution (5%). There is no water use while making the catalyst slurry, as the pristine perovskite(PCo) is unstable in normal water. A homogeneously dispersed solution was obtained after the mixture was ultrasonicated for 4 min, followed by bath sonication for 30 min. To avoid contamination, the 3 mm glassy carbon electrode was properly polished using a polishing pad before coating the catalysts. A 30  $\mu$ L of the catalyst slurry was coated and dried under an IR lamp to use it as a working electrode

#### 2.2. Hg/HgO reference electrode calibration and conversion to RHE

The calibration of Hg/HgO was carried out using a standard three-electrode system where the Pt RDE electrode was used as a working electrode (WE), and Pt wire was used as a counter electrode (CE). Hg/HgO was used as a reference electrode (RE) under H<sub>2</sub>-saturated 0.1 M KOH solution as an electrolyte. The linear sweep voltammogram (LSV) was recorded at a scan rate of 0.50 mV/s under the rotation of 1600 RPM. The thermodynamic potential for the hydrogen electrode reactions was taken when the current crossed the zero point during the LSV measurement. The potential at the zero current for Hg/HgO was measured at - 0.8737 V. Hence, considering these experimentally observed values, the conversion of Hg/HgO to RHE (E <sub>vs. RHE</sub>) was done for all the cases in this work. The following equation is used for the conversion of Hg/HgO reference electrode potential to RHE:

$$E_{vs. RHE} = E_{vs. Hg/Hgo} + 0.8737 \tag{1}$$

#### 2.3. Electrocatalytic activity analysis

All the electrochemical analyses (CV, LSV and RRDE) were carried out using a BioLogic SP-300 potentiostat in a conventional three-electrode test cell. A Hg/HgO electrode and platinum wire were used as reference and counter electrodes. All the ORR and OER activity were performed in an alkaline 0.1 M KOH electrolyte solution. All reported potentials have been converted to the reversible hydrogen electrode (RHE) using  $E_{RHE} = E_{Hg/HgO} + 0.0591$ pH + $E^{o}_{Hg/HgO}$ , if otherwise mentioned. The CV and LSV for the OER and ORR measurements were performed using a glassy carbon (RDE) working electrode with an area of 0.07065 cm<sup>2</sup>. For Oxygen evolution reaction (OER) measurements, the cyclic voltammogram (CV) was obtained under N<sub>2</sub>-saturated conditions. Linear sweep voltammetry (LSV) results were corrected by 85% iR compensation to investigate the OER. A rotating ring disc electrode (RRDE) experiment with a rotation of 900 RPM was carried out to calculate the faradaic efficiency at different potentials during the OER process. The electrochemically active

surface area (ECSA) was evaluated by CV at different scan rates (i.e., 20, 30, 40,50, 60, 80, and 100 mV s<sup>-1</sup>) in the potential window of 0.972-1.072 V and ensuring that there is no Faraday current in this voltage window. The average value of the anode current or cathode current is taken as the double-layer capacitor current, *j*, and the j curve relative to the scanning rate v is drawn. *j* follows the ideal linear behavior of the ideal capacitor. If j = vCdl, then the slope of the line is the double-layer capacitance Cdl. Cdl was measured from the plot of the current density at 1.02 V against the scan rate. The stability measurements for OER were performed using both CV and chronoamperometry tests.

For Oxygen reduction reaction (ORR) measurements, the cyclic voltammetry (CV) measurements were carried out in a N<sub>2</sub>- or O<sub>2</sub>-saturated 0.1 M KOH solution with a scan rate of 50 mV s<sup>-1</sup>. Linear sweep voltammetry (LSV) was performed in the O<sub>2</sub>-saturated 0.1 M KOH electrolyte with a rotation rate of 1600 rpm and a scan rate of 10 mV s<sup>-1</sup>. The electrolyte solution was initially bubbled with oxygen for at least 30 min before each experiment during the whole test. During the RRDE analysis, the H<sub>2</sub>O<sub>2</sub> produced was monitored by its oxidation, while the disc electrode was subjected to variable ORR potential. the disk electrode was scanned at a rate of 5 mV s<sup>-1</sup>, and a constant potential of 1.26 V vs. RHE was maintained at the ring (Pt) electrode to oxidize the H<sub>2</sub>O<sub>2</sub> during the RRDE analysis. The RRDE electrode was kept under rotation at 1600 RPM.

Moreover, the yield of hydrogen peroxide percentage  $(H_2O_2\%)$  and the electron transfer number (n) were determined by the following equations :

$$H_2 O_2 (\%) = \frac{200 I_r / N}{(I_d + \frac{I_r}{N})}$$
(2)

$$n = \frac{4I_d}{(I_d + \frac{I_r}{N})} \tag{3}$$

Where  $I_d$  and  $I_r$  are the voltammetric currents of the disk and ring, respectively. N = 0.37 is the collection efficiency of the Pt ring.

All of the experiments were performed at room temperature if not stated otherwise. All the electrochemical tests were carried out at least three times to avoid the contingency of the experimental data.

#### 2.4. Fabrication and test of solid-state ZAB device

A homemade 3D-printed rechargeable Zn-air battery was assembled by using zinc foil (0.2 mm thickness) as the anode, a PVA-KOH-Zn(CH<sub>3</sub>COO)<sub>2</sub> as the gel electrolyte membrane, and an NPCo catalyst slurry coated over carbon paper as the air cathode. Typically, the air

cathode was prepared by casting the catalyst ink containing 10 mg of the NPCo powder, 0.97 mL of isopropyl alcohol, and 40  $\mu$ L of Nafion® solution. The prepared slurry was coated on pre-cleaned carbon paper (GDL) and then dried at 60 <sup>o</sup>C for further application. A piece of Ni-foam was used as a current collector at the cathode site. The loading of the cathode was 1 mg cm<sup>-2</sup>. For comparison, Pt/C (40 wt%) + RuO<sub>2</sub> (1:1) air electrode was fabricated similarly with the same mass loading. A PVA-KOH- Zn(CH<sub>3</sub>COO)<sub>2</sub> was fabricated and used as the quasi-solid electrolyte and separator.<sup>7</sup> The gel electrolyte membrane was synthesized by taking 1g PVA powder into 10 ml H<sub>2</sub>O at room temperature under stirring for 45 min and heating up to 95 0C until the solution transformed into a transparent gel. 1 ml 6 M KOH was added to the transparent solution. The gel was poured onto a petri dish after stirring for 30 min and frozen in a freezer.

Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range from 0.01 Hz to 100 kHz upon an AC voltage amplitude of 5 mV. To get the power density of the ZAB battery, the polarization curves of the charge and discharge processes were evaluated by LSV at a sweep rate of 5 mV s<sup>-1</sup>. The galvanodynamic charge-discharge cycling test was conducted at the current density of 5 mA cm<sup>-2</sup> to test the rechargeability of the fabricated battery. Each cycle contains a charge process for 10 min and another discharge process for 10 min maintained during the cycling test. The Steady-state polarization curve and impedance analysis of Zn air batteries were tested in an ambient atmosphere using a BioLogic SP-300 electrochemical workstation (BioLogic Science Instruments SAS, France). Moreover, all the other electrochemical battery testing was done using the Neware Battery Testing System (Neware Technology Limited, China).

#### 2.5. Fabrication and test of flexible ZAB device

The flexible Zn-air battery device is fabricated by using NPCo catalyst coated over carbon cloth as an air cathode, thin and flexible Zn foil as an anode, and a synthesized PVA-KOH- $Zn(CH3COOH)_2$  gel membrane as an electrolyte and separator. The flexibility test was done by bending the battery device at different angles (0<sup>0</sup>, 90<sup>0</sup>, and 180<sup>0</sup>), and the charge-discharge data was recorded at 3 mA cm<sup>-2</sup>.

## 3.0 Computational methodology

We performed ab initio calculations using the Vienna Ab initio Simulation Package (VASP)<sup>8</sup> and projector augmented wave (PAW)<sup>9</sup> pseudopotentials to describe electron-ion interactions.<sup>10, 11</sup> The exchange-correlation energy was treated using a generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE). Bulk (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>[CoCl<sub>4</sub>],

is a layered organometallic compound in which  $CoCl_4^-$  tetrahedral groups are isolated. They are connected to the organic cations phenylethyl ammonium (PEA) by N—H···Cl hydrogen bonds via the NH<sub>3</sub>-groups. Therefore, to treat the weak interactions in the compound and systems with water and graphene, we used Grimme's D3 method within the density functional theory (DFT+D3). A set of 3X3X1 k points represented the Brillouin zone.<sup>12-14</sup> The total energy was converged with a tolerance of 10-5 eV while the ionic positions were relaxed until the absolute value of each force component on each ion became less than 0.001 eV/Å. First, we optimized the bulk perovskite, and the calculated lattice parameters are 7.320/23.771/11.167, which compares well with the experimental values.

Next, we constructed a supercell by considering a bilayer slab of the perovskite containing four CoCl<sub>4</sub> and eight PEA cation molecules. We kept the b and c lattice parameters the same as for the bulk perovskite, introduced a vacuum space of about 16 Å along the direction, and added 92 water molecules in the vacuum space arbitrarily. The Brillouin zone integrations were performed for the supercell by considering a 3x3x1 k-points mesh. Furthermore, we added a KOH molecule in water to treat an alkaline medium. The whole system was relaxed so that the orientations of the water molecules improved, but these were not fully optimized. Subsequently, we performed ab initio molecular dynamics at 300 K for 5ps.

In order to show the effect of introducing graphene layers to protect the perovskite from water, we inserted a graphene fragment with edges truncated with hydrogen atoms so that it covered the surface of the perovskite layer well. Again, we performed ab initio MD simulations, and the water molecules remain well separated from the perovskite layer with large values of the bond lengths. Also, it is to be noted that the graphene fragment becomes quite distorted during the simulation, but water remains well separated from the perovskite layer. Further calculations were performed by considering a nitrogen-doped graphene. In this case, we removed a carbon dimer and replaced four carbon atoms around this hole with nitrogen atoms, which were terminated with H atoms. Again, the simulation and the bond length variation are shown. In this case, some hydrogen atoms point towards the graphene, and the N-O bond length, as discussed above, becomes shorter while the other bond lengths remain significant. Accordingly, using such a nitrogen-doped graphene can control the amount of water that can interact with the perovskite layer.

# 4.0 Results and Discussion

# 4.1. Structural data of PCo from single crystal XRD analysis:

Table S1: Single crystal XRD data and structural refinement parameters of compound (PEA)<sub>2</sub>CoCl<sub>4</sub> (PCo)

Structural parameter	(PEA)2CoCl4
CCDC No.	797110
Empirical formula	$(C_8H_{12}N)_2CoCl_4$
Formula weight	445.12
T(K)	273.15
$\lambda$ (Mo Ka) (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/c
a (Å)	7.45380
b (Å)	24.6491
c (Å)	11.18770
α (deg.)	90
β (deg.)	91.786
γ (deg.)	90
V (Å)	2054.5116
Z	12
D (g cm-3 )	1.756
μ (mm-1 )	2.44
F (000)	1109
$\theta$ range (deg.)	2.46 to 28.16
Reflections collected	5099
Unique data	3656
R indexes [ $I > 2 \zeta$ (I)]	R1 = 0.0628
	wR2 = 0.1350
R indexes (all data)	R1 = 0.0923
	wR2 = 0.1660
GOF on F2	1.027

# 4.2. Single crystal structure of the (PEA)<sub>2</sub>CoCl<sub>4</sub>:



**Fig. S1:** (A) Schematic presentation of  $(PEA)_2CoCl_4$  crystal structure drawn using VESTA software using the crystallographic data; (B) Illustrations of hydrogen bonding interactions  $(N-H\cdots Cl)$ .

**Discussion:** The bulk crystal of  $(PEA)_2CoCl_4$  consists of single tetrahedra  $(CoCl_4)$  layers separated by one layer of organic PEA<sup>+</sup> cations. The tetrahedra layers are separated by 12.28 A<sup>0</sup> from each other. The N atom of the PEA<sup>+</sup> cation makes hydrogen bonding with the Cl atom of the CoCl<sub>4</sub><sup>-</sup> tetrahedra framework.

4.3. Chemical stability of the (PEA)<sub>2</sub>CoCl<sub>4</sub>:



Fig. S2: Digital photographs of PCo (A) in KOH solution and; (B) in water solution.

#### 4.4. Powder XRD analysis of materials:



**Fig. S3:** PXRD patterns of PCo, NrGO, and NPCo showing the diffraction peaks where NPCo exhibits a sharp peak at 26.5° corresponding to the (002) graphitic plane of NrGO and multiple peaks (e.g., 32.1° and 40.5°) confirming the crystalline perovskite structure of PCo.

#### 4.5. Raman spectra analysis of the materials:



**Fig. S4:** Raman spectra of PCo, NrGO, and NPCo displaying characteristic D (~1350 cm<sup>-1</sup>) and G (~1600 cm<sup>-1</sup>) bands. NPCo shows an enhanced D/G intensity ratio of ~1.2, indicating defect introduction due to NrGO incorporation.

#### 4.6. Thermogravimetric analysis:



**Fig. S5:** TGA analysis of NrGO, PCo, NPCo(phy), and NPCo under air atmosphere where NPCo exhibits ~30% cobalt oxide residue, confirming higher cobalt content compared to NPCo(phy) (~25%). The decomposition starts at ~200 °C and stabilizes around 600 °C.

4.7. Survey scan X-ray photoelectron spectroscopy analysis:



**Fig. S6:** XPS survey spectra of PCo, NrGO, NPCo(phy), and NPCo, showing peaks corresponding to C1s, N1s, O1s, and Co2p. NPCo exhibits higher Co2p intensity than NPCo(phy), indicating better cobalt dispersion.

# 4.8. C1s X-ray photoelectron spectroscopy analysis:



**Fig. S7:** C1s XPS spectra of PCo, NrGO, NPCo(phy) and NPCo showing no shift in binding energy.

#### 4.9. Deconvoluted Cl 2p X-ray photoelectron spectroscopy analysis:



**Fig. S8:** Deconvoluted Cl 2p and O 1s spectra of PCo, NPCo(phy), and NPCo show the shifting of binding energy of (A) Cl 2p and (B) O 1s spectra after incorporating NrGO.

**Discussion:** The shifting of Cl  $2p_{3/2}$  and Cl  $2p_{1/2}$  peaks from higher in PCo to lower in NPCo and NPCo(phy) indicates the interaction of the Cl atom with the NrGO. After incorporating NrGO, the distances between CoCl<sub>4</sub> <sup>tetrahedra increase, which, as a result, enhances the electron density of Cl, and the <sup>binding energy has shifted to a</sup> lower energy. Similarly, O 1s peak also shift towards lower binding energy after incorporating NrGO in the case of NPCo, indicating the electron transfer from PCo to oxy functional groups of NrGO.</sup>

# 4.10. FTIR analysis:



**Fig. S9:** FTIR spectra showing the stretching frequencies of the of PCo, NrGO, and NPCo catalysts.

#### **(B)** (C) $(\mathbf{A})$ Element overlay Carbon(C) **(D) (E) (F)** Nitrogen(N) Cobalt(Co) Chlorine(Cl) 1.70K (G) Element Weight % 1.53K С 29.87 52.93 13.26 1.36K 1.19K Ν 9.51 14.45 19.49 1.02K Cl 44.87 26.93 3.47 0.85K 15.75 5.69 18.74 Co 0.68K 0.51K CI K C 0.34K 0.17 Co K Co K 0.00K 1.00 4.00 5.00 7.00 2.00 3.00 6.00 8.00 9.00

### 4.11. FESEM and elemental analysis of (PEA)<sub>2</sub>CoCl<sub>4</sub>

**Fig. S10:** (A) FESEM image and EDAX mapping of PCo catalyst; (B) element overlay of PCo C catalyst; (C-F) elemental mapping of C, N, Cl, and Co in the NPCo catalyst; (G) EDX spectra of PCo showing the elemental composition.

# 4.12. FESEM and elemental analysis of NPCo and NPCo(phy):



Fig. S11: SEM images of (A) NPCo(phy); (B) NPCo and; (C) EDX analysis showing the elemental composition of NPCo.

#### 4.13. TEM analysis of NPCo:



**Fig. S12:** (A) Transmission electron microscopy (TEM) images NPCo catalyst at different magnifications showing NrGO coated PCo and their interface; (B) TEM image at higher magnification; (C) line profile of the fringes observed in (B) showing the fringe width.

# 4.14. BET surface area analysis



**Fig. S13:** Nitrogen adsorption/desorption isotherms at 77 K of (A) PCo and (B) NPCo, BET surface area (inset) with pore size distributions of (C) PCo and (D) NPCo.

# 4.15. Electrochemical calibration of Hg/HgO electrode:



**Fig. S14:** The LSV was recorded under an H<sub>2</sub>-saturated electrolyte solution to calibrate the Hg/HgO reference electrode.



4.16. Cyclic voltammogram in the non-Faradaic potential region:

**Fig. S15:** Cyclic voltammogram (CV) of (A) NPCo; (B) NPCo(phy); (C) NrGO and; (D) PCo recorded under 0.1 M KOH electrolyte solution at various scan rates (20, 30, 40, 50, 60, 80 and 100 mV s<sup>-1</sup>) in the non-faradaic potential region to calculate electrochemical surface area (ECSA).

4.17. Cyclic voltammogram and electrical double-layer capacitance calculation in the non-Faradaic potential region:



**Fig. S16:** Plots of (A) CV of Pt/C at different scan rates (10, 20, 40, 60, 80 and 100 mV s<sup>-1</sup>) in the non-faradaic potential region measured in 0.1 M KOH electrolyte solution; (B) The plot between the peak current density and scan rate shows the slope of the curve directly proportional to the ECSA.

4.18. Cyclic voltammogram and electrical double-layer capacitance calculation in the non-Faradaic potential region:



**Fig. S17:** Plots of (A) CV of RuO<sub>2</sub> at different scan rates (10, 20, 40, 60, 80, and 100 mV s<sup>-1</sup>) in the non-faradaic potential region measured in 0.1 M KOH electrolyte solution; (B) The plot between the peak current density and scan rate shows the slope of the curve directly proportional to the ECSA.



4.19. RRDE analysis showing the ring and disc current:

**Fig. S18:** RRDE analysis of PCo, NrGO, NPCo(phy), and NPCo recorded at 1600 RPM in 0.1 M KOH solution, showing the generated H<sub>2</sub>O<sub>2</sub> yield and electron transfer number.

# **4.20.** Durability analysis of the catalysts:



**Fig. S19:** (A) Durability of NPCo catalyst for 3000 CV cycle; (B) durability comparison of PCo, NPCo and NPCo(phy) catalysts for OER performance.

# 4.21. Catalyst loading-dependent ORR activity evaluation:



**Fig. S20:** Linear sweep voltammogram of the NPCo catalyst with different loading amounts with the same experiment conditions (0.1M KOH, 1600 RPM).

# 4.22. Bifunctional ORR and OER activity evaluation:



**Fig. S21:** Comparison of bifunctional OER+ORR linear sweep voltammogram (LSV) for all the catalysts PCo, NrGO, NPCo(phy) with state-of-the-art catalysts.

# 4.23. Comprehensive electrocatalytic activity of NPCo:



**Fig. S22:** Comprehensive comparison of OER and ORR performance of all the catalysts in terms of OER onset potential ( $E_{j=10}$ ), ORR halfwave potential( $E_{1/2}$ ), and  $\Delta E$ .

# 4.24. Post-electrochemical powder XRD analysis:



**Fig. S23:** XRD patterns of as-synthesized NPCo, NPCo after electrocatalytic OER performance, and NPCo after electrocatalytic ORR performance.

# 4.25. Post-electrochemical EPR analysis:



**Fig. S24:** Comparative EPR spectra of NPCo catalyst as synthesized, NPCo after OER, and NPCo after ORR.

# 4.26. Post-electrochemical powder XRD analysis:



**Fig. S25:** Raman spectra of as-synthesized NPCo, NPCo after electrocatalytic OER performance, and NPCo after electrocatalytic ORR performance.

# 4.27. Post-electrochemical FESEM image of the PCo catalyst:



**Fig. S26:** SEM images of NPCo after OER performance show the changes in the morphology of NPCo catalyst, having all the elements in the structure.

# 4.28. Post-electrochemical FESEM image of the NPCo catalyst:



**Fig. S27:** SEM images of NPCo after ORR performance show the changes in the morphology of NPCo catalyst having all the elements in the structure.

# 4.29. Quasi-solid-state Zn-air battery showing the OCV:



**Fig. S28:** Open circuit voltage (OCV) of 3D printed quasi-solid state Zn air battery using NPCo as air cathode with Zn as anode and PVA+KOH membrane.





**Fig. S29:** Discharge-specific capacity curves at a discharge current density of 10 mA cm<sup>-2</sup>, 20 mA cm<sup>-2</sup>, and 50 mA cm<sup>-2</sup> show that even at higher current density, the NPCo air cathode shows a high specific capacity comparable to the commercial catalysts.



4.31. Charge-discharge profile of the Zn-air battery at different current densities:

**Fig. S30:** The charge/discharge cycling stability of NPCo air cathode from low to high current densities (3, 6, 8, 10 mA cm<sup>-2</sup>) and high to low current density.

**Discussion:** The charge/discharge cycling stabilities of NPCo-based ZAB were also measured without updating the electrolyte. Significantly, ZAB based on NPCo also exhibited excellent cycling stability, with the voltage gap increasing by only 76 mV ( $\approx$ 10% relative to the initial) and a high round-trip efficiency of 59% after continuous operation for over 60 h. This result confirms that the prepared NPCo catalysts with highly coordinated structures have good potential for practical applications.

4.32. Discharge profile of the Zn-air battery fabricated by using PCo as cathode electrode:



**Fig. S31:** Discharge-specific PCo air cathode capacity curves at a discharge current density of 3 mA cm<sup>-2</sup> and, 5 mA cm<sup>-2</sup>.

**4.33.** Overall performance of the flexible zinc-air battery fabricated by using NPCo catalyst:



**Fig. S32:** (A) Measured open circuit voltage (OCV) of flexible Zn air battery using NPCo as air cathode with Zn as anode and PVA+KOH membrane. (B) The same OCV at different bending angles shows the flexibility of the device for practical uses.



**Fig. S33:** Nyquist plots under different bending angles 0°, 90° and 180° showing similar charge transfer and interfacial resistances in different bending conditions.

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