

## Br/Co/N Co-doped porous carbon frameworks with enriched defects for high-performance electrocatalysis

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### EXPERIMENTAL SECTION

Chemicals and Reagents: Cobalt Nitrate Hexahydrate  $\text{Co}(\text{NO}_3)_2$ , Nickel Nitrate Hexahydrate  $\text{Ni}(\text{NO}_3)_2$ , 2-methylimidazole (2-Melm) were bought from Aladdin. Pt/C (Pt nominally 20% on high surface area carbon support) was purchased from Alfa Aesar. N, N-Dimethylformamide (DMF) and Methanol (Anhydrous) were obtained from Xilong scientific Corporation. Dimethyldioctadecylammonium bromide was purchased from Sigma-Aldrich. Nafion solution (5 wt. % in lower aliphatic alcohols and water) was obtained from Sigma-Aldrich. All the reagents were used as received without any further purification. All solutions used for electrochemical measurements were prepared in milliQ water.

**Synthesis of ZIF-67:** ZIF-67 was synthesized through solvothermal process. Typically, a solution of fixed moles of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was prepared using anhydrous methanol to which a solution of 2-Methylimidazole was added. The colour of the solution changed from light pink to purple, which was stirred for four hours. The resulting purple powered ZIF-67 was obtained followed by successive centrifugation at 10,000 rpm and washed with anhydrous methanol to remove unreacted metal impurities followed by drying in vacuum oven at 60°C.

**Synthesis of Co@NC:** ZIF-67 was pyrolyzed at 750°C to get Co@NC and the obtained product was leached through 2M HCl for a day to remove unreacted contents and then further washed by water three times followed by drying under vacuum at 60 °C and denoted as Co@NC.

**Room Temperature Synthesis of DODAB Modified ZIF-67** Surfactant modified ZIF-67 was synthesized using a fixed molar solution of Co (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and dimethyldioctadecylammonium bromide in anhydrous methanol, followed by addition of to which a solution of 2-Methylimidazole was added. The colour of the solution changed from orange pink to dark. The resulting homogenous stirred at room temperature for four hours. DODAB Modified ZIF-67 was collected through centrifuge at 10,000 rpm the obtained followed by washing with anhydrous methanol and dried in vacuum dried at 60°C.

**Synthesis of BrRT@CoNC:** DODAB Modified ZIF-67 was subjected to a controlled pyrolysis in Ar at 750 °C for two hours. The obtained product was leached through 2M HCl for a day to remove unreacted contents and subsequently washed by water three times and finally dried under vacuum at 60° C and was denoted as BrRT@CoNC.

**Solvothermal Synthesis of DODAB Modified ZIF-67** Surfactant modified ZIF-67 was synthesized using a fixed molar solution of Co (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and dimethyldioctadecylammonium bromide in anhydrous methanol, followed by addition of to which a solution of 2-Methylimidazole was added. The colour of the solution changed from orange pink to dark. The colour of the solution changed from orange pink to dark purple which was transferred to steel lined Teflon cup and heated set temperature of 180°C for 12 hours. The obtained product was separated by was centrifugation at 10,000 rpm followed by washing with anhydrous methanol and dried in vacuum dried at 60°C.

**Synthesis of BrHT@CoNC:** Solvo-thermally synthesized DODAB Modified ZIF-67 was pyrolyzed in Ar at 750 °C for two hours. The obtained product was leached through 2M HCl for a day to remove unreacted contents and subsequently washed by water three times and finally dried under vacuum at 60° C and was denoted as BrHT@CoNC.

### **Evaluation of Electrocatalytic Performance**

All the electrochemical tests were experimented in three electrode system at room temperature using electrocatalytic CHI 760e, electrochemical workstation. The catalyst inks were prepared by using fixed amount of catalyst in DMF and 0.5% nafion solution followed by ultrasonication for 30 minutes to obtain homogenous catalyst ink. All potentials used were calibrated to reversible hydrogen electrode. All LSV curves were corrected by ohmic compensation, and all current densities were calculated to the geometrical area of electrode.

For ORR the catalyst ink was dropped on a polished glassy carbon rotating ring disk electrode (RRDE) with a catalyst loading of 0.3 mg cm<sup>-2</sup> and dried at ambient conditions. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed using the prepared glassy carbon electrode as working electrode while Ag/AgCl (saturated with 3M KCl) and Platinum wire as reference and counter electrode respectively. 0.1M KOH was used as electrolyte. For electrochemical performance in acid (0.1 M HClO<sub>4</sub>) the reference electrode was replaced by Hg calomel electrode. The cyclic voltammetry and RRDE were performed in both Ar and O<sub>2</sub> saturated electrolyte while ring disk electrode (RDE) measurements were recorded under O<sub>2</sub> saturated electrolyte at a scan rate of 10 mV s<sup>-1</sup>.

Calculation of electron transfer number n

RDE measurements were used to calculate the electron transfer number (n) by using Koutechy-Levich (K-L) equation at various potentials.

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

Where j is the measured current density (mA/cm<sup>2</sup>), j<sub>k</sub> represents the kinetic current density (mA/cm<sup>2</sup>) and j<sub>L</sub> is diffusion-limiting current density (mA/cm<sup>2</sup>), ω represents the rotating rate of the disk electrode. B is the slope of the Koutechy-Levich equation. The K-L data was plotted by linearly among reciprocal of rotating speeds and reciprocal of current density. Slope B was determined directly by linear fitting of K-L plots. The transfer number of electrons was then determined by using the equation

$$B = 0.2nF (D_{O_2})^{3/2} \nu^{-1/6} C_{O_2} \quad (2)$$

Where n accounts for the number of electrons transferred during the process of oxygen reduction, F represents the Faraday constant, C<sub>O<sub>2</sub></sub> is the bulk concentration of O<sub>2</sub>, D<sub>O<sub>2</sub></sub> represents the diffusion coefficient of O<sub>2</sub>, ν denotes the kinematic velocity of the electrolyte, while k is the electron transfer rate constant. The constant 0.2 is adopted when the rotation speed is in rpm.

The electron transfer number per molecule (n) and %yield of peroxide ions, were calculated by RRDE measurements by using the following equations.

$$H_2O_2\% = \frac{200I_{ring}/N}{I_{ring}/N + I_{disk}} \quad (3)$$

$$n = \frac{4I_{disk}}{I_{ring}/N + I_{disk}} \quad (4)$$

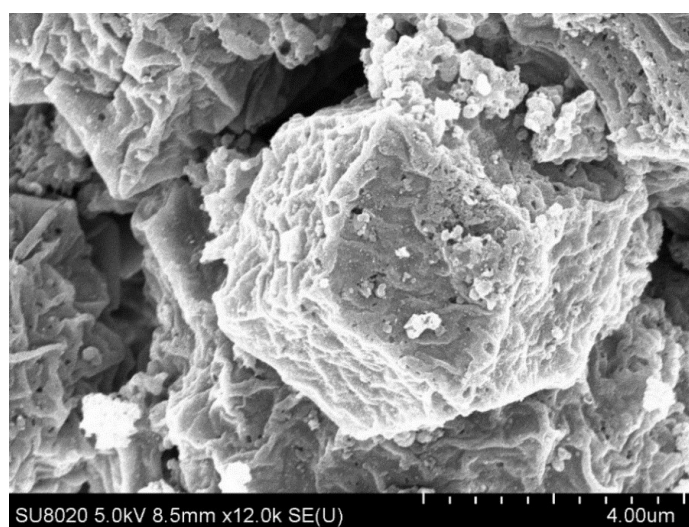
Where I<sub>ring</sub> accounts for ring current, N represents the collection efficiency of the Pt ring calibrated by the K<sub>3</sub>Fe(CN)<sub>6</sub> redox reaction as 0.40 while I<sub>disk</sub> denotes the voltammetric current at the disk electrode. HER and OER were analysed by using same three electrode system with the difference that graphite rod was used as counter electrode for HER instead of Pt wire. The working electrodes were prepared by dropping catalyst ink on pre-treated carbon cloth (CC) and drying under ambient conditions. Electrochemical measurements for OER were recorded in O<sub>2</sub> saturated electrolyte while for HER, Ar saturated environment was used. Both HER and OER were tested under alkaline conditions using 1 M KOH. All potentials for OER and HER were referenced to reversible hydrogen electrode. Long term stability for both was tested using chronoamperometric technique. The electrolyte was stirred at constant speed in order to avoid accumulation of bubbles generated by evolution of H<sub>2</sub> and O<sub>2</sub> which may block the catalysis by covering the catalytic sites for oxygen and hydrogen production. For bifunctional oxygen electrocatalysis 0.1 M KOH was used as electrolyte and LSV was recorded using full potential range for ORR and OER.

## Fabrication of Zinc Air Battery

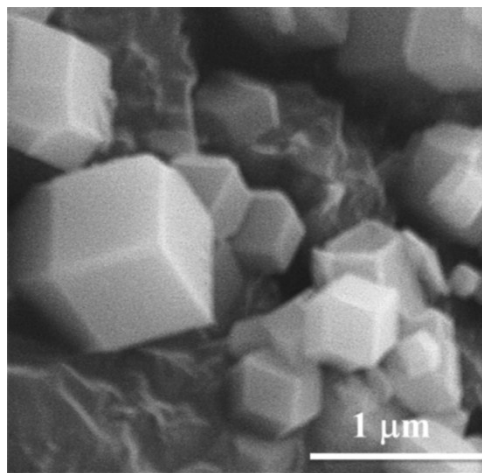
Zinc air battery was assembled using zinc anode, air cathode and a separator. The air cathode was prepared by using the as prepared BrHT@CoNC while anode was prepared by zinc powder in 6M KOH. The catalyst loading was  $6 \text{ mg cm}^{-2}$ . Cu sheet and Ni foam were used as current collector while Nylon filter was used as separator. A 1:1 mixture of 20% Pt/C and  $\text{IrO}_2$  was used for comparison.

## Structural Characterization

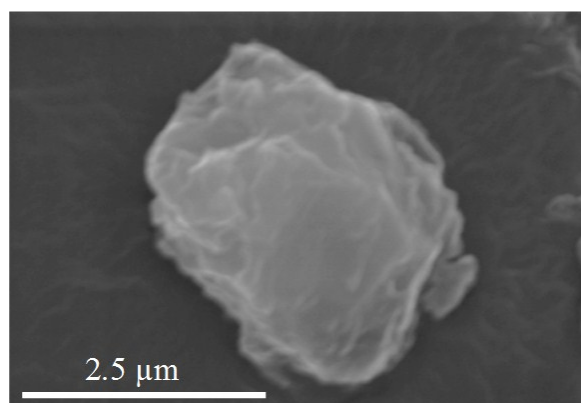
Powder X-ray diffraction (PXRD) patterns were recorded by X'Pert PRO PANalytical diffractometer operating at 40 kV and 30 mA with Cu  $\text{K}\alpha_1$  as radiation source ( $\lambda = 0.15418 \text{ nm}$ ). Scanning electron microscopy (SEM) was carried out with JOEL JSM-7610F microscope. The transmission electron microscopy (TEM) images were obtained by field-emission JEM-2100F microscope at an operating voltage of 200 kV. X-ray photoelectron spectroscopy was carried out for the elemental analysis of the samples (ESCALab220i-XL). Nitrogen adsorption–desorption isotherms were measured at 77 K (Autosorb-IQ, quantachrome). Brunauer–Emmett–Teller (BET) method was used to calculate specific surface area of the electrocatalyst and the total pore volume and the surface was examined by V-t method. Discrete-Fourier-Transform (DFT) method was applied to measure the pore size distribution (PSD). The samples were degassed for twelve hours at 200 °C under vacuum. To monitor weight changes with temperature changes thermogravimetric analysis (TG/DTA) was carried out by TA instruments (SDT Q600) under argon or air flow at a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$  from room temperature to 900 °C. Raman spectrum was recorded by Raman spectrophotometer (Renishaw Raman system, inVia Reflex) with an excitation wavelength of 532 nm for the 20mW air cooled argon ion laser source. The power of laser positioned at the sample was 4.0 mW with diameter 1 mm. Data acquisition time was set to 10 s.



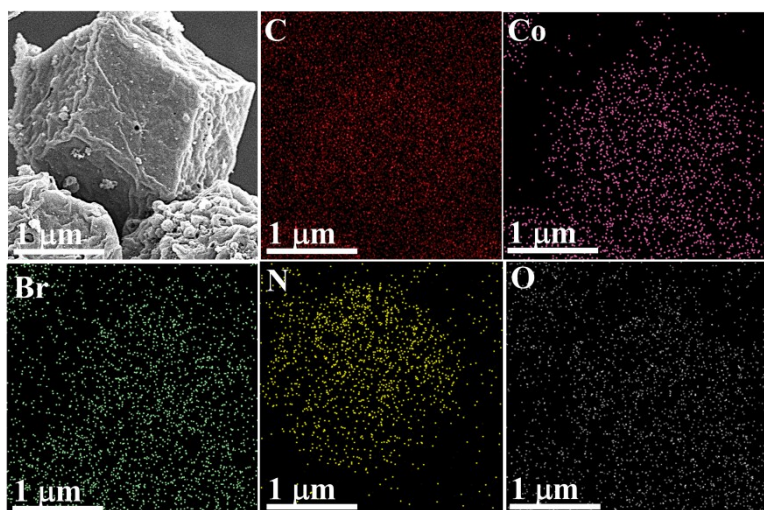
**Figure S1.** SEM images of BrHT@CoNC



**Figure S2.** SEM images of Co@NC



**Figure S3.** SEM images of BrRT@CoNC



**Figure S4.** Elemental mapping of BrHT@CoNC

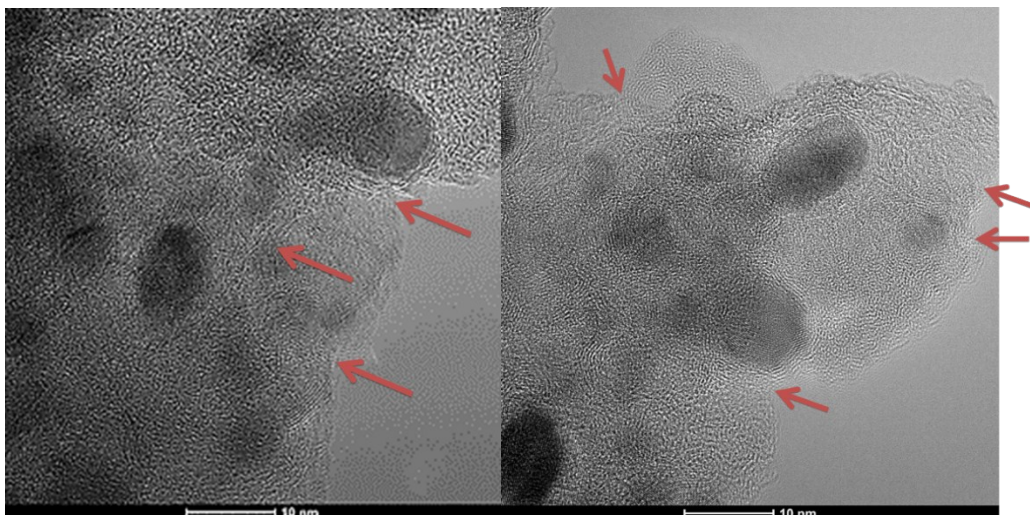


Figure S5. HRTEM images of BrHT@CoNC (defects)

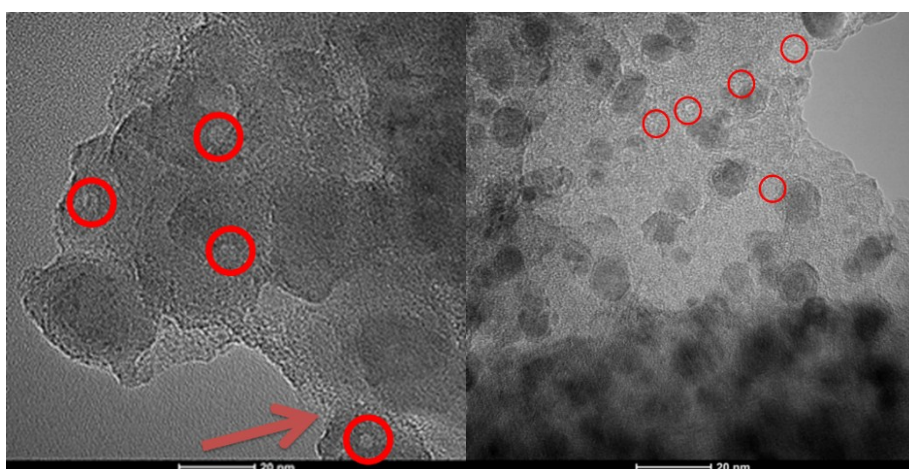


Figure S6. HRTEM images of BrHT@CoNC (defects and pores)

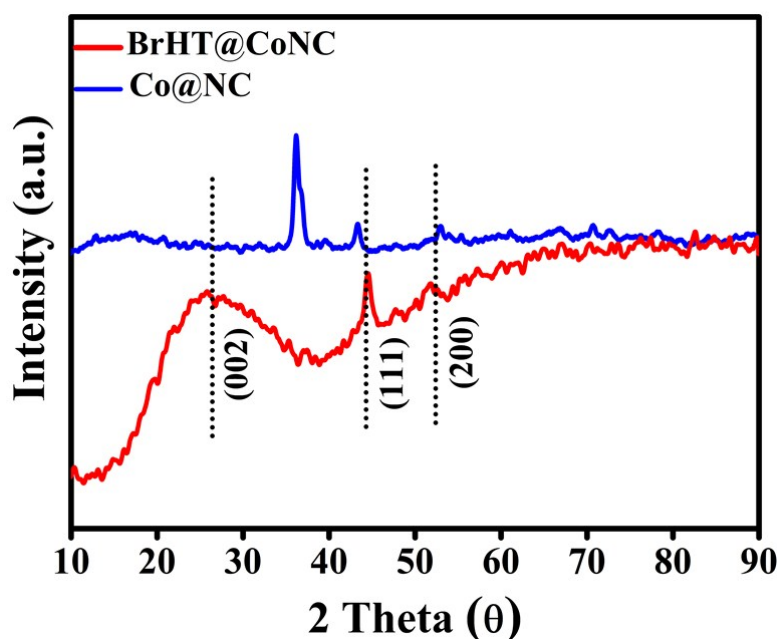


Figure S7. XRD analysis of BrHT@CoNC compared with Co@NC

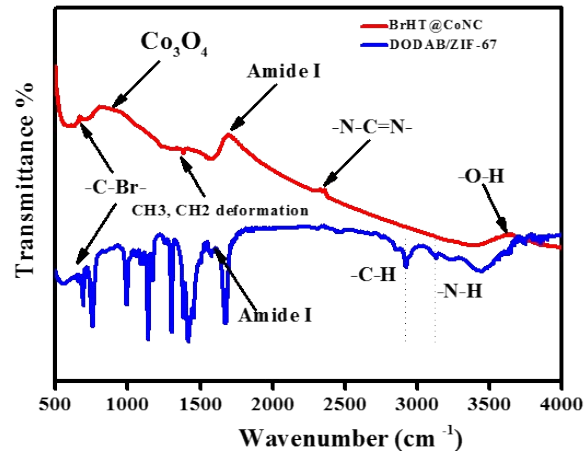


Figure S8. FTIR analysis of BrHT@CoNC (before and after carbonization)

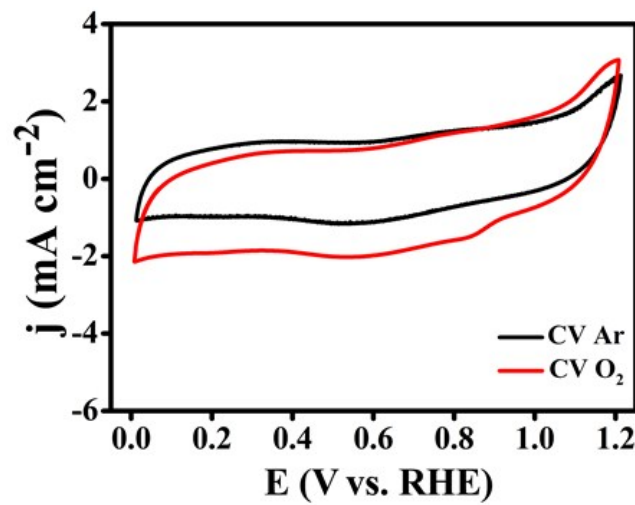


Figure S9. CV of BrHT@CoNC in Ar and O<sub>2</sub> saturated electrolyte

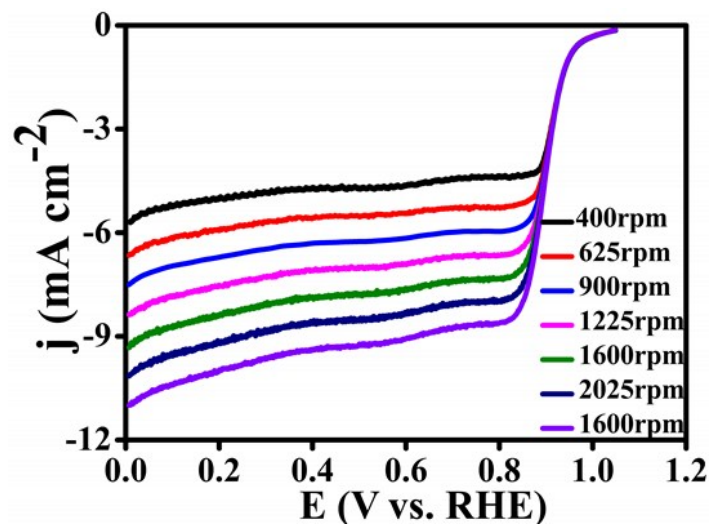
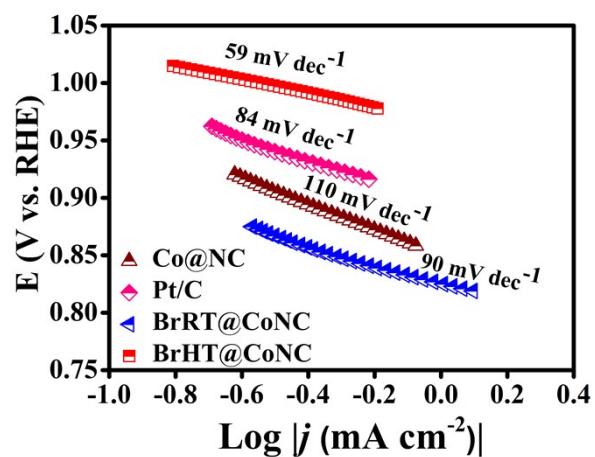
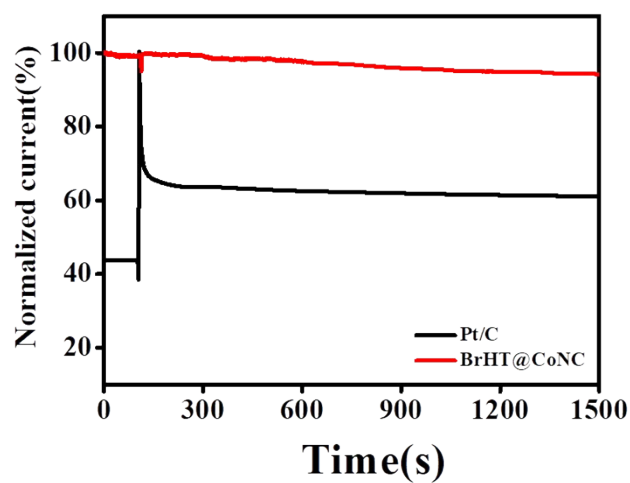


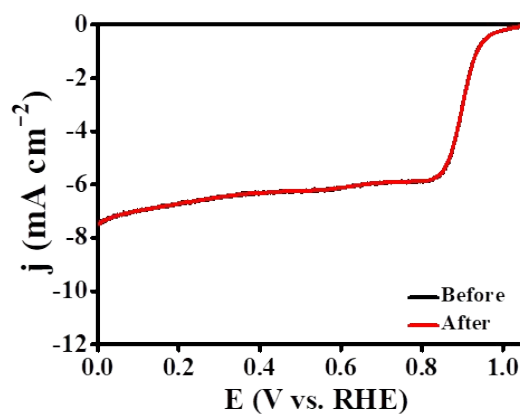
Figure S10. LSV curves of BrHT@CoNC at varying rotational speeds with a scan rate of 10 mV/s



**Figure S11.** Comparison of tafel slopes of of BrHT@CoNC, BrRT@CoNC and Co@NC

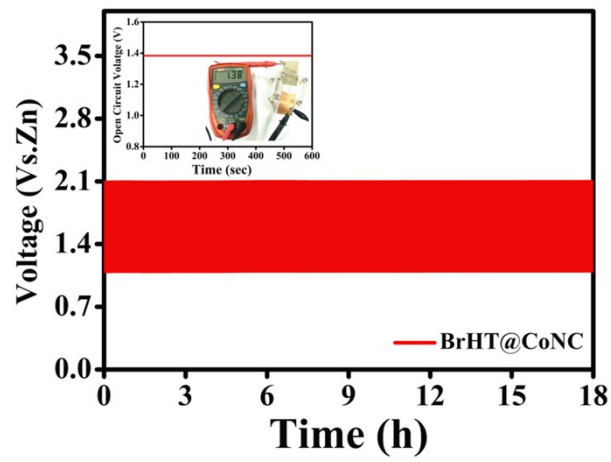


**Figure S12.** Methanol tolerance for BrHT@CoNC

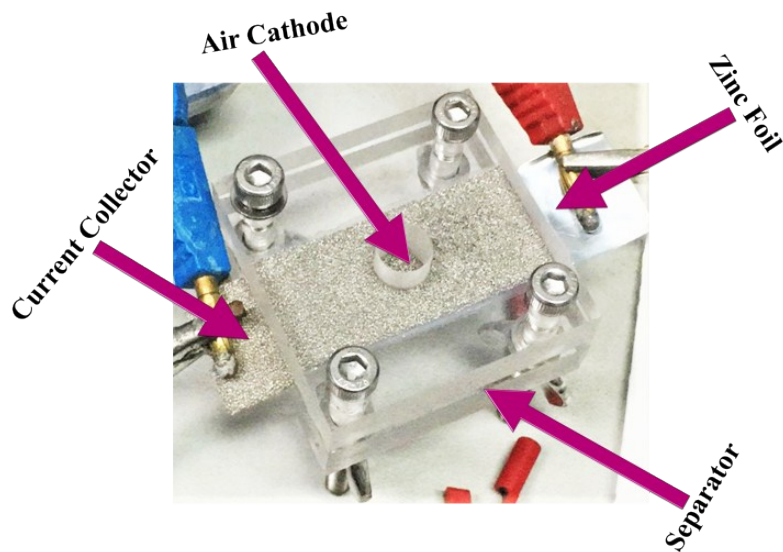


**Figure S13.** Durability test for BrHT@CoNC





**Figure S14.** Charging-discharging cycling performance of rechargeable Zn-air battery assembled with BrHT@CoNC at  $5 \text{ mA cm}^{-2}$  with a pulse cycling interval of 200 seconds per cycle (inset) OCV stability with time.



**Figure S15.** Fabrication of Zn air battery

Materials	ORR		OER $\eta_{10}$ vs, RHE (mV)	Bifunctional Electrocatalysis $\Delta E/V$ ( $E_{\text{OER}}-E_{\text{ORR}}$ )	HER $\eta_{10}$ vs, RHE	Water Splitting $E_{\text{Cell}}$	References
Pt/C (20 wt%)	0.96	0.82	630	1.01	20	---	This work
Co@NC	0.91	0.8	660	1.09	340	--	This work
Pt/C (20 wt%)    IrO <sub>2</sub>	---	---	---	---	---	1.70	This work
CoBrRT@CoNC	0.98	0.86	257	0.62	365	--	This work
CoBrHT@CoNC	1.02	0.90	257	0.60	77	1.55	This work
N-Co 3 O 4 @NC	0.89	0.77	266	0.78	---	---	S1
B-N-C	0.98	0.84	340	0.712	--	---	S2
CNT/ HDC-1000	0.92	0.82	--	--	--	--	S3
NSG@CNT-2	1.03	0.87	370	0.83	350	---	S4
CoSe 2-x Pt	--	--	255	--	--	--	S5
CoP-DC	---	0.81	320	0.76	--	--	S6
NFPGN	---	---	340	--	330	1.91	S7

**Table S1.** Comparison of electrocatalytic activities of recently reported electrocatalysts

## References

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