

Electronic Supplementary Information (ESI) for Chem. Commun.

A Twisted Carbonaceous Nanotube as the Air-Electrode for Flexible Zn-Air Batteries

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1. Experimental section

1.1 Materials

All chemicals were used without any further purification. L-glutamic acid (L-Glu, 99%), stearoyl chloride (98%), pyrrole (99%), ammonium persulfate (APS, 99%), methanol (AR, 99.5%), KOH (AR, 95%), $\text{Co}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$ (99.99%), and potassium persulfate (AR, 99%) were purchased from the Sinopharm Group Chemical Reagent Co., Ltd. Acetone (99.7%) was bought from Tianjin Fuyu Fine Chemical Co., Ltd. NaOH (AR, 96%) was purchased from the Guangdong Guanghua Sci-Tech Co., Ltd. 2-methylimidazole (AR, 99%), acrylic acid (AR, 99%), *N,N*-methylene bisacrylamide (AR, 99%), KI (AR, 95%), and KOH (AR, 95%) were bought from the Energy Chemical. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (AR, 99%) was bought from Tianjin Chemical Reagent Co., Ltd. Polyvinylpyrrolidone K30 (PVP K30, 99%) and polyvinyl alcohol (PVA, 99%) were purchased from the Aladdin.

1.2 Synthesis of Chiral surfactant *N*-stearoyl-glutamic acid

Generally, 3.53 g of L-glutamic acid and 1.92 g of NaOH were added to a mixture of deionized water (DIW, 14 mL) and acetone (12 mL), stirring until dissolved and maintaining the pH = 12. Subsequently, 6.05 g of stearoyl chloride and 10 mL NaOH solution (0.2 mol L^{-1}) were slowly introduced into the above mixture keeping pH = 12 for 1 h. Then, slowly drop HCl to adjust pH = 1. Finally, wash the above-obtained sample with DIW until the pH = 7. After, wash it with petroleum ether to remove impurities and dry it in the freeze dryer for 12 h to obtain $\text{C}_{18}\text{-L-Glu}$.

1.3 Synthesis of HPPy.

Typically, 0.0245 g of $\text{C}_{18}\text{-L-Glu}$ was added into 12.88 mL methanol and stirred for 30 min to form a uniform solution. Then, slowly add 166 μL pyrrole and 60 mL DIW into the above solution. After stirring for 10 min, add 1.2 mL pre-cooled ($0 \sim 5 \text{ }^\circ\text{C}$) ammonium persulfate (APS) solution (containing 0.548 g APS) and stir for 30 min to obtain a black suspension. After that, the black solid of HPPy was obtained by filtration washing with DIW and ethanol and dried at $60 \text{ }^\circ\text{C}$ for 12 h in an oven.

1.4 Synthesis of HPPy@Co.

Firstly, 30 mg of HPPy was added in 10 mL methanol and ultrasound for 30 min to obtain a uniform solution. Next, 1 mmol $\text{Co}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$ was introduced into the above solution and kept stirring for 5 h. After, the sample was collected by centrifugation (13000 rpm, 2 min) and washed with methanol 2 times, which the HPPy@Co was obtained after drying at $60 \text{ }^\circ\text{C}$ for 12 h in an oven.

1.5 Synthesis of HPPy@Co-NC.

The obtained HPPy@Co was dispersed in 5 mL methanol, then slowly 10 mL methanol,

which was dissolved with 10 mmol of 2-methylimidazole and continuously stirred for 12 h. After, the sample was collected by centrifugation and washed with methanol several times, and the HPPy@Co-MIM was obtained after drying at 60 °C for 12 h in an oven. Subsequently, 100 mg of HPPy@Co-MIM was transferred to a porcelain boat for pyrolysis at 900 °C for 3 h with a rate of 2 °C min⁻¹ under Ar atmosphere, finally, the HPPy@Co-NC was obtained.

1.6 Synthesis of ZIF-67 and Co-NC.

First, Co(NO)₃·6H₂O was dissolved in 15 mL methanol to form solution A. Then, 2-methylimidazole was also dissolved in 15 mL methanol to form solution B with the molar ratio of Co(NO)₃·6H₂O and 2-methylimidazole ~ 1 : 4. Next, solution B was slowly poured into solution A continuously stirred for 5 min and aging for 24 h. After that, the ZIF-67 was collected by centrifugation (7000 rpm, 3 min) washed with methanol 3 times, and dried at 60 °C for 12 h in an oven. Finally, the Co-NC was obtained by pyrolysis at 900 °C for 3 h with a rate of 2 °C min⁻¹ under the Ar atmosphere.

1.7 Characterization

Scanning electron microscopy (SEM, Hitachi SU8020) at an accelerating voltage of 5 kV and transmission electron microscope (TEM, JEOL JEM-2100) with a field emission gun operating at 200 kV were used to observe the morphology of the samples. EDS analysis was conducted on an AMETEK Materials Analysis EDX equipped on the TEM. Infrared spectra were collected by the Brüker TENSOR 27 instrument. Powder X-ray diffraction (PXRD) patterns of the materials were conducted on an X-ray diffractometer (Bruker, D8 Advance, Cu K α , λ = 1.5406 Å, 40 kV/ 40 mA). Micromeritics ASAP 2020 was used to measure the Brunauer-Emmett-Teller (BET) specific surface area of the materials. X-ray photoelectron spectroscopic (XPS) spectra were collected by a Kratos AXIS ULTRA XPS. The Raman spectrometer (Renishaw, in Via Reflex) and X-ray photoelectron spectroscopic (XPS) spectra were carried out to analyze the structural composition, valence state, and bonding state of the materials.

1.8 Electrochemical measurement

All the relevant ORR/OER tests were carried out on the CHI 760E (CH Instruments) electrochemical workstation and a Pine Modulated Speed Rotator (Pine Research Instrumentation, Inc.) at 30 °C by a three-electrode system. The potentials in this experiment were converted to a reversible hydrogen electrode (RHE) ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.197 + 0.0591 \times \text{pH})$). For ORR tests, the graphite rod as the counter electrode, Ag/AgCl as the reference electrode, and the rotating disk electrode (RDE) (5 mm, 0.196 cm²) or rotating ring disk electrode (RRDE) (5.61 mm, 0.247 cm²) was severed as working electrode. In detail, the homogeneous catalyst ink was prepared by mixing 2 mg of catalyst, 333 μL of deionized water, 166 μL of ethanol, and 10 μL of Nafion solution, then ultrasonating for 1 h. Subsequently, slowly dropped 20 μL catalyst ink

on each working electrode and dried at room temperature with a load of $\sim 0.4 \text{ mg cm}^{-2}$. Then, continuously injecting Ar/O₂ for ~ 15 min to reach a saturation state before testing. Following, the cyclic voltammetry (CV) curves were operated in Ar/O₂-saturated 0.1 M KOH with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$. Linear sweep voltammetry (LSV) was conducted from 400 to 2025 rpm with a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ after 100% IR compensation. Current-time (*j*-*t*) chronoamperometric responses were performed at 0.664 V (vs. RHE). Moreover, for the OER test, the catalyst ink was the same as ORR, in which the dosage was 6 μL , and glassy carbon (GC) (3 mm, 0.07 cm^2) as the working electrode. LSV testing was measured in 1.0 M KOH with a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ after 100% IR compensation. The overpotential (η) is calculated by the formula: $\eta = E_{\text{RHE}} - 1.23$.

The RDE were conducted to calculate the number of electron transfers (*n*) by the Koutecky-Levich (*K-L*) formula:

$$\frac{1}{j} = \frac{1}{j_l} + \frac{1}{j_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}$$

Where *j* represents the measured current density; *j_l* and *j_k* are on behalf of the diffusion and dynamic current density, respectively; ω is the rotational speed (rpm); *B* can be calculated by the Koutecky-Levich (*K-L*) formula:

$$B = 0.2nFC_0(D_0)^{2/3}/\nu^{-1/6}$$

where *F* is the Faraday constant (96485 C mol^{-1}); *C₀* is the concentration of O₂ in 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$); *D₀* is the diffusion coefficient of O₂ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the viscosity of 0.1 M KOH ($0.1 \text{ cm}^2 \text{ s}^{-1}$).

Besides, the number of electron transfers (*n*) and yield percentage (*H₂O₂*%) also can be verified by RRDE by the following equation:

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

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

1.9 Assembly and performance test of flexible Zn-air batteries

A Zn foil with a thickness of 0.8 mm (2 cm \times 4 cm) is polished and as the anode. The preparation method of the gel polymer electrolyte was as follows: 0.67 g and 0.33 g of the polyvinyl alcohol (type 1788 and 1799) were dissolved in 20 mL deionized water and stirred at 90 °C for 2 h to obtain a transparent solution. Then, 10.08 g of acrylic acid, 3.696 g sodium hydroxide (8.4 mol L^{-1}), and 0.025 g of *N,N*-methylene bisacrylamide were added into the above solution and stirred at 60 °C for 30 min. After that, add 0.171 g ammonium persulfate (0.15 mol L^{-1}) and stir at room temperature for

40 min. Finally, dry it at 70 °C for 3 h and soak it in a mixture solution of KOH (4 M) and KI (2 M) for 24 h to obtain the gel polymer electrolytes. The catalyst ink was uniformly dripped on nickel foam (thickness 0.8 mm, 2 cm × 4 cm) as the air-electrode with a load of ~ 1 mg cm⁻². Relevant electrochemical performance tests were conducted on the CHI 660E electrochemical workstation at room temperature. The discharge characteristic curves were tested under a current density of 1 mA cm⁻² and 5 mA cm⁻². Also, every charge-discharge cycle curve consists of 10 min charge process and 10 min discharge process with a current density of 1 mA cm⁻².

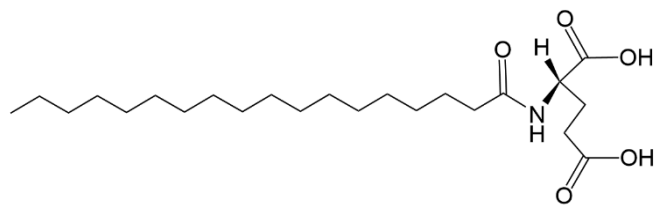


Fig. S1. Molecular structure of C₁₈-L-Glu.

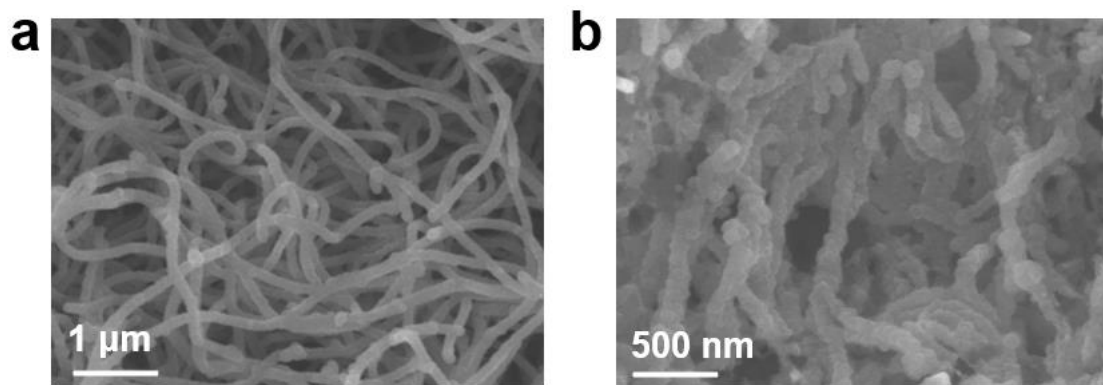


Fig. S2. SEM images of (a) HPPy@Co and (b) HCNT@Co-NC.

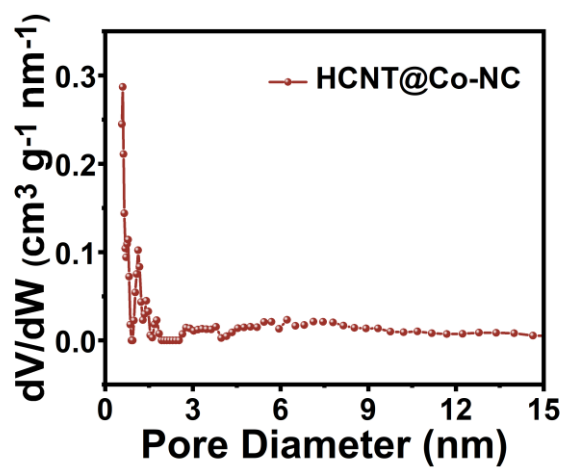


Fig. S3. The pore size distribution plots of HCNT@Co-NC.

The microporous surface area is calculated based on t -plot method, while the mesoporous surface is calculated based on the equation: $S_{\text{meso}} = S_{\text{BET}} - S_{\text{micro}}$.

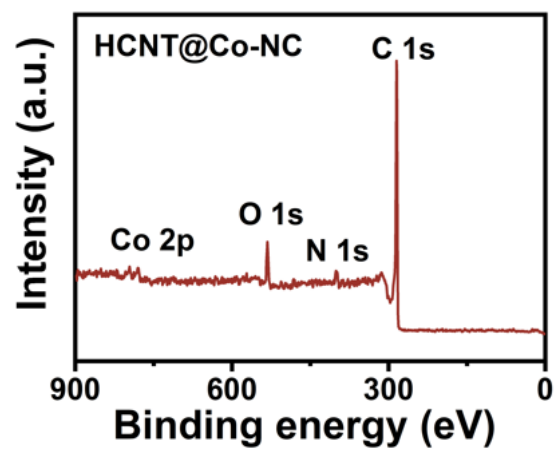


Fig. S4. XPS spectra of HCNT@Co-NC.

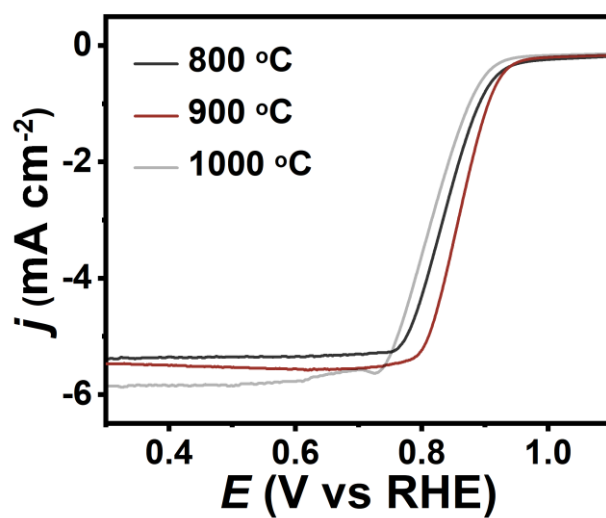


Fig. S5. LSV curves of catalysts at different pyrolysis temperatures of 800°C, 900°C and 1000°C.

As show in LSV curves, the electrocatalyst calcined at 900 °C exhibits a higher ORR activity ($E_{1/2} = 0.850$ V) than the electrocatalysts calcined at 800 °C ($E_{1/2} = 0.825$ V) and 1000 °C ($E_{1/2} = 0.806$ V).

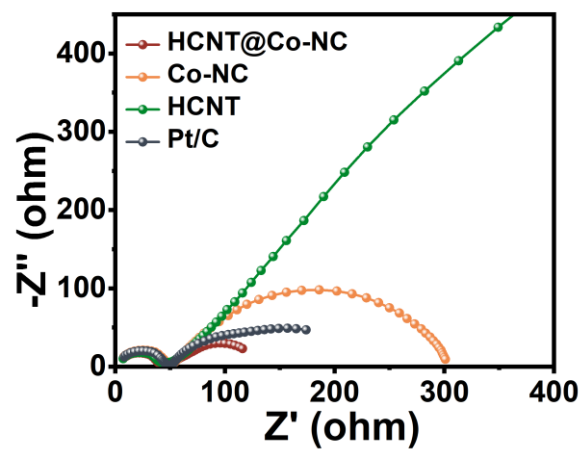


Fig. S6. EIS plots of HCNT@Co-NC, Co-NC, HCNT, and Pt/C in 0.1 M KOH.

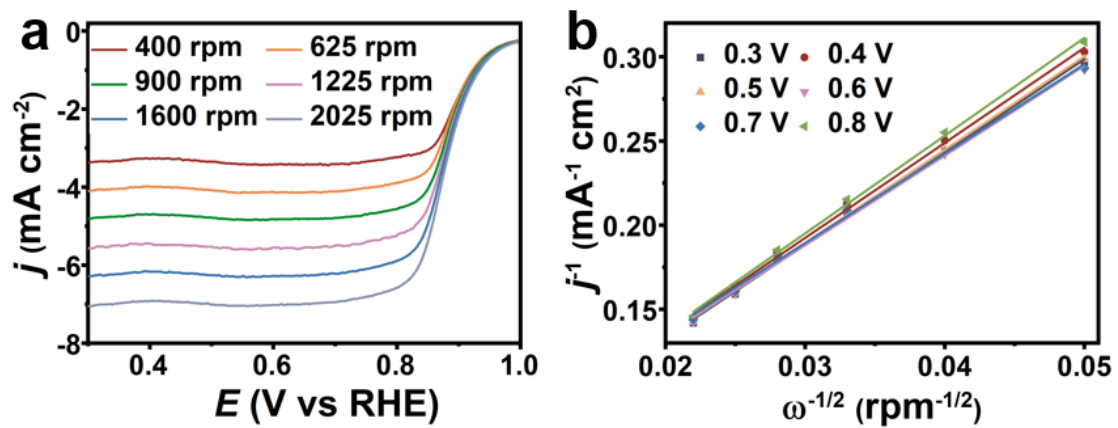


Fig. S7. (a) LSV curves of Pt/C in O₂-saturated 0.1 M KOH solution under different rotation speeds and (b) the corresponding K - L curves.

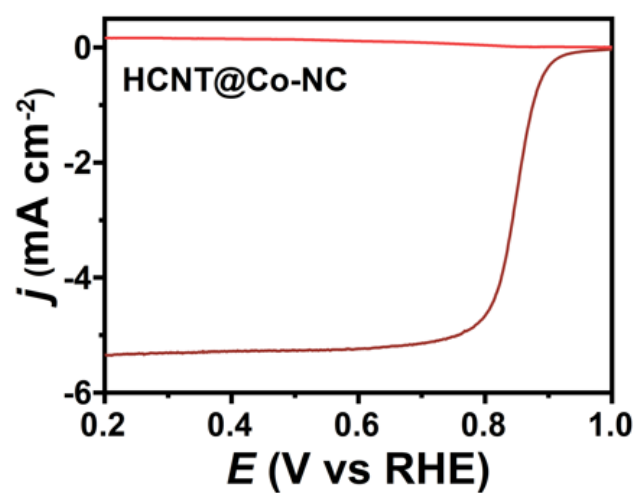


Fig. S8. LSV curve of HCNT@Co-NC with RRDE.

LSV curve of HCNT@Co-NC has been tested in O₂-saturated 0.1 M KOH solution at 1600 rpm, the n of HCNT@Co-NC is 3.87.

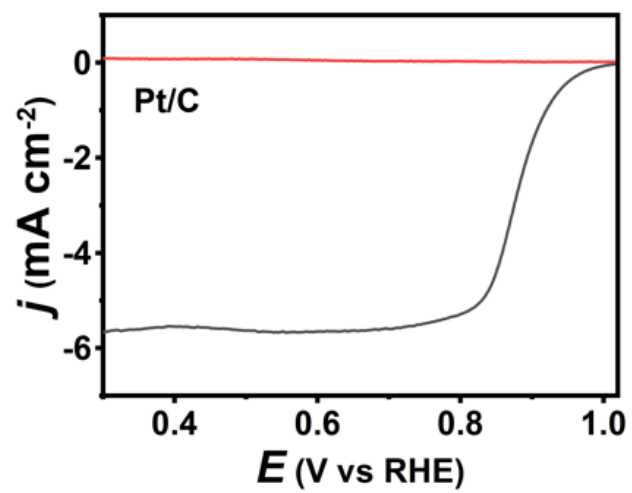


Fig. S9. LSV curve of Pt/C with RRDE.

LSV curve of Pt/C has been tested in O₂-saturated 0.1 M KOH solution at 1600 rpm, the n of Pt/C is 3.97.

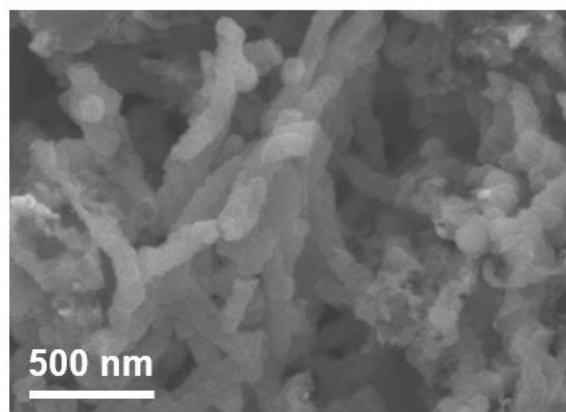


Fig. S10. SEM image after 2000 CV cycles of HCNT@Co-NC.

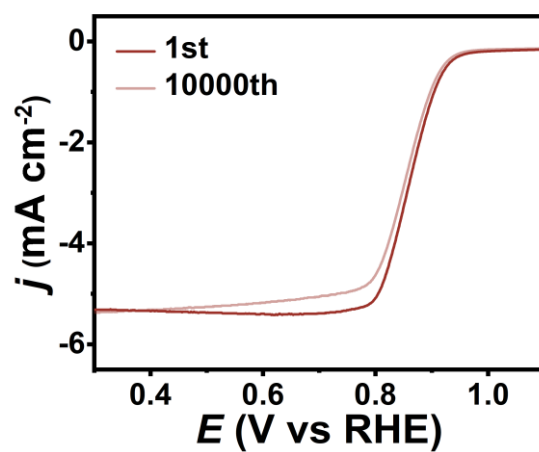


Fig. S11. LSV curves of HCNT@Co-NC for the ADT of 10 k cycles at 0.1 M KOH.

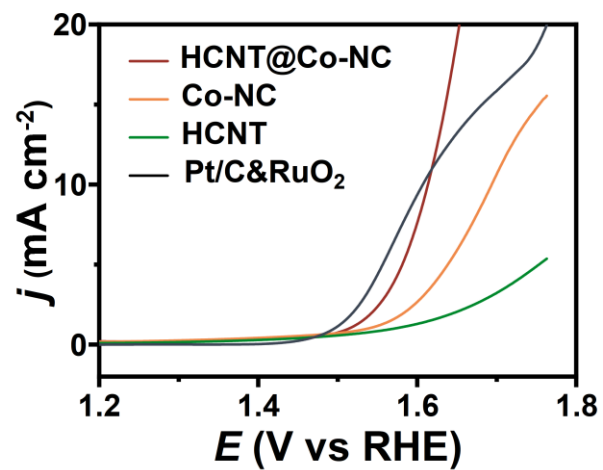


Fig. S12. LSV curves of the HCNT@Co-NC, Pt/C&RuO₂, Co-NC, and HCNT in 1.0 M KOH solution.

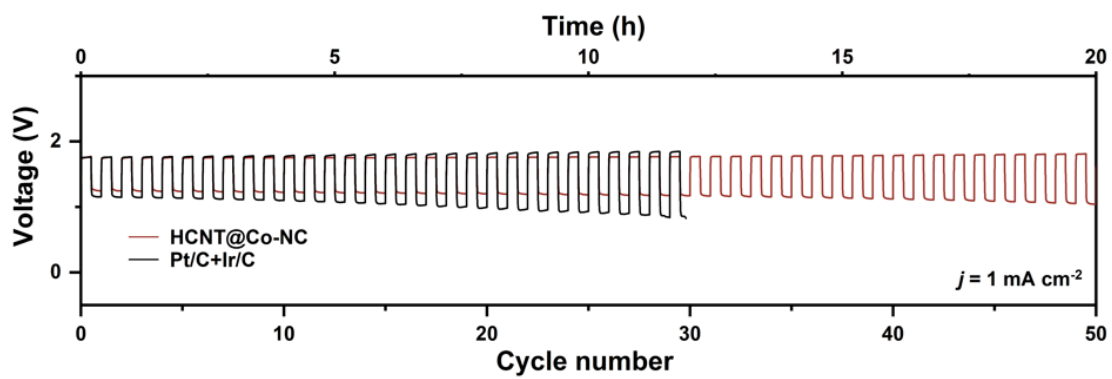


Fig. S13. Stability test of flexible Zn-air batteries assembled with HCNT@Co-NC and Pt/C+Ir/C at the current density of 1 mA cm^{-2} .

Table S1. Estimated percent of Co, and N obtained by the overall XPS spectra of HCNT@Co-NC.

Elements	C	N	O	Co
Atom Content (at.%)	86.46	4.47	7.92	1.15

Table S2. Comparison of electrocatalytic activity of the HCNT@Co-NC with recently reported highly active ORR/OER bifunctional electrocatalysts.

Catalyst	$E_{1/2}$ (vs RHE)	$E_{j=10}$ (vs RHE)	$\Delta E_{(ORR-OER)}$	Ref.
HCNT@Co-NC	0.85 V	1.60 V	0.75 V	This work
CoZn-NC-700	0.84 V	1.62 V	0.78 V	<i>Adv. Funct. Mater.</i> 2017, 27 , 1700795
Co _p @CoNC	0.84 V	1.52 V	0.68 V	<i>Energy Storage Mater.</i> 2022, 46 , 553-562
NiCo/MNC	0.83 V	1.61 V	0.78 V	<i>J. Alloy. Compd.</i> 2019, 797 , 1041-1049
CoFe@NC-SE	0.82 V	1.62 V	0.8 V	<i>J. Power. Sources.</i> 2020, 455 , 227975
3D Co/N-C	0.84 V	1.56 V	0.72 V	<i>Chem. Eng. J.</i> 2022, 433 , 134500
Co@Co ₃ O ₄ @NC-900	0.80 V	1.60 V	0.8 V	<i>J. Mater. Chem. A</i> , 2018, 6 , 1443-1453
CS Co@NC-700	0.86 V	1.64 V	0.78 V	<i>J. Energy. Chem.</i> 2021, 58 , 391-396
Co@N-CNTF-2	0.81 V	1.58 V	0.77 V	<i>J. Mater. Chem. A</i> . 2019, 7 , 3664-3672
Co@NCNTA-600	0.77 V	1.66 V	0.89 V	<i>Small.</i> 2020, 4 , 1900571

Table S3. Comparison of the recently reported flexible Zn-air batteries.

Catalysts	Peak power density (mW cm ⁻²)	Open circuit voltage (V)	Time (h)	Ref.
HCNT@Co-NC	57.1	1.44	50	This work
Co/N@CNTs/CNMF	26.5	1.4	9	<i>Adv. Funct. Mater.</i> , 2020, 30 , 2003407
P-CoO@PWC-2	68	1.48	67	<i>Adv. Sci.</i> , 2021, 8 , 2101314
NiSAs/HCNFs/Co-NAs	40.5	1.38	16	<i>Adv. Sci.</i> , 2021, 8 , 2101314.
NF/CCO/FCH	35.2	1.55	10	<i>Appl. Catal. B Environ.</i> , 2023, 325 , 122332
FeSAC/PCMT	58	1.43	5	<i>Carbon Energy</i> , 2022, 5 , 1-10
Co-NDC	45.9	/	20	<i>Sci. Bulletin</i> , 2018, 63 , 548-555
Fe ₁ /d-CN	78	1.5	20	<i>Energy Environ. Sci.</i> , 2021, 14 , 6455-6463
Ru-RuO ₂ @NPC	29	1.43	6	<i>Appl. Catal. B Environ.</i> , 2022, 302 , 120838
CoNCNTF/CNF	63	1.21	11	<i>Carbon</i> , 2019, 142 , 379-387