Supplementary Information (SI) for ChemComm.

Supporting Information

Hierarchically porous Co-N-C catalysts derived from metal-tetrazole frameworks for efficient oxygen reduction

S1. Experimental Section

All reagents were analytical grade and used without further purifification. All solutions used in electrochemical experiments were prepared with Millipore water (≥ 18 MΩ).

Synthesis of Co-4ptz

Add 4-(5-tetrazolyl)pyridine (51.3 mg, 0.35 mmol) and $Co(OAc)_2·4H_2O$ (49.5 mg, 0.2 mmol) into 2.5 mL of deionized water separately, and ultrasonically disperse each for 10 minutes. Then, slowly pour the $Co(OAc)_2·4H_2O$ aqueous solution into the dispersion of 4-(5-tetrazolyl)pyridine while stirring at 1000 rpm for 30 min. Next, transfer the mixed solution into a 25 mL autoclave and conduct a hydrothermal reaction in an oven at 180 °C for 24 h. After the reaction is complete, wash and dry the product to obtain pink crystals (Co-4ptz). During this process, the molar ratio of metal ions to 4-(5-tetrazolyl)pyridine is 0.57, with a drying temperature of 110 °C and a drying time of 12 h. IR (KBr, cm^{-1}): 3159.69 (m), 1602.56 (s), 1561.49 (w), 1453.26 (m), 1446.40 (s), 1387.02 (m), 1312.84 (w), 1254.56 (w), 1145.62 (w), 1014.76 (m), 723.75 (s).

Synthesis of Co-4ptz-K-M-800

Weigh 20 mg of Co-4ptz prepared earlier and 6 mg of Ketjenblack (KB), grind them together, and place the mixture downstream in a ceramic boat. Simultaneously, weigh 200 mg of melamine (M) and place it upstream in the ceramic boat. Under an argon atmosphere, heat the setup at a rate of 5 °C/min to a temperature of 800 ℃ and maintain this temperature for 2 h. After cooling to room temperature, a cobalt and nitrogen co-doped porous carbon-based oxygen reduction electrocatalyst (Co-ptz-K-M-800) is obtained, derived from Co-4ptz. When the amount of KB was tailored to 20, 30, and 40% of the mass of Co-4ptz, the corresponding products were marked as Co-4ptz-K(4)-M-800, Co-4ptz-K(6)-M-800 (Co-ptz-K-M-800), and Co-4ptz-K(8)-M-800, respectively.

Synthesis of Co-4ptz-K-800 and Co-4ptz-800

The operating conditions for Co-4ptz-K-800 are the same as Co-4ptz-K-M-800, except that melamine was not introduced. The operating conditions for Co-4ptz-800 are the same as Co-4ptz-K-M-800, except that melamine and KB were not introduced.

Characterizations

Powder X-Ray diffraction (PXRD) patterns were recorded on a D8 DAVANCI X-ray powder diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.5406 Å). The diffractometer was operated with working voltage and current of 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a JEM-2100 apparatus working at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was carried out with a S-4800 (JEOL) apparatus working at an S4acceleration voltage of 2 kV. X-ray photon spectroscopy (XPS) was performed on an ESCA Lab250 X-ray microprobe corrected by C1s peak at 284.6 eV. Nitrogen sorption experiments and pore size distribution (PSD) were measured using an ASAP 2020 surface area detecting instrument by N_2 physisorption at 77 K. Prior to the measurement, the samples were degassed at 120°C for 6 h.

Electrochemical Measurements

All electrochemical experiments were conducted on a CHI 760 E electrochemical station (Shanghai Chenhua Co., China) in a standard three electrode cell in O_2-saturated 0.1 M KOH at room temperature. A glassy carbon electrode (GCE, 5 mm in diameter), a saturated calomel electrode (SCE), and a Pt wire were used as the working, reference and counter electrode, respectively. All electrode potentials were expressed in reference to the reversible hydrogen electrode (RHE). 5 mg of the catalysts were dispersed in 1 mL of 1:1 v/v water/alcohol with 40 μL Nafion by sonication to form a homogeneous suspension. Typically, 5 μL well-dispersed suspension was dropped on the glassy carbon electrode and then dried in an ambient environment for measurements. Linear sweep voltammetry (LSV) was tested with a scan rate of 10 mV s^{-1} at 1600 rpm on rotating disc electrode (RDE). The chronoamperometry (CA) was tested at an overpotential of 0.8 V vs RHE after equilibrium. Calibrate the SCE electrode: During calibration, select a specific range near the open-circuit voltage for cyclic voltammetry (CV) testing. The CV scan rate should be as slow as possible, typically 1 mV/s, to ensure the reaction system is in equilibrium. Choose the two electrode potentials corresponding to the zero current density, take their average, which will be the corrected reference electrode potential value.

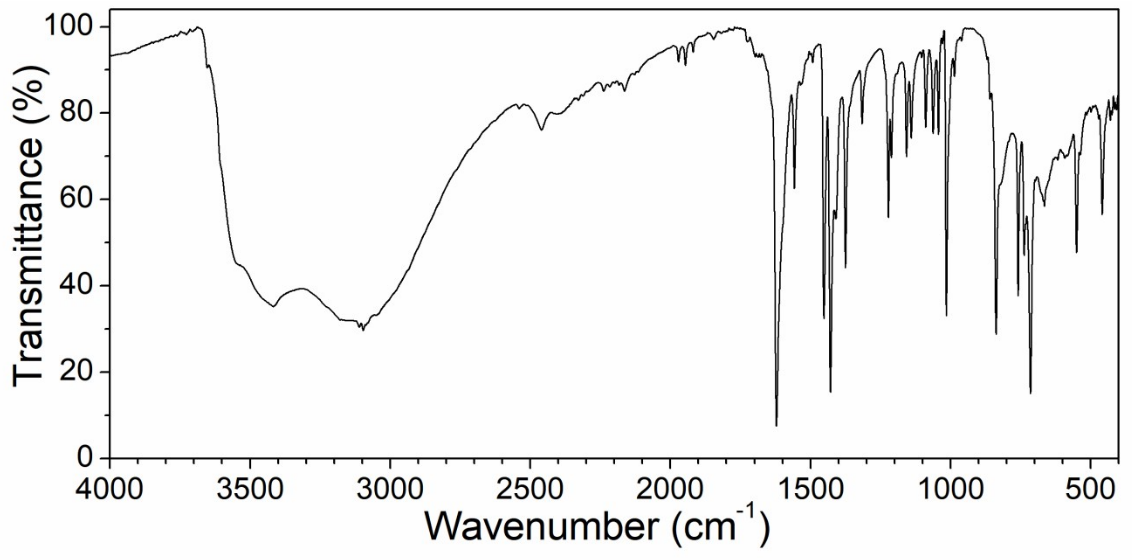

Fig. S1. FTIR image of Co-4ptz.

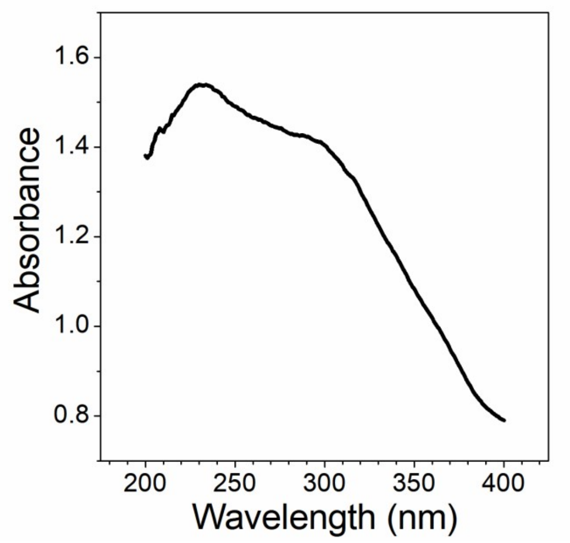

Fig. S2. UV spectrum image of Co-4ptz.

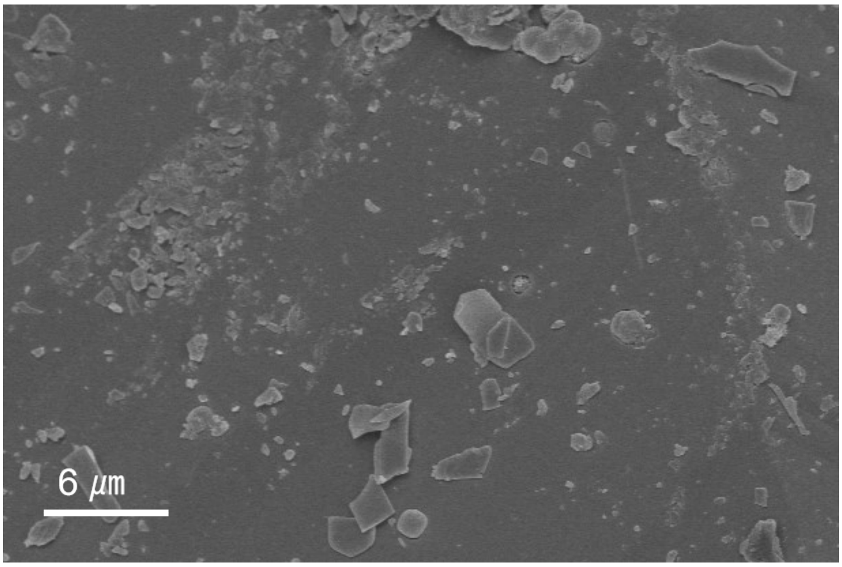

Fig. S3. SEM image of Co-4ptz.

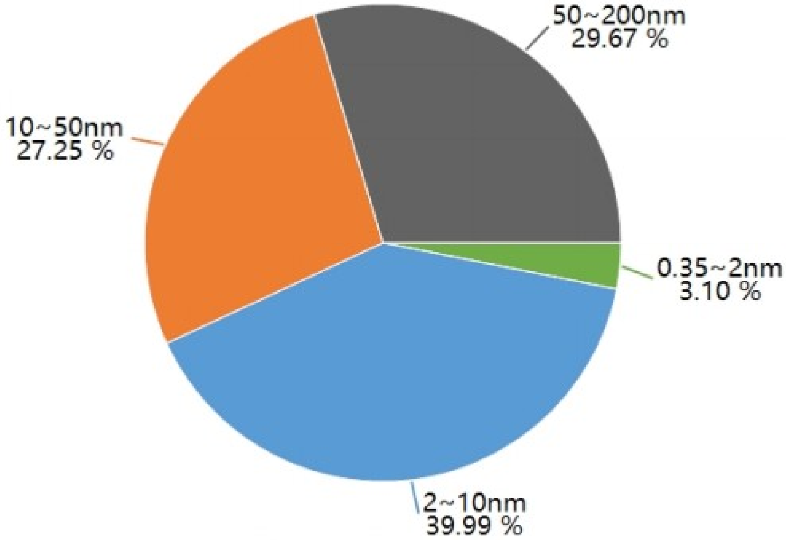

Fig. S4. Pore volume distribution diagram of Co-4ptz-K-M-800.

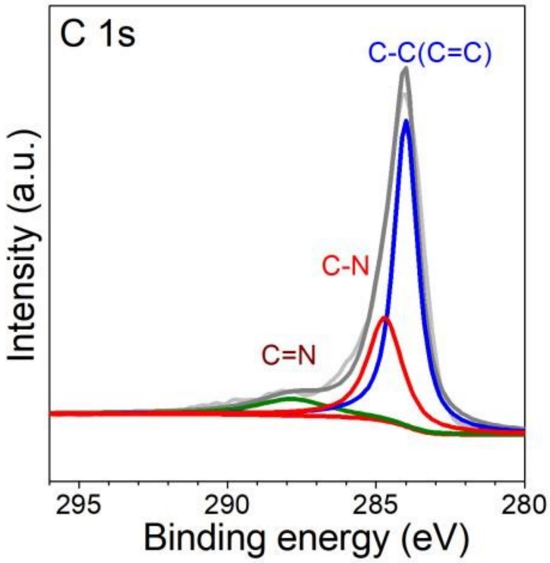

Fig. S5 XPS spectrum of C 1s of Co-4ptz-K-M-800.

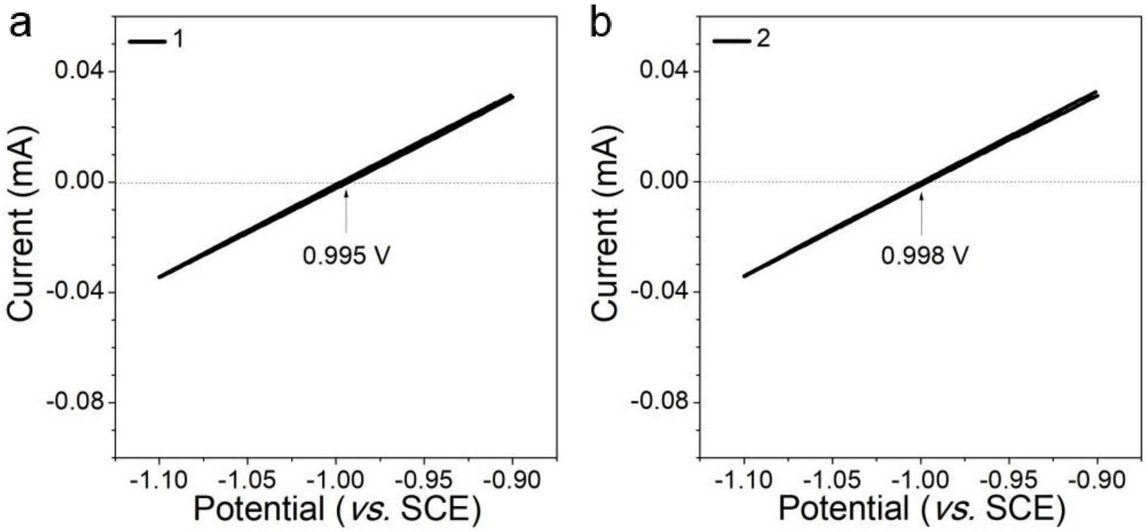

Fig. S6 (a) **1st** and (b) **2nd** cycle CV curves of SCE electrode calibration in 0.1 M KOH at 20 °C.

As shown in Fig. S8a, the SCE electrode was calibrated in 0.1 M KOH, resulting in a difference of 0.995 V between RHE and the calomel electrode potential after calibration. The second test yielded 0.998 V, with an average of 0.997 V. Therefore, in this paper, E (RHE) = E (SCE) + 0.997 V.

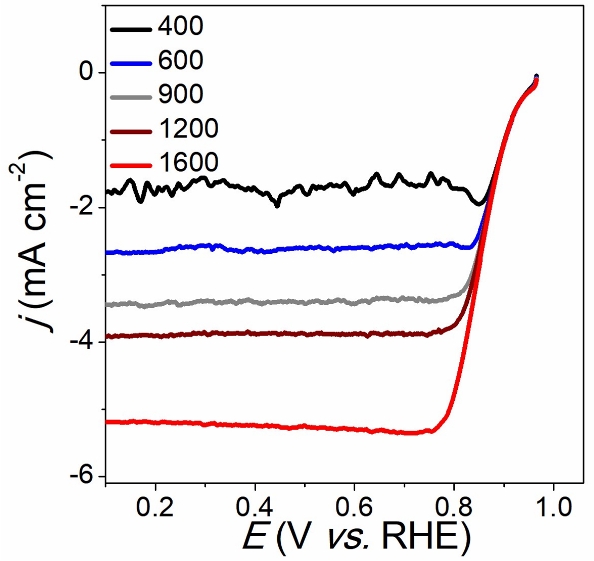

Fig. S7 LSV curves of Co-4ptz-K-M-800 at different rotation rates.

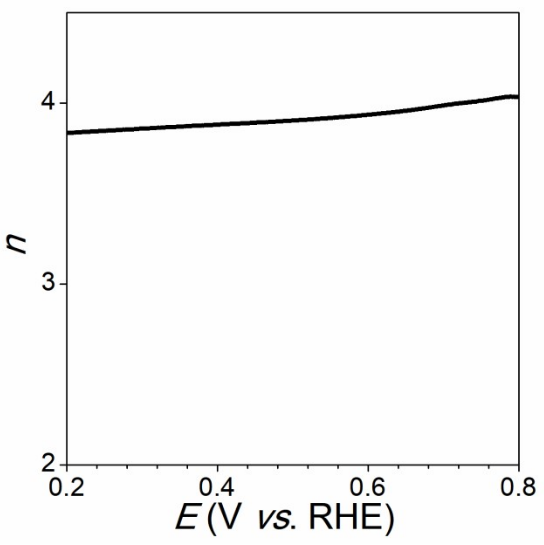

Fig. S8 The electron transfer number (*n*) of Co-4ptz-K-M-800.

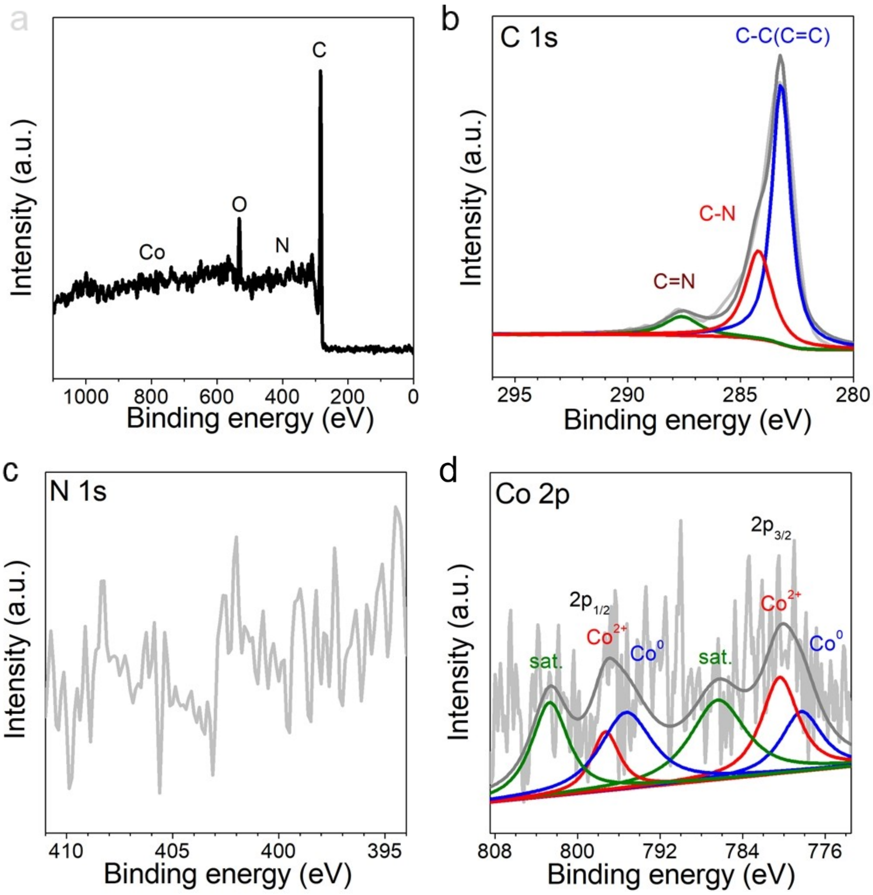

Fig. S9 XPS spectra of full (a), C 1s (b), N 1s (c) and Co (d) of Co-4ptz-K-800.

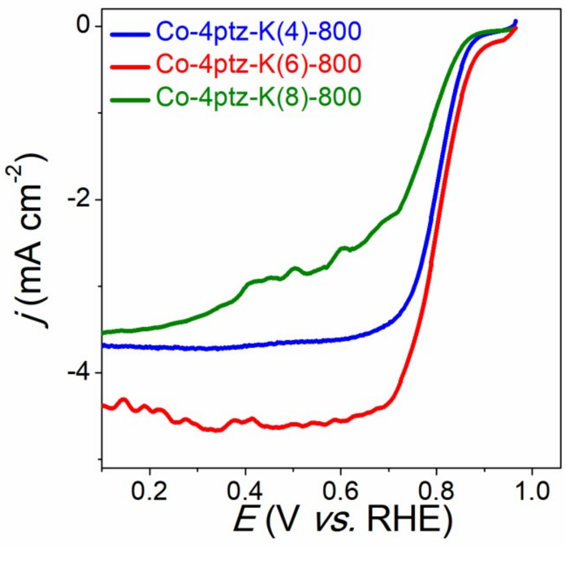

Fig. S10 LSV curves of Co-4ptz-K(4)-M-800, Co-4ptz-K(6)-M-800 and Co-4ptz-K(8)-M-800.

Table S1. Comparison of ORR catalytic performances of reported Co-containing catalysts in 0.1 M KOH solution.

Catalysts	$E_{1/2}$ **[V]**	***Reference***
Co-4ptz-K-M-800	**0.858**	**This work**
CoP/HNBs@NCL-2	0.88	*Chem. Eng. J.*, **2023**, 475, 146154.
$ZnCo_2$@NCNTs-800	0.85	*Chem. Eng. J.*, **2022**, 429, 132199.
Co/NHCB	0.84	*Adv. Funct. Mater.*, **2024**, 2415326.
Co@hNCTs	0.87	*Nano Energy*, **2020**, 71, 104592.
H-Co@FeCo/N/C	0.91	*Appl. Catal. B Environ. Energy*, **2020**, 278, 119259.
CoSAs@NC-920	0.882	*Chem. Eng. J.*, **2024**, 495, 153670.
CoSA/NPC	0.87	*J. Mater. Chem. A*, **2021**, 9, 22643-22652.
CoFe@NC/KB-800	0.845	*Chem. Eng. J.*, **2022**, 427, 131614.

Table S2. The performance of liquid Zn-air batteries with various ORR electrocatalysts reported in literature.

Catalysts	**Peak power density (mW cm^{-2})**	***Reference***
Co-4ptz-K-M-800	**166**	**This work**
Co_3HITP_2	164	*Angew. Chem. Int. Ed.*, **2019**, 59, 286–294.
Co/N-PCC	127.86	*J. Catal.*, **2019**, 369, 143–156.
Co-NC@Al_2O_3	72.4	*Adv. Mater.*, **2018**, 30, 1805268.
Co@N-CNTF	91	*J. Mater. Chem. A*, **2019**, 7, 3664–3672.
Co@NHCC-800	248	*Appl. Catal. B*, **2019**, 254, 55–65.
Co-BTC-bipy-700	336	*Nano Energy*, **2019**, 61, 245–250.
Co@Co_3O_4@NC-900	64	*J. Mater. Chem. A*, **2018**, 6, 1443–1453.
$Co_{0.85}Se$@NC	268	*J. Mater. Chem. A*, **2017**, 5, 7001–7014.