Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

1. Material and methods

1.1 Characterization of the as-prepared composite

The catalysts' morphology and structure were analysed using a Hitachi SU 8010 scanning electron microscope (SEM). The morphology of the composites was observed by a high-resolution transmission electron microscope (JEM-2100F, Talos F200S), operating at 200 k. X-ray photoelectron spectroscopy (XPS) was performed with monochromatic Al Ka radiation (1486.6 eV) using a Quantum 2000 system (Nexsa). The crystal phase identification of the sample was studied by a X-ray powder diffraction (XRD, BRUKER) in the 2h of 0 to 90°using Cu Kα (! = 0.1546 nm) radiation. A Raman spectroscopy with 532 nm laser light (HORIBA) was used to analyse the structure changes in carbon materials. The actual amount of Pt and Co loading in the catalysts was measured by inductively coupled plasma Optical emission spectrometer (ICP-OES) (Optima 8000). The Brunauer-Emmett-Teller (BET) specific surface area and pore structure distribution of the materials were analysed using McASAP 2460 instrument.

1.2 Electrochemical measurements

A CHI 760E electrochemical workstation (CH Instrument) was used to make cyclic voltammetry (CV), linear sweep voltammograms (LSVs) measurements and electrochemical impedance spectroscopy (EIS). All electrochemical studies were conducted using a conventional three electrode system at the temperature of 30°C, and a flow of N_2 or O_2 was maintained during the measurements to ensure an N_2 or O_2 saturated electrolyte, and an Hg/HgO (1 M KOH) and a Pt wire were used as the reference and counter electrodes, respectively. All the potentials mentioned below are relative to the reversible hydrogen electrode (RHE) by adding a value of (0.0989 + 0.059 × pH) V. A rotating disk electrode (RDE, Area:0.19625 cm^2) or a rotating disk ring electrode (RRDE) was polished carefully with 0.3 mm and 0.05 mm alumina powders on the silk. The electrocatalysts were treated as follows: 5mg of PtCoCN(CDs-X) were added to a mixture containing 460 µL of isopropanol and 40 µL of 0.5 % Nafion-ethanol solution. The above solution was sonicated for 30 min, and a uniformly mixed solution was obtained. For the preparation of the working electrode, 5 µL inks were dropped onto RDE and dried at the room temperature. The catalyst loading on the surface of the RDE electrode reaches 12.5 $\mu g/cm^2$.

The ORR kinetic were analysed by Koutecky-Levich plot (K-L) equation and the electron transfer number (n) of the electrocatalyst can be derived from it:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

in which, j is the current density at the applied voltage, j_K is the kinetic current density, j_L is the limiting diffusion currents density, and ω is the electrode rotating rate (rpm). The parameter B at different applied voltages could be obtained from the slope of K-L plots. Meanwhile, n values at different voltages have a relationship with parameter B according to the Levich equation as below in the alkaline solution:

$$B = 0.2nFC_O D_O^{2/3} v^{-1/6}$$

where the constant 0.2 is adopted when the rotation speed is expressed in rpm in alkaline solution. n represents the overall transferred electron number per oxygen molecule, F is the Faraday constant with the value of 96485 C mol^{-1}, D_O is the diffusion coefficient of O_2 in 0.1M KOH (1.9×10^{-5} cm^2 s^{-1}), ν is the kinetic viscosity of the solution (0.01 cm^2 s^{-1}), and C_O is the bulk concentration of O_2 (1.2×10^{-6} mol cm^{-3}). Electrochemical characterizations were carried out in an O_2-saturated potassium hydroxide (0.1 M KOH) aqueous solution. Throughout the test, the RRDE hits 1600 rpm. All the recorded potentials were corrected to the reversible hydrogen electrode (RHE). The selectivity of H_2O_2 production and the number of electrons transferred (n) were obtained from the following equations:

$$H_2O_2 = 200 \times \frac{I_R}{I_D N + I_R}$$

$$n = 4 \times \frac{I_D}{I_D + \frac{I_R}{N}}$$

where I_R is the ring current and I_D is the absolute value of the disk current, N is the current collecting efficiency of the Pt ring and determined to be 37%.

The catalytic durability was evaluated by accelerated durability tests (ADTs) recorded at a potential range from 0.6 V to 1.1 V and a scan rate of 50 mV s^{-1} in N_2-saturated 1 M KOH for 5000 CV cycles.

Zn-Air Battery Assembly and Measurements: Primary ZABs were assembled by using polished zinc foil as the anode and aqueous solution containing 6 M KOH and 0.2 M $Zn(Ac)_2$ as the electrolyte. The total catalyst loading amount on carbon paper was 2 mg cm^{-2}, PtCoCN(CDs-0.10) and RuO_2 (with a mass ration of 1:1) or Pt/C and RuO_2 (with a mass ration of 1:1). The galvanostatic discharge/charge cycling stability for the ZABs was performed using a CHI 760E with a cycling interval of 20 min (10 min for discharging and 10 min for charging) under ambient condition.

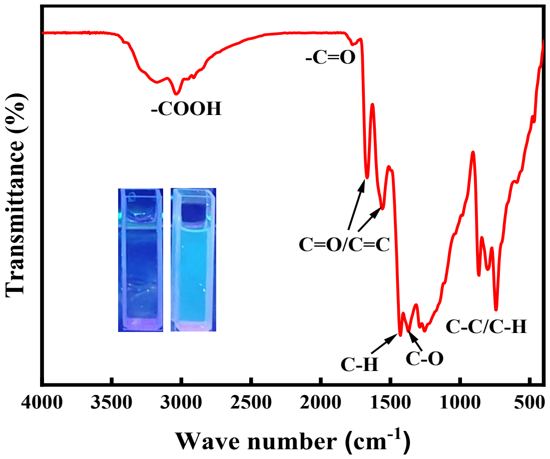

Fig.S 1 FT-IR spectra of CDs and the corresponding photographs of the filtrates exposed to an ultraviolet light at 365 nm.

Table S 1 Surface relative contents of CoCN(CDs-0.10), PtCoCN and PtCoCN(CDs-X) obtained by XPS.

	C-C /C=C	**C-N**	**O-C=O**	**Pyridinic N**	**Graphitic N**	**Co^0**	**Co^{2+}**	**Pt^0**	**Pt^{2+}**
CoCN(CDs-0.1)	69.9	21.7	8.4	52.9	47.1	49.2	50.8	/	/
PtCoCN(CDs-0)	59.5	27.9	12.6	68.5	31.5	45.4	54.6	51.5	48.5
PtCoCN(CDs-0.05)	61.3	25.8	12.9	63.3	36.7	43.5	56.5	64.1	35.9
PtCoCN(CDs-0.10)	64.1	22.1	13.8	55.0	45.0	36.7	63.3	75.2	24.8
PtCoCN(CDs-0.15)	69.3	21.5	9.2	52.4	47.6	42.2	57.8	68.5	31.5

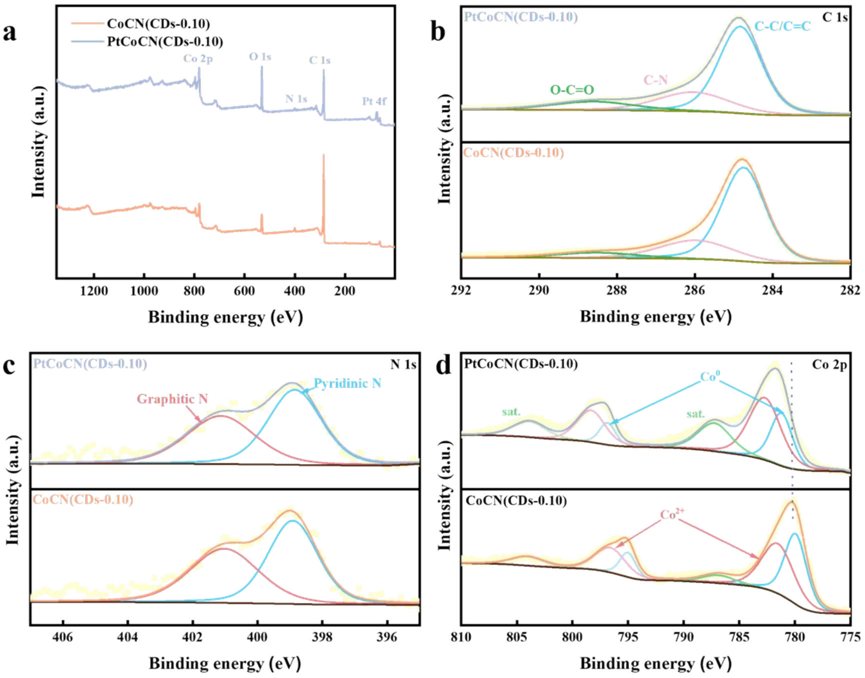

Fig.S 2 XPS spectra of CoCN(CDs-0.10) and PtCoCN(CDs-0.10): (a)survey, (b) C 1s, (c) N 1s, and (d) Co 2p.

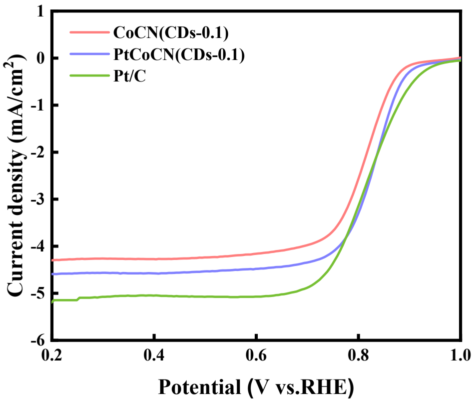

Fig.S 3 ORR polarization curves of different catalysts in O_2-saturated 0.1 M KOH solution.

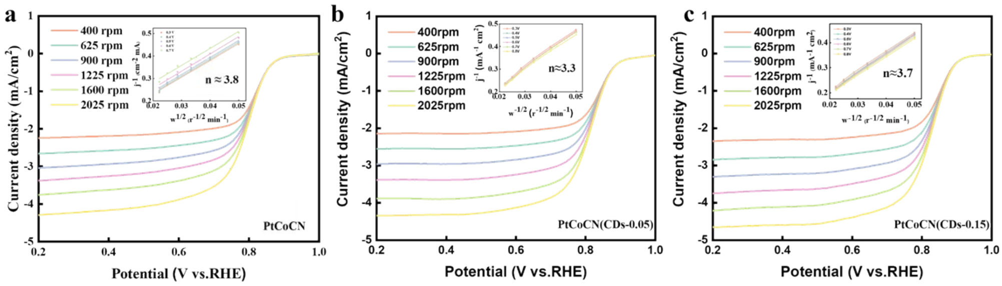

Fig.S 4 The LSV curves at various rotating speeds, with the inset showing the K-L plots at different potentials: (a) PtCoCN, (b) PtCoCN (CDs-0.05) and (c) PtCoCN (CDs-0.15).

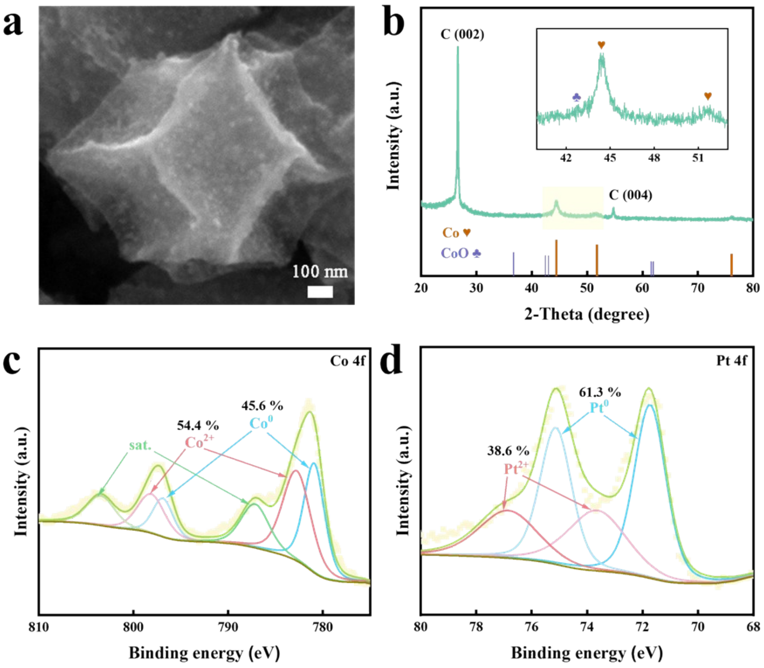

Fig.S 5 (a) SEM image, (b) XRD pattern, (c) Co 4f XPS and (d) Pt 4f XPS spectra of PtCoCN(CDs-0.10) after accelerated degradation tests.