Supplementary Materials:

Experimental section

Chemicals

$Ce(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, 2-methylimidazole (2-MI, $C_4H_6N_2$), Na_2SO4, $KMnO_4$, hexamethylenetetramine (HMT) with purity $>$ 99.5% were obtained from Sigma and used without further purification.

The preparation of $Ce_2(OH)_4SO_4 \cdot 2H_2O$

A $Ce_2(OH)_4SO_4 \cdot 2H_2O$ sample was synthesized by applying the homogeneous alkalization process. In a typical synthesis, $Ce(NO_3)_3 \cdot 6H_2O$ (5 mmol), Na_2SO_4 (2.5 mmol), and HMT (3 mmol) were dissolved in 1000 mL of deionized water. The solution was magnetically stirred and heated to the boiling temperature under N_2 flow, yielding a white precipitate. The mixture was further aged at the refluxing condition for 6 h and then recovered by filtration. The sample was washed with copious amounts of water and ethanol, conditioned at a relative humidity (about 70%) to a constant weight, and stored in a sealed bottle for further characterization and application.

The preparation of Ce-modified 2D-hexagonal-leaf-like ZIFs lamella

Initially, 192 mg of $Zn(NO_3)_2 \cdot 4H_2O$ and 48 mg of $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 20 mL of deionized water to form solutions. Similar steps, 550 mg 2-methylimidazole and 50 mg $Ce_2(OH)_4SO_4 \cdot 2H_2O$ were dissolved in 30 mL of deionized water and stirred for 10 min at room temperature (RT). And then they were mixed together with stirring for 30 min. Then, the mixed solution was stood at RT for 12 h. Finally, lilac colour solid powders were collected and washed with deionized water and ethanol several times and dried under vacuum for 6 h at 60 °C. Similarly, 2D-hexagonal-leaf-like ZIFs are formed without cerium precursors. The 3D Co-Zn-ZIFs are synthesized mainly by using methanol replace deionized water during the synthesis process, following with the same purification process.

The preparation of Ce-HPCN, HPCN and 3D-Co-Zn/C

In a typical process, Ce-modified 2D-hexagonal-leaf-like ZIFs (Ce-ZIF-L) were transferred into a ceramic boat and then heated up to 850 ℃ at a rate of 2 ℃ min^{-1} and kept for 2 h under Ar flow in a tube furnace. After being cooled tort, the black powders of Ce-HPCN were achieved. HPCN and 3D-Co-Zn/C were achieved by the same pyrolyzation process.

Characterization

The field emission scanning electron microscopy (FE-SEM) images were obtained using Hitachi S-4800 microscope with an acceleration voltage of 30 kV. Transmission electron microscopy (TEM) images were captured on a JEM-2100 instrument microscope at an acceleration voltage of 200 kV. HRTEM (Philips Tecnai G2), and STEM (FEI Tecnai G2 F30 S-TWIN). The specific surface area, pore size distribution, and pore volume were characterized with a Micrometrics ASAP2020 analyzer (USA) at 77 K. Powder X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker D8 X-ray diffraction meter with monochromatic Cu Kα radiation (λ = 0.154056 nm). XPS measurements were carried out on Kratos AXIS Ultra spectrometer with a source gun of Al Kα and spot size of 400 μm.

Electrochemical Measurements

The electrocatalyst inks were prepared by ultrasonically dispersing catalyst (2.0 mg) in a mixed solution which consist of 950 μL isopropyl alcohol, 50 μL 5 wt % Nafion solution (Alfa Aesar). After ultrasound for 1 h, 20 μL of the ink was dropped onto a rotating disk electrode (RDE, 5 mm diameter, 0.196 cm^2 geometric surface areas; RRDE, 5.6 mm diameter, 0.246 cm^2 geometric surface areas) and rest at room temperature without any interruption for 1h. The loading of the catalyst is 0.16 mg cm^{-2}. Electrochemical measurements were conducted using a three-electrode cell with saturated calomel electrode (SCE), and a platinum sheet was used as the reference and counter electrodes, respectively. CV, RDE, and RRDE tests were carried out in 0.1 M KOH electrolyte at room temperature on a CHI760D electrochemical workstation assembled with MSR Electrode Rotator (Pine Research Instrumentation). The electrode potential was calibrated based on the equation: E (RHE) = E (SCE) + 0.2415 + 0.0591 × PH. Considering the contribution of the electrical double layer capacity for current response, the obtained electrochemical curves in N_2-saturated electrolyte were subtracted from those in O_2-saturated electrolyte. The four-electron selectivity was evaluated based on the HO_2^- yield and electron transfer number (n), calculated from the following equations:

$$HO_2^{-}(\%) = 200 \times \frac{I_R / N}{I_R / N + I_D} \tag{1}$$

$$n = 4 \times \frac{I_D}{I_R / N + I_D} \tag{2}$$

Here, I_D and I_R are the disk and ring currents, respectively, and N is the ring collection efficiency (0.37).

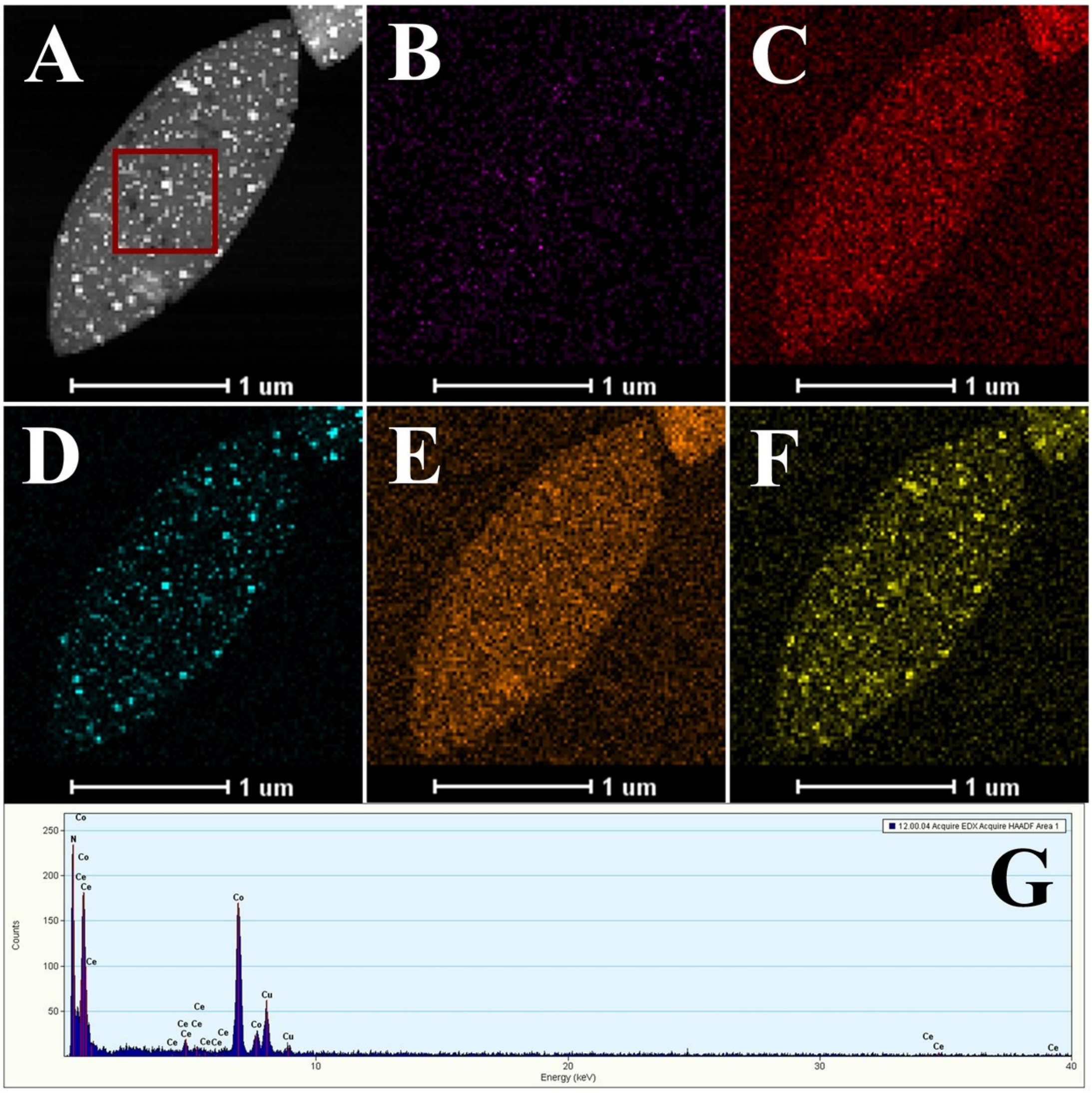

Figure S1. (A-F) STEM and elemental mapping images of Ce-HPCN; (G) Energy Dispersive Spectrometer analysis corresponding to the square region marked in STEM.

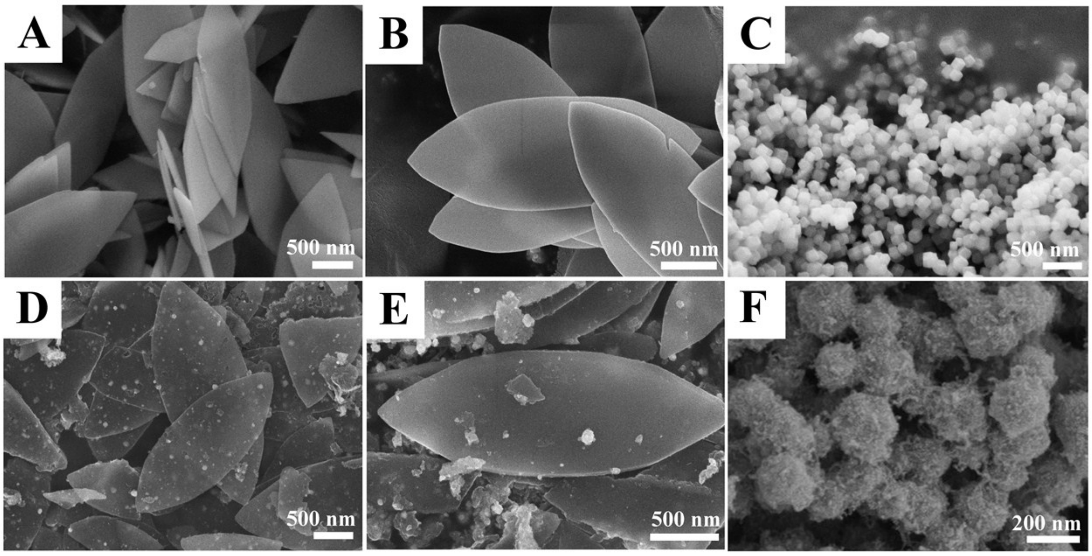

Figure S2. (A-C) FSEM image of the as-prepared Ce-HPCN, HPCN and 3D-Co-Zn/C precursor; (D-F) FSEM image of the Ce-HPCN, HPCN and 3D-Co-Zn/C.

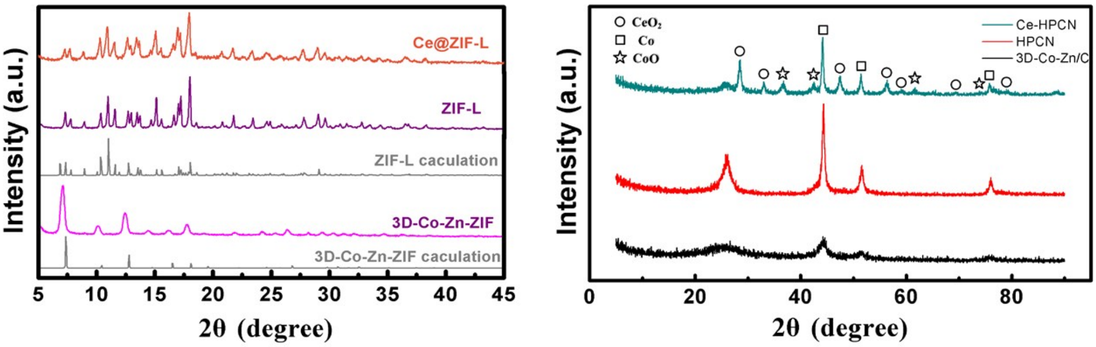

Figure S3. (a) XRD patterns of Ce@ZIF-L, ZIF-L and 3D-Co-Zn-ZIF; (b) XRD patterns of Ce-HPCN, HPCN and 3D-Co-Zn/C.

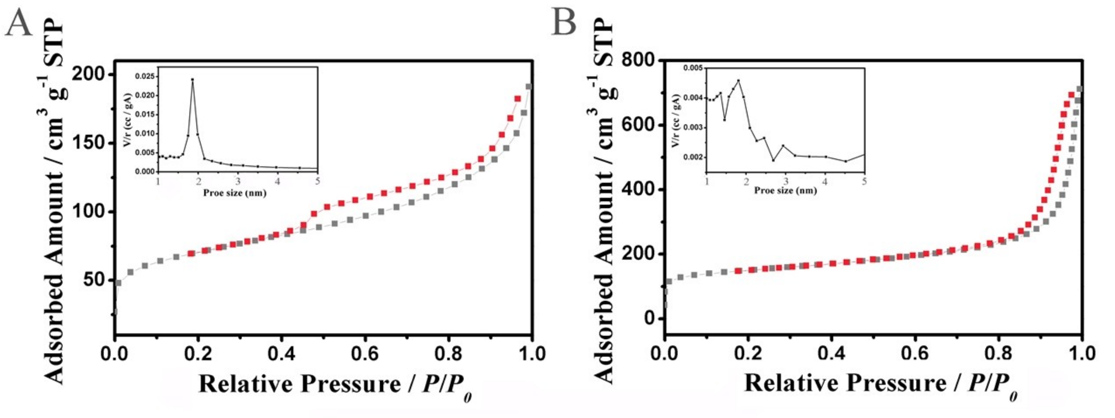

Figure S4. Nitrogen sorption isotherms of 3D-Co-Zn/C (A) and Ce-HPCN (B) (insert: the corresponding pore size distribution).

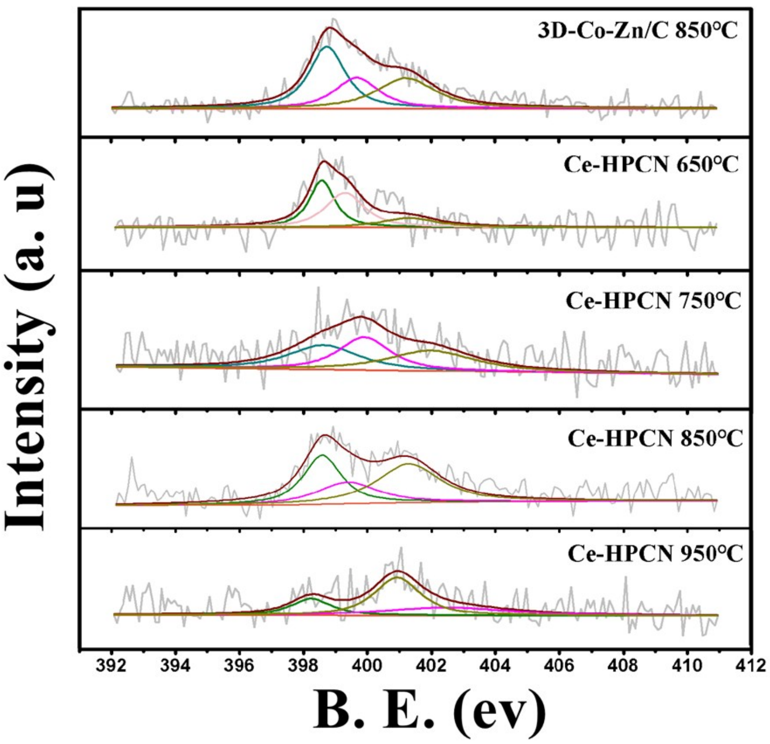

Figure S5. High-resolution XPS N1s spectra of 3D-Co-Zn/C and Ce-HPCN obtained at different heat treatment temperatures.

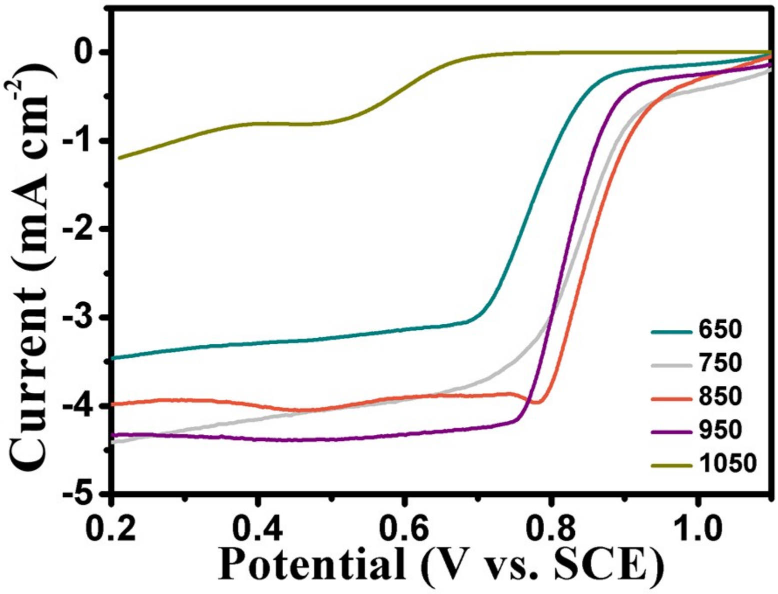

Figure S6. LSV curves (5 mV s^{-1}. 1600 rpm) of Ce-HPCN obtained at different heat treatment temperatures. (Prepared catalyst loading: 0.5 mg cm^{-2})

Taking the surface properties of prepared catalysts into consideration, such outstanding activity for Ce-HPCN must be attributed to the synergistic effect of Ceria with Co-pyridinic and graphitic N sites that maximally exposed on the surface of the 2D open carbon framework. It was found that heat treatment at 850 ℃ led to the best catalytic activity (Figure S6). Combined with the results of XPS (Figure S5), such performance of Ce-HPCN obtained at 850 ℃ should be ascribed to the high content of pyridinic and graphitic N sites.

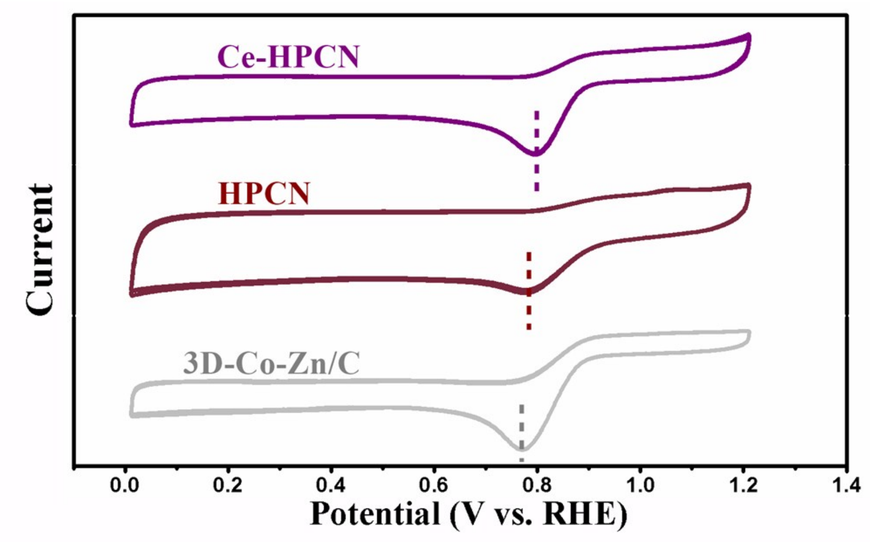

Figure S7. CV curves (50 mV s^{-1}) of Ce-HPCN , HPCN and 3D-Co-Zn/C.

As shown in Figure S7, three obvious cathodic peaks at 0.805 V, 0.792 V, 0.780 V (vs. RHE) were observed for Ce-HPCN , HPCN and 3D-Co-Zn/C, suggesting the best oxygen reduction electrocatalytic activity of Ce-HPCN among these prepared catalysts.

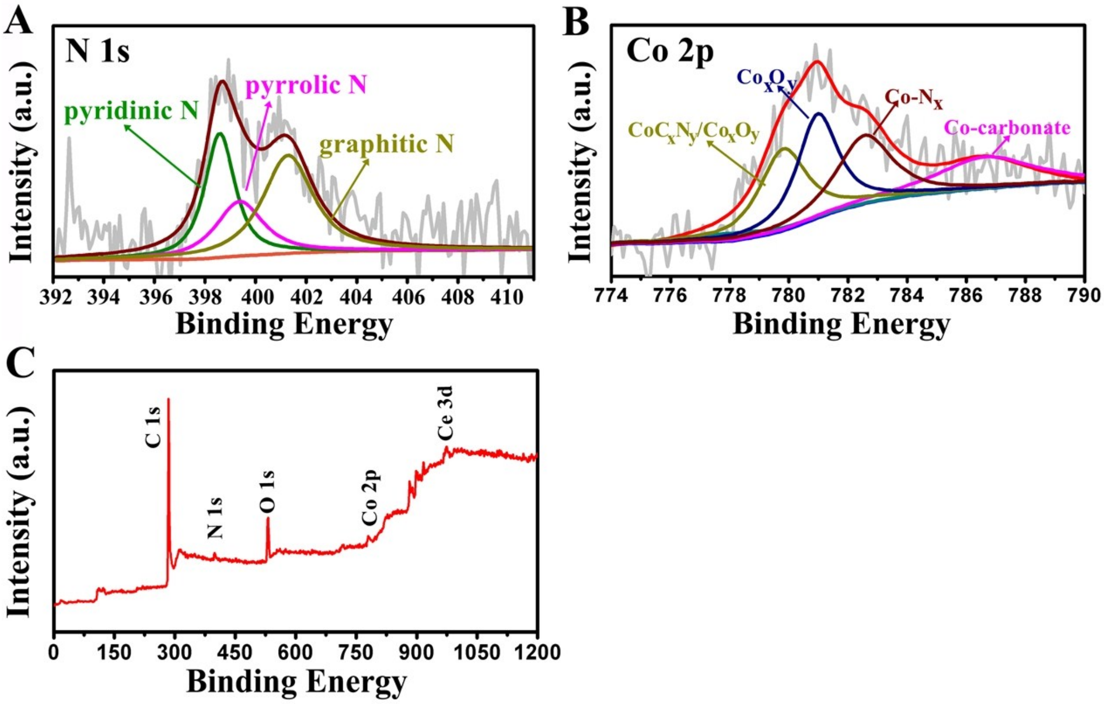

Figure S8. (A) High-resolution XPS N1s spectra of Ce-HPCN; (B) High-resolution XPS Co 2p spectra of Ce-HPCN; (C) Wide-scan XPS survey spectra of Ce-HPCN.