

Electronic Supplementary Information

Zinc hydroxide – organic framework for electrochemical synthesis of H₂O₂

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Methods

Synthesis of Zn-AB-MOF, Zn-A-MOF and Zn-B-MOF

Zn-AB-MOF: Zn(NO₃)₂·6H₂O (1.895 g, 6.37 mmol), A (1,4-terephthalic acid) (0.176 g, 1.06 mmol) and B (3,4-Pyridinedicarboxylic acid) (0.177 g, 1.06 mmol) were dissolved in 60 ml DMF. The solution was transferred into a 100 ml Teflon-lined autoclave and heated at 100 °C for 12 h in an oven. Finally, the obtained product was washed with DMF and ethanol several times and dried at 60 °C.

Zn-A-MOF: Zn(NO₃)₂·6H₂O (1.895 g, 6.37 mmol) and A (1,4-terephthalic acid) (0.352 g, 2.12 mmol) were dissolved in 60 ml DMF. The solution was transferred into a 100 ml Teflon-lined autoclave and heated at 100 °C for 12 h in an oven. Finally, the obtained product was washed with DMF and ethanol several times and dried at 60 °C.

Zn-B-MOF was synthesized using the same procedure as Zn-A-MOF, except for that A was replaced by B (3,4-Pyridinedicarboxylic acid) (0.331 g, 2.12mmol).

Synthesis of Zn-HOF, A-ZnO, B-ZnO, and ZnO

Zn-HOF: Zn-AB-MOF was deposited on a conducting substrate (e.g., glassy carbon or carbon paper) and subjected to cyclic voltammetry (CV) from 0.1 to 0.8 V (vs. RHE) at 50 mV s⁻¹ for 20 cycles in 0.1 M KOH.

A-ZnO: Zn-A-MOF loaded on a conducting substrate was subjected to same electrochemical sweeping (0.1 to 0.8 V vs. RHE at 50 mV s⁻¹ for 20 cycles in 0.1 M KOH).

B-ZnO: Zn-B-MOF loaded on a conducting substrate was subjected to same electrochemical sweeping (0.1 to 0.8 V vs. RHE at 50 mV s⁻¹ for 20 cycles in 0.1 M KOH).

ZnO: Zn(NO₃)₂·6H₂O (4.0121 g, 13.5 mmol) and KOH (0.27 g, 5 mmol) were dissolved in 50 ml of deionized water and stirred for 30 min. The above solution is then transferred to a 100 ml PTFE-lined autoclave, heated in an oven at 120 °C for 12 h. The powder was washed several times with deionized water and ethanol, and dried overnight at 60 °C.

Structural characterization

SEM images were obtained on a JSM-7800F (JEOL Ltd., Japan). XRD patterns were collected on a powder X-ray diffractometer (RIGAKU, D/MAX 2550 VB/PC, Japan) equipped with Cu K α radiation source operating at 40 kV, scanning rate: 2° min⁻¹, 2 θ

range: 5–80°. TEM images were recorded using a FEI Talos F200X system (Thermo Fisher Scientific) at an acceleration voltage of 200 kV. XPS measurements were acquired on an ESCALAB 250Xi system (Thermo Fisher Scientific) with Al K α radiation source. FTIR spectra were recorded on Nicolet 6700 (Thermo Fisher Scientific). UV-Vis spectra were obtained using a U-3310 spectrophotometer (Hitachi Ltd., Japan). ICP-OES measurements were performed on a PerkinElmer Optima 8000.

Electrode fabrication

RRDE: The catalyst ink was prepared as follows: 3 mg of catalyst, 950 μ L of ethanol solution, and 50 μ L of 5% Nafion solution are mixed. The mixture is then treated with ultrasound for 1 h to ensure uniform dispersion. 20 μ L of the prepared ink was coated onto the rotating ring disk electrode (RRDE, electrode area: 0.2475 cm²). The electrode is left to dry at room temperature.

GDE: A 3 \times 3 cm² carbon paper (GDL, YLS30T) was coated on the hydrophobic side by 10% PTFE solution via spin coating. It was placed in a tube furnace and annealed at 350 °C for 2 h. Meanwhile, 10 mg electrocatalyst was dispersed in 250 μ L deionized water, 1710 μ L isopropanol and 40 μ L Nafion solution. The catalyst ink was evenly sprayed onto the hydrophilic side of the carbon paper as the working electrode using a spray pen device. The spraying area was 2 \times 2 cm², the actual working area was 1 \times 1 cm², and the catalyst load was 0.48 mg cm⁻². Pure O₂ was supplied to the cathode chamber at a rate of 50 mL min⁻¹.

Electrochemical measurements

The ORR performances were evaluated using an electrochemical station (Autolab N302) and RRDE setup (PINE Research Instrumentation) in a three-electrode system. A Hg/HgO electrode and a graphite rod were used as the reference electrode and counter electrode, respectively. The Hg/HgO reference electrode was experimentally calibrated and all potentials reported were converted to RHE. All potentials reported were converted to a RHE.

Linear sweep voltammetry (LSV): The polarization curve was measured at a scan rate of 5 mV s⁻¹ at 1600 rpm (the Pt-ring potential was set to 1.4 V vs. RHE, and the collection efficiency (N) of the ring electrode was determined to be 37% as in Fig S9) in the N₂-saturated electrolyte.

Based on the catalyst ring current (I_R) and disk current (I_D), the H₂O₂ selectivity and the electron transfer number (n) were calculated using the following equations:

$$H_2O_2\% = \frac{I_R/N}{\frac{I_R}{N} + I_D} \times 200\% \quad (1)$$

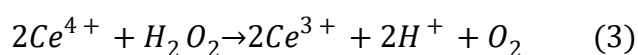
$$n = 4 \times \frac{I_D}{\frac{I_R}{N} + I_D} \quad (2)$$

H₂O₂ production in GDE

The electrosynthesis of H₂O₂ was conducted in a customized H-type electrolytic cell. The cathode chamber and the anode chamber were separated by an anion exchange membrane (Fumasep FAB-PK-130). The electrolyte in the cathode chamber was stirred magnetically at 600 rpm. 60 mL of 1 M KOH was placed in the cathode and anode chambers as the electrolyte, and the electrolyte was replaced every hour during

the chronoamperometric test. A carbon plate was used as the anode and a Hg/HgO electrode was used as the reference electrode.

The yield of H₂O₂ was determined through titration with 1 mM Ce (SO₄)₂. H₂O₂ is able to reduce Ce⁴⁺ to Ce³⁺ with high efficiency according to the following equation:



Ce⁴⁺ is yellow in color while Ce³⁺ is colorless. As the Ce⁴⁺ concentration decreases, the solution gradually transitions from yellow to colorless. The decreased concentration of Ce⁴⁺ ions ($\Delta C_{Ce^{4+}}$) could be calculated from the absorbance decrease. The concentration of H₂O₂ could be calculated by the following formula :

$$C_{H_2O_2} = \frac{1}{2} \times \Delta C_{Ce^{4+}} \quad (4)$$

A series of Ce (SO₄)₂ solutions with concentration ranging from 0.5 mM, 0.4 mM, 0.3 mM, 0.2 mM, 0.1 mM to 0.05 mM were prepared and their UV-Vis spectra were collected. The absorbance at 318 nm was plotted against Ce(SO₄)₂ concentration to obtain the calibration curve (Fig. S11).

By tracking the change in Ce⁴⁺ concentration after adding the collected electrolyte liquid phase, the yield of H₂O₂ can be determined. The calculation for the FE of H₂O₂ generated is as follows:

$$FE_{H_2O_2} = \frac{2CVF}{Q} \quad (5)$$

Where C is the concentration of H₂O₂ in the electrolyte (mol L⁻¹), V is the product of the electrolyte (L), F is Faraday's constant (96485 C mol⁻¹), and Q is the amount of charge passed through (C).

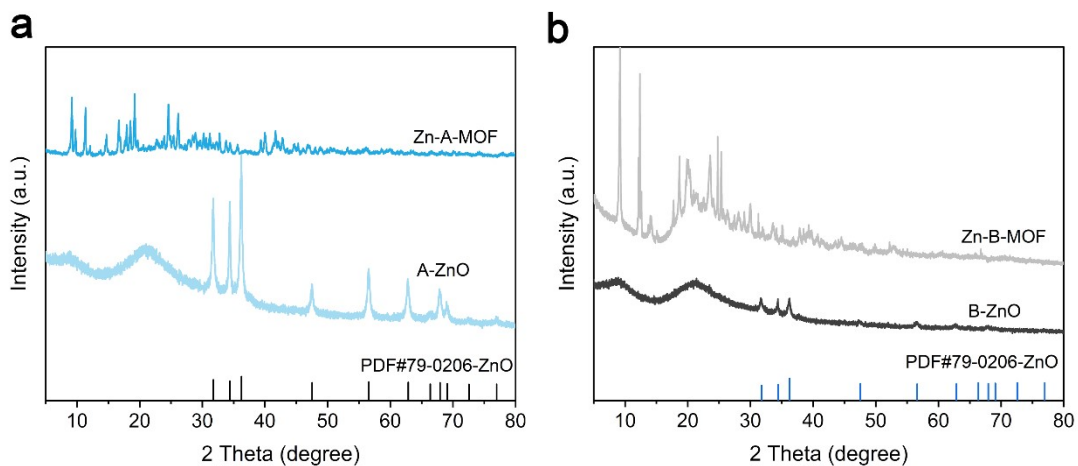


Fig. S1 XRD patterns of (a) Zn-A-MOF and A-ZnO; (b) Zn-B-MOF and B-ZnO.

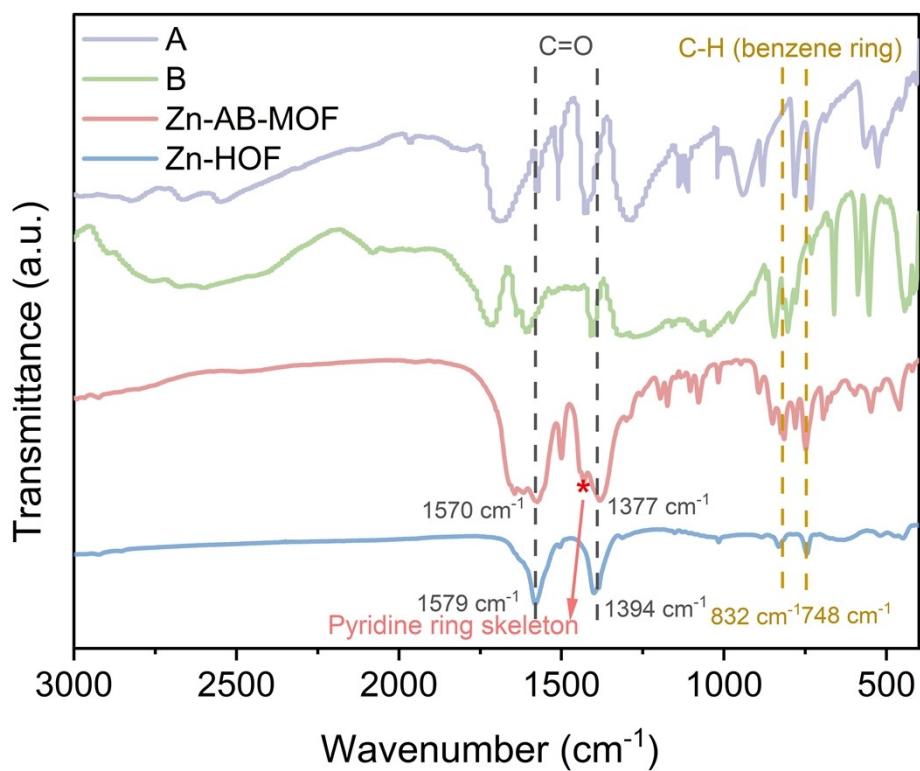


Fig. S2 FTIR spectra of Zn-AB-MOF, Zn-HOF, ligand A and ligand B.

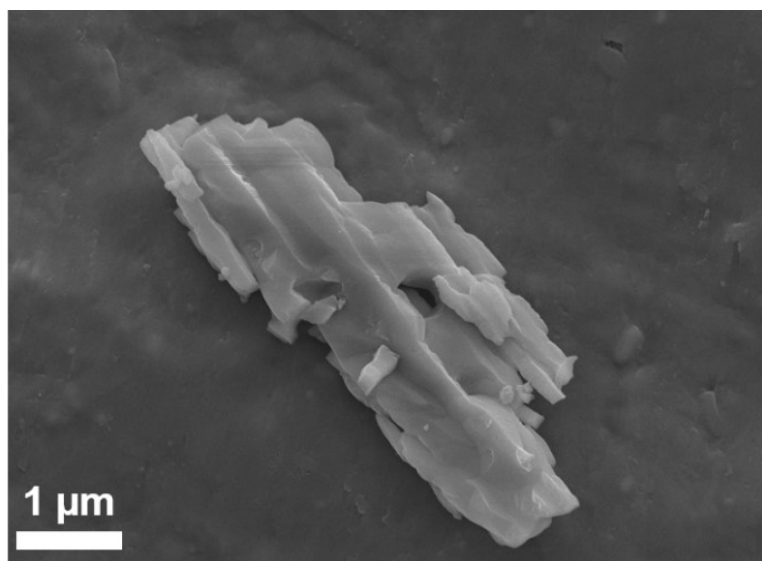


Fig. S3 SEM image of Zn-AB-MOF.

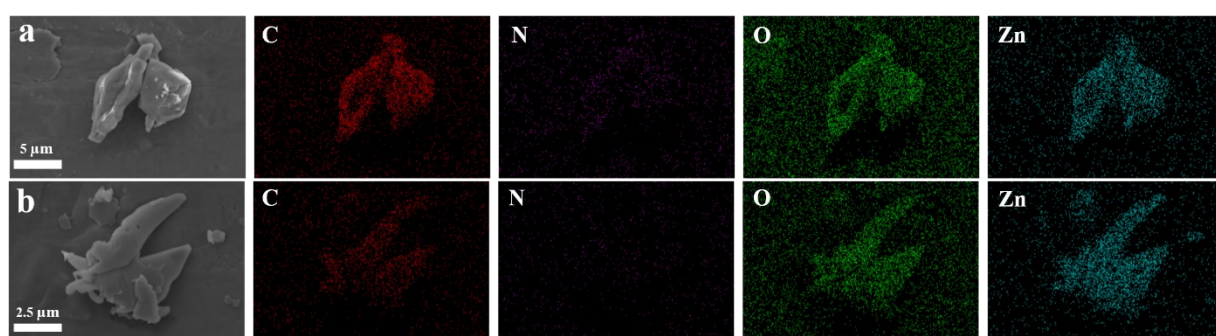


Fig. S4 EDS images of (a) Zn-AB-MOF and (b) Zn-HOF.

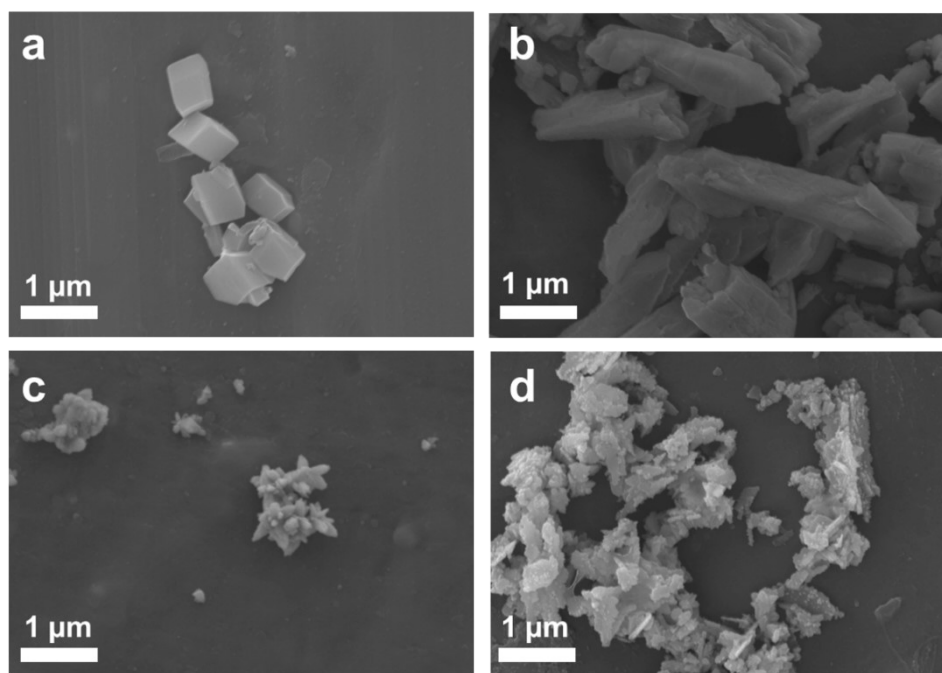


Fig. S5 SEM images of (a) Zn-A-MOF; (b) Zn-B-MOF; (c) A-ZnO and (d) B-ZnO.

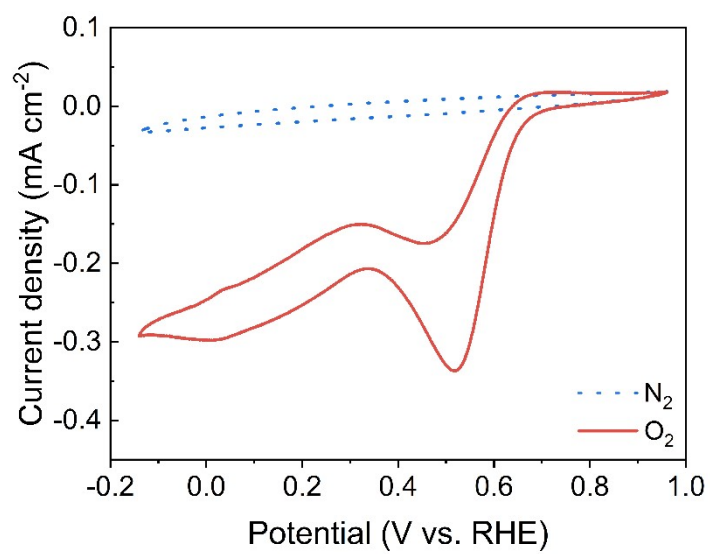


Fig. S6 CV curves of Zn-HOF test in O₂ / N₂ -saturated 0.1 M KOH.

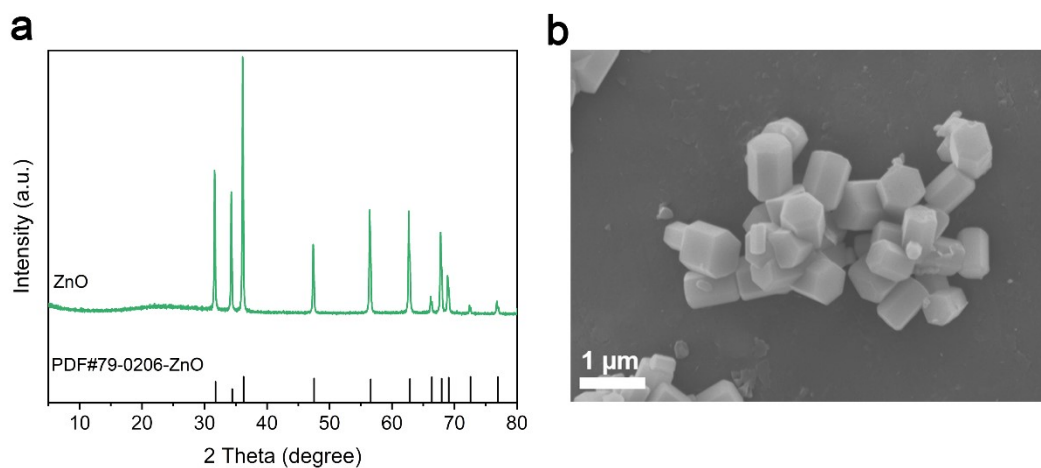


Fig. S7 (a) XRD pattern and (b) SEM image of ZnO synthesized via hydrothermal reaction (synthetic details provided in Methods section above).

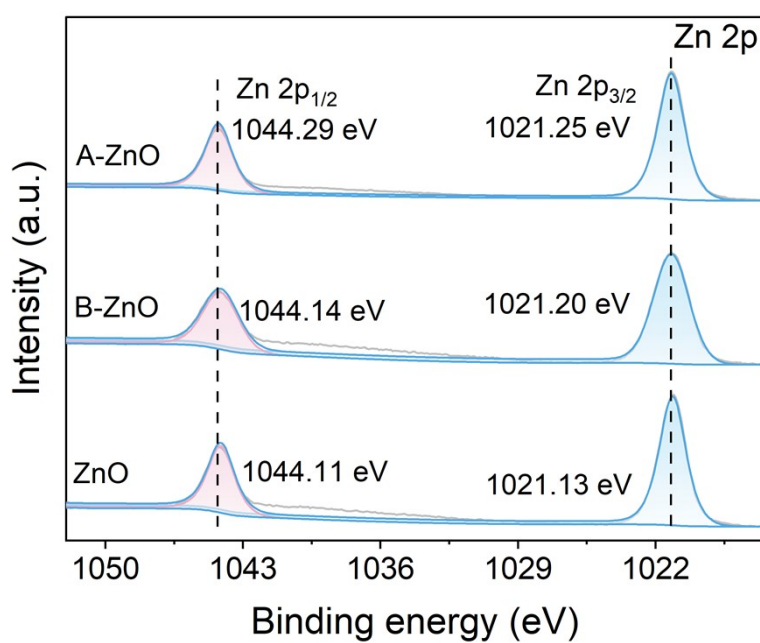


Fig. S8 XPS Zn 2p spectra of A-ZnO, B-ZnO and ZnO.

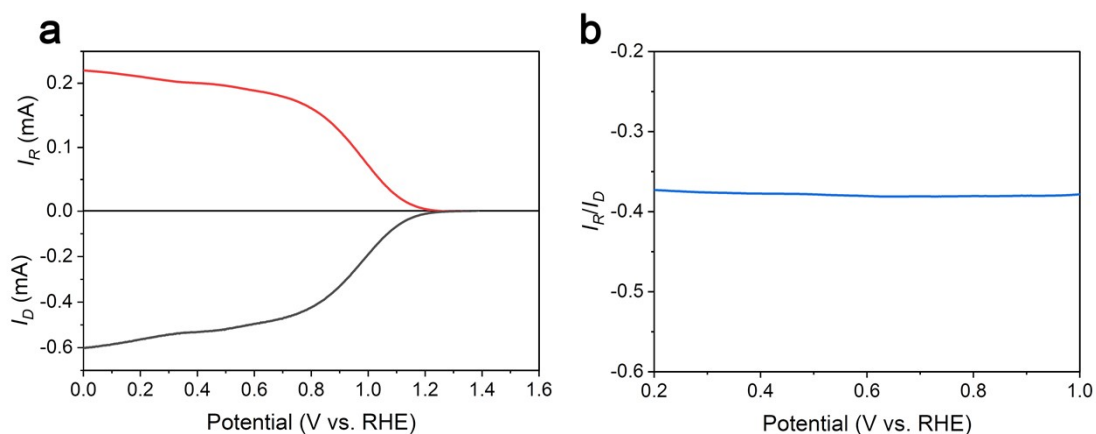


Fig. S9 Experimental determination of the collection efficiency of RRDE used in present work. (a) Polarization curves of the RRDE in degassed 0.1 M KOH solution containing 5 mM of $K_3Fe(CN)_6$ at 1600 rpm. The potential of the disk electrode was negatively scanned from 1.5 V vs. RHE at 5 mV s^{-1} and the potential of ring electrode was held at 1.4 V. A Hg/HgO reference electrode was used and all the potentials were converted vs. RHE. (b) Collection efficiency of the RRDE at different potentials derived from (a).

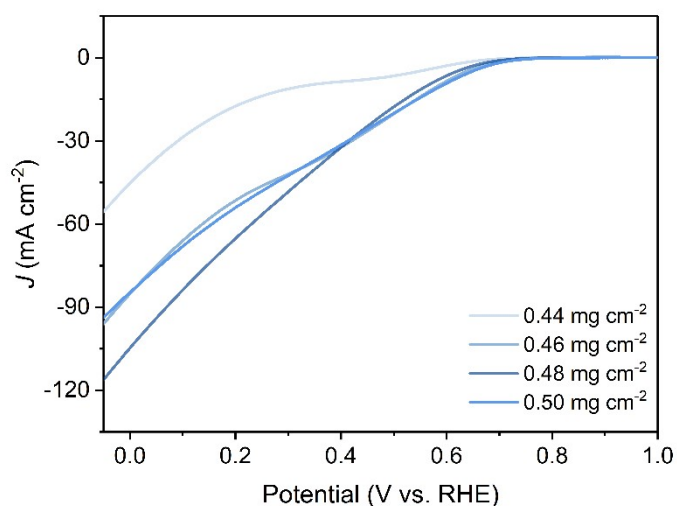


Fig. S10 Polarization curves of Zn-HOF with different loads in the O_2 -feeding 1 M KOH in GDE.

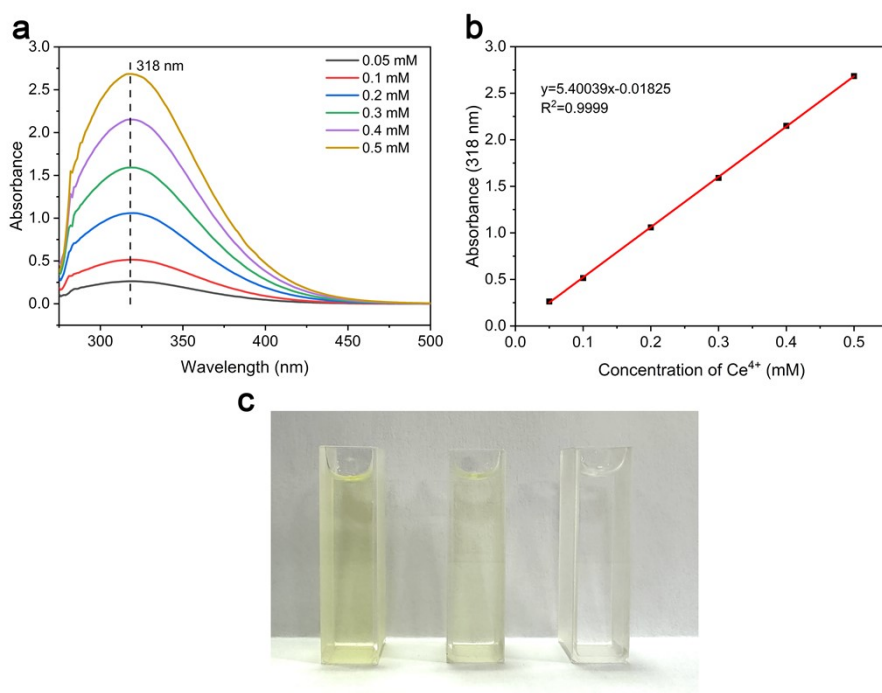


Fig. S11 (a) UV-Vis spectra of different concentration $\text{Ce}(\text{SO}_4)_2$ solutions. (b) The linear calibration curve between the concentration of Ce^{4+} and the absorbance at 318 nm. (c) Image of the $\text{Ce}(\text{SO}_4)_2$ solutions after using electrolyte to titration. (From left to right: 1 mM $\text{Ce}(\text{SO}_4)_2$, 4 mL; 1 mM $\text{Ce}(\text{SO}_4)_2$, 4 mL + 25 μL electrolyte, 1 mM $\text{Ce}(\text{SO}_4)_2$, 4 mL + 75 μL electrolyte. The electrolyte was taken from the cathode chamber of Zn-HOF after electrolysis at 100 mA cm^{-2} for 1 h.)

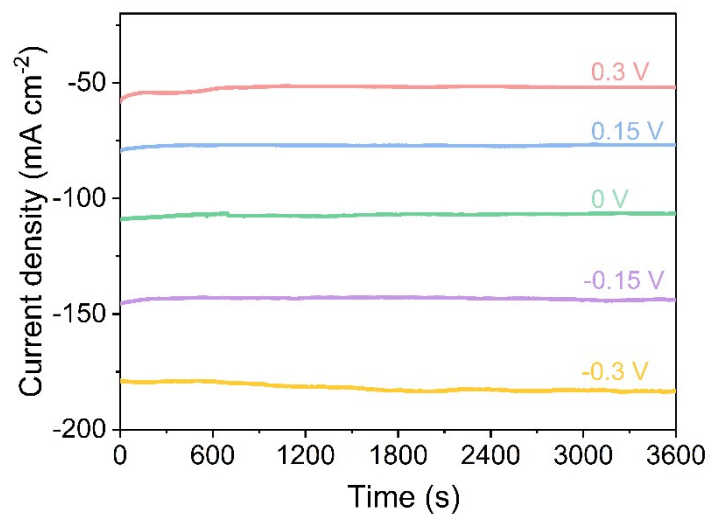


Fig. S12 Chronoamperometric curves of Zn-HOF at different potentials in 1 M KOH in GDE.

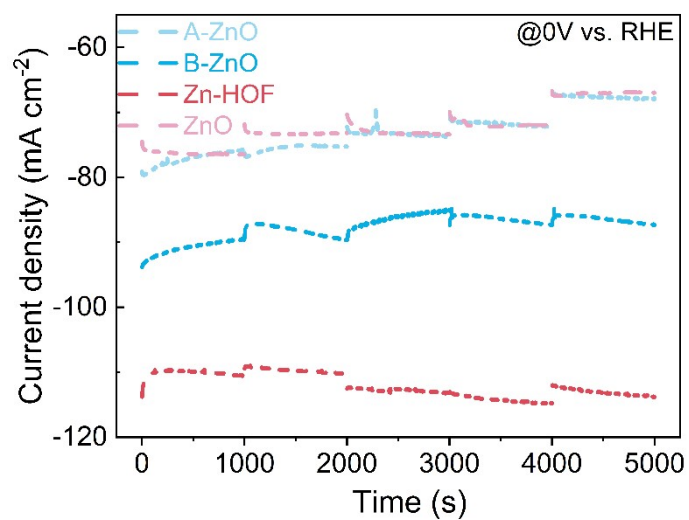


Fig. S13 Chronoamperometric curves of A-ZnO , B-ZnO, Zn-HOF and ZnO at 0 V vs. RHE in 1 M KOH in GDE.

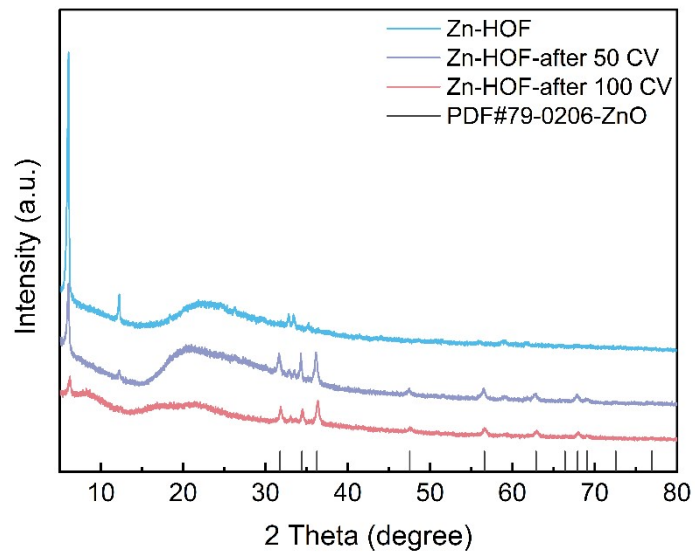


Fig. S14 XRD patterns of Zn-HOF after ORR.

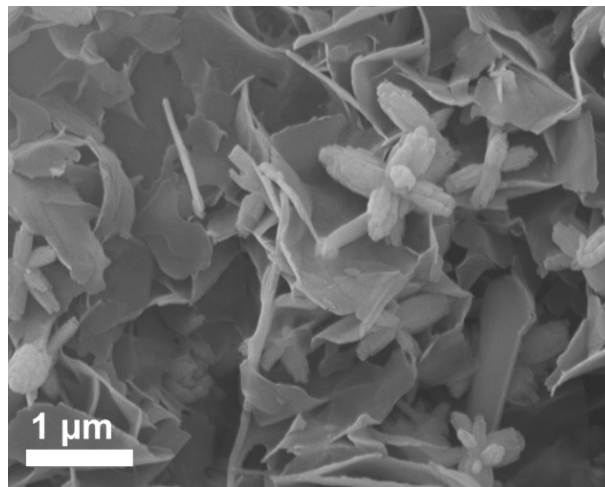


Fig. S15 SEM image of Zn-HOF after ORR.