Single-step thermal synthesis of bimetallic Co/Zn@NC under solvent-free conditions as an efficient dual-functional oxygen electrocatalyst in Zn-air battery

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1. Experimental Section

1.1 Materials

All chemical reagent, solvents were purchased from Aladdin Company and directly used without further purification.

1.2 Electrochemical Characterizations

The electrochemical performance tests for ORR/OER were examined on a conventional three-electrode system on CHI660E electrochemical workstation at room temperature. In the electrochemical tests of ORR, the platinum wire was selected as the counter electrode and the reference electrodes was the Hg/HgO (in alkaline media). In the electrochemical tests of OER, the counter electrode and the reference electrode were platinum wire and oxidized mercury, respectively. The measured potentials were then converted potentials vs reversible hydrogen electrode (RHE) according to the Nernst equation. All the electrochemical properties of ORR were tested in a saturated N_2/O_2 solution, so N_2/O_2 was required to pass through the electrolyte for 20 minutes to ensure

solution saturation. The OER was LSV tested at room temperature at a scanning rate of 5 mV s^{-1} in 1.0 M KOH solution, and the compensation potential was corrected by electrochemical impedance spectroscopy. After measuring the LSV curve of the ORR, the net ORR curve was obtained by subtracting the background capacitance recorded by 0.1 M KOH saturated N_2 solution. To ensure oxygen saturation, oxygen should be supplied continuously during the test. The linear sweep voltammetry (LSV) of the catalyst was measured with a rotating disk electrode (RDE). To obtain the catalyst ink, 5 mg of the prepared catalysts were added into 980 μL of isopropanol/ deionized water (1:1) and 20 μL of Nafion (5%), sonicated for 20 minutes. Then take 20 μl of catalyst ink onto the glassy carbon electrode and dry naturally. The ink preparation method of the commercial Pt/C catalyst was almost the same, 5 mg of Pt/C was dissolved in the solution, and then 20 μL of the ink was dropped onto the electrode.

1.3 Zinc-air Battery Tests

In the zinc-air battery test, zinc foil and carbon paper evenly distributed in catalyst ink were selected as anode and air cathode respectively. A mixed solution of 0.2 M zinc acetate and 6.0 M KOH was used as the electrolyte. The amount of catalyst on carbon paper was 2.0 mg cm^{-2}. An all-solid zinc-air battery was prepared by using carbon paper supported with catalyst as cathode, polished zinc foil as anode and PVA film as solid electrolyte. The preparation process of PVA film is as follows: add 5 g PVA powder to 50 mL deionized water, dissolve 5.94 g KOH and 0.0028 g $Zn(Ac)_2$, stir at 95℃ for 0.5 h until the solution becomes a transparent gel. The gel was then poured into a petri dish and frozen in the fridge for 12 hours.

1.4 Kinetic Current Calculation

The Tafel slope is calculated by the formula η = a + b log |j|, where η is the overvoltage, b is the Tafel slope, and j is the current density. The number of electron transfer (n) in the ORR process is calculated based on the Koutecky-Levich equation at different electrode potentials:

$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{1/2}}+\frac{1}{J_K} \quad (1)$$

$$B=0.2nFC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current density. ω is the angular velocity and n is the number of electron transfer. F is the Faraday constant (96485 C mol^{-1}), C_0 is the volume concentration of oxygen (1.2×10^{-6} mol cm^{-3}), and D_0 is the diffusion coefficient of oxygen at 0.1 M KOH and 0.1 M perchloric acid (1.9×10^{-5} cm^2 s^{-1}), and ν is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}). The specific current density can be calculated by:

$$J_K=\frac{J_L\times J}{J_L-J} \quad (3)$$

2. Characterization

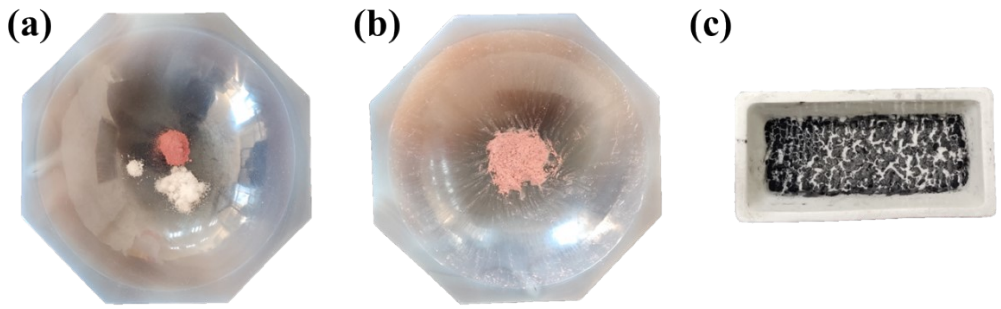


Figure S1. CoZn@NC_IST before grinding (a), after grinding (b), and after pyrolysis at 600°C under 5% H_2/Ar (c).

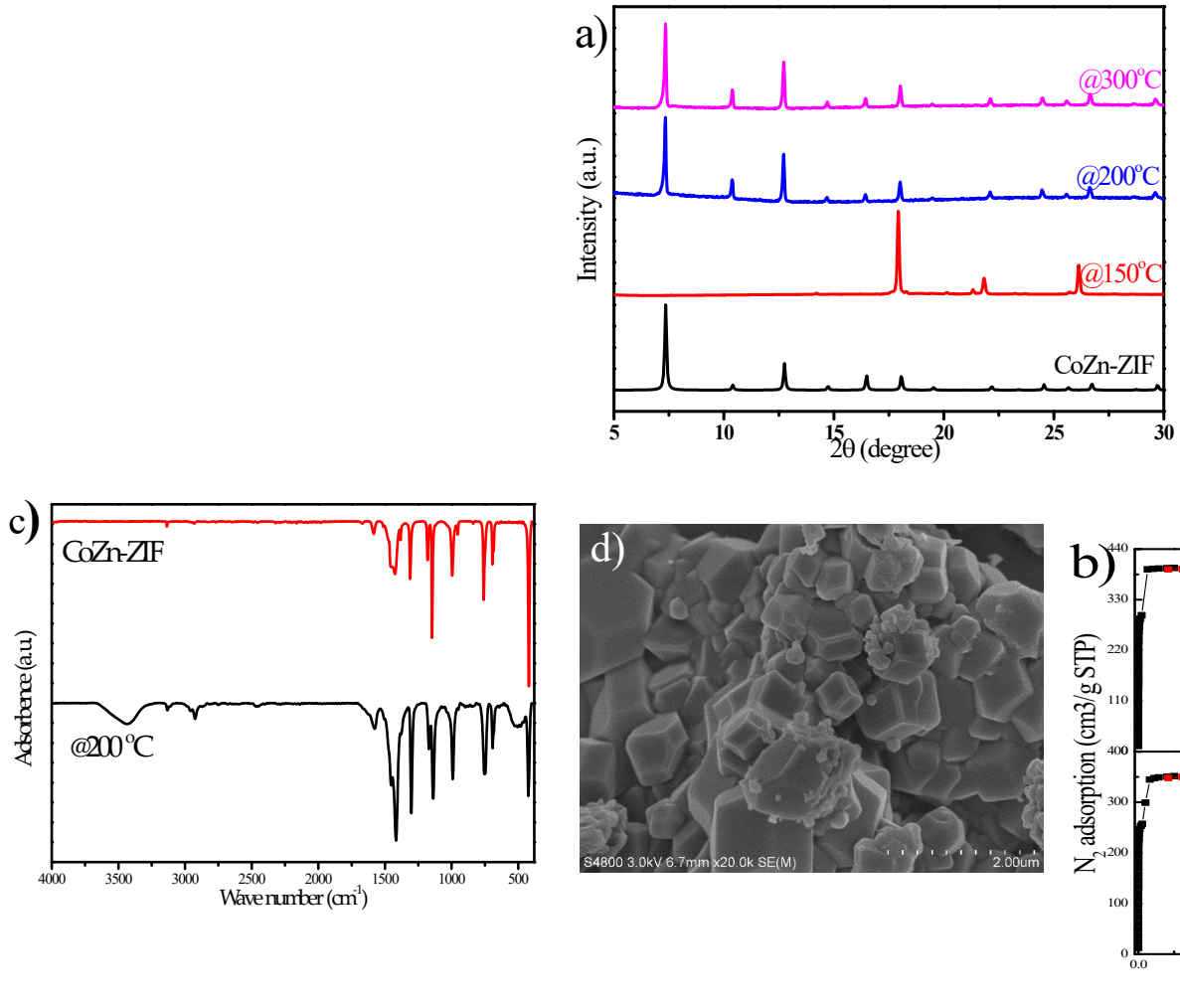


Figure S2. Characteristic properties of materials at low temperature zone, (a) XRD patterns, (b) Isotherm of N_2 adsorption, (c) FTIR analysis and (d) Material morphology of thermal-programmed sample at 200°C.

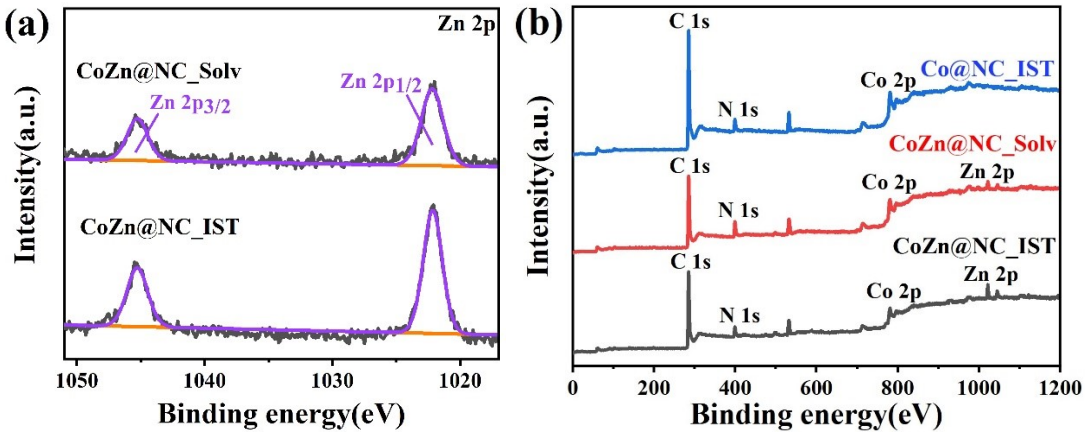


Figure S3. (a) Zn 2p XPS spectra, (b) XPS survey scan.

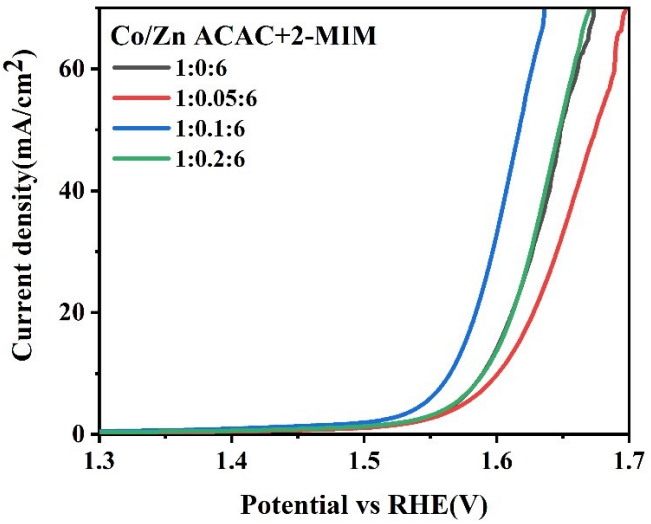


Figure S4. OER performance comparison of different zinc acetylacetonate loading (Zn ACAC) with contain cobalt acetylacetonate (1mmol) and 2-methylimidazole (2-MIM, 6mmol).

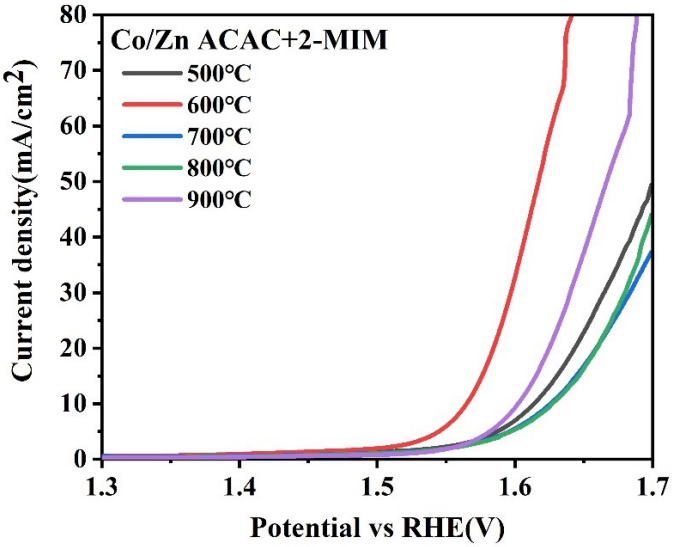


Figure S5. OER performance comparison at different pyrolysis temperatures of the physically mixed precursor (Co/Zn/2-MIM: 1/0.1/6).

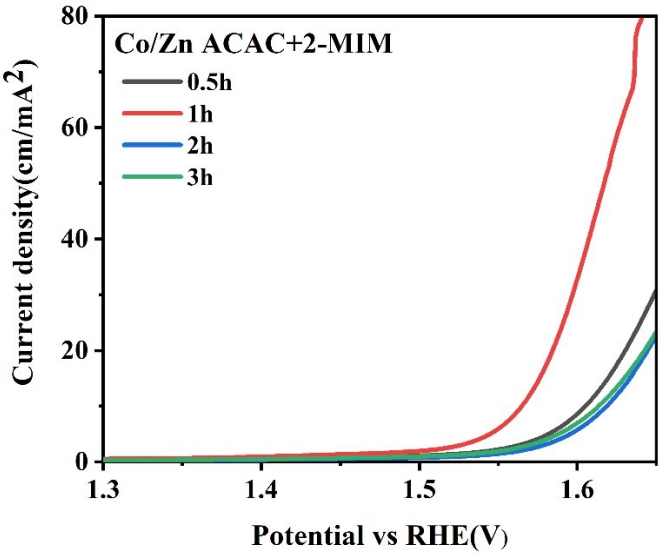


Figure S6. OER performance comparison at different pyrolysis times of the physically mixed precursor (Co/Zn/2-MIM: 1/0.1/6).

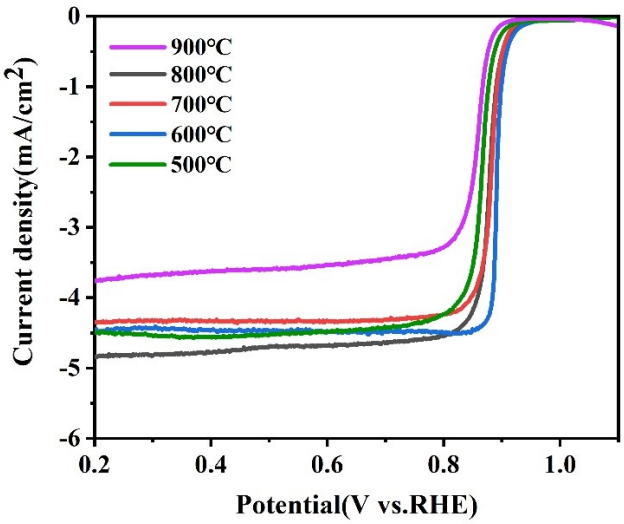
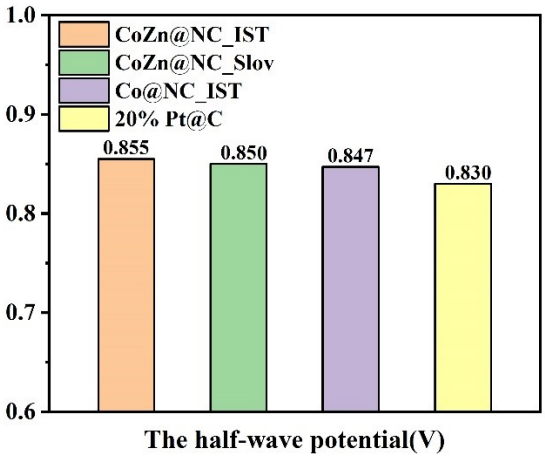
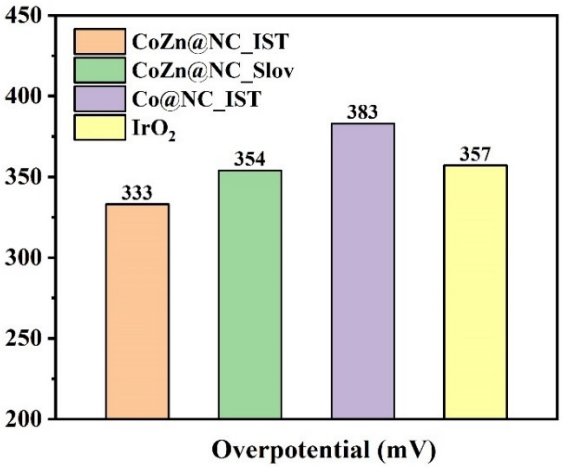


Figure S7. ORR performance comparison at different temperatures.





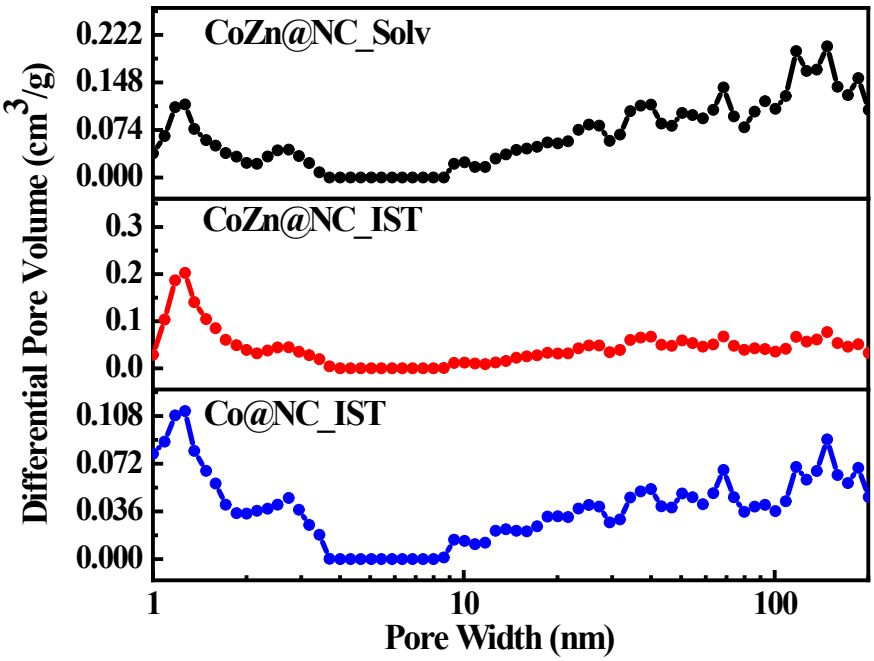
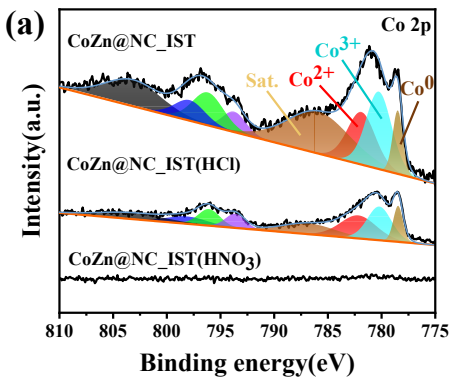


Figure S8. Pore size distribution of synthesized materials.



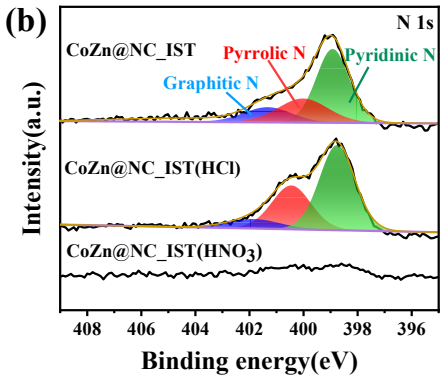


Figure S9. XPS comparison of pickling samples. (a) Co 2p, (b) N 1s.

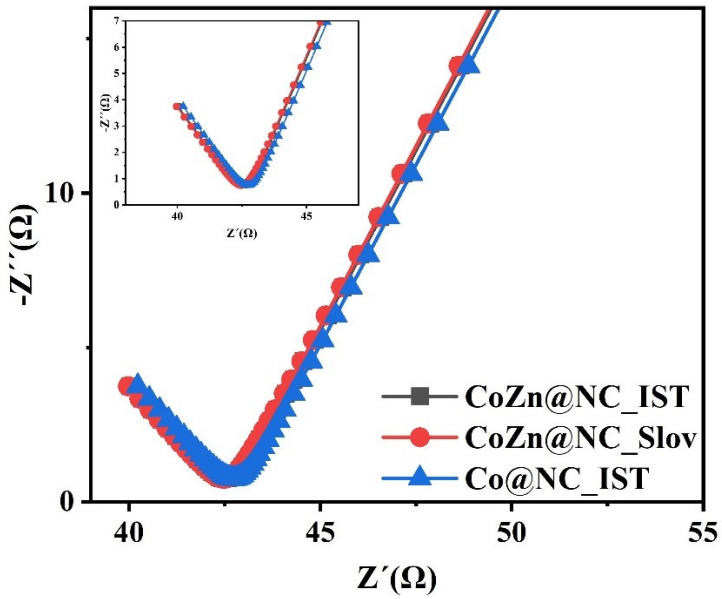


Figure S10. Nyquist plots for CoZn@NC_IST, Co@NC_IST and CoZn@NC_Slov obtained under the open circuit voltage;

Table1： The BET surface areas, langmuir surface areas, pore volume and pore sizes of CoZn@NC_IST, Co@NC_IST and CoZn@NC_Slov

element content（%）	C	N	Co	Zn
CoZn@NC_IST	44.48	5.44	18.34	1.56
CoZn@NC_Slov	38.76	9.00	18.59	1.33
Co@NC_IST	42.00	5.53	26.62	0.03

Table2：Table of elemental contents for CoZn@NC_IST, Co@NC_IST and CoZn@NC_Slov

Sample	BET Surface Area (m^2g^{-1})	Langmuir Surface Area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
CoZn@NC_IST	200	210	0.08	1.180
CoZn@NC_Slov	212	223	0.08	1.088
Co@NC_IST	266	278	0.10	1.082