

Electronic Supplementary Information (ESI) for CrystEngComm

**A Bimetallic 3D Interconnected Metal-Organic Framework with 2D Morphology
and Its Derived Electrocatalyst for Oxygen Reduction**

Zijia Bao,^{†, a} Guojun Zhou,^{†, b} Xinrong Liu,^a Yuxin Peng,^a Zhehao Huang,^{*b} Haoquan Zheng^{*a, c}

^aKey Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China

^bDepartment of Materials and Environmental Chemistry, Stockholm University, Stockholm, SE-10691, Sweden

^cInternational Joint Research Center on Advanced Characterizations of Xi'an City, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China

Correspondence Email: zhenghaoquan@snnu.edu.cn; zhehao.huang@mmk.su.se

1. Experimental section

1.1 Materials

Co(NO)₃·6H₂O (AR, 99%), Zn(NO)₃·6H₂O (AR, 99%), 2-methylimidazole (AR, 99%), KOH (AR, 95%), Zn(CH₃COO)₂·2H₂O (AR, 99%) and were purchased from the Energy Chemical. NaOH (AR, 96%), isopropanol (AR, 99.7%) and ethanol (AR, 99.7%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. All chemicals were used without further purification.

1.2 Preparation of ZIF-EC1

Typically, 1 mL of 0.24 M Zn(OAc)₂·2H₂O aqueous solution was added in 2 mL of 1.92 M 2-methylimidazole aqueous solution. The mixture was kept vigorously stirring for 4 h. White powder was obtained by centrifugation at 10000 rpm for 3 min and washed with deionized water 3-5 times and dried at 60 °C for 24 h.

1.3 Preparation of ZIF-EC1(ZnCo)-X

Typically, 1 mL of aqueous solution contained 0.24 M Zn(OAc)₂·2H₂O and X M Co(OAc)₂·4H₂O for different percentages (0.036 M for 15%, 0.048 M for 20% and 0.06 M for 25%) was added in 2 mL of 1.92 M 2-methylimidazole aqueous solution. The mixture was kept vigorously stirring for 4 h. The obtained powder was collected by centrifugation at 10000 rpm and washed with deionized water for 3-5 times and dried at 60 °C for 24 h.

1.4 Preparation of ZIF-EC1-900 and ZIF-EC1(ZnCo)-900

50 mg precursor (ZIF-EC1 and ZIF-EC1-X%Co) was pyrolyzed in a tube furnace at 900 °C for 2 h with a heating speed and cooling speed of 5 °C/min to obtain ZIF-EC1-900 and ZIF-EC1(ZnCo)-X-900.

1.5 Preparation of ZIF-L(Zn) and ZIF-L(Zn)-900

Typically, 2 mmol of Zn(NO)₃·6H₂O was dissolved in 40 mL deionized water, stirred for 10 min to obtain solution A. 16 mmol of 2-methylimidazole was dissolved in 40 mL deionized water, stirred for 10 min to obtain solution B. Then, solution A was poured into solution B under stirring condition and the mixture was kept stirring for 4 h to obtain a white suspension. The white powder (denoted by ZIF-L(Zn)) was obtained by centrifuging at 10000 rpm for 3 min and drying at 60 °C for 12 h. Synthesis of ZIF-L(Zn)-900: 50 mg of ZIF-L(Zn) powder was transferred to a quartz boat and pyrolyzed at 900 °C with a heating speed and cooling speed of 5 °C/min under Ar flow.

1.6 Characterization

The morphology of the materials was characterized with a scanning electron microscopy (SEM, Hitachi SU8020) at an accelerating voltage of 3 kV and a

transmission electron microscope (TEM, JEOL JEM-2100) with a field emission gun operating at 200 kV. EDS analysis was conducted on an AMETEK Materials Analysis EDX equipped on the TEM. Powder X-ray diffraction (PXRD) patterns of materials were tested on an X-ray diffractometer (Bruker, D8 Advance, Cu $K\alpha$, $\lambda = 1.5406 \text{ \AA}$, 40 kV/40 mA). 3DED data were collected with a Timepix pixel detector QTPX-262k (512 x 512 pixels, Amsterdam Sci. Ins.) on a JEOL JEM2100 microscope at 200 kV. Brunauer-Emmett-Teller (BET) specific surface area was measured in Micromeritics ASAP 2020.

1.7 Electrochemical measurement

All ORR electrochemical tests were carried out on a CHI 660E (CH Instruments) electrochemical workstation and a Pine Modulated Speed Rotator (Pine Research Instrumentation, Inc.) at 30 °C. A three-electrode system was used to conduct ORR tests. The counter electrode is a graphite rod, and the reference electrode is a saturated Ag/AgCl electrode. The working electrode is a rotating disk electrode (RDE) (5 mm, 0.196 cm²). The catalyst ink consists of 2 mg catalyst, 10 μL of Nafion solution (5 wt%, DuPont), 100 μL of deionized water, and 400 μL of isopropanol. The mixture was ultrasonicated for about 1 h to prepare a homogeneous catalyst ink. Then, 20 μL catalyst ink was evenly dropped on the RDE, the catalyst load is 0.08 mg. The cyclic voltammetry (CV) curves were tested in O₂/Ar-saturated 0.1 M KOH solution at the scan rate of 50 mV s⁻¹. The linear sweep voltammetry (LSV) tests were carried out in O₂-saturated 0.1 M KOH solution at a rotational speed range of 400 to 1600 rpm at the scan rate of 5 mV·s⁻¹ after 100% IR compensation.

The potentials corresponding to the reversible hydrogen electrode (RHE) electrode were calculated with the following equation:

$$E_{RHE} = E_{Ag/AgCl} + (0.197 + 0.0591 \times pH)$$

The number of electron transfers (n) is calculated by the Koutecky-Levich (K-L) formula:

$$\frac{1}{j} = \frac{1}{j_l} + \frac{1}{j_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}$$

j is the measured current density; j_l is the diffusion current density; j_k is the dynamic current density; ω is the rotational speed (rpm); B can be confirmed by the Koutecky-Levich (K-L) formula:

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

Where F is the Faraday constant (96485 C mol^{-1}); C_0 is the concentration of O_2 in 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$); D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the viscosity of 0.1 M KOH ($0.1 \text{ cm}^2 \text{ s}^{-1}$).

Table S1. Electrochemical ORR activities of Co-based electrocatalysts in this work and other reported works.

Catalyst	Electrolyte	$E_{1/2}$ vs RHE	Ref.
ZIF-EC1(ZnCo)-20-900	0.1M KOH	876 mV	This work
Co@DMOF-900	0.1M KOH	866 mV	<i>Angew. Chem. Int. Ed.</i> 2021, 60 , 21685-21690 ¹
Co(PO ₃) ₂ /NC	0.1M KOH	780 mV	<i>J. Catal.</i> 2020, 387 , 129-137 ²
Co-TpBpy-800 nanocages	0.1M KOH	830 mV	<i>Chem. Eng. J.</i> , 2020, 401 , 126149 ³
Co-PTS-COPs@MWCNTs	0.1M KOH	835 mV	<i>J. Mater. Chem. A</i> , 2022, 10 , 5918-5924 ⁴
Co SA/N-CNS-900	0.1M KOH	872 mV	<i>J. Energy Chem.</i> , 2022, 68 , 184-194 ⁵
Co/Co ₃ O ₄ @CoS-SNC	0.1M KOH	860 mV	<i>Chem. Eng. J.</i> , 2021, 419 , 129619 ⁶
Co-N-C/CNF	0.1M KOH	859 mV	<i>Nano Res.</i> , 2022, 16 , 545-554 ⁷
HEO/CoNC-3-1	0.1M KOH	850 mV	<i>Appl. Surf. Sci.</i> , 2023, 610 , 155624 ⁸
C-Co(OH) ₂ @ZIF-8-10%-1000	0.1M KOH	840 mV	<i>J. Alloy. Compd.</i> , 2022, 912 , 165198 ⁹
MPF/Co ₅ wt. %	0.1M KOH	800 mV	<i>Chem. Eng. J.</i> , 2023, 458 , 141468 ¹⁰
Co/N/C-1000	0.1M KOH	860 mV	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11 , 41258-41266 ¹¹

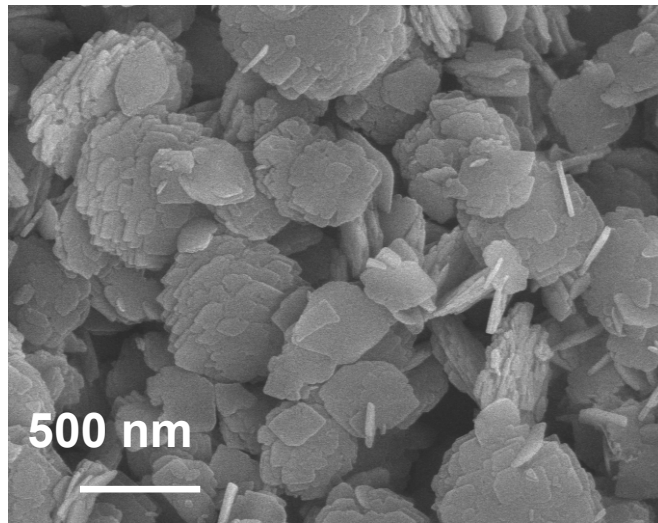


Fig. S1. SEM image of ZIF-EC1.

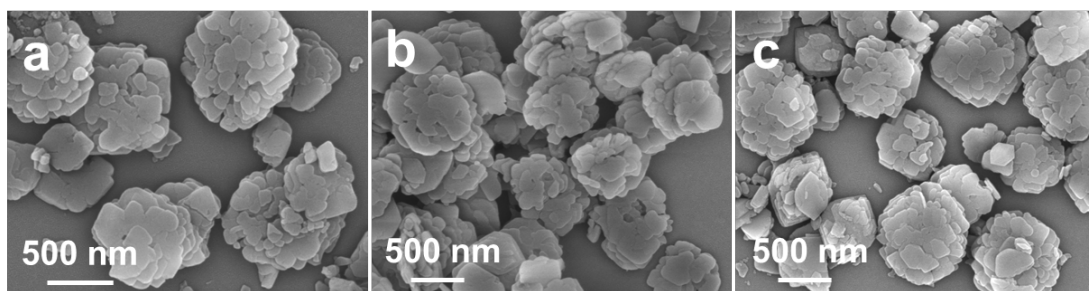


Fig. S2. SEM images of ZIF-EC1(ZnCo)-15 (a), ZIF-EC1(ZnCo)-20 (b), and ZIF-EC1(ZnCo)-25 (c).

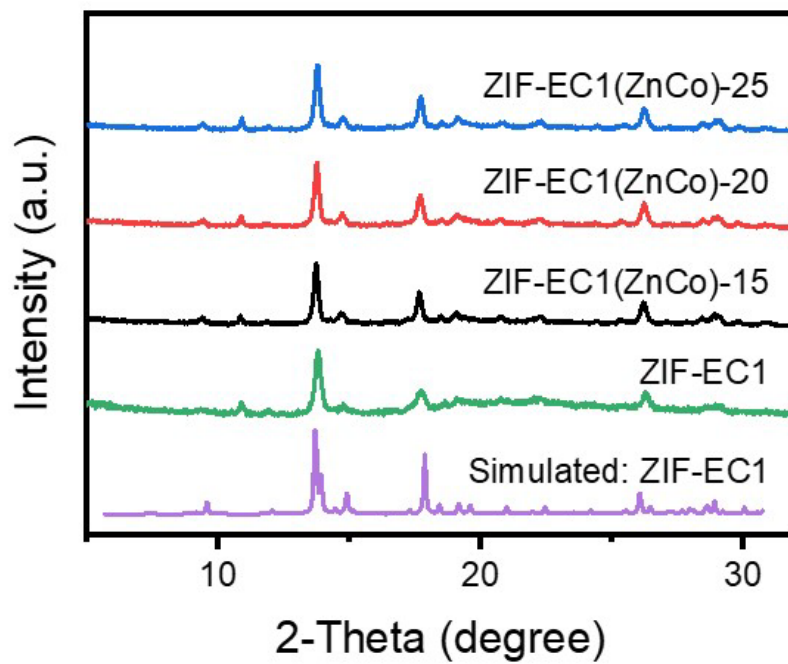


Fig. S3. PXRD patterns of ZIF-EC1, ZIF-EC1(ZnCo)-15, ZIF-EC1(ZnCo)-20, and ZIF-EC1(ZnCo)-25.

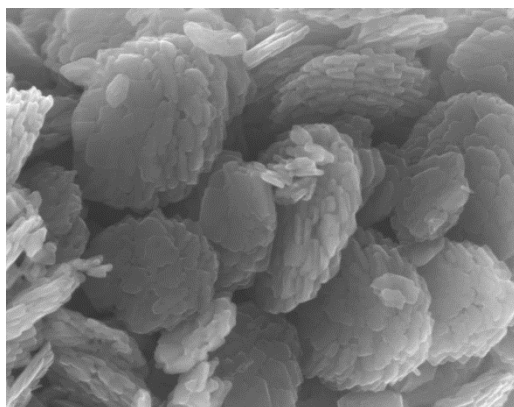


Fig. S4. SEM image of ZIF-EC1-900.

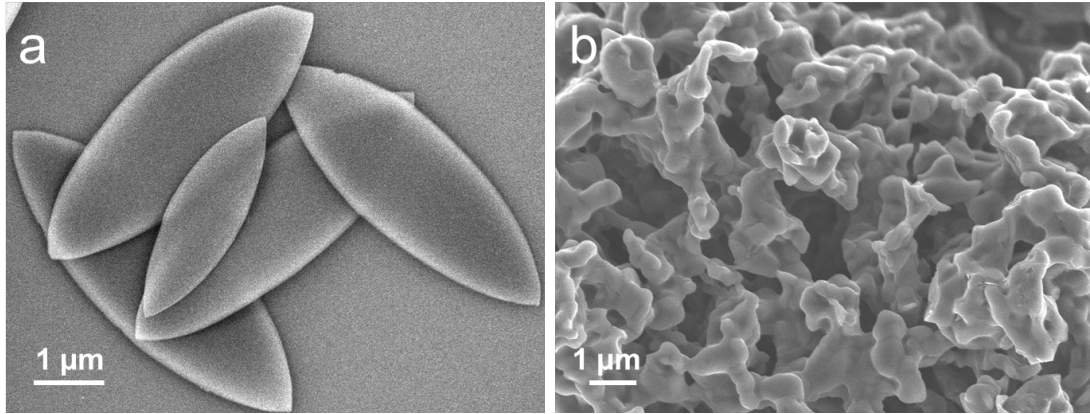


Fig. S5. SEM images of ZIF-L(Zn) (a) and ZIF-L(Zn) pyrolyzed in Ar at 900 °C (b).

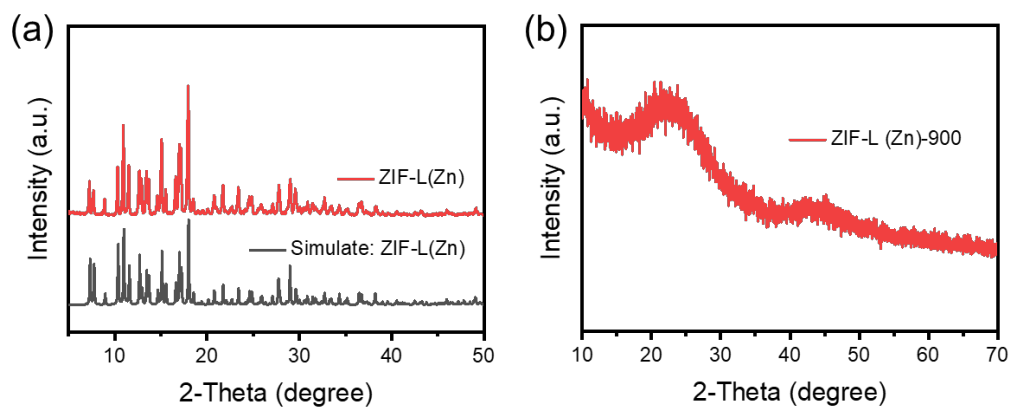


Fig. S6. (a) XRD patterns of ZIF-L(Zn) and simulated ZIF-L(Zn). (b) The XRD pattern of ZIF-L(Zn)-900.

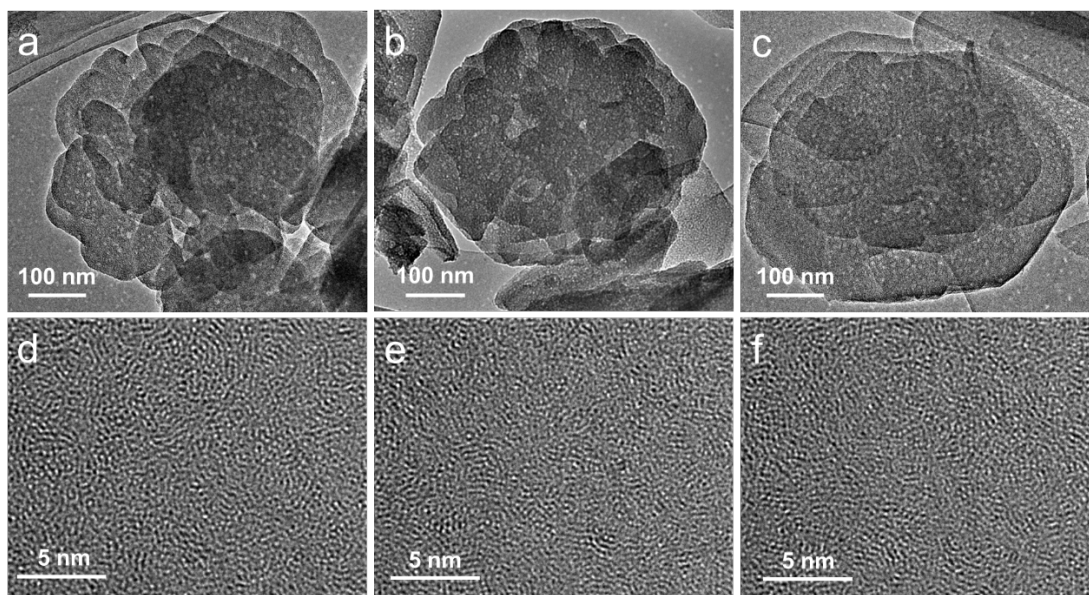


Fig. S7. TEM images of ZIF-EC1(ZnCo)-15-900 (a), ZIF-EC1(ZnCo)-20-900 (b), and ZIF-EC1(ZnCo)-25-900 (c). High-resolution TEM images of ZIF-EC1(ZnCo)-15-900 (a), ZIF-EC1(ZnCo)-20-900 (b), and ZIF-EC1(ZnCo)-25-900(c).

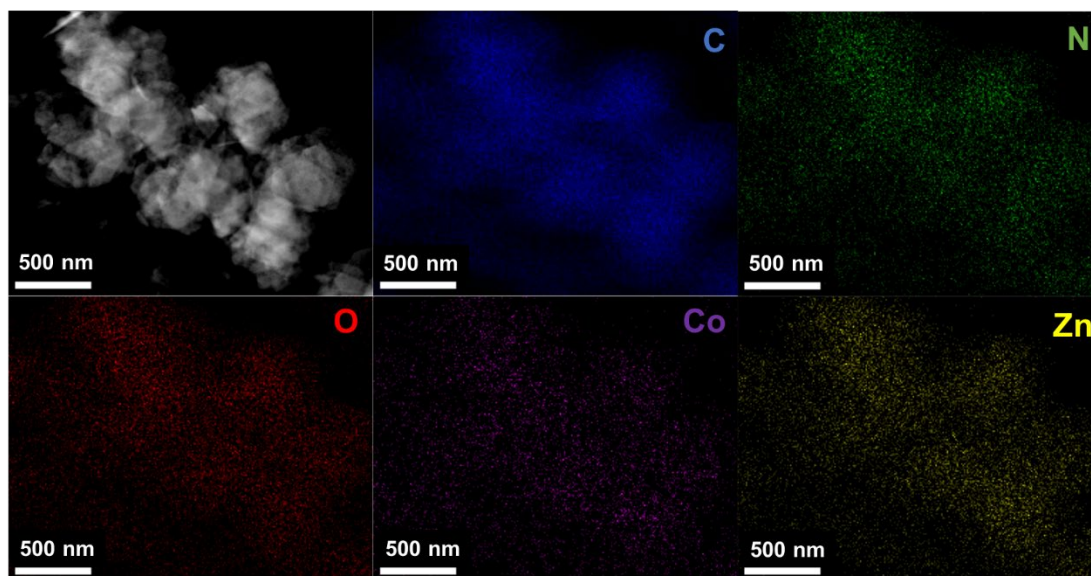


Fig. S8. HAADF-STEM image and corresponding element mapping images of ZIF-EC1(ZnCo)-20-900.

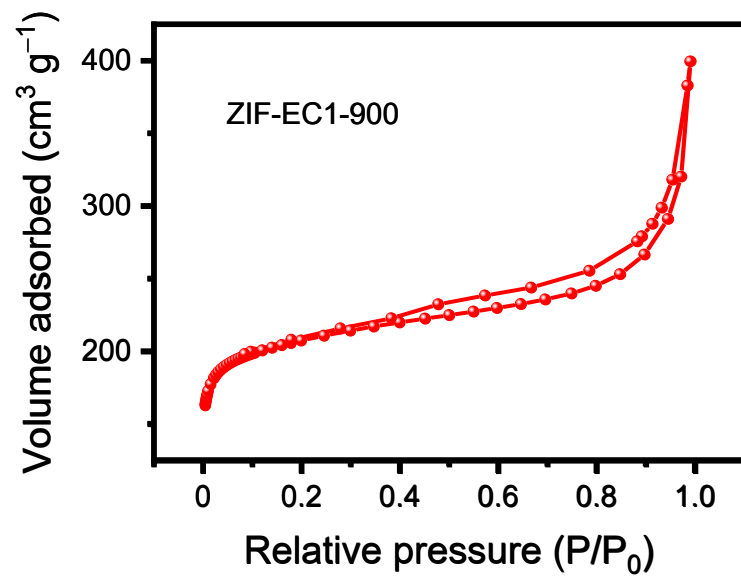


Fig. S9. N₂ adsorption-desorption isotherm of ZIF-EC1(ZnCo)-20-900, from which the Brunauer-Emmett-Teller (BET) surface areas are estimated as 802 m² g⁻¹.

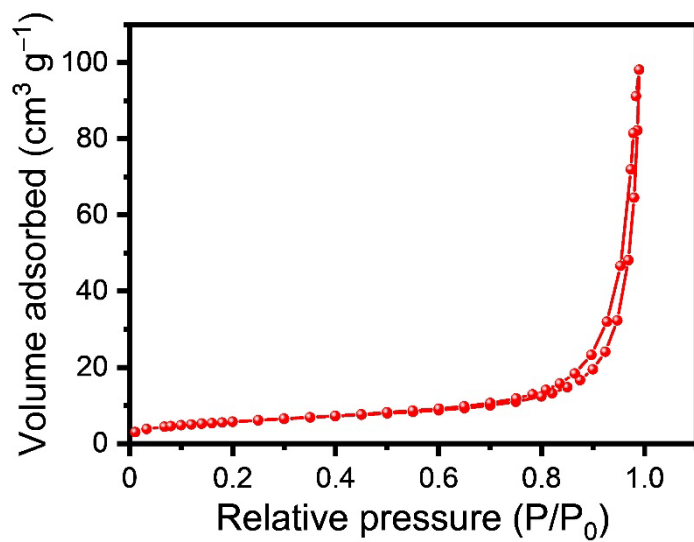


Fig. S10. N₂ adsorption-desorption isotherm of ZIF-EC1(ZnCo)-20, from which the Brunauer-Emmett-Teller (BET) surface areas are estimated as 20.3 m² g⁻¹.

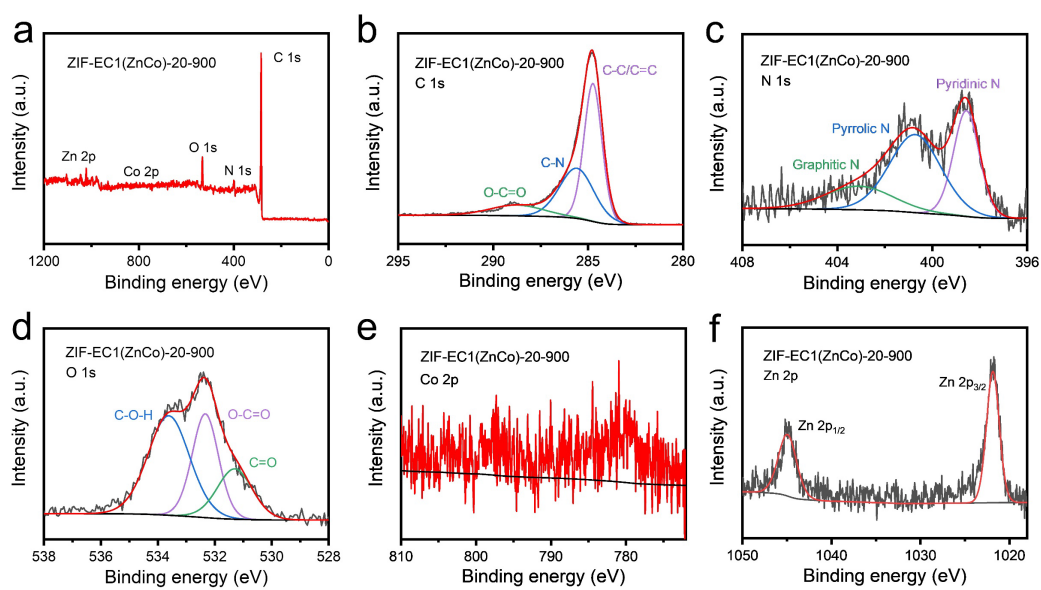


Fig. S11. (a) XPS survey spectra of ZIF-EC1(ZnCo)-20-900. High-resolution XPS spectra of C 1s (b), N 1s (c), O 1s (d), Co 2p (e) and Zn 2p (f) for ZIF-EC1(ZnCo)-20-900.

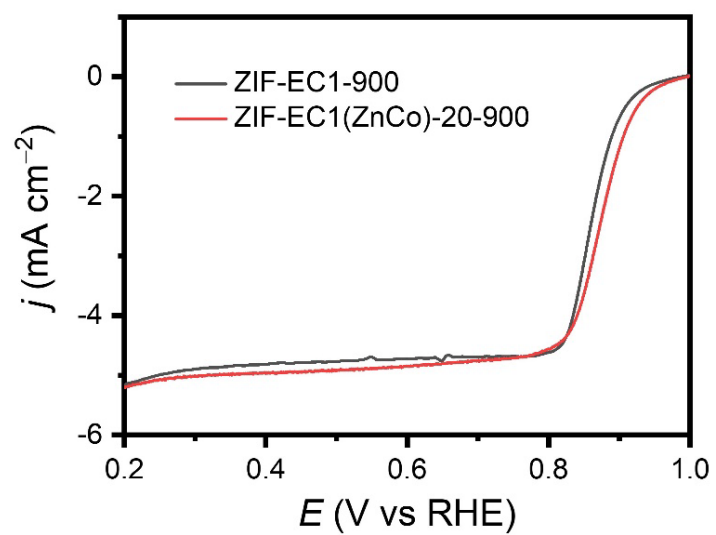


Fig. S12. LSV curves of ZIF-EC1-900 and ZIF-EC1(ZnCo)-20-900.

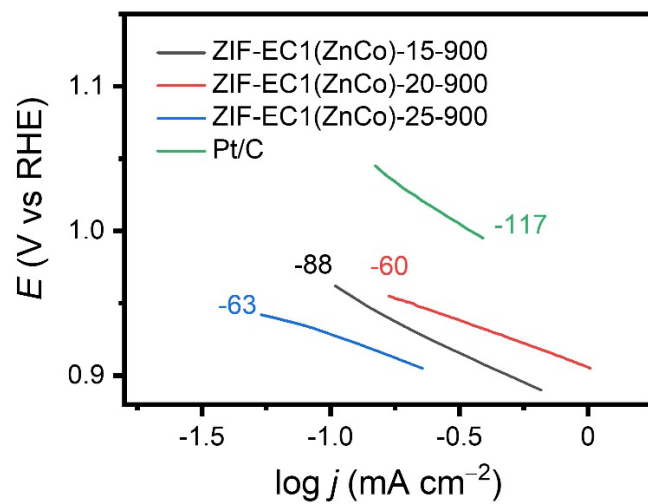


Fig. S13. Tafel slopes derived from Fig. 4b.

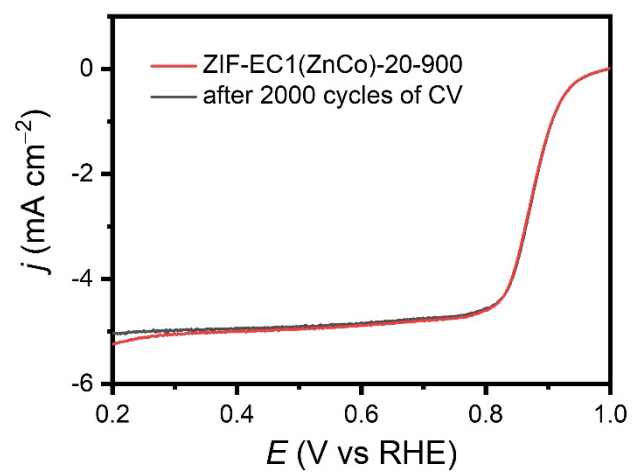


Fig. S14. LSV curve of ZIF-EC1(ZnCo)-20-900 and LSV curve after 2000 cycles of CV.

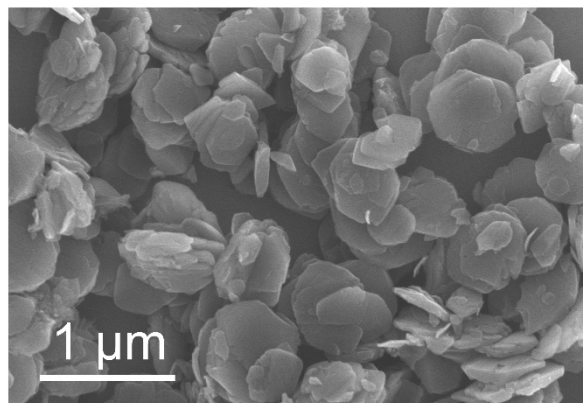


Fig. S15. SEM image of ZIF-EC1(ZnCo)-20-900 after 2000 cycles of CV.

References:

- 1 S. Yuan, J. Zhang, L. Hu, J. Li, S. Li, Y. Gao, Q. Zhang, L. Gu, W. Yang, X. Feng and B. Wang, *Angew. Chem. Int. Ed.*, 2021, **60**, 21685-21690.
- 2 L.-H. Xu, S.-L. Zhang, S.-Y. Guo, X.-J. Zhang, S. Cosnier, R.S. Marks, W.-J. Wang, H.-B. Zeng and D. Shan, *J. Catal.*, 2020, **387**, 129-137.
- 3 H. Chen, Q.-H. Li, W. Yan, Z.-G. Gu and J. Zhang, *Chem. Eng. J.*, 2020, **401**, 126149.
- 4 R. Ma, X. Cui, Y. Wang, Z. Xiao, R. Luo, L. Gao, Z. Wei and Y. Yang, *J. Mater. Chem. A*, 2022, **10**, 5918-5924.
- 5 T. Shen, X. Huang, S. Xi, W. Li, S. Sun and Y. Hou, *J. Energy Chem.*, 2022, **68**, 184-194.
- 6 H. Pan, X. Huang, Z. Lu, Z. Zhang, B. An, D. Wu, T. Wang, X. Chen and F. Cheng, *Chem. Eng. J.*, 2021, **419**, 129619.
- 7 B. Zhang, Y. Zhao, L. Li, Y. Li, J. Zhang, G. Shao and P. Zhang, *Nano Res.*, 2022, **16**, 545-554.
- 8 T. Yu, H. Xu, Z. Jin, Y. Zhang and H.-J. Qiu, *Appl. Surf. Sci.*, 2023, **610**, 155624.
- 9 J.-M. Yang, K.-A. Wang and H.-B. Zhu, *J. Alloy. Compd.*, 2022, **912**, 165198.
- 10 S. Akula, M. Mooste, J. Kozlova, M. Käärrik, A. Treshchalov, A. Kikas, V. Kisand, J. Aruväli, P. Paiste, A. Tamm, J. Leis and K. Tammeveski, *Chem. Eng. J.*, 2023, **458**, 141468.
- 11 W. Sun, L. Du, Q. Tan, J. Zhou, Y. Hu, C. Du, Y. Gao and G. Yin, *ACS Appl. Mater. Interfaces*, 2019, **11**, 41258-41266.