

Supporting Information

Supporting Information contains:

Supplementary Discussions

Number of Figures: 6 (Figure S1 – S6)

Number of Tables: 1 (Table S1)

Supplementary Discussions

Experimental Section

Materials and reagents

All chemicals, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR), 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%), phosphotungstic acid (AR), platinum carbon black, and methanol (CH_3OH), were purchased from Shanghai Sinopharm Chemical Reagent and used without further treatment or purification. All aqueous solutions were prepared with high-purity deionized water (DI-water, resistance $18 \text{ M}\Omega \text{ cm}^{-1}$).

Synthesis of ZIF-8

In a typical synthesis, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8924 g, 3 mmol) was dissolved in 30 mL of methanol, then 2-Methylimidazole (0.9852 g, 12 mmol) was dissolved in 10 mL of methanol. These two solutions were mixed and stirred at room temperature. After stirring for 24 h, the resulting white precipitates were collected by centrifuging (4000 rpm, 5min), washed with methanol subsequently for three times, and finally dried at

60 °C for 24 h.

Synthesis of ZIF-8@ZIF-67

Co(NO₃)₂·6H₂O (0.1500g) and 2-Methylimidazole (0.0382g) were dissolved in 10 mL of methanol, and then added into the solution of 30 mL methanol with the above white precipitates (0.1000g), later the mixture was stirred for 24 h at room temperature. After centrifuging (4000 rpm, 5min), the purple precipitates were obtained by washing them for 3 times using methanol and drying them at the temperature of 60 °C for 24 h.

Synthesis of ZIF-8@ZIF-67@POM

Phosphotungstic acid (0.0500g) was dissolved in 20 mL deionized water, and the above-mentioned purple precipitates (0.0500g) were dissolved in 40 mL methanol and under ultrasonic treatment. Those two solutions were mixed, then the mixture was stirred for 6 h at room temperature. Finally, the obtained samples were centrifuged (4000 rpm, 5min) and washed with methanol for few times to remove impurities and dried in air naturally.

Electrochemical measurements

Electrochemical measurements were carried out on an electrochemical working station (CHI 760E, CH Instruments, Shanghai, China). A conventional three-electrode system was widely applied for electrochemical measurements, which consisted of an Ag/AgCl (saturated KCl) electrode as the reference electrode, a modified glassy carbon electrode as the working electrode, and platinum foil as the auxiliary electrode.

Characterization of ZIF-8@ZIF-67@POM hybrids

Powder X-ray diffraction (PXRD) patterns are recorded on a Bruker D8 Advanced X-ray Diffractometer under the following conditions: 40 kV, 40 mA, Cu K α radiation ($\lambda = 0.154$ nm).

Scanning electron microscopy (SEM) images are obtained using a Zeiss-Supra 55.

High-resolution transmission electron microscopy (HRTEM) images and **energy dispersive X-ray (EDX)** analytical data are collected on a Tecnai G2 F30 instruments electron microscope operating at 200 kv acceleration voltage, TEM equipped with an EDX detector.

X-ray photoelectron spectroscopy (XPS) measurements were performed with monochromatized Al K α exciting X-radiation (PHI Quantera SXM).

Fourier transform infrared (FT-IR) spectroscopy was collected on a TENSOR 27 with samples prepared as KBr pellets at wavenumbers ranging from 4000 to 400 cm $^{-1}$.

Textural properties of samples were measured by nitrogen sorption at 77 K on a Micromeritics ASAP 2020 system. Prior to the measurement, the samples were degassed at 110 °C for 10 h. SAED images and energy dispersive X-ray spectroscopy mapping were captured on a Tecnai G2 F30 transmission electron microscopy at an acceleration voltage of 300 kV. The specific surface area of catalyst was obtained with a Brunauer Emmet Teller (BET) analysis system with a N $_2$ adsorptive medium.

Fabrication of working electrodes. To fabricate working electrode, each sample (4

mg) and Nafion solution (5 wt%, 120 μL) in 666 μL of water solution and 334 μL of ethanol solution, followed by ultrasonication for 1 h. 5 μL of the catalyst dispersion was deposited on the surface of a glassy carbon electrode (GCE, loading density of 0.25 mg cm^{-2}) and dried naturally at room temperature.

Electrochemical characterization on working electrodes. The electrochemical water oxidation experiments were carried out on an electrochemical working station (CHI 760E, Shanghai Chenhua). A conventional three-electrode system was implemented for all the electrochemical measurements by utilizing GCE (diameter: 3.0 mm) as working electrode, Pt wire as counter electrode, and Hg-HgO electrode as reference electrode in 1.0 M KOH solution. According to the **Nernst equation**:

$$E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098$$

the current density was normalized to the geometrical surface area and the measured potential vs. Hg/HgO was converted to a reversible hydrogen electrode (RHE). Prior to the electrochemical test, we first passed half an hour of N_2 gas in the electrolyte (1 M KOH) to ensure the $\text{O}_2/\text{H}_2\text{O}$ equilibrium at 1.23 V vs. RHE. The working electrodes were scanned for several times until the signals were stabilized, then LSV data were collected, corrected for the iR contribution within the battery. CV and LSV were applied for confirming the electrocatalytic properties of working electrodes. Through adjusting to the **Tafel equation**:

$$\eta = b \log j + a$$

where η is the overpotential, b is the Tafel slope, j is the current density and a is the exchange current density. The Tafel slopes and exchange current densities could be

calculated for POM@MOF. In addition, the transfer number per oxygen molecule

involved in oxygen reduction can be determined by **Koutecky-Levich equations**:

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

$$B = 0.62nFC_0(D_0)^{\frac{2}{3}}\nu^{-\frac{1}{6}}$$

$$j_k = nFKC_0$$

which j represents the measured current density, j_l and j_k are the diffusion-limiting and kinetic current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, where N is the linear rotation speed), n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O_2 ($C_0 = 1.1 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient of O_2 ($D_0 = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the electrolyte ($\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant. The **Turn Over Frequency (TOF)** value is calculated from the following equation:

$$\text{TOF} = jA/4Fm$$

$$\text{TOF} = JA/(4 \times F \times m)$$

j is the current density at overpotential of 300 mV at 10 mA cm^{-2} , A is the area of the electrode, F is the Faraday constant of 96485 C mol^{-1} , m is the number of moles of the active materials that are deposited onto the GC.

Supplementary Figures

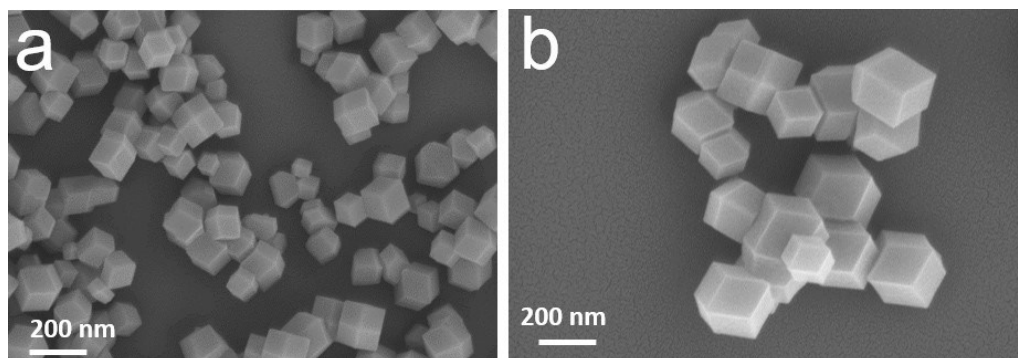


Figure S1. a, b) SEM images of ZIF-8.

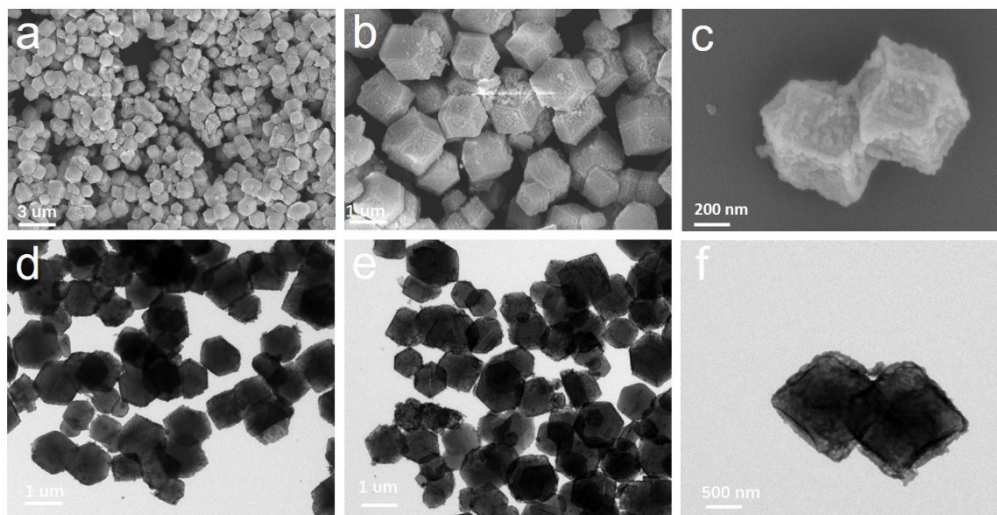


Figure S2. a-c) SEM images of ZIF-8@ZIF-67@POM. d-f) TEM images of ZIF-8@ZIF-67@POM.

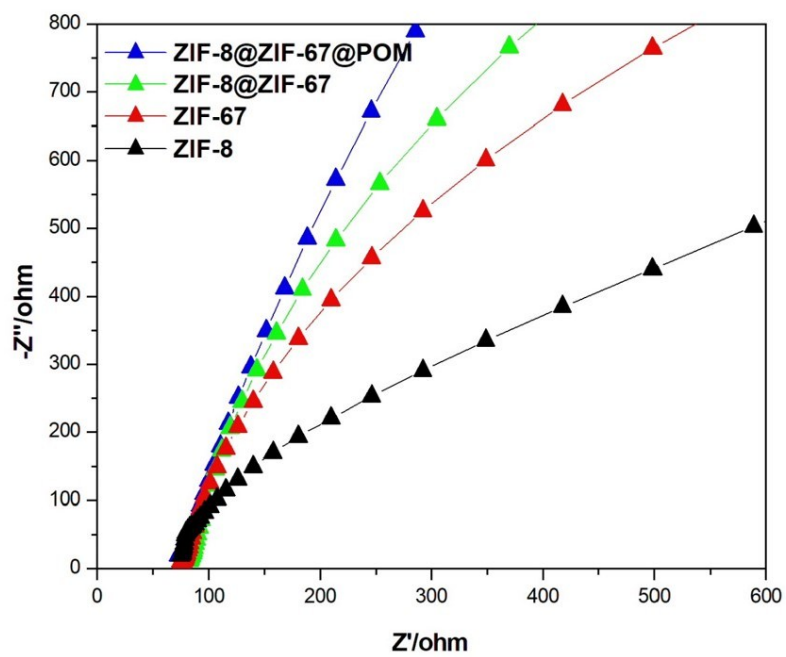


Figure S3. Nyquist plots of the catalysts obtained by the EIS measurement at a constant potential of 0.2 V.

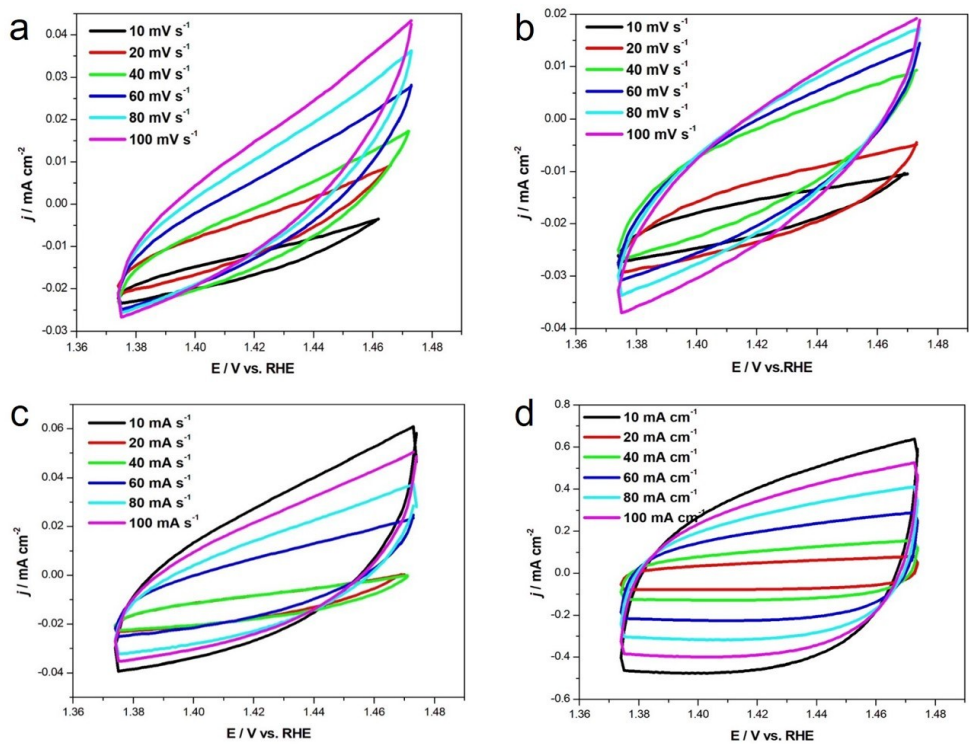


Figure S4. CV curves of a) ZIF-67, b) ZIF-8, c) ZIF-8@ZIF-67 and d) ZIF-8@ZIF-67@POM.

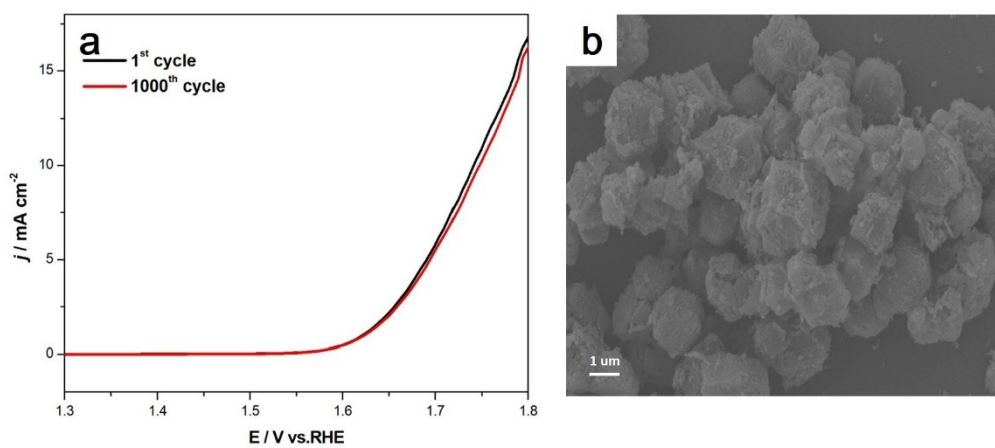


Figure S5. a) The LSV curve of ZIF-8@ZIF-67@POM before and after 1000 cycles. b) SEM image of ZIF-8@ZIF-67@POM after the chronoamperometric testing.

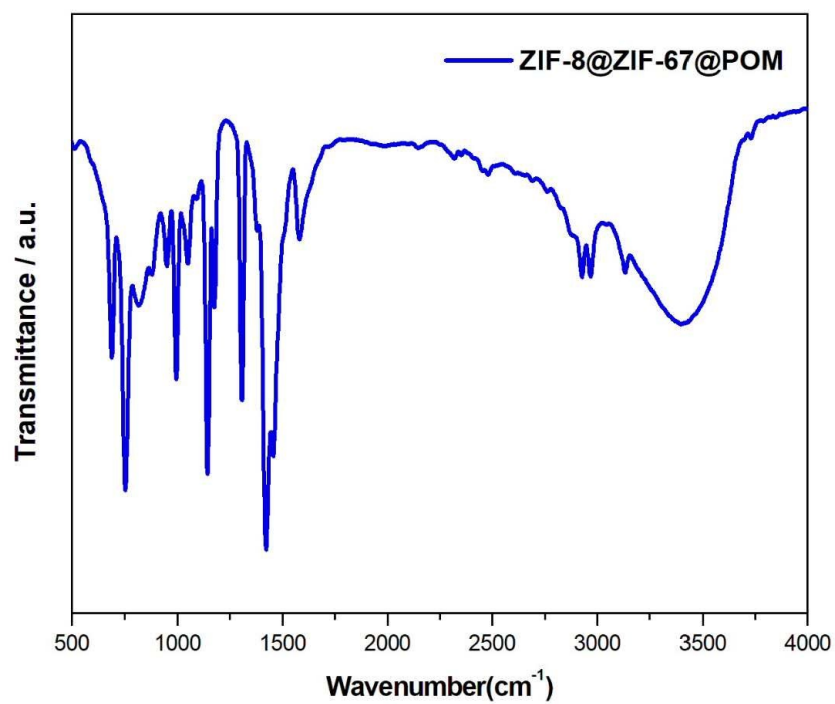


Figure S6. FTIR spectra of ZIF-8@ZIF-67@POM hybrids.

Table S1. Comparison of OER performance for the reported ZIFs and their derivatives catalysts that loaded on a glass carbon electrode.

Catalysts	Electrolyte	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Refence
Fe-N-HPC-900	1 M KOH	520@10 mA cm ⁻²	119	1
EG/Co(OH) ₂ /ZIF-67 hybrid	1.0 M KOH	280@10 mA cm ⁻²	63	2
CoP/NCNHP	1 M KOH	310@10 mA cm ⁻²	70	3
MnCo ₂ O ₄ @Co ₃ O ₄	1.0 M KOH	280@100 mA cm ⁻²	109.6	4
Co-B-O@Co ₃ O ₄	0.1 M KOH	350@10 mA cm ⁻²	32.7	5
Co-B-O@Co ₃ O ₄	1.0 M KOH	342@10 mA cm ⁻²	40.3	5
ZIF-67@POM	1.0 M KOH	287@10 mA cm ⁻²	58	6
Co ₃ O ₄ /NPC	1 M KOH	330@10 mA cm ⁻²	79	7
CoNiP/NC700	1.0 M KOH	300@10 mA cm ⁻²	66	8
ZIF-67@NPC-2 (2:1)	0.1 M KOH	~410@10 mA cm ⁻²	114	9
CoO _x -ZIF	0.1M NaOH	318@10mA cm ⁻²	70.3	10
Co-ZIF-9	0.1 M KOH	510@1mA cm ⁻²	93	11
Ti@TiO ₂ /CdS/ZIF-67	0.5M NaOH	287@10mA cm ⁻²	42	12
ZIF-67@POM	1.0 M KOH	490@10 mA cm ⁻²	88	this work

Supplementary References

References

- 1 J. Xiong, J. Zhao, Z. Xiang, C. Li, M. Wu, X. Wang, Y. Pan, W. Lu and R. Liu, *J. Solid State Electrochem.*, 2019, **23**, 2225–2232.
- 2 J. Cao, C. Lei, J. Yang, X. Cheng, Z. Li, B. Yang, X. Zhang, L. Lei, Y. Hou and K. (Ken) Ostrikov, *J. Mater. Chem. A*, 2018, **6**, 18877–18883.
- 3 Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W.-C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen and Y. Li, *J. Am. Chem. Soc.*, 2018, **140**, 2610–2618.
- 4 J.-J. Zhou, X. Han, K. Tao, Q. Li, Y.-L. Li, C. Chen and L. Han, *Chem. Eng. J.*, 2018, **354**, 875–884.
- 5 D. Kim, D. Kim, Y. Jeon, Y. Li, J. Lee, J. Kang, L. Y. S. Lee and Y. Piao, *Electrochim. Acta*, 2019, **299**, 213–221.
- 6 Q. Y. Li, L. Zhang, Y. X. Xu, Q. Li, H. Xue and H. Pang, *ACS Sustain. Chem. Eng.*, 2019, **7**, 5027–5033.
- 7 G. Zhuang, Y. Gao, X. Zhou, X. Tao, J. Luo, Y. Gao, Y. Yan, P. Gao, X. Zhong and J. Wang, *Chem. Eng. J.*, 2017, **330**, 1255–1264.
- 8 J. Li, G. Du, X. Cheng, P. Feng and X. Luo, *Chinese J. Catal.*, 2018, **39**, 982–987.
- 9 H. Wang, F.-X. Yin, B.-H. Chen, X.-B. He, P.-L. Lv, C.-Y. Ye and D.-J. Liu, *Appl. Catal. B Environ.*, 2017, **205**, 55–67.
- 10 S. Dou, C.-L. Dong, Z. Hu, Y.-C. Huang, J. Chen, L. Tao, D. Yan, D. Chen, S. Shen,

- S. Chou and S. Wang, *Adv. Funct. Mater.*, 2017, **27**, 1702546.
- 11 S. Wang, Y. Hou, S. Lin and X. Wang, *Nanoscale*, 2014, **6**, 9930.
- 12 T. Zhang, J. Du, H. Zhang and C. Xu, *Electrochim. Acta*, 2016, **219**, 623–629.