

Synthesis of metal-organic framework microrings via an anisotropic growth-etching approach

Yue Zhang^a, Rong Deng^a, Ling Yuan^a, Chaoqi Zhang^{*a}, Jing Wang^{*b}, and Chao Liu^{*a}

Experimental section

Chemicals

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd), 2-methylimidazole (2-MeIM, Aldrich), cetyltrimethylammonium bromide (CTAB, Adamas-beta), ethanol (AR, 99%, Adamas-beta) and methanol (AR, 99%, Adamas-beta) were used as received. Deionized water was used in all experiments.

Synthesis of ZIF-L

583 mg of 2-MeIM was dissolved in 20 mL of deionized water with stirring for 5 min. Afterwards, 20 mL of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (22.5 mg/mL) was poured into the above mixture solution with stirring for 3 h at room temperature. The products were collected by centrifugation, then washed with methanol for three times before drying at 60 °C for 5 h.

Synthesis of ZIF-8

10.08 g of 2-MeIM was dissolved in 170 mL of deionized water, followed by adding 4.5 mL of 0.01 M CTAB aqueous solution with stirring for 5 min. Then, 30 mL of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (23.7 mg/mL) was added into the above solution. After reaction for 4 h at room temperature, the samples were collected by centrifugation, then washed with methanol for three times before drying at 60 °C for 5 h.

Synthesis of ZIF-R

Typically, 583 mg of 2-MeIM was dissolved in 20 mL of deionized water with stirring for 5 min, followed by adding 20 mL of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (22.5 mg/mL). After reaction for 1 h at room temperature, 4 mL of 2-MeIM solution (0.13 g/mL) was added with further stirring for 20 min. The products were collected by centrifugation, then washed with methanol for three times before drying at 60 °C for 5 h.

Synthesis of ZIF-8-C and ZIF-R-C

The as-synthesized ZIF-8 and ZIF-R were pyrolyzed at 800 °C for 3 h with a heating rate of 5 °C

min⁻¹ under nitrogen atmosphere to form ZIF-8-C and ZIF-R-C, respectively.

Characterization

Wide-angle X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance Powder X-ray diffractometer (Bruker AXS, Germany) operating at 40 mA and 40 kV with Cu-K α radiation source. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo ESCALAB 250 using an Al K α radiation and C 1s (284.8 eV) as a reference to correct the binding energy. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEM-2100F (JEOL, Japan) with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were acquired by a scanning electron microscope (HITACHI-S4800).

Electrochemical measurement

Rotating ring-disk electrode (RRDE) tests were conducted in a standard three-electrode system on a CHI-760C electrochemical analyzer (CH Instruments Inc.) in O₂-saturated 0.1 M KOH solution at ambient temperature with platinum wire as counter electrode, Ag/AgCl (KCl, 3.5 M) as reference electrode and catalyst-modified glassy carbon as working electrode. The catalyst inks were prepared by dispersing 10 mg of sample into 1 mL of isopropanol containing 30 μ L of Nafion solution to form a homogeneous suspension. The prepared ink was deposited on the polished glassy carbon disk with a mass loading of 0.61 mg cm⁻² and dried under an infrared lamp. Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 5 mV s⁻¹. The Tafel slope (b) was obtained by fitting the linear part of the Tafel plots according to the Tafel equation ($\eta = a + b \log(j)$) to evaluate the kinetic performance of as-prepared catalysts for ORR.

The electrochemical active surface area (ECSA) was evaluated based on the double-layer capacitances (C_{dl}) of the catalysts on RDE by cyclic voltammograms (CV) curves at different scanning rates of 10-100 mV s⁻¹ in the non-Faradaic voltage region. A straight line can be obtained by plotting the current density against the scan rate at a specific potential in the CV curves. The slope of the line is defined as electrochemical double-layer capacitance (C_{dl}). Furthermore, the ECSA can be calculated as: $ECSA = C_{dl} / (A \times C_s)$, where A is the amount of the material coating on the surface of electrode (mg·cm⁻²), C_s is an empirical constant representing the capacitance per unit area (40 μ F·cm⁻²). Electrochemical impedance spectroscopy (EIS) was measured in 0.1 M KOH solution in the frequency range of 1000 kHz to 0.01 Hz with an

amplitude of 10 mV. The electron-transfer number (n) involved in a typical ORR process was estimated by Koutecky-Levich (K-L) equation: $1/J=1/J_K+1/J_L=1/J_K+1/B\omega^{1/2}$. J , J_K , and J_L are the measured current density, the kinetic current density, and the diffusion-limited current density, respectively. ω is the angular velocity (rad s^{-1}). B is the Levich constant, determined from the slope of Koutecky-Levich plots based on Levich equation as followed: $B=0.62nFC_0D^{2/3}\nu^{-1/6}$. n is the overall number of electrons transferred in the ORR process. F is the Faraday constant. C_0 is the concentration of O_2 . D is the diffusion coefficient of O_2 in the electrolytes, and ν is the kinetic viscosity of the electrolyte.

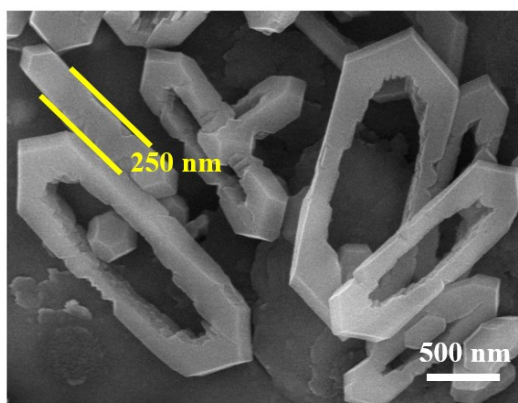


Figure S1. SEM image of ZIF-R.

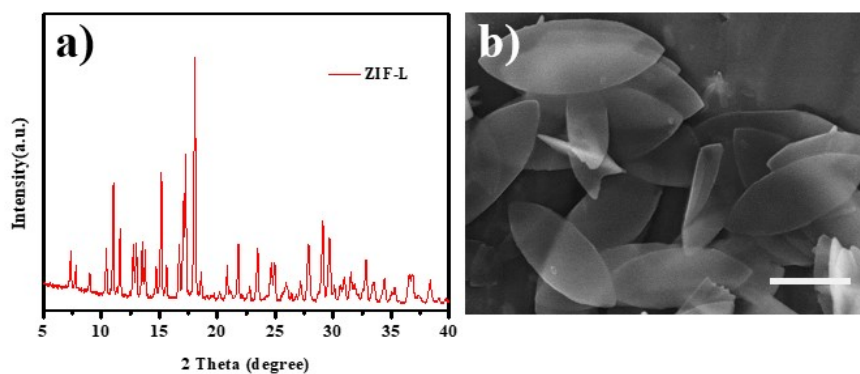


Figure S2. a) XRD pattern and b) SEM image of ZIF-L. The scale bar is $1\mu\text{m}$.

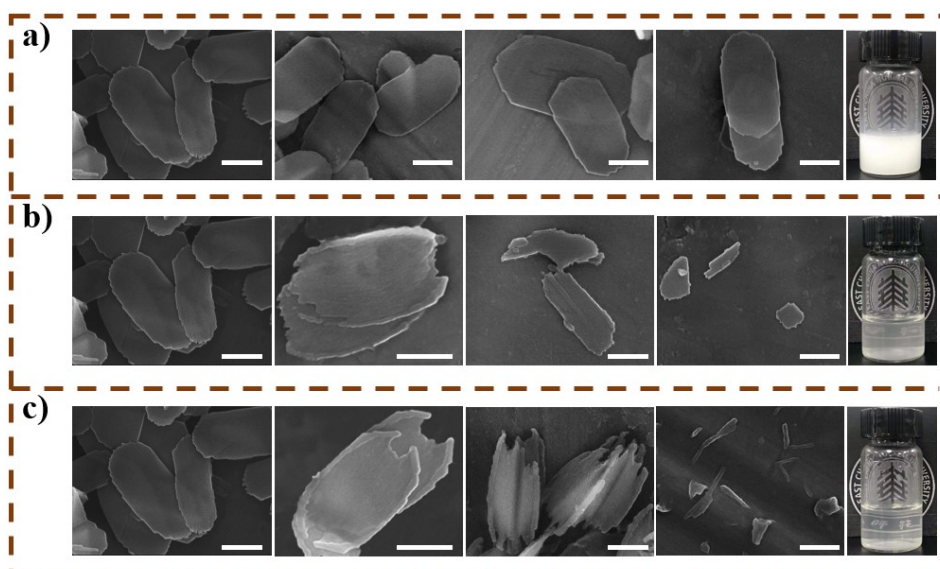


Figure S3. SEM images of ZIF-L dissolved in a) buffer solution with 2-MIM (PH=7.62), b) NaOH solution (PH=11.16), c) 2-MeIM solution (PH=11.14) for 0, 5, 10 and 15 min. The corresponding digital photos at 15 min are also presented. The scale bar is 1 μm.

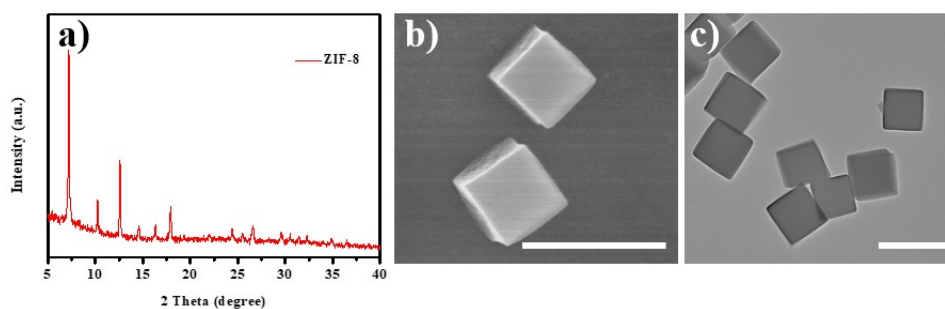


Figure S4. a) XRD pattern, b) SEM and c) TEM images of ZIF-8. The scale bar is 500 nm.

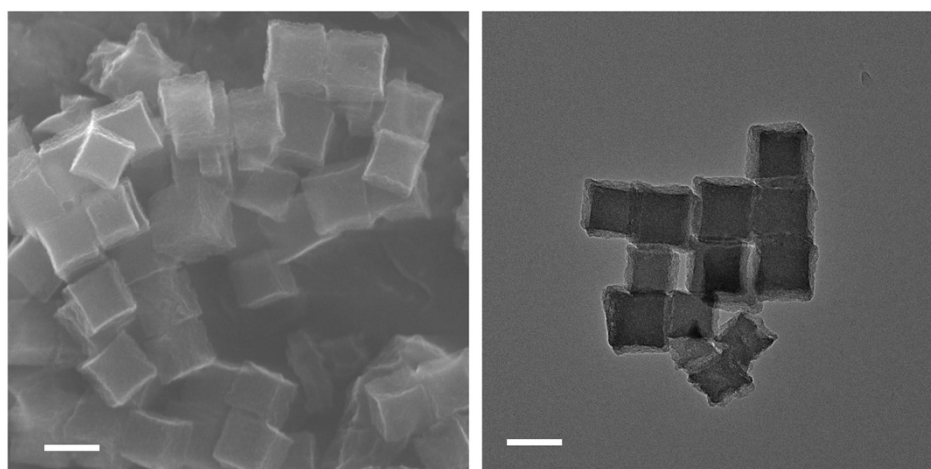


Figure S5. SEM and TEM images of ZIF-8-C. Scale bar is 200 nm.

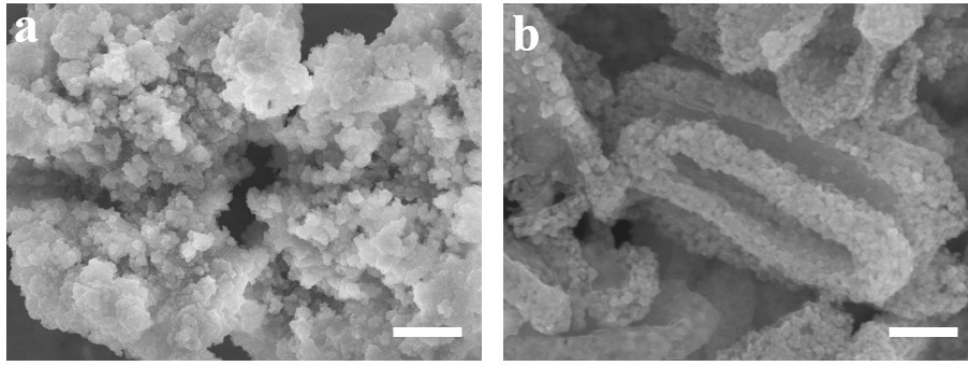


Figure S6. SEM images of (a) ZIF-L-C and (b) ZIF-L@ZIF-8-C. Scale bar is 500 nm.

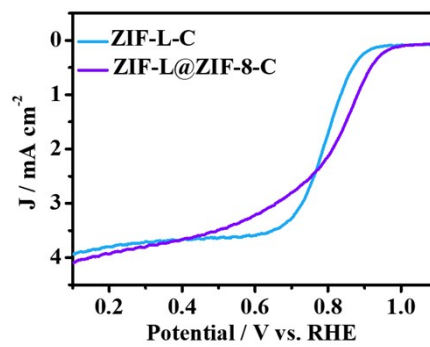


Figure S7. LSV curves of ZIF-L-C and ZIF-L@ZIF-8-C.

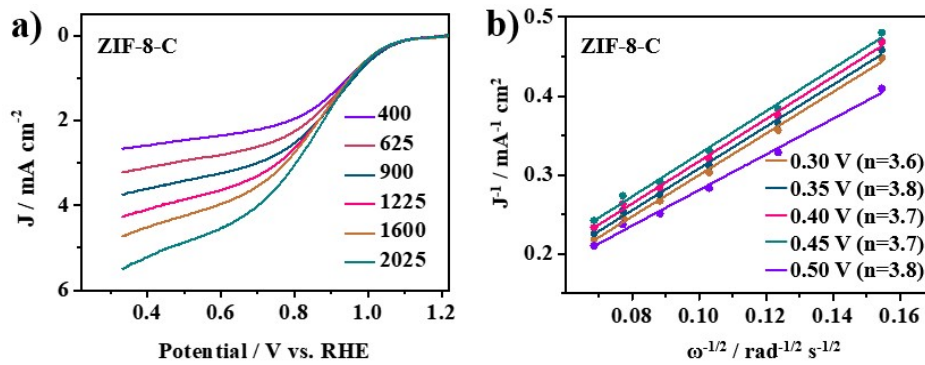


Figure S8. (a) LSV curves for ZIF-8-C at different rotation rates and (b) K-L plot of J^{-1} versus $\omega^{-1/2}$ of ZIF-8-C.

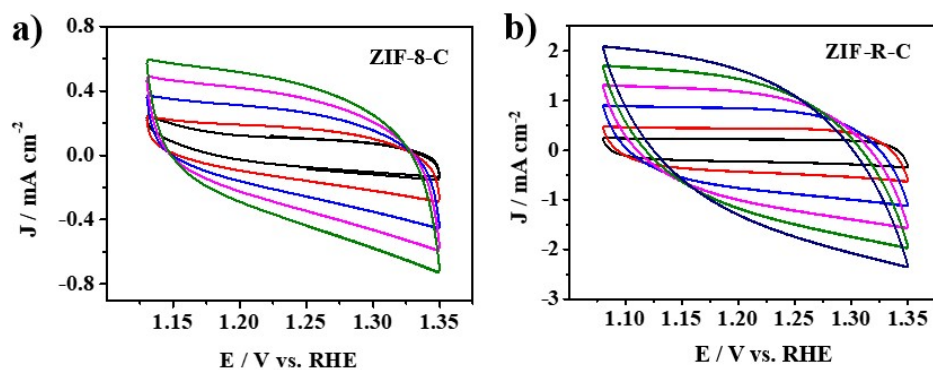


Figure S9. CV curves of (a)ZIF-8-C and (b) ZIF-ring-C at different scan rate.

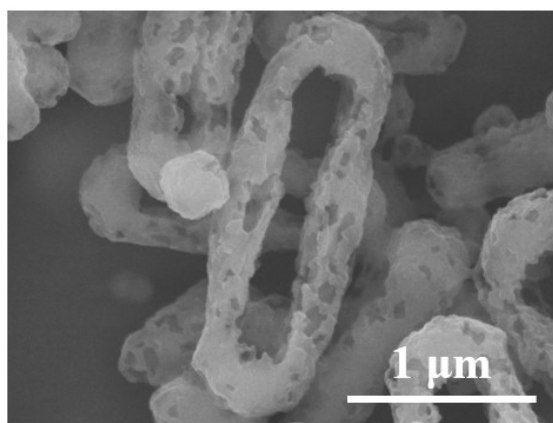


Figure S10. SEM image of ZIF-R-C after 24 h stability test.

Table S1. Performance comparison of ZIF-R-C with reported ZIF-based ORR electrocatalysts.

Catalysts	Electrolyte	$E_{1/2}$ (V)	Ref.
ZIF-R-C	0.1 M KOH	0.88V	-
Cu@Fe-N-C	0.1 M KOH	0.89V	1
Glc-Fe-ZIF	0.1 M H ₂ SO ₄	0.874V	2
La ₂ O ₃ -Co/AB	0.1 M KOH	0.86V	3
Fe/HCP	0.1 M KOH	0.85V	4
FeCo@NC-N	0.1 M KOH	0.84V	5
Co _{0.6} -N/C-800	0.1 M KOH	0.825V	6
Co/Zn-ZIF Nanosheet	0.1 M KOH	0.60V	7

References

- [1] Z. Wang, H. Jin, T. Meng, K. Liao, W. Meng, J. Yang, D. He, Y. Xiong, S. Mu, *Adv. Funt. Mater.*, **2018**, 28, 1802596.
- [2] J. Zhong, L. He, Q. Yang, X. Duan, W. Yang, *Chemistry Select*, **2021**, 6, 1271-1275.
- [3] Q. Zhou, L. Zhang, X. Wang, *Appl. Surf. Sci.*, **2023**, 601, 155551.
- [4] Y. Pei, Z. Qi, X. Li, R. V. Maligal-Ganesh, T. W. Goh, C. Xiao, T. Wang, W. Huang, *J. Mater. Chem. A*, **2017**, 5, 6186-6192.
- [5] X. Wu, S. Zhang, J. Gao, X. Liu, Q. Yuan, Y. Wu, W. Gan, *J. Electrochem. Soc.*, **2022**, 169, 016507.
- [6] J. Li, W. Xia, J. Tang, H. Tan, J. Wang, Y. V. Kaneti, Y. Bando, T. Wang, J. He, Y. Yamauchi, *Nanoscale Horiz.*, **2019**, 4, 1006-1013.
- [7] F. Yang, J. Xie, X. Liu, G. Wang, X. Lu, *Small*, **2021**, 17, 2007085.