

Fig. S1 Scanning electron microscopy (SEM) images of ZIF-8 (a), FeCl3-CZIF (b), PB-CZIF (c).



Fig. S2 SEM EDS (a) and TEM image (b) of Fe-CZIF-800-10.



Fig. S3 XPS survey spectra (a) and high-resolution N 1s X-ray photoelectron spectroscopy (b-f) of different Fe-CZIF samples and CZIF-900.



Fig. S4 Thermogravimetric analysis (TGA) curves of different Fe-CZIF samples under air atmosphere.



Fig. S5 Nitrogen adsorption–desorption isotherms of FeCl₃-CZIF at 77 K (inset shows the corresponding DFT pore size distributions).



Fig. S6 (a) Rotating disk electrode (RDE) polarization curves of the Fe-CZIF-T-10 samples, (b) The Koutecky-Levich (K-L) plots of Fe-CZIF-800-10 from the RDE polarization curves at rotation rates from 400 to 2025 rpm.



Fig. S7 LSV curves for ORR on Fe-CZIF-800-10 (a) and CZIF-900 (b) at 1600 rpm in O₂-saturated 0.1 M KOH with and without 10 mM KSCN.



Fig. S8 LSV curves of Fe-CZIF-800-10 tested in wide potential at 1600 rpm





Fig. S9 (a) LSV curves of the samples at different rotation rates and corresponding (b) K-L plots at different potentials.



Fig. S10 Electron transfer numbers of Pt/C and Fe-CZIF catalysts derived from their corresponding LSV curves at a scan rate of 1600 rpm.



Fig. S11 The impedance characteristics of Fe-CZIF-800-n (a) and CZIF-900 (b).



Fig S12 (a) The CV curves at 5 mV s⁻¹ and (b) GCD curves at 1 A g⁻¹ of Fe-CZIF-800-n.



Fig. S13 Specifc capacitance versus current density for Fe-CZIF-T-10 (a) and Fe-CZIF-800-n (b).

| | C (at%) | N (at%) | O (at%) | Fe (at%) |
|----------------|---------|---------|---------|----------|
| Fe-CZIF-800-10 | 81.36 | 13.78 | 4.21 | 0.65 |
| Fe-CZIF-800-5 | 81.93 | 12.07 | 5.46 | 0.54 |
| Fe-CZIF-800-15 | 89.51 | 6.69 | 3.09 | 0.72 |
| Fe-CZIF-900-10 | 92.66 | 3.68 | 3.17 | 0.49 |
| Fe-CZIF-700-10 | 74.98 | 19.06 | 5.29 | 0.67 |
| CZIF900 | 89.97 | 8.09 | 1.93 | / |

Table S1 Elemental qualification of various catalysts determined using XPS

Table S2 The iron content of CZIF-900 and Fe-CZIF samples calculated by the thermogravimetric analysis (TGA)

| | Sample | Iron content(wt%) | | |
|------|------------------|-------------------|--|--|
| | CZIF900 | / | | |
| | Fe-CZIF-900-10 | 5.90 | | |
| | Fe-CZIF-800-10 | 6.13 | | |
| | Fe-CZIF-700-10 | 8.77 | | |
| | Fe-CZIF-800-5 | 2.09 | | |
| | Fe-CZIF-800-15 | 7.58 | | |
| Pt/C | 0.979 | 0.828 | | |

 Table S3 ORR performance of porous carbon-based materials reported in the

 representative literature. All catalysts were tested in 0.1 M KOH

| | Electrode materials | Onset potential (V vs. NHE) | Half-wave potential (V vs. NHE) | Limiting Current Density (mA/cm ²) | References |
|----------|------------------------|-----------------------------------|--|---|----------------------|
| | | 0.96 | 0.70 | 4.50 | Energy Environ. Sci. |
| Carbon-L | 0.80 | 0.70 | 4.39 | 2014. 7, 442-450 | |

| Pt/C | 0.979 | 0.826 | 5.75 | This work |
|-------------------------|-------|-------|------|---|
| Fe-CZIF-800-10 | 0.982 | 0.830 | 5.68 | This work |
| Fe,S/NGC-900 | 0.95 | 0.77 | 4.9 | ACS Appl. Mater. Inter. 2016, 8, 19533- 19541 |
| LDH@ZIF-67-800 | 0.94 | 0.83 | 5.5 | Adv. Mater. 2016, 28, 2337-2344 |
| Fe/N-CNT | 0.96 | 0.82 | / | J. Mater. Chem. A. 2016, 4, 1694 |
| Fe ₃ C/C-800 | 1.05 | 0.83 | / | Angew. Chem. Int.Ed. 2014, 53, 3675 |
| Fe-N-CNFs-800 | 0.944 | 0.824 | 5.1 | Angew. Chem. Int. Ed. 2015, 54, 8179- 8183 |
| FNCT800-100 | 0.933 | 0.828 | 5.32 | Nanoscale. 2017, 9, 17364- 17370 |
| LHNHPC | 0.98 | 0.865 | 4.4 | Appl Catal B-Environ 2017, 210, 57–66 |
| Fe-SNC-900 | 0.979 | 0.834 | 7.2 | Adv. Energy Mater. 2017, 7, 1602002 |

| Electrode | Capacitance (F g ⁻¹) | Current density | References | |
|--------------------|-------------------------------------|----------------------|--------------------------|--|
| | | (A g ⁻¹) | | |
| Carbon-L-950 | 228 | 0.1 | J. Mater. Chem. A. | |
| | | | 2014, 2, 12873 | |
| Carbon-ZS | 285.8 | 0.1 | Carbon. | |
| | | | 2015, 85, 51-59 | |
| | 251 | 0.05 | Chemical Communications. | |
| AS-ZC-800 251 0.25 | | 0.25 | 2014, 50, 1519-1522 | |
| PC1000@C | 225 | 0.5 | Electrochimica Acta. | |
| | | | 2016, 196, 699–707 | |
| Fe-CZIF-800-10 | 246 | 0.5 | This work | |
| CZIF-900 | 207 | 0.5 | This work | |

Table S4 Capacitive performance of ZIF-8 derived materials reported in therepresentative literature. All Samples were tested in 6 M KOH