Electronic Supplementary Information

A "micropores & active species protection" strategy for the preparation of high-performance Fe/S/N-composited porous carbon catalyst with efficient oxygen reduction reaction and zinc-air batteries

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Characterization

FESEM images were observed on field-emission scanning electron microscope (SEM, Quant 250FEG). High-resolution transmission electron microscopy images were collected at an acceleration voltage of 200 kV (TEM, JEM-2100F). X-ray diffraction patterns were performed on a Rigaku UItima IV X-Ray Diffractometer. Raman spectra were carried out on a laser Raman microscope system (HORIBA Evolution Raman scope) with the excitation wavelength of 532 nm. The N_2 adsorption-desorption isothermal curve and the BET surface area were calculated via MicroASAP2020 at 77 K. XPS was measured by Thermo ESCALAB 250 surface analysis system.

Electrochemical measurements

The electrochemical measurements were evaluated using a CHI660E electrochemical work station in a standard three-electrode setup with a glass carbon electrode (GC, diameter of 5 mm) loaded with the catalysts was used as the working electrode. The procedure for the preparation of a working electrode was as following: 5 mg of the catalyst powder was dispersed in 800 μL of absolute ethanol and 30 μL of Nafion (5 wt%, Sigma-Aldrich) to obtain a homogeneous ink under ultrasonication, then 10 μL of the ink was slightly dropped on the glassy carbon electrode. For ORR tests, cyclic voltammetry (CV) curves were tested in a N_2-saturated or O_2-saturated 0.1 M KOH

electrolyte with a scan rate of 50 mV s^{-1}, respectively. RDE/RRDE tests were measured in O_2-saturated 0.1 M KOH electrolyte at 10 mV s^{-1}, respectively.

Zinc-air battery tests:

The measurements of zinc-air batteries were evaluated under ambient conditions. A polished zinc plate and 6.0 M KOH solution were used as anode and electrolyte, respectively. The cathode was prepared by loading catalysts on the carbon paper (catalyst loading amount of 1.0 mg cm^{-2}).

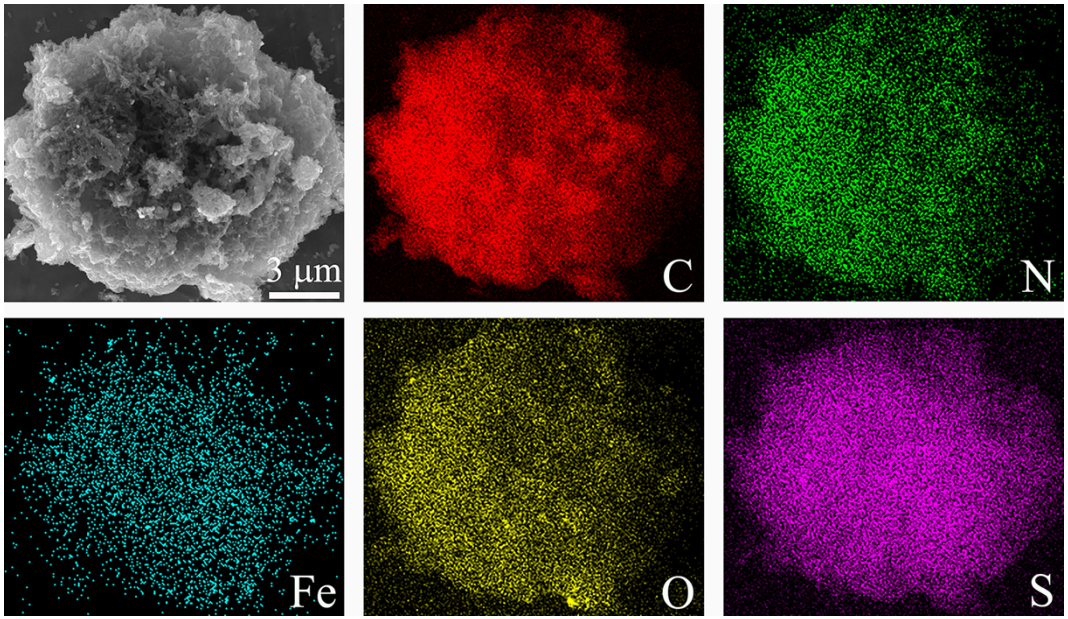

Fig. S1. SEM images of FeTPP-MP@PTh-900 used in the EDS mapping area revealing the elemental distribution of C, N, Fe, O and S.

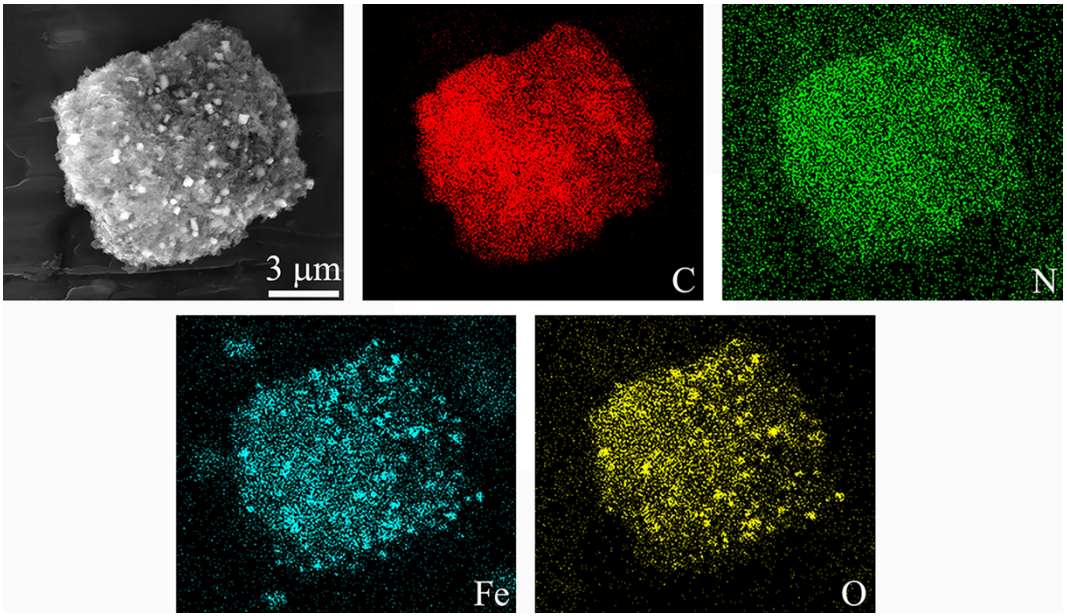

Fig. S2. SEM images of FeTPP-MP-900 used in the EDS mapping area revealing the elemental distribution of C, N, Fe and O.

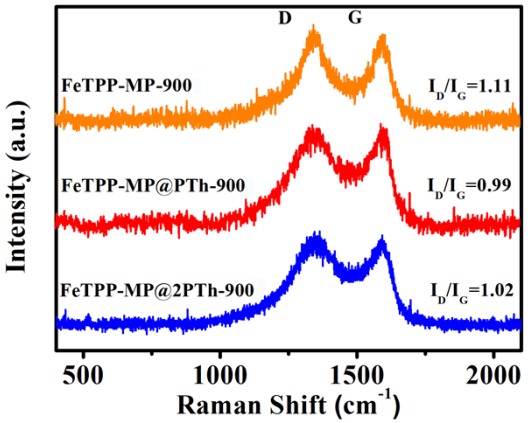

Fig. S3. Raman spectra of FeTPP-MP-900, FeTPP-MP@PTh-900 and FeTPP-MP@2PTh-900.

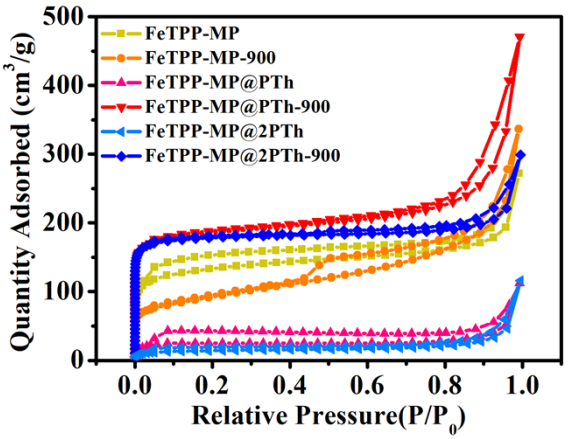

Fig. S4. N_2 adsorption/desorption isotherm plots of precursors (FeTPP-MP, FeTPP-MP@PTh and FeTPP-MP@2PTh) and catalysts (FeTPP-MP-900, FeTPP-MP@PTh-900 and FeTPP-MP@2PTh-900).

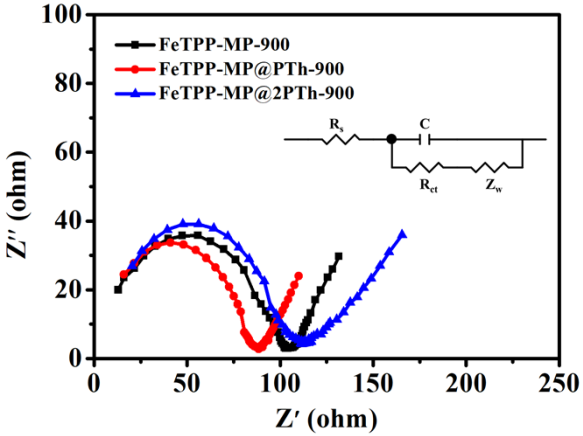

Fig. S5. Nyquist plots of FeTPP-MP-900, FeTPP-MP@PTh-900 and FeTPP-MP@2PTh-900 catalysts-modified electrodes in 0.1 M KOH solution in the frequency range of 0.1-10000 Hz, respectively, (Inset: corresponding equivalent circuit).

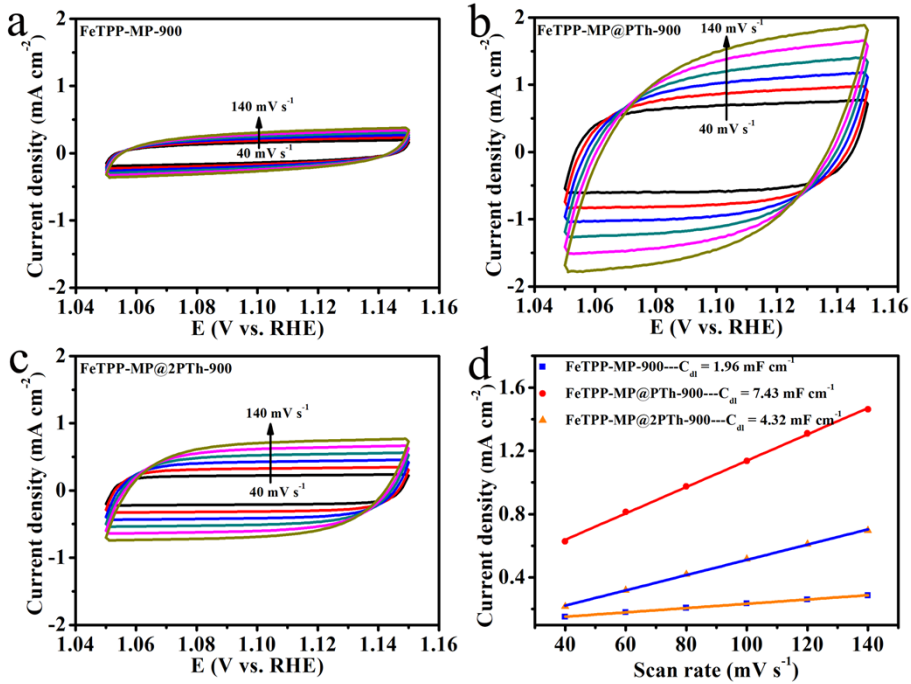

Fig. S6. Cyclic voltammograms (CV) at various scan rates of (a) FeTPP-MP-900, (b) FeTPP-MP@PTh-900, (c) FeTPP-MP@2PTh-900 in 0.1 M KOH solution; (d) Plots of the capacitive currents as a function of scan rate for samples as well as the double-layer capacitance values for samples.

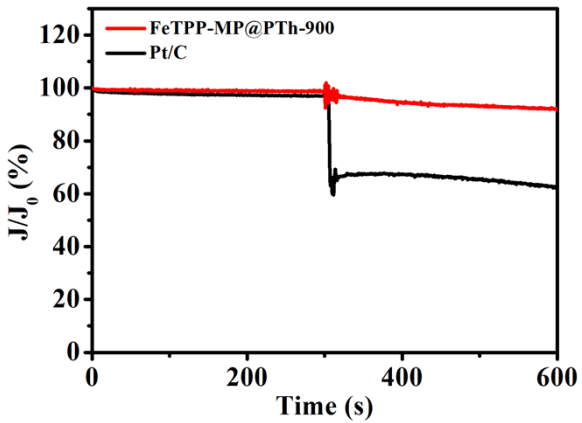

Fig. S7. Upon the addition of 3 M methanol in O_2-saturated 0.1 M KOH solution with the rotation speed of 1600 rpm.

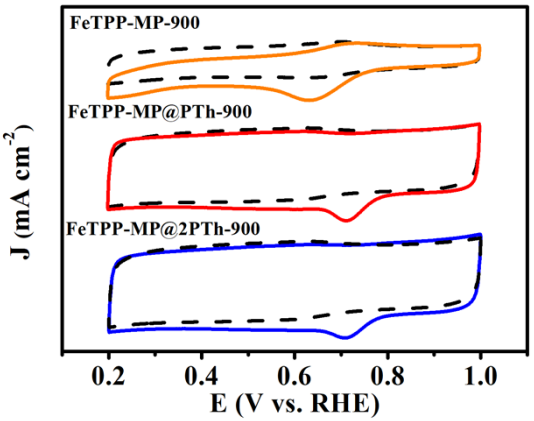

Fig. S8. CV curves of FeTPP-MP-900, FeTPP-MP@PTh-900 and FeTPP-MP@2PTh-900 in O_2-saturated (solid lines) and N_2-saturated (dot lines) 0.5 M H_2SO_4 at 50 mV s^{-1}, respectively.

Table S1. The electrocatalytic activities of the recently reported catalysts for ORR in 0.1 M KOH.

Catalyst	E_{onset}/ V	$E_{1/2}$/V	Reference
FeTPP-MP@PTh-900	0.96	0.89	This Work
FN_3SG	0.99	0.80	Carbon. 2019, 142: 1-12
Cu-Fe-N-C	0.97	0.86	Appl. Catal. B-Environ. 2019, 242: 209-217
Fe-N-HMCTs	0.99	0.87	Adv. Funt. Mater. 2021, 31: 2009197
Fe_3C-FeN/NC-2	0.95	0.80	J. Mater. Chem. A 2021, 9: 6831-6840
Zigzag-type-GO	0.96	0.82	Adv. Mater. 2018, 30: 3819-3828
Fe@N-Go	0.98	0.85	Nano Res. 2020, 11: 2217-2228.
Fe SA-NSC-900	0.94	0.86	ACS Energy Lett. 2021, 6: 379-386.

Table S2. The electrocatalytic activities of the recently reported catalysts for ORR in 0.5 M H_2SO_4.

Catalyst	E_{onset}/ V	$E_{1/2}$/V	Reference
FeTPP-MP@PTh-900	0.80	0.75	This Work
Fe-SAC/NC	0.85	0.69	Nano Energy 2020, 72: 104670
Fe@NSC20-7001-9001	0.85	0.79	J. Catal. 2019, 370: 130-137
Fe-N-C spheres	0.861	0.73	ACS Catal. 2017, 7: 1655-1663
FeNC-D0.5	0.85	0.75	Small 2020, 16: 2006178
Fe-SAs/NSC	0.84	0.70	J. Am. Chem. Soc. 2019, 141: 20118-20126
Fe/N-HCS-0.5-800	0.80	0.59	J. Colloid InterfaceSci. 2019, 544: 178-187
Fe-N-C/N-OMC	0.91	0.73	Appl. Catal. B-Environ. 2021, 280: 119411