Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Synthesis of Nanoporous Structured Iron Carbide/ Fe–N–Carbon Composites for Efficient Oxygen Reduction Reaction in Zn-Air Batteries†

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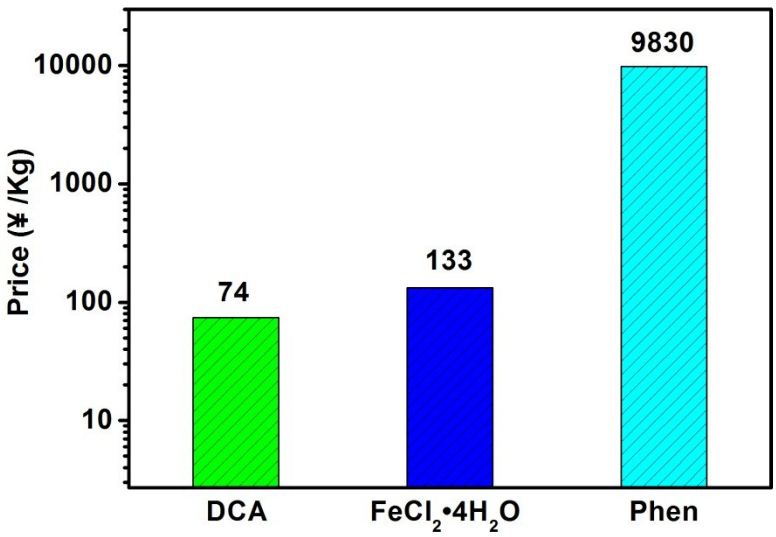

Fig. S1 The price of chemicals for the preparation of Fe−Phen−N catalysts. The data was from Sinopharm Chemical Reagent Co. Ltd.. Website: http://www.sinoreagent.com.

Evaluating the cost of the Fe−Phen−N−800 sample: 0.99 g Phen: ¥ 9.73 + 0.33 g $FeCl_2{\cdot}4H_2O$: ¥ 0.043 +4.5 DCA: ¥ 0.33 = ¥ 10.10 Fe−Phen−N−800 (~ 20% yield compared with the starting materials). Therefore the cost is about ¥ 8.69 /g for Fe−Phen−N−800.

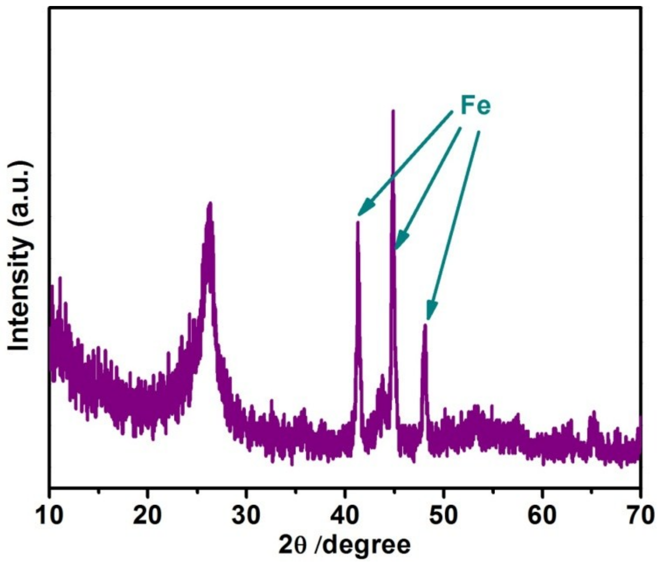

Fig. S2 XRD pattern of Fe−Phen−N−800 catalyst before leaching in 6 M HCl solution.

Fig. S3 shows that the decomposition of the Fe−Phen−N−800 sample divided in two stages: (i) a slight mass loss of 8.42% (crystal water release) and (ii) a sharp mass loss of 86.25% due to the decomposition of Fe−Phen−N−800 to produce Fe_2O_3 material.

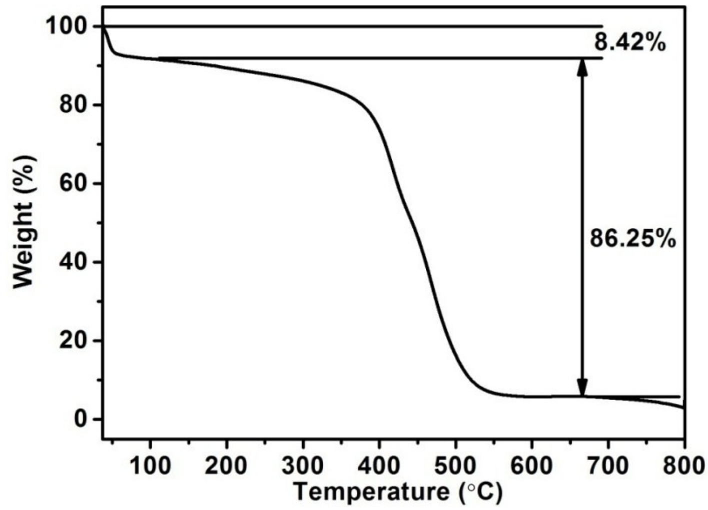

Fig. S3 TG curve of the Fe−Phen−N−800 sample in air.

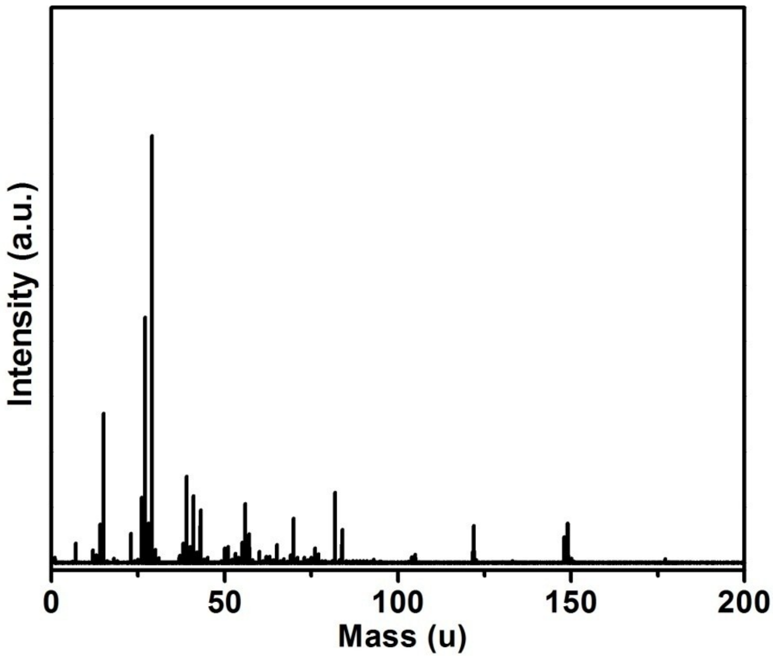

Fig. S4 TOF-SIMS spectrum of Fe−Phen−N−800 sample.

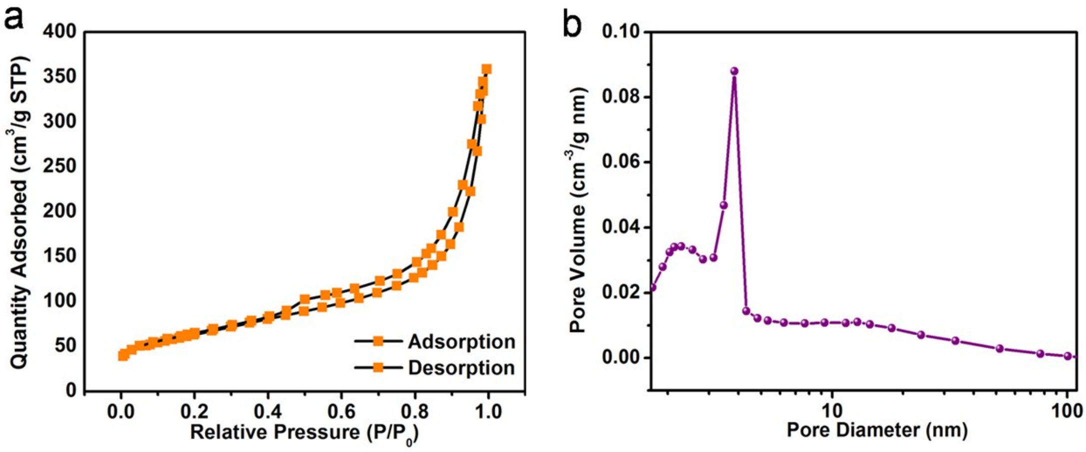

Fig. S5 (a) N_2 adsorption/desorption isotherms and (b) pore distribution of Fe−Phen−N−800 catalyst.

Table S1. The Comparison of ORR performance of NPMCs from the recent literature and this work (electrode 1600 rpm in 0.1 M KOH medium).

Catalysts	Catalyst loading (mg cm^{-2})	Onset potential (V vs RHE)	Current density (mA cm^{-2})	Electron transfer numbers	Reference
Fe3C−Fe−N/C−800	0.1	0.99	5.7	4.02	This work
LDH@ZIF-67−800	0.2	0.94	5.5	4.0	Adv. Mater., 2016,28, 2337
Co3O4/rmGO	0.17	0.88	4.5	3.9	Nat. Mater. 2011, 10, 780
Co/N-carbon fibres	0.306	0.95	2.2	3.9	Chem. Eur. J. 2015, 21, 2165
CoP-CMP800	0.6	0.85	4.8	3.94	Adv. Mater., 2014, 26, 1450
Fe-N-CNFs	0.6	0.93	5.12	3.95	Angew. Chem. Int. Ed., 2015, 54, 8179
Fe−N−CNFs	0.6	0.93	5.1	3.93	Angew. Chem. Int. Ed., 2015, 54,1
CoII-A-rG-O	0.6	0.88	5.3	3.95	Angew. Chem. Int. Ed., 2015, 54, 12622
N-Carbon nanotube frameworks	0.2	0.95	5.2	3.97	Nature Energy, 2016, 1, 15006.
Fe/N/C HNSs.	0.255	/	5.8	3.80	Nanoscale, 2015, 7, 1501
rGO/($Co2^{+}$–THPP)$_7$	1.0	0.86	4	3.85	Angew. Chem. Int. Ed., 2013, 52, 5585
Co–N–C–NS	0.464	0.93	5.7	3.7	Nanoscale,

					2015, 7, 10334
Fe/N/C	0.458	0.91	3.75	3.96	Sci. Rep., 2014, 4, 43866
Fe−Nx−C	0.36	0.95	5	3.3	Carbon, 214, 78 49
Fe_3C@NG800−0.2	0.2	0.95	5.5	3.5	ACS Appl. Mater. Interfaces，2015,7，21511

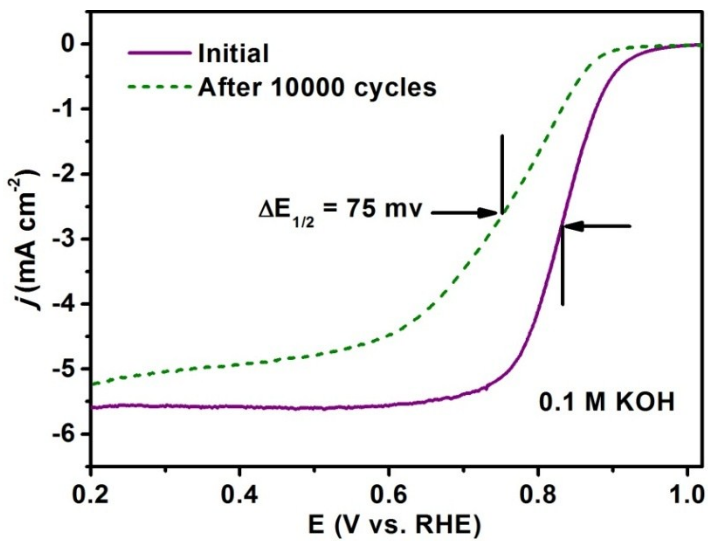

Fig. S6 Durability test of the Pt/C catalyst for 10000 cycles in O_2-saturated 0.1 M KOH solution.

Table S2. The Comparison of ORR performance of non-precious catalysts from the recent literature and this work (electrode 1600 rpm in 0.1 M $HClO_4$ medium)

Catalysts	Catalyst loading (mg cm^{-2})	Onset potential (V vs RHE)	Current density (mA cm^{-2})	Electron transfer numbers	Reference
Fe_3C−Fe−N/C−800	0.1	0.85	5.6	3.98	This work
FP−Fe−TA−N−850	0.3	0.83	5.5	3.5	Angew. Chem. Int. Ed., 2015, 54, 1
N-mesoporous carbon	0.8	0.80	4.5	3.2	J. Am. Chem. Soc., 2011, 133, 206
N,P-mesoporous nanocarbon	0.45	0.83	5.6	4.0	Nature Nanotech., 2015, 10,444
Co/N/C	0.6	0.83	3.8	3.5	Chem. Eur. J., 2011, 17, 2063
Fe−N−C−750	0.6	0.89	4.05	3.96	ACS Catal., 2014, 4, 3928

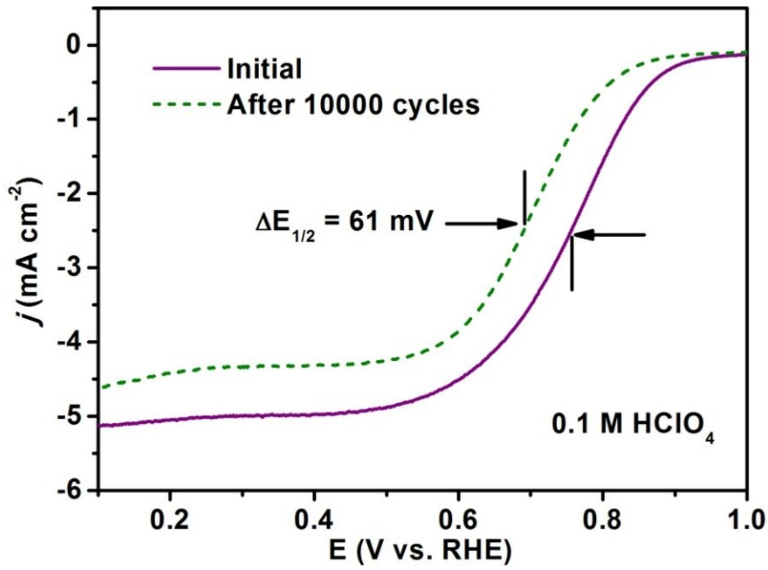

Fig. S7 Durability test of the Pt/C catalyst for 10000 cycles in O_2-saturated 0.1 M $HClO_4$ solution.

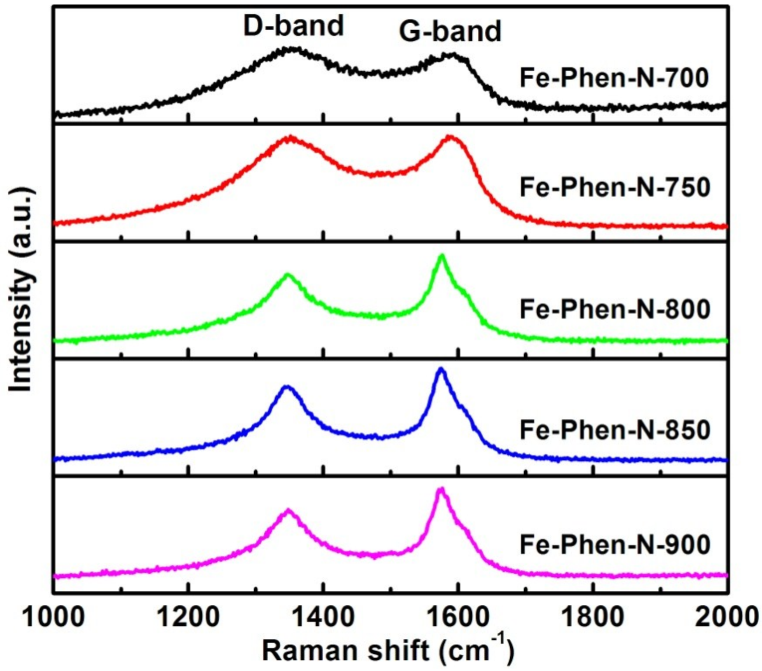

Fig. S8 Raman spectra of Fe−Phen−N catalysts pyrolyzed at different temperatures.

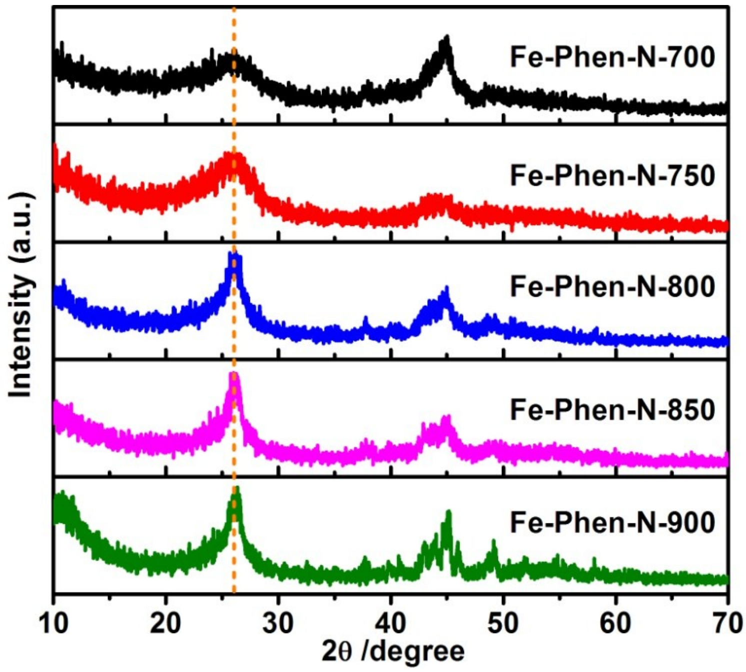

Fig. S9 XRD patterns of Fe−Phen−N samples pyrolyzed at different temperatures.

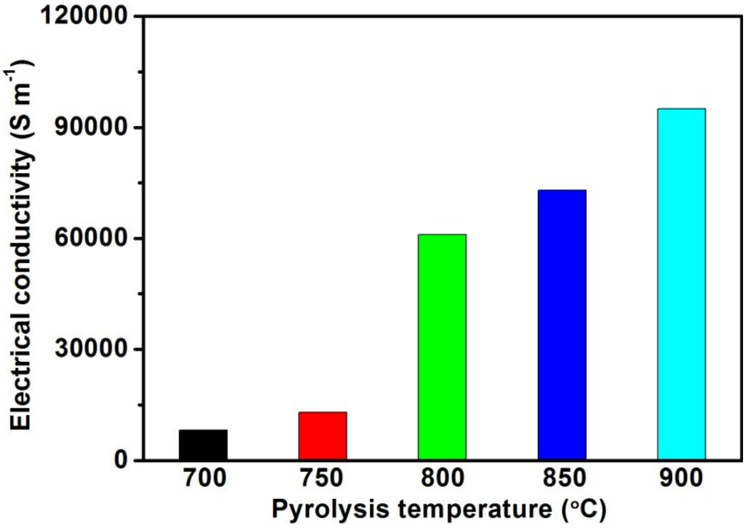

Fig. S10 Electrical conductivity of Fe−Phen−N samples as a function of pyrolysis temperature.

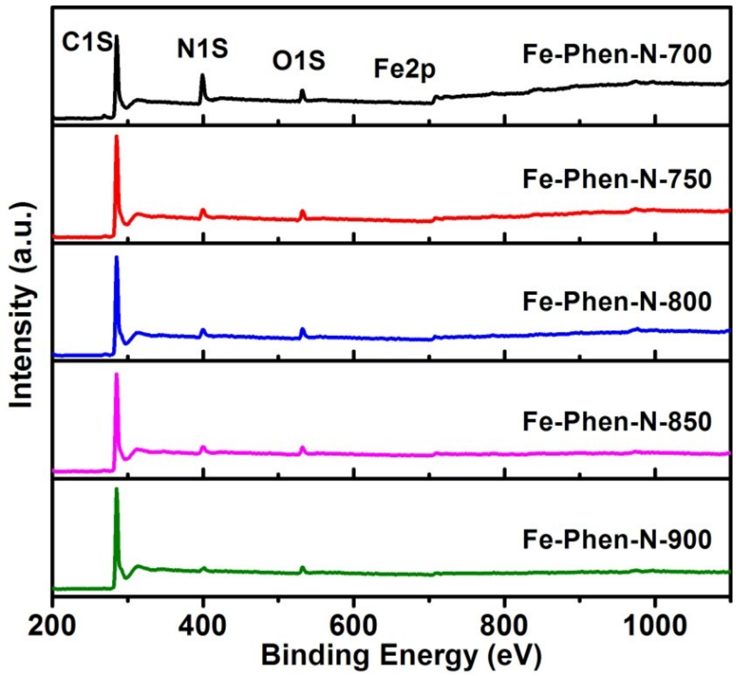

Fig. S11 XPS survey scan of Fe−Phen−N samples pyrolyzed at different temperatures.

Table S3. Elemental compositions of Fe−Phen−N samples pyrolyzed at different temperatures determined by XPS.

Temp (ºC)	C atom %	N atom %	Fe atom %	O atom %
700	75.53	19.22	0.93	4.32
750	82.27	12.93	0.81	3.90
800	89.32	6.25	0.78	3.65
850	90.36	5.81	0.62	3.21
900	93.58	2.92	0.52	2.98

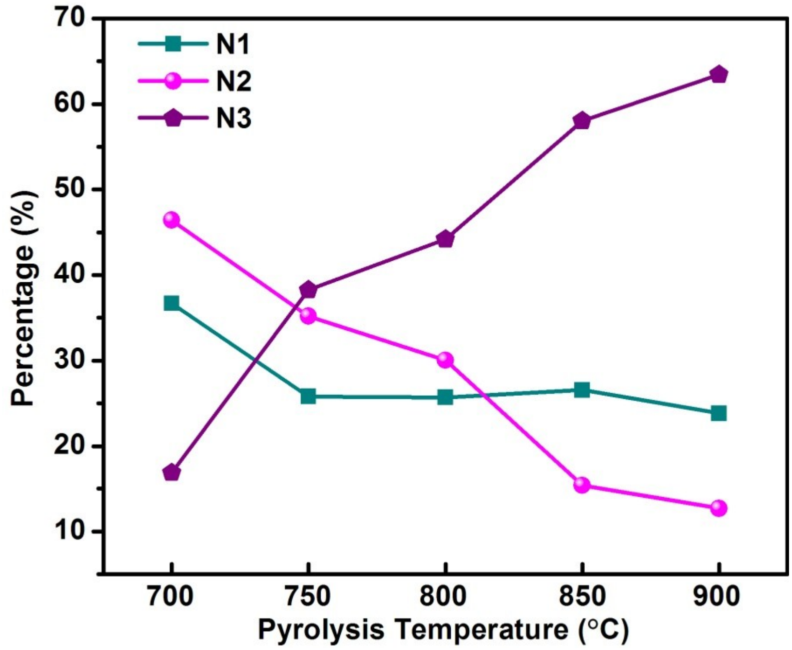

Fig. S12 Percentage of various nitrogen species as a function of pyrolysis temperature.

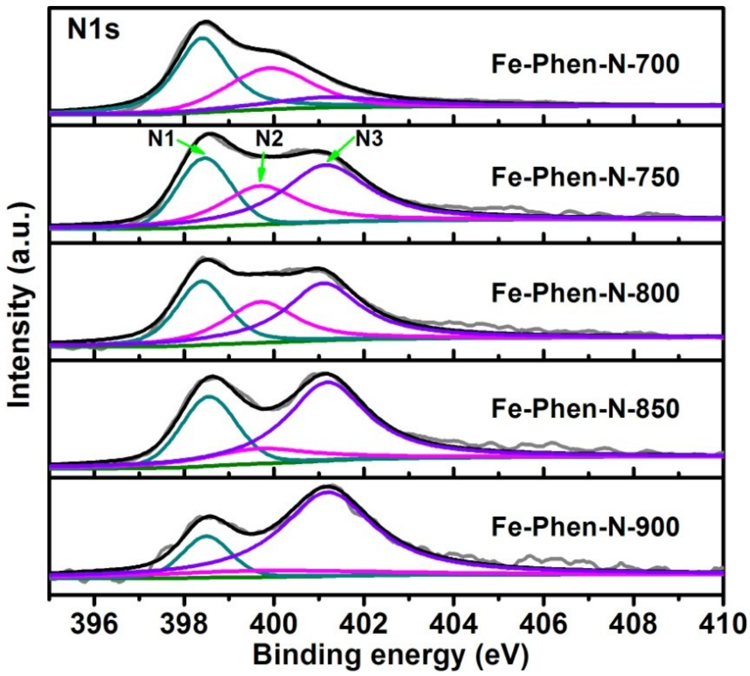

Fig. S13. High-resolution XPS N1s spectra of Fe−Phen−N catalysts pyrolyzed at different temperatures.

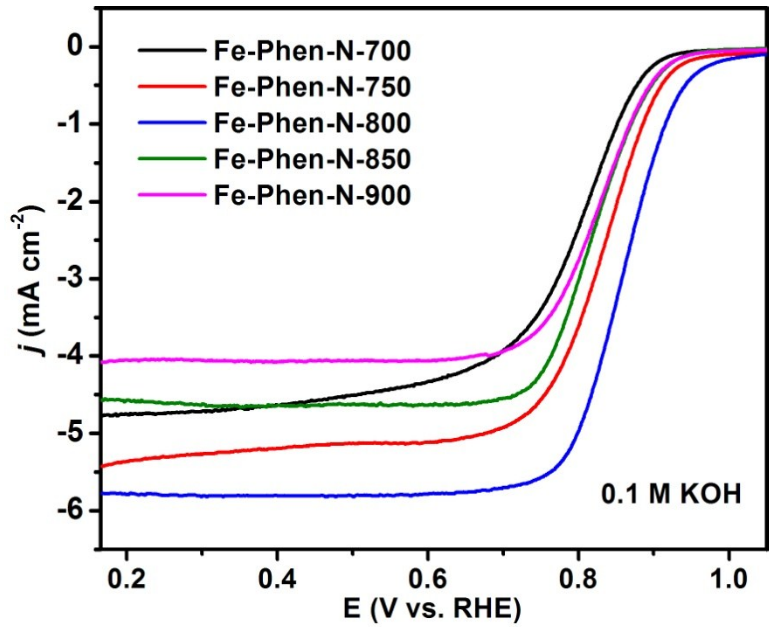

Fig. S14 Comparison of the RDE polarization curves of Fe−Phen−N catalysts pyrolyzed at different temperatures in O_2 -saturated 0.1 M KOH solution at a sweep rate of 10 mV s^{-1} and electrode rotation speed of 1600 rpm (the catalyst loading is 0.1 mg cm^{-2}).

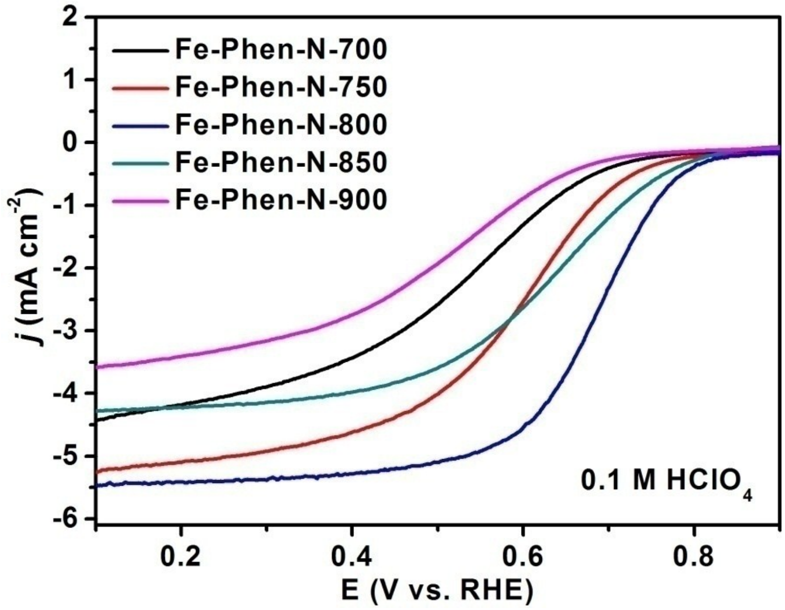

Fig. S15 Comparison of the RDE polarization curves of Fe−Phen−N catalysts pyrolyzed at different temperatures in O_2 -saturated 0.1 M $HClO_4$ solution at a sweep rate of 10 mV s^{-1} and electrode rotation speed of 1600 rpm (the catalyst loading is 0.1 mg cm^{-2}).

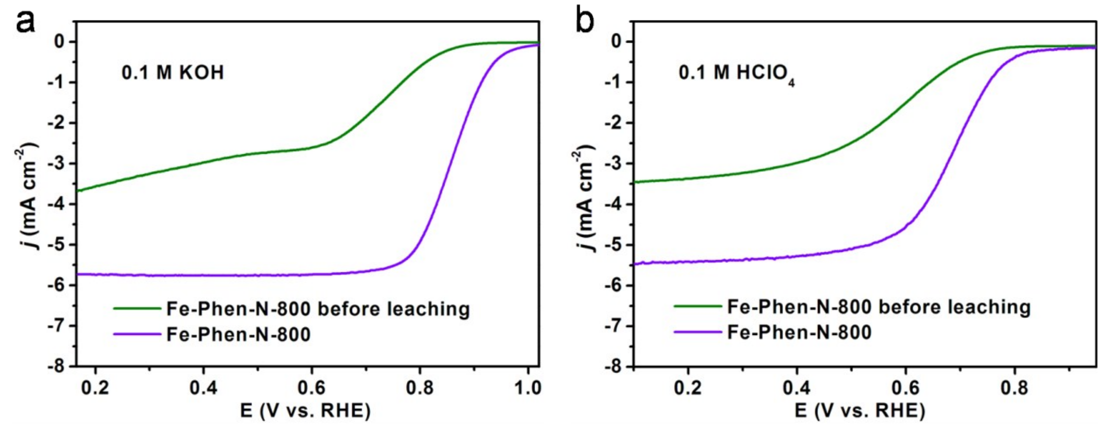

Fig. S16 RDE polarization curves of Fe−Phen−N−800 catalyst in O_2-saturated 0.1 M KOH (a) and 0.1 M $HClO_4$ (b) before and after being leached in acid.

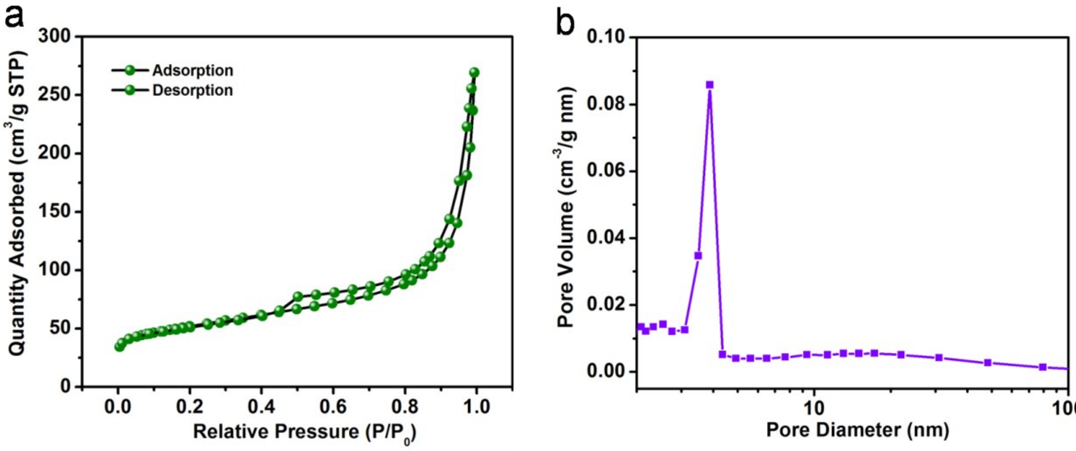

Fig. S17 (a) N_2 adsorption/desorption isotherms and (b) pore distribution of Fe−Phen−N−800 catalyst before leaching.

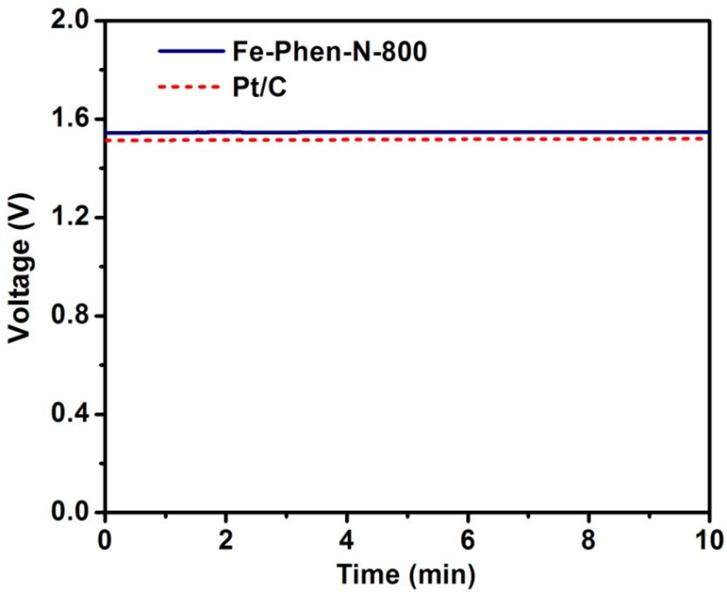

Fig. S18 Open circuit voltage measurements of the Zn-Air batteries with Fe−Phen−N−800 and commercial Pt/C as the cathode catalysts.

Table S4. Comparasion of the Zn-air battery performance of Fe−Phen−N−800 catalyst with reported values.

ORR Catalyst	Zn electrode	Electrolyte	Voltage @ 10 mA cm^{-2}	Reference
Fe−Phen−N−800	**Zn foil**	**6 M KOH**	**1.26**	**This work**
N,S-GO	Zn plate	6 M KOH	1.24	Electrochim. Acta 2015, 183, 63.
FePc-Py-CNT	Zn powder	6 M KOH	1.25	Nat. Commun. 2013, 4, 2076
Fe-N-CNFs	Zn foil	6 M KOH	1.21	Angew. Chem. Int. Ed. 2015, 54, 8179.
Amorphous MnO_x/C	Zn powder	6 M KOH	1.24	Nano Lett. 2011, 11, 5362
N-doped CNTs	Zn plate	6 M KOH	1.22	Electrochim. Acta 2011, 56, 5080.
N-CNF aerogel	Zn foil	6 M KOH	1.25	Nano Energy 2015, 11, 366.