Supporting Information

Manganese, nitrogen co-doped porous carbon with high-loading active sites as the oxygen reduction catalyst for Zn-air battery

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Materials

KOH (99.999 %), manganese acetylacetonate ($Mn(acac)_3$, 97%) and 2-methylimidazole (2-MeIm, 98 %) were acquired from Shanghai Aladdin. $Zn(NO_3)_2 \cdot 6H_2O$ (99 %) was acquired from Sinopharm. Nafion solution (5 %) was obtained from Dupont. Methanol (99.5 %) and isopropanol solution (99 %) were obtained from Tianjin Fuyu.

Electrochemical measurements

All electrochemical measurements were conducted by standard three-electrode configuration controlled by an electrochemical workstation (CHI 760E) at room temperature. A glassy carbon rotating disk electrode with surface area of 0.196 cm^2 served as working electrode. Graphite sheet and mercury/mercury oxide (Hg/HgO) were used as counter and reference electrodes, respectively, in 0.1 M KOH. To prepare catalyst ink, 2.5 mg of catalyst was dispersed into 500 μL of a mixed solution containing 20 μL of a Nafion solution, 300 μL of a ultrapure water, and 180 μL of an isopropanol solution, followed by ultrasonication for 60 min. All potentials have been converted to the reversible hydrogen electrode (RHE) potential.

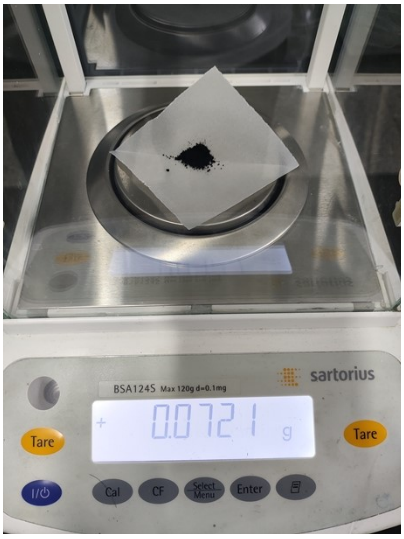

Fig. S1. The mass yield of Mn-N-C-900

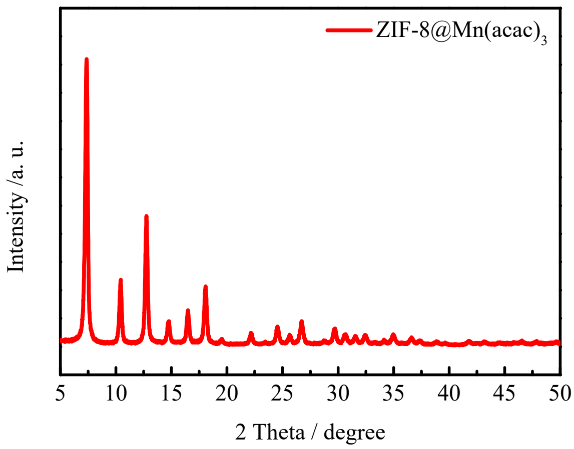

Fig. S2. XRD spectrum of ZIF-8@Mn(acac)$_3$

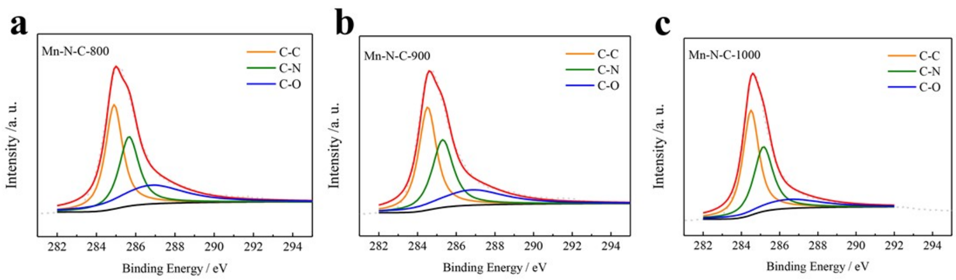

Fig. S3. C 1s XPS spectra of (a) Mn-N-C-800, (b) Mn-N-C-900 and (c) Mn-N-C-1000 catalysts.

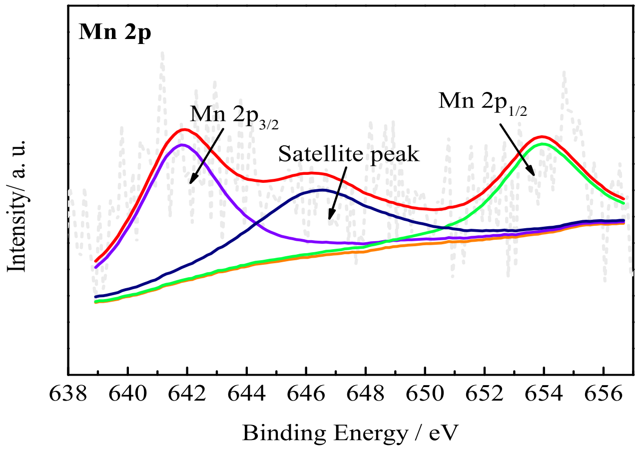

Fig. S4. Mn 2p XPS spectra of Mn-N-C-900 catalyst.

Table S1 The percentage of different N-sites derived from high-resolution XPS scans of N 1s

Sample	Pyridinic-N (%)	$Mn-N_x$ (%)	Pyrrole N (%)	Graphitic-N (%)	Oxidized-N (%)
Mn-N-C-800	27.82	24.19	12.97	20.73	14.29
Mn-N-C-900	44.8	27.47	12.72	4.63	10.38
Mn-N-C-1000	25.31	16.97	23.81	19.5	14.41

Table S2 Comparison of the ORR performance of various M-N-C catalysts in alkaline environment from the recent literature and this work

Catalysts	Electrolyte	Half-wave potential (V vs. RHE)	Reference
Mn-N-C-900	**0.1 M KOH**	**0.882**	**This work**
Fe-N-C HNSs	0.1 M KOH	0.84	Adv. Mater. 2019, 31, 1806312
Fe_2N/NPCF	0.1 M KOH	0.865	J. Colloid Interf. Sci. 2022, 616, 539-547.
SA-Fe-NC	0.1 M KOH	0.88	Chem. Mater. 2021, 33, 5542-5554.
Fe SA-NSC-900	0.1 M KOH	0.86	ACS Energy Lett. 2021, 6. 379-386.
Mn-N-C	0.1 M KOH	0.88	ACS Sustainable Chem. Eng. 2020, 8, 9367-9376

Co@hNCTs-800	0.1 M KOH	0.887	Nano Energy 2020, 71, 104592.