Rational Design of N-doped Carbon Nanobox supported $Fe/Fe_2N/Fe_3C$ nanoparticles as Efficient Oxygen Reduction Catalyst for Zn-air Batteries

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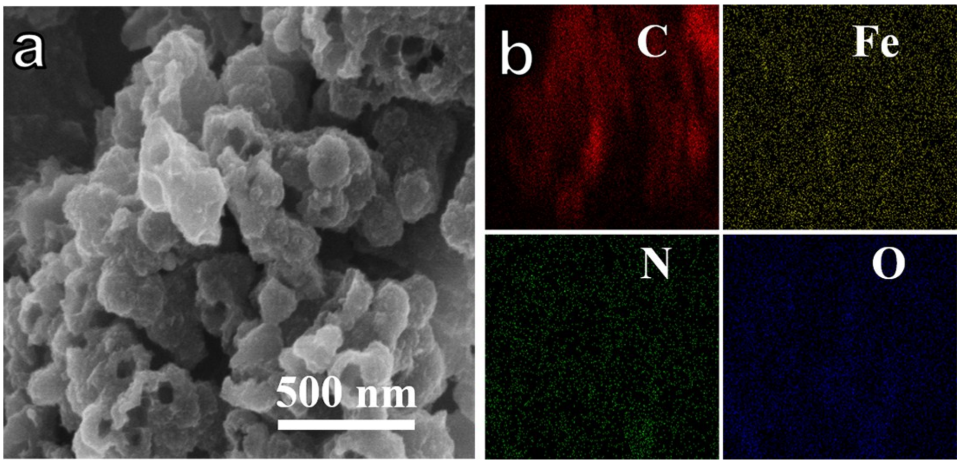

Fig. S1 (a) SEM images and (b) corresponding elemental mapping images of Fe-N-CNBs-600.

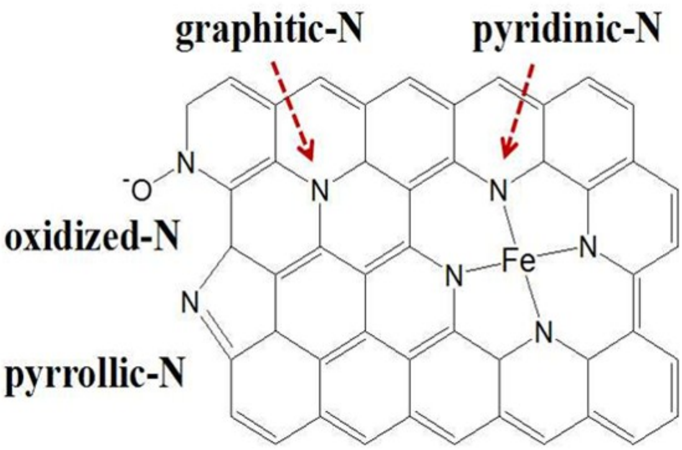

Fig. S2 Schematic illustration of four types of nitrogen in Fe-N-CNBs.

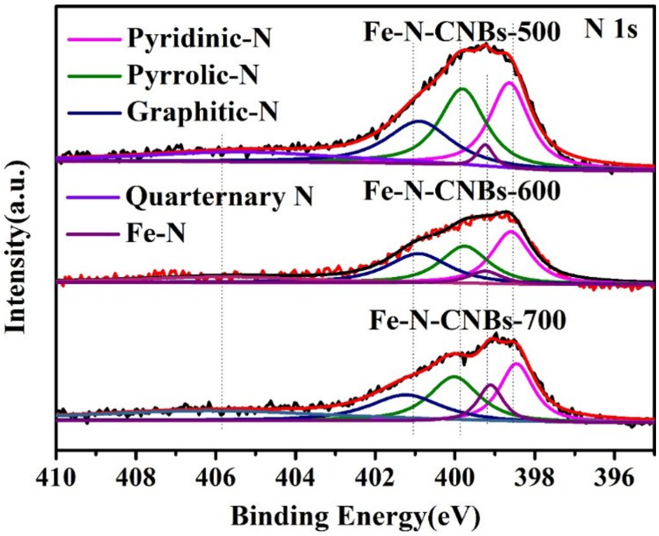

Fig. S3 XPS N 1s spectrum of Fe-N-CNBs with different calcination temperature.

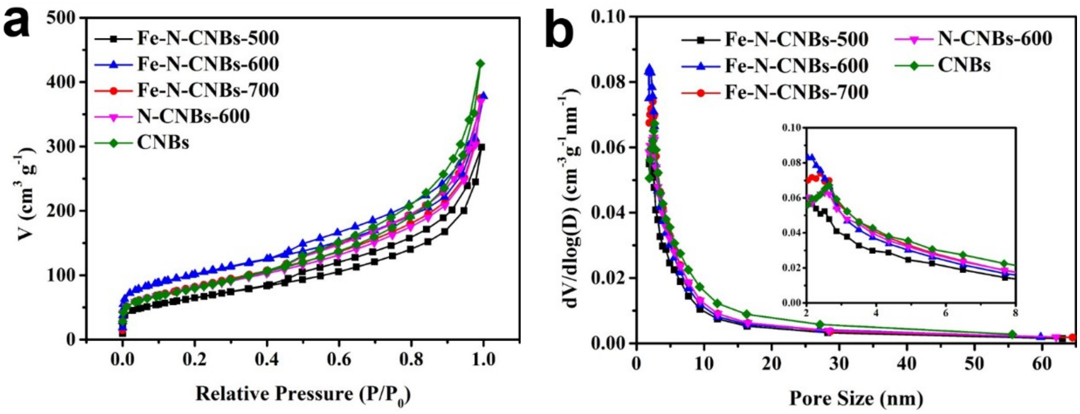

Fig. S4 (a) N_2 adsorption/desorption isotherm curves and (b) corresponding pore size distribution curves of CNBs, Fe-CNBs-600, N-CNBs-600 and Fe-N-CNBs-500, Fe-N-CNBs-600 and Fe-N-CNBs-700.

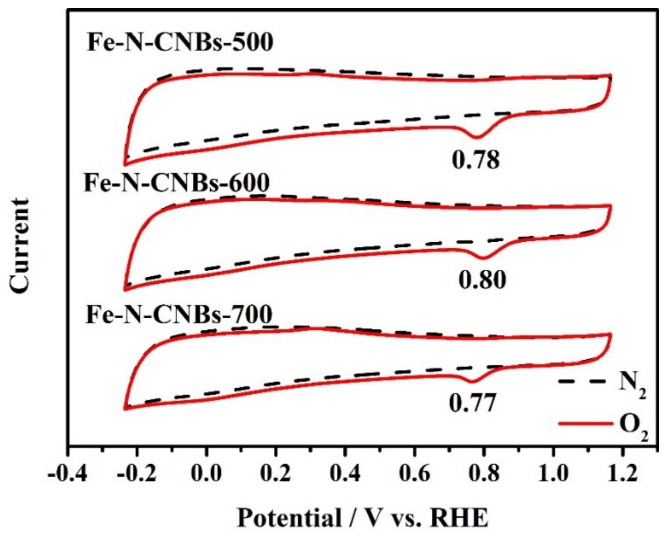

Fig. S5 CV curves for the Fe-N-CNBs electrodes with different calcination temperature with O_2 and N_2-saturatedin 0.1 M of KOH.

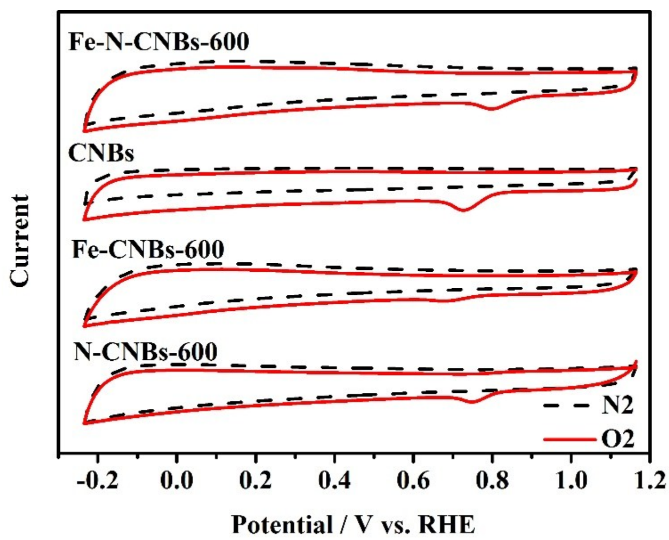

Fig. S6 CV curves for CNBs, Fe-CNBs-600, N-CNBs-600 and Fe-N-CNBs-600 electrodes with N_2 and O_2-saturated in 0.1 M KOH solution.

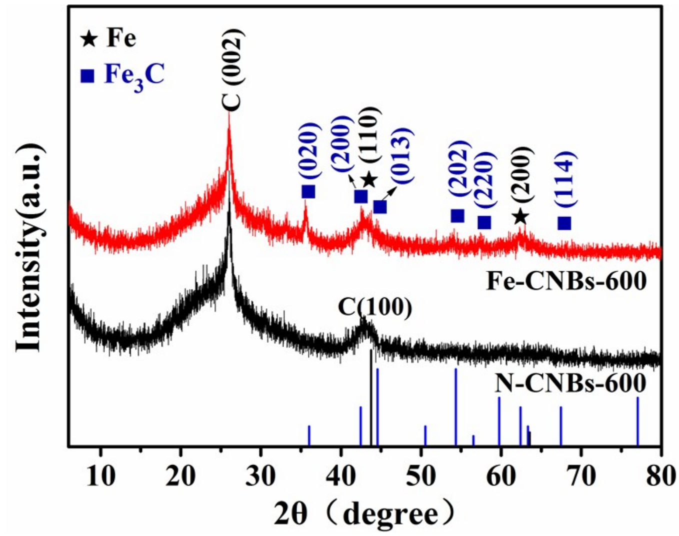

Fig. S7 XRD spectra of N -CNBs-600 and Fe -CNBs-600.

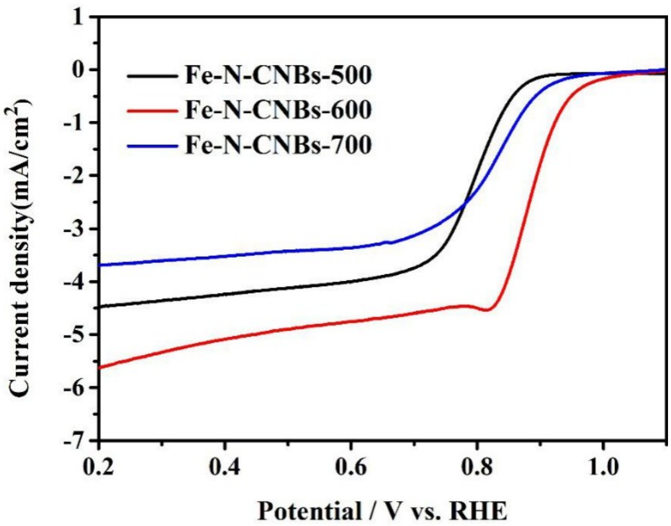

Fig. S8 LSV curves for the Fe-N-CNBs electrodes with different calcination temperature at 1600 rpm.

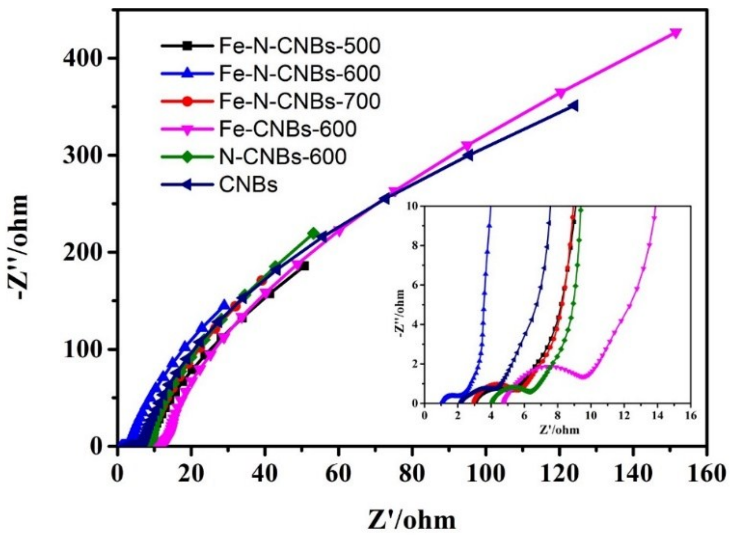

Fig. S9 Electrochemical impedance spectroscopy (EIS) curves plots of the CNBs, Fe-CNBs-600, N-CNBs-600, Fe-N-CNBs-500, Fe-N-CNBs-600 and Fe-N-CNBs-700 electrodes in 0.1M KOH solution.

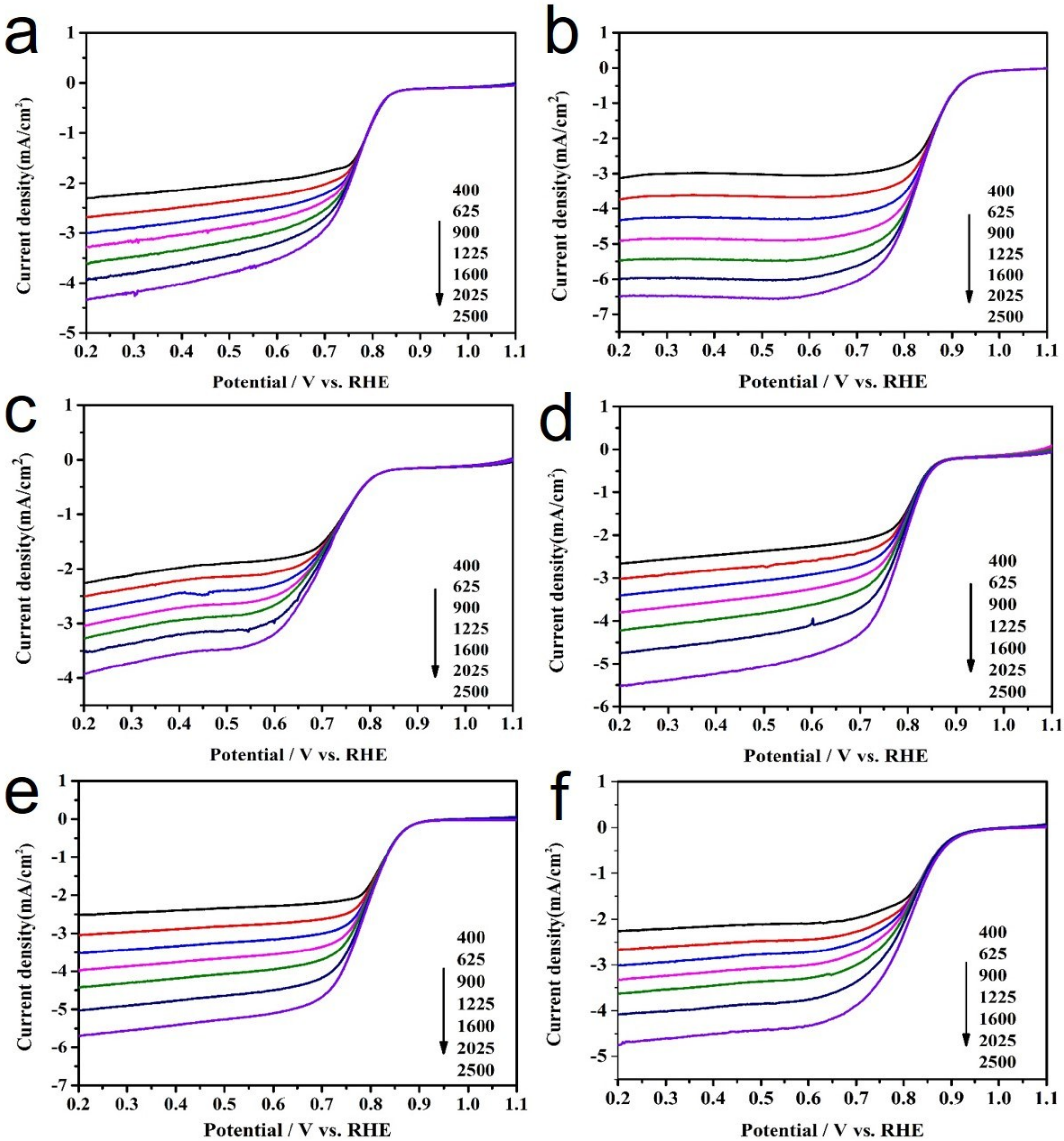

Fig. S10 LSV curves at various rotation speeds of (a) CNBs, (b) Pt/c, (c) Fe-CNBs-600, (d) N-CNBs-600, (e) Fe-N-CNBs-500 and (f) Fe-N-CNBs-700 in O_2-saturated 0.1 M KOH solution.

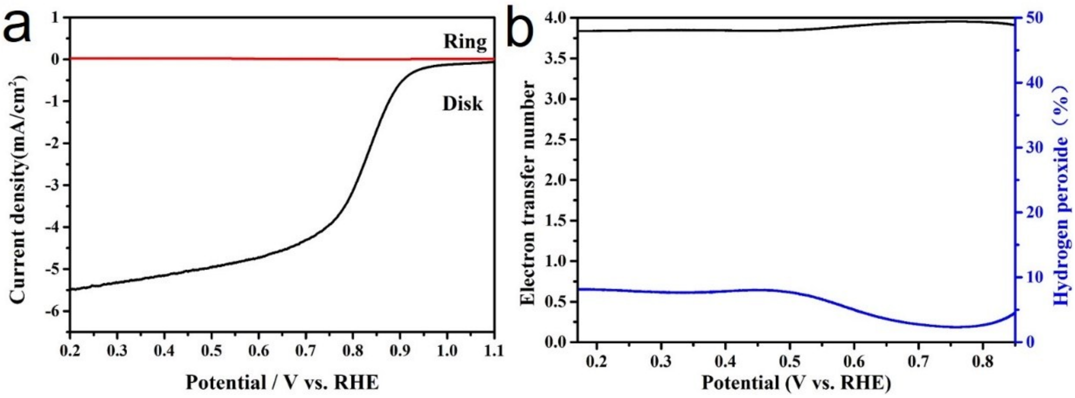

Fig. S11 (a) RRDE voltammograms, (b) plots of H_2O_2 yield and number of electron transfer of Fe-N-CNBs-600 at the rotation speed of 1600 rpm.

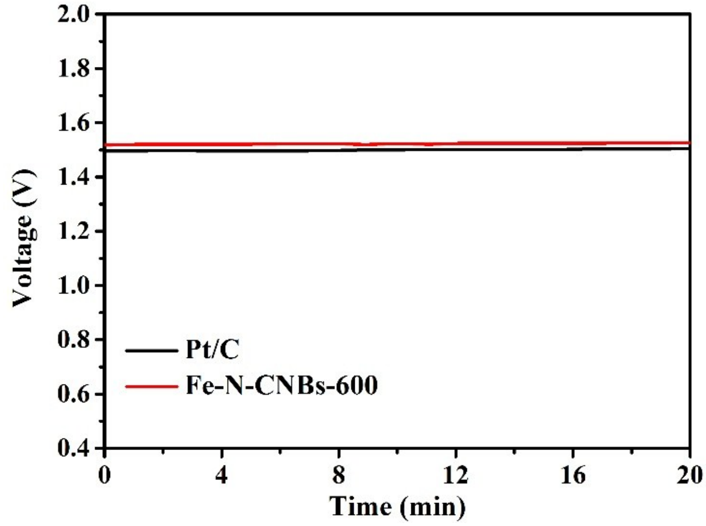

Fig. S12 The open circuit voltage measurements of ZAB with Fe-N-CNBs-600 and Pt/C as the cathode catalysts.

Table S1 Elemental composition of CNBs, N-CNBs-600, Fe-N-CNBs-500, Fe-N-CNBs-600 and Fe-N-CNBs-700 catalysts.

Sample	C [at%]	N [at%]	O [at%]	Fe [at%]
CNBs	96.10	/	3.90	/
N-CNBs-600	94.34	2.35	3.31	/
Fe-N- CNBs -500	90.02	5.50	4.14	0.34
Fe-N- CNBs -600	90.24	3.55	3.92	0.29
Fe-N- CNBs -700	92.10	4.35	3.40	0.14

Table S2 Textural properties of CNBs, N-CNBs-600, Fe-N-CNBs-500, Fe-N-CNBs-600 and Fe-N-CNBs-700 catalysts.

Sample	BET surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter (nm)
CNBs	216.38	0.43	8.03
N-CNBs-600	282.64	0.57	8.10
Fe-N- CNBs -500	231.88	0.46	7.97
Fe-N- CNBs -600	353.98	0.58	6.62
Fe-N- CNBs-700	295.95	0.58	7.85

Table S3 Comparison of ORR performance in 0.1 M KOH electrolyte of Fe-N-CNBs-600 and with literature values.

Sample	Catalyst loading (mg/cm^2)	Onset potential (V vs. RHE)	Half potential (V vs. RHE)	Reference
Fe-N-CNBs-600	0.429	1.03	0.875	This work
Fe_3C@NCNF-900	0.120	-0.035 (vs. Ag/AgCl)	-0.121 (vs. Ag/AgCl)	1
Fe_3C/NG-800	0.400	1.03	0.86	2
N-doped Fe/ Fe_3C@C/RGO	0.556	1.00	0.93	3
Fe-N/C-800	0.796	0.98	\	4
Fe-N/C-800	0.100	0.923	0.809	5
Fe-N-PGC-800	0.305	-0.017 (vs. Ag/AgCl)	-0.15 (vs. Ag/AgCl)	6
FP-Fe-TA-N-850	0.300	0.98	\	7
Fe-N-CNFs	0.600	0.93	0.81	8
NG-900-4	0.300	0.885	0.752	9

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