Electronic Supplementary Information

Hierarchically porous Fe/N-C hollow spheres derived from melamine/Fe-incorporated polydopamine for efficient oxygen reduction reaction electrocatalysis

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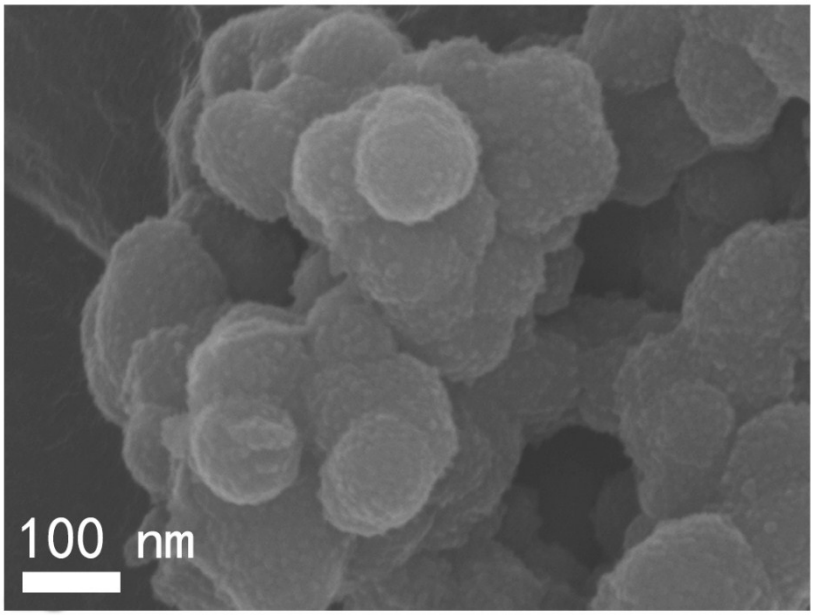

Fig. S1 SEM image of PDA-Fe-melamine precursor.

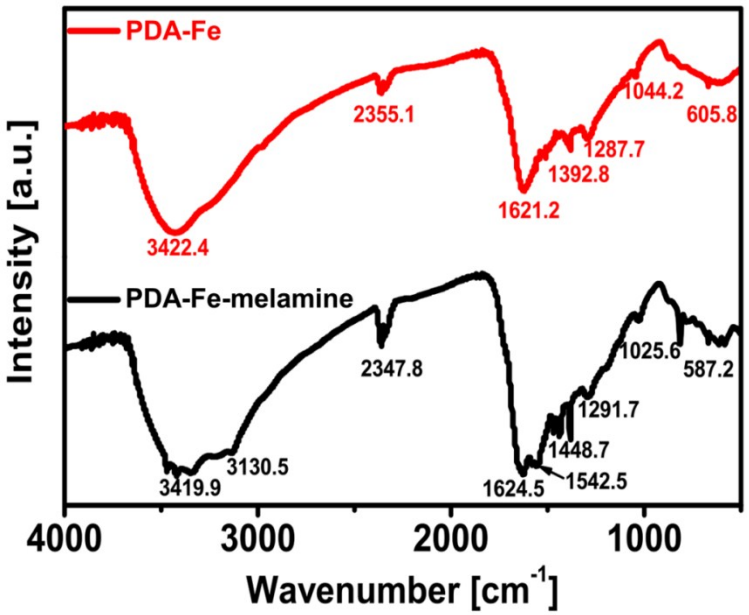

Fig. S2 FTIR spectra of PDA-Fe-melamine precursor and PDA-Fe precursor.

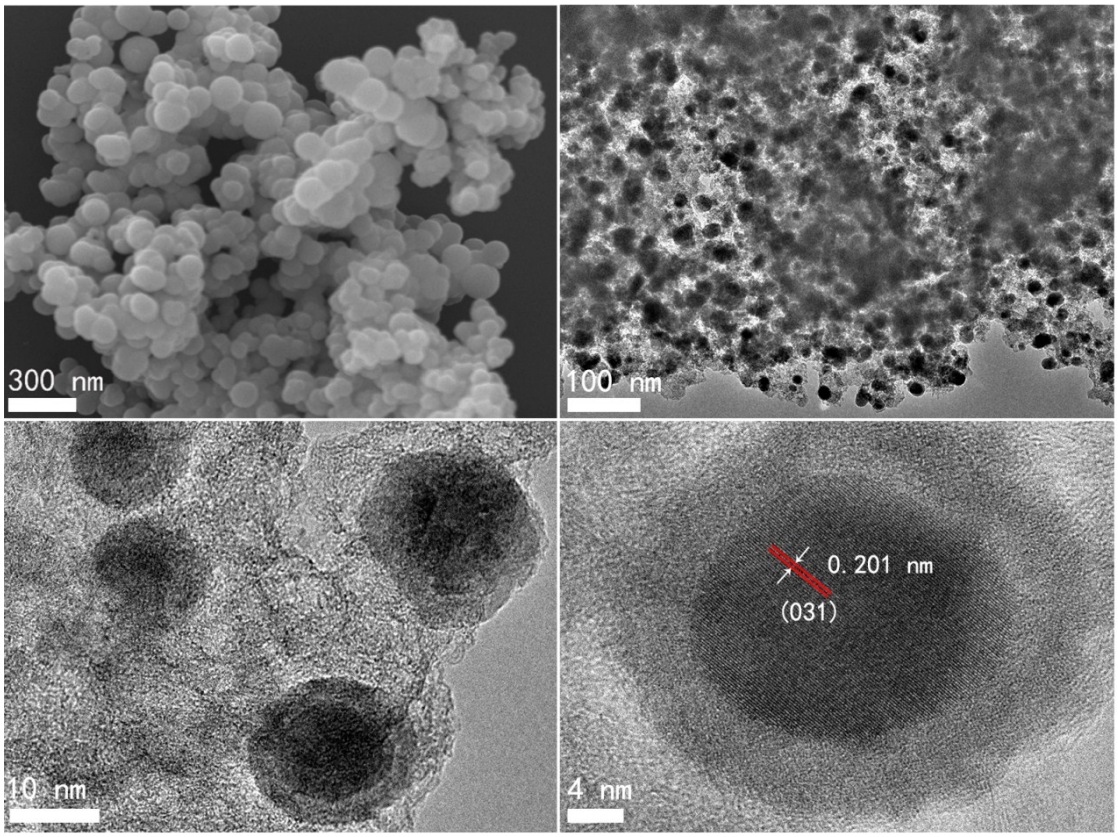

Fig. S3 FESEM and TEM images of Fe_3C@N-C catalyst synthesized by pyrolysis of PDA-Fe precursor.

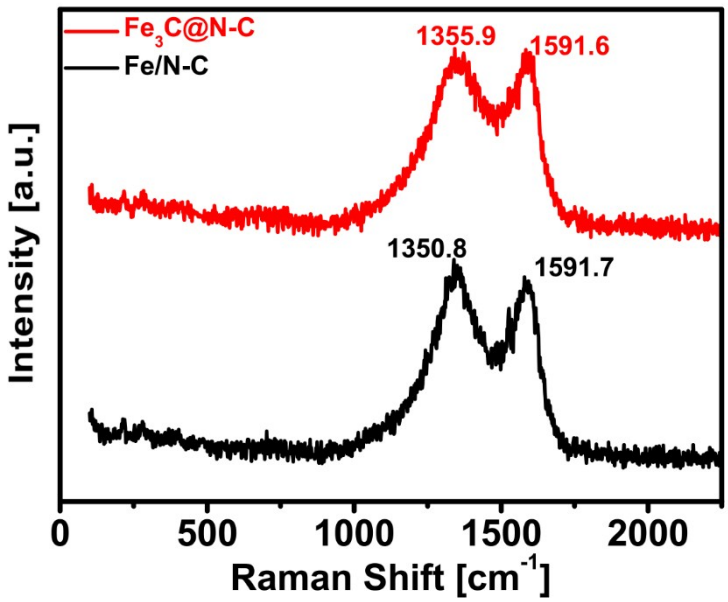

Fig. S4 Raman spectra of Fe/N-C and Fe_3C@N-C catalyst.

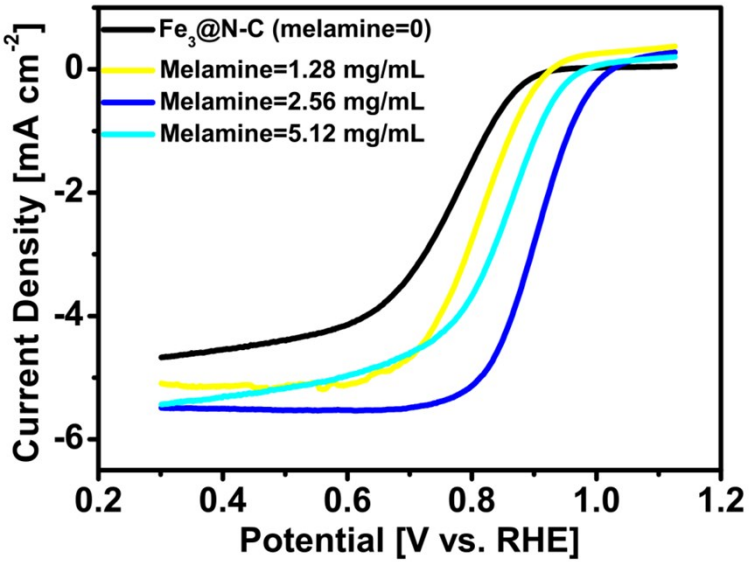

Fig. S5 Optimizing alkaline ORR activity of Fe/N-C catalysts by changing the dosage of melamine. LSV curves of a batch of Fe/N-C catalysts synthesized with different concentration of melamine at 0, 1.28, 2.56 and 5.12 mg mL^{-1}, respectively. (Other parameters remain constant including DA=1.28 mg mL^{-1}, Fe concentration=1 mM, pyrolysis at 800 °C. LSV curves measured in O_2-satruated 0.1 M KOH, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

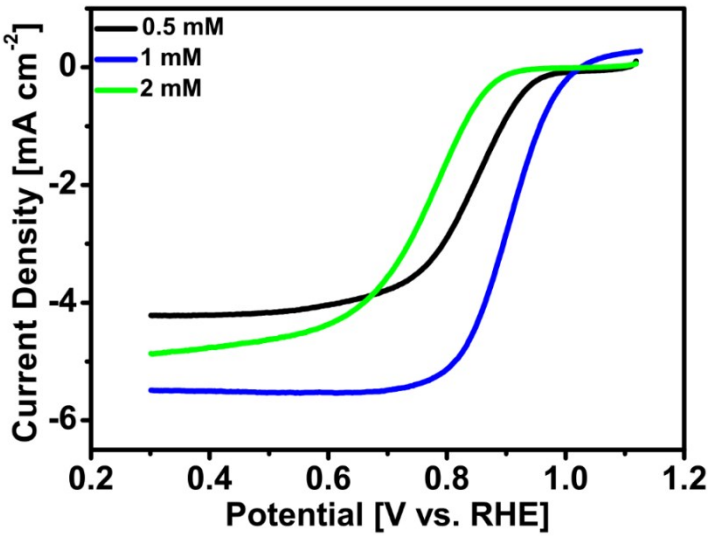

Fig. S6 Optimizing alkaline ORR activity of Fe/N-C catalysts by changing the dosage of Fe^{3+} concentration from 0.5 to 2.0 mM. (Other parameters remain constant including DA=1.28 mg mL^{-1}, melamine concentration=2.56 mg mL^{-1}, pyrolysis at 800 °C. LSV curves measured in O_2-satruated 0.1 M KOH, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

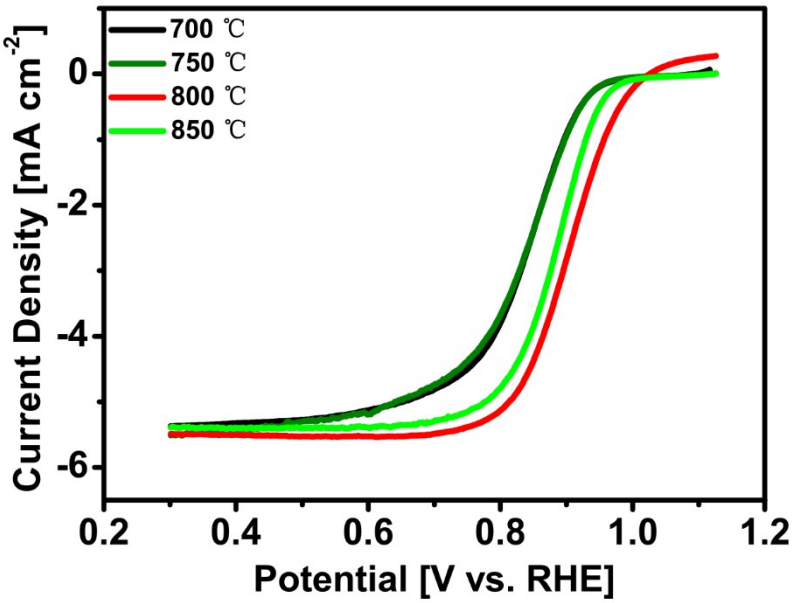

Fig. S7 Optimizing alkaline ORR activity of Fe/N-C catalysts by changing the pyrolysis temperature. (Other parameters remain constant including DA=1.28 mg mL^{-1}, melamine concentration=2.56 mg mL^{-1}, Fe^{3+} concentration 1.0 mM. LSV curves measured in O_2-satruated 0.1 M KOH, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

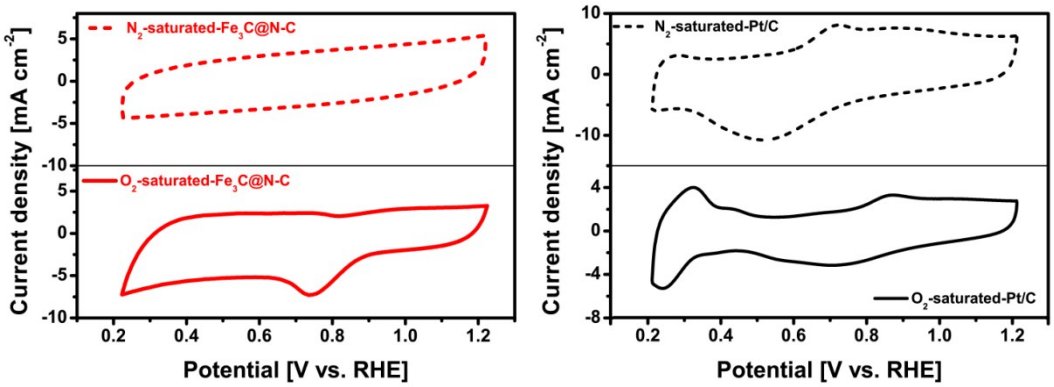

Fig. S8 CV curves of Fe_3C/N-C catalyst and Pt/C catalyst measured in O_2-satruated and N_2-satruated 0.1 M KOH, scan rate: 100 mV s^{-1}.

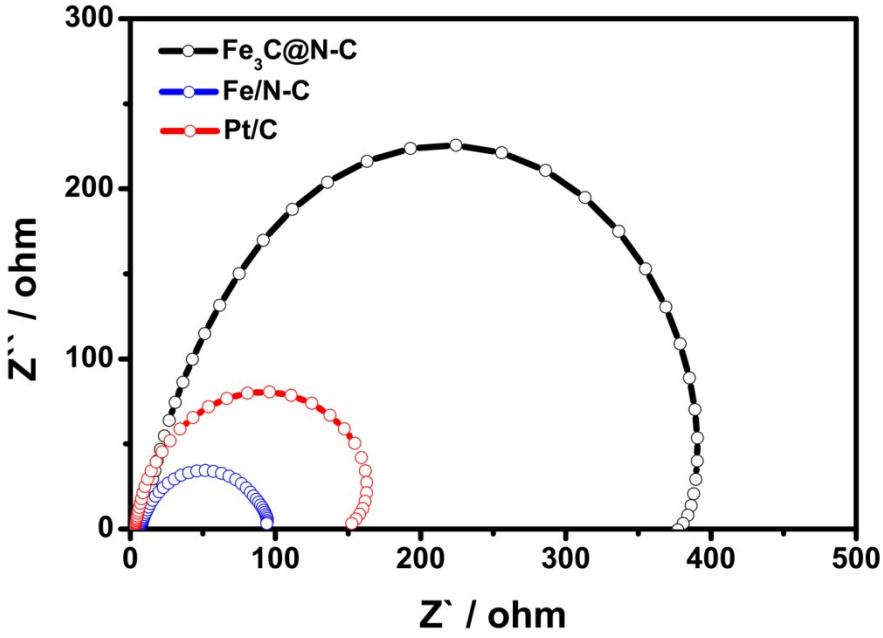

Fig. S9 EIS curves of Fe/N-C, Fe_3C/N-C and Pt/C catalysts measured in O_2-satruated 0.1 M KOH. (Applied potential: 0.95 V vs. RHE, amplitude of AC signal perturbation: 5 mV, frequency range: 100 kHz to 10 mHz.

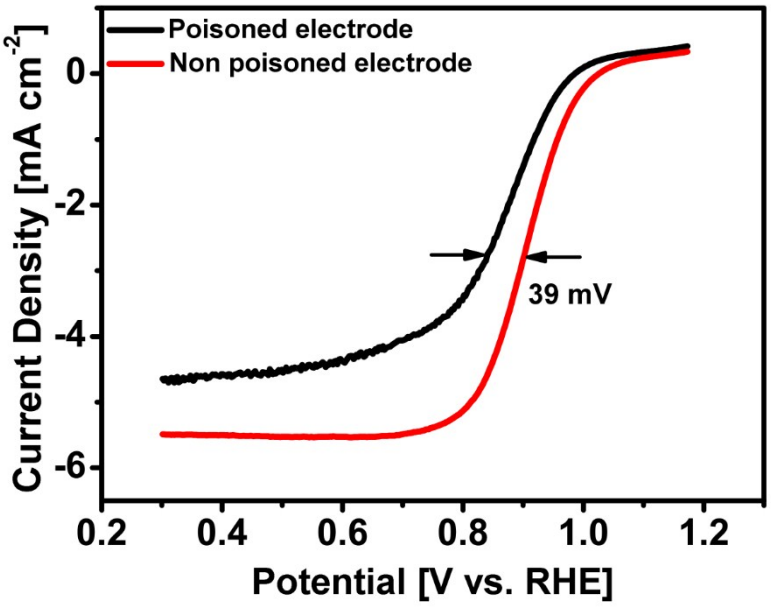

Fig. S10 Alkaline ORR activity of Fe/N-C catalysts before and after immersing in 10 mM KSCN for 1 h. (Electrolytes: O_2-satruated 0.1 M KOH, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

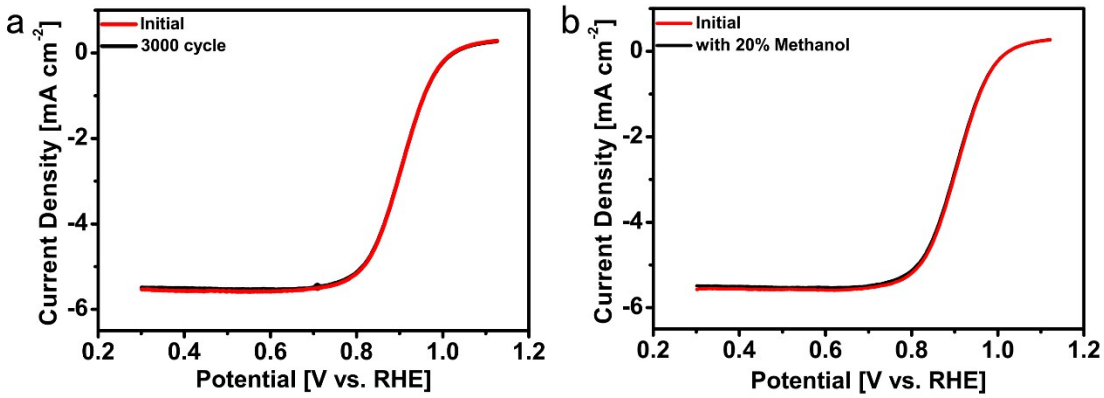

Fig. S11 (a) LSV curves of Fe/N-C before and after 3000-cycle ADT. (b) LSV curves with and without 20 % methanol (v/v). (Electrolytes: O_2-satruated 0.1 M KOH, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

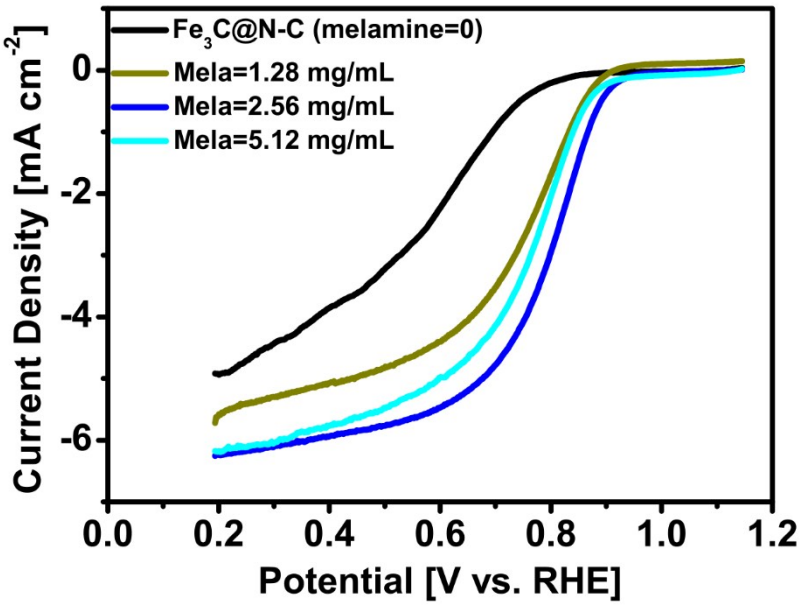

Fig. S12 Optimizing acidic ORR activity of Fe/N-C catalysts by changing the dosage of melamine. LSV curves of a batch of Fe/N-C catalysts synthesized with different concentration of melamine at 0, 1.28, 2.56 and 5.12 mg mL^{-1}, respectively. (Other parameters remain constant including DA=1.28 mg mL^{-1}, Fe concentration=1 mM, pyrolysis at 800 °C. LSV curves measured in O_2-satruated 0.1 M $HClO_4$, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

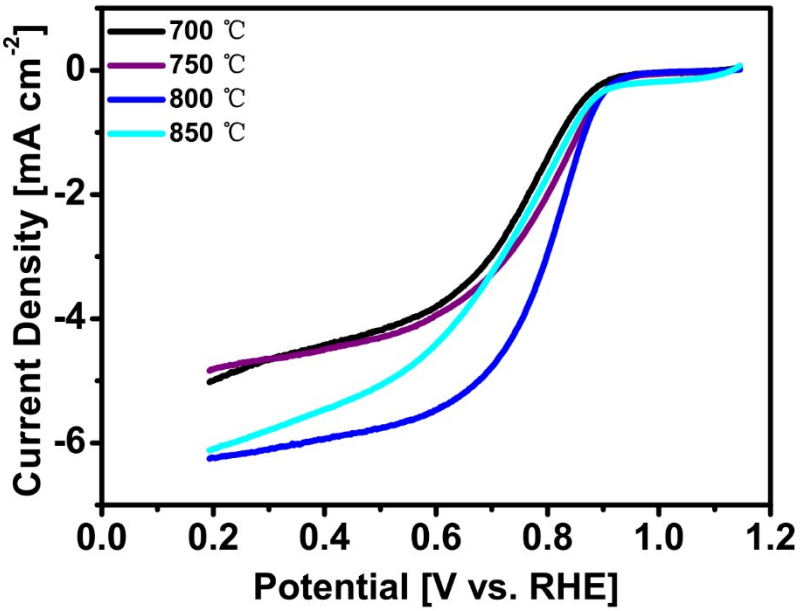

Fig. S13 Optimizing acidic ORR activity of Fe/N-C catalysts by changing the pyrolysis temperature. (Other parameters remain constant including DA=1.28 mg mL^{-1}, melamine concentration=2.56 mg mL^{-1}, Fe^{3+} concentration 1.0 mM. LSV curves measured in O_2-satruated 0.1 M $HClO_4$, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm). (Electrolytes: O_2-satruated 0.1 M $HClO_4$, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

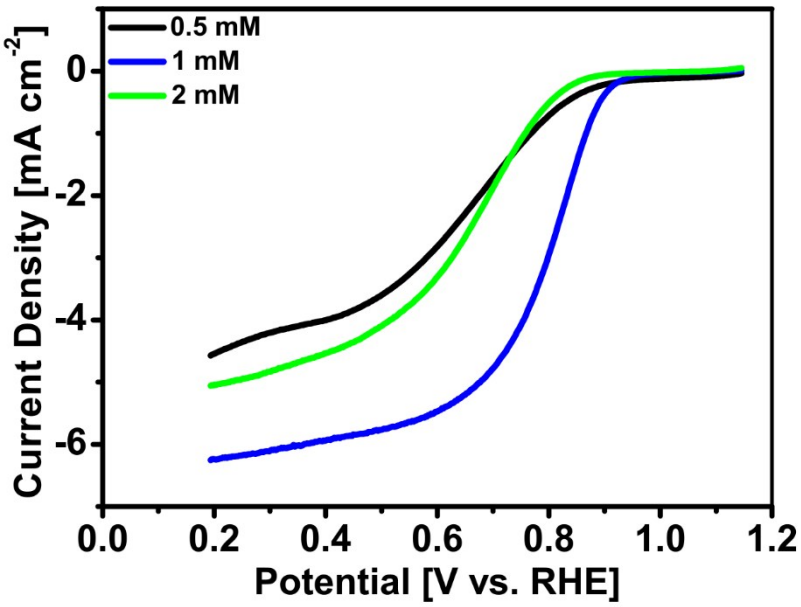

Fig. S14 Optimizing acid ORR activity of Fe/N-C catalysts by changing the dosage of Fe^{3+} concentration from 0.5 to 2.0 mM. (Other parameters remain constant including

DA=1.28 mg mL^{-1}, melamine concentration=2.56 mg mL^{-1}, pyrolysis at 800 °C. LSV curves measured in O_2-satruated 0.1 M $HClO_4$, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

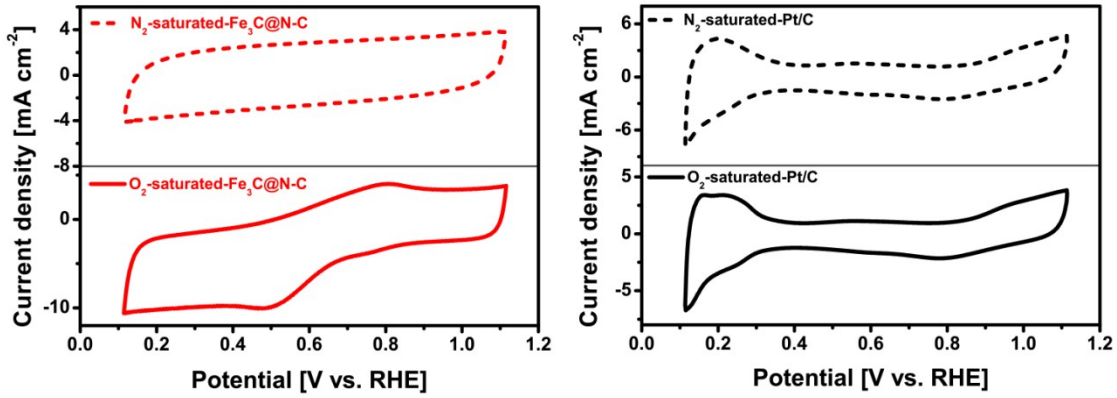

Fig. S15 CV curves of Fe_3C/N-C catalyst and Pt/C catalyst measured in O_2-satruated and N_2-satruated 0.1 M $HClO_4$, scan rate: 100 mV s^{-1}.

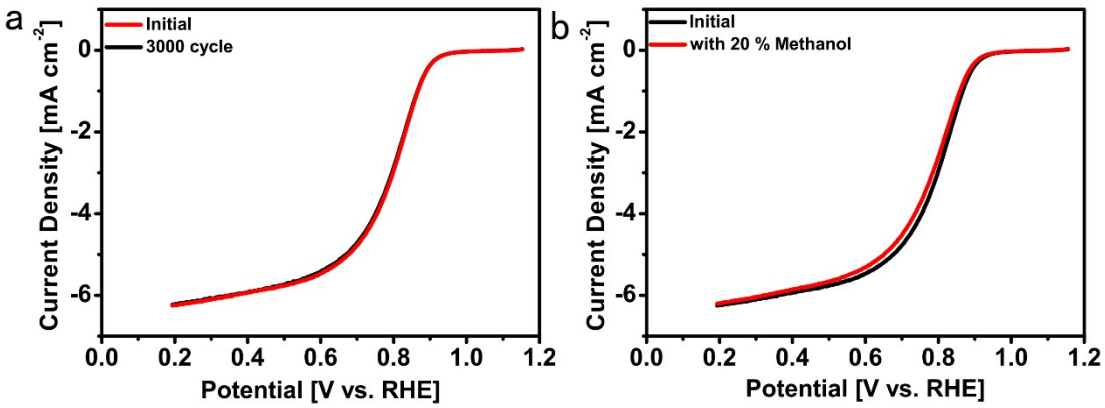

Fig. S16 (a) LSV curves of Fe/N-C catalyst before and after 3000-cycle ADT. (b) LSV curves with and without 20 % methanol (v/v). (Electrolytes: O_2-satruated 0.1 M $HClO_4$, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

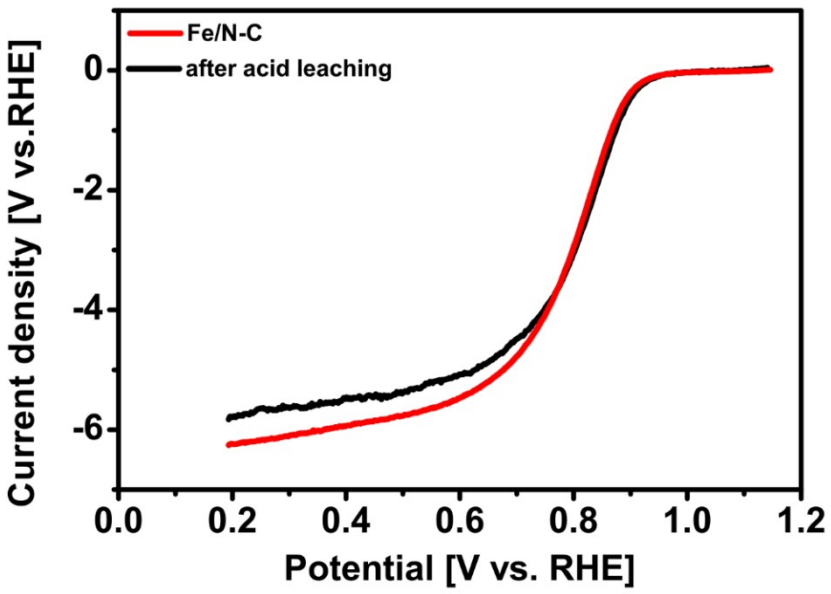

Fig. S17 (a) LSV curves of Fe/N-C catalyst before and after acid leaching and the second heat-treatment. (Electrolytes: O_2-satruated 0.1 M $HClO_4$, scan rate: 10 mV s^{-1}, rotation rate: 1600 rpm).

Table S1. ORR activity of Fe/N-C catalysts in alkaline media reported in recent literature.

Catalyst	Medium	$E_{1/2}$ (V vs. NHE)	$\Delta E_{1/2}$ (mV, relative to Pt/C)	n	Max H_2O_2 (%)	Ref.
Fe-N/C	0.1 M KOH	0.915	+45	3.81-3.99	5	This work
3D-Fe-N-CNS	0.1 M KOH	0.88	+20	3.83-3.95	-	[1]
Fe-ISAs/CN	0.1 M KOH	0.9	+58	3.9	5	[2]
Fe/SNC	0.1 M KOH	0.79	+40			[3]
Fe-N/C-800	0.1 M KOH	0.81	-	3.97	5	[4]
Fe SAC/N-C	0.1 M KOH	0.89	+40	4	2	[5]
SA-Fe-HPC	0.1 M KOH	0.89	+50	4	2.5	[6]
Fe-N-SCCF*	0.1 M KOH	0.883	-	3.9-4	5	[7]
Fe_{50}–N–C-900*	0.1 M KOH	0.92	+70	3.95	10	[8]
FeGH-ArNH3	0.1 M KOH	-	-27	3.95	5.6	[9]
Fe/N/C	0.1 M KOH	0.84	0	3.96	-	[10]
Fe SAs-N/C-20	0.1 M KOH	0.909	+59	3.8	-	[11]
Fe@Aza-PON	0.1 M KOH	-	+13	3.7	15	[12]
N-Fe-CNT/CNP	0.1M NaOH	0.93	+20	3.92	-	[13]
SA-Fe/NG	0.1 M KOH	0.88	+30	3.87-3.96	8.6	[14]
Fe@C-FeNCs	0.1 M KOH	0.899	+15	3.95-3.99	2.5	[15]
Fe−N/C−700*	0.1 M KOH	0.84	+5	4.02	3	[16]
Fe−N−CC	0.1 M KOH	0.83	+50	3.7	10	[17]
Fe_{SA}-N-C*	0.1 M KOH	0.891	+43	4	5.5	[18]
Fe-N-S*	0.1 M KOH	0.91	+60	4	2	[19]
Fe@NC-800*	0.1 M KOH	0.81	+40	3.98	3.55	[20]

Fe/Fe_3C@N-C*	0.1 M KOH	0.804	-16	4.08-4.15	3.5	[21]
Fe-N-C*	1 M NaOH	0.9	+20	3.9	-	[22]
Fe-N-C900*	0.1 M KOH	0.91	+32	3.988	2.5	[23]
CNT@f-FeNC170*	0.1 M KOH	0.84	0			[24]
SC-Fe*	0.1 M KOH	0.869	-	3.7	-	[25]
C-FeHZ8@g-C3N4-950*	0.1 M KOH	-	+30	3.96	-	[26]
Fe@N-CNTs@rGO *	0.1 M KOH	0.83	0	4.1	7	[27]

Table S2. ORR activity of Fe/N-C catalysts in acidic media reported in recent literature.

Catalyst	**Medium**	**$E_{1/2}$ (V vs. NHE)**	**$\Delta E_{1/2}$ (mV, relative to Pt/C)**	**n**	**Max H_2O_2 (%)**	**Ref.**
Fe-N/C	0.1 M $HClO_4$	0.810	-55	>3.95	2	This work
C-Fe-Z8-Ar*	0.1 M $HClO_4$	0.82	-40	3.98	1	[28]
FeCo-NC	0.1 M $HClO_4$	0.74	-	3.9	-	[29]
Fe-ISAs/CN	0.1 M $HClO_4$	-	-90	-	-	[2]
Fe/SNC	0.5 M H_2SO_4	0.77	-50	3.9	6	[3]
SA-Fe-HPC	0.1 M $HClO_4$	0.81	-30	3.9	-	[6]
Fe−g-C3N4@C	0.1 M $HClO_4$	0.75	-	3.95	2.6	[30]
Fe-NMCS	0.1 M $HClO_4$	-	-59	3.92-3.94	6	[31]
Fe/N/S-PCNTs	0.5 M H_2SO_4	0.62	-14	3.84	-	[32]
PmPDAFeNx/C	0.1 M H_2SO_4	0.82	-65	-	1.5	[33]
(CM+PANI)-Fe-C	0.5 M H_2SO_4	0.8	-	3.95	2.5	[11]
Fe/N/C-SCN	0.1 M H_2SO_4	0.836	-48	-	1.5	[34]
Fe–N–C/VA-CNT	0.5 M H_2SO_4	0.79	-	3.92-3.98	1-5	[35]

SA-Fe/NG	0.1 M $HClO_4$	0.8	-30	3.95	5	[14]
Fe−N/C−700*	0.1 M $HClO_4$	-	-18	3.98	5	[16]
Fe−N−CC*	0.5 M H_2SO_4	0.56	-80	3.8	8	[17]
Fe_{SA}-N-C*	0.1 M $HClO_4$	0.776	-5	4	1	[18]
Fe-N-S*	0.5 M H_2SO_4	0.78	-15	4	1	[19]
Fe@NC-800*	0.5 M H_2SO_4	0.58	-140	3.74	-	[20]
Fe-N-C900	0.5 M H_2SO_4	0.80	-	3.955	2	[23]
CNT-Fe/NHCNS	0.1 M $HClO_4$	0.84	+20	3.93-3.98	2	[36]
C-FeHZ8@g-C3N4-950*	0.1 M $HClO_4$	-	-60	3.7	-	[26]

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