

Electronic Supplementary Material

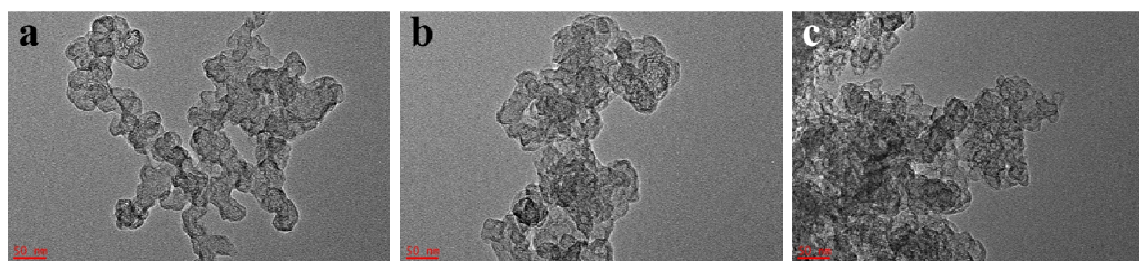


Fig. S1 TEM images of (a) Fe-N-C-0, (b) Fe-N-C-5, and (c) Fe-N-C-15. Scale bar: 50 nm.

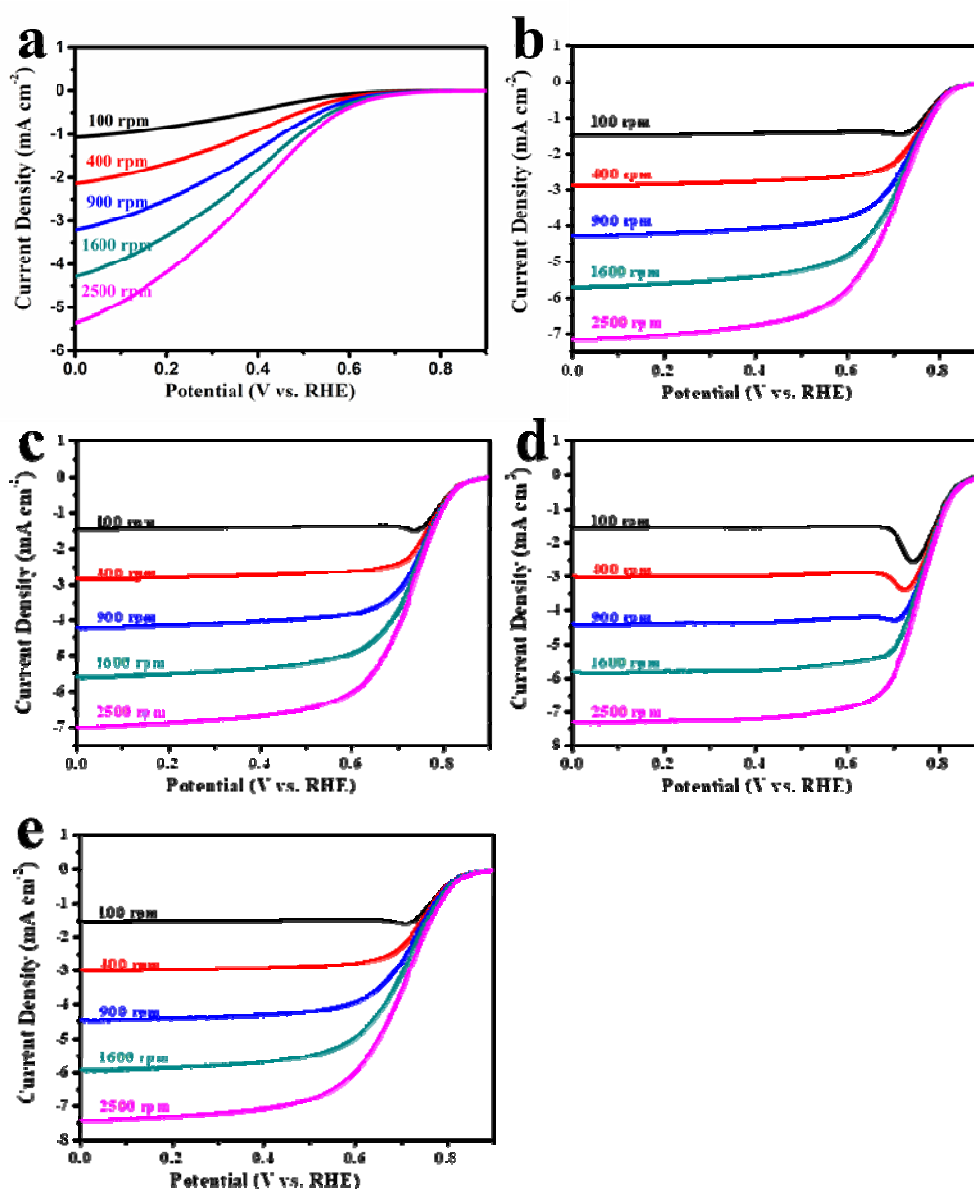


Fig. S2ORR polarization curves in O_2 -saturated 0.1 M HClO_4 solution with a scan rate of 5 mV s^{-1} at different rotation rate of (a) Fe-N-C-0, (b) Fe-N-C-5, (c) Fe-N-C-15, (d) Fe-N-C-20 and (e) Fe-N-C-30.

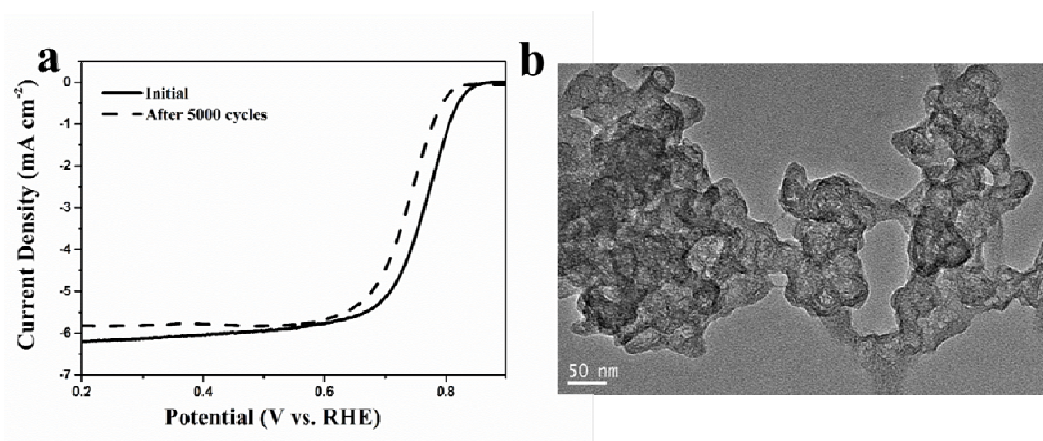


Fig. S3(a) LSV curves of the Fe-N-C-20 electrocatalyst in O_2 -saturated 0.1 M $HClO_4$ solution with a scan rate of 5 mV s^{-1} at 1600 rpm before and after 5000 cycles. (b) TEM image of Fe-N-C-20 after 5000 cycles.

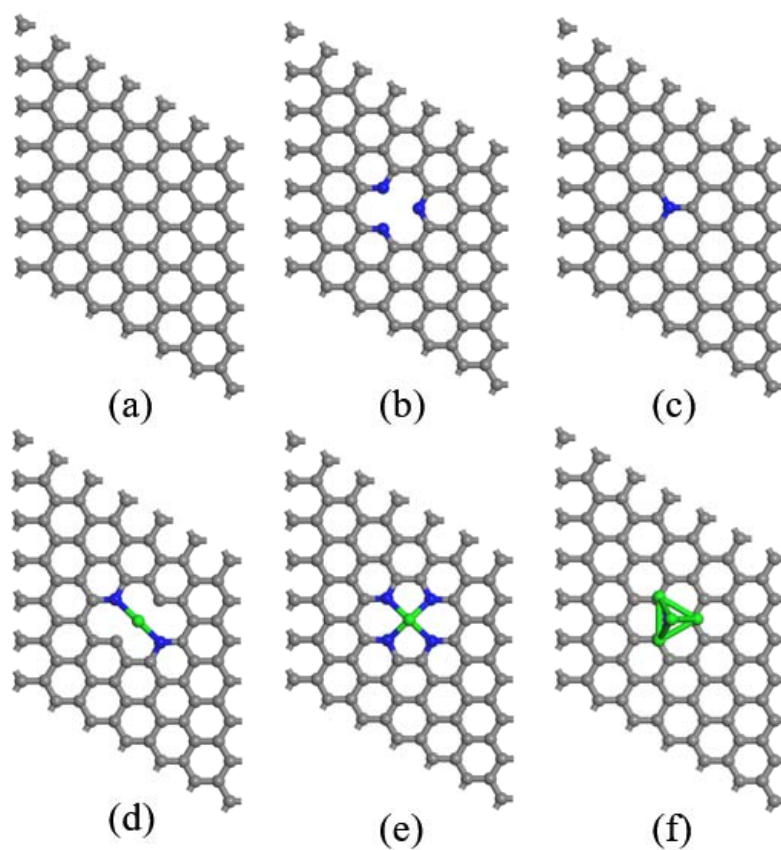


Fig. S4 Calculation model: (a) monolayer graphite (b) pyridinic N-doped graphite (c) quaternary N-doped graphite (d) $Fe-N_2-C$ (e) $Fe-N_4-C$ (f) metallic Fe_4-N-C . Atoms in different color: Gray-C, Blue-N, Green-Fe.

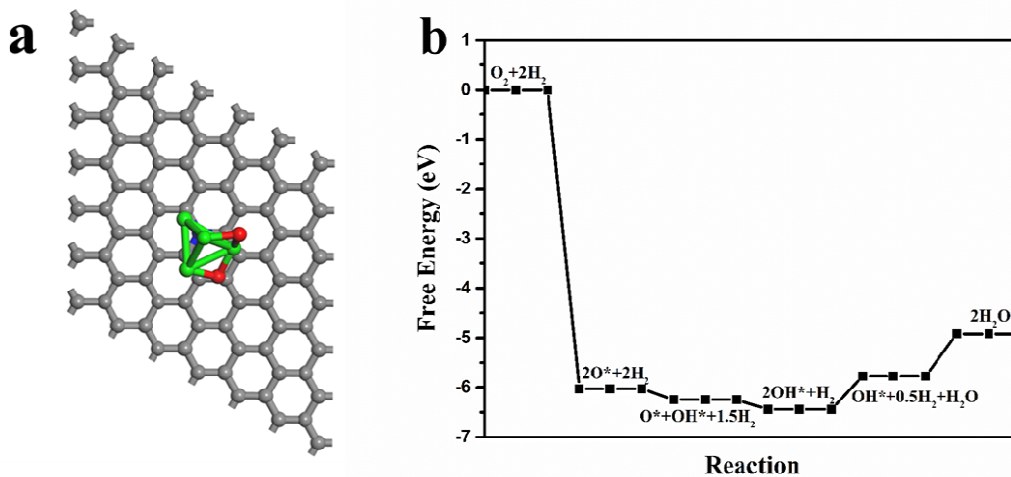


Fig. S5(a) The model of oxygen adsorbed on metallic Fe₄-N-C. (b) Free energy change diagram during ORR on metallic Fe₄-N-C.

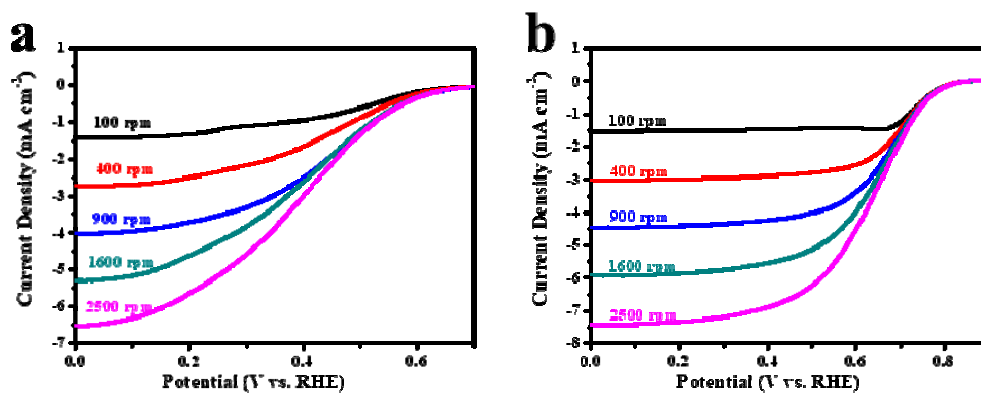


Fig. S6 ORR polarization curves in O₂-saturated 0.1 M HClO₄ solution with a scan rate of 5 mV s⁻¹ at different rotation rate of (a) Fe-N-C-5-II-0, (b) Fe-N-C-5-II-10.

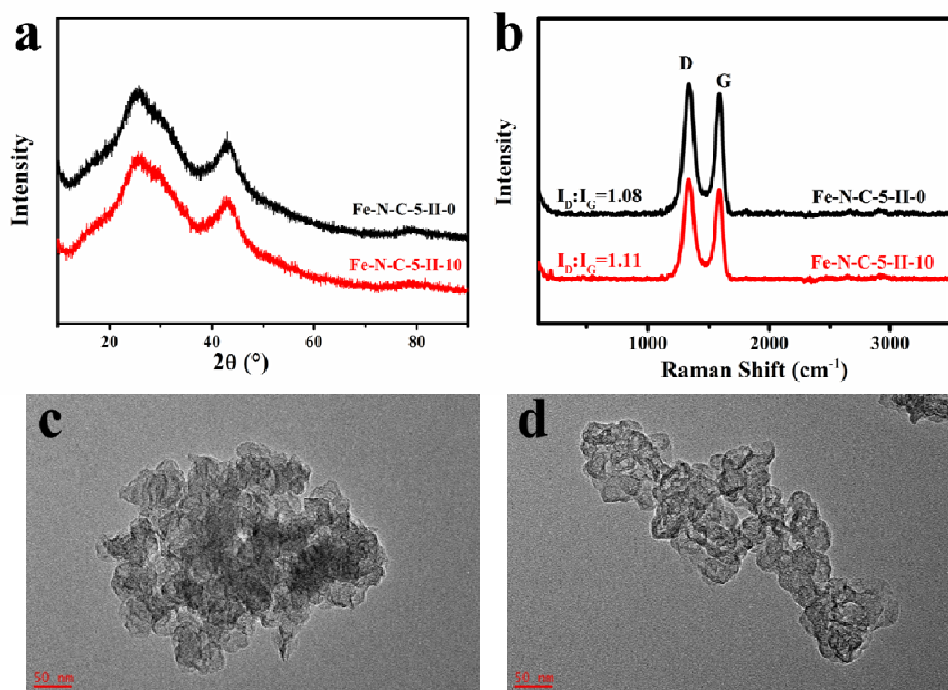


Fig. S7 (a) XRD patterns (b) Raman spectra of Fe-N-C-5-II-Y catalysts with second heat treatment and different Fe addition (c) TEM image of Fe-N-C-5-II-0 and (d) TEM image of Fe-N-C-5-II-10.

Table S1 Content of Fe, N as well as different nitrogen species in as-prepared Fe-N-C-X catalysts

Sample	Fe-N-C-0	Fe-N-C-5	Fe-N-C-15	Fe-N-C-20	Fe-N-C-30
Fe content (wt.%)	0.247	0.677	0.865	1.598	1.925
N content (at.%)	1.76	1.51	1.16	1.04	0.93
Pyridinic N(at.%)	0.36	0.19	0.07	0.05	0.10
Fe-N _x (at.%)	0	0.19	0.20	0.23	0.19
Pyrrolic N (at.%)	0.20	0	0.24	0.08	0.15
Quaternary N (at.%)	0.67	0.79	0.36	0.52	0.29
Oxidized N (at.%)	0.53	0.34	0.29	0.16	0.20

Table S2 Fitting parameters of Fe K-edge EXAFS spectra of Fe foil and Fe-N-C-20

Sample	Scattering path	R (Å)	CN	$\sigma^2(\text{Å}^2)$	E_0/eV	R factor
Fe foil	Fe-Fe ₁	2.472±0.002	7.3±0.2	0.0063	6.2	0.004
	Fe-Fe ₂	2.834±0.003	8.2±0.5	0.0103	5.1	
Fe-N-C-20	Fe-N	1.969±0.004	4.2±0.1	0.0145	10.4	0.003

Notes: . CN: Coordination number; σ^2 : mean-square disorder; E_0 : energy shift