Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

A Facile Synthesis of Fe/N-doped Ultrathin Carbon Sheet for Highly Efficient Oxygen Reduction Reaction

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1. Supplementary Figures

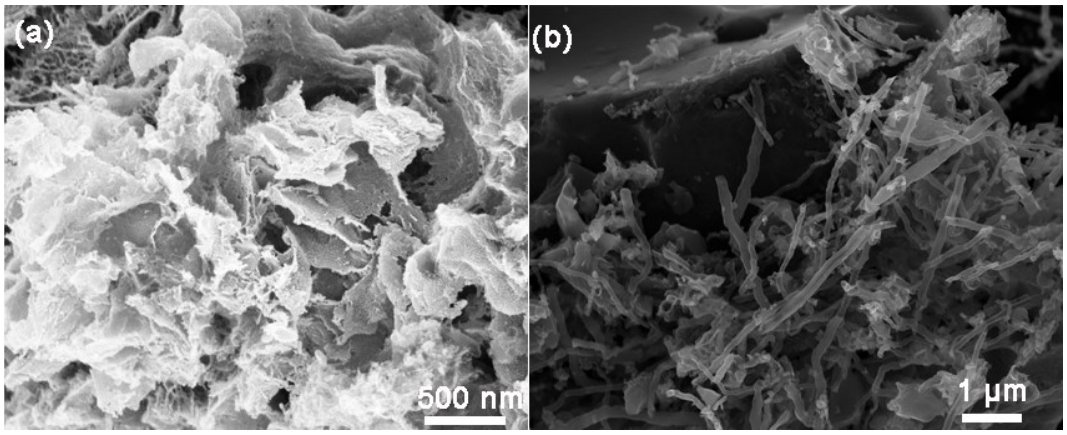

Figure S1. SEM images of the catalysts Fe_3C/NC-800 and FeNC-800-M.

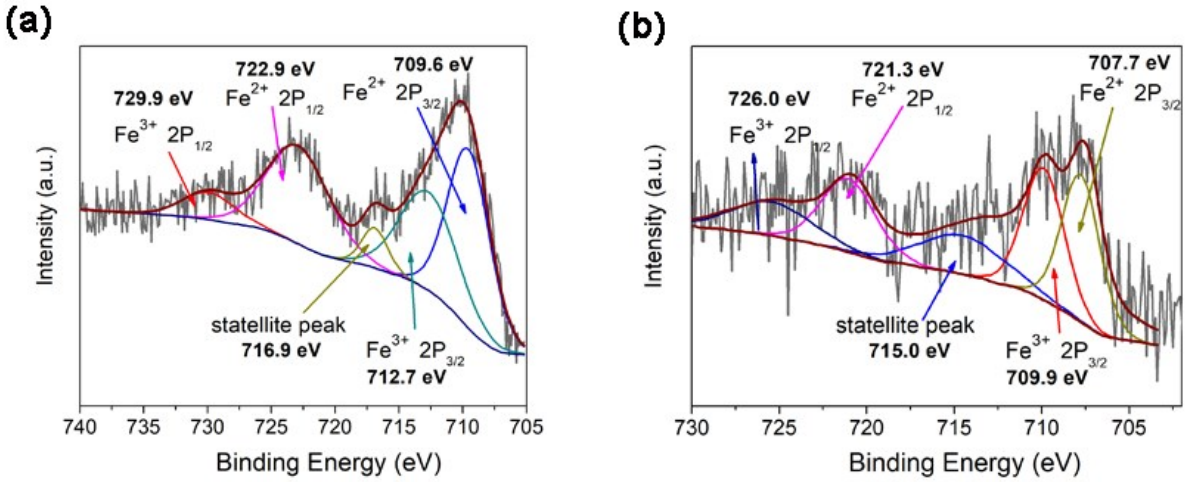

Figure S2. High resolution of Fe 2p of (a) Fe_3C/NC-800 and (b) FeNC-800-M.

(Fe_3C/NC-800 exhibited a much larger binding energy than that of FeNC-800-M, and Fe (II) and Fe (III) type with different binding energy can be distinguished. The peak of Fe^{3+} $2p_{3/2}$ was considered to be Fe connected to N, the resulting FeN_4 structure is generally recognized as the active sites, especially in alkaline solution.)

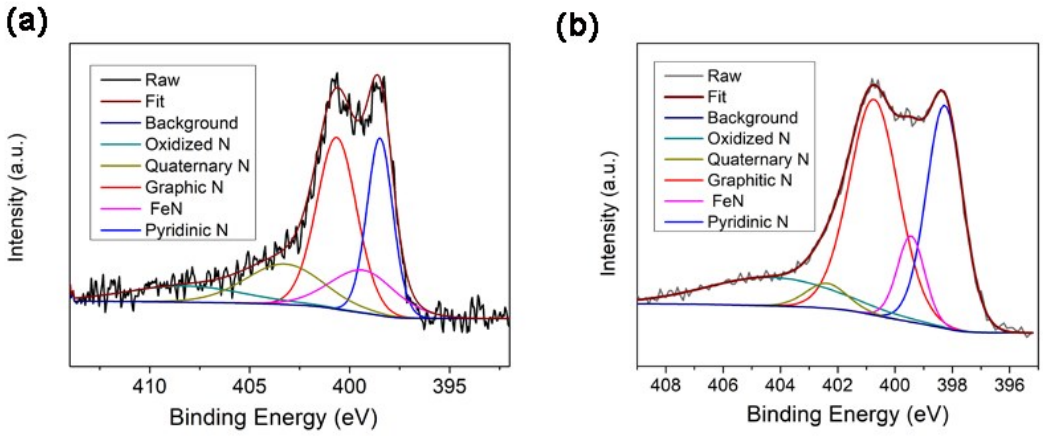

Figure S3. High resolution of N 1s of (a) Fe_3C/NC-800 and (b) FeNC-800-M.

(The binding energy could be divided into five types: graphitic N, pyridinic N, oxidized N, quatemary N and FeN. In ORR catalytic process, pyridinic N and FeNx was thought to be the major contributor to enhance the electrochemical performance.)

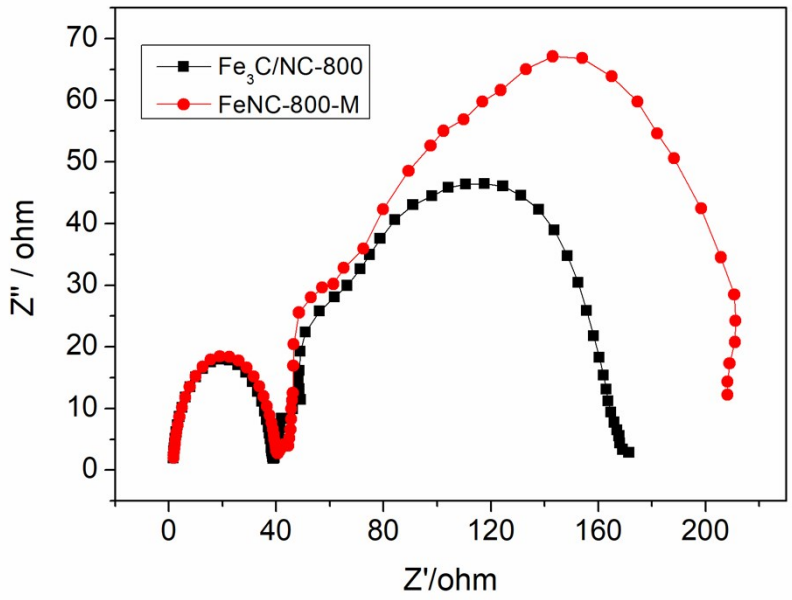

Figure S4. Electrochemical impedance spectroscopy data for FeNC-800-M (red line) and Fe_3C/NC-800 (black line).

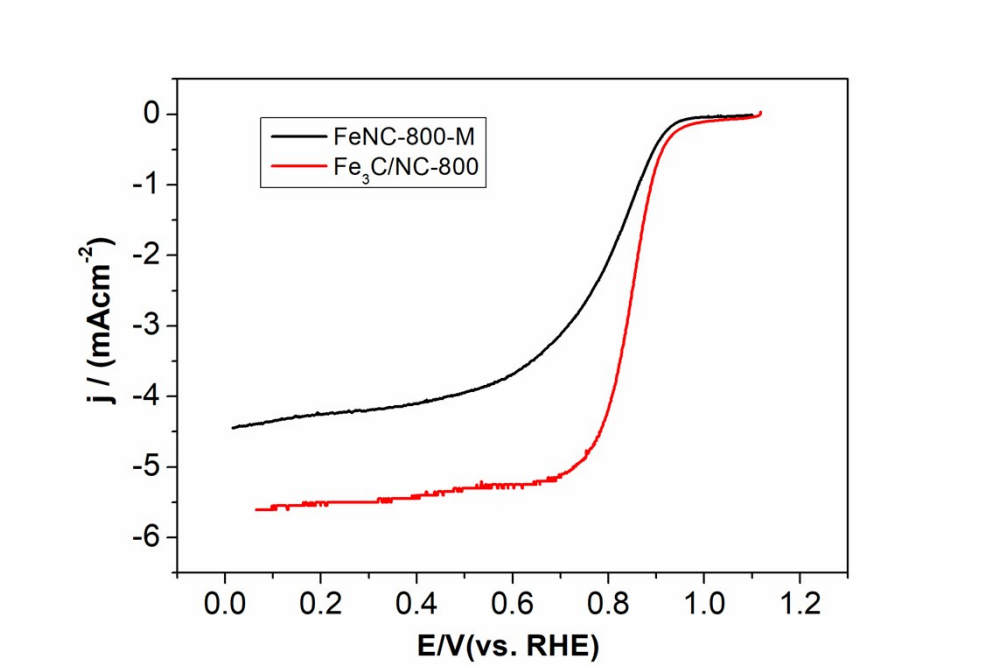

Figure S5. Steady-state polarization curves of ORR for Fe_3C/NC-800 (red line) and FeNC-800-M (black line) in 0.1M KOH solution.

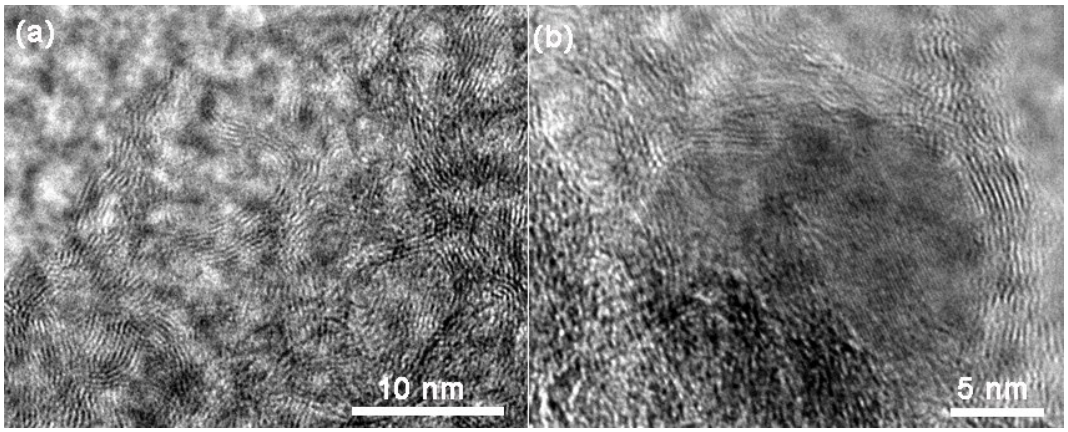

Figure S6. HRTEM images of the catalysts Fe_3C/NC-800.

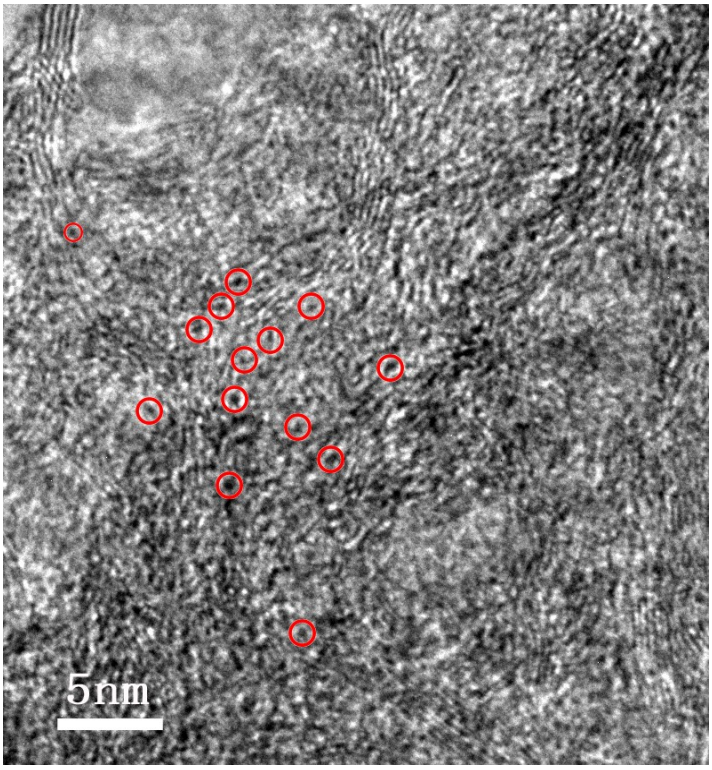

Figure S7. High resolution TEM image of Fe_3C/NC-800.

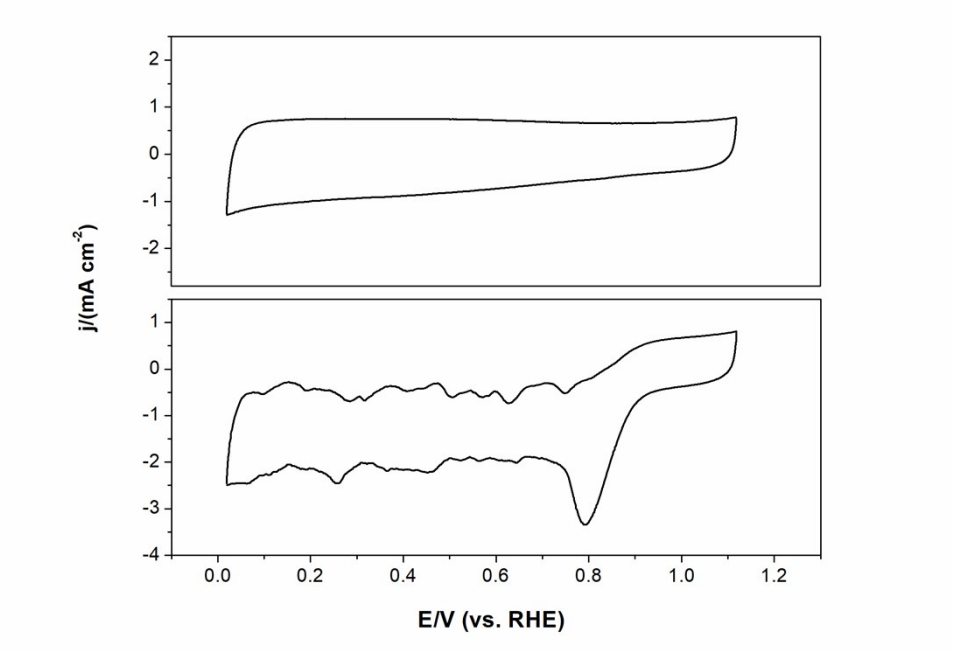

Figure S8. Cyclic voltammograms for Fe_3C/NC-800 obtained in 0.1 M KOH with Ar (up) and O_2 (down) saturated. The scan was performed negatively.

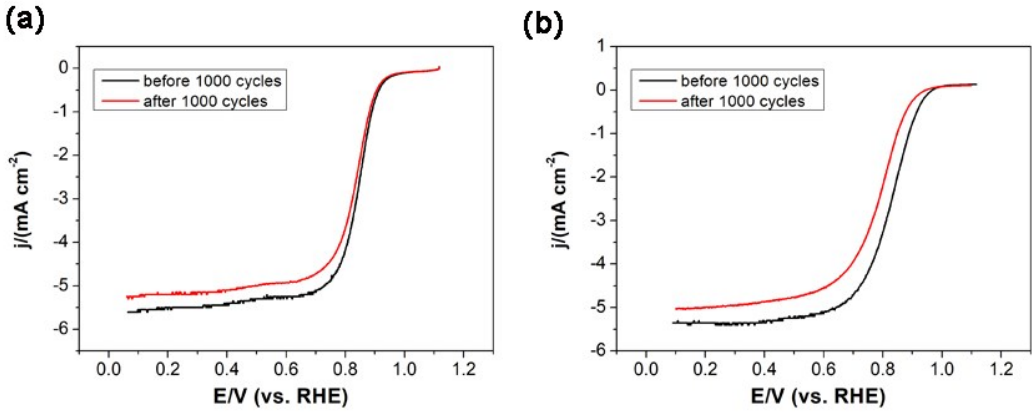

Figure S9. The activities after 1000 cycles of Fe_3C/NC-800 and Pt/C in an O_2-saturated 0.1 M KOH solution.

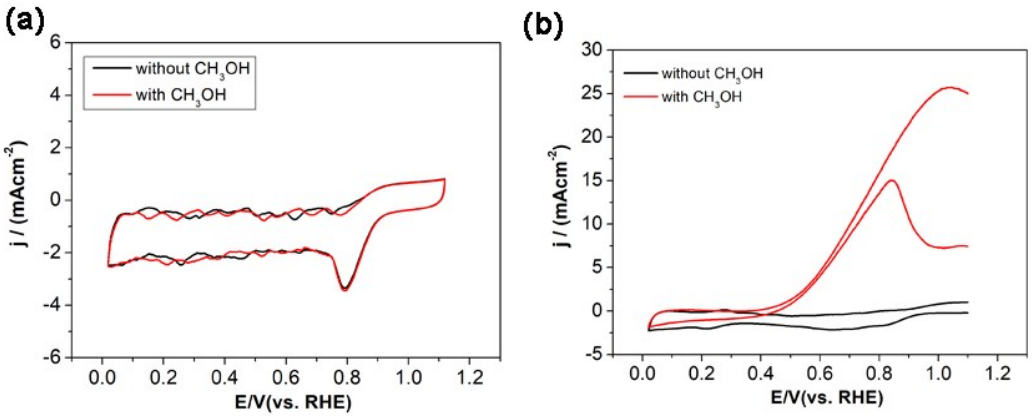

Figure S10. Cyclic voltammograms of (a) Fe_3C/NC-800 and (b) Pt/C in an O_2-saturated 0.1 M KOH solution containing 1M methanol. The scan was performed negatively.

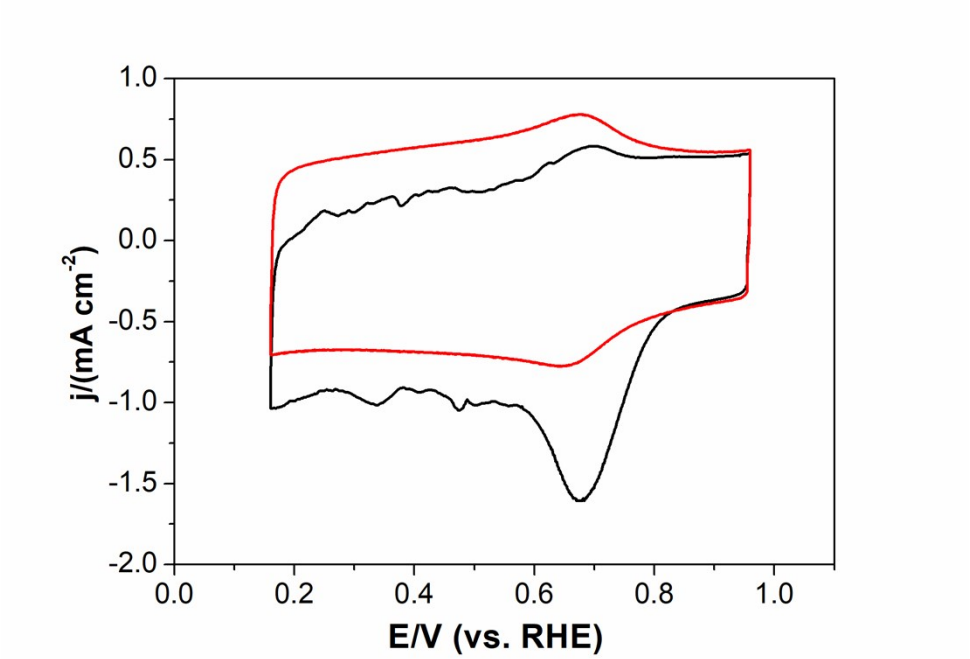

Figure S11. Cyclic voltammograms for Fe_3C/NC-800 obtained in 0.1 M $HClO_4$ at a scanning rate of 50 mV/s with O_2 saturated (black line) and Ar saturated (red line). The scan was performed negatively.

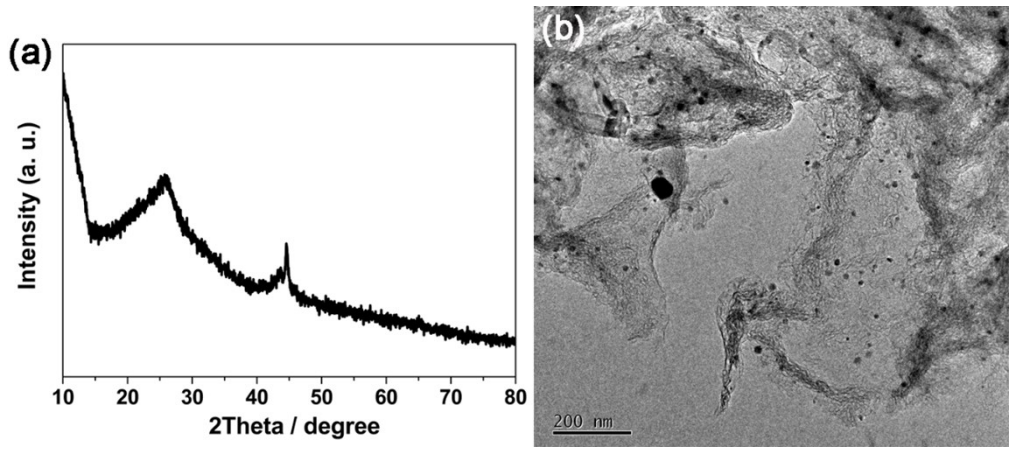

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Figure S12. Fe_3C/NC-800 catalyst after *i*–t test: (a) XRD pattern; (b) TEM image.

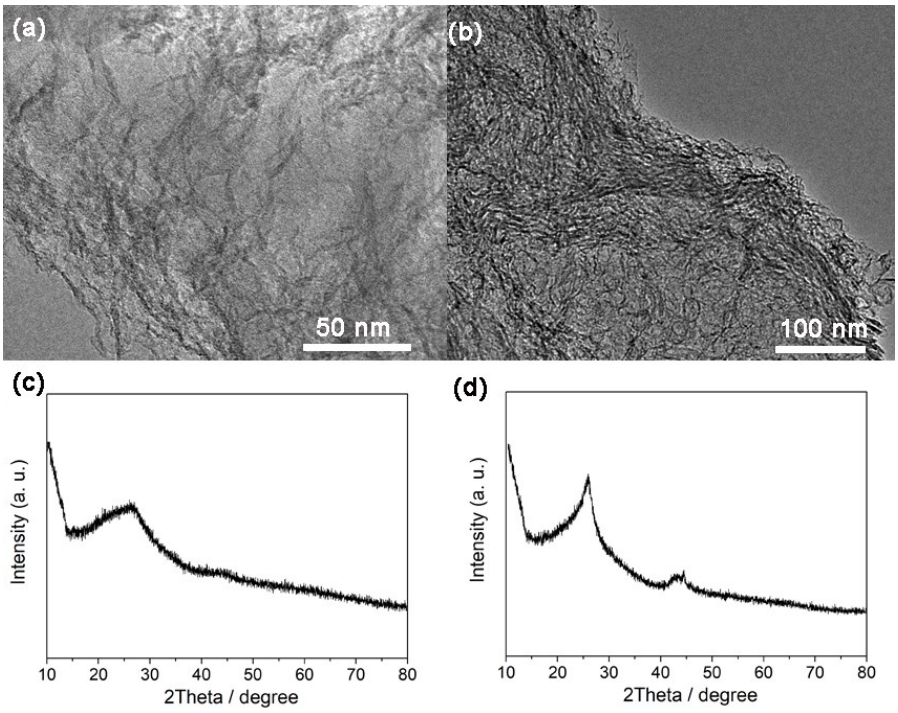

Figure S13. TEM images and XRD patterns of the FeNC-700 (a, c) and FeNC-900 (b, d).

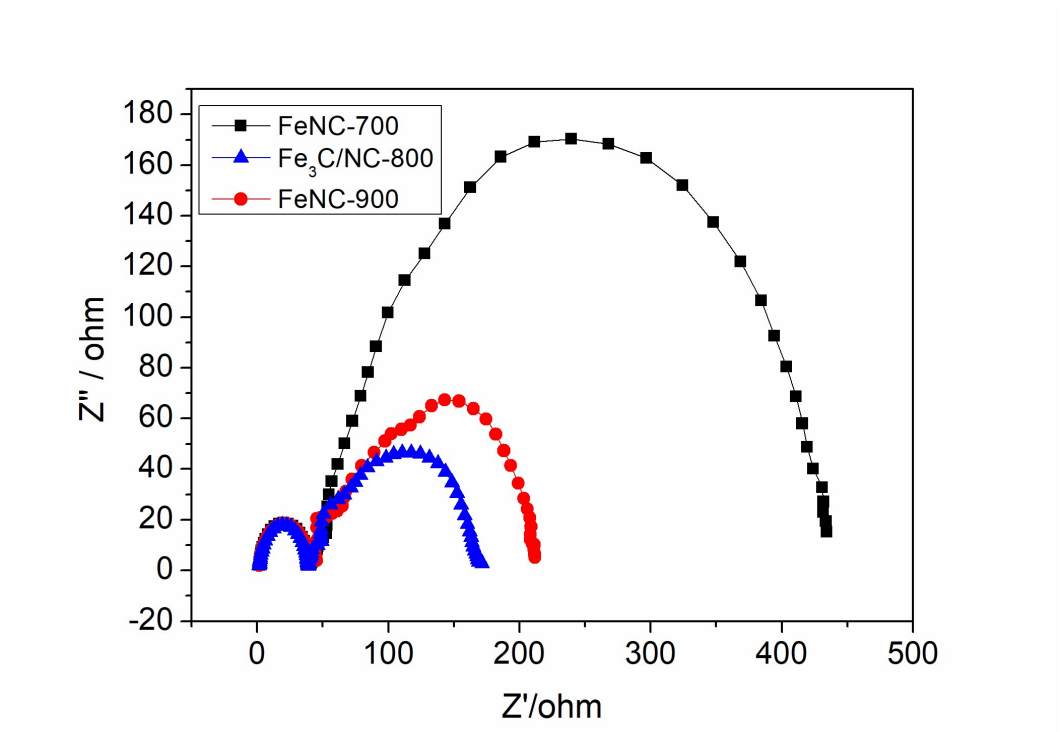

Figure S14. Electrochemical impedance spectroscopy data for samples obtained at 700, 800 and 900℃, respectively.

2. Supplementary Tables

Table S1. Percentage of different kinds of N in Fe_3C/NC-800 and FeNC-800-M.

Sample	N content	graphitic N	pyridinic N	FeN	oxidized N	pyrrolic N
Fe_3C/NC-800	7.8%	36.5%	33.8%	14.5%	5.9%	9.3%
FeNC-800-M	4.5%	41.0%	31.4%	9.1	14.5%	13.1%

Table S2. Comparison of ORR catalytic performances in alkaline solution between Fe_3C/NC-800 and other non-precious metal-based catalysts reported previously.

Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Mass loading ($\mu g\ cm^{-2}$)	Ref.
Fe_3C/NC-800	1.0	0.85	150	This work
NCNT/CoO-NiO-NiCo	1.0	0.83	210	1
D-AC@2Mn–4Co	0.88	0.80	160	2
GNPCSs-800	0.957	0.82	200	3
Fe−N/C−800	0.92	0.81	100	4
NCNT/Ni–NiMn2O4		0.71	210	5
Co@Co_3O_4@ C-CM	0.93	0.81	350	6
Fe_1/N, S-PC	1.0	0.90	510	7
NC-900	0.83	0.68	100	8
Fe-N-C/rGO	0.94	0.81	3939	9
FePhen@MOF-ArNH_3	1.03	0.86	3000	10
S–Fe/N/C	0.91	0.80	160	11
Fe-NCB-900	–	0.8	4000	12

Fe@C–NG/NCNTs	0.93	0.84	240	13
N-Fe/G(100)-900	0.89	0.81	50	14
Fe_3C/C-800	1.05	0.83	600	15
Fe-N_2-800	−0.077 V (vs. SCE)	−0.25 V (vs. SCE),	313	16
Fe_3O_4/FeNSG-3	0.95	0.81	200	17
Co@CoO@NC/C	0.92	0.81	420	18
CNPs	1.03	0.85	385	19
Fe-BC-800	0.94	0.80	420	20

Table S3. Comparison of ORR catalytic performances in acid media between Fe_3C/NC-800 and other non-precious metal-based catalysts reported previously.

Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Mass loading (μg cm^{-2})	Ref.
FeNC-800	0.88	0.7	150	This work
Fe_3C/C-700	0.9	0.73	600	15
Fe-N-HCMS	0.81	0.6	1199	21
Fe_3O_4/FeNSG-3	0.75	/	200	17
CPANIFe-NaCl	0.91	0.74	600	22
PANI-Fe	0.85	/	600	23
Fe-N/C-800	0.8	0.68	100	24
pPMF-800	0.89	0.71	1200	25
Fe_3C/NG-800	0.92	0.77	400	26

NH_3-$Fe_{0.25}$-N/C-900	0.94	0.68	125	27
FeNC-700	0.8	/	100	28
NH_3-$Fe_{0.25}$-N/C-900	0.94	0.71	400	27
H–Fe@N–C/RGO	0.89	0.67	315	29
N–Fe/G (60)-900-S	0.83	0.72	500	14
FeCo-PANI-TPP-NH_3	0.85	0.73	2550	30
Fe−g-C_3N_4@C		0.75	600	31
PpPD-Fe-C	0.83	0.72	200	32
Fe-N-GC-900	/	0.74	600	33
N, P-CGHNs	0.9	0.68	600	34
Fe-N/MPC2	0.82	0.7	637	35
$(Fe_{1-x}S/N, S\text{-}MCNS)_{0.2}$	0.81	0.73	400	36
N/Fe-CG	0.93	0.73	170	37
Fe-N/C	0.8	0.55	270	38

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