Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Unexpected catalytic performance of Fe-M-C (M=N, P and S) electrocatalysts towards oxygen reduction reaction: surface heteroatoms boost the activity of Fe_2M/graphene nanocomposites

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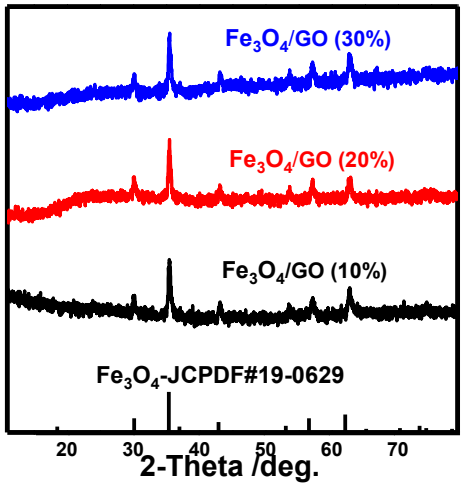


Figure S1. XRD patterns of Fe_3O_4/graphene catalysts prepared with various weight ratio.

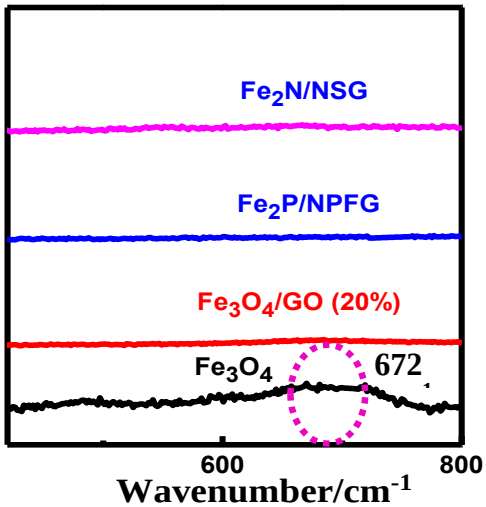


Figure S2. Raman spectra of Fe_3O_4 (black), Fe_3O_4/GO (red), (c) Fe_2P/NPFG (blue), and (d) Fe_2N/NSG (purple).

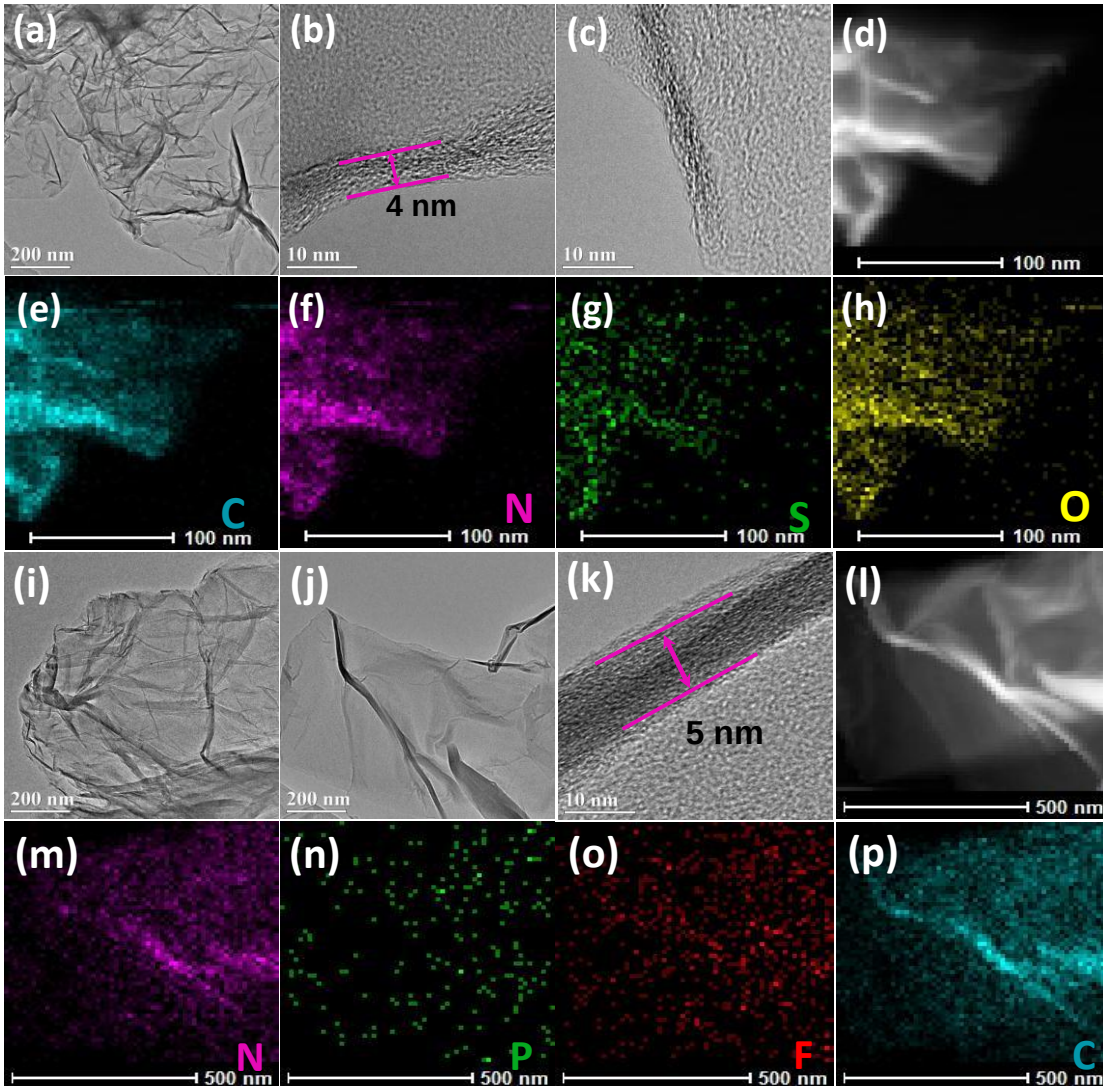


Figure S3. TEM, HR-TEM, and HAADF-STEM images of (a-h) N, S dual-doped graphene; (i-p) N, P, and F tri-doped graphene.

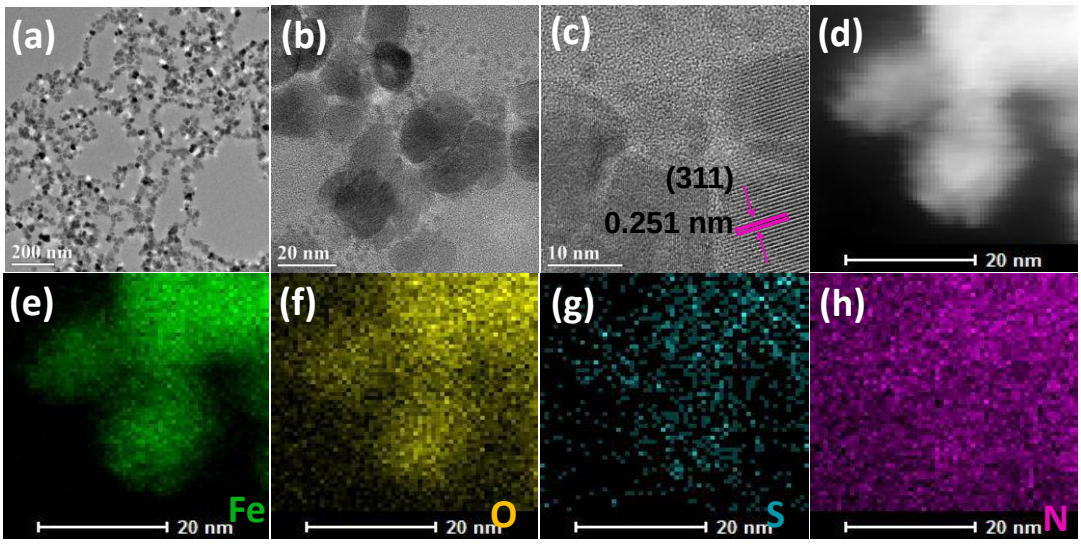


Figure S4. TEM, HR-TEM, and HAADF-STEM images of N, S co-doped Fe_2N catalysts.

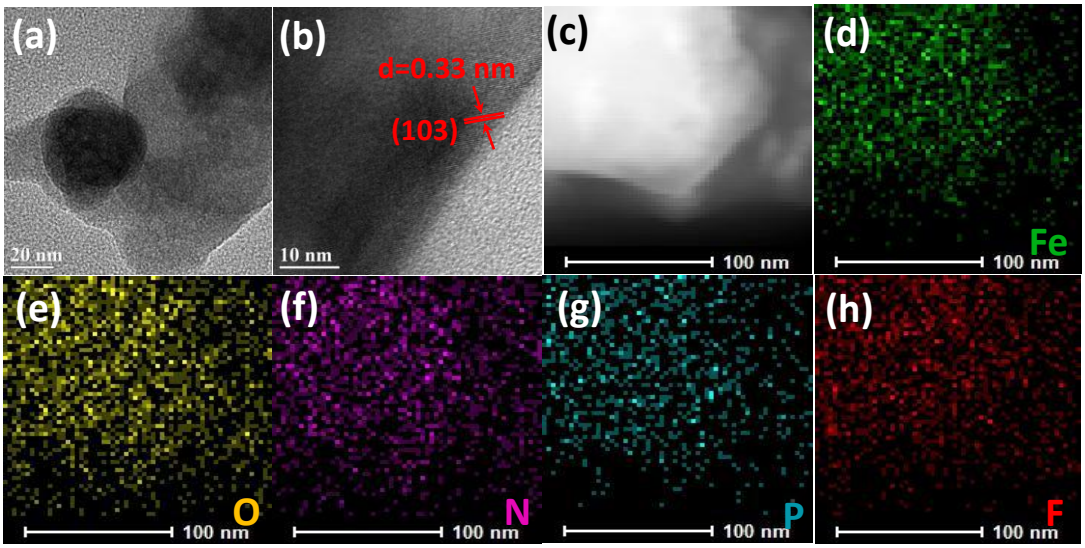


Figure S5. TEM, HR-TEM, and HAADF-STEM images of N, P, F tri-doped Fe_2P.

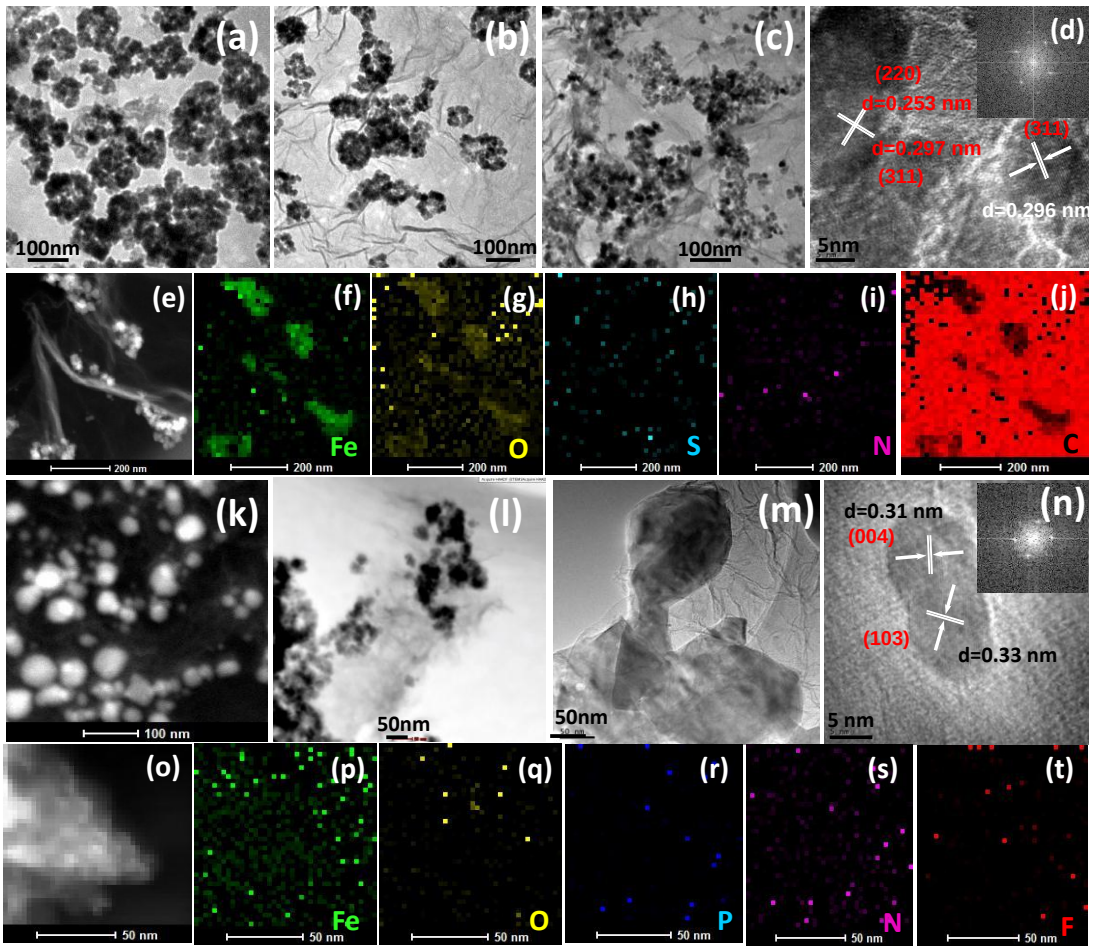


Figure S6. TEM, HR-TEM images, and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images of (a-j) Fe_3O_4/NSG; (k-t) $Fe_3(PO_4)_2(OH)_2$/NPFG.

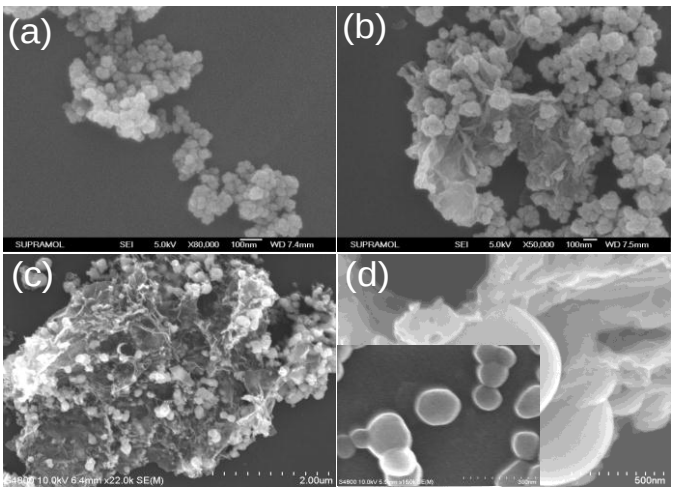


Figure S7. SEM images of (a) Fe_3O_4, (b) Fe_3O_4/GO (20%), (c) Fe_2N/NSG, and (d) Fe_2P/NPFG catalysts.

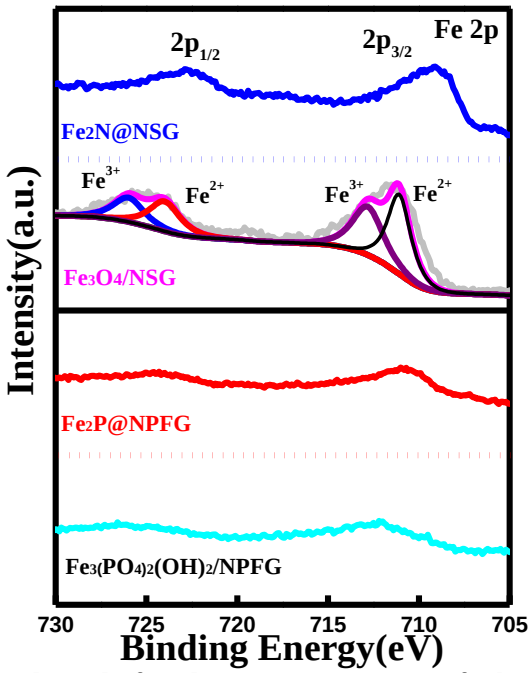
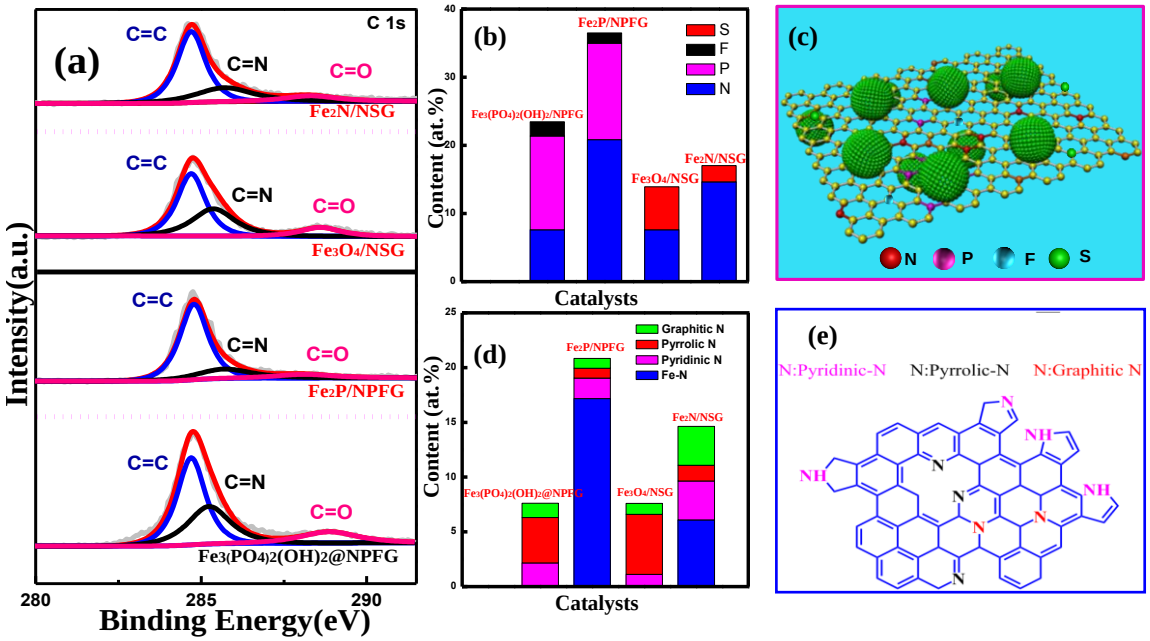


Figure S8. Experimental and fitted Fe 2p spectra of the fresh precursor and their corresponding calcined catalysts.



(f)

Samples	C (At. %)	O (At. %)	N (At.%)	Fe (At. %)	S (At. %)	P (At. %)	F (At. %)
Fe_3O_4/NSG	57.33	31.55	1.63	8.31	1.37	----	----
$Fe_3(PO_4)_2(OH)_2$ @NPFG	67.37	25.01	2.18	1.53	----	3.67	0.24
Fe_2N/NSG	64.24	19.88	7.76	7.31	0.91	----	----
Fe_2P/NPFG	68.38	11.05	10.24	3.61	----	6.71	0.01

Figure S9. Experimental and fitted XPS spectra of the fresh precursor and their corresponding calcined catalysts: (a) C 1s; (b) Concentration and (c) Illustration of the N, P, F, and S heteroatoms; (d) Concentration of four types of nitrogen in these catalysts; and (e)

Illustration of the three types of nitrogen in graphene, (f) atomic percentages of the elements obtained in the XPS survey spectra.

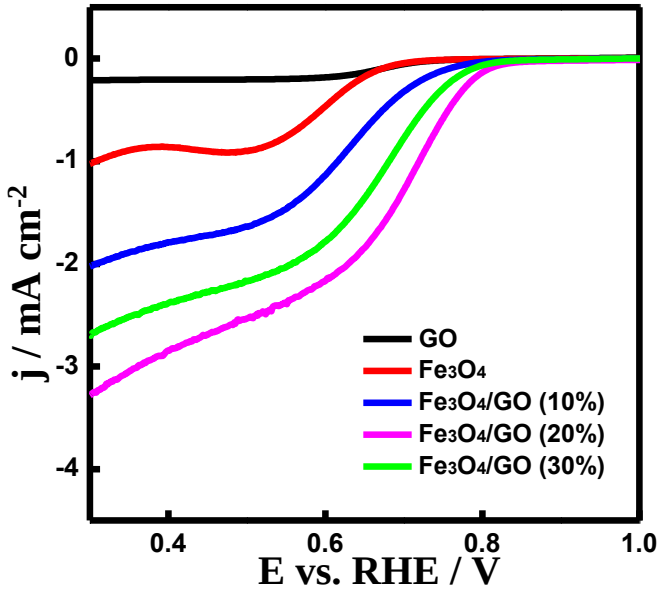


Figure S10. ORR property for these catalysts.

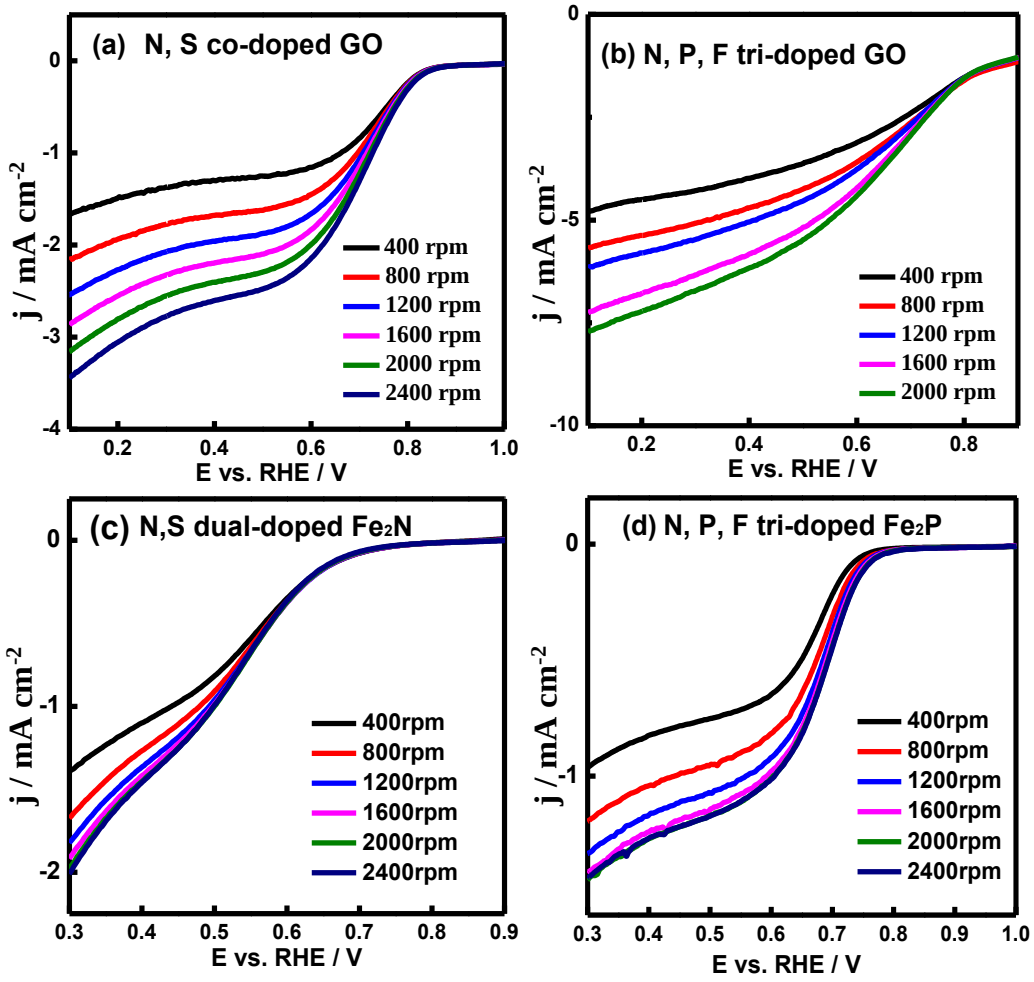


Figure S11. ORR properties for the (a) N, S co-doped graphene, (b) N, P, F tri-doped graphene, (c) N, S dual-doped Fe_2N, and (d) N, P, F tri-doped Fe_2P.

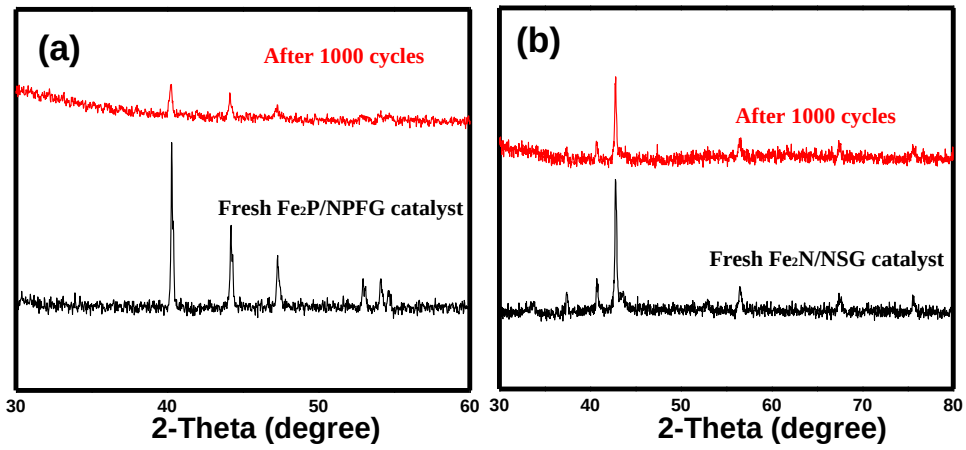


Figure S12. XRD patterns of the (a) Fe_2P/NPFG and (b) Fe_2N/NSG catalysts after cycling test.

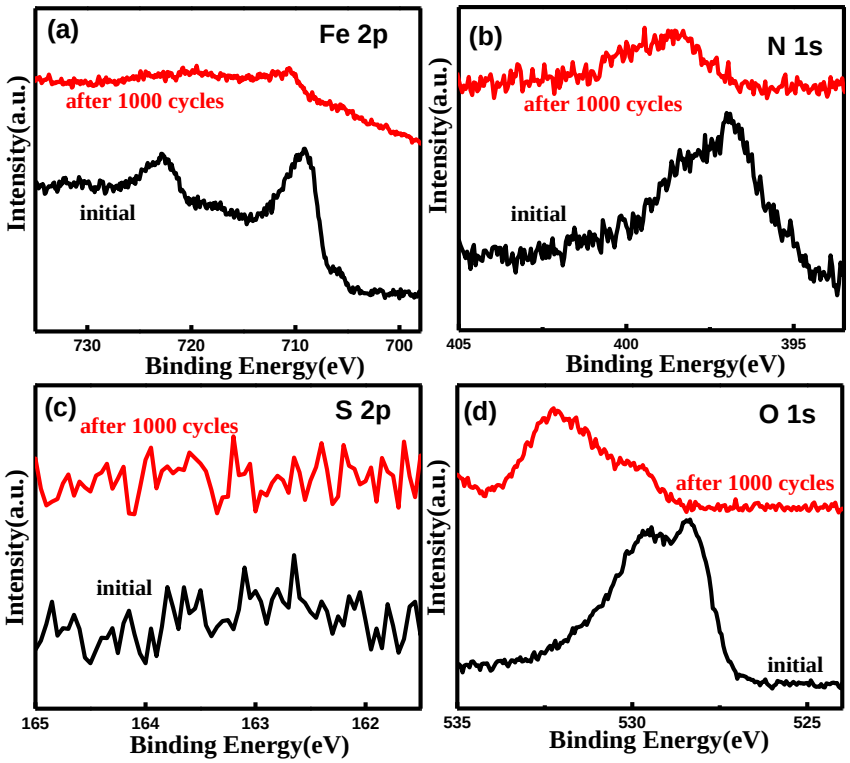


Figure S13. XPS spectra of the initial Fe_2N/NSG and their corresponding catalysts after 1000 cycles: (a) Fe 2p, (b) N 1s, (c) S 2p, and (d) O 1s.

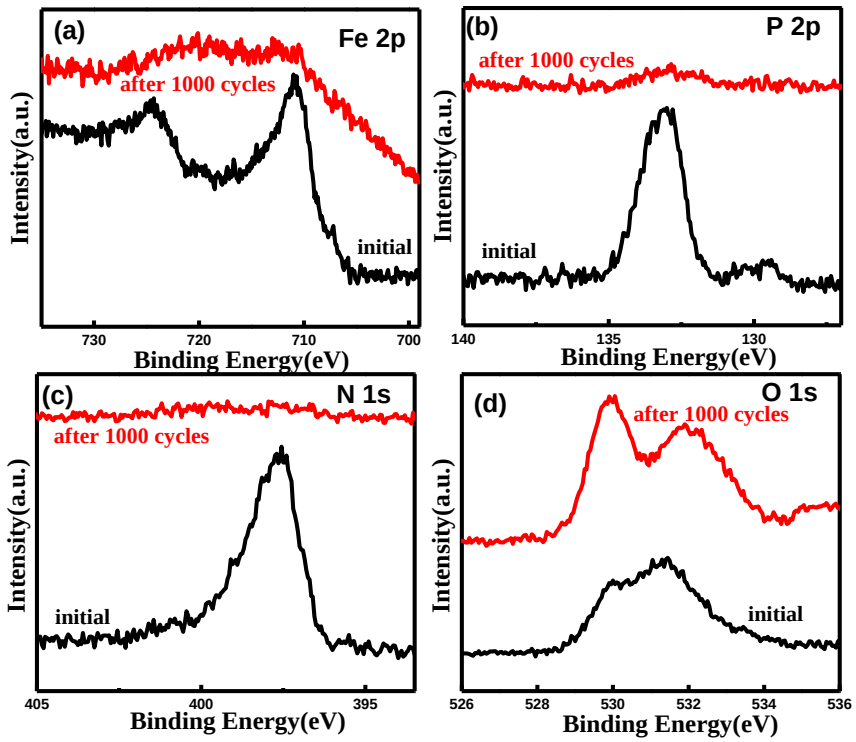


Figure S14. XPS spectra of the initial Fe_2P/NPFG and their corresponding catalysts after 1000 cycles: (a) Fe 2p, (b) P 2p, (c) N 1s, and (d) O 1s.

The XRD patterns of the Fe_2P/NPFG and Fe_2N/NSG catalysts indicated that there was no significant change in the crystalline structures of the samples after cycling test. And the peak intensity was decreased, probably due to the lower crystallinity degree after the electrochemical cycling test. The crystalline structure and composition of these catalysts remained almost identical after electrochemical reaction, demonstrating the high stability of Fe_2N/NSG and Fe_2P/NPFG as an ORR electrocatalyst.(Figure S12-Figure S14)

Table S1 Comparison of ORR catalytic performance for different catalysts reported in this work.

Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Limiting Current density (mA/cm^{-2})	Electron transfer number (n)	Tafel slop (mV dec-1)
Fe_2N/NSG	0.97	0.82	5.21	3.9	80
Fe_2P/NPFG	0.97	0.83	5.02	3.9	76
Fe_3O_4	0.74	0.59	0.43	0.4	87
GO	0.72	0.57	0.08	1.4	89
Fe_3O_4-GO	0.87	0.67	0.3	1.3	75
Pt−C (20wt%)	0.91	0.78	5.3	-	84

Table S2 Comparison of ORR electrocatalytic activity of Fe-based catalysts reported in this work and some other representative ORR eletrocatalysts that have been recently reported in alkaline medium.

Catalyst	Electrolyte	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Limiting Current density (mA/cm^{-2})	Electron transfer number (n)	Tafel slop ($mV\ dec^{-1}$)	Reference
Fe_2N/NSG	0.1 M KOH	0.97	0.82	5.21	3.9	80	This work
Fe_2P/NPFG	0.1 M KOH	0.97	0.83	5.02	3.9	76	This work
Fe−P−C	0.1 M KOH	0.95	0.78	5.01	3.61		J. Am. Chem. Soc. 2015, 137, 3165−3168
Meso-Fe-N-C/ N-G	0.1 M KOH	1.03	0.89	5.41	4	63	J. Mater. Chem. A. 2017, 5, 4868-4878
S-Fe/N/C	0.1M KOH	1.0	0.825	5.05	3.96		ACS Appl. Mater. Interfaces 2016, 8, 19379−19385
Fe,S/NGC-900	0.1 KOH	0.95	0.83	4.95	3.99	77	ACS Appl. Mater. Interfaces 2016, 8, 19533−19541
Fe-N-CC	0.1 KOH	0.94	0.83	5.0	3.7		ACS Nano 2016,10,5922 −5932
Fe-N/rGOsonic	0.1 KOH	0.906	0.737	3.4		86	J Solid State Electrochem, 2016, 20, 3507–3523
Fe/Fe_3C@N–C–NaCl	0.1 KOH	0.970	0.869		3.9		J. Mater. Chem. A, 2016, 4,7781–7787
CNT/PC	0.1 KOH	0.95	0.88	5.9	4		J. Am. Chem. Soc, 2016,138, 15046−15056
Fe_2N/N-graphitic carbon	0.1 M KOH	0.896	0.789	7.18	3.86	-	Nano energy, 2016, 24, 121-129
FeN_2	0.1 M KOH	0.90	0.83	5.01	4.0		Nano energy, 2016, 24, 121-129

Table S3 The charge transfer of Fe, P, N, F, S and C atoms, ΔQ_{Fe}, ΔQ_{P}, ΔQ_{N}, ΔQ_{F}, ΔQ_{S} and ΔQ_{C}, respectively. Fe, P_1, N_1, F_1 and S_1 denote the atoms in the doped Fe_2P (111) or Fe_2N (111). C, P_2, N_2, F_2 and S_2 denote the atoms in the doped graphene. "-" and "+" indicate the loss and gain of charge, respectively.

	N, F doped Fe_2P(111)		S doped Fe_2N(111)	
	Without graphene	With graphene	Without graphene	With graphene
ΔQ_{Fe}	-4.814	-5.648	-3.936	-4.021
ΔQ_{P1}	+2.468	+2.584		
ΔQ_{N1}	+1.568	+1.320	+3.391	+3.015
ΔQ_{F1}	+0.778	+0.675		
ΔQ_{S1}			+0.545	+0.723
ΔQ_{C}		+0.448		-0.493
ΔQ_{P2}		-1.303		
ΔQ_{N2}		+1.313		+1.156
ΔQ_{F2}		+0.611		
ΔQ_{S2}				-0.380

Reference

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[4] S. Grimme, J. Comput. Chem. **2006**, *27*, 1787.

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