Supporting Information

Efficient oxygen reduction electrocatalyst from graphene by simultaneously generating pores and nitrogen doped active sites

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Results

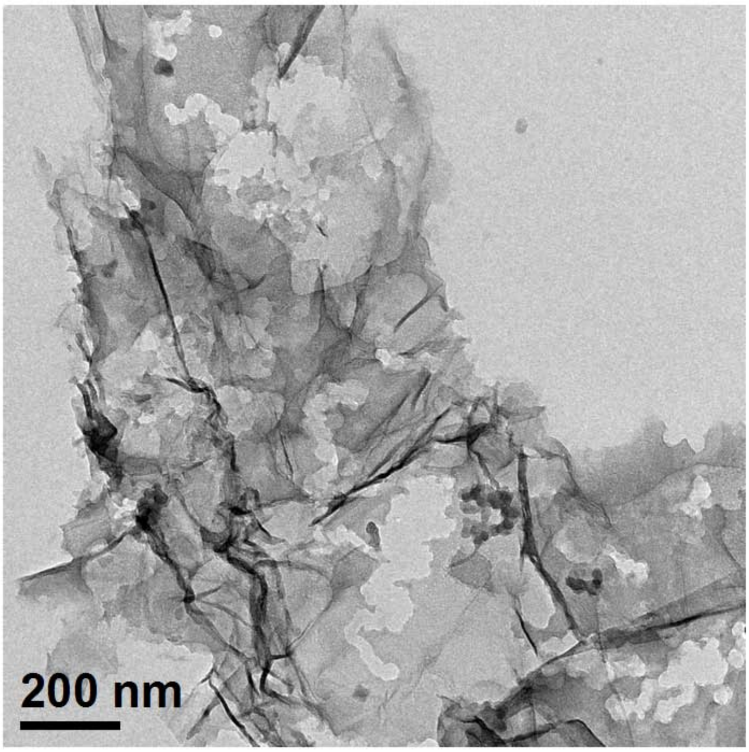


Fig. S1: HRTEM image of the porous graphene derived from larger and aggregated Fe_2O_3 particles.

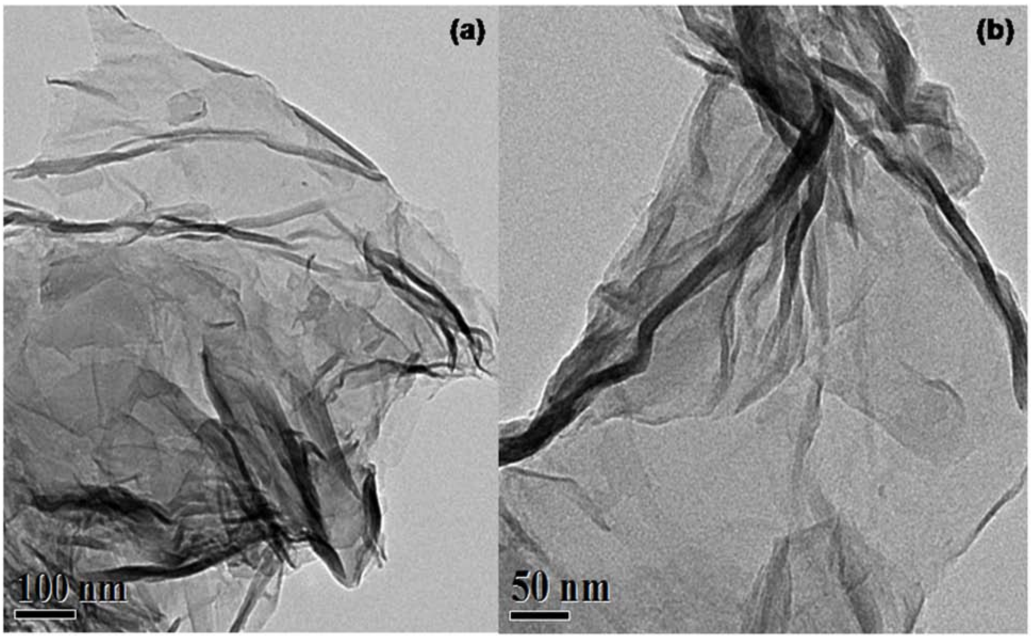


Fig. S2. HRTEM images of the nitrogen doped graphene (N-Gr). The sample was prepared by avoiding the Fe precursor during the pyrrolyzis step.

The HRTEM images of N-Gr (shown in Fig. S2) clearly show the few-layer nitrogen doped Gr, where the graphene layers are stacked together. There are no indications of the formation of pores in these samples due to the absence of the Fe precursor in the preparation process.

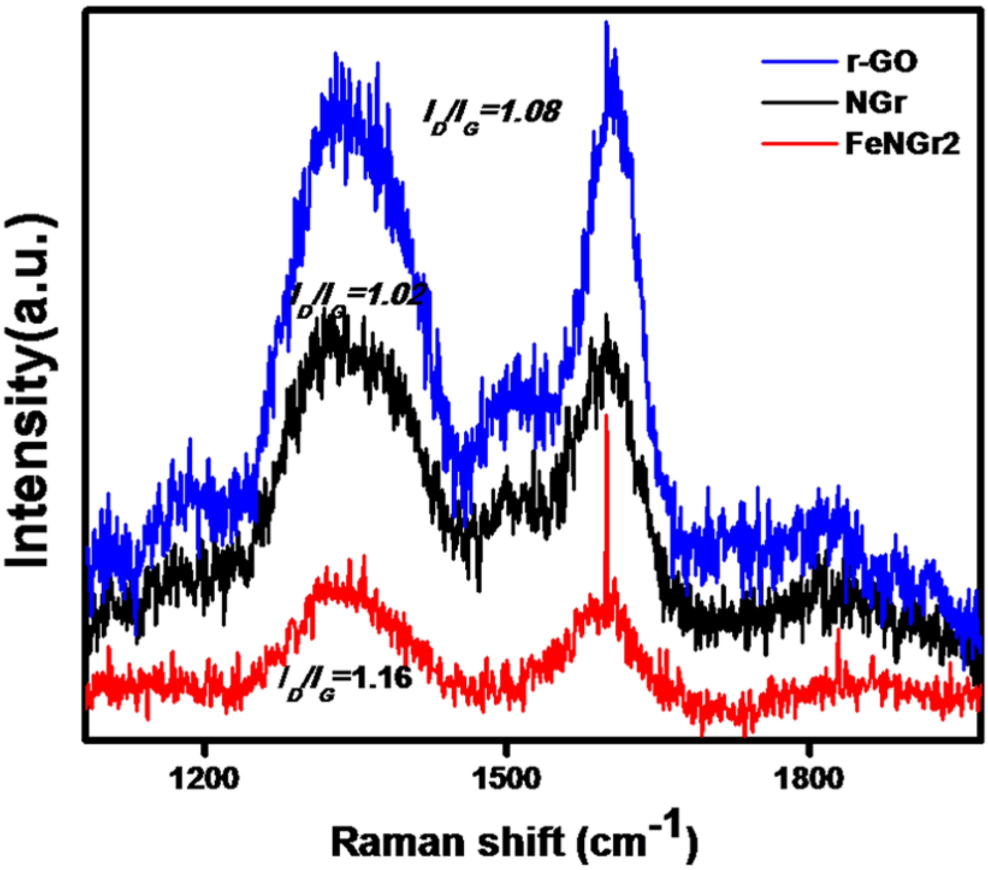


Fig. S3 . Raman spectra of r-GO, N-Gr and FeNGr2.

Since Raman spectroscopy is an important tool to deduce the structure in particularly defects and disorder nature of Gr based materials, we took Raman spectra of all the samples (Fig. S3). The Raman spectra of the samples exhibit two remarkable peaks at around 1340 and 1506 cm^{-1} corresponding to the well defined D band and G band, respectively. The graphitic peak (G band) at 1506-1510 cm^{-1} is due to the E_{2g} vibrational mode of the C-C bond stretching and the disorder peak (D-band) at 1330-1345 cm^{-1} is due to the A_{1g} vibrational mode. The intensity ratio of the D and G bands *i.e* (I_D/I_G ratio) helps to estimate the defects of Gr based samples where a higher ratio ensures more defects on Gr. The calculated I_D/I_G ratios of r-GO, N-Gr and FeNGr2 are 1.08, 1.02, and 1.16 respectively. The higher I_D/I_G ratio of FeNGr2 compared to the other nitrogen based Gr materials clearly depicts the defective nature of FeNGr2 due its porous structure. This conclusion is well in agreement with the conclusions derived from the XRD, XPS and HRTEM analyses.

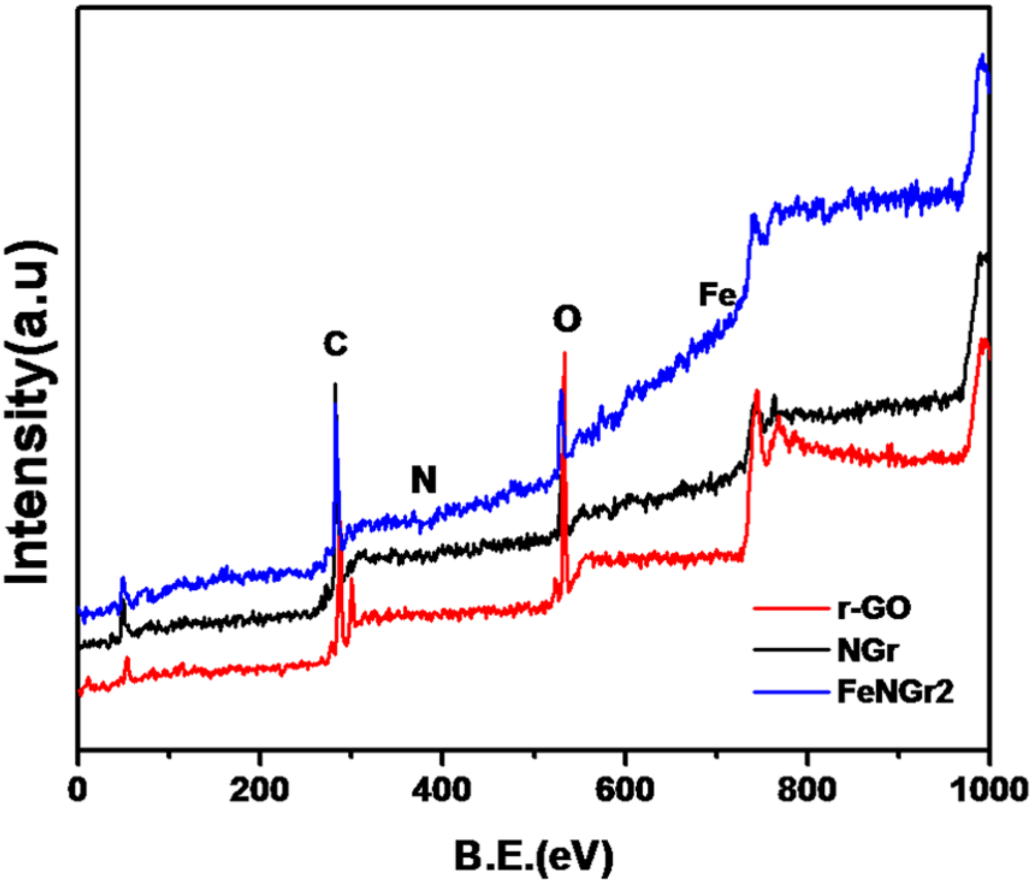
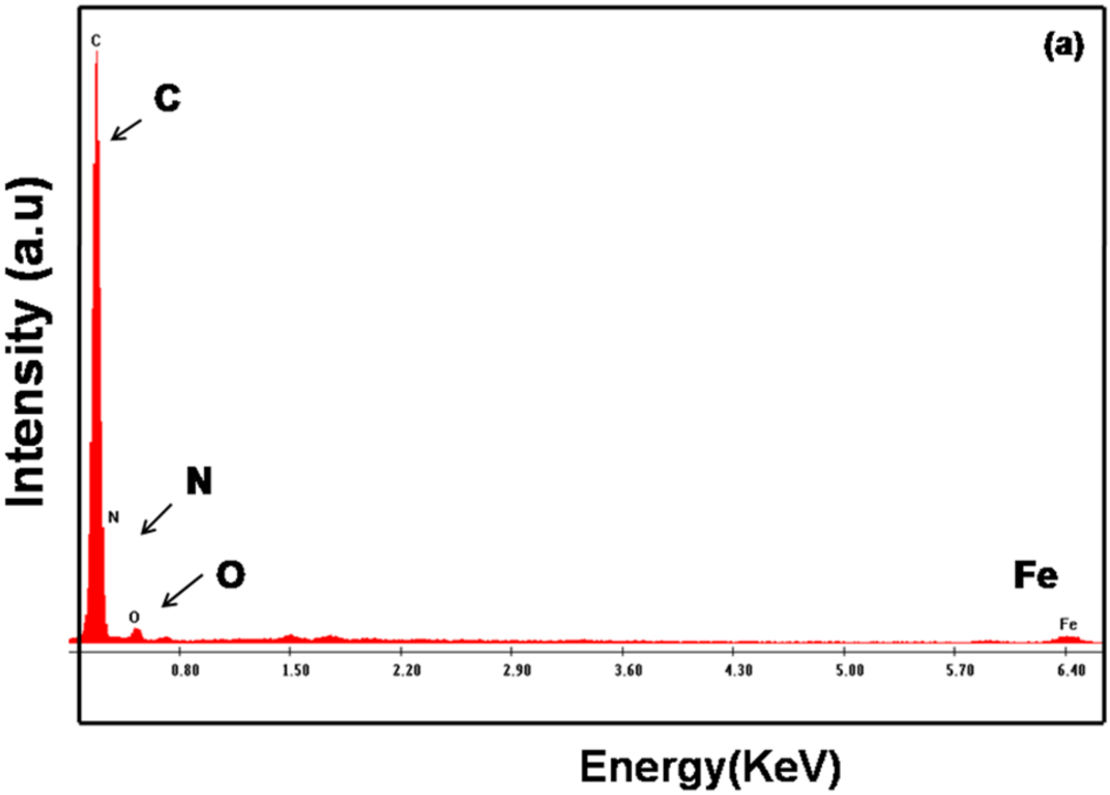


Fig. S4. Full range XPS survey of (a) r-GO (b) N-Gr and (c) FeNGr2

The elemental surface compositions r-GO, N-Gr and FeNGr2 were evaluated using XPS. The full range XPS survey spectra of r-GO, N-Gr and FeNGr2 are shown in Fig. S4, which clearly show the presence of carbon (C), oxygen (O_2), nitrogen (N_2), and iron (Fe). The main peak at 284.3 eV is due to the sp^2 -carbon, which indicates the predominant graphitic nature of the carbon. The additional peaks at 398, 532 and 702 eV correspond to N_2, O_2 and Fe respectively. The peak for O_2 arises mainly due to the O_2 functional groups at the surface of the basal plane of Gr.

EDAX analysis



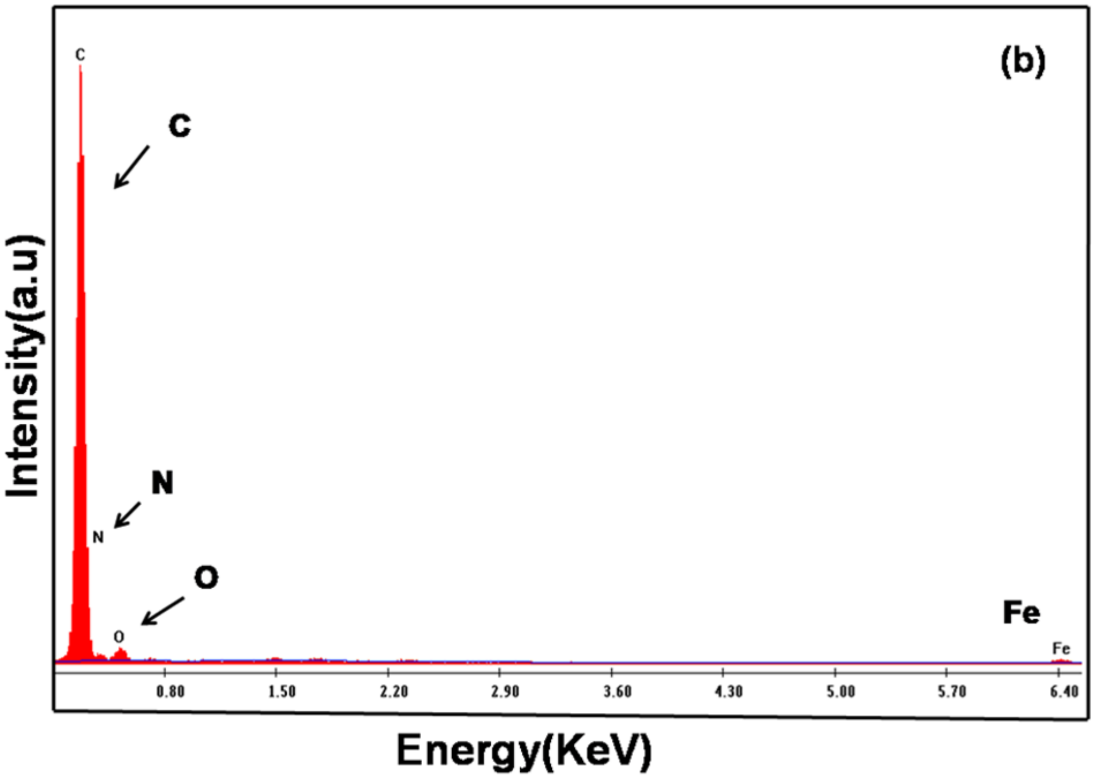


Fig. S5. EDAX spectra of (a) FeNGr2 and (b) FeNGr3 showing 5.9 and 9.75 % of nitrogen doping, respectively.

EDAX quantification of FeNGr2

Elem	Wt %	At %	K-Ratio	Z	A	F
C K	88.11	90.85	0.7458	1.0028	0.8440	1.0001
N K	5.92	5.24	0.0046	0.9948	0.0783	1.0001
O K	4.70	3.64	0.0055	0.9876	0.1184	1.0000
FeK	1.26	0.28	0.0111	0.8432	1.0425	1.0000
Total	100.00	100.00				

EDAX quantification of FeNGr3

Elem	Wt %	At %	K-Ratio	Z	A	F
C K	83.94	86.82	0.7031	1.0025	0.8354	1.0001
N K	9.75	8.65	0.0079	0.9945	0.0819	1.0001
O K	5.64	4.38	0.0065	0.9873	0.1169	1.0000
FeK	0.66	0.15	0.0058	0.8429	1.0425	1.0000
Total	100.00	100.00				

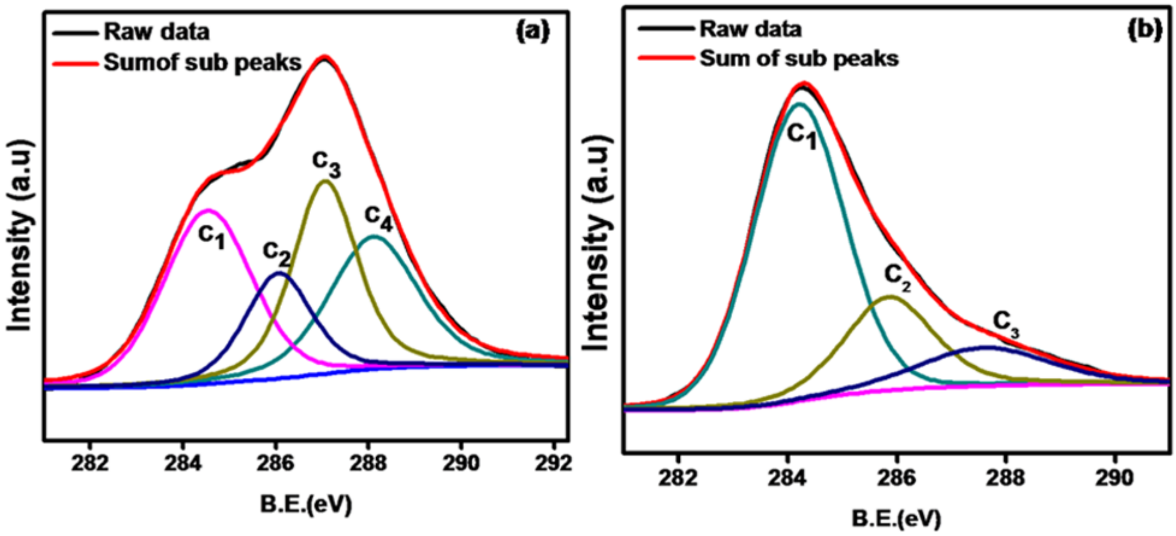


Fig. S6. C 1s spectra of (a) r-GO and (b) FeNGr2.

The C1s spectra of r-GO and FeNG2r are shown in Fig. S6. The C1s spectra of r-GO (Fig. S6a) are deconvoluted into four different peaks. The peak at 284.5 eV is assigned as C_1 corresponding to graphitic carbon. The peaks at 286.7, 287.1 and 288.1 eV can be recognized as C_2, C_3 and C_4 are corresponding to the sp^3 carbon (*i.e.* carbon bound with oxygen (C-O)), epoxy carbon (C-O-C) and carbonyl carbon (C=O) respectively. Similarly, in the case of

FeNGr2 (Fig. S6b), the C1s spectra are deconvaluted into three peaks. The peak at 284.3, 285.7 and 287.5 eV are corresponding to the graphitic carbon, C-O and sp3 carbon (either carbon bound with oxygen or nitrogen) and epoxy carbon respectively. Fig. S6b also reveals strong suppression of the oxygen functional groups especially carbonyl functional groups compared to r-GO which ensures the proficient reduction of the oxygen functional groups during the thermal treatment.

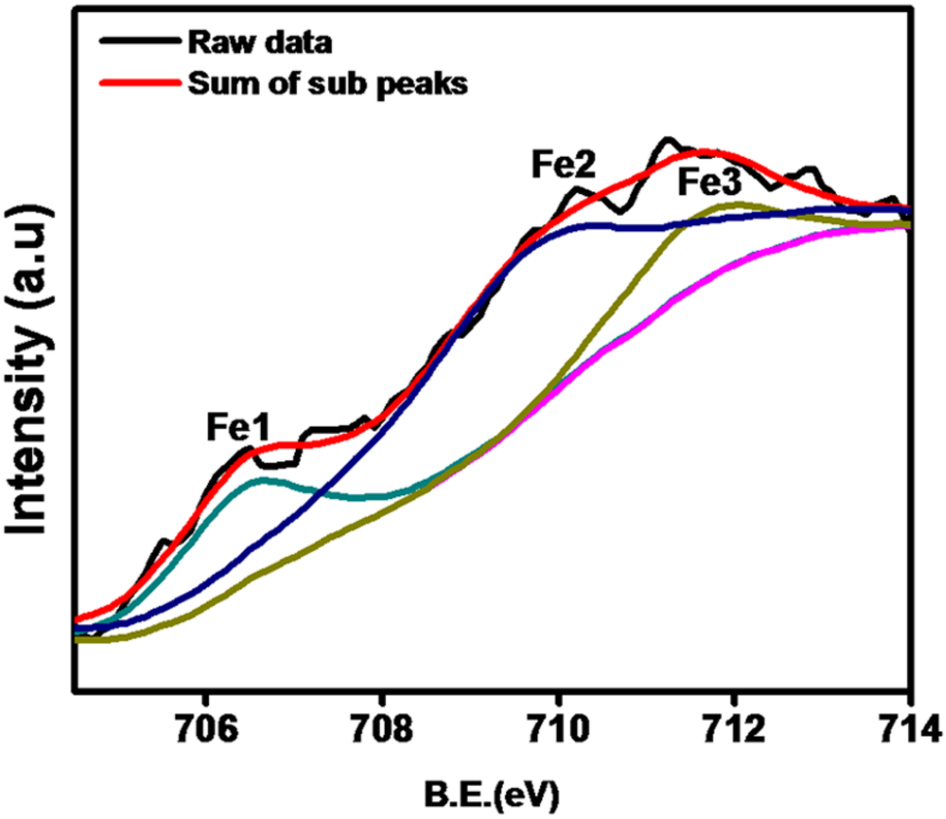


Fig. S7. Fe2p spectra of FeNGr2.

The Fe2p spectra of FeNGr2 have been deconvaluted into three different peaks which are shown in Fig. S7. The peak at the low binding energy of 706.6 eV, named as Fe1, corresponds to metallic iron carbide (Fe2p$_{3/2}$) emphasizing the presence of trace amount of Fe$_3$C which is well line up with the XRD results. The pair of peaks at 709.8.0 and 711.8 e V which are assigned as Fe2 and Fe3, respectively, correspond to the ionic state of Fe (Fe2p$_{1/2}$)

and this result discloses that Fe in the ionic state arises either from the iron coordinated with nitrogen or residual iron oxide.

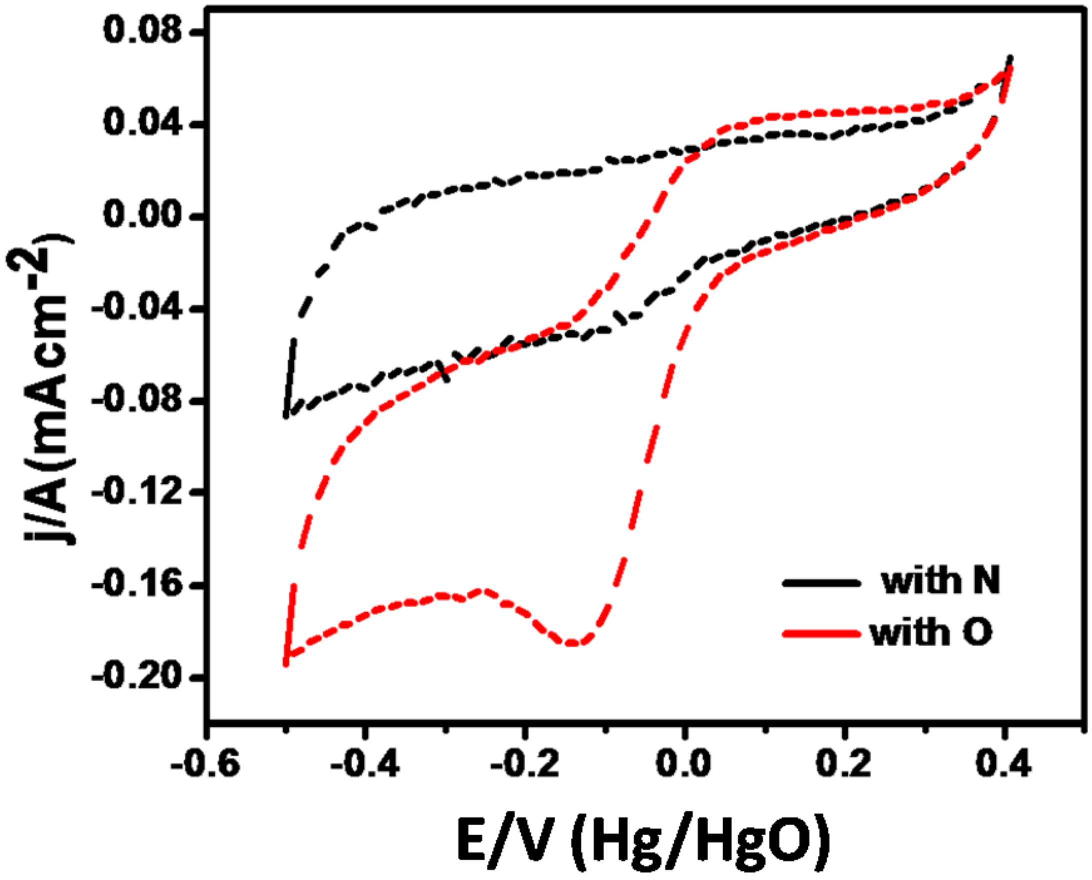
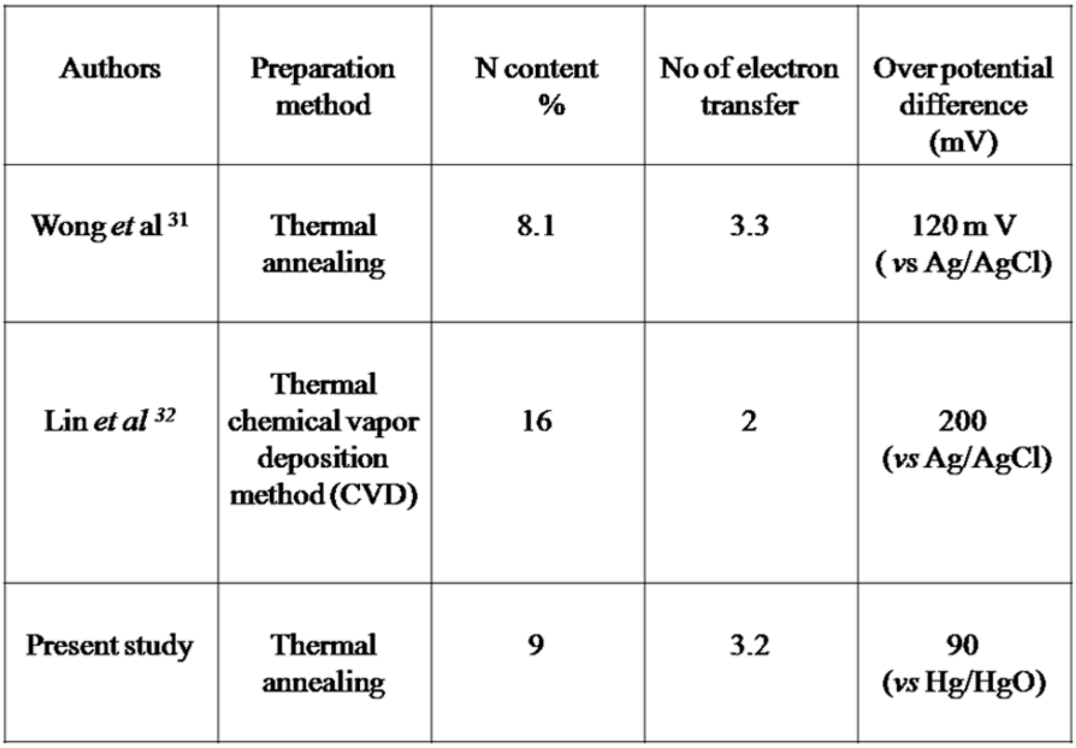


Fig. S8. CV for N-Gr recorded in 0.1 KOH at a scan rate of 5 m V/s under nitrogen and oxygen enriched conditions.

Fig. S8 shows the cyclic voltammograms of N-Gr) cycled between 0.4 V to -0.5 V against Hg/HgO reference electrode at a scan rate of 5 mV/s under nitrogen and oxygen enriched conditions. As can be seen, NGr shows well resolved cathodic peak corresponding to ORR under oxygen saturated conditions.

Table S1. Summary of performance of nitrogen doped catalysts.



Authors	Preparation method	N content %	No of electron transfer	Overpotential difference (mV)
Wong *et* al [31]	Thermal annealing	8.1	3.3	120 m V (*vs* Ag/AgCl)
Lin *et al* [32]	Thermal chemical vapor deposition method (CVD)	16	2	200 (*vs* Ag/AgCl)
Present study	Thermal annealing	9	3.2	90 (*vs* Hg/HgO)

The reference numbers are as given in the manuscript.