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Supporting information

Three Dimensional Mn_3O_4 Network Supported on Nitrogenated Graphene Electrocatalyst with Enhanced Oxygen Reduction Reaction

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Keywords: nitrogen doped graphene, Mn_3O_4, electrodeposition, oxygen reduction reaction, hybrids.

XPS survey spectrum of NrGO and Mn_3O_4/NrGO/nafion

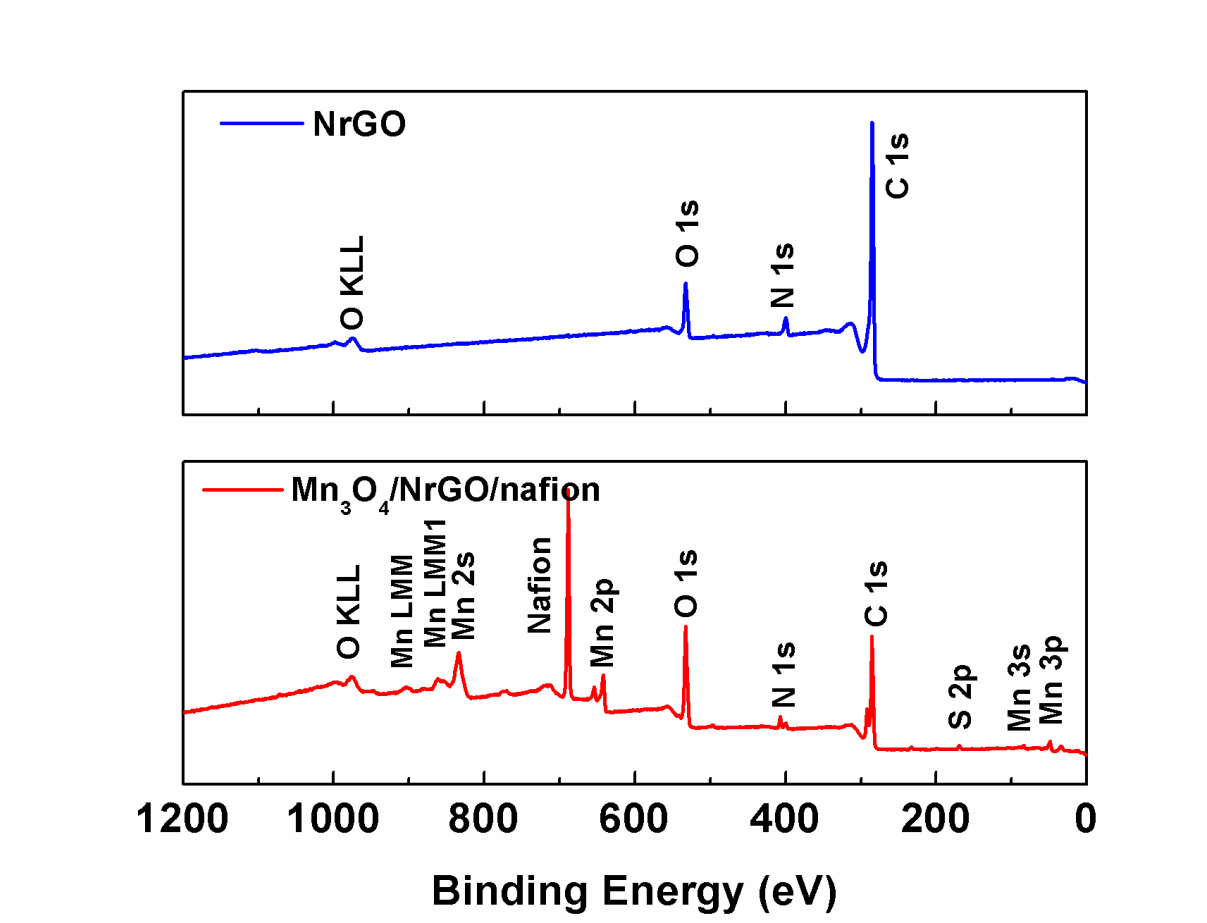

Figure S1. XPS survey scans of NrGO and Mn_3O_4/NrGO.

Figure S1 shows the wide XPS spectrum of NrGO and Mn_3O_4/NrGO. In the case of NrGO the material is drop dried on silicon substrate with 70% ethanol as solvent and dried for 24 hrs at 60^0C in oven under vaccum. The survey spectrum of NrGO shows only carbon, oxygen and nitrogen peaks. The survey scan of Mn_3O_4/NrGO/nafion shows additional peals related to sodium and sulphur. The presence of these peaks might indicate that the Mn_3O_4 or NrGO is slightly doped with sodium and sulphur.

High resolution XPS spectrum of O 1s and Mn 3s

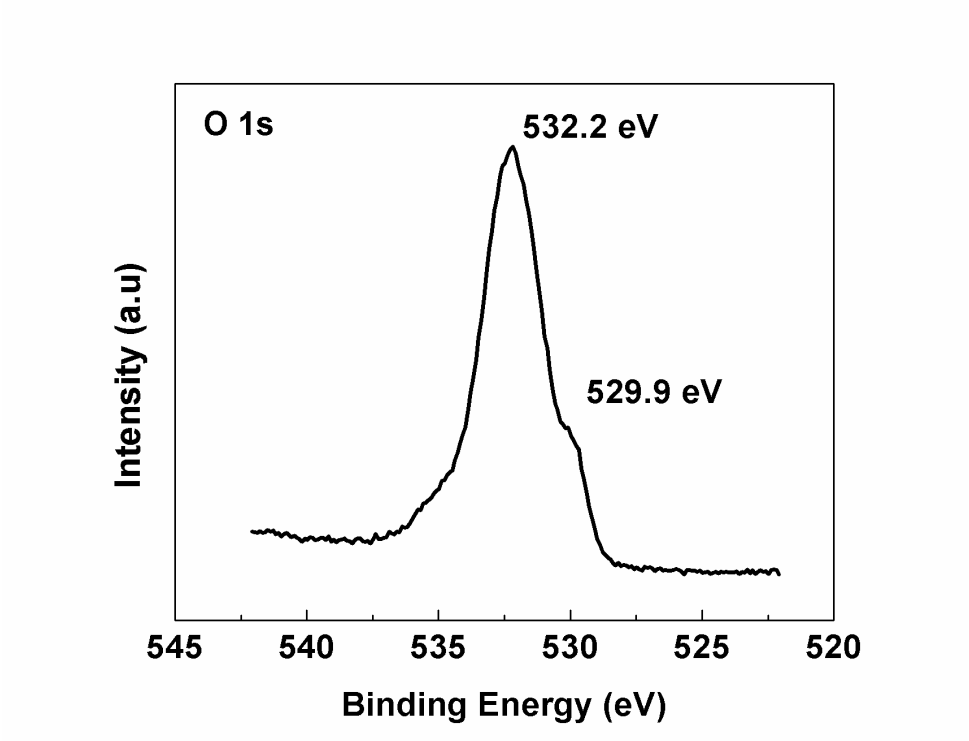

Figure S2. High resolution O 1s XPS spectra of Mn_3O_4/NrGO.

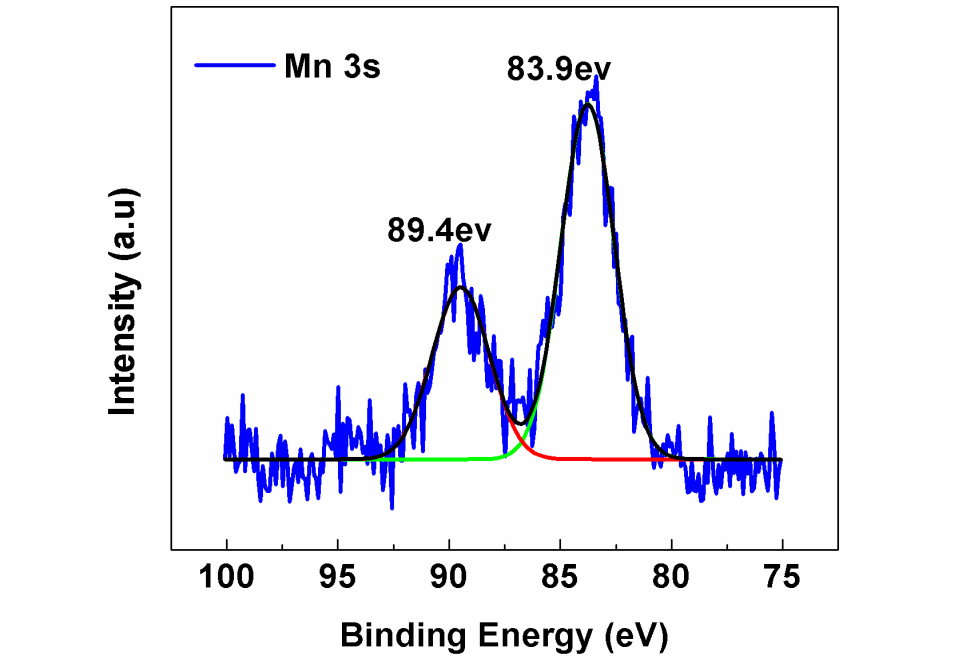

Figure S3. Mn 3s XPS spectra of Mn_3O_4/NrGO.

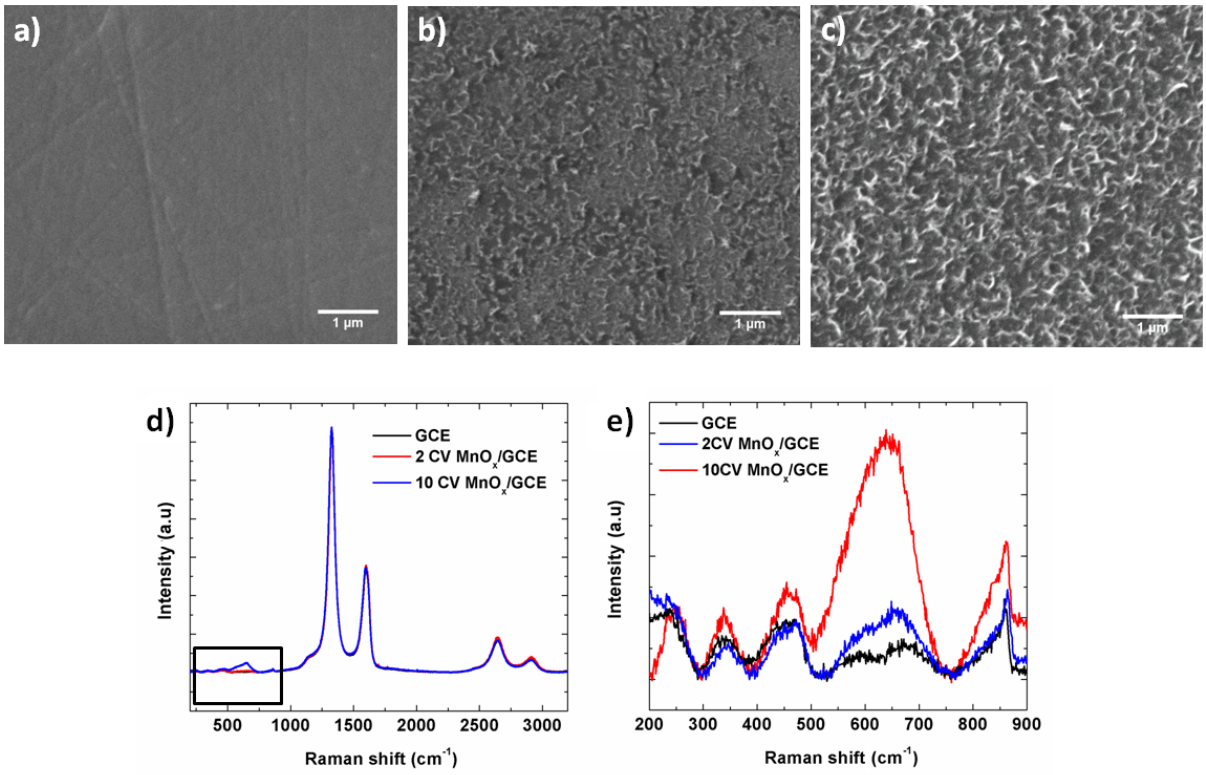

Figure S4. (a) SEM image of GCE (b) SEM image of 2CV MnO_x/GCE (c) SEM image of 10CV MnO_x/GCE (d) Raman wide spectra of GCE, 2CV and 10CV MnO_x/GCE (e) magnified version of the region indicated in the square in (d).

Figure S4 shows the SEM images of GCE, 2CV MnO_x/GCE and 10CV MnO_x/GCE. It can be seen that there is progressive growth of MnO_x nanoflakes between 2 and 10 CVs on the GCE, which is getting more dense and uniform at 10CVs. A comparison of SEM images in Figures 3(b) and S4(b) which show MnO_x 2 CV deposition on GCE and NrGO reveals that Mn_3O_4 nanoflakes grow at a higher rate on NrGO than on GCE.

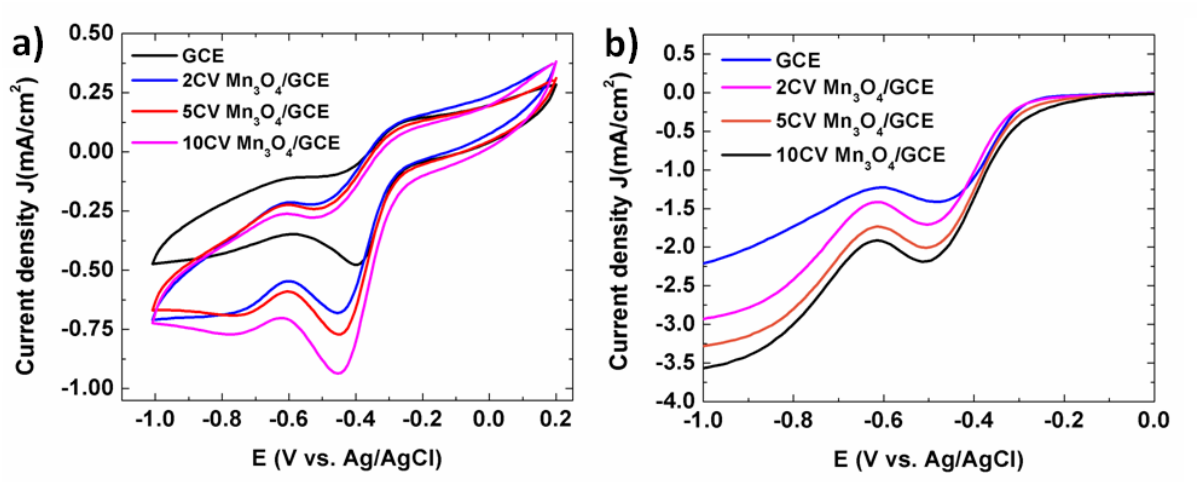

Figure S5. (a) CVs of GCE, 2CV MnO_x/GCE, 5CV MnO_x/GCE, 10CV MnO_x/GCE in O_2-saturated 0.1 M KOH solutions (b) LSV of 2CV MnO_x/GCE, 5CV MnO_x/GCE, 10CV MnO_x/GCE in O_2 saturated 0.1 M KOH solution at 1600 rpm.

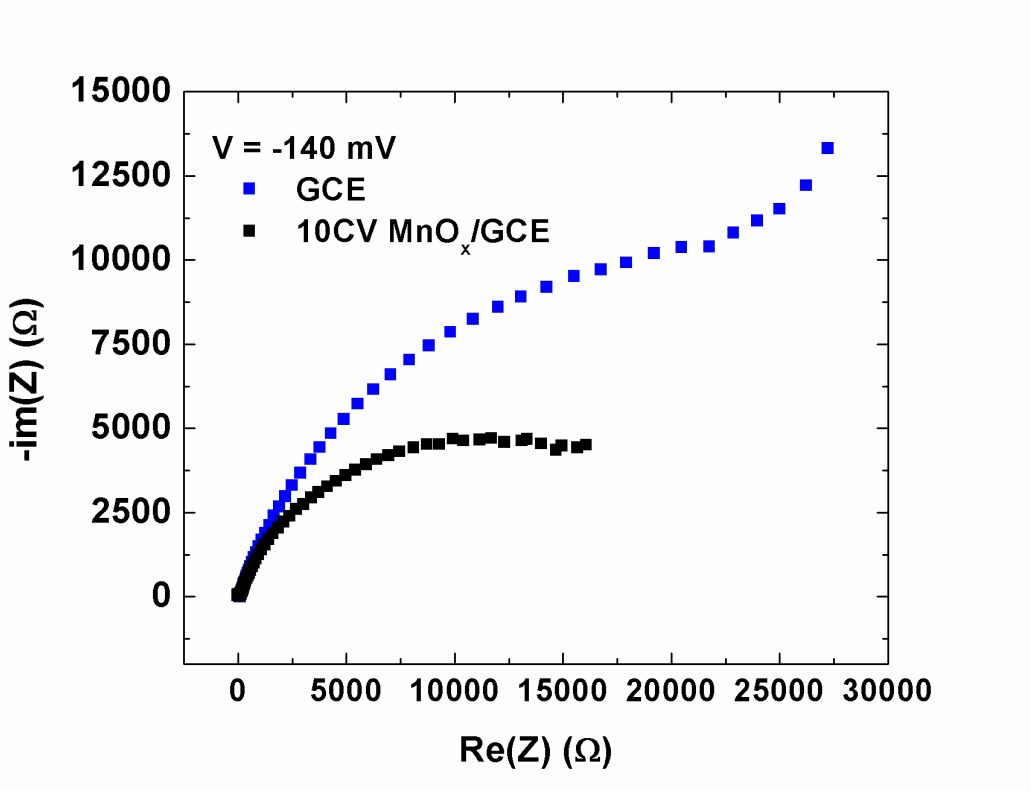

Figure S6. Nyquist plot of GCE and 10CV MnO_x/GCE at V = -140 mV over the frequency range 100 kHz to 10 mHz

Figure S6 presents the Nyquist plots of GCE and 10CV MnO_x/GCE at -140 mV. The smaller semi circle of the 10CV MnO_x/GCE indicates the smaller resistance to the charge transfer when compared to the bare GCE.

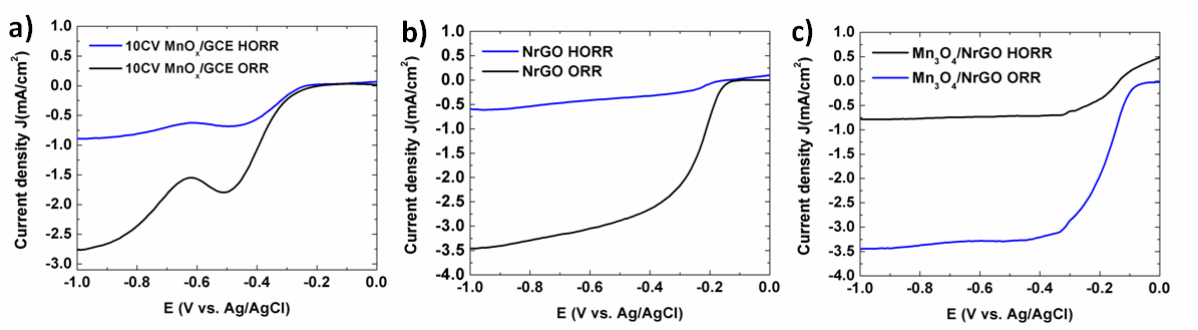

Figure S7. (a) LSV at 1600 rpm of ORR and HORR of 10CV MnO_x/GCE (b) LSV at 1600 rpm of ORR and HORR of 20 µg NrGO (c) LSV at 1600 rpm of ORR and HORR of 2CV Mn_3O_4/ 20 µg NrGO. ORR linear sweeps were measured in O_2 saturated 0.1 M KOH solution and HORR linear sweeps were measured in Ar-saturated 0.1 M KOH solution containing 1.3 mM H_2O_2.

TEM analysis of Mn_3O_4/NrGO

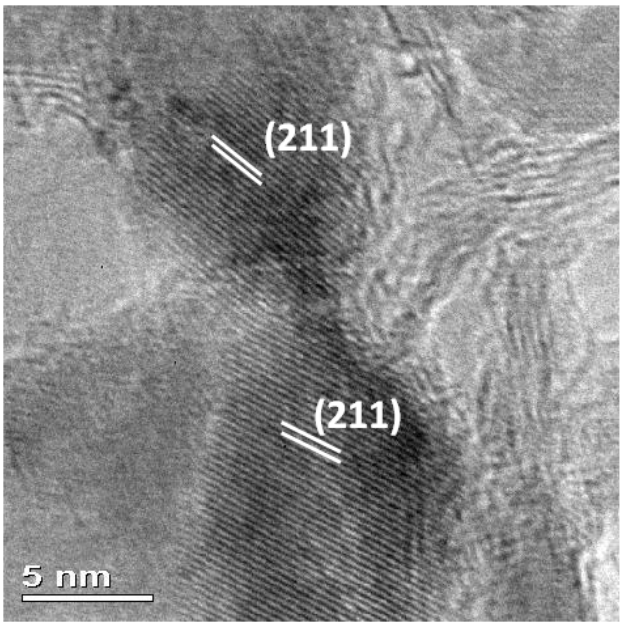

Figure S8. HRTEM image of Mn_3O_4/NrGO, showing two Mn_3O_4 nanocrystallites and their connection. The marked fringes have a d-spacing of 0.246 nm, corresponding to the (211) planes of the tetragonal Mn_3O_4.

Subtraction from argon(Ar) saturation

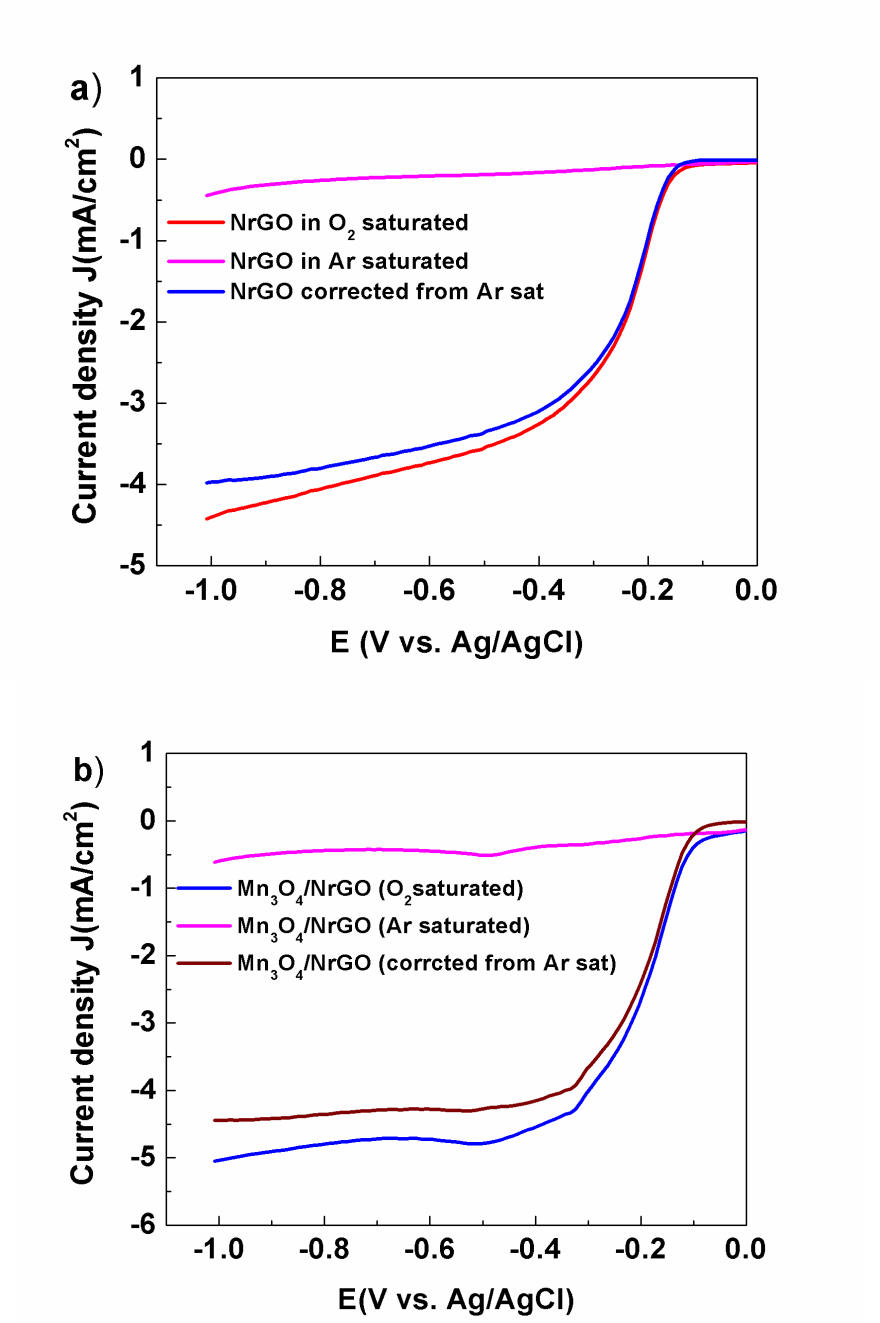

Figure S9. (a) LSV of NrGO in O_2 saturation (red), LSV of NrGO in Ar saturation (pink), corrected LSV of NrGO from Ar saturation (blue). (b) LSV of Mn_3O_4/NrGO in O_2 saturation (blue), LSV of Mn_3O_4/NrGO in Ar saturation (pink), corrected LSV of Mn_3O_4/NrGO from Ar saturation (brown).

In the case of NrGO and Mn_3O_4/NrGO after subtraction from Ar saturation the current is decreased due to the elimination of the capacitive currents. In the case of the NrGO decrease

in the current is less when compared to the Mn_3O_4/NrGO, which indicates that the Mn_3O_4/NrGO has higher capacitance than the NrGO.

Methanol poisoning of Pt/C

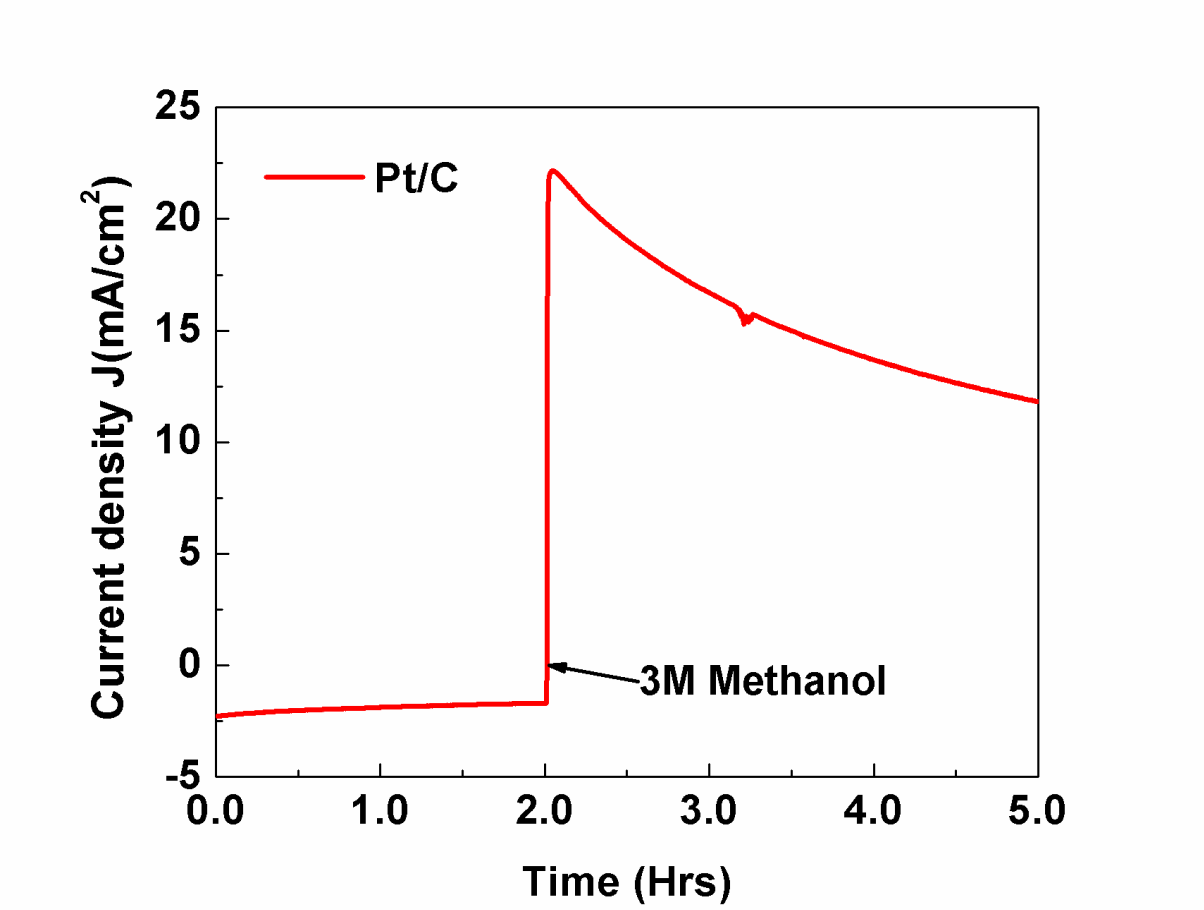

Figure S10. Shows the current of the Pt/C electrode under half wave potential at 1600 rpm. After 2 hrs of chronoamperometry methanol is added to O_2 saturated 0.1 M KOH solution (the resulting concentration of methanol is 3M), showing that the current is shifted from cathodic to anodic, which is called methanol poisoning of the catalyst.

Annealing studies of NrGO and Mn_3O_4/NrGO on carbon fiber paper

We have conducted annealing experiments on both NrGO and Mn_3O_4/NrGO hybrid coated on carbon fiber paper at 225 ^oC in air atmosphere and at 300 ^oC in nitrogen atmosphere compared their ORR performance. Figure S11 reveals that annealing causes a decrease in ORR performance in both NrGO and Mn_3O_4/NrGO hybrid structures, when compared to the as deposited samples, causing negative shifts on the onset potentials. However the beneficial effect of the Mn_3O_4 is always present independent of the annealing temperature as can be judged from the higher current densities observed in the hybrid structures when compared to the NrGO alone (see figure S12).

The XRD spectra of the as prepared Mn_3O_4/NrGO, annealed Mn_3O_4/NrGO at 225 ^oC in air for 120 min and Mn_3O_4/NrGO at 300 ^oC in nitrogen atmosphere for 150 min are shown in Figure S13. The crystallinity of all the samples has not been improved most probably due to low temperatures employed here. We should note that further annealing at higher temperatures results in progressive decomposition of NrGO.

Figure S14 shows that stability of the as prepared and annealed Mn_3O_4/NrGO at 225 ^oC. Stability of the each electrode is measured for 500 cycles (3.5 hrs) in the voltage range 0 to -1.0 V vs. Ag/AgCl at scan rate of 100 mV/sec. The LSV presented in figure S14 are before and after accelerated stability test. In the case of the as prepared Mn_3O_4/NrGO a shift of 0.61 V vs . Ag/AgCl is measured at 50 mA/cm^2 where as in the case of Mn_3O_4/NrGO annealed at 225 0C a shift of 0.35 V is measured at 50 mA/cm^2. This shows that the Mn_3O_4/NrGO annealed shows better stability when compared to as prepared Mn_3O_4/NrGO.

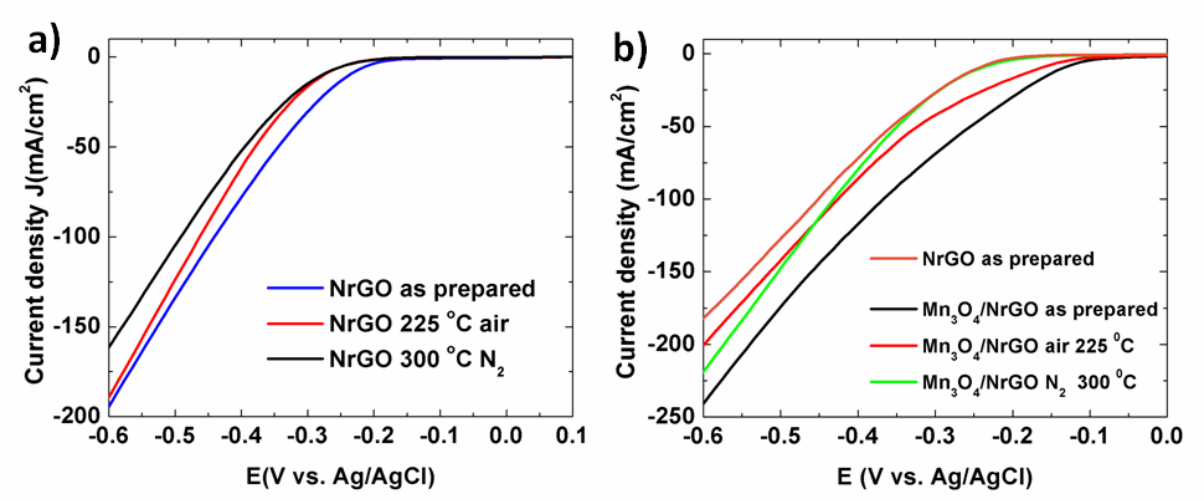

Figure 11. (a) LSV of NrGO, annealed NrGO in air at 225 °C and annealed NrGO in N_2 at 300 °C. (b) LSV of as prepared Mn_3O_4/NrGO; annealed Mn_3O_4/NrGO in air at 225 °C and annealed Mn_3O_4/NrGO in N_2 at 300 °C on carbon fiber paper in O_2 saturated 0.1 M KOH at a scan rate of 10 mV/sec. (catalyst loading 0.2 mg/cm^2).

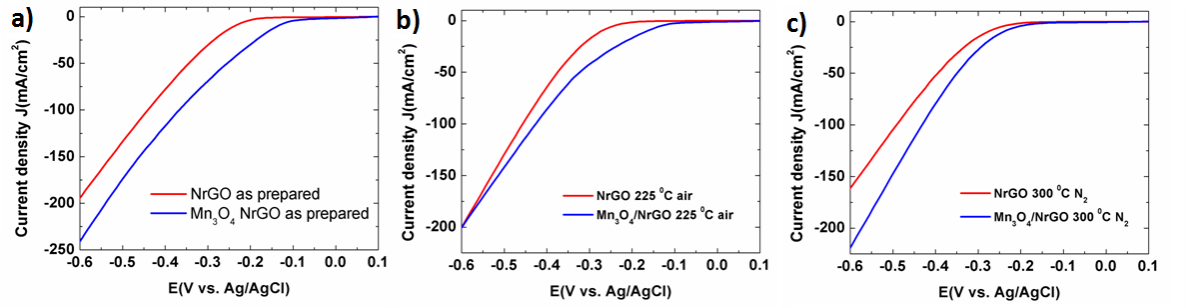

Figure S12. (a) LSV of as prepared NrGO and Mn_3O_4/NrGO (b) LSV of annealed NrGO and Mn_3O_4/NrGO at 225 °C in air atmosphere (c) LSV of NrGO and Mn_3O_4/NrGO at 300 °C in N_2 atmosphere.

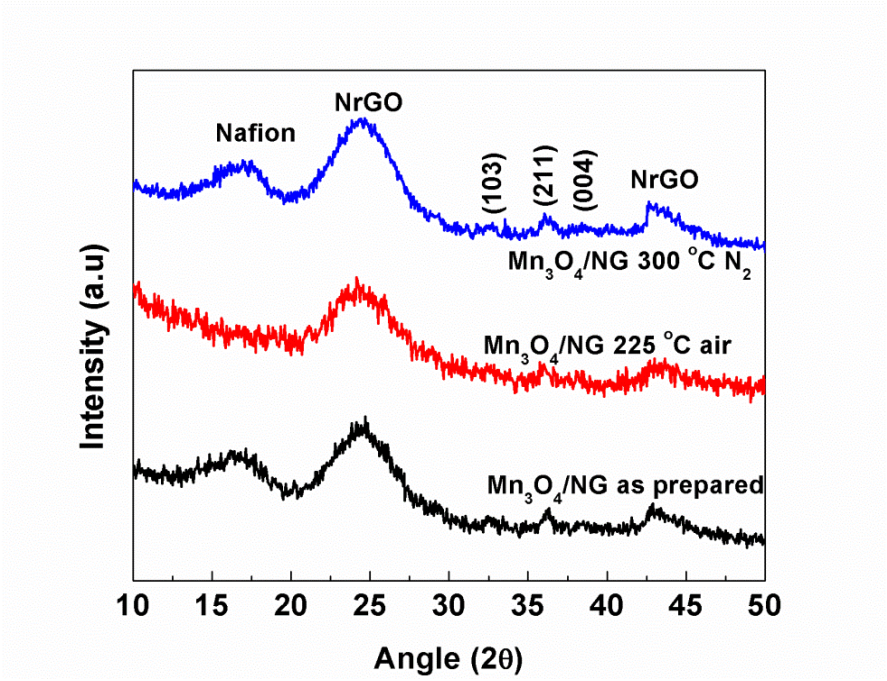

Figure S13. XRD of as prepared Mn_3O_4/NrGO and annealed Mn_3O_4/NrGO in air at 225 ^oC and Mn_3O_4/NrGO in air at 300 ^oC in nitrogen atmosphere at 300 C (blue)

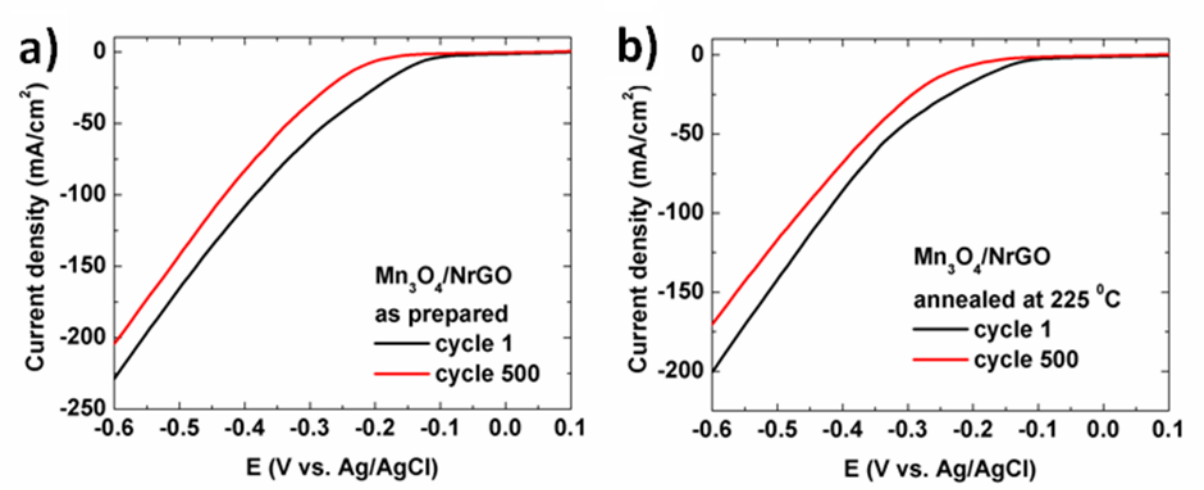

Figure S14. (a) stability of as prepared Mn_3O_4/NrGO (b) stability of annealed Mn_3O_4/NrGO at 225 ^oC in air. LSV are not subtracted from Argon saturation (Catalyst loading: 0.2 mg/cm^2).

Table S1: Fitting parameters of Nyquist Plots

	NrGO	Mn_3O_4/NrGO
Solution resistance (R_s)	60 Ω	60 Ω
CPE-T	0.0014 F	0.0020 F
CPE-P	0.87 F	0.77 F
Charge transfer resistance(R_{ct})	5 KΩ	1.2 KΩ

Table S2: Summary of ORR activities on manganese oxide/carbon published in literature.

S.No	Catalyst	Half wave potential V(vs. Ag/AgCl)	Limiting current density J(mA/cm^2)	Catalyst loading (mg/cm^2)	ref
1	Mn_3O_4/Nano-C	-0.13	4.4	0.5	18
2	Mn_3O_4/rGO-IL	-0.28	3.7	0.085	16
3	MnO_x /Ketjenblack	-0.27	7.6(3200 rpm)	0.085	17
4	MnO-m-N-C	-0.14	5.0	0.1	19
5	Cu- αMnO_2/GLC Ni-α-MnO_2/GLC	-0.24 -0.30	3.5(2500 rpm) 4.2(2500 rpm)	0.51 0.51	24
6	Mn_3O_4/C nanofiber+KB	-0.15	0.06 mA (1200 rpm)	-	26
7	Mn_2O_3/GCE	-0.21	5.4	-	31
8	Mn_3O_4/NrGO	-0.23	4.0	0.2	25
9	MnOOH/carbon	-0.11	4.5	0.2	27
10	Mn_2O_3/carbon	-0.22	0.47 mA	-	21
11	Mn_3O_4/pGC	-0.25	6.0	-	09
12	MnO_2/graphene	-0.20	3.0	0.15	20
13	Mn_3O_4/NrGO	-0.3	3.7(-0.6V)	0.1	22
14	Mn_3O_4/NrGO	-0.3	2.0	0.1	23
15	Mn_3O_4/ NrGO	-0.20	4.4	0.45	This work

*Limiting currents (I_L) were recorded at 1600 rpm; otherwise, the rotation rate is indicated in the table.

Conversion between reference electrodes

$E_{R.H.E} = E_{Ag/AgCl} + 0.95$ V (0.1 M KOH)

$E_{Hg/HgO} = E_{Ag/AgCl} + 0.05$ V (0.1 M KOH)