

## Supplementary Information for

### Porphyrin-based graphene oxide frameworks with ultra- large d-spacings for electrocatalyzation of oxygen reduction reaction

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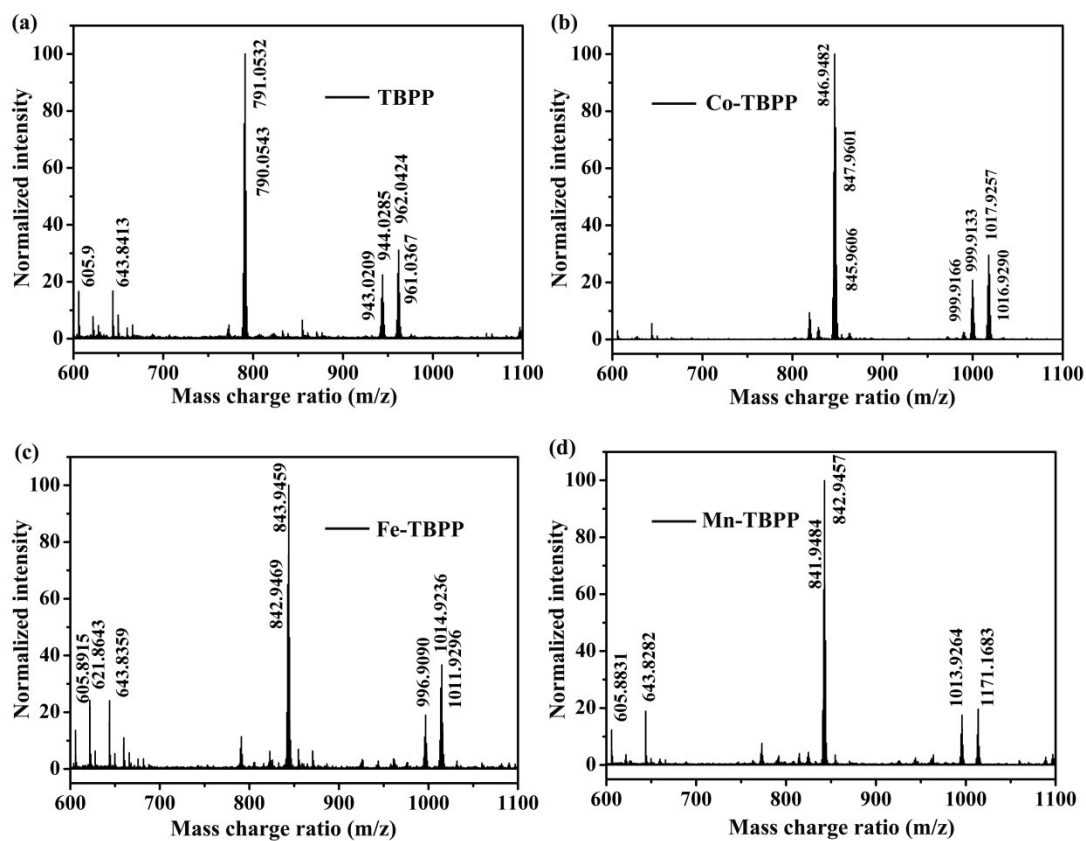
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**Table S1** Elemental atomic contents of GO, GO<sub>NH3</sub> and P-GOF calculated from their XPS spectra

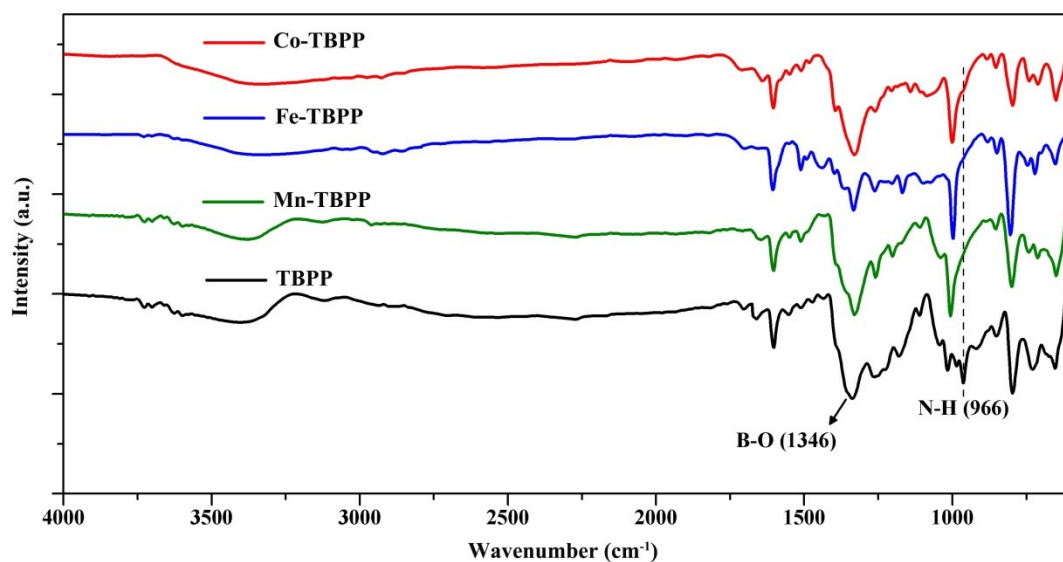
Sample	C (%)	O (%)	N (%)	B (%)
GO	65.2	33.5	0.92	0.35
GO <sub>NH3</sub>	67.9	27.9	3.86	0.31
P-GOF	68.8	25.0	4.50	2.50

**Table S2** The fitting results of the modified electrodes from EIS spectra with Randles equivalent circuits

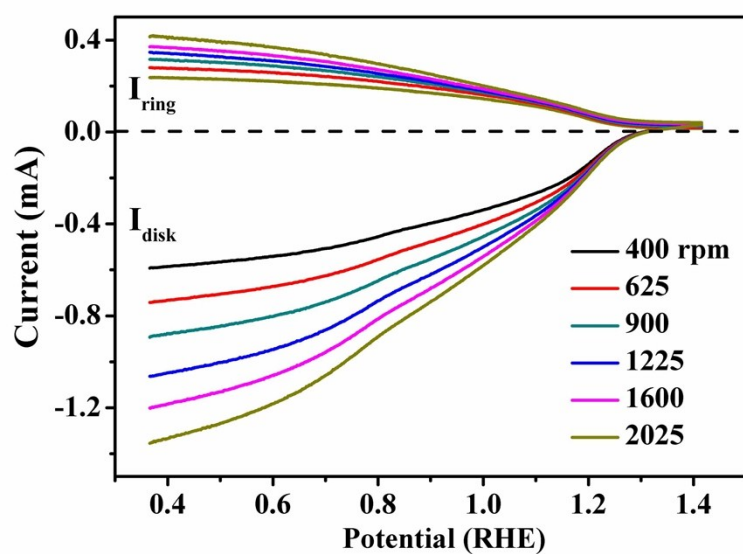
Catalysts	R <sub>Ω</sub>	R <sub>ct</sub>	CPE <sub>1</sub> (μF)	p <sub>1</sub>	CPE <sub>2</sub> (mF)	p <sub>2</sub>
P-GOF	15.90	305.1	9.4	0.862	0.520	0.387
P-rGOF	14.08	2.5	2043.0	0.477	2.860	0.190
Mn-GOF	14.53	218.0	9.3	0.858	0.459	0.338
Mn-rGOF	12.81	3.3	1960.0	0.439	2.570	0.818
Fe-GOF	14.26	229.2	7.1	0.872	0.419	0.366
Fe-rGOF	14.03	2.6	2247.0	0.461	2.570	0.827
Co-GOF	14.03	336.3	6.4	0.870	0.477	0.385
Co-rGOF	12.99	4.5	2582.0	0.741	1.450	0.530



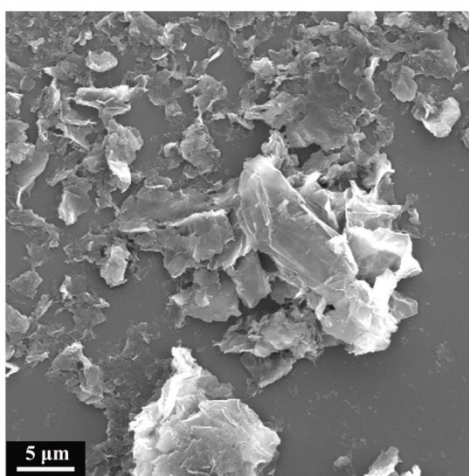
**Fig. S1** Mass spectra of (a) TBPP, (b) Co-TBPP, (c) Fe-TBPP and (d) Mn-TBPP.



**Fig. S2** IR spectra of TBPP, Co-TBPP, Fe-TBPP and Mn-TBPP indicate that MnP, FeP and CoP were obtained as evidenced by the disappearance of N-H stretch vibration at around 966 cm<sup>-1</sup>.



**Fig. S3** RRDE measurement of Co-rGOF electrode in 0.1 M NaOH solution containing 10 mM  $K_3Fe(CN)_6$  at scan rate of  $50 \text{ mV s}^{-1}$ . Collection efficiency was calculated from the equation:  $N=I_r/I_d$ .



**Fig. S4** SEM images of GO.

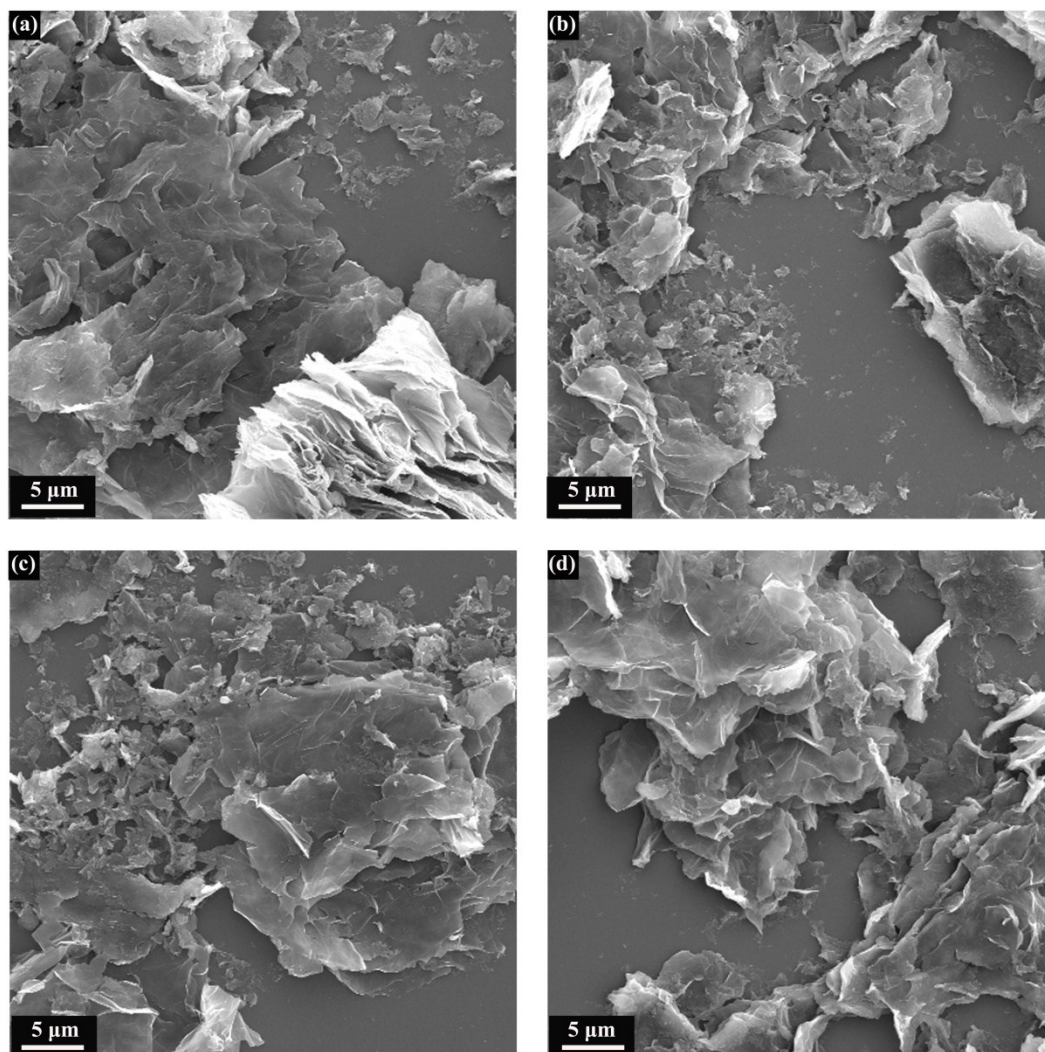


Fig. S5 SEM images of (a) P-GOF, (b) Co-GOF, (c) Fe-GOF and (d) Mn-GOF.

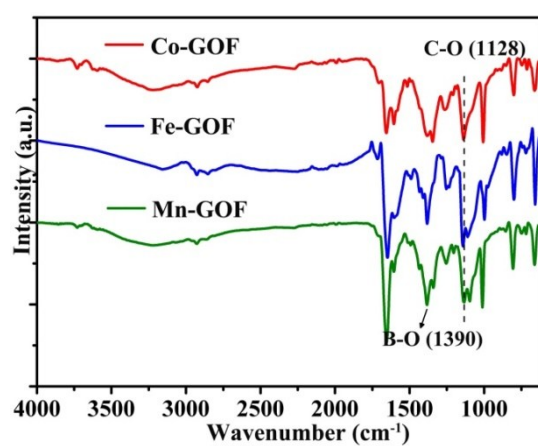
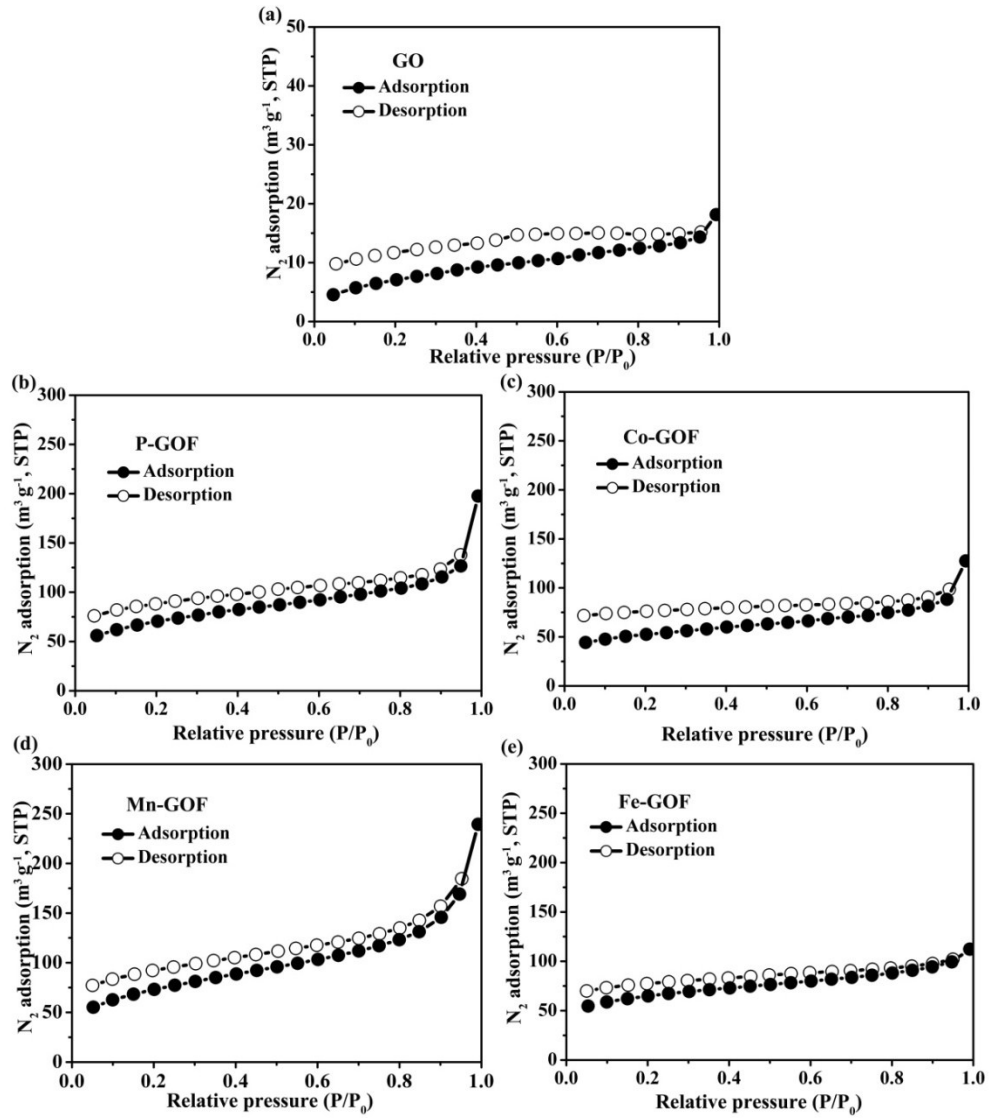
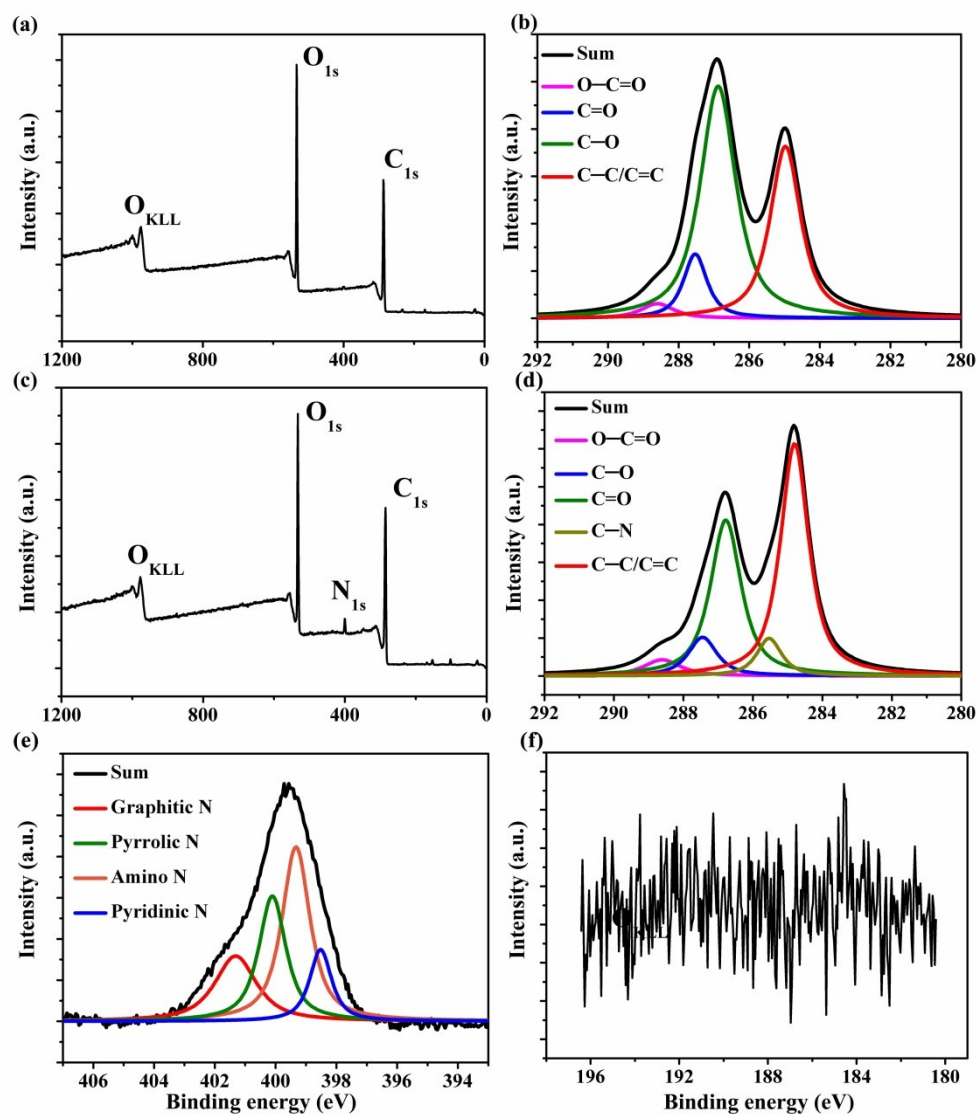


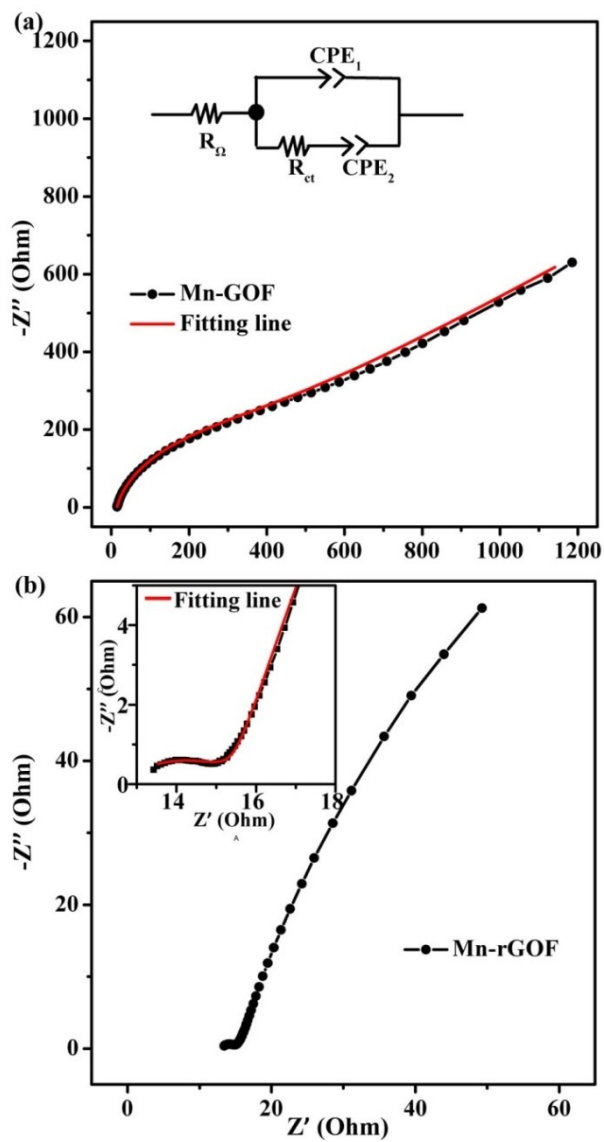
Fig. S6 IR spectra of Co- Fe- and Mn-GOFs



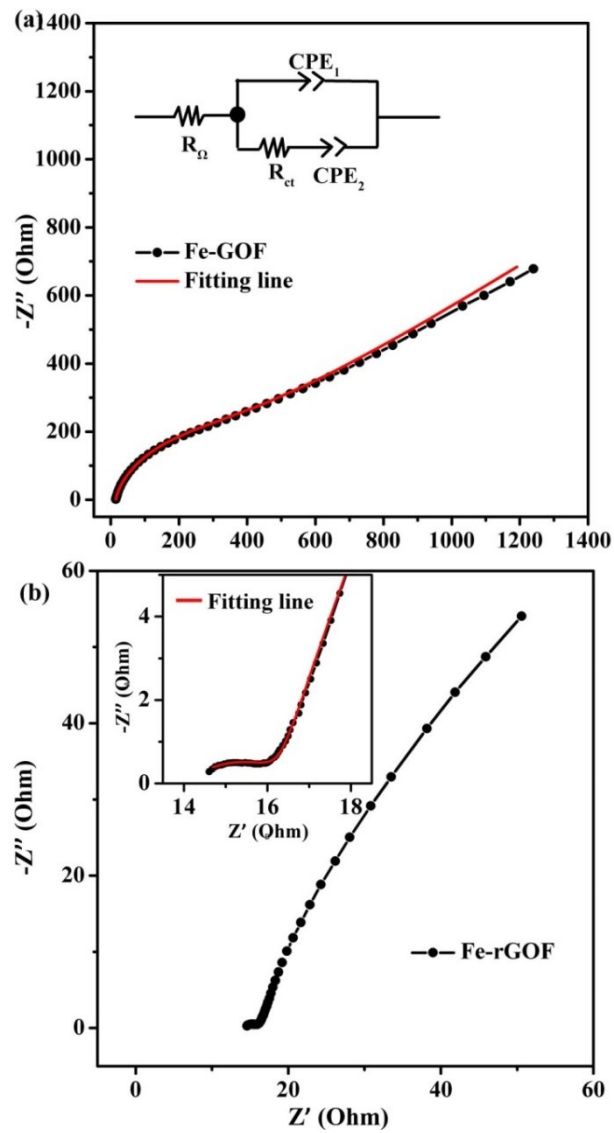
**Fig. S7**  $N_2$  adsorption and desorption of (a) GO, (b) P-GOF, (c) Co-GOF, (d) Mn-GOF, and (e) Fe-GOF.



**Fig. S8** XPS survey scan spectra (a) and  $\text{C}_{1s}$  spectra (b) of GO. XPS survey scan spectra (c),  $\text{C}_{1s}$  spectra (d),  $\text{N}_{1s}$  spectra (e) and  $\text{B}_{1s}$  spectra (f) of  $\text{GO}_{\text{NH}_3}$ .

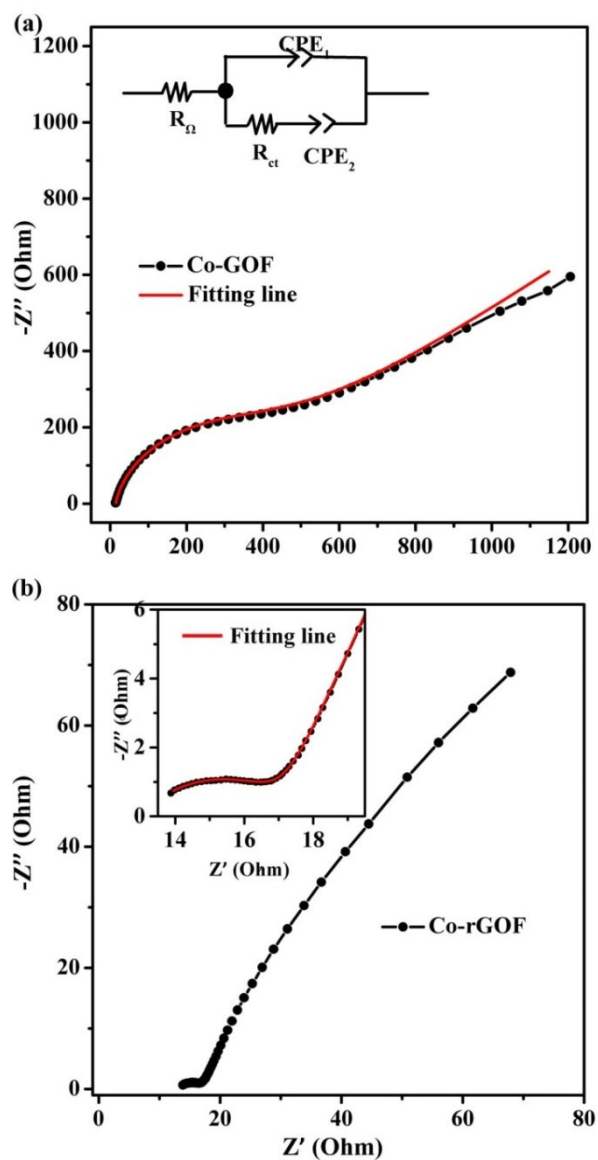


**Fig. S9** Nyquist plots of (a) Mn-GOF and (b) Mn-rGOF from  $10^5$  to 1 Hz at the open circuit potential (the red lines are fitting results).

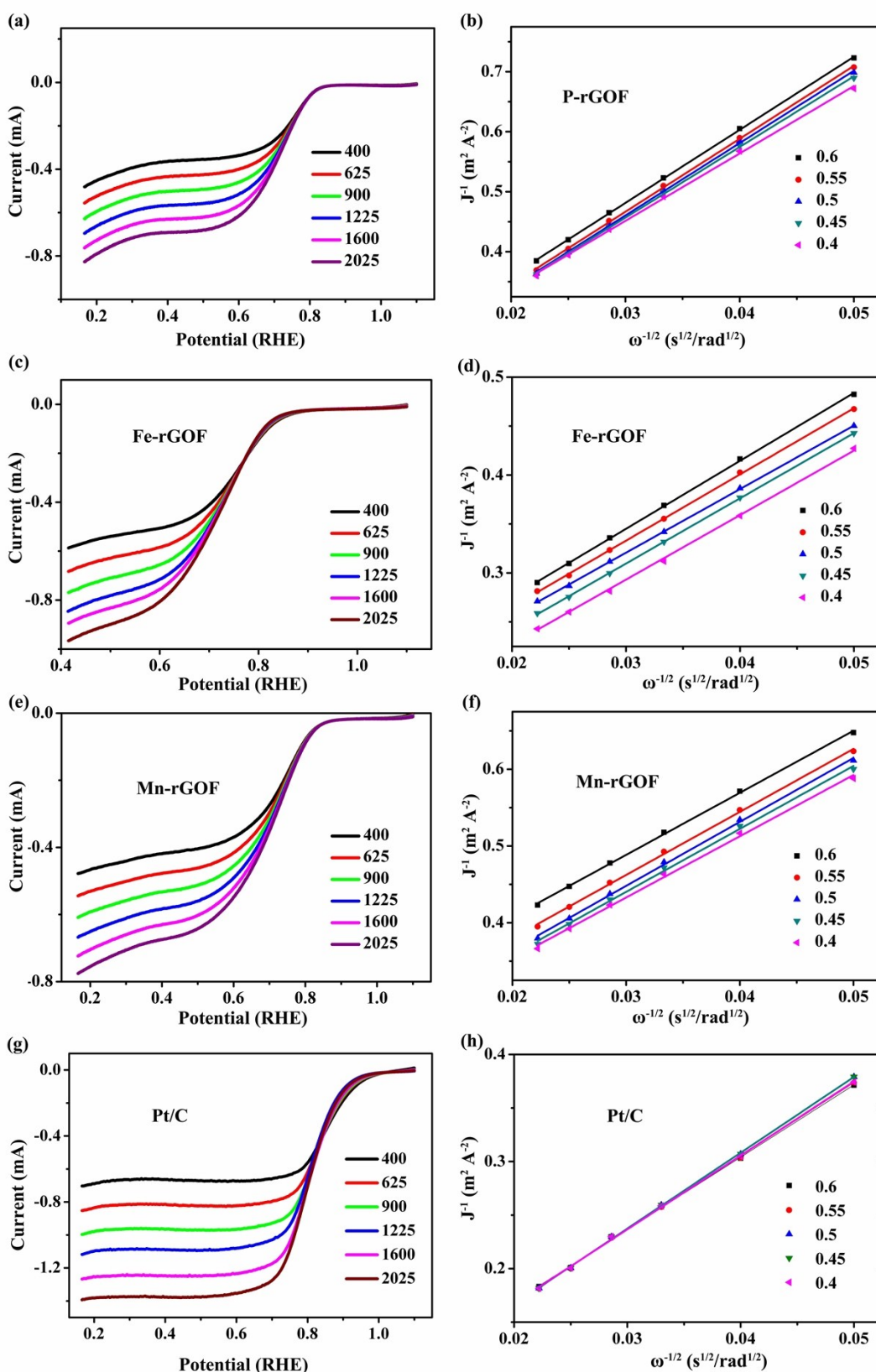


**Fig. S10** Nyquist plots of (a) Fe-GOF and (b) Fe-rGOF from  $10^5$  to 1 Hz at the open circuit potential (the red lines are fitting results).

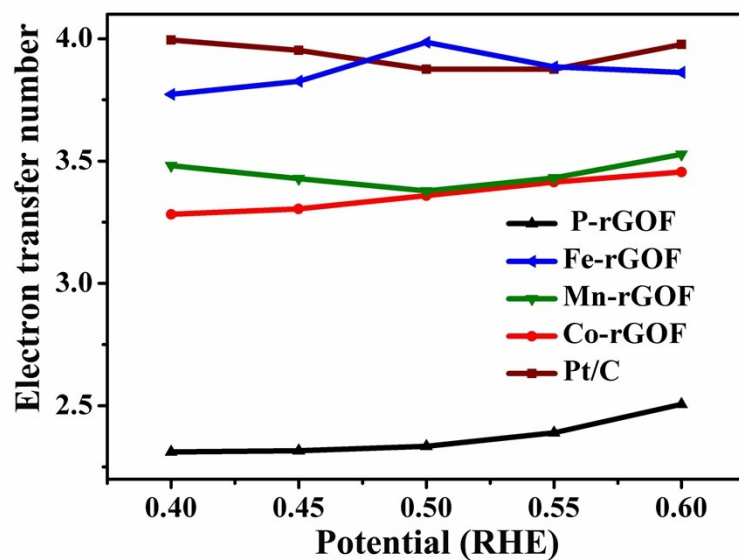




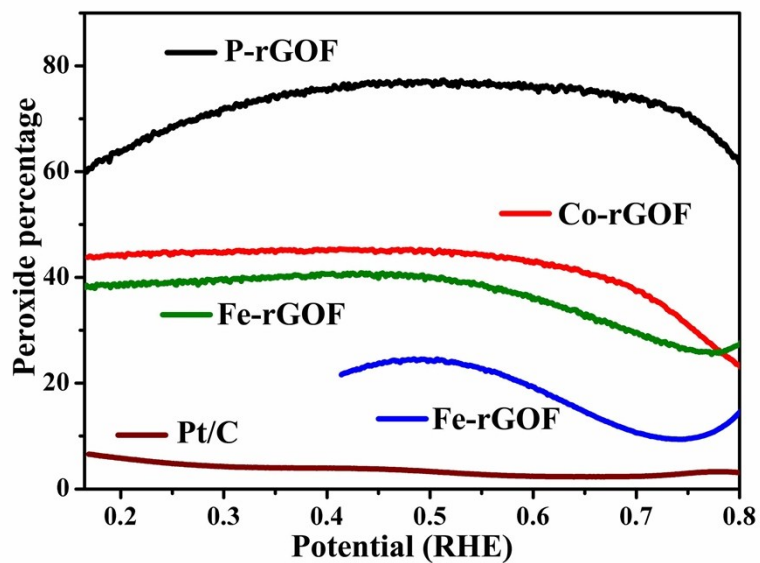
**Fig. S11** Nyquist plots of (a) Co-GOF and (b) Co-rGOF from  $10^5$  to 1 Hz at the open circuit potential (the red lines are fitting results).



**Fig. S12** RDE measurements of ORR on (a) P-rGOF, (c) Fe-rGOF, (e) Mn-rGOF and (g) Pt/C modified glassy carbon electrode in oxygen-saturated 0.1 M KOH solution with rotating speeds varying from 400 to 2025 rpm at the a scan rate of  $10 \text{ mV s}^{-1}$  and the obtained K-L plots for (b) P-rGOF, (d) Fe-rGOF, (f) Mn-rGOF and (h) Pt/C, respectively.



**Fig. S13** Plots of K-L equation derived electron transfer number versus potential on different modified electrodes.



**Fig. S14** Peroxide percentages in the ORR products on P-rGOF, Co-rGOF, Fe-rGOF, Mn-rGOF and Pt/C electrodes.