**Supporting Information** 

## High-Rate Oxygen Electroreduction over Metal-Free Graphene Foams embedding P-N coupled moieties in Acidic Media

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## Electrode preparation and electrochemical measurement.

It is reported that the oxygen adsorption induced by the self-assembly of Nafion on graphic carbon layers can potentially decrease the measured catalyst activities. <sup>S1,S2</sup> The total oxygen reduction current can be expressed as a sum of two contributions, one from oxygen diffusing from the bulk of solution and another corresponding to the surface confined oxygen. Thus, in order to find out a proper quantity of Nafion used in the preparation of the catalyst inks, which containing variable quantity of Nafion® were prepared. The ratio of the volume ( $\mu$ l) of 5% Nafion® solution to the weight (mg) of carbon-based catalyst used for the catalyst ink preparation will be denoted by R, where R = 1 corresponds to 1  $\mu$ l of the 5% Nafion® solution used for 1 mg of the carbonbased catalyst. Cyclic voltammograms were recorded for our catalysts inks containing 0.5 to 7 $\mu$ l of 5%Nafion® per 1 mg of the carbon-based catalyst (0.5 $\leq$ R $\leq$ 7) and the catalyst loading on the working electrode is 0.36 mg cm<sup>-2</sup> in 0.1 M KOH solution and 0.6 mg cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub> solution, as shown in Fig.S1



**Fig. S1**. Cyclic voltammograms recorded for the prepared P-N-GFs-HMPA mixed with various quantities of 5% Nafion® solution in  $O_2$  saturated (A) 0.1 M HClO<sub>4</sub> (B) 0.1M KOH at 10 mV s<sup>-1</sup>. The catalyst loading on the working electrode is 0.36 mg cm<sup>-2</sup> in 0.1 M KOH solution and 0.6 mg cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub> solution.

It can be seen from Fig.S1 that the increasing quantities of Nafion® solution in catalyst ink have no obvious influence on the oxygen reduction peak current density for all Nafion contents corresponding to  $R \leq 5$  in acidic or alkaline media, which suggests that the oxygen reduction processes on the catalysts P-N-GFs-HMPA may almost be a diffusion controlled process.

For preparation of the working electrode, 10 mg of as-prepared samples or commercial

Pt/C catalyst (Johnson Matthey, 20 wt % Pt) were dispersed in a mixture of 1.25 ml ethanol and 0.03 ml Nafion (5 %; R=3), and treated with an ultrasonic to obtain a homogeneous catalyst inks. Before the electrochemical measurement, a desired amount of such catalyst inks were spread on the GC electrode and dried at room temperature. In order to understand the current character of ORR produced over the prepared catalysts, we research the relationships between the peak current ( $i_p$ ) (non-faradaic charging currents was subtracted from the measured currents) and the scan rate (v), as shown in Fig. S2.



**Fig. S2.** (A) CVs of the prepared P-N-GFs-HMPA in  $O_2$  saturated 0.1 M HClO<sub>4</sub> under different scan rate, and (B) peak current density for the P-N-GFs-HMPA electrode plotted vs. the square root of the scan rate in 0.1 M HClO<sub>4</sub> solution. (C) peak current density plotted against the scan rate 0.1 M HClO4 solution. (D) CVs of the prepared P-N-GFs-HMPA in  $O_2$  saturated 0.1M KOH under different scan rate and (E) peak current density for the P-N-GFs-HMPA electrode plotted vs. the square root of the scan rate in  $O_2$  saturated 0.1M KOH under different scan rate in  $O_2$  saturated 0.1M KOH solution. (F) peak current density plotted against the scan rate in  $O_2$  saturated 0.1M KOH solution. (F) peak current density plotted against the scan rate in 0.1M KOH solution. In the electrochemical measurement, the capacitive contribution to the current, due to double layer charging, that has be subtracted from the measured currents. The catalyst loading on the working electrode is 0.36 mg cm<sup>-2</sup> in 0.1 M KOH solution and 0.6 mg cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub> solution.

These plots display an obvious linear relationship between peak current and the square root of scan rate in both acidic and alkaline electrolytes. Both plots clearly obey the Nicholson and shain equation, demonstrating that the oxygen reduction process is totally irreversible in these electrolytes. At the same time, it can also be seen that the linear dependencies of the peak current on square root of scan rate ( $v^{1/2}$ ) and the non-linear dependencies of the peak current on the scan rate (v) in Fig. S2, corresponding to the diffusion controlled process in the ORR.

All the CV, RDE and RRDE techniques for the ORR were carried out in  $O_2$ saturated 0.1 M KOH solution or 0.1 M HClO<sub>4</sub> solution, and all these date were recorded at a scan rate of 10 mV s<sup>-1</sup>. All the RDE curves were obtained at a rotation speed of 1600 rpm. The loadings of the prepared samples on the working electrode are 0.36 and 0.60 mg cm<sup>-2</sup> in  $O_2$ -saturated 0.1 M KOH and 0.1 M HClO<sub>4</sub>, respectively. The loadings of commercial Pt/C catalysts on the working electrode are 0.10 mg cm<sup>-2</sup> in both electrolytes. The onset potential reported in this work was defined when ORR current density is 3  $\mu$ A cm<sup>-2</sup> in RDE polarization curves.

Hydrogen peroxide yields and the electron transfer number (n) were calculated using the equations below:

$$n = \frac{4I_D}{I_D + I_R/N}; \text{ (Equation 1)}$$
  
% $HO_2^- = 200 \times \frac{I_R/N}{I_D + I_R/N}; \text{ (Equation 2)}$ 

where  $I_D$ ,  $I_R$  and N are the disk current, ring current and the ring collection efficiency, respectively. In this measurement, N= 0.37.

For Tafel plots, the kinetic current was determined after mass-transport correction of RDE curves by

$$J_{K} = \frac{J \times J_{L}}{J_{L} - J}$$

**Fig.S3.** Chronoamperometric responses of P-N-GFs-HMPA and commercial Pt/C with injection of 2 wt% methanol after 500s (A) in O<sub>2</sub>-saturated 0.1 M KOH; (B) in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. The current density degradation of P-N-GFs-HMPA and commercial Pt/C (C) in O<sub>2</sub>-saturated 0.1 M KOH; (D) in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. The corresponding current densities are recorded at 0.55 V in alkaline medium and 0.57 V in acidic medium at 1600 rpm with a scan rate of 10 mV s<sup>-1</sup>. The catalyst loading on the working electrode is 0.36 mg cm<sup>-2</sup> in 0.1 M KOH solution and 0.6 mg cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub> solution.



**Fig. S4.** SEM images of (A) P-GFs-TPP, (B) N-GFs-TPA, (C) N,P-GFs-TPA-TPP (D) P-N-GFs-HMPA, respectively.



**Fig. S5.** (A) N<sub>2</sub> adsorption/desorption isotherms of P-GFs-TPP, N-GFs-TPA, and N,P-GFs-TPA-TPP. The insert is the pore size distribution. (B) Roman spectra of P-GFs-TPP, N-GFs-TPA, and N,P-GFs-TPA-TPP.



**Fig. S6.** (A) XPS survey spectra of the prepared P-GFs-TPP, N-GFs-TPA, and N,P-GFs-TPA-TPP; (B) High resolution P2p XPS spectra of P-GFs-HMPA and N,P-GFs-TPA-TPP; (C) High resolution N1s XPS spectra of N-GFs-TPA and N,P-GFs-TPA-TPP; (A) FT-IR spectra for N,P-GFs-TPA-TPP.



Fig. S7. (A) CVs of the prepared P-GFs-TPP, N-GFs-TPA, and N,P-GFs-TPA-TPP. (B) RDE and (C) RRDE polarization curves of the prepared materials at 1600 rpm. (D) Calculated electron transfer number and peroxide yields based on the corresponding RRDE polarization curves. All these measurements are carried out in  $O_2$  -saturated 0.1 M HClO<sub>4</sub> with a scan rate of 10 mV s<sup>-1</sup>. The catalyst loading on the working electrode is 0.6 mg cm<sup>-2</sup> in 0.1 M HClO<sub>4</sub> solution.



**Fig. S8.** (A) CVs of the prepared P-GFs-TPP, N-GFs-TPA, and N,P-GFs-TPA-TPP. (B) RDE and (C) RRDE polarization curves of the prepared materials at 1600 rpm. (D) Calculated electron transfer number and peroxide yields based on the corresponding RRDE polarization curves. All these measurements are carried out in  $O_2$  -saturated 0.1 M KOH with a scan rate of 10 mV s<sup>-1</sup>. The catalyst loading on the working electrode is 0.36 mg cm<sup>-2</sup> in 0.1 M KOH solution.



**Fig. S9.** Tafel plots of the prepared P-GFs-TPP, N-GFs-TPA, N,P-GFs-TPA-TPP, and commercial Pt/C catalysts in O<sub>2</sub> -saturated 0.1 M KOH.



Samples			C (at%)	N (at <sup>c</sup>	%)	O (at%)	P (at%)
P-GFs-TPP			94.6	-		5.6	0.8
N-GFs-TPA			89.3	3.9		6.8	-
N,P-GFs-TPA-TPP			86.9	4.8		7.1	1.2
P-N-GFs-HMPA			83.4	6.1		8.2	2.3
Samples	P-C	P-N	P-O	pyridini	pyrrolic-	Graphiti	pyridinic-N-
	(%)	(%)	(%)	c-N(%)	N(%)	c-N(%)	O(%)
P-GFs-TPP	45.2	-	54.8	-	-	-	-
N-GFs-TPA	-	-	-	33.0	16.2	46.5	4.3
N,P-GFs- TPA-TPP	38.3	-	62.7	39.5	22.6	32.3	5.6
P-N-GFs- HMPA	28.9	49.5	21.6	43.7	23.3	26.5	6.5

**Table S1.** The surface composition and the relative content of the component elements in different catalysts evaluated from the XPS analysis.

## Reference

- S1. J. Chlistunoff, J. M. Sansiñena, J. Electroanal. Chem., 2016, 780, 134-146.
- S2. J. Chlistunoff, J. M. Sansiñena, J. Phys. Chem. C., 2016, 120, 28038-28048.