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.\textsuperscript{S1,S2} 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 (μl) 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 μl of the 5% Nafion® solution used for 1 mg of the carbon-based catalyst. Cyclic voltammograms were recorded for our catalysts inks containing 0.5 to 7μl of 5%Nafion® per 1 mg of the carbon-based catalyst (0.5≤R≤7) and the catalyst loading on the working electrode is 0.36 mg cm\textsuperscript{-2} in 0.1 M KOH solution and 0.6 mg cm\textsuperscript{-2} in 0.1 M HClO\textsubscript{4} solution, as shown in Fig.S1.

![Cyclic voltammograms](image)

**Fig. S1.** Cyclic voltammograms recorded for the prepared P-N-GFs-HMPA mixed with various quantities of 5% Nafion® solution in O\textsubscript{2} saturated (A) 0.1 M HClO\textsubscript{4} (B) 0.1M KOH at 10 mV s\textsuperscript{-1}. The catalyst loading on the working electrode is 0.36 mg cm\textsuperscript{-2} in 0.1 M KOH solution and 0.6 mg cm\textsuperscript{-2} in 0.1 M HClO\textsubscript{4} 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≤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.

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$_4$ solution, and all these data were recorded at a scan rate of 10 mV s$^{-1}$. 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$^{-2}$ in O$_2$-saturated 0.1 M KOH and 0.1 M HClO$_4$, respectively. The loadings of commercial Pt/C catalysts on the working electrode are 0.10 mg cm$^{-2}$ in both electrolytes. The onset potential reported in this work was defined when ORR current density is 3 $\mu$A cm$^{-2}$ in RDE polarization curves.

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

\[
n = \frac{4I_D}{I_D + I_R/N}; \quad \text{(Equation 1)}
\]

\[
\%\text{HO}_2^- = 200 \times \frac{I_R/N}{I_D + I_R/N}; \quad \text{(Equation 2)}
\]

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 O₂-saturated 0.1 M KOH; (B) in O₂-saturated 0.1 M HClO₄. The current density degradation of P-N-GFs-HMPA and commercial Pt/C (C) in O₂-saturated 0.1 M KOH; (D) in O₂-saturated 0.1 M HClO₄. 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⁻¹. The catalyst loading on the working electrode is 0.36 mg cm⁻² in 0.1 M KOH solution and 0.6 mg cm⁻² in 0.1 M HClO₄ 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\textsubscript{2} 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; (D) 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 O₂-saturated 0.1 M HClO₄ with a scan rate of 10 mV s⁻¹. The catalyst loading on the working electrode is 0.6 mg cm⁻² in 0.1 M HClO₄ 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 O₂-saturated 0.1 M KOH with a scan rate of 10 mV s⁻¹. The catalyst loading on the working electrode is 0.36 mg cm⁻² 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 O₂-saturated 0.1 M KOH.
Table S1. The surface composition and the relative content of the component elements in different catalysts evaluated from the XPS analysis.

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<th>Samples</th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
<th>P (at%)</th>
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<td>P-GFs-TPP</td>
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<tr>
<th>Samples</th>
<th>P-C (%)</th>
<th>P-N (%)</th>
<th>P-O (%)</th>
<th>pyridinic-N (%)</th>
<th>pyrrolic-N (%)</th>
<th>Graphitic-N (%)</th>
<th>pyridinic-N-O (%)</th>
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<td>26.5</td>
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Reference