Supporting Information

Superiority of boron, nitrogen and iron ternary doped carbonized graphene oxide–based catalyst for oxygen reduction in microbial fuel cells

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Table S1: The details of feeding raw for preparation of different catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>GO content (mg)</th>
<th>PAN content (g)</th>
<th>Mass ratio (PAN/GO)</th>
<th>H$_3$BO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFe–C</td>
<td>0</td>
<td>0.6</td>
<td>Non</td>
<td>Non</td>
</tr>
<tr>
<td>BNFe–C</td>
<td>0</td>
<td>0.6</td>
<td>Non</td>
<td>Y</td>
</tr>
<tr>
<td>BNFe–C–G1</td>
<td>10</td>
<td>0.6</td>
<td>60</td>
<td>Y</td>
</tr>
<tr>
<td>BNFe–C–G2</td>
<td>20</td>
<td>0.6</td>
<td>30</td>
<td>Y</td>
</tr>
<tr>
<td>BNFe–C–G3</td>
<td>40</td>
<td>0.6</td>
<td>15</td>
<td>Y</td>
</tr>
<tr>
<td>BNFe–C–G4</td>
<td>80</td>
<td>0.6</td>
<td>7.5</td>
<td>Y</td>
</tr>
</tbody>
</table>

Non represents H$_3$BO$_3$ was not introduced, while Y means H$_3$BO$_3$ was introduced.

Fig. S1: SEM images of PAN microsphere and the particle size distribution (insert graph).
Fig. S2 The FTIR spectrum of PAN (a) and GO/PAO (b).

Fig. S3 TEM images of GO.

Fig. S4 the images of (a) GO/PAN, (b) G/PAO and (c) BNFe–C–G.
Fig. S5 The low-magnification SEM images of BNFe–C–G.

Fig. S6 The SEM–EDS images of carbon layer in BNFe–C–G: (a) SEM image, (b) C element, (c) B element, (d) Fe element, (e) N element and (f) O element.

Fig. S7 The SEM–EDS images of graphene that introduced in BNFe–C–G: (a) SEM image, (b) C element, (c) B element, (d) Fe element, (e) N element and (f) O element.
Fig. S8 (a) the variation of C and O in different catalysts; the high-resolution XPS of nitrogen for BNFe–C–G1 (b), BNFe–C–G3 (c) and BNFe–C–G4 (d).
Fig. S9 The high-resolution XPS of Fe 2p within different catalysts.

Fig. S10 The CV curves (a) and electrochemical BET (b) of different catalysts measured by well-known Matsuda's equation. The electrolyte was a mixed solution of 5mM potassium ferrocyanide and 0.2 M Na2SO4, and the scan potential window was 0 – 0.5 V (vs. Ag/AgCl) with the scan rate of 10 mV s⁻¹.
Fig. S11 The CV curves (a) and electrochemical BET (b) of different catalysts measured by well–known Matsuda's equation. The electrolyte was a mixed solution of 5mM potassium ferrocyanide and 0.2 M Na$_2$SO$_4$, and the scan potential window was 0 – 0.5 V (vs. Ag/AgCl) with the scan rate of 10 mV s$^{-1}$.

Fig. S12 The CV curves of different catalysts in O$_2$–saturated (a) and N$_2$–saturated (b) PBS solution.
Fig. S13 The LSV curves of different catalysts in O$_2$–saturated PBS solution at different rotation speeds: (a) NFe – C, (b) BNFe – C, (c) BNFe – C – G1, (d) BNFe – C – G2, (e) BNFe – C – G3, (f) BNFe – C – G4.

Fig. S14 The EIS plots of different catalysts on RDE (electrolyte: 50 mM PBS).
Table S2 the internal resistance (Rs) and the charge transfer resistance (Rct) of different catalysts on RDE (electrolyte: 50 mM PBS).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rs (ohm)</th>
<th>Rct (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFe – C</td>
<td>125</td>
<td>38</td>
</tr>
<tr>
<td>BNFe – C</td>
<td>121</td>
<td>32</td>
</tr>
<tr>
<td>BNFe – C – G2</td>
<td>105</td>
<td>27</td>
</tr>
</tbody>
</table>

Koutecky–Levich equations:
\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}
\]

Eq. S(1)

Where, \( j \) represents the measured current density; \( \omega \) is the angular velocity of the disk (\( \omega=2\pi N \), \( N \) represents the linear rotation speed (rpm s\(^{-1}\)); \( j_L \) and \( j_k \) represent the limiting diffusion and kinetic current density, respectively; \( B \) can be determined from the slope of the Koutecky–Levich plots based on the Levich equation as follows, Eq. (2):
\[
B = 0.62nFC_0(D_0)^{2/3} \nu^{-1/6}
\]

Eq. S(2)

Where, \( n \) represents the overall number of electrons transferred in oxygen reduction; the constant 0.62 is adopted when the rotating speed is expressed in rad s\(^{-1}\); \( C_0 \) is the bulk concentration of \( O_2 \) (\( C_0=1.2 \times 10^{-3} \) mol L\(^{-1}\)); \( F \) is the Faraday constant (\( F=96,485 \) C mol\(^{-1}\)); \( \nu \) is the kinetic viscosity of the electrolyte (\( \nu=0.01 \) cm\(^2\) s\(^{-1}\) in 0.1 M PBS); and \( D_0 \) is the diffusion coefficient of \( O_2 \) in 0.1 M PBS (\( D_0 = 1.9 \times 10^{-5} \) cm\(^2\) s\(^{-1}\)).
Fig. S15 The Koutecky–Levich plots of different catalysts: (a) BNFe – C, (b) BNFe – C – G1, (c) BNFe – C – G2, (d) BNFe – C – G3, (e) BNFe – C – G4, (f) NFe – C.

Fig. S16 The electron transfer number of different catalysts calculated from Koutecky–Levich plots.
Fig. S17 The SEM image of BNFe–C–G2 after stability testing.

Fig. S18 i–t technique: the stability and resistance to poisoning of BNFe–C–G1, BNFe–C–G2, BNFe–C–G3 and BNFe–C–G4.