Supporting Information

Solution Plasma Synthesis of Boron-Carbon-Nitrogen Catalyst with Controllable Bond Structure

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Koutecky–Levich (K–L) analysis 43

\[
\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} \quad \text{(1)}
\]

\[
\frac{1}{j} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \quad \text{(2)}
\]

\[
B = 0.201 \, n \, F \, A \, C_0 \, D_o^{2/3} \, \nu^{-1/6} \omega^{1/2} \quad \text{(3)}
\]

where, \( j \) is the measured current density (mA/cm\(^2\)), \( j_k \) and \( j_L \) are the kinetic and diffusion-limiting current densities (mA/cm\(^2\)), \( \omega \) is the angular velocity of the disk in rpm, \( F \) is the Faradays constant (F = 96485 C mol\(^{-1}\)), \( n \) is the number of electrons transferred per oxygen molecule, \( C_0 \) and \( D_o \) are the oxygen bulk concentration (1.2 \times 10^{-3} mol cm\(^{-3}\)) and diffusion coefficient of O\(_2\) (1.9 \times 10^{-5} cm\(^2\) s\(^{-1}\), respectively, and \( \nu \) is the kinematic viscosity of the electrolyte (1.1 \times 10^{-2} cm\(^2\) s\(^{-1}\)).
Fig. S1 Electrochemical measurements of B/N uncoupling: (a) CV curves of the ORR in O\textsubscript{2} and N\textsubscript{2}-saturated 0.1M KOH solutions at a scan rate of 10 mV s\textsuperscript{-1}. (b) LSV curves of the ORR in O\textsubscript{2}-saturated 0.1 M KOH solution at a scan rate of 10 mV s\textsuperscript{-1} with different rotation speeds from 400 to 2500 rpm. (c) The Koutecky-Levich (K-L) plots of current density\textsuperscript{-1} versus ω\textsuperscript{-1/2} at various potentials obtained from LSV curves in an O\textsubscript{2}-saturated 0.1 M KOH solution at a scan rate of 10 mV s\textsuperscript{-1}. (d) The number of transferred electrons calculated from the slopes of the K-L plots in (c).
Fig. S2 Electrochemical measurements of B/N coupling: (a) CV curves of the ORR in O$_2$ and N$_2$-saturated 0.1M KOH solutions at a scan rate of 10 mV s$^{-1}$. (b) LSV curves of the ORR in O$_2$-saturated 0.1 M KOH solution at a scan rate of 10 mV s$^{-1}$ with different rotation speeds from 400 to 2500 rpm. (c) The Koutecky-Levich (K-L) plots of current density$^{-1}$ versus $\omega^{-1/2}$ at a various potentials obtained from LSV curves in an O$_2$-saturated 0.1 M KOH solution at a scan rate of 10 mV s$^{-1}$. (d) The number of transferred electrons calculated from the slopes of the K-L plots in (c).
**Fig. S3** Wide-field TEM images with selected-area electron diffraction (SAED) of (a) CB, (b) CN, and (c) B/N coupling. (d) SEM images of all nanocarbons.

**Fig. S4** Contrast line profiles of B/N uncoupling.
**Fig. S5** Narrow scan XPS of (a) B/N uncoupling and (b) B/N coupling for C1s. The four deconvoluted peaks in the high resolution C1s spectrum at 283.4, 284.7, 286.2 and 288.3 eV can be attributed to C-B, C=C, C-N and C-O bonds, respectively.\(^\text{13}\)

**Fig. S6** Possible schematic structure of BCN nanocarbon: (a) B/N uncoupling and (b) B/N coupling.
Table S1 Relative content of (a) B atom (b) N atom and (c) Pt atom before and after chronoamperometry test.

(a) Chemical state containing B atom (%)

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<th></th>
<th>B cluster</th>
<th>B&lt;sub&gt;4&lt;/sub&gt;C</th>
<th>BC&lt;sub&gt;3&lt;/sub&gt;</th>
<th>BC&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>BCO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>B-N</th>
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<tr>
<td>Before</td>
<td>23.2</td>
<td>8.9</td>
<td>8.9</td>
<td>25</td>
<td>14.3</td>
<td>16.1</td>
<td>3.6</td>
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<tr>
<td>After</td>
<td>5.5</td>
<td>12.7</td>
<td>12.7</td>
<td>18.2</td>
<td>25.5</td>
<td>21.8</td>
<td>3.6</td>
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(b) Chemical state containing N atom (%)

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<th></th>
<th>B-N</th>
<th>Pyridinic N</th>
<th>Pyrrolic N</th>
<th>Graphitic N</th>
<th>Oxidic N</th>
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<tr>
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<td>28.6</td>
<td>31.4</td>
<td>39.4</td>
<td>0.6</td>
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<tr>
<td>After</td>
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<td>31.3</td>
<td>31.6</td>
<td>32.6</td>
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(c) Chemical state containing Pt atom (%)

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<th>Pt&lt;sup&gt;4+&lt;/sup&gt;(4f&lt;sub&gt;5/2&lt;/sub&gt;)</th>
<th>Pt&lt;sup&gt;4+&lt;/sup&gt;(4f&lt;sub&gt;7/2&lt;/sub&gt;)</th>
<th>Pt&lt;sup&gt;2+&lt;/sup&gt;(4f&lt;sub&gt;5/2&lt;/sub&gt;)</th>
<th>Pt&lt;sup&gt;2+&lt;/sup&gt;(4f&lt;sub&gt;7/2&lt;/sub&gt;)</th>
<th>Pt&lt;sup&gt;0&lt;/sup&gt;(4f&lt;sub&gt;5/2&lt;/sub&gt;)</th>
<th>Pt&lt;sup&gt;0&lt;/sup&gt;(4f&lt;sub&gt;7/2&lt;/sub&gt;)</th>
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<tr>
<td>Before</td>
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<td>3.1</td>
<td>7.5</td>
<td>11</td>
<td>40.8</td>
<td>34.8</td>
</tr>
<tr>
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<td>5.6</td>
<td>15.8</td>
<td>20.1</td>
<td>26</td>
<td>27.9</td>
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Fig. S7 XPS narrow scan after durability experiment of (a) Pt4f of 20 wt.% Pt/C and the relative element contents before and after the chronoamperometry for (b) Pt.

Fig. S8 OES spectra of the SPP in pure pyridine for synthesis CN (nitrogen doped carbon).