Supporting information

Effect of pyrolysis gas

From the nitrogen sorption measurement, the BET surface area of the PNCEs-900-NH$_3$ (719.4 m$^2$/g) is significantly higher than that of the PNCEs-900-N$_2$ (104.08 m$^2$/g). Figure S1 displays the pore distribution of the PNCEs-900-NH$_3$ and PNCEs-900-N$_2$. The ratio of macropore and the mesoporous is significantly increased for the PNCE-N$_2$. Moreover, the micropores are significantly increased. This proves that the reactions between carbon and NH$_3$ involve the replacement of oxygen-bearing species by nitrogen-containing groups and the etching of carbon fragments by the radicals generated by the decomposition of NH$_3$ at high temperatures, which forms more pores in carbon framework.$^{[1,2]}

![Figure S1. N$_2$ sorption isotherms of the resultant PNCEs carbon catalysts prepared under different atmosphere;](image-url)
Figure S2. High resolution XPS spectra of Fe 2p N1s (a) PNCEs -1000 (b) NNCEs-1000

Table S1. Physical characteristic of the PNCEs synthesized at different temperature

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{micro}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{ext}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{micro}$ (cm$^3$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNCEs-700</td>
<td>432.7</td>
<td>334.08</td>
<td>98.6</td>
<td>0.154</td>
<td>0.329</td>
</tr>
<tr>
<td>PNCEs-800</td>
<td>528.2</td>
<td>378.4</td>
<td>149.9</td>
<td>0.173</td>
<td>0.412</td>
</tr>
<tr>
<td>PNCEs-900</td>
<td>719.4</td>
<td>497.4</td>
<td>222</td>
<td>0.228</td>
<td>0.553</td>
</tr>
<tr>
<td>PNCEs-1000</td>
<td>924.6</td>
<td>502.2</td>
<td>502.17</td>
<td>0.227</td>
<td>0.715</td>
</tr>
<tr>
<td>PNCEs-1100</td>
<td>756.6</td>
<td>263.8</td>
<td>492.7</td>
<td>0.117</td>
<td>0.518</td>
</tr>
<tr>
<td>NNCEs-1000</td>
<td>523</td>
<td>329.1</td>
<td>194.03</td>
<td>0.151</td>
<td>0.547</td>
</tr>
</tbody>
</table>

$S_{BET}$: Surface area calculated by the Brunauer-Emmet-Teller(BET) method, $S_{micro}$: micropore surface area calculated by t-plot method; $S_{ext}$: External surface area calculated by t-plot analysis; $V_{micro}$: micropore volume calculated by t-plot analysis and $V_t$: total pore volume at $P/P_0=0.995$;
Figure S3. (a) Normalized XANES of NNCEs-1000 and PNCEs-1000 with reference compounds at the Fe K-edge.

(b) Magnitudes of k3-weighted Fourier-transformed (phase-uncorrected) EXAFS data for NNCE-1000 and PNCEs-1000 with some reference compounds.

Figure S4. Oxygen reduction polarization curves for the catalysts PNCEs-1000 and 20%Pt/C in O₂-purged 0.5 M H₂SO₄; rotating rate is 1600 rpm. Scan rate=5 mV s⁻¹

Reference