Supporting Information

Unraveling the relationship between morphologies of metal-organic frameworks and properties of their derived carbon materials

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Physical and chemical characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a RigakuDmax 2500 diffractometer equipped with Cu-Kα radiation (λ= 1.54056 Å) over the 2θ range of 4-50° for MOFs and 4-80° for carbon materials with a scan speed of 3° min⁻¹ at room temperature. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ by using an SDT Q600 thermogravimetric analyser. N₂ sorption isotherms for MOFs and the derived carbon materials were measured by using a Micrometrics ASAP 2020 instrument at 77 K. Before the measurement, the samples were activated at 393 K in vacuum for 12 h. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained on a FEIT 20 instrument at an accelerating voltage of 200 kV. Raman spectra of dried samples were obtained on Lab-RAM HR800 with excitation by an argon ion laser (532 nm). Elemental analyses of C, H, and N were carried out on an ElementarVario EL III analyzer. The morphologies of MOFs were studied using a (JSM-6700F) scanning electron microscope (SEM) working at 10 KV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Kα source (15 kV, 10 mA).

Fig. S1 Size distribution of 45 nm spherical shape ZIF-7-S (from a total number of 400).
Fig. S2 Size distribution of 125 nm polyhedral shape ZIF-7-D (from a total number of 300).

Fig. S3 Rod ZIF-7-R with (a) 3\(\mu\)m in length and (b) 0.6 \(\mu\)m in diameter.
Fig. S4 PXRD patterns of ZIF-7-S, ZIF-7-D and ZIF-7-R.

Fig. S5 N$_2$ sorption isotherms of ZIF-7-S, ZIF-7-D and ZIF-7-R.
Fig. S6 Thermogravimetric analysis (TGA) of ZIF-7-S, ZIF-7-D and ZIF-7-R.

Fig. S7 Linear sweep voltammetry (LSV) curves for NC-D-700, NC-D-800 and NC-D-900 at an RDE rotation rate of 1600 rpm with a scan rate of 5 mVs$^{-1}$.

We have investigated the effect of different carbonization temperatures for NC-D-$x$ ($x = 700, 800, 900$) materials on the performance of ORR reactions. The LSV measurement results of the NC-D-$x$ prepared at different temperatures were shown in Fig. S7. NC-D-800 showed the most positive onset (0.87 V vs RHE), which was superior to NC-D-700 (0.77 V) and NC-D-900 (0.83 V), suggesting a pronounced electrocatalytic activity of NC-D-800 for ORR.
Table S1 Textural properties of ZIF-derived porous N-doped carbon materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-S-800</td>
<td>352</td>
<td>0.43</td>
</tr>
<tr>
<td>NC-D-800</td>
<td>538</td>
<td>0.41</td>
</tr>
<tr>
<td>NC-R-800</td>
<td>272</td>
<td>0.17</td>
</tr>
<tr>
<td>NC-D-NH₃</td>
<td>636</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Fig. S8 Pore size distributions of NC-S-800, NC-D-800 and NC-R-800, respectively.
Table S2 Nitrogen atom percentage of obtained porous N-doped carbon materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ncontent (wt%)</th>
<th>Ncontent (wt%)</th>
<th>pyridinic-N (%)</th>
<th>pyrrolic-N (%)</th>
<th>graphitic-N (%)</th>
<th>pyridine-N-oxide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-S-800</td>
<td>11.05</td>
<td>9.91</td>
<td>37.7</td>
<td>30.9</td>
<td>25.3</td>
<td>6.1</td>
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<tr>
<td>NC-D-800</td>
<td>10.30</td>
<td>9.42</td>
<td>39.5</td>
<td>23.3</td>
<td>30.4</td>
<td>6.8</td>
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<tr>
<td>NC-R-800</td>
<td>10.24</td>
<td>8.58</td>
<td>38.3</td>
<td>25.7</td>
<td>28.4</td>
<td>7.6</td>
</tr>
<tr>
<td>NC-D-NH₃</td>
<td>2.28</td>
<td>2.09</td>
<td>19.1</td>
<td>13.2</td>
<td>54.6</td>
<td>13.1</td>
</tr>
</tbody>
</table>

*a* Based on elemental analysis results.

*b* Based on X-ray photoelectron spectroscopy (XPS).

![Fig. S9](image-url) (a) LSV curve of NC-D-800 at different rotation rates, (b) Linear fitting curve of K-L plots.
Fig. S10 (a) LSV curve of NC-S-800 at different rotation rates, (b) Linear fitting curve of K-L plots.

Fig. S11 (a) LSV curve of NC-R-800 at different rotation rates, (b) Linear fitting curve of K-L plots.
Fig. S12 Linear sweep voltammetry (LSV) curves for NC-D-800, NC-D-NH$_3$(800) and NC-D-NH$_3$(1000) at an RDE rotation rate of 1600 rpm with a scan rate of 5 mVs$^{-1}$.

NC-D-800 was treated at 800 °C for 30 min under flowing NH$_3$ to obtain NC-D-NH$_3$(800), while treated at 1000 °C for 30 min under flowing NH$_3$ to obtain NC-D-NH$_3$(1000).

The LSV measurement results of the NC-D-NH$_3$(x) (x = 800, 1000) prepared at different temperatures were shown in Fig. S12. NC-D-NH$_3$(1000) showed the best ORR activity with the most positive onset of 1.0 V (vs RHE) and half-wave potentials of 0.82 V, which was superior to NC-D-NH$_3$(800) with positive onset of 0.89 V and half-wave potentials of 0.77 V. Furthermore, compared with the NC-D-NH$_3$(800), NC-D-NH$_3$(1000) showed higher diffusion-limiting current density of 5.65 mA cm$^{-2}$ at 0.2 V, indicating that NC-D-NH$_3$(1000) obtained at 1000 degrees with NH$_3$ atmosphere has better ORR activity.
Fig. S13 The NC-D-NH$_3$ of (a-b) SEM images with different scale bars, (c) TEM image (d) HRTEM image.

Fig. S14 (a) N$_2$ sorption isotherms and (b) pore size distributions for NC-D-NH$_3$. Solid symbols denote adsorption, open symbols denote desorption ($P/P_0$ = partial pressure).
Fig. S15 N 1s spectra of NC-D-NH$_3$ with four kinds of nitrogen species (pyridinic-N, pyrrolic-N, graphitic-N, and pyridinic-N-oxide)