Electronic Supplementary Information (ESI)

Efficient oxygen electroreduction over ordered mesoporous Co-N-doped carbon derived from cobalt porphyrin

C. Li, Z. Han, Y. Yu, Y. Zhang, B. Dong, A. Kong*, and Y. Shan*

School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, P.R. China.

E-mail: agkong@chem.ecnu.edu.cn

Content

Experimental section

Fig. S1. Calibration to reversible hydrogen electrode (RHE)

Fig. S2. (A) is the SEM image of the Co-N-GC-800 used in the EDS mapping test; (B) The overall EDS-mapping images for Co, N, O and C elements in Co-N-GC-800; (C) The Co element mapping image; (D) The N element mapping image; (E) The O element mapping image; (F) The C element mapping image.

Fig. S3. The Uv-vis diffuse reflection spectra for Co-porphyrin and Co-N-GC

Fig. S4. CVs recorded on the mesoporous materials prepared at different temperature and Pt/C in an O₂-saturated 0.1 M KOH solution;

Table S1. The physical parameters of the prepared materials

Table S2. The surface composition and the relative content of different types of doped nitrogen evaluated from the XPS analysis.

References
Experimental section

Preparation of SBA-15

Ordered mesoporous silica SBA-15 was prepared according to the previously reported method.\textsuperscript{S1,S2} In the typical preparation, P123 (4.0 g, $M_w = 5800$, Aldrich), deionized (DI) water (144 g), and HCl (160 ml, 1.6 M) was stirred at 40 °C. After P123 was completely dissolved, tetraethyl orthosilicate (8.3 g) was added in the solution, followed by stirring at 40 °C for 24 h, and then, the mixtures were transferred to a Teflon-lined autoclave and heated at 150 °C for 24 h. The resulting white precipitates were filtered, and washed with DI water, and dried at 100 °C for 24 h. Finally, mesoporous SBA-15 silica was obtained after it was further calcined at 550 °C in air for 4 h, with heating rate of 1 °C min\textsuperscript{-1}. 
The ICP measurements for Co content of Co-N-GC materials.

The metal content of each catalyst were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II). By heating treatment of Co-N-GC-700(a), Co-N-GC-800(b), Co-N-GC-900(c) at 700 °C for 30 min in an air atmosphere, with a heating rate of 3 °C min⁻¹, residue species Co₃O₄ have been obtained. The XRD patterns of these residue species have been shown as follows:

These residue species may contain some impurity such as SiO₂, which haven’t been detected by XRD analysis. The weight percentage of Co in Co-N-GC-700, Co-N-GC-800 and Co-N-GC-900 is 3.4, 3.6 and 1.8 wt% respectively.
**Fig. S1.** Calibration to reversible hydrogen electrode (RHE).

We used Ag/AgCl (3 M, KCl) electrode as the reference electrode in all measurements. It was calibrated with respect to RHE. The crossing potential at zero current was taken to be the potential for the reaction of $\text{H}^+/\text{H}_2$ reaction in a H$_2$-saturated electrolyte using the platinum wires as the working electrode and the counter electrode. Using these crossing potential in different electrolytes, all the reported potentials were calibrated to the RHE potentials according to the reported method$^{33}$. 

\[
E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.268V
\]

\[
E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.949V
\]
**Fig. S2.** (A) is the SEM image of the Co-N-GC-800 used in the EDS mapping test; (B) The overall EDS-mapping images for Co, N, O and C elements in Co-N-GC-800; (C) The Co element mapping image; (D) The N element mapping image; (E) The O element mapping image; (F) The C element mapping image.
Fig. S3. The Uv-vis diffuse reflection spectra for Co-porphyrin and Co-N-GC
Fig. S4. CVs recorded on the mesoporous materials prepared at different temperature and Pt/C in an O$_2$-saturated 0.1 M KOH solution;
Table S1. The physical parameters of the prepared materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area (m² g⁻¹)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N-GC-700</td>
<td>723</td>
<td>3.9</td>
<td>0.95</td>
</tr>
<tr>
<td>Co-N-GC-800</td>
<td>682</td>
<td>4.4</td>
<td>1.09</td>
</tr>
<tr>
<td>Co-N-GC-900</td>
<td>622</td>
<td>4.7</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Table S2. The surface composition and the relative content of different types of doped nitrogen evaluated from the XPS analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (at %)</th>
<th>N (at %)</th>
<th>O (at %)</th>
<th>Co (at %)</th>
<th>Py-N*-O* (%)</th>
<th>Py-like (%)</th>
<th>G-like (%)</th>
<th>Pyr-N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N-GC-700</td>
<td>81.9</td>
<td>8.1</td>
<td>11.3</td>
<td>0.5</td>
<td>5.5</td>
<td>32.3</td>
<td>25.9</td>
<td>36.3</td>
</tr>
<tr>
<td>Co-N-GC-800</td>
<td>83.3</td>
<td>6.8</td>
<td>9.3</td>
<td>0.6</td>
<td>5.1</td>
<td>43.3</td>
<td>27.2</td>
<td>24.4</td>
</tr>
<tr>
<td>Co-N-GC-900</td>
<td>87.2</td>
<td>3.5</td>
<td>9.1</td>
<td>0.2</td>
<td>4.1</td>
<td>38.9</td>
<td>40.7</td>
<td>16.3</td>
</tr>
</tbody>
</table>
References

