Porous Cobalt, Nitrogen-Codoped Carbon Nanostructures from Carbon Quantum Dots and VB12 and Their Catalytic Properties for Oxygen Reduction

Supporting Information

Fig. S1 (a) TEM image of CQDs. Inset is the HRTEM image of a single CQDs. (b) The particle size distribution of CQDs.

Fig. S2 Raman spectrum of CQDs.
Fig. S3 FTIR spectrum of CQDs.

Fig. S4 The molecular structure of VB12.
**Fig. S5** TEM image of pyrolyzed VB12 at 700 °C for 4h.

**Fig. S6** The high resolution N1s spectrum of (a) Co$_{1.23}$/N$_{3.05}$/C-500, (b) Co$_{1.12}$/N$_{2.92}$/C-700 and (c) Co$_{1.03}$/N$_{2.79}$/C-900.
**Fig. S7** TEM images of (a) Co$_{1.23}$/N$_{3.05}$/C-500 and (b) Co$_{1.03}$/N$_{2.90}$/C-900.

**Fig. S8** CVs of (a) Co$_0$/N$_0$/C, (b) Co$_{0.68}$/N$_{1.22}$/C, (c) Co$_{1.87}$/N$_{5.02}$/C and (d) Co$_{3.68}$/N$_{5.88}$/C in 0.1 M HClO$_4$ solution saturated with N$_2$ (red line) and O$_2$ (black line) at a scan rate of 50 mV·s$^{-1}$. 
Table S1 Finely tuned contents for Co and N.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CQDs:VB12 [mg/mg]</th>
<th>Raw materials:Products for Co concentration</th>
<th>Raw materials:Products for N concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:0</td>
<td>0:0</td>
<td>0:0</td>
</tr>
<tr>
<td>2</td>
<td>9:1</td>
<td>0.435:0.68</td>
<td>1.45:1.22</td>
</tr>
<tr>
<td>3</td>
<td>4:1</td>
<td>0.87:1.12</td>
<td>2.89:2.92</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>2.175:1.87</td>
<td>7.23:5.02</td>
</tr>
<tr>
<td>5</td>
<td>0:1</td>
<td>4.35:3.68</td>
<td>14.46:5.88</td>
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</table>

Table S2 Deconvolution results (at%) for N 1s high-resolution spectra. Compared with other samples, the Co_{1.12}/N_{2.92}/C-700 possesses the highest levels of quaternary nitrogen content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyridinic (398.5 eV)</th>
<th>Pyrrolic (399.8 eV)</th>
<th>Quaternary (401 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co_{1.22}/N_{3.06}/C-500</td>
<td>1.8</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Co_{1.12}/N_{2.92}/C-700</td>
<td>1.2</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Co_{1.03}/N_{2.79}/C-900</td>
<td>1.7</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Co_{0}/N_{0}/C-700</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Co_{0.68}/N_{1.22}/C-700</td>
<td>0.6</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Co_{1.87}/N_{5.02}/C-700</td>
<td>1.8</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Co_{3.68}/N_{5.48}/C-700</td>
<td>2.3</td>
<td>2.1</td>
<td>1.1</td>
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</table>
**Table S3** The Co, N concentrations and BET area of the samples prepared at 500 and 900 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature [°C]</th>
<th>Co concentration [%]</th>
<th>N concentration [%]</th>
<th>BET area [m²·g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>1.23</td>
<td>3.05</td>
<td>137.51</td>
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<tr>
<td>2</td>
<td>900</td>
<td>1.03</td>
<td>2.79</td>
<td>142.38</td>
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</tbody>
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**Table S4** The peak current density of ORR in 0.1 M KOH and HClO₄ solution saturated with O₂ at the scan rate of 50 mV·s⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak current density (mA·cm⁻¹)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Alkaline</td>
</tr>
<tr>
<td>Co₀/N₀/C</td>
<td>0.46</td>
</tr>
<tr>
<td>Co₀.₆₈/N₁.₂₂/C</td>
<td>0.39</td>
</tr>
<tr>
<td>Co₁.₁₂/N₂.₉₂/C</td>
<td>0.57</td>
</tr>
<tr>
<td>Co₁.₈₇/N₅.₀₂/C</td>
<td>0.55</td>
</tr>
<tr>
<td>Co₃.₆₈/N₅.₈₈/C</td>
<td>0.23</td>
</tr>
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Table S5 Various electrocatalysts for oxygen reduction reaction.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Peak potential (vs. RHE) [V]</th>
<th>Pyrolysis temperature [°C]</th>
<th>Literature</th>
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</thead>
<tbody>
<tr>
<td>Co-N-GN</td>
<td>0.781</td>
<td>---</td>
<td>S1</td>
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<tr>
<td>Co/N/rGO(NH$_3$)</td>
<td>0.626</td>
<td>850</td>
<td>S2</td>
</tr>
<tr>
<td>Co/N/C</td>
<td>0.756</td>
<td>800</td>
<td>S3</td>
</tr>
<tr>
<td>N-CoO</td>
<td>0.486</td>
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<td>S4</td>
</tr>
<tr>
<td>700°C/GC</td>
<td>0.776</td>
<td>700</td>
<td>S5</td>
</tr>
<tr>
<td>Co-N-C</td>
<td>0.766</td>
<td>900</td>
<td>S6</td>
</tr>
<tr>
<td>Co-PPy/BP</td>
<td>0.809</td>
<td>---</td>
<td>S7</td>
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<tr>
<td>Co/N/C</td>
<td>0.844</td>
<td>700</td>
<td>Our work</td>
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References


