Supplementary Information for

A Large-scale Synthesis of Heteroatom (N and S) co-doped Hierarchically Porous Carbon (HPC) Derived from Polyquaternium for Superior Oxygen Reduction Reactivity

Mingjie Wu, Jinli Qiao, Kaixi Li, Xuejun Zhou, Yuyu Liu, Jiujun Zhang

a College of Environmental Science and Engineering, Donghua University, 2999 Ren’min North Road, Shanghai 201620, P. R. China, qiaojl@dhu.edu.cn
b College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China
c Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, P. R. China
d Institute of Functional Materials, Donghua University, 2999 Ren’min North Road, Shanghai 201620, P. R. China
e Multidisciplinary Research on the Circulation of Waste Resources, Graduate School of Environmental Studies, Tohoku University, Aramaki, aza Aoba 6-6-11, Aoba-ku, Sendai 980-8579, Japan, liu@mail.kankyo.tohoku.ac.jp
f Energy, Mining & Environment, National Research Council of Canada, Vancouver, BC, Canada, Jiujun.Zhang@nrc-cnrc.gc.ca
The peroxide percentage ($\text{H}_2\text{O}_2\%$) was determined from RRDE measurements based on the disk current ($I_d$) and ring current ($I_r$) via the following equation:

$$\text{H}_2\text{O}_2\% = 100 \times \frac{2I_r/N}{I_d + I_r/N}$$

The electron transfer number ($n$) was based on the following equation:

$$n = \frac{4I_d}{I_d + I_r/N}$$

where $N = 0.36$ is the current collection efficiency of Pt ring, which is calibrated in 0.1M KOH with a 10 mM $\text{K}_3\text{Fe(CN)}_6$ electrolyte.
Fig. S1 (a) SEM image and (b) TEM image of N-S-HPC catalyst with different magnifications, showing the highly porous structures. (c) XRD pattern of N-S-HPC sample. (d) EDS spectrum of the N-S-HPC sample (Insert: composition of the N-S-HPC). (e) FT-IR spectra of N-S-HPC in the range of 4000–400 cm$^{-1}$. 

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.78</td>
</tr>
<tr>
<td>N</td>
<td>1.16</td>
</tr>
<tr>
<td>O</td>
<td>11.98</td>
</tr>
<tr>
<td>S</td>
<td>1.08</td>
</tr>
</tbody>
</table>
Fig. S2 (a) RRDE test of the ORR on N-S-HPC and Pt/C catalysts in an O$_2$-saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm; (b) Linear sweep ORR voltammetric curves for N-S-HPC catalysts obtained at different heat-treatment temperatures, measured in O$_2$-saturated 0.1 M KOH solution at a scan rate of 5 mV s$^{-1}$. 
Fig. S3 (a) Cyclic voltammograms of N-S-HPC in N₂- and O₂-saturated 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹ (100 µg cm⁻²); (b) Linear sweep voltammograms of N-S-HPC catalysts with different loadings in an O₂-saturated 0.5 M H₂SO₄ electrolyte at a rotation rate of 1500 rpm; (c) RRDE test of the ORR on N-S-HPC and Pt/C catalyst in an O₂-saturated 0.5 M H₂SO₄ electrolyte at a rotation rate of 1600 rpm. The loading was 0.5 mg cm⁻² for N-S-HPC and 0.1 mg cm⁻² for Pt/C; (d) Linear sweep voltammograms of N-S-HPC on a rotating disk electrode (1500 rpm) before and after 5000 cycles in O₂-saturated 0.1 M H₂SO₄ at a scan rate of 5 mV s⁻¹.
Fig. S4 (a) Linear sweep voltammograms of N-S-HPC on a rotating disk electrode (1500 rpm) in O$_2$-saturated 0.5 M H$_2$SO$_4$ (with and without NaSCN) at a scan rate of 5 mV s$^{-1}$. (b) Linear sweep voltammograms of N-S-HPC on a rotating disk electrode (1500 rpm) in O$_2$-saturated 0.1 M KOH (with and without NaSCN) at a scan rate of 5 mV s$^{-1}$. 
**Supplementary Table 1.** Summary of reported ORR performance of heteroatom-doped carbon catalysts (All catalysts were tested in 0.1 M KOH, rpm = 1600).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst loading (mg cm(^{-2}))</th>
<th>Half-wave potential (V vs. RHE)</th>
<th>Current density at 0.8 V (mA cm(^{-2}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meso/micro-PoPD Pt/C</td>
<td>0.1</td>
<td>0.85</td>
<td>4.32</td>
<td>Nat. Commun. 2014, 5, 4973</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.87</td>
<td>4.95</td>
<td></td>
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<tr>
<td></td>
<td>0.1</td>
<td>0.85</td>
<td>3.98</td>
<td></td>
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<tr>
<td>Hierarchically porous N-doped carbon nanoflakes</td>
<td>0.1</td>
<td>0.80</td>
<td>2.0</td>
<td>Carbon, 2014, 78, 60</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.86</td>
<td>4.5</td>
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<tr>
<td>N and S dual-doped graphene</td>
<td>0.42</td>
<td>0.67</td>
<td>&lt; 2.0</td>
<td>Adv. Mater. 2013, 25, 6226</td>
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<td>B/N co-doped carbon nanosheets</td>
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<td>0.69</td>
<td>&lt; 2.0</td>
<td>J. Mater. Chem. A, 2014, 2,7742</td>
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<tr>
<td>Pt/C</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>nitrogen-doped carbon nanosheets</td>
<td>0.6</td>
<td>0.83</td>
<td>3.2</td>
<td>Angew. Chem. Int. Ed. 2014, 53, 1570</td>
</tr>
<tr>
<td>Carbon nanotube–graphene (NT–G) complexes</td>
<td>0.485</td>
<td>0.87</td>
<td>5.0</td>
<td>Nat Nanotechnol. 2012, 7, 394</td>
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<tr>
<td>Cobalt Porphyrin-Based Conjugated Mesoporous Polymers</td>
<td>0.6</td>
<td>0.64</td>
<td>4.8</td>
<td>Adv. Mater. 2014, 26, 1450</td>
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<tr>
<td>Pt/C</td>
<td>0.15</td>
<td>0.80</td>
<td>2.5</td>
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<td>Heteroatom (N and S) co-doped hierarchically porous carbons (N-S-HPC)</td>
<td>0.1</td>
<td>0.83</td>
<td>4.1</td>
<td>This work</td>
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<tr>
<td></td>
<td>0.5</td>
<td>0.87</td>
<td>5.8</td>
<td></td>
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<tr>
<td></td>
<td>0.1</td>
<td>0.82</td>
<td>3.42</td>
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**Supplementary Table 2.** Summary of reported ORR performance of heteroatom-doped carbon catalysts (All catalysts were tested in 0.5 M H$_2$SO$_4$, rpm = 1600).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst loading (mg cm$^{-2}$)</th>
<th>Half-wave potential (V vs. RHE)</th>
<th>Current density at 0.5 V (mA cm$^{-2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meso/micro-PoPD</td>
<td>0.5</td>
<td>0.71</td>
<td>3.8</td>
<td>Nat. Commun. <strong>2014</strong>, 5, 4973</td>
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<td>Hierarchically porous N-doped carbon nanoflakes</td>
<td>0.25</td>
<td>0.47</td>
<td>4.5</td>
<td>Carbon, <strong>2014</strong>, 78, 60</td>
</tr>
<tr>
<td>Mesoporous Fe-N-Doped Carbon Nanofibers</td>
<td>0.6</td>
<td>0.58</td>
<td>3.7</td>
<td>Angew. Chem. Int. Ed. <strong>2015</strong>, 54, 8179</td>
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<tr>
<td>Cobalt Porphyrin-Based Conjugated Mesoporous Polymers Pt/C</td>
<td>0.6</td>
<td>0.64</td>
<td>4.8</td>
<td>Adv. Mater. <strong>2014</strong>, 26, 1450</td>
</tr>
<tr>
<td>Nitrogen-doped carbon nanosheets</td>
<td>0.6</td>
<td>0.56</td>
<td>3.5</td>
<td>Angew. Chem. Int. Ed. <strong>2014</strong>, 53, 1570</td>
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<td>Carbon nanotube–graphene (NT–G) complexes</td>
<td>0.485</td>
<td>0.76</td>
<td>5.6</td>
<td>Nat Nanotechnol. 2012, 7, 394</td>
</tr>
<tr>
<td>Heteroatom (N and S) co-doped hierarchically porous carbons (N-S-HPC)</td>
<td><strong>0.5</strong></td>
<td><strong>0.71</strong></td>
<td><strong>6.2</strong></td>
<td>This work</td>
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<tr>
<td>Pt/C</td>
<td><strong>0.8</strong></td>
<td><strong>0.73</strong></td>
<td><strong>6.9</strong></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td><strong>0.1</strong></td>
<td><strong>0.73</strong></td>
<td><strong>5.3</strong></td>
<td>This work</td>
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</tbody>
</table>
**Supplementary Table 3:** Peak power density of primary Zn-air batteries with several key parameters extracted from literatures.

<table>
<thead>
<tr>
<th>ORR catalyst used</th>
<th>Zn electrode/electrolyte</th>
<th>Current Density @ V = 1.0 V (mA cm(^{-2}))</th>
<th>Peak power density (mW cm(^{-2}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO/N-CNT</td>
<td>Zn foil/6 M KOH</td>
<td>197</td>
<td>265</td>
<td><em>Nat Commun.</em> 2013, 4, 1805</td>
</tr>
<tr>
<td>MnOx/Ketjenblack carbon</td>
<td>Zn powders/6 M KOH</td>
<td>120</td>
<td>190</td>
<td><em>Nano Lett.</em> 2011, 11, 5362</td>
</tr>
<tr>
<td>MnOx/C</td>
<td>zinc plate/6 M KOH</td>
<td>97</td>
<td>122</td>
<td><em>Int J Hydrogen Energ.</em> 2014, 39, 3423</td>
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<tr>
<td>Mn(_3)O(_4)/Graphene</td>
<td>zinc plate/6 M KOH</td>
<td>70</td>
<td>120</td>
<td><em>Energy Environ. Sci.</em> 2011, 4, 4148</td>
</tr>
<tr>
<td>α-MnO(_2)/XC72</td>
<td>zinc plate/6 M KOH</td>
<td>40</td>
<td>67.5</td>
<td><em>J of Power Sources</em> 2011, 6, 108</td>
</tr>
<tr>
<td>N-doped CNTs</td>
<td>zinc plate/6 M KOH</td>
<td>50</td>
<td>69.5</td>
<td><em>Electrochim. Acta</em> 2011, 56, 5080</td>
</tr>
<tr>
<td>N-doped porous carbon nanofibers</td>
<td>zinc plate/6 M KOH</td>
<td>150</td>
<td>194</td>
<td><em>J. Power Sources</em> 2013, 243, 267</td>
</tr>
<tr>
<td>N-S-HPC</td>
<td>zinc plate/6 M KOH</td>
<td>317</td>
<td>536</td>
<td>This work</td>
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</table>