A dual-template strategy to engineer hierarchically porous Fe-N-C electrocatalyst for high-performance cathode of Zn-air batteries

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Fig. S1 SEM images of (a) Fe-N-HPC, (b) Fe-N-C(Z) and (c) Fe-N-C(M).
Fig. S2 TEM images of Fe-N-C(M).
**Fig. S3** (a) TEM and (b) HRTEM images of Fe-N-C(Z).
Fig. S4 The XRD patterns of (a) Fe-N-C(Z), (b) Fe-N-C(M) and (c) Fe-N-HPC before acid etching.
Fig. S5 XPS survey spectrum of Fe-N-C(Z), Fe-N-C(M) and Fe-N-HPC.
**Fig. S6** High-resolution C1s XPS spectra of Fe-N-C(Z), Fe-N-C(M) and Fe-N-HPC.
Fig. S7 High-resolution Fe2p XPS spectra of Fe-N-C(Z), Fe-N-C(M) and Fe-N-HPC.
Fig. S8 CV curves of Fe-N-C(Z), Fe-N-C(M) and Fe-N-HPC in O₂-saturated and N₂-saturated 0.1 M KOH solution, respectively.
Fig. S9 Electrochemical impedance spectroscopy (EIS) of Fe-N-C(Z), Fe-N-C(M) and Fe-N-HPC in 0.1 M KOH.
Fig. S10 CV curves of (a) Fe-N-C(Z), (b) Fe-N-C(M) and (c) Fe-N-HPC, respectively, at various scan rates (5 mV/s, 10 mV/s, 15 mV/s, 20 mV/s and 25 mV/s). (d) Plots of the extraction of the $C_{dl}$ from CV curves at various scan rates.
Fig. S11 The $j_K$@0.90 V with respect to $C_{dl}$ for Fe-N-C(Z), Fe-N-C(M) and Fe-N-HPC in 0.1 M KOH.
**Fig. S12** Chronoamperometric responses of Fe-N-HPC and 20% Pt/C at 0.75 V in O$_2$-saturated 0.1 M KOH followed by adding methanol.
Fig. S13 ORR polarization curves of 20% Pt/C before and after 10 000 potential cycles in alkaline media.
Fig. S14 ORR polarization curves of 20% Pt/C before and after 5 000 potential cycles in acidic media.
Fig. S15 (a) Structure of Pt(111) plane and the adsorption configurations of the ORR intermediates on the surface of Pt(111) plane where dark cyan, red, and white balls represent platinum, oxygen, and hydrogen atoms, respectively; * denotes the adsorption state. Free energy diagrams of ORR on Pt(111) plane in (b) alkaline and (c) acidic media.
Fig. S16 Galvanostatic discharge curves at 10 mA cm$^{-2}$ of Zn-air batteries employing Fe-N-HPC and Pt/C as the cathode catalysts.
Fig. S17 Charge/discharge curves of the Zn-air battery using Fe-N-HPC catalyst at a current density of 10 mA cm$^{-2}$ (20 min per cycle).
Fig. S18 A digital image of the as-prepared flexible PVA gel film.
Table S1. The content of C, N, O and Fe of the prepared catalysts obtained from XPS.

<table>
<thead>
<tr>
<th></th>
<th>Atomic Concentration %</th>
<th>Mass Concentration %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>Fe-N-C(Z)</td>
<td>94.97</td>
<td>1.10</td>
</tr>
<tr>
<td>Fe-N-C(M)</td>
<td>87.90</td>
<td>2.88</td>
</tr>
<tr>
<td>Fe-N-HPC</td>
<td>90.23</td>
<td>3.93</td>
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</table>
Table S2. The content of different types of N (%) for the prepared catalysts obtained from XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyridinic N</th>
<th>Fe-N</th>
<th>Pyrrolic N</th>
<th>Graphitic N</th>
<th>Oxidized N</th>
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<tbody>
<tr>
<td>Fe-N-C(Z)</td>
<td>16.2</td>
<td>14.3</td>
<td>22.5</td>
<td>25.8</td>
<td>21.2</td>
</tr>
<tr>
<td>Fe-N-C(M)</td>
<td>13.8</td>
<td>14.7</td>
<td>21.5</td>
<td>33.9</td>
<td>16.1</td>
</tr>
<tr>
<td>Fe-N-HPC</td>
<td>18.7</td>
<td>18.0</td>
<td>16.4</td>
<td>30.3</td>
<td>16.6</td>
</tr>
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</table>
Table S3. A comparison table of the ORR performance between this work and recently reported Fe-N-C catalysts in alkaline and acidic media.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_{1/2}$ (V) vs. RHE in 0.1 M KOH</th>
<th>$E_{1/2}$ (V) vs. RHE in 0.1 M HClO$_4$ or 0.5 M H$_2$SO$_4$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N-HPC</td>
<td>0.910</td>
<td>0.800 (HClO$_4$)</td>
<td>This work</td>
</tr>
<tr>
<td>Fe-N-C</td>
<td>0.82</td>
<td>0.54 (HClO$_4$)</td>
<td>J. Mater. Chem. A, 2017, 5, 3336-3345.</td>
</tr>
<tr>
<td>Fe$_3$C/NG-800</td>
<td>0.86</td>
<td>0.77 (HClO$_4$)</td>
<td>Adv. Mater., 2015, 27, 2521-2527.</td>
</tr>
<tr>
<td>SA-Fe-NHPC</td>
<td>0.93</td>
<td>0.76 (HClO$_4$)</td>
<td>Adv. Mater. 2020, 1907399</td>
</tr>
<tr>
<td>Fe-N/C-700</td>
<td>0.84</td>
<td>0.672 (HClO$_4$)</td>
<td>Small, 2016, 12, 5710-5719.</td>
</tr>
<tr>
<td>Fe-Phen-N-800</td>
<td>0.86</td>
<td>0.71 (HClO$_4$)</td>
<td>J. Mater. Chem. A, 2016, 4, 19037-19044.</td>
</tr>
<tr>
<td>Fe-N-CNT/PC</td>
<td>0.88</td>
<td>0.79 (HClO$_4$)</td>
<td>J. Am. Chem. Soc., 2016, 138, 15046-15056</td>
</tr>
<tr>
<td>FePhen@MOF-ArNH3</td>
<td>0.86</td>
<td>0.79 (HClO$_4$)</td>
<td>Nat. Commun., 2015, 6, 7343.</td>
</tr>
<tr>
<td>Fe SA/NPCs</td>
<td>0.83</td>
<td>0.77 (H$_2$SO$_4$)</td>
<td>Appl. Catal. B Environ., 2020, 278, 119270</td>
</tr>
<tr>
<td>Sample</td>
<td>Activity</td>
<td>Selectivity</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------</td>
<td>-------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>SA-Fe-N-1.5-800</td>
<td>0.910</td>
<td>0.812 (H$_2$SO$_4$)</td>
<td>Adv. Energy Mater. 2018, 1801226</td>
</tr>
<tr>
<td>Fe-N/MPC2</td>
<td>0.88</td>
<td>0.70 (H$_2$SO$_4$)</td>
<td>Appl. Catal. B Environ., 2017, 205, 637-653</td>
</tr>
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</table>
Table S4. A summary of the performance of liquid and all-solid-state Zn-air batteries with M-N-C cathode catalysts.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Liquid Zn-air batteries</th>
<th>All-solid-state Zn-air batteries</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak power density (mW cm(^{-2}))</td>
<td>Specific capacity (mAh·g(_{Zn})(^{-1}))</td>
<td>Energy density (Wh kg(_{Zn})(^{-1}))</td>
</tr>
<tr>
<td>Fe-N-HPC</td>
<td>164.8</td>
<td>735.2</td>
<td>952.8</td>
</tr>
<tr>
<td>Fe-N-C/N-OMC</td>
<td>113</td>
<td>711</td>
<td>—</td>
</tr>
<tr>
<td>FeCo-N-C-700</td>
<td>150</td>
<td>518</td>
<td>—</td>
</tr>
<tr>
<td>NGM-Co</td>
<td>152</td>
<td>750</td>
<td>840</td>
</tr>
<tr>
<td>Fe-N-C-(PANI+CM+g-C(_3)N(_4))</td>
<td>120</td>
<td>686</td>
<td>—</td>
</tr>
<tr>
<td>SilkNC/KB</td>
<td>91.2</td>
<td>614.7</td>
<td>727.6</td>
</tr>
</tbody>
</table>

References:
- J. Mater. Chem. A, 2020, 8, 9355-9363
- J. Mater. Chem. A, 2020, 8, 7273
<table>
<thead>
<tr>
<th>Sample</th>
<th>s (°)</th>
<th>d-spacing (Å)</th>
<th>Bond Length (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe@C-NG/NCNTs</td>
<td>101.3</td>
<td>682.6</td>
<td>764.5</td>
<td>J. Mater. Chem. A, 2018, 6, 516-526</td>
</tr>
<tr>
<td>FeNC-1000</td>
<td>55</td>
<td>680</td>
<td>—</td>
<td>ACS Appl. Mater. Interfaces, 2018, 10, 10778-10785</td>
</tr>
</tbody>
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