Electronic Supplementary Information for

A general dual-templating approach to biomass-derived hierarchically porous heteroatom-doped carbon materials for enhanced electrocatalytic oxygen reduction

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Fig. S1 High-resolution TEM image of N_{0.54-Z_3/M_1-900}.

Fig. S2 XRD pattern of N_{0.54-Z_3/M_1-900}.
Fig. S3 Raman spectrum of N_{0.54}-Z_3/M_{1-900}.

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**Fig. S10** FESEM images of hierarchically porous heteroatom-doped carbon materials derived from (a) cirsium setosum leaves, (b) lavender flowers, (c) mother chrysanthemum leaves, (d) stigma of corn, (e) bamboo fungus, (f) felon herb, (g) rabdosia rubescens stems, (h) rhus typhina fruit, (i) kowkui leaves, (j) loofah fruit, (k) mother chrysanthemum flowers, (l) peanut leaves, (m) honeysuckle flowers, (n) chili and (o) malachium aquaticum leaves.
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Fig. S12 N$_2$ sorption isotherms of hierarchically porous heteroatom-doped carbon materials derived from (a) cirsium setosum leaves, (b) lavender flowers, (c) mother chrysanthemum leaves, (d) stigma of corn, (e) bamboo fungus, (f) felon herb, (g) rabdosia rubescens stems, (h) rhus typhina fruit, (i) kowkui leaves, (j) loofah fruit, (k) mother chrysanthemum flowers, (l) peanut leaves, (m) honeysuckle flowers, (n) chili and (o) malachium aquaticum leaves.
Fig. S13 Pore size distributions of hierarchically porous heteroatom-doped carbon materials derived from (a) cirsium setosum leaves, (b) lavender flowers, (c) mother chrysanthemum leaves, (d) stigma of corn, (e) bamboo fungus, (f) felon herb, (g) rabdosia rubescens stems, (h) rhus typhina fruit, (i) kowkui leaves, (j) loofah fruit, (k) mother chrysanthemum flowers, (l) peanut leaves, (m) honeysuckle flowers, (n) chili and (o) malachium aquaticum leaves.
Fig. S14 CV curves of (a) N_{0.54}-Z_{3}/M_{1}-900, (b) N_{0.54}-Z_{3}/M_{0}-900, (c) N_{0.54}-Z_{0}/M_{1}-900, (d) N_{0.54}-Z_{0}/M_{0}-900 and (e) N_{0}-Z_{0}/M_{0}-900 modified electrodes in the double-layer region at scan rates of 10, 20, 30, 40 and 50 mV s\(^{-1}\) in 0.1 M KOH aqueous electrolyte; (f) current density (taken at the potential of 1.115 V) as a function of scan rate derived from (a) to (e).
Fig. S15 (a) FESEM image, (b) TEM image, (c) N\textsubscript{2} sorption isotherms, (d) pore size distribution, (e) XPS survey and (f) N 1s spectra of N\textsubscript{0.27-}Z\textsubscript{3}/M\textsubscript{1-900}. 
**Fig. S16** (a) FESEM image, (b) TEM image, (c) N$_2$ sorption isotherms, (d) pore size distribution, (e) XPS survey and (f) N 1s spectra of N$_{1.05}$-Z$_3$/M$_1$-900.

**Fig. S17** LSV curves of N$_{0.27}$-Z$_3$/M$_1$-900 and N$_{1.05}$-Z$_3$/M$_1$-900.
Fig. S18 (a) FESEM image, (b) TEM image, (c) N$_2$ sorption isotherms, (d) pore size distribution, (e) XPS survey and (f) N 1s spectra of N$_{0.54}$-Z$_3$/M$_{0.5}$-900.
Fig. S19 (a) FESEM image, (b) TEM image, (c) $\text{N}_2$ sorption isotherms, (d) pore size distribution, (e) XPS survey and (f) $\text{N}$ 1s spectra of $\text{N}_{0.54}$-$\text{Z}_3$/M$_{1.5}$-900.
Fig. S20 (a) FESEM image, (b) TEM image, (c) N\textsubscript{2} sorption isotherms, (d) pore size distribution, (e) XPS survey and (f) N 1s spectra of N\textsubscript{0.54}-Z\textsubscript{2}/M\textsubscript{1}-900.
Fig. S21 (a) FESEM image, (b) TEM image, (c) N$_2$ sorption isotherms, (d) pore size distribution, (e) XPS survey and (f) N 1s spectra of N$_{0.54}$-Z$_{4}$/M$_{1}$-900.
Fig. S22 LSV curves of $N_{0.54-Z3/M0.5-900}$, $N_{0.54-Z3/M1.5-900}$, $N_{0.54-Z2/M1-900}$ and $N_{0.54-Z4/M1-900}$.

Fig. S23 (a) FESEM and (b) TEM images of the $N_{0.54-Z3/M1-900}$ sample after the stability test for 24 h.
Fig. S24 LSV curves of hierarchically porous heteroatom-doped carbon materials derived from (a) carrots, (b) Chinese yam stems, (c) ginkgo leaves, (d) tung flowers, (e) long beans, (f) cirsium setosum leaves, (g) lavender flowers, (h) mother chrysanthemum leaves, (i) stigma of corn, (j) bamboo fungus, (k) felon herb, (l) rabdosia rubescens stems, (m) rhus typhina fruit, (n) kowkui leaves, (o) loofah fruit, (p) mother chrysanthemum flowers, (q) peanut leaves, (r) honeysuckle flowers, (s) chili and (t) malachium aquaticum leaves.
Fig. S25 Koutecky-Levich plots ($j^{-1} \text{ vs. } \omega^{-1/2}$) from the LSV curves (Fig. S24) of hierarchical porous heteroatom-doped carbon materials derived from (a) carrots, (b) Chinese yam stems, (c) ginkgo leaves, (d) tung flowers, (e) long beans, (f) cirsium setosum leaves, (g) lavender flowers, (h) mother chrysanthemum leaves, (i) stigma of corn, (j) bamboo fungus, (k) felon herb, (l) rabdosia rubescens stems, (m) rhus typhina fruit, (n) kowkui leaves, (o) loofah fruit, (p) mother chrysanthemum flowers, (q) peanut leaves, (r) honeysuckle flowers, (s) chili and (t) malachium aquaticum leaves.
Table S1. Structural and compositional information and electrocatalytic performance of different Nₓ-Zᵧ/Mz-T samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET}^a (m² g⁻¹)</th>
<th>V_{total}^b (ml g⁻¹)</th>
<th>d_{average}^c (nm)</th>
<th>N content^d (at.%)</th>
<th>V_{onset}^e (V)</th>
<th>V_{half-wave}^f (V)</th>
<th>j^g (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₀-Z₀/M₀-900</td>
<td>630</td>
<td>0.28</td>
<td>1.78</td>
<td>0</td>
<td>0.78</td>
<td>0.574</td>
<td>1.8</td>
</tr>
<tr>
<td>N₀.54-Z₀/M₀-900</td>
<td>420</td>
<td>0.22</td>
<td>2.12</td>
<td>1.24</td>
<td>0.90</td>
<td>0.620</td>
<td>1.7</td>
</tr>
<tr>
<td>N₀.54-Z₀/M₁-900</td>
<td>797</td>
<td>1.00</td>
<td>5.05</td>
<td>2.98</td>
<td>0.91</td>
<td>0.806</td>
<td>3.0</td>
</tr>
<tr>
<td>N₀.54-Z₃/M₀-900</td>
<td>1255</td>
<td>0.76</td>
<td>2.43</td>
<td>2.89</td>
<td>0.94</td>
<td>0.820</td>
<td>3.3</td>
</tr>
<tr>
<td>N₀.54-Z₃/M₁-900</td>
<td>1394</td>
<td>0.96</td>
<td>2.77</td>
<td>3.62</td>
<td>0.94</td>
<td>0.824</td>
<td>4.3</td>
</tr>
<tr>
<td>N₀.27-Z₃/M₁-900</td>
<td>1689</td>
<td>1.20</td>
<td>2.86</td>
<td>1.56</td>
<td>0.92</td>
<td>0.784</td>
<td>3.6</td>
</tr>
<tr>
<td>N₁.05-Z₃/M₁-900</td>
<td>1952</td>
<td>1.64</td>
<td>3.36</td>
<td>3.66</td>
<td>0.93</td>
<td>0.800</td>
<td>4.3</td>
</tr>
<tr>
<td>N₀.54-Z₃/M₀.5-900</td>
<td>1314</td>
<td>0.73</td>
<td>2.22</td>
<td>3.48</td>
<td>0.90</td>
<td>0.714</td>
<td>2.8</td>
</tr>
<tr>
<td>N₀.54-Z₃/M₁.5-900</td>
<td>1392</td>
<td>0.93</td>
<td>2.70</td>
<td>3.04</td>
<td>0.94</td>
<td>0.753</td>
<td>3.9</td>
</tr>
<tr>
<td>N₀.54-Z₃/M₁-900</td>
<td>1371</td>
<td>1.15</td>
<td>2.61</td>
<td>2.96</td>
<td>0.94</td>
<td>0.778</td>
<td>3.1</td>
</tr>
<tr>
<td>N₀.54-Z₄/M₁-900</td>
<td>2077</td>
<td>1.33</td>
<td>2.57</td>
<td>3.28</td>
<td>0.94</td>
<td>0.806</td>
<td>3.9</td>
</tr>
</tbody>
</table>

^a BET specific surface area. ^b Total pore volume. ^c Average pore diameter. ^d Nitrogen content. ^e Onset potential. ^f Half-wave potential. ^g Diffusion-limited current.
Table S2. Structural and compositional information and electrocatalytic performance of hierarchically porous heteroatom-doped carbon materials derived from different biomass precursors.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>$S_{\text{BET}}^a$ (\text{m}^2 \text{ g}^{-1})</th>
<th>$V_{\text{total}}^b$ (\text{cm}^3 \text{ g}^{-1})</th>
<th>$d_{\text{average}}^c$ (nm)</th>
<th>N content $^d$ (\text{at.}%)</th>
<th>$V_{\text{onset}}^e$ (V)</th>
<th>$V_{\text{half-wave}}^f$ (V)</th>
<th>$j^g$ (\text{mA cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrot</td>
<td>1630</td>
<td>1.68</td>
<td>4.14</td>
<td>2.92</td>
<td>0.94</td>
<td>0.783</td>
<td>4.5</td>
</tr>
<tr>
<td>Chinese yam stem</td>
<td>1548</td>
<td>1.27</td>
<td>3.29</td>
<td>2.78</td>
<td>0.93</td>
<td>0.803</td>
<td>3.5</td>
</tr>
<tr>
<td>Ginkgo leaves</td>
<td>1366</td>
<td>1.25</td>
<td>3.66</td>
<td>2.25</td>
<td>0.93</td>
<td>0.768</td>
<td>3.5</td>
</tr>
<tr>
<td>Tung flower</td>
<td>1316</td>
<td>1.08</td>
<td>3.29</td>
<td>1.89</td>
<td>0.92</td>
<td>0.764</td>
<td>3.7</td>
</tr>
<tr>
<td>Long bean</td>
<td>1517</td>
<td>1.45</td>
<td>3.83</td>
<td>2.82</td>
<td>0.98</td>
<td>0.774</td>
<td>4.2</td>
</tr>
<tr>
<td>Cirsium setosum</td>
<td>1548</td>
<td>1.32</td>
<td>3.41</td>
<td>2.53</td>
<td>0.94</td>
<td>0.807</td>
<td>4.0</td>
</tr>
<tr>
<td>Lavender</td>
<td>1358</td>
<td>1.19</td>
<td>3.52</td>
<td>2.57</td>
<td>0.95</td>
<td>0.807</td>
<td>3.9</td>
</tr>
<tr>
<td>Mother chrysanthemum leaves</td>
<td>1492</td>
<td>1.28</td>
<td>3.43</td>
<td>3.16</td>
<td>0.94</td>
<td>0.780</td>
<td>3.8</td>
</tr>
<tr>
<td>Stigma of corn</td>
<td>1451</td>
<td>0.97</td>
<td>2.68</td>
<td>1.06</td>
<td>0.94</td>
<td>0.729</td>
<td>3.8</td>
</tr>
<tr>
<td>Bamboo fungus</td>
<td>1466</td>
<td>1.27</td>
<td>3.47</td>
<td>2.73</td>
<td>0.93</td>
<td>0.768</td>
<td>3.6</td>
</tr>
<tr>
<td>Felon herb</td>
<td>1621</td>
<td>1.42</td>
<td>3.52</td>
<td>1.5</td>
<td>0.94</td>
<td>0.818</td>
<td>3.8</td>
</tr>
<tr>
<td>The stems of rabdosia rubescens</td>
<td>1426</td>
<td>1.01</td>
<td>2.85</td>
<td>2.59</td>
<td>0.95</td>
<td>0.809</td>
<td>3.6</td>
</tr>
<tr>
<td>The fruits of rhus typhina</td>
<td>1049</td>
<td>0.84</td>
<td>3.22</td>
<td>2.71</td>
<td>0.95</td>
<td>0.792</td>
<td>3.8</td>
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<tr>
<td>Kowkui</td>
<td>1679</td>
<td>1.11</td>
<td>2.66</td>
<td>2.48</td>
<td>0.95</td>
<td>0.827</td>
<td>3.5</td>
</tr>
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<td>Loofah</td>
<td>1752</td>
<td>1.20</td>
<td>2.74</td>
<td>2.61</td>
<td>0.94</td>
<td>0.820</td>
<td>3.6</td>
</tr>
<tr>
<td>Mother chrysanthemum</td>
<td>1548</td>
<td>1.24</td>
<td>3.20</td>
<td>2.61</td>
<td>0.95</td>
<td>0.811</td>
<td>4.2</td>
</tr>
<tr>
<td>Peanut leaf</td>
<td>1390</td>
<td>1.12</td>
<td>3.22</td>
<td>0.66</td>
<td>0.94</td>
<td>0.795</td>
<td>4.0</td>
</tr>
<tr>
<td>Honeysuckle</td>
<td>1548</td>
<td>1.24</td>
<td>3.20</td>
<td>1.79</td>
<td>1.01</td>
<td>0.806</td>
<td>4.6</td>
</tr>
<tr>
<td>Chili</td>
<td>1459</td>
<td>1.49</td>
<td>4.10</td>
<td>2.45</td>
<td>0.93</td>
<td>0.789</td>
<td>3.4</td>
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<tr>
<td>Malachium aquaticum</td>
<td>1734</td>
<td>1.43</td>
<td>3.30</td>
<td>2.95</td>
<td>0.96</td>
<td>0.773</td>
<td>4.3</td>
</tr>
</tbody>
</table>

$^a$ BET specific surface area. $^b$ Total pore volume. $^c$ Average pore diameter. $^d$ Nitrogen content. $^e$ Onset potential. $^f$ Half-wave potential. $^g$ Diffusion-limited current.
Table S3. Summary of various carbon-based electrocatalysts for ORR.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$V_{\text{onset}}^a$ (V)</th>
<th>$V_{\text{half-wave}}^b$ (V)</th>
<th>$j^c$ (mA cm$^{-2}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_{0.54}$-Z$_3$/M$_1$-900</td>
<td>0.96</td>
<td>0.825</td>
<td>4.3</td>
<td>This study</td>
</tr>
<tr>
<td>N-graphene</td>
<td>0.77</td>
<td>NA</td>
<td>0.8</td>
<td>ACS Nano 2010, 4, 1321</td>
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<tr>
<td>Undoped CNT</td>
<td>0.92</td>
<td>NA</td>
<td>4.5</td>
<td>J. Am. Chem. Soc. 2011, 133, 5182</td>
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<tr>
<td>Intrinsic carbon</td>
<td>0.88</td>
<td>NA</td>
<td>NA</td>
<td>ACS Catal. 2015, 5, 6707</td>
</tr>
<tr>
<td>N-doped carbon</td>
<td>0.86</td>
<td>0.70</td>
<td>4.6</td>
<td>Energy Environ. Sci. 2014, 7, 442</td>
</tr>
<tr>
<td>Zigzag-type graphene</td>
<td>0.96</td>
<td>0.819</td>
<td>4.8</td>
<td>Adv. Mater. 2018, 30, 3819</td>
</tr>
<tr>
<td>N/S co-doped carbon</td>
<td>0.86</td>
<td>0.75</td>
<td>5.1</td>
<td>Adv. Funct. Mater. 2016, 26, 5893</td>
</tr>
<tr>
<td>N-S-doping porous carbons</td>
<td>0.87</td>
<td>0.74</td>
<td>5.5</td>
<td>Adv. Funct. Mater. 2016, 26, 8651</td>
</tr>
<tr>
<td>N, S doped graphene</td>
<td>0.90</td>
<td>NA</td>
<td>NA</td>
<td>Angew. Chem. Int. Ed. 2012, 51, 11496</td>
</tr>
<tr>
<td>C$_3$N$_4$/carbon</td>
<td>0.82</td>
<td>NA</td>
<td>NA</td>
<td>Angew. Chem. Int. Ed. 2012, 51, 3892</td>
</tr>
<tr>
<td>Macro/meso-NC-NH$_3$</td>
<td>NA</td>
<td>0.82</td>
<td>6.6</td>
<td>Energy Environ. Sci. 2015, 8, 3274</td>
</tr>
<tr>
<td>Porous carbon</td>
<td>0.94</td>
<td>0.85</td>
<td>4.2</td>
<td>Nat. Nanotechnol. 2015, 10, 444</td>
</tr>
<tr>
<td>Hierarchically porous carbon</td>
<td>0.96</td>
<td>0.84</td>
<td>5.2</td>
<td>ACS Catal. 2017, 7, 6082</td>
</tr>
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</table>

$^a$ Onset potential. $^b$ Half-wave potential. $^c$ Diffusion-limited current.