Supplementary information

A General Approach for the Direct Fabrication of Metal Oxide-Based Electrocatalysts for Efficient Bifunctional Oxygen Electrodes

Jie Wang, a Zexing Wu, a Lili Han, c Cuijuan Xuan, a Jing Zhu, a Weiping Xiao, a Jianzhong Wu, a Huolin L. Xin b and Deli Wang a,*

a Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

b Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

c School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China
Fig. S1 (a) XRD pattern of Co@CoO/NDC-700, MnO/NDC-700, Ni@NiO/NDC-700 and NDC-700 catalysts; (b) XRD pattern of Co/CoO/C, MnOx/C and Ni/NiO/C catalysts.

Fig. S2 Thermogravimetric Analysis (TGA) of Co@CoO/NDC-700, MnO/NDC-700 and Ni@NiO/NDC-700 catalysts.
Fig. S3 Stick models of EDTA molecular and EDTA-Co chelating agent.

Fig. S4 Particle size distribution of Co@CoO/NDC-700 (a), Ni@NiO/NDC-700 (b) and MnO/NDC-700 (c) catalysts.
**Fig. S5** Selected area electron diffraction (SAED) pattern of MnO/NDC-700 catalyst.

**Fig. S6** High-resolution XPS spectra of Mn 2p (a) and Ni 2p (b).
Fig. S7 Cyclic voltammetry comparison of Co@CoO/NDC-700, MnO/NDC-700, Ni@NiO/NDC-700, NDC-700 and Vulcan XC-72 at a scan rate of 50 mV s\(^{-1}\) in N\(_2\)- and O\(_2\)- saturated 1 M KOH solution.
Fig. S8 (a) Bifunctional catalytic comparison of Co@CoO/NDC-600, Co@CoO/NDC-700 and Co@CoO/NDC-800; (b) Bifunctional catalytic comparison of MnO/NDC-600, MnO/NDC-700 and MnO/NDC-800; (c) Bifunctional catalytic comparison of Ni@NiO/NDC-600, Ni@NiO/NDC-700 and Ni@NiO/NDC-800 in O$_2$- saturated 1 M KOH solution.
Fig. S9 Bifunctional catalytic comparison of Co/CoO/C, MnOx/C and Ni/NiO/C in O2-saturated 1 M KOH solution.

Fig. S10 (a) polarization curves of the ring current density on Ni/NDC-700, MnO/NDC-700 and Co@CoO/NDC-700 (The ring potential was 1.2 V). (b) The electron-transfer number n and H2O2 yield on Ni/NDC-700, MnO/NDC-700 and Co@CoO/NDC-700 catalysts.
**Fig. S11** Cyclic voltammetry curves of Co@CoO/NDC-700 in O$_2$-purged 1 M KOH solution at room temperature for various numbers of potential cycles.

**Fig. S12** XRD patterns of Co@CoO/NDC-700 after chronoamperometric stability measurement and chronopotentiometry stability measurement.
Fig. S13 Discharge/charge cycling curves of MnO/NDC-700 at current density of 10 mA cm$^{-2}$.

Fig. S14 Discharge/charge cycling curves of Ni@NiO/NDC-700 at current density of 10 mA cm$^{-2}$. 
Table S1 Comparison of Mulliken atomic charges for EDTA and EDTA-Co (The red rows are corresponding to the bonding atoms).

<table>
<thead>
<tr>
<th>Atom Number</th>
<th>Atom</th>
<th>EDTA</th>
<th>EDTA-Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>-0.105</td>
<td>-0.0237</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>-0.0909</td>
<td>-0.0239</td>
</tr>
<tr>
<td>3</td>
<td>N</td>
<td>-0.447</td>
<td>-0.434</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
<td>-0.456</td>
<td>-0.433</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>-0.175</td>
<td>-0.109</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>-0.148</td>
<td>-0.110</td>
</tr>
<tr>
<td>15</td>
<td>C</td>
<td>0.497</td>
<td>0.543</td>
</tr>
<tr>
<td>16</td>
<td>O</td>
<td>-0.415</td>
<td>-0.562</td>
</tr>
<tr>
<td>17</td>
<td>O</td>
<td>-0.555</td>
<td>-0.498</td>
</tr>
<tr>
<td>18</td>
<td>C</td>
<td>0.516</td>
<td>0.535</td>
</tr>
<tr>
<td>19</td>
<td>O</td>
<td>-0.419</td>
<td>-0.570</td>
</tr>
<tr>
<td>20</td>
<td>O</td>
<td>-0.555</td>
<td>-0.493</td>
</tr>
<tr>
<td>21</td>
<td>C</td>
<td>-0.109</td>
<td>-0.109</td>
</tr>
<tr>
<td>24</td>
<td>C</td>
<td>-0.190</td>
<td>-0.109</td>
</tr>
<tr>
<td>27</td>
<td>C</td>
<td>0.498</td>
<td>0.535</td>
</tr>
<tr>
<td>28</td>
<td>O</td>
<td>-0.416</td>
<td>-0.571</td>
</tr>
<tr>
<td>29</td>
<td>O</td>
<td>-0.553</td>
<td>-0.570</td>
</tr>
<tr>
<td>30</td>
<td>C</td>
<td>0.482</td>
<td>0.535</td>
</tr>
<tr>
<td>31</td>
<td>O</td>
<td>-0.422</td>
<td>-0.571</td>
</tr>
<tr>
<td>32</td>
<td>O</td>
<td>-0.553</td>
<td>-0.493</td>
</tr>
<tr>
<td>33</td>
<td>Co</td>
<td>—</td>
<td>0.390</td>
</tr>
</tbody>
</table>

Table S2 Elemental composition by XPS (at. %)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s</th>
<th>N 1s</th>
<th>O 1s</th>
<th>M 2p (M = Co, Mn, Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@CoO/NDC-700</td>
<td>92</td>
<td>3.4</td>
<td>3.2</td>
<td>1.4</td>
</tr>
<tr>
<td>MnO/NDC-700</td>
<td>97.3</td>
<td>1.2</td>
<td>1.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni@NiO/NDC-700</td>
<td>91</td>
<td>2.1</td>
<td>6.6</td>
<td>0.8</td>
</tr>
<tr>
<td>NDC-700</td>
<td>97.4</td>
<td>1.5</td>
<td>1.1</td>
<td>—</td>
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</table>
Table S3 Comparison of key performance parameters for rechargeable Zn-air batteries extracted from literature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Loading (mg cm(^{-2}))</th>
<th>Peak power density</th>
<th>Voltage gap</th>
<th>Electrolyte</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-GRW</td>
<td>0.5</td>
<td>65 mW cm(^{-2})</td>
<td>0.91 V @ 2 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnCl(_2)</td>
<td>1</td>
</tr>
<tr>
<td>CoO/N-CNT+NiFe LDH/CNT</td>
<td>1.0</td>
<td>265 mW cm(^{-2})</td>
<td>0.70 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>2</td>
</tr>
<tr>
<td>NCNF-1000</td>
<td>2.0</td>
<td>185 mW cm(^{-2})</td>
<td>0.73 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>3</td>
</tr>
<tr>
<td>Co@NG-acid</td>
<td>1.0</td>
<td>350 mW cm(^{-2})</td>
<td>—</td>
<td>6 M KOH</td>
<td>4</td>
</tr>
<tr>
<td>CuPt-NC</td>
<td>2.0</td>
<td>250 mW cm(^{-2})</td>
<td>—</td>
<td>6 M KOH</td>
<td>5</td>
</tr>
<tr>
<td>MnO(_2)/Co(_3)O(_4)</td>
<td>2.0</td>
<td>33 mW cm(^{-2})</td>
<td>0.90 V @ 15 mA cm(^{-2})</td>
<td>6 M KOH</td>
<td>6</td>
</tr>
<tr>
<td>FeCo@NC-750</td>
<td>1.0</td>
<td>132 mW cm(^{-2})</td>
<td>0.74 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>7</td>
</tr>
<tr>
<td>Pb(_2)Ru(_4)O(_6)(_5)</td>
<td>—</td>
<td>195 mW cm(^{-2})</td>
<td>0.77 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnO</td>
<td>8</td>
</tr>
<tr>
<td>NiFe@NCX</td>
<td>1.0</td>
<td>83 mW cm(^{-2})</td>
<td>0.78 V @ 50 mA cm(^{-2})</td>
<td>6 M KOH</td>
<td>9</td>
</tr>
<tr>
<td>P,S-CNS</td>
<td>0.5</td>
<td>198 mW cm(^{-2})</td>
<td>1.04 V @ 25 mA cm(^{-2})</td>
<td>6 M KOH</td>
<td>10</td>
</tr>
<tr>
<td>C–CoPAN900</td>
<td>1.0</td>
<td>125 mW cm(^{-2})</td>
<td>0.90 V @ 2 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnCl(_2)</td>
<td>11</td>
</tr>
<tr>
<td>A-EPC-900</td>
<td>—</td>
<td>—</td>
<td>0.85 V @ 5 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnCl(_2)</td>
<td>12</td>
</tr>
<tr>
<td>COMT@Ni</td>
<td>1.0</td>
<td>—</td>
<td>0.70 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnCl(_2)</td>
<td>13</td>
</tr>
<tr>
<td>HMC</td>
<td>0.1</td>
<td>—</td>
<td>0.81 V @ 2 mA cm(^{-2})</td>
<td>6 M KOH + 2% ZnO</td>
<td>14</td>
</tr>
<tr>
<td>Co-PDA-C</td>
<td>1.0</td>
<td>—</td>
<td>0.94 V @ 2 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnCl(_2)</td>
<td>15</td>
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<tr>
<td>CoFe@NCNTs</td>
<td>1.0</td>
<td>150 mW cm(^{-2})</td>
<td>0.75 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>16</td>
</tr>
<tr>
<td>BNPC-1100</td>
<td>2.0</td>
<td>—</td>
<td>1.06 V @ 2 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M ZnCl(_2)</td>
<td>17</td>
</tr>
<tr>
<td>α-MnO(_2)/CNT10</td>
<td>—</td>
<td>66.3 mW cm(^{-2})</td>
<td>0.86 V @ 10 mA cm(^{-2})</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>18</td>
</tr>
<tr>
<td>MnO(_2)-2h/KB</td>
<td>1.0</td>
<td>133.17 mW cm(^{-2})</td>
<td>—</td>
<td>6 M KOH</td>
<td>19</td>
</tr>
<tr>
<td>Sample</td>
<td>Mn (1-x)</td>
<td>Current Density</td>
<td>Open Circuit Potential</td>
<td>Electrolyte</td>
<td>Power Density</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------</td>
<td>-----------------</td>
<td>-------------------------</td>
<td>-----------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>NCNT/Co$<em>x$Mn$</em>{1-x}$O</td>
<td>0.5</td>
<td>—</td>
<td>0.57 V @ 7 mA cm$^{-2}$</td>
<td>6 M KOH + 2% ZnO</td>
<td>20</td>
</tr>
<tr>
<td>S-DGF</td>
<td>—</td>
<td>300 mW cm$^{-2}$</td>
<td>0.78 V @ 2 mA cm$^{-2}$</td>
<td>6 M KOH + 0.2 M ZnCl$_2$</td>
<td>21</td>
</tr>
<tr>
<td>NiCo$_2$S$_4$/N-CNT</td>
<td>1.0</td>
<td>147 mW cm$^{-2}$</td>
<td>0.63 V @ 10 mA cm$^{-2}$</td>
<td>6 M KOH + 0.2 M ZnCl$_2$</td>
<td>22</td>
</tr>
<tr>
<td>Ni$_3$Fe/N-C sheets</td>
<td>—</td>
<td>—</td>
<td>0.78 V @ 10 mA cm$^{-2}$</td>
<td>6 M KOH</td>
<td>23</td>
</tr>
<tr>
<td>egg-CMS</td>
<td>3.2</td>
<td>—</td>
<td>0.51 V @ 10 mA cm$^{-2}$</td>
<td>6 M KOH</td>
<td>24</td>
</tr>
<tr>
<td>CuFe alloy</td>
<td>212</td>
<td>—</td>
<td>6 M KOH</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Co@CoO/NDC-700</td>
<td>1.0</td>
<td>192.1</td>
<td>0.68 V @ 10 mA cm$^{-2}$</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>This work</td>
</tr>
<tr>
<td>MnO/NDC-700</td>
<td>1.0</td>
<td>130.2</td>
<td>1.15 V @ 10 mA cm$^{-2}$</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>This work</td>
</tr>
<tr>
<td>Ni@NiO/NDC-700</td>
<td>1.0</td>
<td>109.5</td>
<td>0.77 V @ 10 mA cm$^{-2}$</td>
<td>6 M KOH + 0.2 M zinc acetate</td>
<td>This work</td>
</tr>
</tbody>
</table>