Heterogeneous Assembly of Pt-Clusters on Hierarchical Structured CoO$_x$@SnPd$_2$@SnO$_2$ Quaternary Nanocatalyst Manifesting Oxygen Reduction Reaction Performance

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1. HRTEM analysis of CSP NC (i.e. without Pt decoration).

**Figure S1.** HRTEM images of CSP nanocatalyst.
2. **XRD patterns of control samples**

![Figure S2](image)

**Figure S2.** XRD patterns of control samples. The characteristics diffraction peaks A, B, C, D, E, F, G, H, I, J and K for Co-CNT are corresponding to tetragonal (211), hexagonal (211), (330), (301), (510), (20-24), (321), tetragonal (510), hexagonal (510), tetragonal (411) and hexagonal (411) planes, respectively. Meanwhile two peaks $X_1$ and $X_2$ (denoted in yellow region) are characteristics reflections from tetragonally packed CoO$_2$ planes.

3. **Pd K-edge X-ray absorption spectra of control samples (a) XANES and (b) Fourier transformed EXAFS regions.**

![Figure S3](image)

**Figure S3.** Pd K-edge X-ray absorption spectra of control samples (a) XANES and (b) Fourier transformed EXAFS regions.
4. X-ray absorption spectroscopy analysis at Co k-edge and Sn k-edge of experimental CSPP NCs series and control samples.

Figure S4. X-ray absorption spectroscopy of CSPP NCs and control samples. (a) XANES and (b) FT-EXAFS spectra of CSPP NCs at Co K-edge, compared with control sample. (c) XANES and (d) FT-EXAFS spectra of CSPP NCs at Sn K-edge.
5. Sn K-edge X-ray absorption spectra of control samples (a) XANES and (b) Fourier transformed EXAFS regions.

![Figure S5. Sn K-edge X-ray absorption spectra of control samples (a) XANES and (b) Fourier transformed EXAFS regions.](image)

6. XPS determined composition ratios of experimental CSPP nanocatalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>CSPP-1</td>
<td>23.31</td>
</tr>
<tr>
<td>CSPP-2</td>
<td>25.73</td>
</tr>
<tr>
<td>CSPP-14</td>
<td>32.32</td>
</tr>
</tbody>
</table>
7. Comparative Nyquist plots of CSPP NCs under different applied potentials.

Figure S6. (a) Comparative Nyquist plots of (a) CSPP-1, (b) CSPP-2 and (c) CSPP-14 NCs under different applied potentials.
Table S2. Electrochemical performances of CSPP NCs compared with CSP and commercial catalysts (JM-Pt/C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (0.5V)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt;&lt;sup&gt;V vs RHE&lt;/sup&gt;</th>
<th>E&lt;sub&gt;1/2&lt;/sub&gt;&lt;sup&gt;V vs RHE&lt;/sup&gt;</th>
<th>SA (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>J&lt;sub&gt;k 0.85V&lt;/sub&gt; mA cm&lt;sup&gt;-2&lt;/sup&gt;</th>
<th>M.A. 0.85V (mA mg&lt;sup&gt;-1&lt;/sup&gt; Pt)</th>
<th>M.A. 0.85V (mA mg&lt;sup&gt;-1&lt;/sup&gt; Pd+Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J.M.-Pt/C</td>
<td>4.0</td>
<td>0.910</td>
<td>0.844</td>
<td>0.261</td>
<td>4.37</td>
<td>67.0</td>
<td>67.0</td>
</tr>
<tr>
<td>Pd-standard</td>
<td>4.0</td>
<td>0.895</td>
<td>0.831</td>
<td>N/A</td>
<td>2.33</td>
<td>N/A</td>
<td>41.6</td>
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<tr>
<td>CSP</td>
<td>3.2</td>
<td>0.896</td>
<td>0.834</td>
<td>NA</td>
<td>1.95</td>
<td>NA</td>
<td>36.3</td>
</tr>
<tr>
<td>CSPP-1</td>
<td>4.4</td>
<td>0.926</td>
<td>0.867</td>
<td>0.534</td>
<td>5.23</td>
<td>2146.2</td>
<td>94.0</td>
</tr>
<tr>
<td>CSPP-2</td>
<td>3.9</td>
<td>0.925</td>
<td>0.865</td>
<td>0.603</td>
<td>6.15</td>
<td>1555.7</td>
<td>67.7</td>
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<tr>
<td>CSPP-14</td>
<td>3.9</td>
<td>0.917</td>
<td>0.860</td>
<td>0.711</td>
<td>4.91</td>
<td>223.6</td>
<td>47.9</td>
</tr>
</tbody>
</table>

8. Comparative LSV curves of Pd-standard and CSPP nanocatalysts.

![Figure S7. Comparative LSV curves of Pd-standard and CSPP nanocatalysts.](image-url)
9. Fitted EIS curves of CSPP NCs.

Figure S8. (a) Fitting and (b) as-obtained EIS curves of CSPP NCs.