Supporting Information

Achieving high-performance nitrate electrocatalysis with PdCu nanoparticles confined in nitrogen-doped carbon coralline

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**Fig. S1** SEM images of the prepared catalysts with different PdCu alloy loading amount: (a) N-pC: without metal salts; (b) Pd$_{0.4}$Cu$_{0.4}$@N-pC: 0.4 wt% PdCl$_4^{2-}$ + 0.4 wt% Cu$^{2+}$; (c) Pd$_{0.6}$Cu$_{0.2}$@N-pC: 0.6 wt% PdCl$_4^{2-}$ + 0.2 wt% Cu$^{2+}$; (d) Pd$_{0.2}$Cu$_{0.6}$@N-pC: 0.2 wt% PdCl$_4^{2-}$ + 0.6 wt% Cu$^{2+}$; (e) Pd$_6$Cu$_2$@N-pC: 6 wt% PdCl$_4^{2-}$ + 2 wt% Cu$^{2+}$; (f) Pd$_2$Cu$_6$@N-pC: 2 wt% PdCl$_4^{2-}$ + 6 wt% Cu$^{2+}$.

**Fig. S2** TEM image of catalyst Pd$_{0.4}$Cu$_{0.4}$@N-pC without adding melamine: 4 wt% PdCl$_4^{2-}$ + 4 wt% Cu$^{2+}$. The preparation process is the same as Pd$_4$Cu$_4$@N-pC, except that no melamine is added.
**Fig. S3** Pd 3d XPS spectra and (c) Cu 2p XPS spectra of Pd₄Cu₄@N-pC.

**Fig. S4** (a) XRD patterns, (b) nitrogen sorption isotherms, (c) pore size distribution curves of Pd₀.₄Cu₀.₄@N-pC, Pd₀.₆Cu₀.₂@N-pC, and Pd₀.₂Cu₀.₆@N-pC.
**Fig. S5** LSV patterns of Pd₄Cu₄@N-pC, Pd₆Cu₂@N-pC, Pd₂Cu₆@N-pC.

**Fig. S6** Standard curve for NO₃⁻ to calculate the concentration of electrolyte after electrocatalysis.
Fig. S7 The results including nitrate conversion, removal capacity and selectivity for nitrogen of nitrate reduction of (a) Pd₄Cu₄@N-pC, Pd₆Cu₂@N-pC, and Pd₂Cu₆@N-pC, and (b) Pd₀.₄Cu₀.₄@N-pC, Pd₀.₆Cu₀.₂@N-pC, and Pd₀.₂Cu₀.₆@N-pC; the detailed investigation the nitrate electro-catalysis ability of Pd₄Cu₄@N-pC coralline-like nanostructures (c) at different calcination temperatures of 500 °C, 600 °C, and 700 °C, and (d) under different reduction voltage of -1.0 V, -1.1 V, -1.2 V, -1.3 V and -1.4 V. All composites were reduced after 12 h at -1.3 V.

Fig. S8 Thermal gravimetric analysis (TGA) curves of (a) Pd₄Cu₄@N-pC and (b) Pd₀.₄Cu₀.₄@N-pC, respectively.
**Fig. S9** XRD patterns of Pd$_4$Cu$_4$@N-pC coralline nanostructures obtained at different calcination temperatures of 500 °C, 600 °C, and 700 °C.

**Fig. S10** Testing the respective solutions of NO$_2^-$ and NH$_4^+$ from electrocatalytic corresponding points from 6 h to 48 h.
Table S1: Physicochemical properties of Pd$_x$Cu$_y$@N-pC coralline nanostructures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore diameter$^{[a]}$ (nm)</th>
<th>Pore volume$^{[b]}$ (cm$^3$ g$^{-1}$)</th>
<th>$S_{BET}^{[c]}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{micro}^{[d]}$ (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-pC</td>
<td>1.97</td>
<td>0.26</td>
<td>524.1</td>
<td>440.1</td>
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<tr>
<td>Pd$_4$Cu$_4$@N-pC</td>
<td>2.28</td>
<td>0.25</td>
<td>444.8</td>
<td>368.3</td>
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<td>Pd$_6$Cu$_2$@N-pC</td>
<td>2.6</td>
<td>0.21</td>
<td>470.6</td>
<td>372.7</td>
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<tr>
<td>Pd$_2$Cu$_6$@N-pC</td>
<td>2.99</td>
<td>0.19</td>
<td>455.2</td>
<td>338.1</td>
</tr>
<tr>
<td>Pd$<em>{0.4}$Cu$</em>{0.4}$@N-pC</td>
<td>3.02</td>
<td>0.17</td>
<td>318.8</td>
<td>241.4</td>
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<tr>
<td>Pd$<em>{0.6}$Cu$</em>{0.2}$@N-pC</td>
<td>2.25</td>
<td>0.18</td>
<td>323.9</td>
<td>256</td>
</tr>
<tr>
<td>Pd$<em>{0.2}$Cu$</em>{0.6}$@N-pC</td>
<td>2.63</td>
<td>0.21</td>
<td>323.6</td>
<td>248.5</td>
</tr>
</tbody>
</table>

$^{[a]}$ Pore diameter were obtained by using Barrett-Joyner-Halenda (BJH) model from the adsorption branches of isotherms.

$^{[b]}$ Pore volume were evaluated at a relative pressure $P/P_0$ of 0.995.

$^{[c]}$ BET surface areas, $S_{BET}$, were determined by common Brunauer-Emmett-Teller (BET) method.

$^{[d]}$ T-plot micropore surface.

Table S2. Leaching atomic concentration of Pd$_4$Cu$_4$@N-pC electrode for electrocatalysis test at the respective electrocatalytic time points.

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>Cu concentration (ppb)</th>
<th>Pd concentration (ppb)</th>
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</thead>
<tbody>
<tr>
<td>6</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>12</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>18</td>
<td>0.07</td>
<td>0.02</td>
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<tr>
<td>24</td>
<td>0.08</td>
<td>0.03</td>
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<tr>
<td>36</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>48</td>
<td>0.06</td>
<td>0.02</td>
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