Support information

Synthesis of Single-crystal Hyperbranched Rhodium Nanoplates with Remarkable Catalytic Properties
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Table S1. Typical examples of branched nanostructures that have been reported in the literature.

<table>
<thead>
<tr>
<th>Noble metals</th>
<th>Morphologies (TEM or SEM images)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au Ref.</td>
<td><img src="1.png" alt="Image" /> <img src="2.png" alt="Image" /> <img src="3.png" alt="Image" /> <img src="4.png" alt="Image" /> <img src="5.png" alt="Image" /></td>
</tr>
<tr>
<td>Ag Ref.</td>
<td><img src="6.png" alt="Image" /> <img src="7.png" alt="Image" /></td>
</tr>
<tr>
<td>Pt Ref.</td>
<td><img src="8.png" alt="Image" /> <img src="9.png" alt="Image" /> <img src="10.png" alt="Image" /> <img src="11.png" alt="Image" /> <img src="12.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td><img src="13.png" alt="Image" /> <img src="14.png" alt="Image" /> <img src="15.png" alt="Image" /> <img src="16.png" alt="Image" /> <img src="17.png" alt="Image" /></td>
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<tr>
<td></td>
<td><img src="18.png" alt="Image" /> <img src="19.png" alt="Image" /></td>
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<tr>
<td>Pd Ref.</td>
<td>20</td>
</tr>
<tr>
<td>--------</td>
<td>----</td>
</tr>
<tr>
<td>Rh Ref.</td>
<td>25</td>
</tr>
<tr>
<td>Alloys Ref.</td>
<td>28</td>
</tr>
<tr>
<td>33</td>
<td>34</td>
</tr>
<tr>
<td>Alloys</td>
<td>Au-Pt35</td>
</tr>
<tr>
<td>Pt-Cu40</td>
<td>Pt-Cu41</td>
</tr>
</tbody>
</table>
### Table S2. ECSAs obtained based on CO stripping and corresponding onset potentials for as-prepared hyperbranched Rh NCs and commercial Rh black.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECSA (m²/gₚ₆₅) Based on CO stripping</th>
<th>Onset potentials/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh branch-4:4</td>
<td>42.6</td>
<td>0.30</td>
</tr>
<tr>
<td>Rh branch-6:2</td>
<td>43.7</td>
<td>0.27</td>
</tr>
<tr>
<td>Rh branch-8:0</td>
<td>21.1</td>
<td>0.33</td>
</tr>
<tr>
<td>Commercial Rh black</td>
<td>18.6</td>
<td>0.35</td>
</tr>
</tbody>
</table>

### Table S3. Positive-going peak current densities for the electrooxidation of 1 M ethanol in 1 M NaOH solution (scan rate: 50 mV/s).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific activity (mA cm⁻²) Based on CO stripping</th>
<th>Mass activity (A mgₚ₆₅⁻¹) Based on mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh branch-4:4</td>
<td>0.27</td>
<td>96.7</td>
</tr>
<tr>
<td>Rh branch-6:2</td>
<td>0.34</td>
<td>146.6</td>
</tr>
<tr>
<td>Rh branch-8:0</td>
<td>0.19</td>
<td>41.9</td>
</tr>
<tr>
<td>Commercial Rh black</td>
<td>0.15</td>
<td>28.4</td>
</tr>
</tbody>
</table>
Fig. S1 Typical SEM image of the as-prepared hyperbranched Rh triangle nanoplates.

Fig. S2 (A) Typical low-magnification TEM image of as-prepared hyperbranched Rh triangle nanoplates. The vertical orientation of the branched Rh NCs were marked by white ellipses. (B) Statistical analysis of the thickness by counting more than 60 nanobranches.

Fig. S3 Typical low-magnification TEM images of hyperbranched Rh triangle nanoplates obtained at different volume ratios of ODA and TBA: (A) 8 mL : 0 mL, (B) 6 mL : 2 mL, and (C) 4 mL : 4 mL.
Fig. S4 Box-counting estimation of the fractal dimension for the as-prepared hyperbranched Rh triangle nanoplates when the volume ratio of ODA and TBA was (A) 6:2 and (B) 4:4.
**Fig. S5** Representative TEM image of the product obtained by replacing 8 mL ODA with the same volume of TBA.

**Fig. S6** Representative TEM images of the products obtained at different reaction temperatures: (A) 160 °C, (B) 220 °C.
Fig. S7 Typical low-magnification TEM images of Rh NCs that were produced by using different amounts of precursors RhCl₃: (A) 0.25 mg, (B) 0.5 mg, (C) 2 mg, (D) 30 mg. Inset in (A) shows lots of nanoparticles.

Fig. S8 (A) CVs of as-prepared hyperbranched Rh triangle nanoplates and commercial Rh black in 0.1M HClO₄ solution (26 °C). (B) Zoom-in view of (E) range from -0.1 to 0.8 V. The ECSAs of the catalysts were determined by the mass.
**Fig. S9.** TEM image of state-of-the-art commercial Rh black catalyst purchased from Alfa Aesar (Johnson Matthey). Clearly, it is composed of the agglomerated Rh nanoparticles of about 8 nm.

**Fig. S10** Roughly determination of the density of edge sites of hyperbranched Rh NCs.

For roughly evaluating the density of edge sites, we measured the total length of single hyperbranched Rh NC (marked in red in Figure S8), and divided by the area (S). As measured in the Figure 3D, we know the branch length (a) of the NC, so we can roughly determinate the area of NC by assuming the threefold symmetrical hyperbranched NC was an equilateral triangle. And the $S = (\sqrt{3} / 4) (\sqrt{3}a)^2$. By measuring more than 50 hyperbranched Rh NCs with different sizes, the density of edge sites are 12.7±3.3%, 19.6±4.3% and 17.9±2.5% for Rh branch-8:0, Rh branch-6:2, and Rh branch-4:4, respectively.
**Fig. S11** CVs of ethanol electrooxidation by the as-prepared hyperbranched Rh NCs and commercial Rh black in 1.0 M ethanol + 1.0 M NaOH solution (scan rate: 50 mV/s). The ECSAs of the catalysts were determined by the areas of CO stripping peaks in the cyclic voltammetry measurements performed in 0.1 M HClO₄ solution.

**Fig. S12** TEM images of the as-prepared Rh branch NCs after CO stripping, ethanol electrooxidation and stability experiments: (A) Rh branch-8:0, (B) Rh branch-6:2, and (C) Rh branch-4:4.

**Fig. S13** TEM images of the as-prepared hyperbranched Rh triangle nanoplates: (A) Rh branch-8:0, (B) Rh branch-6:2, and (C) Rh branch-4:4 after storage at room temperature for 6 months.
References


37 Weiner RG, Skrabalak SE, Metal dendrimers: synthesis of hierarchically stellated nanocrystals by sequential seed-directed overgrowth. Angew Chem Int Ed, 2015, 54: 1181-1184


