Supporting Information

Self-stabilized Pt-Rh bimetallic nanoclusters as durable electrocatalyst for dioxygen reduction in PEM fuel cells

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**Figure S1.** FESEM images of supportless nanoclusters of SL Pt$_3$Rh NC (a & b) and VC supported Pt$_3$Rh NC (c & d).
Figure S2. (a) EDX pattern, (b) SEM and elemental mappings of (c) Pt, (d) Rh for supportless Pt$_3$Rh nanoclusters.
Figure S3. Comparison of (a) cyclic voltammograms in N₂ and (b) linear scan voltammograms in O₂ saturated 0.5 M H₂SO₄ for SL Pt-Rh nanoclusters with different atomic wt. % compositions at 25 °C.
**Figure S4.** Comparison of (a) mass transfer corrected Tafel plots and (b) K-L plots of SL Pt-Rh nanoclusters with different atomic wt. % compositions in O\textsubscript{2} saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} at a scan rate of 0.01 V s\textsuperscript{-1} at 25 °C.
Figure S5. Mass transfer corrected Tafel plots of supportless Pt₃Rh and Pt₃Rh/VC nanoclusters in O₂ saturated 0.5 M H₂SO₄ at 2400 rpm at a scan rate of 0.01 V s⁻¹ at 25 °C.
Figure S6. ADT (a) CVs and (b) LSVs of Pt₃Rh/VC nanoclusters and (c) comparison of normalized ECSA for both supportless and VC supported Pt₃Rh nanoclusters during potential cycling.
Figure S7. (a) TEM image, (b) EDX pattern, (c) CV in N₂ and (d) LSVs at different rotation rates in O₂ saturated 0.5 M H₂SO₄ for SL Pt@Pt₃Rh nanoclusters at 25 °C.
Figure S8. Comparison of LSVs for supportless Pt@Pt$_3$Rh and Pt$_3$Rh nanoclusters at rotation rate of 2400 rpm in O$_2$ saturated 0.5 M H$_2$SO$_4$ nanoclusters at 25 °C.
Table S1. Comparison of ORR kinetic parameters for supportless Pt-Rh nanoclusters with different atomic weight percentage composition.

<table>
<thead>
<tr>
<th>Pt-Rh (atomic wt. % composition)</th>
<th>$j_d$ (mA cm$^{-2}$)</th>
<th>Onset Potential (V)</th>
<th>$b$ (mV dec$^{-1}$)</th>
<th>$E_{1/2}$ (V)</th>
<th>$10^6 \times i_0$ (A cm$^{-2}$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>3.92</td>
<td>0.73</td>
<td>132</td>
<td>0.61</td>
<td>1.30</td>
<td>4.0</td>
</tr>
<tr>
<td>1:1</td>
<td>2.96</td>
<td>0.68</td>
<td>143</td>
<td>0.57</td>
<td>0.57</td>
<td>2.65</td>
</tr>
<tr>
<td>1:3</td>
<td>2.78</td>
<td>0.59</td>
<td>159</td>
<td>0.45</td>
<td>0.35</td>
<td>2.61</td>
</tr>
</tbody>
</table>

$j_d$-limiting current density; $E_{1/2}$-half-wave potential; $b$-Tafel slope; $\alpha$-electron transfer coefficient; $i_0$-exchange current density; $n$-number of electron transfer.