Supplementary Information

Deposition of Pd/graphene aerogel on nickel foam as a binder free electrode for direct electrooxidation of methanol and ethanol

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Figure captions

Fig S1. Digital image of (a) front, and (b) back of the 7.65 wt.% Pd/GA/NF, and optical microscope image of the 7.65 wt.% Pd/GA/NF and the NF, (c-d) low magnification (scale bar: 1000 μm), and (e-f) high magnification (scale bar: 400 μm).

Fig S2. (a-c) TEM images of 0.8 wt.% Pd/GA/NF in 3 random areas (scale bar: (a) and (b): 100 nm, (c): 200 nm), and (d) size distributions of Pd NPs.

Fig S3. (a-c) TEM images of 2.17 wt.% Pd/GA/NF in 3 random areas (scale bar: (a) and (b): 200 nm, (c): 0.5 μm), and (d) size distributions of Pd NPs.

Fig S4. (a-c) TEM images of 7.65 wt.% Pd/GA/NF in 3 random areas (scale bar: 200 nm), and (d) size distributions of Pd NPs.

Fig S5. CV of 2.17 wt.% Pd/GA/NF in 1 M EtOH/1 M KOH (-0.845 to +0.955 V).

Fig S6. The 25th cycle of CV in 1 M MeOH/1 M KOH (-0.245 to +0.955 V) of (a) NF, GA/NF and 7.65 wt.% Pd/GA/NF, and (b) NF; the 25th cycle of CV in 1 M EtOH/1 M KOH (-0.845 to +0.955 V) of (c) NF, GA/NF and 7.65 wt.% Pd/GA/NF, and (d) NF.

Fig S7. CV of 7.65 wt.% Pd/GA/NF in 1 M KOH solution at the 11th cycle (scan rate: 0.05 V s⁻¹).
Table captions

Table S1. Variation of anodic scan $J_f$, $I_f/I_b$ and onset potential of 7.65 wt.% Pd/GA/NF in methanol oxidation.

Table S2. Variation of anodic scan $J_f$, $I_f/I_b$ and onset potential of 7.65 wt.% Pd/GA/NF in ethanol oxidation.

Table S3. Comparison of the best values of current density in the anodic scan ($J_f$) and $I_f/I_b$ ratio of some Pd based electrocatalyst for methanol and ethanol oxidation.
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**CV behavior of 7.65 wt.% Pd/GA/NF in 1 M KOH**

In-depth analysis of electrocatalytic performance of 7.65 wt.% Pd/GA/NF was performed. Fig. S7 shows the CV curve of 7.65 wt.% Pd/GA/NF in 1 M KOH solution at the 11th cycle at 25 °C. The result indicated an obvious cathodic peak at -0.43 V in the reverse scan, which was due to oxygen desorption from the Pd NPs in alkaline solution.¹

![CV curve of 7.65 wt.% Pd/GA/NF in 1 M KOH solution](image)

Fig. S7. C CV of 7.65 wt.% Pd/GA/NF in 1 M KOH solution at the 11th cycle (scan rate: 0.05 V s⁻¹).
Table S1 Variation of anodic scan $J_f$, $I_f/I_b$ and onset potential of 7.65 wt.% Pd/GA/NF in methanol oxidation.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$J_f$ (A g$^{-1}$) (MeOH)</th>
<th>$I_f/I_b$ (MeOH)</th>
<th>Variation rate of $J_f$ (MeOH)</th>
<th>Onset potential (V) (MeOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>593.3</td>
<td>4.15</td>
<td>0.74</td>
<td>-0.476</td>
</tr>
<tr>
<td>5</td>
<td>715.2</td>
<td>3.46</td>
<td>0.90</td>
<td>-0.476</td>
</tr>
<tr>
<td>6</td>
<td>733.2</td>
<td>2.86</td>
<td>0.92</td>
<td>-0.476</td>
</tr>
<tr>
<td>9</td>
<td>755.8</td>
<td>3.51</td>
<td>0.95</td>
<td>-0.496</td>
</tr>
<tr>
<td>14</td>
<td>798.8</td>
<td>3.11</td>
<td>1</td>
<td>-0.496</td>
</tr>
<tr>
<td>25</td>
<td>787.97</td>
<td>3.03</td>
<td>0.99</td>
<td>-0.496</td>
</tr>
<tr>
<td>29</td>
<td>788</td>
<td>3.05</td>
<td>0.99</td>
<td>-0.536</td>
</tr>
<tr>
<td>54</td>
<td>729.9</td>
<td>2.96</td>
<td>0.91</td>
<td>-0.516</td>
</tr>
<tr>
<td>104</td>
<td>670.2</td>
<td>3.03</td>
<td>0.84</td>
<td>-0.516</td>
</tr>
<tr>
<td>254</td>
<td>590</td>
<td>2.70</td>
<td>0.74</td>
<td>-0.516</td>
</tr>
<tr>
<td>504</td>
<td>492.4</td>
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<tr>
<td>1004</td>
<td>316</td>
<td>1.61</td>
<td>0.40</td>
<td>-0.496</td>
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Table S2 Variation of anodic scan $J_f$, $I_f/I_b$ and onset potential of 7.65 wt.% Pd/GA/NF in ethanol oxidation.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$J_f$ (A g$^{-1}$ (EtOH))</th>
<th>$I_f/I_b$ (EtOH)</th>
<th>Variation rate of $J_f$ (EtOH)</th>
<th>Onset potential (V) (EtOH)</th>
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<tbody>
<tr>
<td>1</td>
<td>60.5</td>
<td>0.52</td>
<td>0.07</td>
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<td>288.3</td>
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<td>25</td>
<td>744.3</td>
<td>2.17</td>
<td>0.85</td>
<td>-0.596</td>
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<td>786</td>
<td>2.22</td>
<td>0.90</td>
<td>-0.616</td>
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<td>32</td>
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<td>801</td>
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<td>-0.596</td>
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<td>807</td>
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<td>55</td>
<td>819.3</td>
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<td>0.95</td>
<td>-0.596</td>
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<td>130</td>
<td>835</td>
<td>2.54</td>
<td>0.96</td>
<td>-0.616</td>
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<tr>
<td>280</td>
<td>874</td>
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<td>1</td>
<td>-0.616</td>
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<td>862</td>
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<td>1004</td>
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<td>2.15</td>
<td>0.69</td>
<td>-0.616</td>
</tr>
<tr>
<td>1030</td>
<td>590.2</td>
<td>2.13</td>
<td>0.68</td>
<td>-0.616</td>
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Table S3 Comparison of the best values of current density in the anodic scan \( (J_f) \) and \( I_f/I_b \) ratio of some Pd based electrocatalyst for methanol and ethanol oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( J_f ) (MeOH/KOH)</th>
<th>( J_f ) (EtOH/KOH)</th>
<th>( I_f/I_b ) (MeOH)</th>
<th>( I_f/I_b ) (EtOH)</th>
<th>Reference electrode</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDG/Pd</td>
<td>27.6 (mA cm(^{-2}))</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Hg/HgO</td>
<td>1</td>
</tr>
<tr>
<td>Porous Pd</td>
<td>238 (A g(^{-1}) Pd)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Hg/HgO</td>
<td>2</td>
</tr>
<tr>
<td>Pd/CNT</td>
<td>274.5 (A g(^{-1}) Pd)</td>
<td>135 (A g(^{-1}) Pd)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>Hg/HgO</td>
<td>3</td>
</tr>
<tr>
<td>Pd/graphene</td>
<td>N/A</td>
<td>0.56 (mA cm(^{-2}))</td>
<td>N/A</td>
<td>4.0</td>
<td>Ag/AgCl</td>
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<tr>
<td>Pd/graphene</td>
<td>522 (A g(^{-1}) Pd)</td>
<td>N/A</td>
<td>6.05</td>
<td>N/A</td>
<td>SCE</td>
<td>5</td>
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<tr>
<td>Pd/C</td>
<td>N/A</td>
<td>102.8 (A g(^{-1}))</td>
<td>N/A</td>
<td>0.7</td>
<td>Hg/HgO</td>
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</tr>
<tr>
<td>Pd/C</td>
<td>N/A</td>
<td>114 (mA cm(^{-2}))</td>
<td>N/A</td>
<td>N/A</td>
<td>Hg/HgO</td>
<td>7</td>
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<tr>
<td>Pd-F/CNT</td>
<td>32.7 (mA cm(^{-2}))</td>
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<td>3.13</td>
<td>N/A</td>
<td>SCE</td>
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<tr>
<td>Pd/LDH-NWs</td>
<td>N/A</td>
<td>2.01 (mA cm(^{-2}))</td>
<td>N/A</td>
<td>0.91</td>
<td>Hg/HgO</td>
<td>9</td>
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<tr>
<td>Pd nanocubes</td>
<td>15.6 (A g(^{-1}))</td>
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<td>&lt;1</td>
<td>NHE</td>
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<tr>
<td>0.8 wt.%</td>
<td>N/A</td>
<td>394.7 (A g(^{-1}))</td>
<td>N/A</td>
<td>2.66</td>
<td>SCE</td>
<td>This</td>
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<tr>
<td>Pd/GA/NF</td>
<td>Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>work</td>
</tr>
<tr>
<td>2.17 wt.%</td>
<td>187.3 (A g(^{-1}))</td>
<td>914.7 (A g(^{-1}))</td>
<td>2.58</td>
<td>1.97</td>
<td>SCE</td>
<td>This</td>
</tr>
<tr>
<td>Pd/GA/NF</td>
<td>Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>work</td>
</tr>
<tr>
<td>7.65 wt.%</td>
<td>798.8 (A g(^{-1}))</td>
<td>874 (A g(^{-1}) Pd)</td>
<td>3.11</td>
<td>2.72</td>
<td>SCE</td>
<td>This</td>
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<td>Pd/GA/NF</td>
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<td></td>
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<td>work</td>
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References:


