Electronic Supplementary Information

Gold nanobipyramid doped with Au/Pd alloyed nanoclusters for high efficiency ethanol electrooxidation

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Supplementary figures

(a) TEM image and (b) corresponding optical spectrum of the AuBPs (Scale bars: 100 nm)

Fig. S1 (a) TEM image and (b) corresponding optical spectrum of the AuBPs (Scale bars: 100 nm)
Fig. S2  (a) UV-vis-NIR absorption spectra of AuBPs@Au$_x$Pd$_{1-x}$ nanostructures with varying Au/Pd proportion in the alloy shell. TEM images of the nanostructures obtained under the addition of varying H$_2$PdCl$_4$ of 2mM (b), 1.5mM (c), 1mM (d) and 0.25mM (e) obtained at 65°C with respective addition of 0.2 mL HAuCl$_4$ and 0.2 mL H$_2$PdCl$_4$ (Scale bars: 100 nm).

Fig. S3  Absorption spectra of 4-NP reduced by NaBH$_4$ in the presence of AuBPs@Au$_x$Pd$_{1-x}$.
(a) AuBPs@Au$_0$Pd$_1$, (b) AuBPs@Au$_{0.2}$Pd$_{0.8}$, (c) AuBPs@Au$_{0.4}$Pd$_{0.6}$, (d) AuBPs@Au$_{0.6}$Pd$_{0.4}$, (e) AuBPs@Au$_{0.8}$Pd$_{0.2}$. 
Fig. S4 (a) Cyclic voltammograms for the AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts in N\textsubscript{2}-saturated KOH (0.3M) solution at a scan rate of 50 mV s\textsuperscript{-1}. (b) CV curves for the AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts in N\textsubscript{2}-saturated KOH (0.3M) solution containing ethanol (0.5M) at a scan rate of 50 mV s\textsuperscript{-1}. (c) CV curves by the ECSAs. (d) Mass activities (green) and specific activities (orange) of AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts from measurement. Note: AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts were obtained with addition of 0.2 mL HAuCl\textsubscript{4} and 0.2 mL H\textsubscript{2}PdCl\textsubscript{4}.
Fig. S5  (a) specific activity of the AuBPs@Au$_x$Pd$_{1-x}$ nanostructures obtained at 65°C with addition of HAuCl$_4$/H$_2$PdCl$_4$ precursor (0.2 mL and 0.4 mL). (b) Cycling measurement of the AuBPs@Au$_x$Pd$_{1-x}$ nanocatalysts obtained at 65°C with addition of HAuCl$_4$/H$_2$PdCl$_4$ precursor (0.2 mL and 0.4 mL). (c) specific activity of the AuBPs@Au$_{0.8}$Pd$_{0.2}$ nanocatalysts obtained at 65°C with addition of different volume of HAuCl$_4$/H$_2$PdCl$_4$ precursor (0.2 mL and 0.4 mL).

Fig. S6  (a) Cycling measurement for AuBPs@Au$_x$Pd$_{1-x}$ nanocatalysts with addition of 0.2 mL HAuCl$_4$/H$_2$PdCl$_4$ precursor. (b) Chronoamperometric curves in mixture solution of KOH (0.3M) and ethanol (0.5M) for 1000s at -0.23V versus Ag/AgCl potential.
**Table S1** The AuBPs@Au$_x$Pd$_{1-x}$ with different concentration for Au and Pd precursors

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of H$_2$PdCl$_4$ (mM)</th>
<th>Concentration of HAuCl$_4$ (mM)</th>
<th>Amount of H$_2$PdCl$_4$ (mL)</th>
<th>Amount of HAuCl$_4$ (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuBPs@Au$<em>{0.8}$Pd$</em>{0.2}$</td>
<td>1</td>
<td>0.25</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>AuBPs@Au$<em>{0.6}$Pd$</em>{0.4}$</td>
<td>1</td>
<td>1.5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>AuBPs@Au$<em>{0.4}$Pd$</em>{0.6}$</td>
<td>1.5</td>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>AuBPs@Au$<em>{0.2}$Pd$</em>{0.8}$</td>
<td>0.5</td>
<td>2</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>AuBPs@Au$<em>{0}$Pd$</em>{1}$</td>
<td>2.5</td>
<td>0</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Table S2** Comparison of the AuBPs@Au$_x$Pd$_{1-x}$ with different mole fractions for Au and Pd precursors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd amount of substance concentration (mg/ L)</th>
<th>Pd mass percent</th>
<th>Au/Pd atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuBPs@Au$<em>{0.8}$Pd$</em>{0.2}$</td>
<td>0.32</td>
<td>40.5%</td>
<td>44.2:55.8</td>
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<td>AuBPs@Au$<em>{0.6}$Pd$</em>{0.4}$</td>
<td>0.50</td>
<td>50.0%</td>
<td>35.0:65.0</td>
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<td>AuBPs@Au$<em>{0.4}$Pd$</em>{0.6}$</td>
<td>0.96</td>
<td>65.3%</td>
<td>25.5:74.5</td>
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<td>AuBPs@Au$<em>{0.2}$Pd$</em>{0.8}$</td>
<td>1.92</td>
<td>80.3%</td>
<td>11.6:83.4</td>
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<td>AuBPs@Au$<em>{0}$Pd$</em>{1}$</td>
<td>3.02</td>
<td>82.9%</td>
<td>9.9:90.1</td>
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