Supplementary Material:

Stable bimetallic Gold–Platinum Nanoparticles Immobilized on Spherical Polyelectrolyte Brushes: Synthesis, Characterization, and Application for the Oxidation of Alcohols

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Figure S1. Decrease of the shell thickness $L$ during ion exchange. Starting with the carrier particle SPB (Stage 0) the value of $L$ is decreased by an increasing amount of $[\text{AuCl}_4^{-}]$-ions (Stage 1). The following ultrafiltration step (Stage 2) is followed by a slightly increasing $L$, indicating the change of ion strength. The introduction of $[\text{PtCl}_6^{2-}]$-ions is followed again by an decreasing $L$ (Stage 3). After reduction (Stage 4) and ultrafiltration (Stage 5) $L$ becomes comparable for all composite systems.
Figure S2. EDX-spectra of an entire SPB/Au-Pt-NP composite (Au$_{73}$Pt$_{27}$) particle. This spectra coincides with the spectra shown in Fig. 3 of the text. Hence, all alloy nanoparticles immobilized on a given carrier particle exhibit the same composition.

Figure S3. Wide-angle X-ray scattering intensities of the composite systems Au$_{73}$Pt$_{27}$, Au$_{55}$Pt$_{45}$, Au$_{45}$Pt$_{55}$, Au$_{25}$Pt$_{75}$ (from bottom to top).
Figure S4. Cryo-TEM image of a catalyst solution (Au$_{55}$Pt$_{45}$) before (top) and after (bottom) use in a catalytic reaction. There is no change of the morphology of the composite particles. This underscores the stability of the composite system (see also Fig. S5).

Table S1. Solutions used for the determination of the catalytic activity

<table>
<thead>
<tr>
<th>catalyst solution</th>
<th>solid content</th>
<th>metal content in solid content</th>
<th>Au content in metal content</th>
<th>Pt content in metal content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$<em>{73}$Pt$</em>{27}$</td>
<td>0.682 wt%</td>
<td>8.210 wt%</td>
<td>73 mol%</td>
<td>27 mol%</td>
</tr>
<tr>
<td>Au$<em>{55}$Pt$</em>{45}$</td>
<td>0.704 wt%</td>
<td>9.029 wt%</td>
<td>55 mol%</td>
<td>45 mol%</td>
</tr>
<tr>
<td>Au$<em>{45}$Pt$</em>{55}$</td>
<td>0.529 wt%</td>
<td>7.935 wt%</td>
<td>45 mol%</td>
<td>55 mol%</td>
</tr>
<tr>
<td>Au$<em>{25}$Pt$</em>{75}$</td>
<td>0.511 wt%</td>
<td>6.798 wt%</td>
<td>25 mol%</td>
<td>75 mol%</td>
</tr>
</tbody>
</table>
Oxygen consumption of benzyl alcohol oxidation (Au-NP)

A 600 ml steel autoclave was charged with 100 ml of water, 37.5 mmol (5.2 g) K$_2$CO$_3$, 12.5 mmol (1.3 ml) benzyl alcohol and 3.9 ml Au-NP. A pressure of 1.1 bar pure O$_2$ (pressure above atmospheric pressure) was used as oxidizing agent. The available gas volume amounts to 496 ml which corresponds to 42 mmol oxygen at the beginning of the reaction. At the stage of a complete conversion 35.75 mmol oxygen should be left, which corresponds to a pressure change of 0.3 bar (found: 0.35 bar after 16 h; conversion > 99 %).

Comparison of catalysts with different Pt content

In a typical experiment, 1 mmol benzyl alcohol (108 mg, 103 µl) is added to a mixture of 8 ml of water and 3 mmol (414 mg) of K$_2$CO$_3$. At the end a catalyst solution in water is added to yield 0.0336 mol% metal (a) 0.31 ml Au-NP; b) 0.12 ml Au$_{73}$Pt$_{27}$; c) 0.1 ml Au$_{55}$Pt$_{45}$-NP; d) 0.16 ml Au$_{45}$Pt$_{55}$-NP; e) 0.19 ml Au$_{25}$Pt$_{75}$-NP; f) 1.16 ml Pt-NP; see table 1). The emulsion is stirred vigorously for 5 h in air at room temperature. After 5 h 0.4 mmol (68 mg, 91 µl) dodecane as internal standard are added. The benzaldehyde is extracted twice using 4 ml of diethylether, the combined organic layers are dried over sodiumsulfate and the conversion is checked via GC.

Recycling experiments

In order to test the stability of the catalytic nanoparticles, several runs have been performed in which the catalysts have been re-used repeatedly. This has been done using the pure Pt-sample and the Au$_{55}$Pt$_{45}$-NP using 1 mmol of benzyl alcohol. After the reaction time of 24 h the products were removed by ether and new educts were added. This was repeated four times. Results are listed in the table. Stirring at 50°C leads to the precipitation of the gold containing samples within one hour.
Table SII. Recycling experiments.

<table>
<thead>
<tr>
<th>sample</th>
<th>run 1</th>
<th>run 2</th>
<th>run 3</th>
<th>run 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-NP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Au&lt;sub&gt;55&lt;/sub&gt;Pt&lt;sub&gt;45&lt;/sub&gt;-NP&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
<td>&gt;99%</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1.16 ml Pt-NP solution in water with a solid content of 0.520 wt% and a metal content of ca. 1.1 wt% Pt correspond to a catalyst loading of 0.0336 mol% Pt.

<sup>b</sup> 0.28 ml Au<sub>55</sub>Pt<sub>45</sub>-NP solution in water with a solid content of 0.339 wt% and a metal content of ca. 7 wt% Au/Pt (60 mol% Au and 40 mol% Pt) correspond to a catalyst loading of 0.0136 mol% Pt and 0.020 mol% Au (total 0.0336 mol%).