Tunable Synthesis of Au-Pd@CeO$_2$ for Semihydrogenation of Phenylacetylene by Ammonia Borane

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Experimental

Preparation of Au@CeO$_2$ and Pd@CeO$_2$

Firstly, 500 mg of PVP and 200 mg of KBr were dissolved in 20 mL of water. The mixed solution was heated for 10 min at 60 °C. Then 1 mL HAuCl$_4$ (20 mM) solution for Au@CeO$_2$ or 1 mL K$_2$PdCl$_4$ (20 mM) solution for Pd@CeO$_2$ and 5 mL Ce(Ac)$_3$ (50 mM) solution were added in sequence followed by dropping a certain amount of diluted ammonia solution (3.5 mL of 25% ammonia solution dissolved in 50 mL water). Such solution was heated at 60 °C for 1 h. Finally, the products were separated and washed by centrifugation with water for several times. Then the sample was dried at 60 °C overnight.

Selectively etching the Pd content

10 mg of the synthesized Au-Pd@CeO$_2$ was re-dispersed in 30 mL of water. Then 1 mL of concentrated nitric acid is added. The reaction was heated at 60 °C for 3 hours. After cooling down to room temperature, the final product was purified by centrifugation and washed with water for five times to complete remove the excess acid.

Preparation of Au-Pd bimetallic nanoparticles

The synthesis of Au-Pd nanoparticles was according to previous reports. Typically 12.13 mL of 15 mM CTAB, 36.38 mL of 15 mM CTAC, 0.625 mL of 10 mM HAuCl$_4$, 0.625 mL of 10 mM H$_2$PdCl$_4$, and 237.5 μL of 100 mM sodium citrate were mixed in a 100 mL glass vessel with cap. Then the vessel was placed in an oven and heated at 90 °C for 16 hours.

Hydrogenation of phenylacetylene for Au-Pd bimetallic nanoparticles

In typical, Au-Pd bimetallic nanoparticles were added into 2 mL of water with the amount of noble metal the same as Au-Pd@CeO$_2$-1. Then 10 mg NH$_3$BH$_3$ dissolved in 3 mL ethanol and 0.2 mmol phenylacetylene were added into the catalyst solution. The reaction temperature was set at 25 °C and the solution was stirred with 500 rpm. After reaction, catalyst was separated by centrifugation at 10000 rpm for 30 s. And the obtained products were analyzed on Bruker 450-GC gas chromatograph. The amount of compound was determined by external standard according to the peak areas. The time for cycle reactions was 60 min for each run.
Fig. S1 Size distribution of (a) Au@CeO$_2$, (b) Au-Pd@CeO$_2$-2, (c) Au-Pd@CeO$_2$-1 and (d) Au-Pd@CeO$_2$-0.5.

Fig. S2 EDS line-scanning spectra of a single Au-Pd@CeO$_2$-1 nanoparticle.
Fig. S3 XRD patterns of (a) Au@CeO$_2$, (b) Au-Pd@CeO$_2$-2, (c) Au-Pd@CeO$_2$-1 and (d) Au-Pd@CeO$_2$-0.5.

Fig. S4 TEM image of the Au-Pd@CeO$_2$-1 treated with HNO$_3$. 
**Fig. S5** UV-VIS spectra of the original Au-Pd@CeO\(_2\)-1 and the sample after etched with HNO\(_3\).

**Fig. S6** TEM images of (a) Au@CeO\(_2\), (b) Au-Pd@CeO\(_2\)-2 and (c) Au-Pd@CeO\(_2\)-0.5.

**Table S1** Au and Pd compositions in different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au (%)</th>
<th>Pd (%)</th>
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<tbody>
<tr>
<td>Au@CeO(_2)</td>
<td>39.4</td>
<td>-</td>
</tr>
<tr>
<td>Au-Pd@CeO(_2)-2</td>
<td>33.04</td>
<td>3.93</td>
</tr>
<tr>
<td>Au-Pd@CeO(_2)-1</td>
<td>23.79</td>
<td>6.33</td>
</tr>
<tr>
<td>Au-Pd@CeO(_2)-0.5</td>
<td>15.51</td>
<td>8.86</td>
</tr>
</tbody>
</table>
Fig. S7 $N_2$ adsorption–desorption isotherms of (a) Au@CeO$_2$, (b) Au-Pd@CeO$_2$-2, (c) Au-Pd@CeO$_2$-1 and (d) Au-Pd@CeO$_2$-0.5.

Fig. S8 UV-VIS spectra of KBr-HAuCl$_4$, KBr-K$_2$PdCl$_4$ and the precursor solutions.
Fig. S9 UV-VIS spectra of the reaction process with different time.

Fig. S10 Compositional changes for Au, Pd and Ce elements of the reaction with different time.
Fig. S11 TEM image of the Pd@CeO$_2$ sample.

Fig. S12 TEM image of the sample after 4 cycles.
**Fig. S13** TEM images of (a) fresh Au-Pd bimetallic nanoparticles, (b) Au-Pd bimetallic nanoparticles after 4 cycles. (c) Catalytic stability of the Au-Pd nanoparticles.

**Fig. S14** XPS spectra of (a) Ce 3d and (b) Pd 3d for (1) Au@CeO$_2$, (2) Au-Pd@CeO$_2$-2, (3) Au-Pd@CeO$_2$-1, (4) Au-Pd@CeO$_2$-0.5 and (5) Pd@CeO$_2$. 