Supporting information

Synergistic catalysis of Au-Co@SiO2 nanospheres in hydrolytic dehydrogenation of ammonia borane for chemical hydrogen storage

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**Synthesis of M@SiO₂ using the reverse micelle method:** A reverse micelle (microemulsion-templating) method¹-⁵ was employed to fabricate core-shell structured M@SiO₂ nanospheres (Fig. S1). Here, the precursors were simply introduced by adding the aqueous solution of metal ammine complexes into the cyclohexane solution of NP-5 in the step of water-in-oil (w/o) reverse micelle (microemulsion) formation. Tetraethylorthosilicate (TEOS) was hydrolyzed with aqueous NH₄OH at the interface between water and oil to form silica nanospheres, resulting in the encapsulation of the metal ammine complexes in the SiO₂ shell (see Fig. S1).

Figure S1. Diagram for the formation of M@SiO₂.
Figure S2. (a) and (b) HAADF-STEM images and (c) the corresponding EDX spectrum (Fig. S2b, point 1) for the as-synthesized Au-Co@SiO₂-RT nanospheres.
Figure S3. (a) and (b) HAADF-STEM images and (c) the corresponding EDX spectrum (Fig. S3a, point 1) for the as-synthesized Au-Co@SiO$_2$-HT nanospheres.
Figure S4. Selected area electron diffraction (SAED) corresponding to Fig. 2 for Au-Co@SiO₂-RT (a) and Au-Co@SiO₂-HT (b) nanospheres.
Table S1. Hydrogen generation from hydrolysis of ammonia borane (AB, 0.16 M, 5 mL) with NaBH₄ (5 mg) in the presence of the as-synthesized nanospheres (Au/AB = 0.015, Co/AB = 0.05).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂ yield (mL)</th>
<th>H₂ productivity (%)</th>
<th>Time to completion (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@SiO₂-RT</td>
<td>45</td>
<td>69.2%</td>
<td>117</td>
</tr>
<tr>
<td>Co@SiO₂-RT</td>
<td>17</td>
<td>26.2%</td>
<td>134</td>
</tr>
<tr>
<td>Au-Co@SiO₂-RT</td>
<td>65</td>
<td>100%</td>
<td>90</td>
</tr>
<tr>
<td>Au@SiO₂-HT</td>
<td>7</td>
<td>10.8%</td>
<td>20</td>
</tr>
<tr>
<td>Co@SiO₂-HT</td>
<td>65</td>
<td>100%</td>
<td>81</td>
</tr>
<tr>
<td>Au-Co@SiO₂-HT</td>
<td>65</td>
<td>100%</td>
<td>34.5</td>
</tr>
</tbody>
</table>
Figure S5. Hydrogen generation from hydrolysis of ammonia borane (AB, 0.16 M, 5 mL) with NaBH₄ (5 mg) in the presence of the as-synthesized Au-Co@SiO₂-HT nanospheres and Au-Co@SiO₂-673K nanospheres (Au/AB = 0.015, Co/AB = 0.05). Similar to the synthesis of Au-Co@SiO₂-HT, Au-Co@SiO₂-673 K was prepared by evacuating the Au-Co@SiO₂-RT nanospheres at 673 K for 5 h.

Figure S6. Hydrogen productivity vs. reaction time for the generation of hydrogen from an aqueous ammonia borane solution (AB, 0.16 M, 5 mL) catalyzed by the as-synthesized Au-Co@SiO₂-HT catalysts at sequential runs by addition of equivalent amounts of AB and by the reused catalyst (recycled by centrifugation).
Figure S7. Nitrogen absorption-desorption isotherms of (a) Au-Co@SiO$_2$-RT and (b) Au-Co@SiO$_2$-HT nanospheres after the hydrolysis of NH$_3$BH$_3$.

Figure S8. Powder X-ray diffraction patterns for the nanospheres after the hydrolysis of NH$_3$BH$_3$. 
Figure S9. (a) HAADF-STEM images and (b) the corresponding EDX spectrum (Fig. S5a, area 1) for the Au-Co@SiO$_2$-RT nanospheres after the hydrolysis of NH$_3$BH$_3$. 
Figure S10. (a) HAADF-STEM images and (b) the corresponding EDX spectrum (Fig S6a, point 1) for the Au-Co@SiO$_2$-HT nanospheres after the hydrolysis of NH$_3$BH$_3$. 
Figure S11. Selected area electron diffraction (SAED) corresponding to Fig. 9 for Au-Co@SiO₂-RT (a) and Au-Co@SiO₂-HT (b) after the hydrolysis of NH₃BH₃. Compared with the samples before reaction (Fig. S4), the samples after the catalytic reaction showed increased degree of crystallinity.
X-ray photoelectron spectroscopic (XPS) measurements: XPS measurements on Au–Co@SiO$_2$-RT and Au–Co@SiO$_2$-HT nanospheres before and after reaction in combination with argon-sputtering were performed to examine the structures of the nanospheres (see below, Fig S12 and S13). The peak intensities of gold 4f and cobalt 2p were too weak to be observed in these samples, which is probably due to the low metal contents of these nanospheres (1.9 wt%). The silicon 2p and oxygen 1s bands of the Au–Co@SiO$_2$-RT and Au–Co@SiO$_2$-HT nanosphere before and after the reaction could be observed during the argon-sputtering. Based on these observations, it can be concluded that the gold and cobalt NPs are well coated by the SiO$_2$ nanospheres, which is in agreement with the TEM results (Fig. 2 and Fig. 9).
Figure S12. The XPS spectra of (a) Au 4f, (b) Co 2p, (c) Si 2p and (d) O 1s obtained from Au-Co@SiO₂-RT nanospheres before (left) and after (right) catalytic reaction.
Figure S13. The XPS spectra of (a) Au 4f, (b) Co 2p, (c) Si 2p and (d) O 1s obtained from Au-Co@SiO₂-HT nanospheres before (left) and after (right) catalytic reaction.
References:


