Electronic Supplementary Information

Fabrication of yolk-shell Pd@ZIF-8 nanoparticles and their excellent catalytic size-selectivity in the hydrogenation of olefins

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Table S1  The ICP data for the Zn and Pd contents in Pd@ZnO and Pd@ZIF-8 NPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn (wt%)</th>
<th>Pd (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd@ZnO</td>
<td>37.6</td>
<td>3.73</td>
</tr>
<tr>
<td>Pd@ZIF-8</td>
<td>26.9</td>
<td>3.42</td>
</tr>
</tbody>
</table>

Fig. S1  (a) The HRTEM image and (b) the EDS spectrum of Pd@ZnO NPs.

Fig. S2  The TEM images of (a) ZnO spheres and (b) hollow ZIF-8 NPs.

Fig. S3  The corresponding histogram of size distribution. In the histogram, the particle size was an average of the edge lengths measured along two orthogonal directions of each nanocube.
**Notes:** For the TGA curve, the weight loss of about 2.0% is due to the removal of the guest molecules, followed by a distinct weight loss caused by the combustion of carbon. The remaining weight of the composites after heating to 400 °C is about 37.0%, corresponding to the calculated value by using the ICP data from the following equation:

\[
m(\text{residue}) = 3.42 \text{ wt.}\% \times \frac{M(\text{PdO})}{M(\text{Pd})} + 26.9 \text{ wt.}\% \times \frac{M(\text{ZnO})}{M(\text{Zn})} = 3.42 \text{ wt.}\% \times \frac{122.4}{106.4} + 26.9 \text{ wt.}\% \times \frac{81.4}{65.4} \approx 37.4 \text{ wt.}\%
\]

**Fig. S4** The TGA curve of the yolk-shell Pd@ZIF-8 nanocomposites.

**Fig. S5** Recycling of the yolk-shell Pd@ZIF-8 composites for the hydrogenation of 1-hexene.
**Fig. S6** The TEM images of yolk-shell nanostructure (a) before catalytic reaction and (b) after the third circle hydrogenation reaction.

**Fig. S7** The PXRD patterns of yolk-shell Pd@ZIF-8 composites before catalytic reaction (dark line) and after the third hydrogenation reaction (blue line).
Preparation of Au nanorods
For the seed solution: To an aqueous CTAB solution (0.2 mol/L, 5 mL) was added the HAuCl₄ solution (0.5 mmol/L, 5 mL) and then the ice-cold NaBH₄ solution (10 mmol/L, 0.6 mL). The color of the seed solution turned from yellow to brownish. The growth solution was prepared by adding CTAB (0.2 mol/L, 25 mL) to AgNO₃ solution (4 mmol/L, 1.0 mL) mixed with HAuCl₄ solution (1 mmol/L, 25 mL). The solution of AA (0.0788 mol/L, 0.35 mL) was then added to the mixture accompanied by a color change from yellow to colorless. Subsequently, the 60 μL seed solution was added to the growth solution. The reaction was left to proceed for 12 h at 30 °C. The dark-blue color of the mixture indicated the formation of the Au nanorods (NRs), and this solution was stored at room temperature for next use without any purification.

Preparation of Au@ZnO nanospheres
To the solution (50 mL) of CTAB (0.5 mmol) and AA (0.3 mmol) was added Zn(NO₃)₂·6H₂O (0.6 mmol) and HMTA (0.6 mmol). Then the 50 mL solution of the preformed Au nanorods was added dropwise and stirred for 10 min. The mixture was heated at 85 ºC for 8 h and then gradually cooled to room temperature. The pink product was centrifuged, washed with distilled water and absolute ethanol three times respectively, and dried in a vacuum at 60 ºC for 12 h to yield Au@ZnO core-shell nanospheres.

Preparation of yolk-shell Au@ZIF-8 nanostructures
Au@ZnO nanospheres (0.02 g) were fully dispersed in 30 mL methanol solution by ultrasonic. To this solution was added dropwise 10 mL of the aqueous solution of 2-methylimidazole (0.30 g). The mixture was shaken slightly for several seconds and was allowed to stand for about 1 h at room temperature. The resulting yolk-shell Au@ZIF-8 nanospheres were centrifuged, washed three times with ethanol and dried at 60 ºC for 12 h.

Fig. S8  The TEM images of (a) Au@ZnO nanospheres and (b) yolk-shell Au@ZIF-8 NPs.