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.

Sample	Zn (wt%)	Pd (wt%)
Pd@ZnO	37.6	3.73
Pd@ZIF-8	26.9	3.42

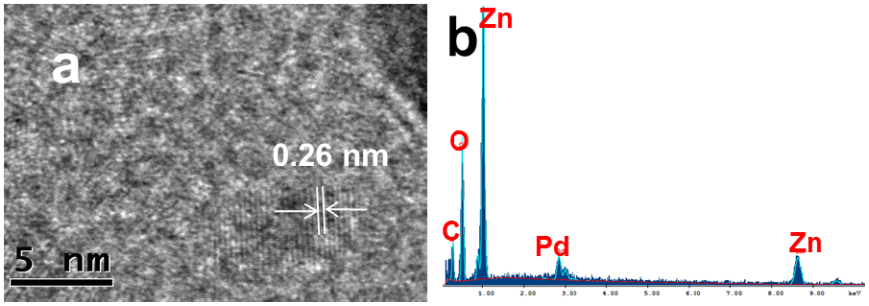

Fig. S1 (a) The HRTEM image and (b) the EDS spectrum of Pd@ZnO NPs.

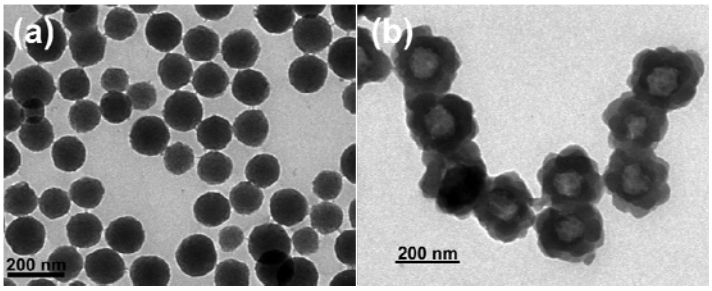

Fig. S2 The TEM images of (a) ZnO spheres and (b) hollow ZIF-8 NPs.

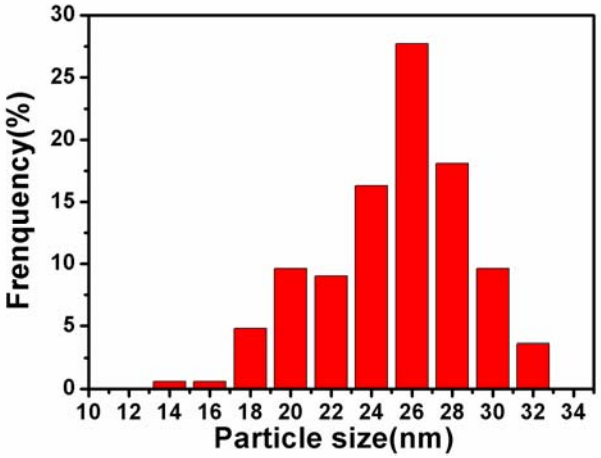

Fig. S3 The corresponding histogram of size distribution. In the histogram, the particle size was an average of the edge lengths measured along two orthogonal directions of each nanocube.

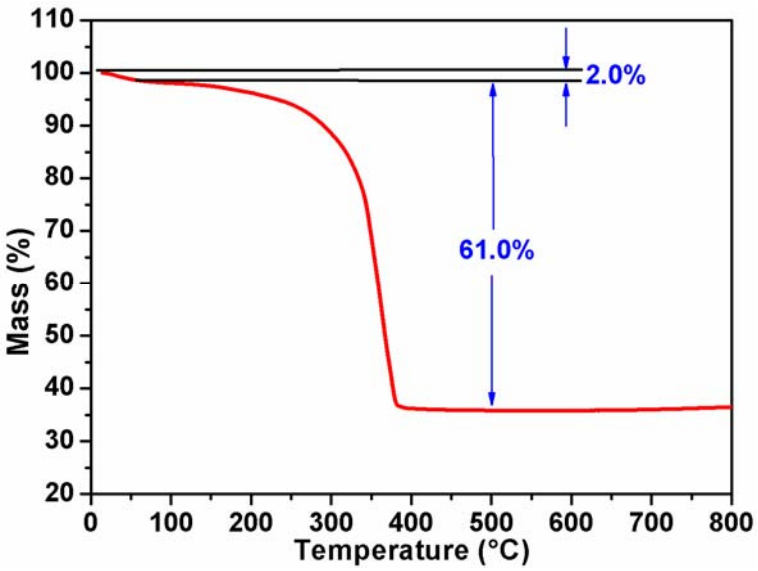

Fig. S4 The TGA curve of the yolk-shell Pd@ZIF-8 nanocomposites.

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 ºC is about 37.0 %, corresponding to the calculated value by using the ICP data from the following equation: m(residue) = 3.42 *wt.*% × M(PdO)/M(Pd) + 26.9 *wt.*% × M(ZnO)/M(Zn) = 3.42 *wt.*% × 122.4/106.4 + 26.9 *wt.*% × 81.4/65.4 ≈ 37.4 *wt.*%

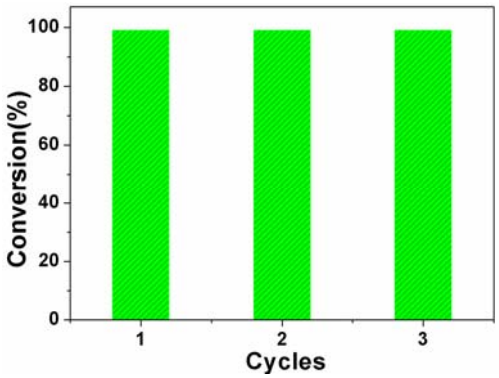

Fig. S5 Recycling of the yolk-shell Pd@ZIF-8 composites for the hydrogenation of 1-hexene.

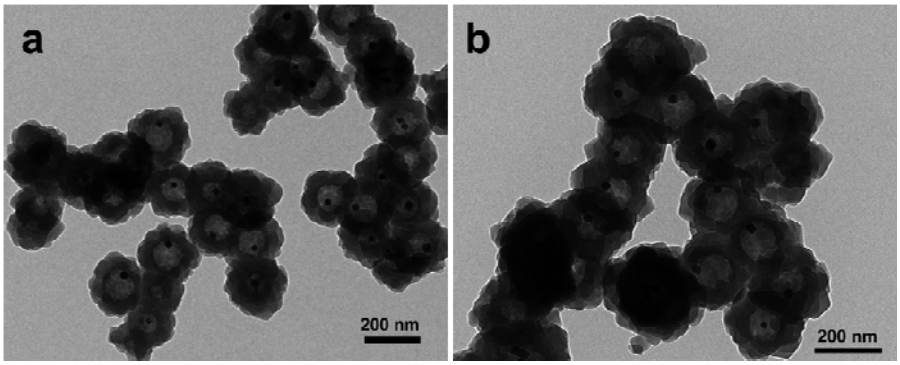

Fig. S6 The TEM images of yolk-shell nanostructure (a) before catalytic reaction and (b) after the third circle hydrogenation reaction.

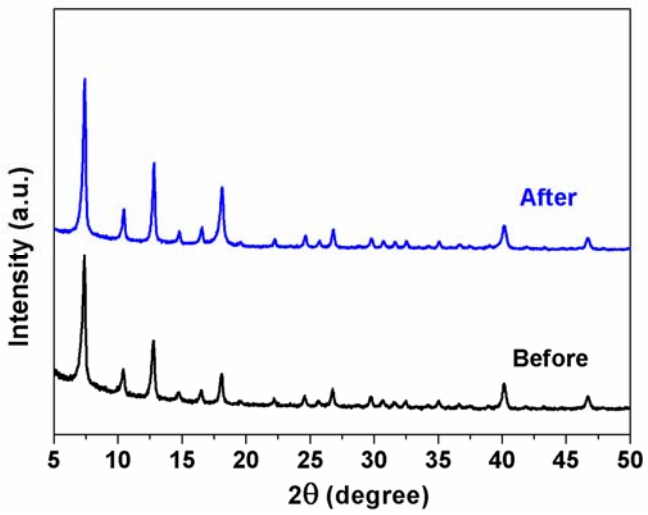

Fig. S7 The **P**XRD patterns of yolk-shell Pd@ZIF-8 composites before catalytic reaction (dark line) and after the third hydrogenation reaction (blue line).

Preparation of Au nanorods

For the seed solution: To an aqueous CTAB solution (0.2 mol/L, 5 mL) was added the $HAuCl_4$ solution (0.5 mmol/L, 5 mL) and then the ice-cold $NaBH_4$ 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 $AgNO_3$ solution (4 mmol/L, 1.0 mL) mixed with $HAuCl_4$ 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 soltution (50 mL) of CTAB (0.5 mmol) and AA (0.3 mmol) was added $Zn(NO_3)_2{\cdot}6H_2O$ (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 shaked 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 °C for 12 h.

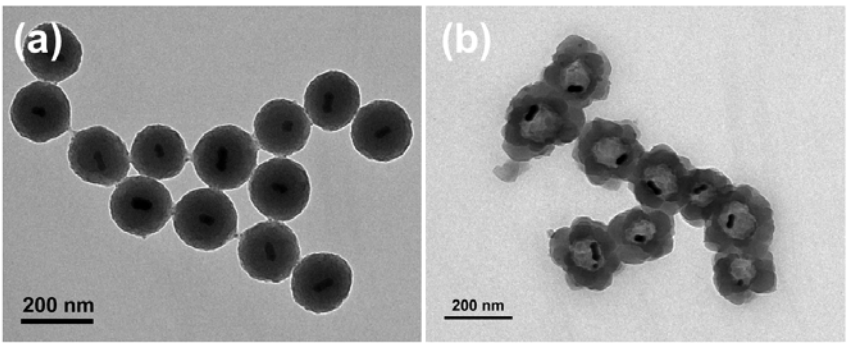

Fig. S8 The TEM images of (a) Au@ZnO nanospheres and (b) yolk-shell Au@ZIF-8 NPs.