Electronic Supplementary Information for

Super-hydrophobic yolk/shell catalyst with enhanced catalytic performance in the reduction of hydrophobic nitroaromatic compounds

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Experiment

Materials:

Methanol (AR), tetraethyl orthosilicate (TEOS) (AR) and ammonium hydroxide (28-30 wt%AR) were purchased from Tianjin Kermel Reagent Co. Ltd. 2-Methyl-4-nitrophenol (2-M-4-NP) (AR), 2,6-dimethyl-4-nitrophenol (2,6-2M-4-NP) (AR) and 4-nitrophenol (4-NP) (AR) were from the Alddin Chemistry Co. Ltd. Isobutyltrimethoxysilane (IBMS) (97%) was from Alfa Aesar. HF (>40%) and ethanol (AR) were from Tianjin Chengxin Co. Ltd. All of the materials were used as received without further purification.

Synthesis of Au NPs:

2 mL of 1 wt% HAuCl₄ was added into 50 mL deionized water, followed by 5 mL 38.8 M citrate sodium solution and then the mixture was heated under reflux for 30 min. Finally, the resultant colloid was cooled to room temperature and 13 nm gold nanoparticles were obtained. For 40 nm gold nanoparticles, the synthetic conditions were the same as described above except using sodium citrate as reduction reagent instead. For the synthesis of 6 nm gold nanoparticles, a HAuCl₄ solution (2 g, 1 wt%) and a sodium tartrate solution (4 mL, 38.8 mM) were added to deionized water (100 mL), finally a NaBH₄ solution (1 mL, 0.145 wt%) was added and gold nanoparticles were formed. For the synthesis of platinum nanoparticles, the procedure is the same with the procedure to prepare 13 nm Au particles, except 4 mL of 1 wt% HPtCl4 was used.

Synthesis of core shell nanoparticle Au@IB-SiO₂:

A fresh solution of polyvinylpyrrolidone (0.3 mL, 12.8 mg/mL) was added to a previously prepared Au NPs solution. The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the gold surface. Then, the solution was centrifuged (20000 rpm, 20 min) and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 10 mL by dilution with ethanol. The colloid was under ultrasonic for 15 min, followed by addition of ethanol (20 mL) and concentrated ammonia solution (1.65 mL, 28–30 wt% NH₃ in water). Afterwards, a solution of TEOS (1.15 mL), IBMS (0.15 mL) in ethanol (1.5 mL) was added. The reaction mixture was then stirred for additional 24 h at room temperature. The resultant colloid was centrifuged and washed with water and ethanol and dried at 353 K. For the synthesis of Au-6@IB-SiO₂, Au-40@IB-SiO₂ and Pt@IB-SiO₂, the procedure is the same except with different nanoparticles were used.

Synthesis of yolk/shell nanoparticle Au@IB-YSN:

0.1 g of the obtained Au@IB-SiO₂ coreshell nanoparticles were dispersed in 20 g methanol for at least 2 h, then 2 g 5 wt% HF solution were added into the turbid liquid. The mixture was stirred vigorously for 25 min at room temperature. The resultant colloid was centrifuged and washed with water and methanol and dried at 353 K. For the synthesis of Au-6@YSN, Au-40@YSN and Pt@YSN, the procedure is the same except with different nanoparticles were used.

Synthesis of Au/C:

0.1 g of the active carbon was added to the freshly prepared Au NPs solution. The resultant solution was stirred for 24 h, followed by centrifugation and washing with water and ethanol and dried at 353 K. The gold content of Au/C was maintained at 9.6 wt%.

Synthesis of Au/SBA-15:

SBA-15 was prepared as previous reported. 0.1 g of the SBA-15 was added to the freshly prepared Au NPs solution. The resultant solution was stirred for 24 h, followed by centrifugation and washing with water and ethanol and dried at 353 K. The gold content of Au/C was 9.6 wt%.

Reduction of nitroaromatic compounds:

First, 3.5 mL of aqueous NaBH₄ (100 mM) solution was added to 0.1 mL of 4-NP (2.5 mM) solution in a quartz cuvette at 25 $^{\circ}$ C. Then, 0.1 mL of the catalyst suspension (1 mg/mL) was added to the mixture. After the addition of catalysts, UV-vis spectra of the mixture were recorded at regular intervals to monitor the reaction progress.

Characterization:

Fourier transform infrared (FT-IR) spectra were collected between 4000 and 400 cm⁻¹ on a Bruker Tensor 27 spectrometer in KBr media. UV-vis spectra were measured on Shimadzu UV-2550. Transmission electron microscope (TEM) was measured on JEM 2000EX. The size distribution of the nanoparticles was measured from the TEM images, and at least one hundred spheres were counted. N₂ adsorption–desorption isomer was performed on Quantachrome Autosorb-1, Water contact angles were performed on contact angle measuring system JC 2000 C1. The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max 2500/PC powder diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). The nuclear magnetic resonance spectra of ²⁹Si with magic-angle spinning (²⁹Si MAS NMR) were performed on a Bruker DRX-400 spectrometer at 79.5 MHz with a spinning frequency of 4 kHz. ICP-AES was performed on ICPS-8100.



Fig. S1 Size distribution of Au NPs.



Fig. S2 Size distribution of Au@IB-SiO₂.



Fig. S3 Size distribution of Au cores in Au@IB-SiO₂.



Fig. S4 Size distribution of Au@IB-YSN.



Fig. S5 Size distribution of Au cores in Au@IB-YSN.



Fig. S6 UV-vis spectra of a) Au NPs, b) Au@IB-SiO₂, c) Au@IB-YSN.



Fig. S7 XRD patterns of a) Au@IB-SiO₂, b) Au@IB-YSN.



Fig. S8 Isotherm and pore size distribution of Au@IB-YSN.



Fig. S9 FT-IR spectra of a) Au@IB-SiO₂, b) Au@IB-YSN.



Fig. S10 magnified TEM image of Au@IB-YSN.



Fig. S11 TEM images of super-hydrophobic yolk/shell nano-reactor with 6 nm Au NPs



Fig. S12 Au particle size distribution of 6 nm Au NPs.



Fig. S13 TEM images of super-hydrophobic yolk/shell nano-reactor with 40 nm Au NPs



Fig. S14 Au particle size distribution of 40 nm Au NPs.



Fig. S15 TEM images of super-hydrophobic yolk/shell nano-reactor with Pt NPs



Fig. S16 TEM image of Au/C and the Au particle size distribution.



Fig. S17 TEM image of Au/SBA-15 and the Au particle size distribution.



Fig. S18 Catalyst distribution between water and cyclohexane, from left to right, Au/SBA-15, Au/C, Au@IB-YSN.



Fig. S19 4-NP reduction in the presence of Au@IB-YSN



Fig. S20 2-M-4-NP reduction in the presence of Au@IB-YSN



Fig. S21 2,6-2M-4-NP reduction in the presence of Au@IB-YSN



Fig. S22 4-NP reduction in the presence of Au/C



Fig. S23 2-M-4-NP reduction in the presence of Au/C



Fig. S24 2,6-2M-4-NP reduction in the presence of Au/C



Fig. S25 4-NP reduction in the presence of Au/SBA-15



Fig. S26 2-M-4-NP reduction in the presence of Au/ SBA-15



Fig. S27 2,6-2M-4-NP reduction in the presence of Au/SBA-15



Fig. S28 Reusability of Au@IB-YSN in the reduction of 4-NP



Fig. S29 TEM images and Au NPs size distribution after third use of Au@IB-YSN