Electronic supplementary information

Amino-functionalized silica nanoparticles with center-radially hierarchical mesopores as ideal catalyst carriers†

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Synthesis of NH_2-MCM-41. Amino functionalized MCM-41 nanoparticles were synthesized under basic conditions using co-condensation method.[1] In a typical synthesis, 0.20 g of CTAB was dissolved in 96 g of deionized water under stirring at room temperature. Then 0.70mL of NaOH (2M) was added into the solution and the temperature of the solution was raised to 80 °C. To this clear solution, 1.2 mL of TEOS and 0.10 mL of APMS were added sequentially. The mixture was continuously stirred for an additional 2 h. The solid product was filtered and washed with water. Template extraction was performed by adding the precipitates in ethanolic HCl (15 mL of conc. HCl in 120 mL of ethanol) followed by stirring at 60 °C for 24 h. Finally, the precipitates were filtered, washed with pure water, and dispersed in water or dried in air at 60 °C.

[1] Zhang, L.; Qiao, S., Jin, Y.; Cheng, L.; Yan, Z.; Lu, G. Q. *Adv. Funct. Mater.* **2008**, *18*, 3834-3842.

Synthesis of SBA-15. Mesoporous silica SBA-15 was synthesized according to the previous literature with a little modification.[2] The typical synthesis process was as follows: at room temperature, 1.0 g of P123 was dissolved in 35 mL of 2.0 M HCl solution, followed by adding 8 mL of deionized water and 0.6 mL of isooctane. After the solution was well stirred for 2 h at 40 °C, 2.0 mL of TEOS was added, then the resulting mixture was kept at 40 °C for 24 h under stirring. The solid product was filtered, washed with water, and dried in an oven at 60 °C for 24 h followed by calcination in air at 550 °C for 6 h to completely remove the Pluronic P123.

Amino-functionalization of SBA-15. 0.2 g of SBA-15 was added in 100 mL of anhydrous toluene. After the mixture was stirred for 1 h under a nitrogen atmosphere, 0.2 mL of APMS was added and stirred at 120 °C for 24 h. After reaction, the amino-functionalized SBA-15 was rinsed with toluene and ethanol, and dried in an oven at 60 °C for 24 h.

[2] Zhao, D. Y.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F. Stucky, G. D. *Science* **1998**, *279*, 548-552.

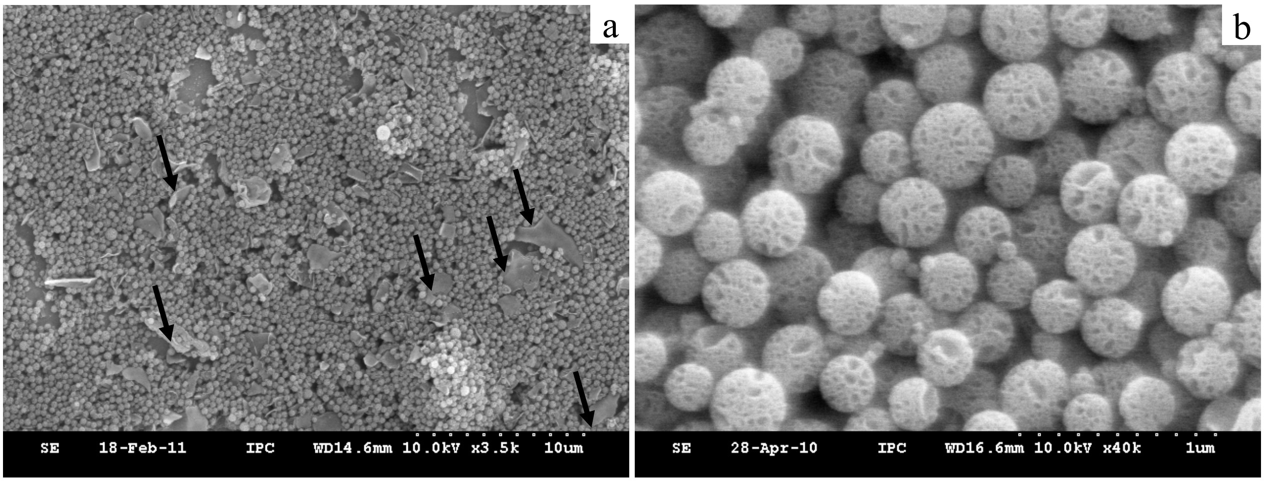

Figure S1. SEM images of as-prepared NH_2-HMSNs. The black arrows in (a) show the appearance of some unexpected sheets in the product.

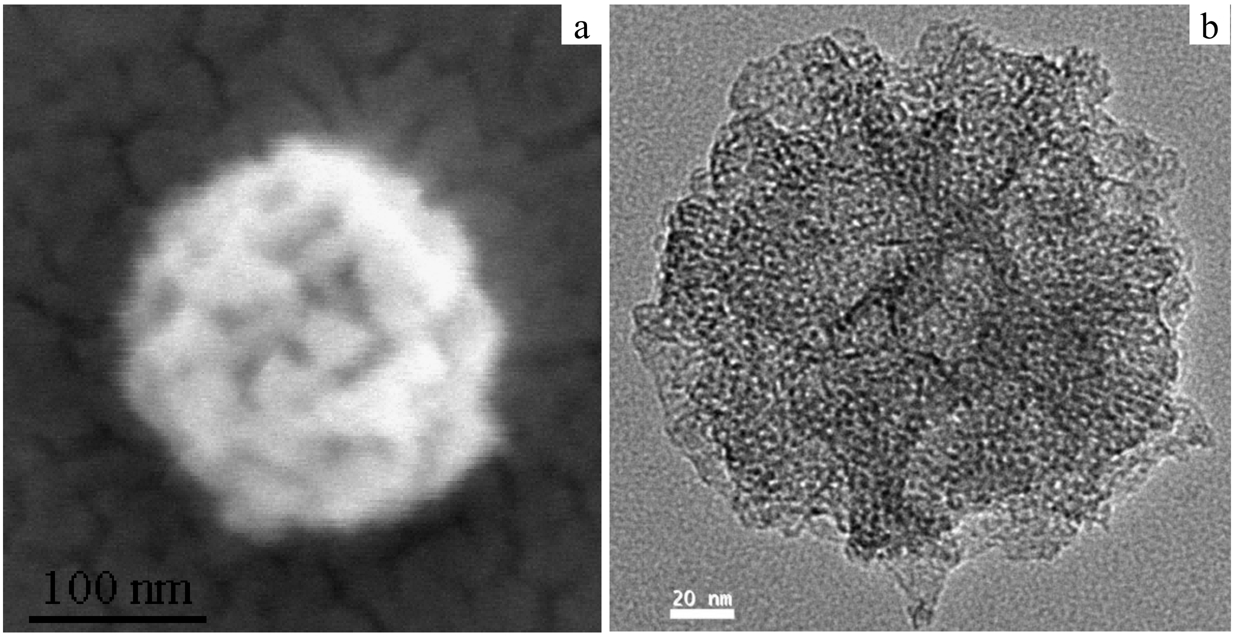

Figure S2. SEM (a) and TEM (b) images of calcined NH_2-HMSNs. After calcination, the worm-like mesopores with a size of 2-4 nm can be seen clearly.

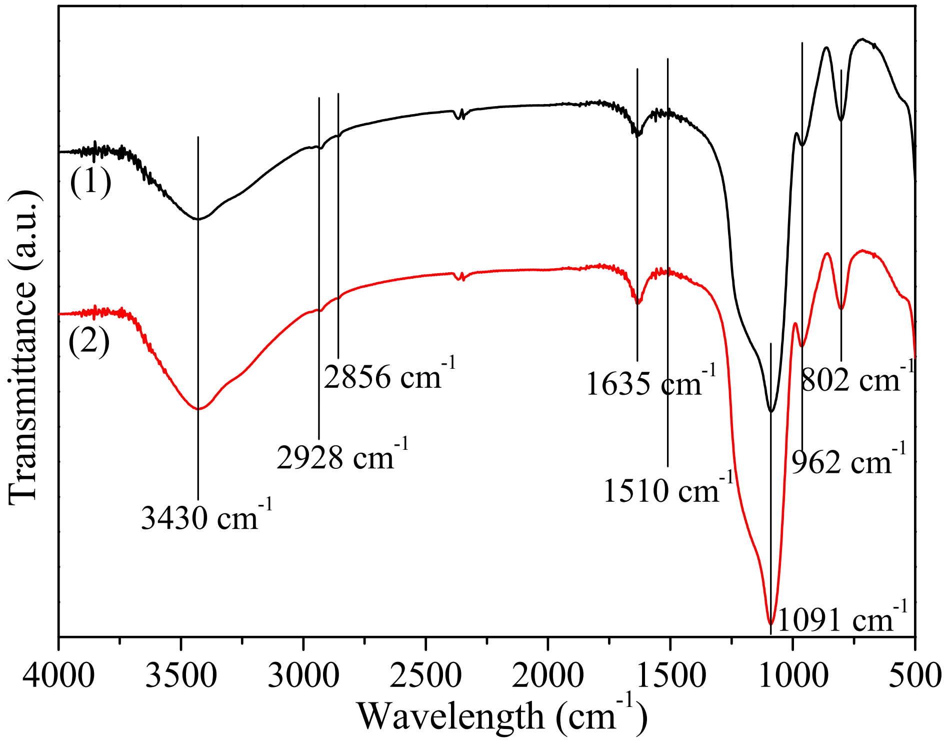

Figure S3. FTIR spectra of the extracted and purified NH_2-HMSNs (1) and Au-NH_2-HMSNs (2). It can be observed that the FTIR spectrum of Au-NH_2-HMSNs is almost identical with that of NH_2-HMSNs, indicating nearly no change of surface groups.

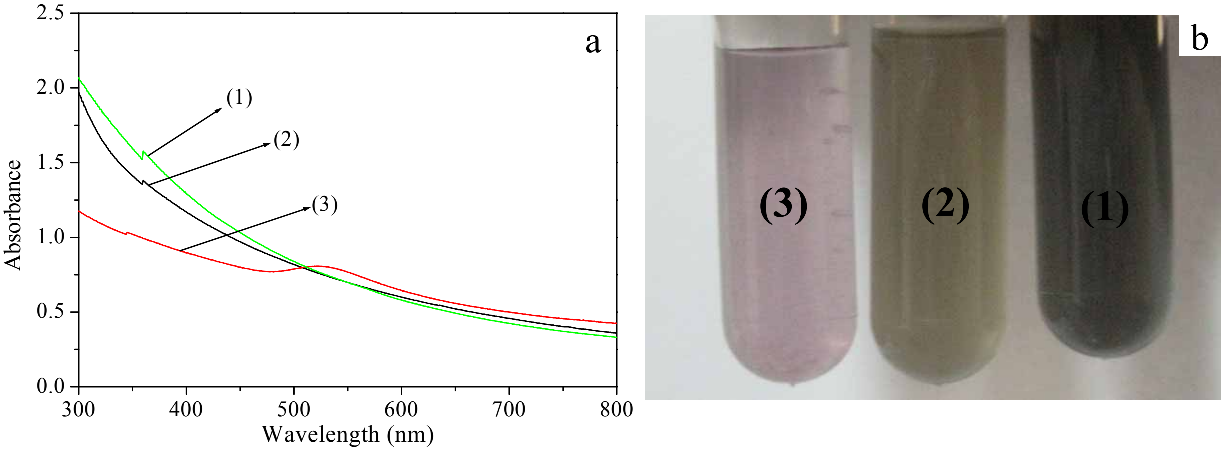

Figure S4. (a) UV-vis absorption spectra of Pt-NH_2-HMSNs suspension (1), Au-Pt-NH_2-HMSNs suspension (2) and aqueous mixture of Au-NH_2-HMSNs and Pt-NH_2-HMSNs (3). (b) The corresponding digital images of Pt-NH_2-HMSNs suspension (1), Au-Pt-NH_2-HMSNs suspension (2) and aqueous mixture of Au-NH_2-HMSNs and Pt-NH_2-HMSNs (3).

Curves (1) and (2) show no peak, but curve (3) shows a peak at 523 nm in the wavelength range of 400–600 nm. The absence of Au surface plasmon resonance band in the absorption spectrum of Au-Pt-NH_2-HMSNs suspension indicates that the obtained Au-Pt NPs are not the mixture of isolated Au NPs and Pt NPs but rather Au-Pt bimetallic NPs.[3,4]

[3] J. He, I. Ichinose, T. Kunitake, A. Nakao, *J. Am. Chem. Soc.* **2003**, *125*, 11034-11040.

[4] L. Wang, B. Qi, L. Sun, Y. Sun, C. Guo, Z. Li, *Mater. Lett.* **2008**, *62*, 1279-1282.

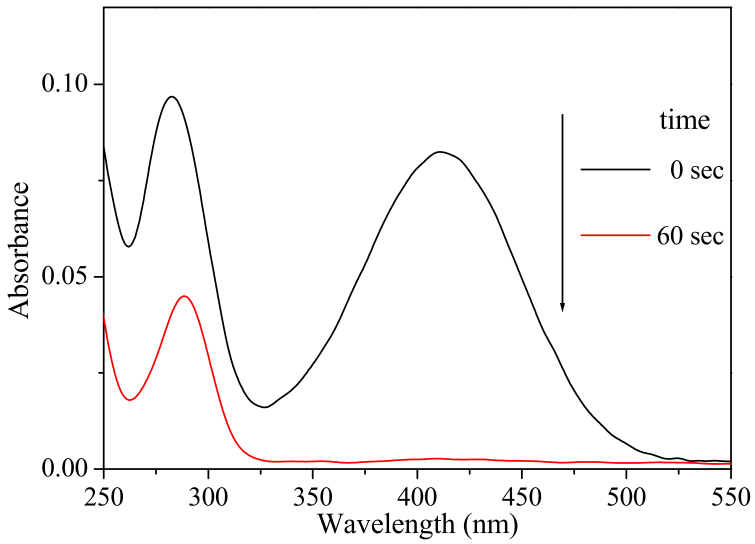

Figure S5. UV-vis absorption spectra of the reaction mixture at 0 and 60 s when the molar ratio of Au:2-NA:$NaBH_4$ in the catalytic reaction was about 1:15:75. The reaction progress was monitored by taking a small portion (0.1mL) of the reaction mixture into 1.9 mL of water for immediate determination of UV-vis absorption spectra.

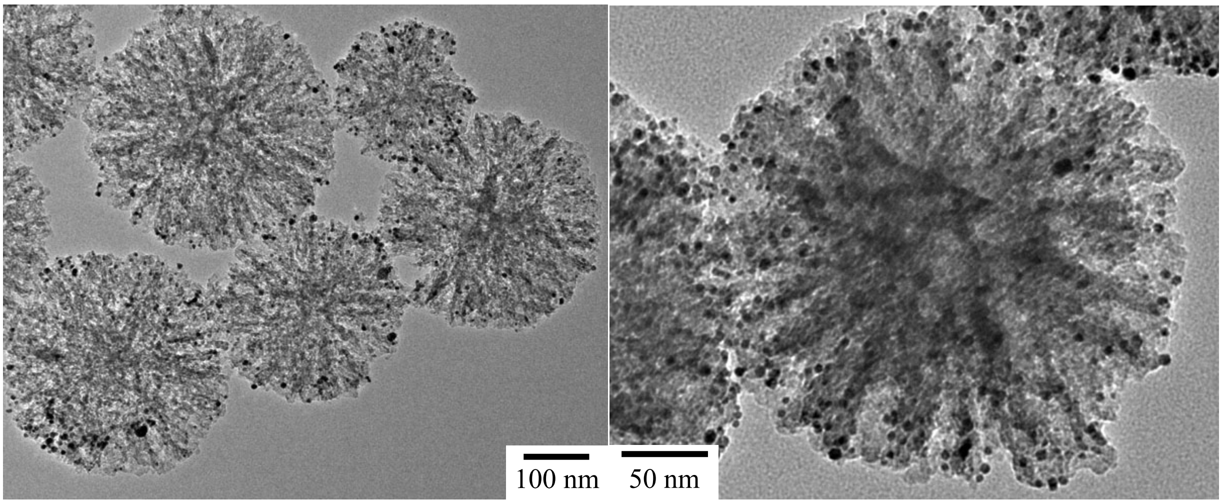

Figure S6. TEM images of the recovered Au-NH_2-HMSNs after 10 cycles of the catalytic reaction when the molar ratio of Au:2-NA:$NaBH_4$ in the catalytic reaction was about 1:15:75.

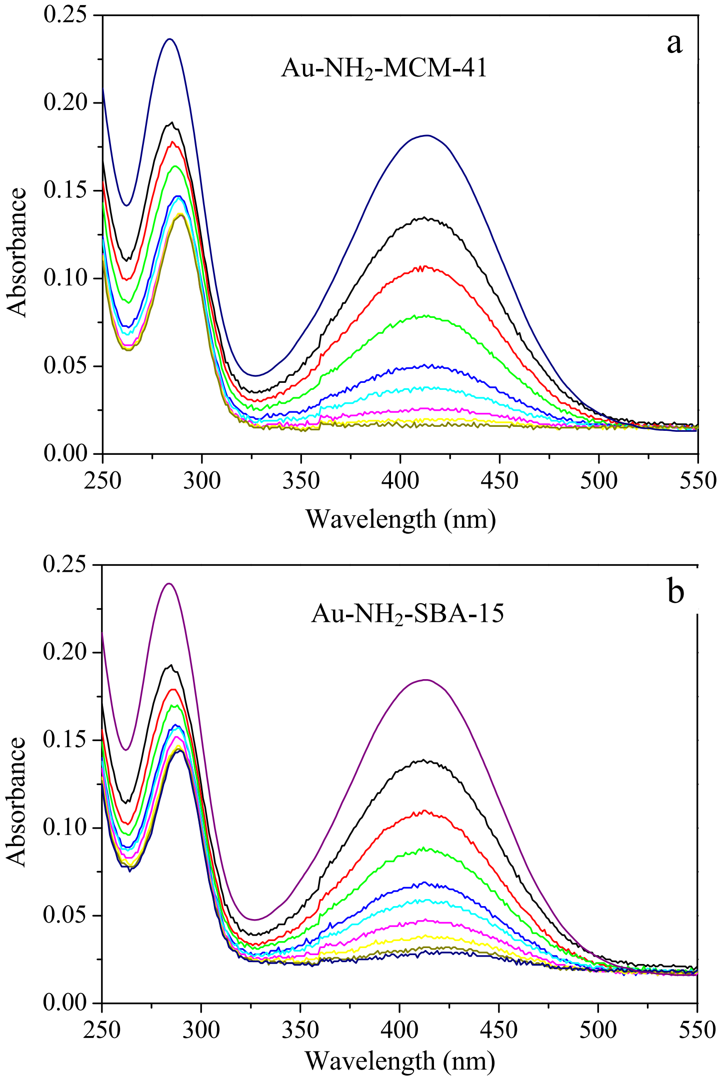

Figure S7. Time-dependent UV-vis absorption spectral changes of the reaction mixtures catalyzed by Au-NH_2-MCM-41 (a) and Au-NH_2-SBA-15 (b), respectively, when the molar ratio of Au:2-NA:$NaBH_4$ was about 1:150:750 in the catalytic reaction.

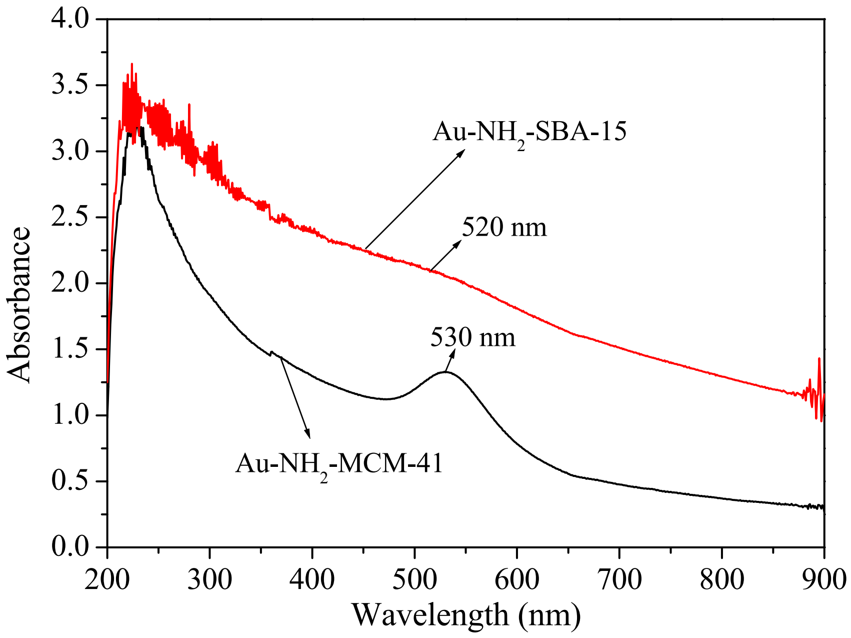

Figure S8. (a) UV-vis absorption spectra of Au-NH$_2$-MCM-41 and Au-NH$_2$-SBA-15 suspensions, respectively.