Supporting Information

Multi-functional Mesoporous Composite Microspheres with Well-designed Nanostructure: A Highly Integrated Catalyst System

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Experimental Section

Thermal stability investigation of Fe_3O_4@SiO_2 –Au@SiO_2 microspheres and Au-impregnated 3-D macroporous silica monolith

The 3-D ordered macroporous silica monolith was synthesized by using a colloidal crystal of monodispersed poly(methyl methacrylate) (PMMA) latexes (~ 380 nm in diameter) as a template and pre-hydrolyzed tetraethyl orthosilicate as a silica source. After being calcined in air to remove the PMMA template, 3-D ordered macroporous silica monolith with the pore size of about 300 nm and window size of about 50 nm was obtained. A piece of 3-D ordered macroporous silica monolith (with a dimension of 1.0 cm x 1.0 cm) was immersed in a solution of the Au nanoparticles with the size of ~ 12 nm (50 mL, 0.1 wt%) for soaking for 2 h. After that, the monolith was quickly rinsed with deioned water for 2 times, blotted up with a filtration paper and finally dried in vacuum at 50 °C. The obtained Au-macroporous silica monolith and Fe_3O_4@SiO_2–Au@SiO_2 microspheres (50 mg) were treated at 300 °C in argon for 2 h in tubular furnace to study their thermal stability. The obtained samples were subject to TEM analysis and X-ray diffraction measurements.

Deposition of Ag nanoparticles on Fe_3O_4@SiO_2 microspheres

The Ag nanoparticles were deposited on the Fe_3O_4@SiO_2 microspheres according to previously reported method.[1] Specifically, 0.026 g of $AgNO_3$ was dissolved in 150 mL of ethanol under ultrasonication, and the resultant solution was mixed with 50 mL of Fe_3O_4@SiO_2 microspheres ethanol dispersion (containing 0.12 g of microspheres) in a polypropylene flask. The dispersion was mechanically stirred at 50 °C. After stirring for 5 min, 1.0 mL of *n*-butylamine ethanol solution (0.01 g/mL) was added with a syringe. The reaction solution was further stirred for 3 h. Finally, the Fe_3O_4@SiO_2-Ag particles were separated with a magnet and washed with ethanol for 3 times. The obtained Fe_3O_4@SiO_2-Ag particles were used for subsequent further coating with mesoporous silica according to procedures for the Fe_3O_4@SiO_2-Au@mSiO_2.

Reference

1. Kim, K.; Kim, H. S.; Park, H. K. *Longmuir* **2006**, *22*, 8083-8088.

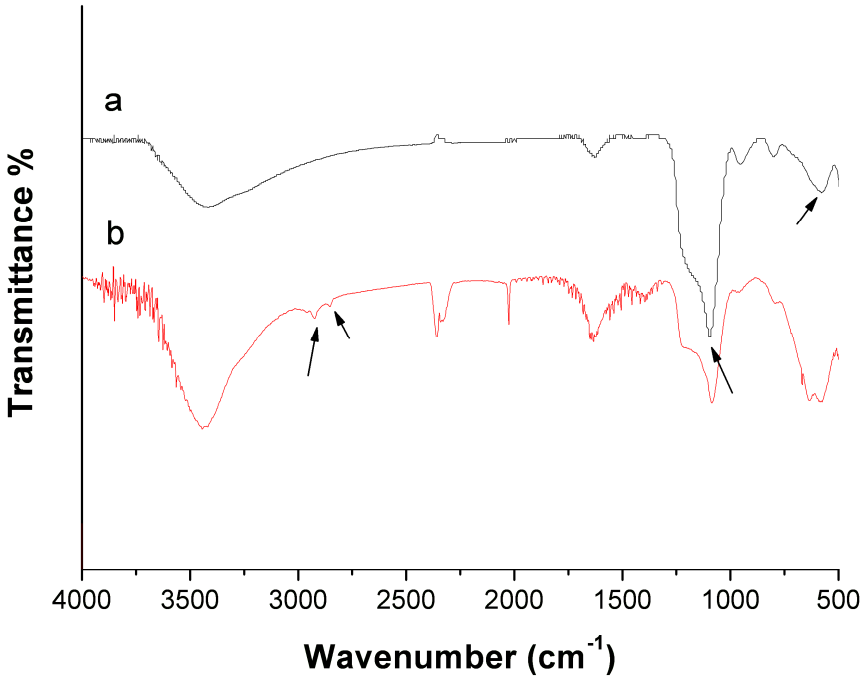

Figure S1. FT-IR spectra of the Fe_3O_4@SiO_2 microspheres before (a) and after (b) surface modification with 3-aminopropyltriethylsilane (APTS), wherein, the absorption bands at 580 and 1090 cm^{-1} are assigned to the Fe-O and Si-O-Si vibrations, respectively, and the new peaks at 2920 and 2852 cm^{-1} correspond to -CH_2- group of aminopropyl from APTS molecules. Contributions from –NH_2 group were probably overlapped by vibration bands related with silanol groups and adsorbed water.

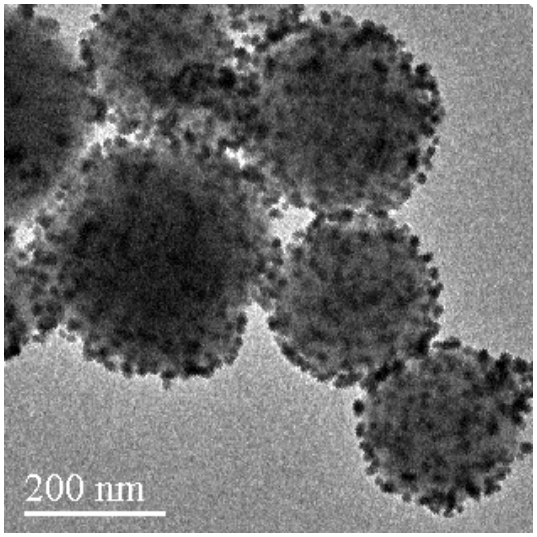

Figure S2. The TEM image of the Fe_3O_4@SiO_2–Au microspheres with a low magnification, showing that the Fe_3O_4@SiO_2 microspheres were evenly decorated with Au nanoparticles of about 12 nm in size.

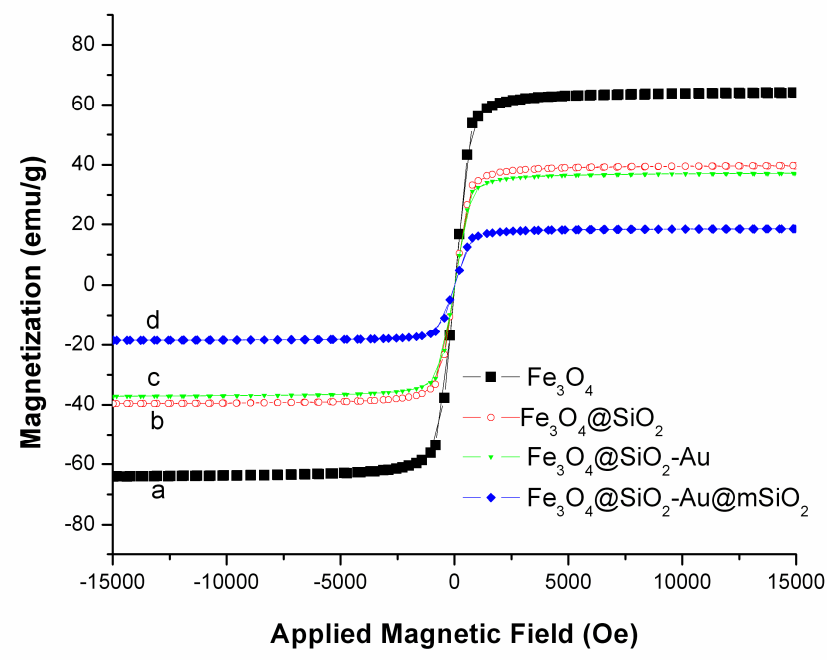

Figure S3. The magnetic hysteresis loops of (a) the Fe_3O_4 particles, (b) the core-shell Fe_3O_4@SiO_2 microspheres, (c) the Fe_3O_4@SiO_2-Au microspheres and (d) the Fe_3O_4@SiO_2-Au@mSiO_2 microspheres with 90-nm thickness outer mesoporous silica layer.

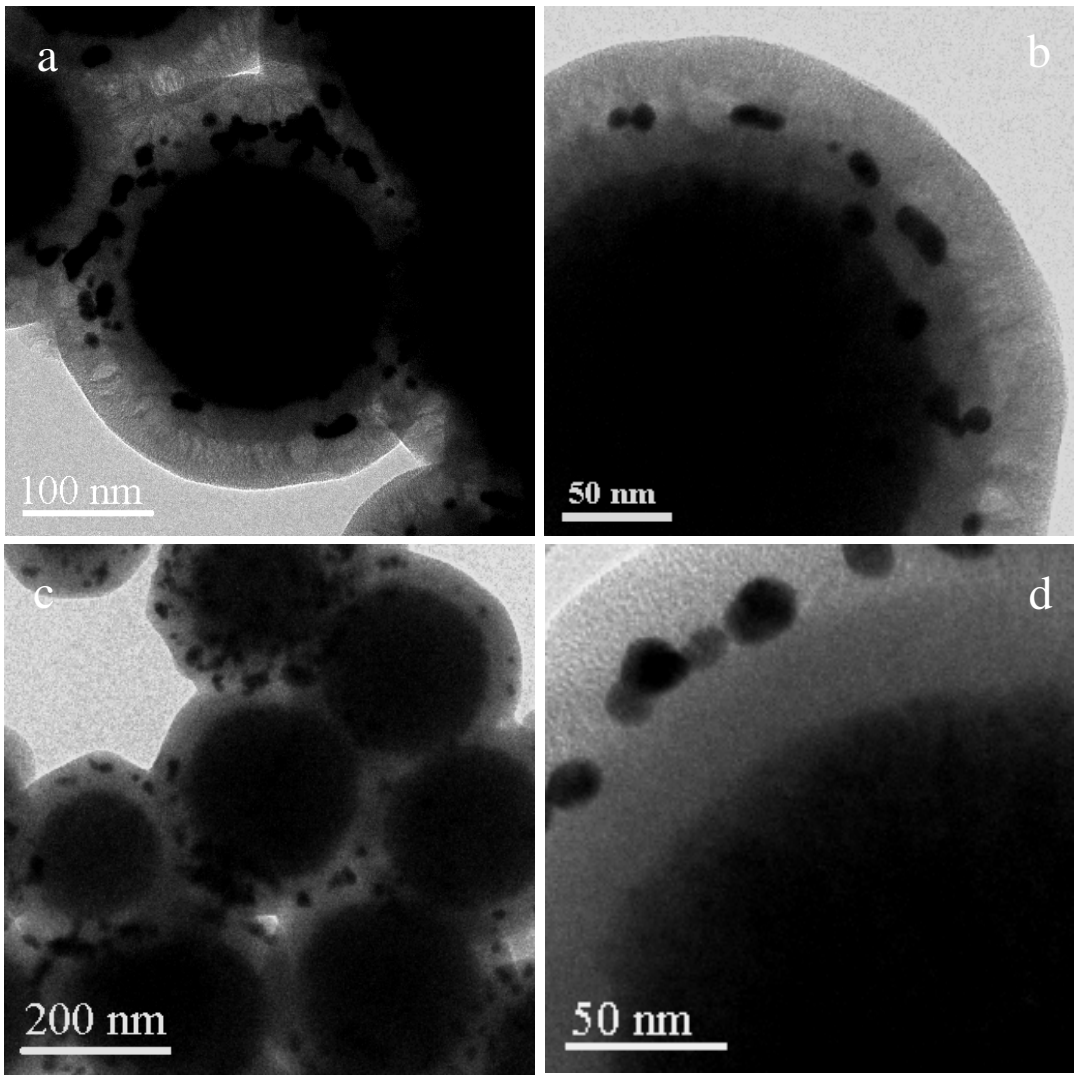

Figure S4. TEM images of the Fe_3O_4@SiO_2-Au@mSiO_2 microspheres with (a, b) 40-nm and (c, d) 20-nm thick mesoporous silica shells, respectively.

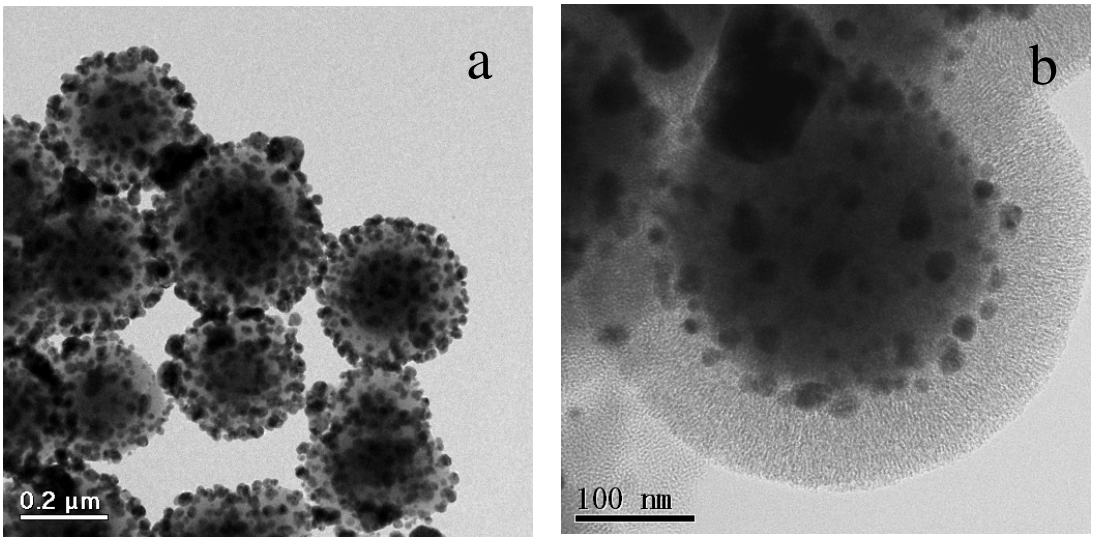

Figure S5. TEM images of (a) the Fe_3O_4@SiO_2-Ag particles and (b) Fe_3O_4@SiO_2-Ag@mSiO_2 microspheres.