

Electronic Supplementary Information

Controlled synthesis of novel cyanopropyl polysilsesquioxane hollow spheres loaded with highly dispersed Au nanoparticles for catalytic applications

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Materials

3-cyanopropyltriethoxysilane (98%), H₂AuCl₄·3H₂O (99.9%), sodium borohydride (99%), 4-nitrophenol (99%), styrene (99%) and polyvinylpyrrolidone (PVP40) were obtained from Sigma-Aldrich. Potassium persulfate (KPS) was supplied by Hayashi Pure Chemicals. Ammonia aqueous solution (28 wt%) was purchased from Junsei Chemical. All chemicals were used as received without any further purification. Distilled water from a Milli-Q water system was used throughout the experiment.

Experimental Methods

1. CPSQ hollow spheres: Polystyrene (PS) latexes were prepared by the method as described elsewhere (Dong et al., *Chem. Commun.*, 2010, 7498). PS suspension (2 g, 0.14 g solid contained) was mixed with NH₃·H₂O (3.5 mL) in 28 ml of water in a water bath of 50°C. Then, 3-cyanopropyltriethoxysilane (5 mmol) was slowly added dropwise under stirring. After reaction for 24 h, the product was isolated by centrifugation and filtration, washed with distilled water, and dried under vacuum. For

control experiments, CPSQ solid spheres were prepared by the same procedure without using the PS template. Methyl-functional polysilsesquioxane (MPSQ) hollow spheres were also fabricated by using methyltrimethoxysilane (10 mmol, for similar particle size to that of CPSQ hollow spheres) as precursor with the same procedure.

2. Au/CPSQ hybrid hollow spheres: The hybrid nanocomposites were fabricated by using CPSQ hollow spheres as support and HAuCl_4 as the gold source through an aqueous impregnation method. 1 mL freshly prepared $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution (10 mM) was added to 29 g of CPSQ hollow sphere suspensions (0.12 g solid containing) under magnetic stirring at room temperature. After stirring for 12 h, 1 mL freshly prepared NaBH_4 (0.03 M) was added into the mixture under stirring at room temperature. After stirring for 3 h, the product was collected by centrifugation and dried at 60 °C overnight in a vacuum oven for further use. MPSQ hollow spheres and CPSQ solid spheres were also used as support for loading Au nanoparticles with the same procedure.

3. Catalytic reduction of 4-nitrophenol: Au/CPSQ hybrid nanocomposite aqueous suspension (5 mL, 0.4 g/L) was added to NaBH_4 aqueous solution (5 mL, 0.3 M), and the mixture was stirred for 10 min at room temperature. 4-nitrophenol (5 mL, 0.003 M) was then added to the mixture, which was stirred until the bright yellow gradually changed to colorless. The reaction progress was monitored by measuring UV-vis absorption spectra of the mixture. To study the catalyst durability, the catalyst was centrifuged after reaction for 60 minutes, and the clear supernatant liquid was decanted carefully. The catalyst was washed thoroughly with water and ethanol, followed by drying at 60 °C for 6 h in vacuum oven. Then, the catalyst was reused for subsequent recycle under the same reaction conditions.

Characterizations

1. TEM images were taken using a JEM-2011 electron microscope operating at 200 kV. Samples were dispersed in ethanol, ultrasonicated for 2 min, and then collected by using carbon-film-covered copper grids for TEM measurements.
2. SEM images were recorded with a field emission XL-30 SEM with energy-dispersive X-ray spectrometer (EDX). A thin Os film was sprayed on the

sample before measurements.

3. The ^{29}Si NMR spectrum was obtained on a Varian Inc., 400 MHz UNITY INOVA spectrometer at room temperature with the resonance frequency of 79.5 MHz, a magic-angle spinning at 5 kHz, 90° pulse length of 6.5 μs and a repetition delay of 60 s.
4. The X-ray photoelectron spectroscopy (XPS) spectrum was recorded using a VG Scientific Model ESCA Lab 250 XPS spectrometer.
5. The X-ray diffraction (XRD) pattern of the sample was recorded using a Philips diffractometer with a Geiger counter . The X-ray tube was operated at 40 kV and 30 mA (Cu $K\alpha$ radiation with Ni filter, $\lambda = 1.5406 \text{ \AA}$). Scans were made from 1.2 to 70° (2θ) at the speed of $1^\circ/\text{min}$.
6. FTIR of KBr powder-pressed pellets was recorded on a JASCO FT/IR-4100 infrared spectrometer.
7. UV-vis absorption spectra were taken on a spectrophotometer (Hitachi UV-2010).
8. TGA analysis was performed using TG instrument Q500 from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 gas.

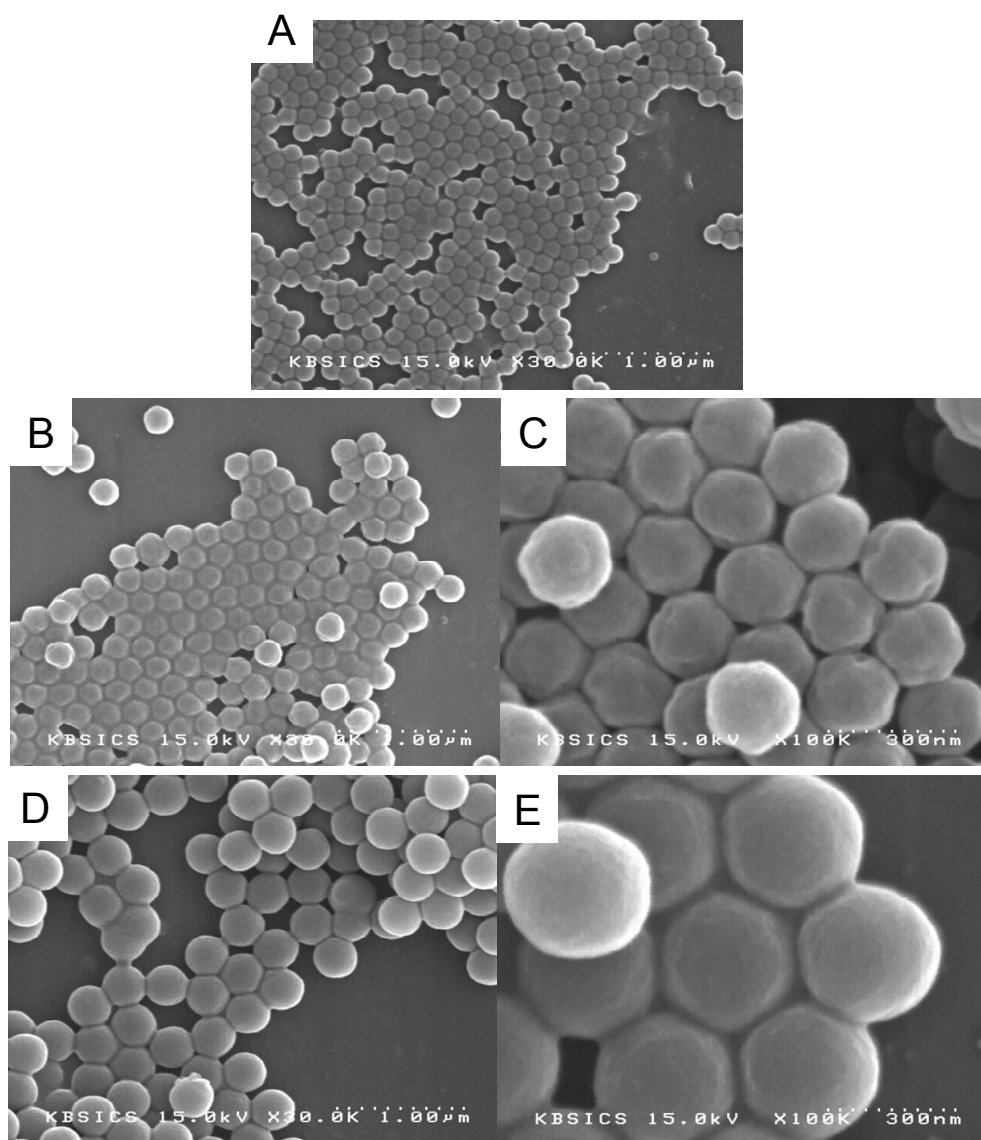


Fig. S1 SEM images of A) the PS latexes and CPSQ hollow spheres generated from different amounts of 3-cyanopropyltriethoxysilane precursor. (B, C) 2.5 mmol; (D, E) 10 mmol.

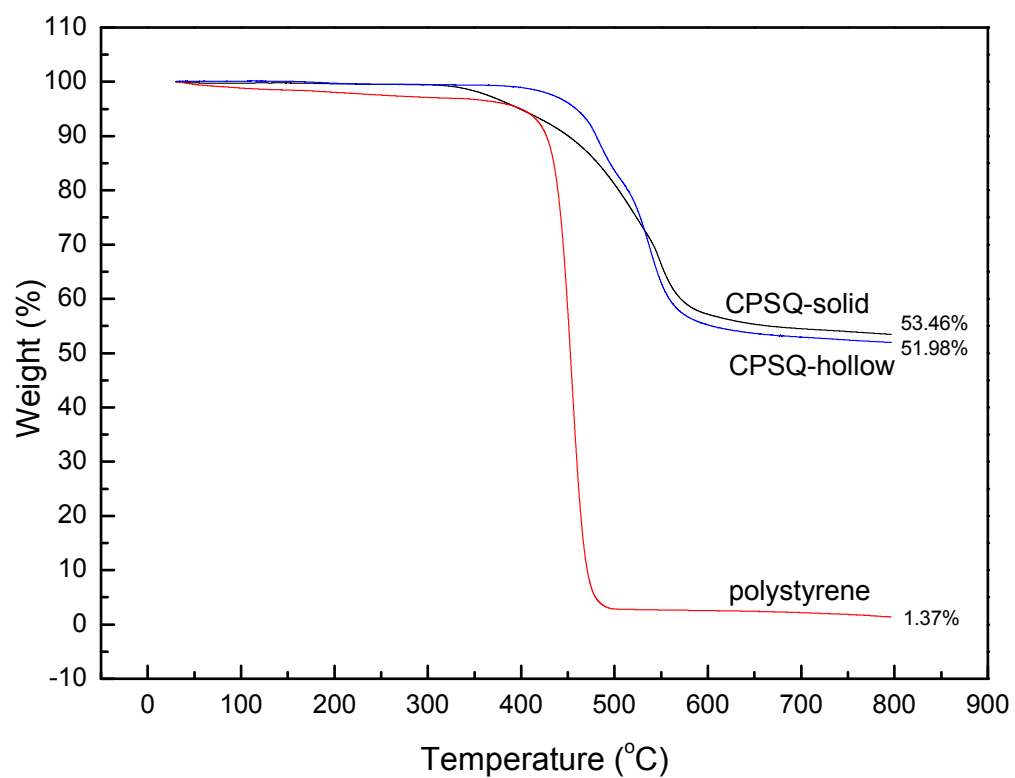


Fig. S2 TGA thermograms of CPSQ solid spheres, CPSQ hollow spheres and polystyrene.

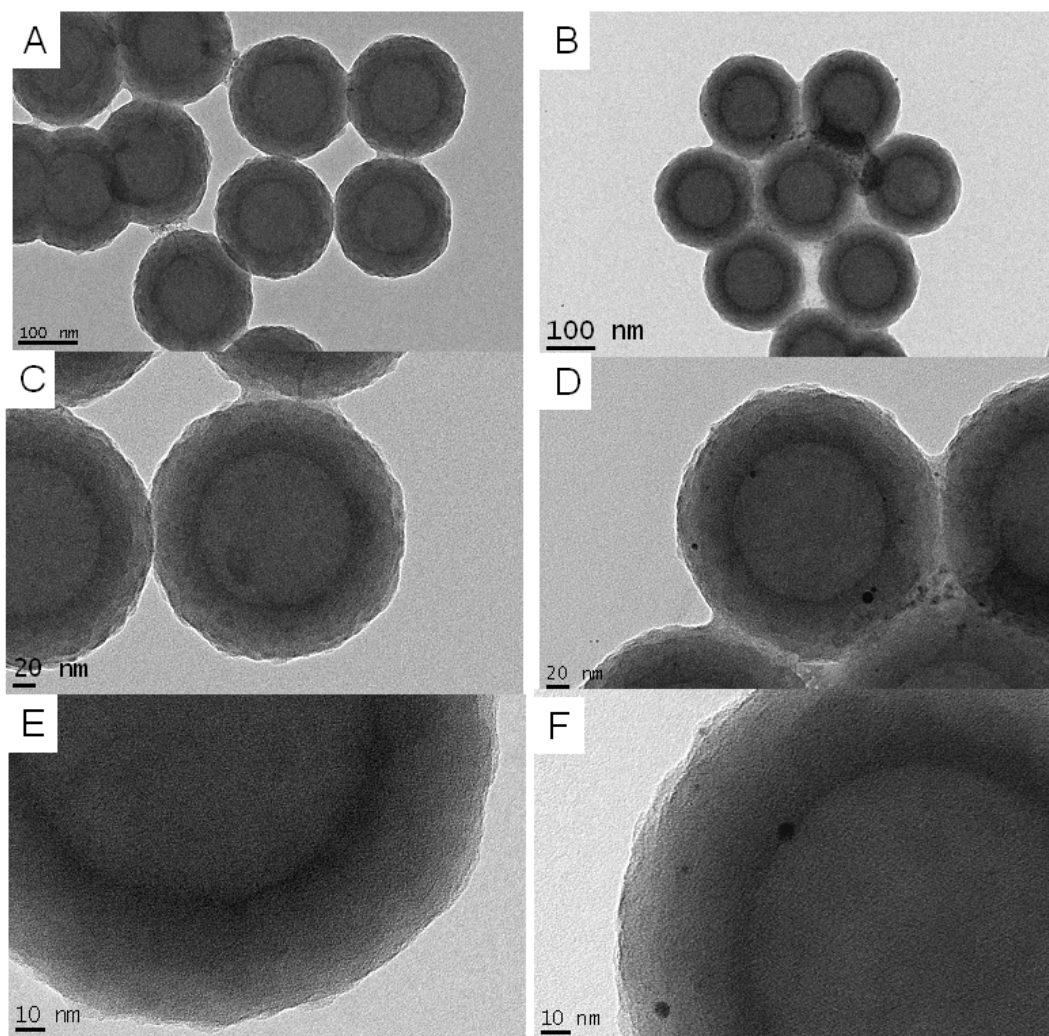


Fig. S3 TEM images of A, C, E) MPSQ hollow spheres and B, D, F) the corresponding Au-loaded MPSQ hollow spheres, where MPSQ stands for methyl-functional polysilsesquioxanes.

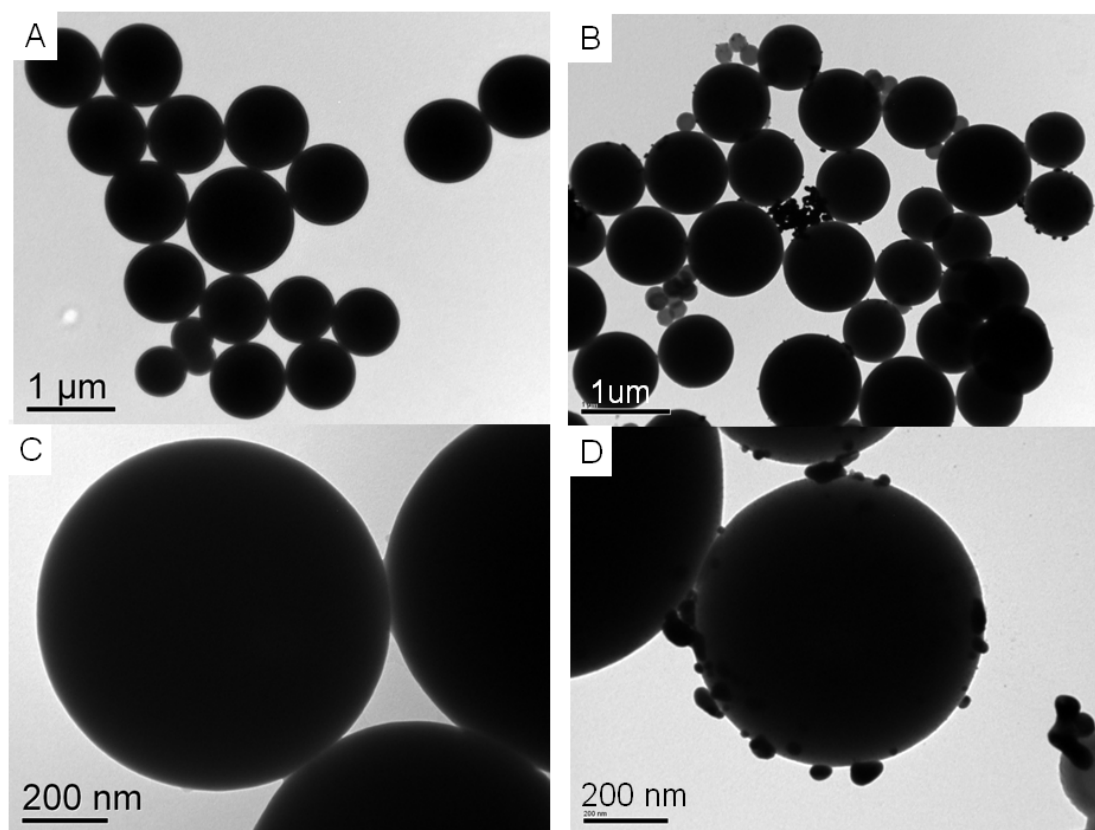


Fig. S4 TEM images of A, C) CPSQ solid spheres and B, D) the corresponding Au-loaded CPSQ solid spheres.