

Supporting Information

A soft-templated method to synthesize sintering-resistant Au/mesoporous-silica core-shell nanocatalysts with sub-5 nm single-core

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Experience:

1 Synthesis of TTAB stabled Au colloids.

The synthesis of TTAB-capped Au nanoparticles was carried out by following the reported method¹ with a modification. Typically, 5 ml of aqueous 10 mM HAuCl₄ and 12.5 ml of 100 mM TTAB were mixed with 29.5 ml of water in a 100 ml round bottom flask at room temperature. The mixture was stirred at room temperature for 10 min and was heated at 50 °C for 10 min. 3 ml of 500 mM ice-cooled NaBH₄ solution was injected through the septum using a syringe. The gas evolved inside the flask was released by inserting a needle through the septum for 20 min. The needle was then removed and the solution was kept at 50 °C for 15 h. The achieved Au colloids were collected for further use.

2 Synthesis of Au@m-SiO₂ core-shell nanoparticles.

The synthesis of the 42 nm dia. single-core Au@m-SiO₂ nanoparticles was carried out as follows: 18 ml as-synthesized gold colloids were mixed with 162 ml TTAB solution (0.15 mmol); 0.90 ml of 1 M NaOH was then added to the solution to adjust the pH to 11.4; 1.8 g TEOS was introduced and kept stirring for 3 hours at 25 °C; the as-synthesised core-shell nanoparticles was obtained after centrifuge and washing with water and ethanol. After drying at 80 °C for 1 hour, the powder was calcined at 550 °C for 3 hours to remove the TTAB surfactant. Single-core nanoparticles with different diameters could be achieved only by changing the TEOS concentration.

Core-shell nanoparticles with different core numbers were prepared in the same way only by changing the gold colloid amount. And addition of TTAB might be needed to keep the required concentration (between 3.33 and 4.17 mM), which guaranteed the formation of spherical structure.

3 Synthesis of Au/SiO₂ supported catalyst

The supported Au/SiO₂ catalyst with 2.9% gold loading was prepared as follows: 22.5 ml gold colloids were mixed with 0.15 g amorphous SiO₂. Then, the mixture was stirred at 50 °C for 12 hours to evaporate the water. The powder was collected and dried at 80 °C for 1 hour. Finally, the powder was calcined at 550 °C for 3 hours to remove the TTAB surfactants.

4 Characterization.

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance diffractometer with Cu K α radiation. Transmission electron microscopy (TEM) images were obtained with a JEM 2100 microscope operated at 200 kV. Scanning electron microscopy (SEM) images were obtained on a S4800 microscope operated at 20 kV. Nitrogen sorption isotherms were measured at 77 K by using a ASAP-2020M system. The surface area and pore size were obtained by using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Elemental analysis was performed using inductivity coupled plasma (ICP) on a PE Optima 2100DV spectrometer.

5 Catalytic test: CO oxidation

The catalysis test was carried out on a Finetec Finesorb-3010. 50 mg Au@m-SiO₂ sample was packed into a U-type quartz tube (i.d.=4 mm) sealed by quartz wool. Before the reaction test, the catalyst was reduced in flowing 10% H₂ (balance Ar) at 450 °C for 1h. The reduced catalyst cooled down and kept at room temperature for more than 10 hours. For the test, a gas stream of 1% CO (balance air, < 1ppm water) flowed through the catalyst at a rate of 30 ml/min (36000 ml_{cat}⁻¹h⁻¹), and the existing stream analyzed by FGA-4100 five components gas analyzer.

References

1. H. Lee, S. E. Habas, S. Kweskin, D. Butcher, G. A. Somorjai and P. Yang, *Angewandte Chemie-International Edition*, 2006, 45, 7824-7828.

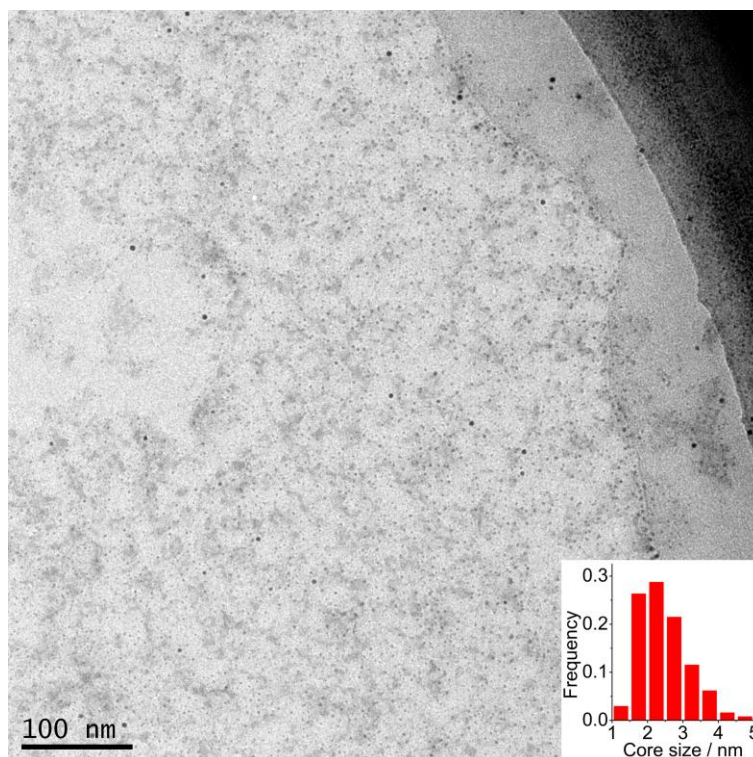


Fig.S1 TEM image of Au-TTAB colloids.

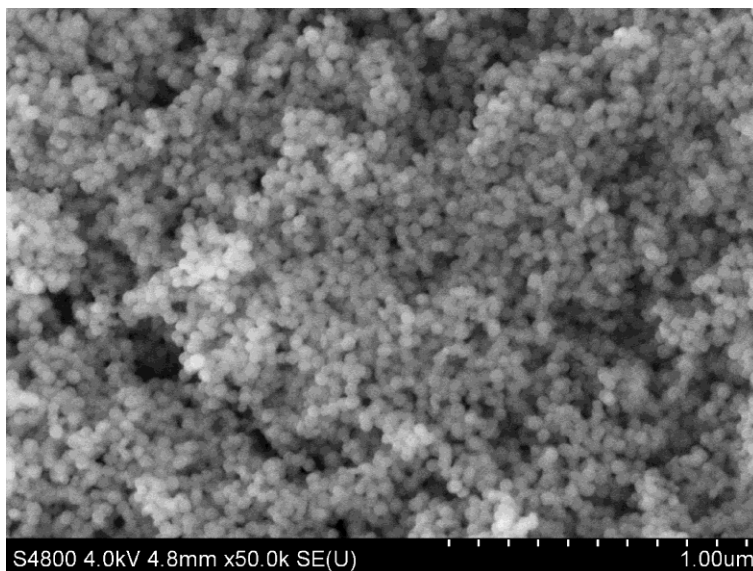


Fig.S2 SEM image of Au@TTAB-SiO₂ nanoparticles.

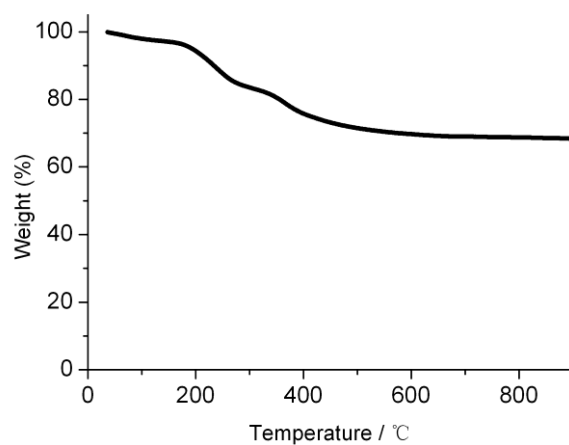


Fig.S3 TG curve of Au@TTAB-SiO₂.

Sphere size (nm)	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
30	1122.4	2.3	1.54
42	735.9	2.2	0.92
48	648.2	2.0	0.46

Table.S4 Surface properties of Au@m-SiO₂ spheres with different sizes.

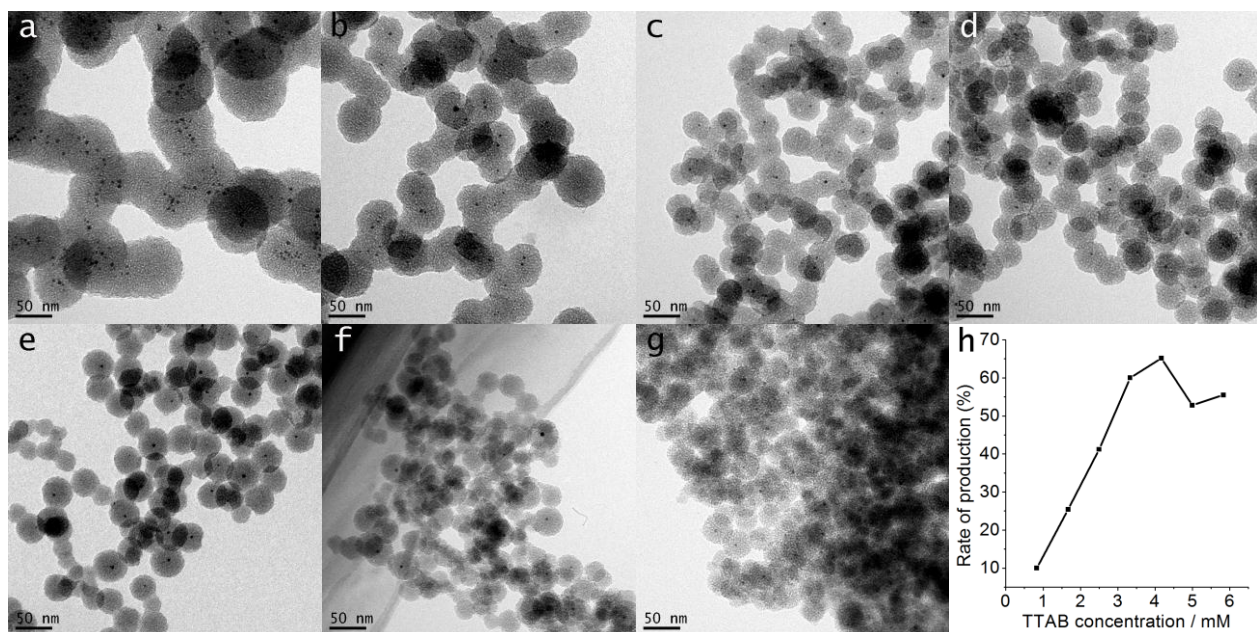


Fig.S5 TEM images of Au@TTAB-SiO₂ nanostructures synthesized in different TTAB concentrations: (a) 0.83 mM, (b) 1.67 mM, (c) 2.50 mM, (d) 3.33 mM, (e) 4.17 mM, (f) 5.00 mM, (g) 5.83mM. (h) The relationship between TTAB concentration and the rate of production. When the TTAB concentration was between 3.33 mM (d) and 4.17 mM (e), monodisperse spherical core-shell nanoparticles can be achieved with a high rate of production. Lower TTAB concentrations lead to connection between SiO₂ spheres (a, b, c) and with low productions. Higher TTAB concentrations result in small SiO₂ fragments and serious aggregation (f, g).

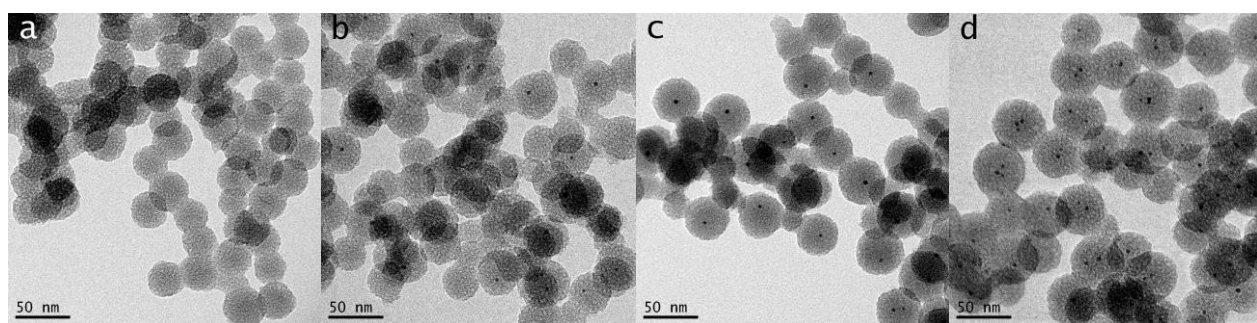


Fig.S6 Whole scale TEM images of Fig.3a-d. The Au@TTAB-SiO₂ nanoparticles obtained at the pH value of 11.4 with different gold concentrations: (a) 0 mM, (b) 0.067 mM, (c) 0.100 mM, (d) 0.167 mM.

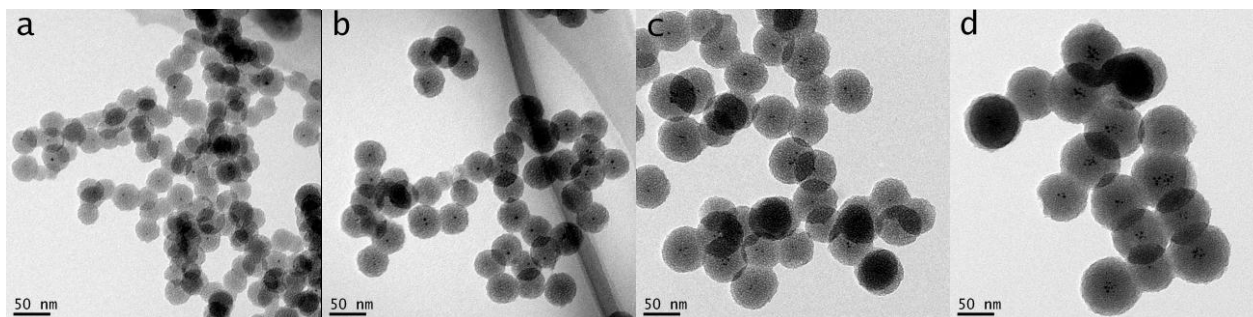


Fig.S7 Whole scale TEM images of Fig.3e-h. The Au@TTAB-SiO₂ nanoparticles obtained with the gold concentration of 0.100 mM at different pH value: (a) 11.1, (b) 11.5, (c) 11.7, (d) 11.8.

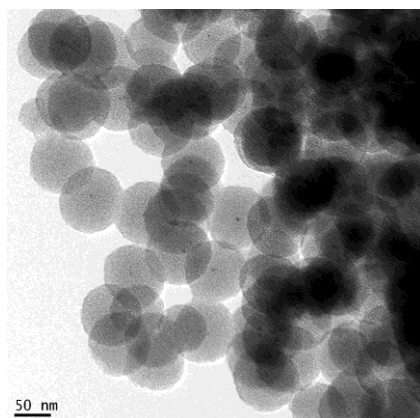


Fig.S8 TEM images of 70~80 nm dia. single-core spheres obtained at pH 11.8 with the gold concentration of 0.033 mM.

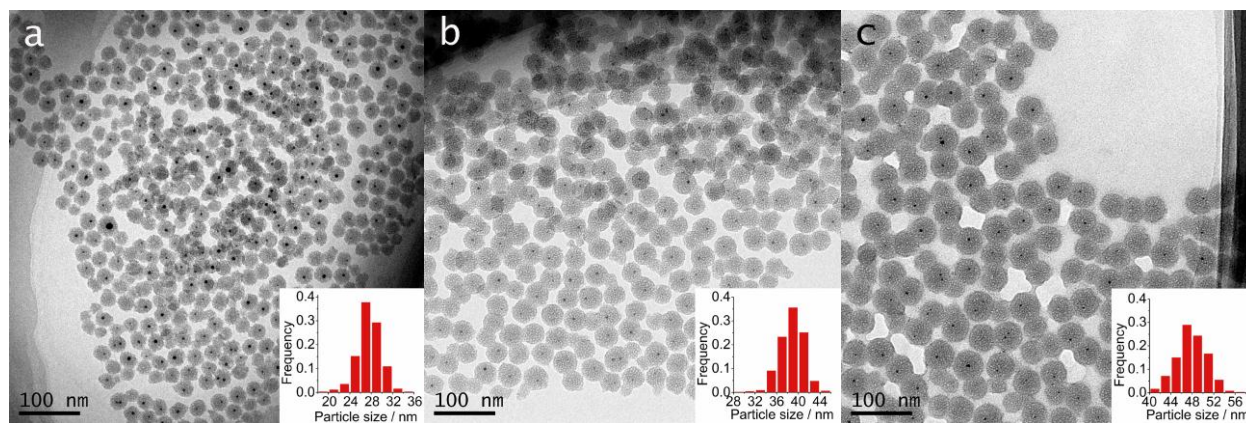


Fig.S9 TEM images of Au@m-SiO₂ spheres with diameters of about: (a) 28 nm, (b) 39 nm, (c) 48 nm in average. The samples were achieved by adjusting the TEOS concentration: (a) 0.016 M, (b) 0.048 M, (c) 0.096 M.

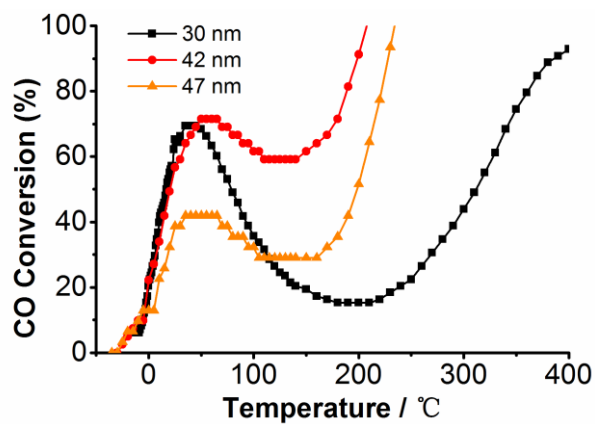


Fig.S10 CO conversion of particles with different sphere size. The curves have adjusted to a same gold content (2.9 wt%).

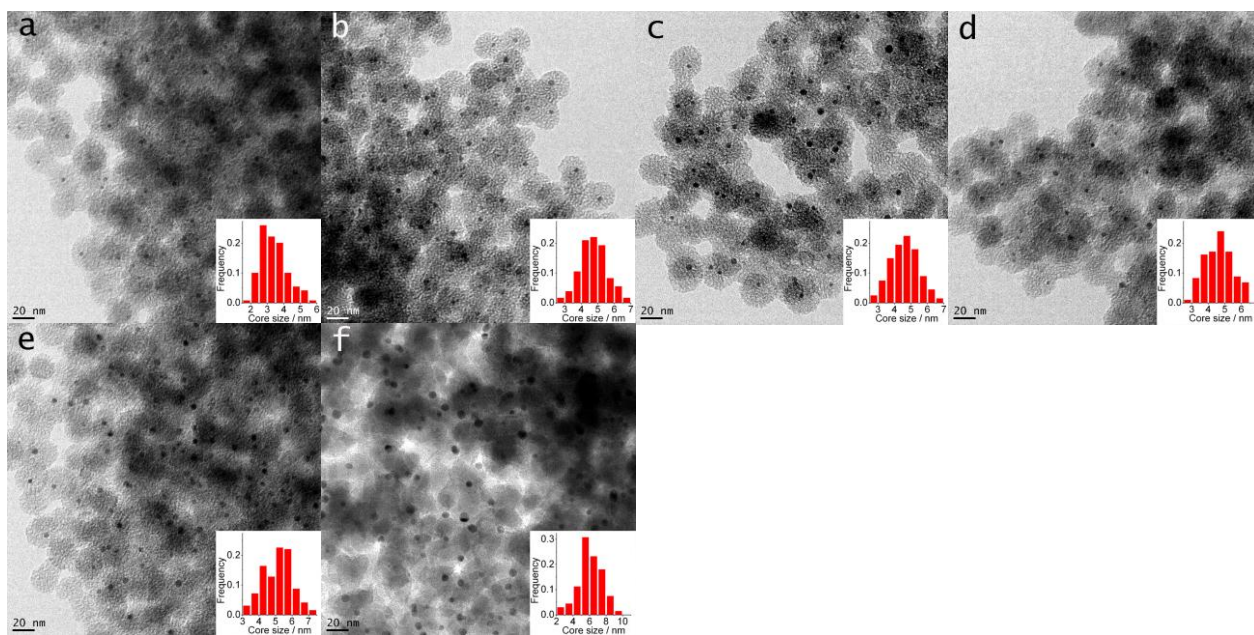
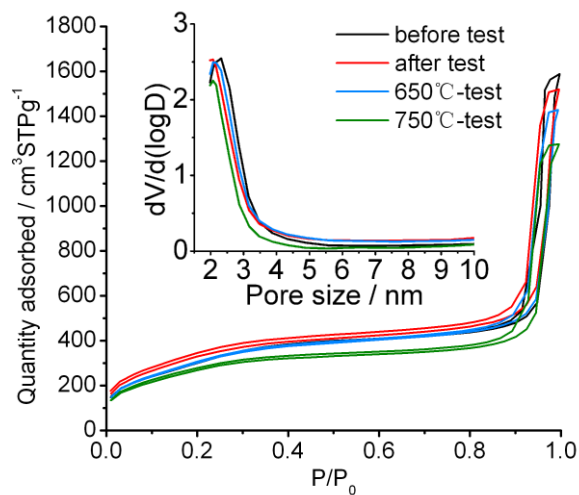


Fig.S11 TEM images of single-core Au@SiO₂ nanoparticles: (a) before removing TTAB by calcining, (b) after removing TTAB and before the test, (c) after the test, (d) after the calcination at 650°C and test, (e) after the calcination at 750°C and the test. (f) TEM images of the Au/SiO₂ samples before removing TTAB by calcining. The average sizes of Au particles were (a) 3.4 nm, (b) 4.6 nm, (c) 4.5 nm, (d) 4.7 nm, (e) 5.1 nm, (f) 6.1 nm.



Au@m-SiO ₂ - 30nm	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
Before the test	1122.4	2.3	1.54
After the test	1232.7	2.1	1.53
650°C calcined – tested	1133.7	2.2	1.51
750°C calcined – tested	1011.1	2.1	1.68

Fig.S12 N₂ sorption isotherms, pore size distributions and detail surface properties of Au@m-SiO₂ particles after different treatments. 6