Supporting Information

for

The encapsulation of metal nanoparticles within porous liquids

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Experimental

Materials

All chemicals were used as received. Pluronic F127, 3-mercaptopropyltrimethoxysilane, tetramethoxysilane, poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt (PEGS), tetrachloroauric(III) acid trihydrate, chloroplatinic(IV) acid hydrate, palladium(II) acetate (all Sigma Aldrich), anhydrous potassium sulfate, mesitylene, toluene, hydrochloric acid (32%), mesitylene (all Merck), acetone, ethanol (both UChem) and *N*,*N*-didecyl-*N*-methyl-*N*-(3-triethoxysilylpropyl)ammonium chloride (organosilane, 40-42% in methanol, Gelest). All water used was de-ionised using a MilliQ (Millipore) Ultra Pure Water System.

Preparation of hollow SiO₂ spheres (SiO₂)

Hollow silica spheres were synthesised based on a procedure by Zheng *et al.*¹ Pluronic F127 (1.4 g) and K₂SO₄ (4.9 g) were dissolved in water (84 mL) and the resulting solution was cooled to 13.5 °C. A solution of 3-mercaptopropyltrimethoxysilane (0.67 mL) in mesitylene (1.62 mL) was added and the mixed solution was stirred at 13.5 °C for 3 h. Tetramethoxysilane (4.11 mL) was added and the mixture was stirred at 13.5 °C for an additional 24 h. The mixture was aged at 100 °C for 24 h in a Teflon-lined autoclave before filtering, washing the solid with excess water and drying at 60 °C to produce F127@SiO₂. To produce pure hollow silica spheres (SiO₂) the F127@SiO₂ was calcined in air at 550 °C for 10 h with a ramp rate of 2 °C min⁻¹.

Preparation of hollow thiol-functionalised SiO₂ spheres (HS-SiO₂)

To produce thiol-functionalised silica (HS-SiO₂), F127@SiO₂ (1.0 g) synthesised as above was refluxed in a solution of hydrochloric acid (3 mL, 32%) in ethanol (200 mL) for 24 h. The mixture was filtered and the solid washed with water then ethanol before drying at 60 °C.

Synthesis of $M@HS-SiO_2$ (M = Au, Pt, Pd)

The encapsulation of the metal nanoparticles within the hollow silica spheres was based on a method by Zheng *et al.*¹ HS-SiO₂ (0.5 g) was stirred in a solution of the metal precursor (HAuCl₄.3H₂O or H₂PtCl₆.xH₂O; ~20 mg metal) in water (50 mL) at room temperature for 24 h before the mixture was filtered and the solid was washed with water and dried at 60 °C. The resulting powder was reduced under a 9% H₂/N₂ flow at 300 °C for 6 h with a 2 °C min⁻¹ ramp rate.

For the encapsulation of Pd the above was repeated using $Pd(OAc)_2$ as the metal precursor and acetone as the solvent.

Synthesis of $Au@SiO_2$

To remove the thiol groups the Au@HS-SiO₂ synthesised above was calcined under an air flow at 350 °C for 10 h with a 2 °C min⁻¹ ramp rate to produce Au@SiO₂.

Synthesis of porous liquids

The porous liquids were synthesised following a procedure by Zhang *et al.*² The silica spheres (1.0 g) were sonicated in an aqueous alkaline solution (20 mL, pH ~9-10, NH₄OH) for 30 min. The organosilane (2.0 mL) was added and the mixture was stirred at room temperature for 24 h. The mixture was filtered and the solid was washed with water then ethanol before drying at 60 °C. The organosilane-functionalised silica (1.0 g) was treated with an aqueous PEGS solution (12.5 %, 30 mL) at 70 °C for 24 h. The excess PEGS was extracted with warm toluene three times and the aqueous phase was dried using a rotary evaporator. The remaining material was dispersed in acetone and centrifuged at 16000 rpm for 20 min and the supernatant was separated. The residual was washed once by being re-suspended in acetone before centrifuging at 16000 rpm for 20 min. The combined supernatants were dried under vacuum at 60 °C overnight to produce a viscous liquid.

Characterisation

Raman spectra were recorded using Bruker MultiRAM FT-Raman Sectrometer. X-ray photoelectron spectroscopy (XPS) data were collected with a Thermo Fisher Scientific K-Alpha+ X-ray Photoelectron Spectrometer. Samples were compressed using a pellet press for XPS analysis. The binding energies were referenced to C1s peak at 284.8 eV from adventitious carbon. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 operating at 200 kV. High Resolution TEM (HRTEM) was performed using a JEOL JEM- 2200FS operating at 200 kV. Thermogravimetric analysis (TGA) was performed using a TA Instruments Discovery TGA.

Inductively coupled plasma – optical emission spectrometry (ICP-OES) was performed using a Perkin Elmer Optima 7000 DV optical emission spectrometer. Samples were prepared by first calcining at 550 °C for 10 h with a 2 °C min⁻¹ ramp rate. Calcined samples containing Au or Pt were stirred in aqua regia overnight before diluting and analysing. Calcined samples containing Pd were stirred in concentrated nitric acid at 70 ° overnight before diluting and analysing.

The N_2 adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosity analyser at 77 K. The samples were degassed at 100 °C before analysis. The specific surface areas and pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models, respectively.



Figure S1. Raman spectra of hollow SiO_2 (red) and HS-SiO₂ (blue) spheres.



Figure S2. TGA trace of HS-SiO₂ completed under nitrogen.



Figure S3. TEM images of Au@SiO₂, synthesised using a vacuum impregnation method. This involved the addition of an aqueous HAuCl₄ solution to SiO₂ under static vacuum, before drying and reducing for 3 h at 300 °C under a H_2/N_2 (9%) flow with a 2 °C min⁻¹ ramp rate.



Figure S4. Histograms of the metal nanoparticles size from the TEM micrographs (Fig. 1) for (a) Au@HS-SiO₂, (b) Pt@HS-SiO₂ and (c) Pd@HS-SiO₂.



Figure S5. TEM images and photographs (inserts) of (a) hollow SiO₂ spheres and (b) SiO₂ porous liquid.



Figure S6. TGA trace of SiO₂ porous liquid completed in air.



Figure S7. N₂ adsorption-desorption isotherms and corresponding pore size distributions (insets) of (a) SiO₂ and OS-SiO₂ hollow spheres and (b) HS-SiO₂ and OS-HS-SiO₂ hollow spheres.

| Sample | S _{BET} (m ² g ⁻¹) | Pore Diameter (nm) |
|------------------------|--|--------------------|
| SiO ₂ | 618 | 10.8 |
| OS-SiO ₂ | 175 | 9.1 |
| HS-SiO ₂ | 429 | 10.8 |
| OS-HS-SiO ₂ | 163 | 11.0 |

Table S1. Surface properties of SiO₂, OS-SiO₂, HS-SiO₂ and OS-HS-SiO₂.

Modification of the hollow SiO₂ spheres with thiol decreased the surface area from 618 m² g⁻¹ to 429 m² g⁻¹ (Table S1). Further functionalisation with the organosilane resulted in an additional reduction in the surface areas of the samples to between 160–175 m² g⁻¹. Although the surface areas of the materials were found to decrease significantly upon organosilane-functionalisation, there was no significant difference in the pore diameters of the samples, which were between 9–11 nm (Table S1). These values correspond well to the diameter of the internal cavity observed from the TEM images (~9 nm). The similarity observed between the pore diameters is significant as it suggests that the internal cavity is unaffected during this functionalisation and, hence, that the porosity of the spheres is maintained during organosilane-functionalisation.



Figure S8. The addition of a small guest molecule (chloroform) to dried porous liquid (bottom left) leads to the displacement of the gas from the silica cavities and the formation of bubbles (bottom right).

Figure S9. Histograms of metal nanoparticle size from the TEM micrographs (Fig. 3) for (a) OS-Au@HS-SiO₂, (b) OS-Pt@HS-SiO₂, (c) OS-Pd@HS-SiO₂, (d) Au@HS-SiO₂ porous liquid, (e) Pt@HS-SiO₂ porous liquid and (f) Pd@HS-SiO₂ porous liquid.

Figure S10. HRTEM images of Pt@HS-SiO₂ porous liquid tilting along the z-axis at (a) 0° , (b) -25° and (c) -55° . The Pt nanoparticles are around 1.2 nm in diameter.

Figure S11. TEM images of Au@SiO₂ porous liquid, synthesised by calcining Au@HS-SiO₂ at 350 °C for 10 h before functionalisation of the external surface by the corona-canopy.

References

- 1. Y. Zheng, X. Zhang, Y. Yao, X. Chen and Q. Yang, *RSC Advances*, 2015, **5**, 105747-105752.
- 2. J. S. Zhang, S. H. Chai, Z. A. Qiao, S. M. Mahurin, J. H. Chen, Y. X. Fang, S. Wan, K. Nelson, P. F. Zhang and S. Dai, *Angewandte Chemie-International Edition*, 2015, **54**, 932-936.