

Engineering microencapsulation of highly catalytic gold nanoclusters for an extreme thermal stability

Ana Sousa-Castillo,^a Mathilde Gauthier,^a Raul Arenal,^{b,c} Moisés Pérez-Lorenzo,^{*a} and Miguel A. Correa-Duarte^{*a}

(a) Department of Physical Chemistry, Biomedical Research Center (CINBIO), and Institute of Biomedical Research of Ourense-Pontevedra-Vigo (IBI), Universidade de Vigo, 36310 Vigo, Spain. E-mail: moisespl@uvigo.es; macorrea@uvigo.es

(b) Laboratorio de Microscopías Avanzadas (LMA), Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain

(c) ARAID Foundation, 50018 Zaragoza, Spain

1. Synthetic procedure

All chemicals were of analytical grade and used without further purification.

1.1. Synthesis of silica bead/gold nanoparticles/microporous silica nanocomposites

- 1.1.1. *Synthesis of silica beads.* Monodisperse silica spheres (504±20 nm) were prepared using a modified Stöber method.¹ Typically, an ethanolic TEOS solution (1.7 mL, 1.2 M) was added to a solution containing ethanol (18.12 mL), ammonium hydroxide (1.96 mL), and water (3.21 mL). This mixture was stirred at room temperature for 2 h. The excess of reagents was removed by three centrifugation-redispersion cycles with ethanol (6000 rpm, 20 min).
- 1.1.2. *Functionalization of silica beads.* Silica beads were functionalized with poly(allylamine hydrochloride) (PAH, Mw ~56000). To this end, PAH was dissolved in 0.5 M NaCl (pH 9.0) with a final polymer concentration of 1 mg/mL. Then, 35 mL of the positively charged PAH solution were added to the silica nanoparticles (39.2 mg) and stirred at room temperature for 20 min. The excess of reagents was removed by three centrifugation-redispersion cycles with water (6000 rpm, 20 min).
- 1.1.3. *Synthesis of 14 and 2.6 nm AuNPs.* 14 nm gold nanoparticles were prepared by the classical method described by Turkevich.² A stable dispersion of 13.8±1.47 nm AuNPs was achieved. 2.6 nm gold nanoparticles were prepared based on the Baiker method.³ A stable dispersion of 2.60±0.64 nm AuNPs was obtained.
- 1.1.4. *Deposition of 14 and 2.6 nm AuNPs on functionalized silica beads.* A 14 nm Au solution (4 mL) and a 2.6 nm Au solution (6 mL) were added to 3.92 mg of functionalized silica nanoparticles. Both mixtures were stirred at room temperature for 20 min. In both cases, the excess of AuNPs was removed by three centrifugation-redispersion cycles with water (3000 rpm, 20 min) with the final redispersion in ethanol (10 mL).
- 1.1.5. *Synthesis and deposition of 0.8–1.2 nm clusters on functionalized silica beads.* 0.8–1.2 nm Au clusters were prepared as described elsewhere.⁴ An aqueous solution of HAuCl₄ (2.5 mL, 8.4×10⁻⁶ M) was added to functionalized silica nanoparticles (0.1 mL, 1.98 mg/mL) and stirred for 2 min. Then, a sodium citrate solution (0.4 mL, citrate/gold=2000) was added. In this case, citrate ion was employed as stabilizer and soft reducing agent. The mixture was stirred at room temperature for 20 min, and then rinsed by three centrifugation-redispersion cycles with water (3000 rpm, 20 min) with the final redispersion in ethanol (1 mL). Small Au nanoclusters in a rather narrow size distribution (1.17±0.14 nm) were obtained.
- 1.1.6. *Silica coating of silica/gold nanocomposites.* Silica coating was performed by following a strategy described elsewhere,⁵ with the appropriate modifications. Thus, 2, 2, and 1 mL of the silica/14, 2.6 and 0.8–1.2 nm AuNPs solutions were centrifuged (3500 rpm, 15 min for 14, and 2.6 AuNPs; 2500 rpm, 20 min for 0.8–1.2 nm AuNPs) and sediments were redispersed in 40, 10 and 3 mL of a 4.2% (v/v) ammonia/ethanol solution, respectively. The mixtures were then stirred for 15 min. After that, 0.3, 0.4 and 0.1 mL of a 10% (v/v) TEOS/ethanol solution were added dropwise to the silica/14, 2.6 and 0.8–1.2 nm Au solutions, respectively. The mixtures were left under magnetic stirring for 48 h. The excess of reagents was removed by three centrifugation-redispersion cycles with ethanol (same conditions as described above) with the final redispersion in 10, 10 and 2.5 mL. As a result, the final concentration referred to the silica beads was set to 0.0784 mg/mL in all cases. We evidenced the molecular transport through the microporous shell by SERS monitoring of benzenethiol.⁶ These tests confirm the diffusion of similar-sized molecules through the microporous silica coating before and after aging.

1.2. Synthesis of void/microporous silica/gold nanoclusters/mesoporous silica nanocomposites

- 1.2.1. *Functionalization of polystyrene beads.* 500 nm polystyrene beads (PS) were functionalized with poly(sodium styrene sulfonate) (PSS, Mw ~70000) and poly(allylamine hydrochloride) (PAH, Mw ~15000) through layer-by-layer self-assembly. To this end, 25 mL of a negatively charged PSS solution (1 mg/mL) were added to the PS beads (10 mg) and stirred at room temperature for 20 min. The excess of reagents was removed by five centrifugation-redispersion cycles with water (9000 rpm, 30 min). After that, PAH was dissolved in 0.5 M NaCl (pH 9.0) with a final polymer concentration of 1 mg/mL. Then, 25 mL of the positively charged PAH solution were added to the PSS-functionalized PS beads following the procedure previously described. The final sediment was redispersed in 10 mL of water.
- 1.2.2. *Silica coating of polymer-functionalized PS beads.* 5 mL of the PS/PSS/PAH solution (1 mg/mL) were added to 70 mL of a 4.2% (v/v) ammonia/ethanol solution. The mixture was then stirred for 10 min. After that, 0.375 mL of a 10% (v/v) TEOS/ethanol solution were added. The mixture was left under magnetic stirring for 2 h. The excess of reagents was removed by three centrifugation-redispersion cycles with a 50% (v/v) ethanol/water solution (4500 rpm, 30 min) with the final redispersion in water (2.5 mL).
- 1.2.3. *Functionalization of silica-coated PS beads.* 1 mL of a silica-coated PS beads solution (2 mg/mL) were functionalized with poly(allylamine hydrochloride) (PAH, Mw ~56000). To this end, PAH was dissolved in 0.5 M NaCl (pH 9.0) with a final polymer concentration of 1 mg/mL. Then, 5 mL of the positively charged PAH solution were added to the PS/SiO₂ composites and stirred at room temperature for 20 min. The excess of reagents was removed by five centrifugation-redispersion cycles with water (4500 rpm, 20 min) with the final redispersion in water (1 mL).
- 1.2.4. *Synthesis and deposition of 0.8–1.2 nm clusters on polymer-functionalized silica-coated PS beads.* 0.8–1.2 nm Au clusters were prepared as described elsewhere.⁴ An aqueous solution of HAuCl₄ (2.5 mL, 8.4×10⁻⁶ M) was added to the PAH-functionalized PS/SiO₂ composites (0.099 mL, 2 mg/mL) and stirred for 2 min. Then, a sodium citrate solution (0.4 mL, citrate/gold=2000) was added. The mixture was stirred at room temperature for 20 min, and then rinsed by three centrifugation-redispersion cycles with water (3000 rpm, 20 min) with the final redispersion in ethanol (1 mL). Small Au nanoclusters in a rather narrow size distribution (1.17±0.14 nm) were obtained.
- 1.2.5. *Mesoporous silica coating of PS/SiO₂/gold nanocomposites.* A solution containing PS/SiO₂/gold clusters (1 mL, 0.99 mg/mL) was added to 10 mL of a CTAB aqueous solution (6.9×10⁻³ M). The mixture was then stirred for 10 min. After that, 120 µL of an aqueous ammonium hydroxide solution (28–30 %), 4 mL of ethanol and finally, 0.15 mL of a 5% (v/v) TEOS/ethanol solution were added. The mixture was left under magnetic stirring for 5 h. The excess of reagents was removed by three centrifugation-redispersion cycles with ethanol (4500 rpm, 20 min) with the final redispersion in ethanol (1 mL). Characterization of silica porosity was performed as described elsewhere.⁷ An experiment comprising three SERS probes with considerably different molecular areas was used in order to evidence the molecular transport through the mesoporous shell before and after aging. These tests clearly demonstrates the diffusion of considerably large molecular systems (up to 2.5 nm) through the mesoporous silica coating.
- 1.2.6. *Hollow micro/mesoporous silica-embedded gold clusters.* Hollow nanocomposites were obtained by calcination of PS beads at 550 °C for 24 h. The final sediment was redispersed in 5 mL ethanol, attaining a final concentration of hollow SiO₂/gold clusters/SiO₂ of 0.198 mg/mL.

2. Characterization

2.1. Electron microscopy

TEM images were obtained using a JEOL JEM 1010 transmission electron microscope operating at an acceleration voltage of 100 kV. HRTEM and elemental mapping by XEDS analysis were carried out with a JEOL JEM 2010F transmission electron microscope operating at an acceleration voltage of 200 kV. HAADF-STEM imaging studies were performed on a probe-corrected FEI Titan Low-Base 60-300 microscope operating at 300 keV (fitted with an X-FEG® gun, a Cs-probe corrector (CESCOR from CEOS GmbH) and an EDAX EDS detector). EDS spectra were recorded using the spectrum-imaging (SPIM in 2D or spectrum-line (SPLI) in 1D) mode.⁸

2.2. Energy-dispersive X-ray spectroscopy

EDS experiments were performed on a JEOL JSM-6700F high resolution transmission electron microscope.

2.3. UV-visible spectroscopy

UV-Vis absorbance spectra were recorded on a HP8453 UV-Vis spectrophotometer fitted with a thermostated holder and collected from a 1-cm pathlength quartz cuvette.

2.4. Dynamic light scattering

The hydrodynamic radius of the hollow nanocomposites in simulated body fluids was measured using a dynamic light scattering instrument (NanoZS, Malvern Instruments) with a 633 nm “red” laser. 3 measurements with 10 runs were performed, and the average size was calculated.

3. Catalytic experiments

3.1. Reaction conditions

Redox reactions were performed over a temperature range of 10–50 °C before and after calcination at 100, 200, 300, 500 and 800 °C. Typical potassium hexacyanoferrate (III) concentrations were $(4.0\text{--}5.0)\times 10^{-4}$ M, while NaBH_4 was always in large excess (0.01 M) over $\text{K}_3[\text{Fe}(\text{CN})_6]$ ensuring pseudo-first-order conditions. UV–Vis absorbance spectra were recorded on a HP8453 UV–Vis spectrophotometer fitted with a thermostated holder and collected from a 1-cm pathlength quartz cuvette. Rates were measured by monitoring the decrease of hexacyanoferrate (III) absorption band at 420 nm. In all cases, the reactions were carried out in a highly basic medium (pH=13) in order to avoid NaBH_4 decomposition.⁹ The absorbance versus time data always fitted satisfactorily to the integrated pseudo-first-order rate law, $A_t = A_\infty - (A_\infty - A_0)\exp(-k_{\text{obs}}t)$.

3.2. Arrhenius kinetic analyses

The Arrhenius equation was used to determine E_a for the 14, 2.6, and ~ 1 nm gold-catalyzed electron-transfer reaction before and after calcination by plotting the logarithm of the pseudo-first order rate constant (k_{obs}) versus the inverse of temperature ($1/T$) (Figure S2).

3.3. Influence of the redispersion procedure on the catalytic behavior of Au clusters deposited onto silica beads

Figure S3 displays the different catalytic activity of the $\text{SiO}_2/\sim 1$ nm clusters depending on how redispersion of the gold-based nanocomposites is performed during the synthesis.

4. Supplementary figures

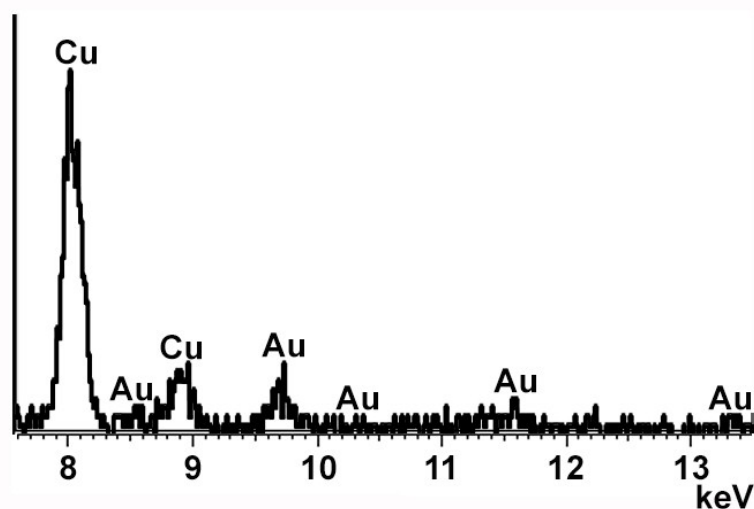


Figure S1. Energy-dispersive X-ray spectrum of MWCNT/0.8–1.2 nm Au clusters showing the presence of gold in the nanostructure.

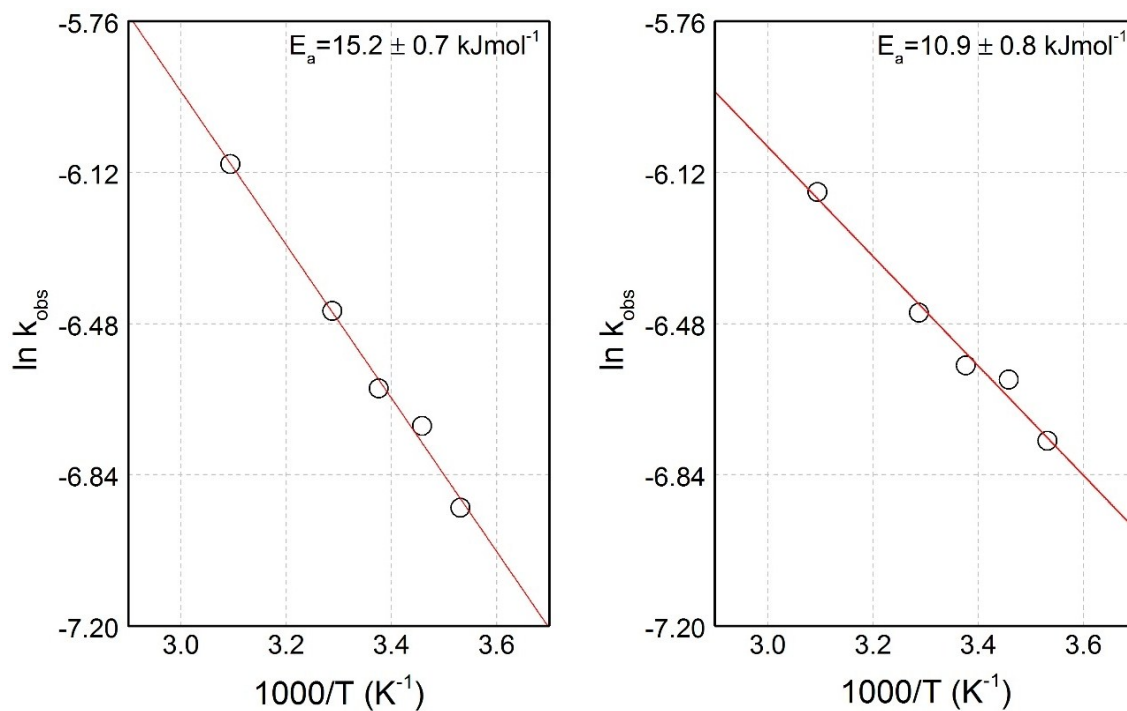


Figure S2. Representative examples of Arrhenius plots for the reduction of ferricyanide upon addition of sodium borohydride in the presence of (left) $\text{SiO}_2/2.6 \text{ nm AuNPs/SiO}_2$ calcined at $300 \text{ }^\circ\text{C}$, and (right) $\text{SiO}_2/\sim 1 \text{ nm AuNPs/SiO}_2$ calcined at $300 \text{ }^\circ\text{C}$. Reduction reactions were performed within the temperature range of $5\text{--}50 \text{ }^\circ\text{C}$. The relative standard error of $\ln k_{obs}$ never exceeded 1%.

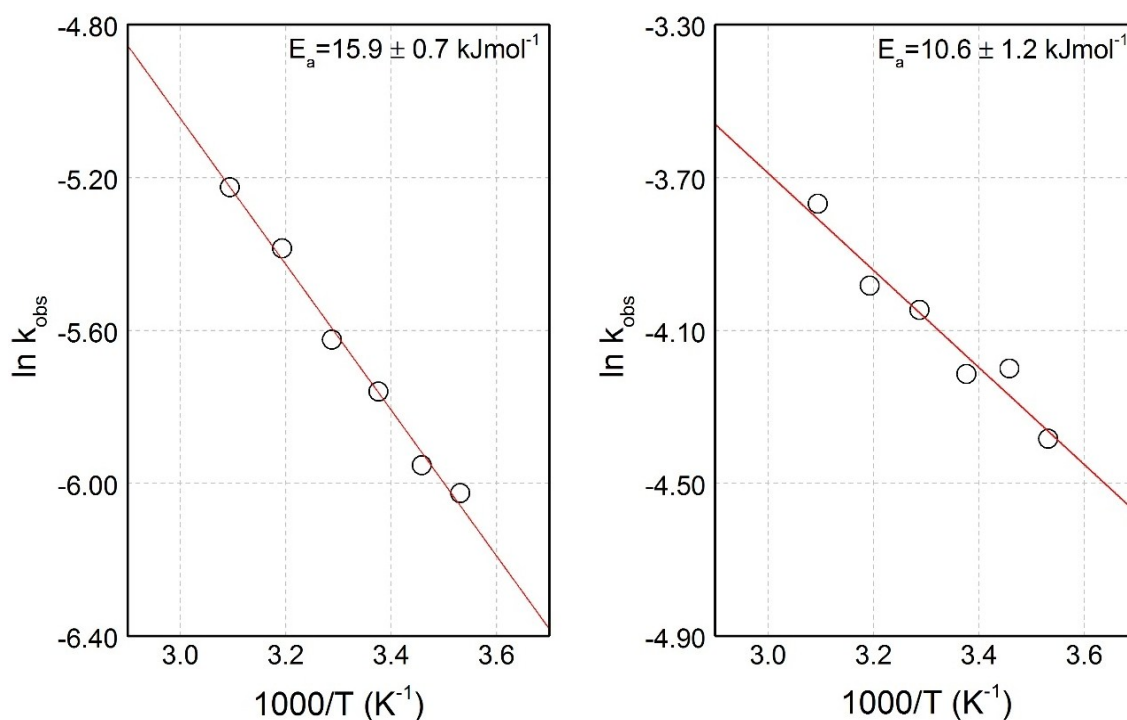


Figure S3. Arrhenius plots for the reduction of ferricyanide upon addition of sodium borohydride in the presence of $\text{SiO}_2/\sim 1 \text{ nm AuNPs}$. (left) Ultrasound-driven redispersion, and (right) Stirring-assisted redispersion. Reduction reactions were performed within the temperature range of $5\text{--}50 \text{ }^\circ\text{C}$. The relative standard error of $\ln k_{obs}$ never exceeded 1%.

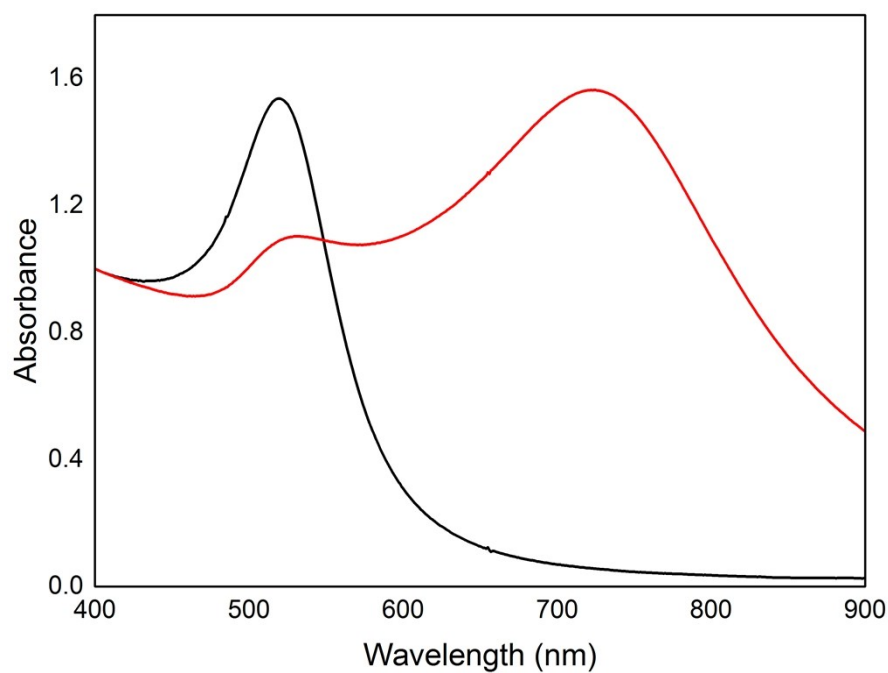


Figure S4. Visible spectra of citrate-stabilized 15 nm Au nanoparticles in water (black), and simulated body fluids (red). An instantaneous aggregation of the particles is observed when using SBF as a solvent.

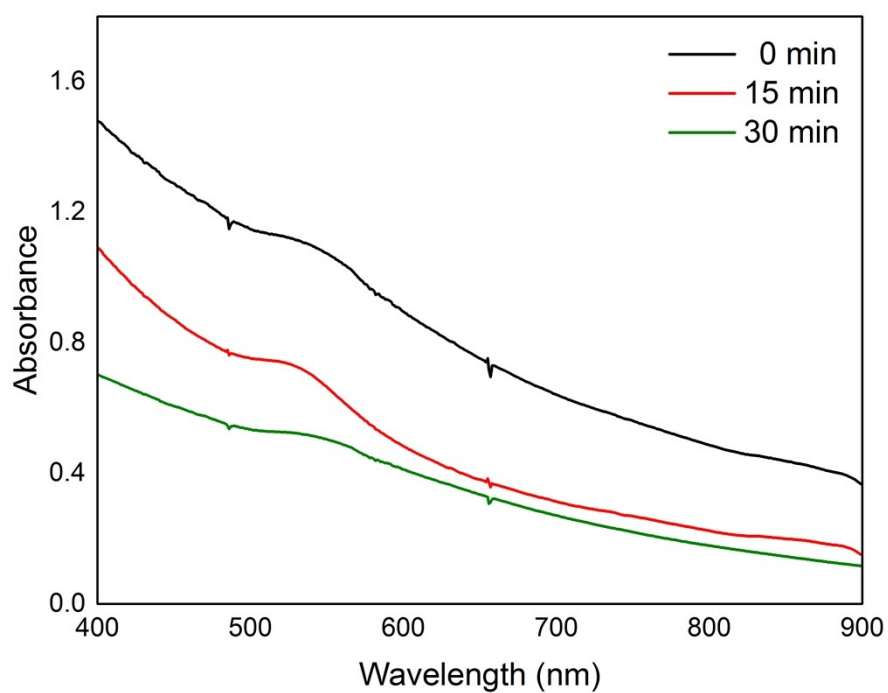


Figure S5. Temporal evolution of visible spectrum of 15 nm Au nanoparticles supported onto silica beads using simulated body fluids as a solvent. In this case, a fast decantation and aggregation can be observed.

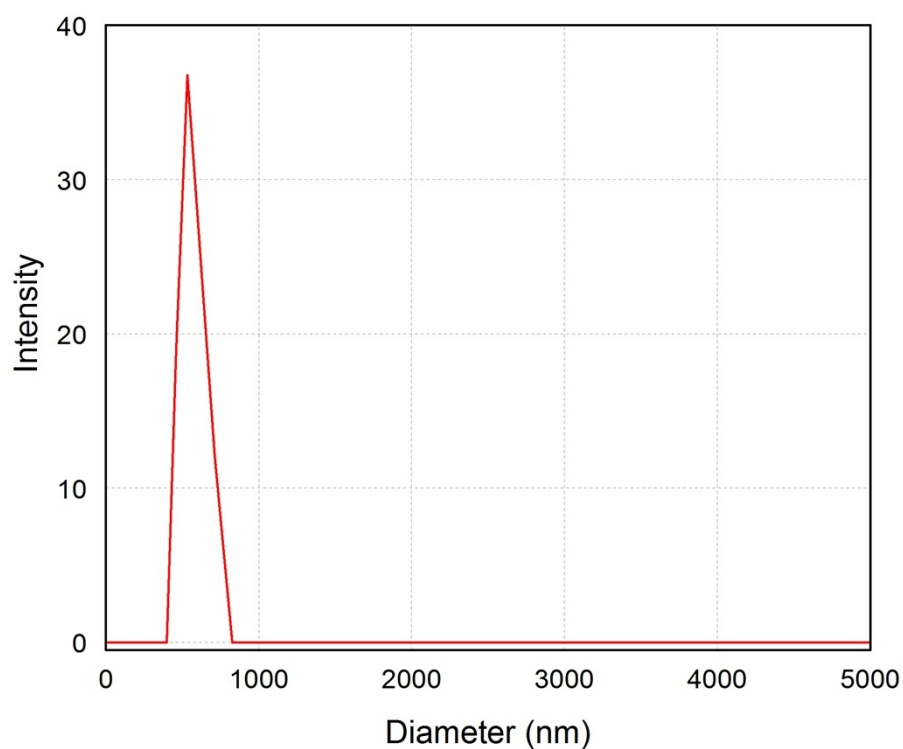


Figure S6. Dynamic light scattering measurements showing the size distribution profile of the hollow nanocomposites in simulated body fluids after 6 h, which evidence the absence of aggregation of the capsules. $T=36.0\text{ }^{\circ}\text{C}$.

5. References

- (1) W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62–69.
- (2) J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55–75.
- (3) D. G. Duff, A. Baiker and P. P. Edwards, *Langmuir*, 1993, **9**, 2301–2309.
- (4) L. Alves, B. Ballesteros, M. Boronat, J. R. Cabrero-Antonino, P. Concepción, A. Corma, M. A. Correa-Duarte and E. Mendoza, *J. Am. Chem. Soc.*, 2011, **133**, 10251–10261.
- (5) C. Graf, D. L. J. Vossen, A. Imhof and A. van Blaaderen, *Langmuir*, 2003, **19**, 6693–6700.
- (6) M. Sanlés-Sobrido, W. Exner, L. Rodríguez-Lorenzo, B. Rodríguez-González, M. A. Correa-Duarte, R. A. Álvarez-Puebla and L. M. Liz-Marzán, *J. Am. Chem. Soc.*, 2009, **131**, 2699–2705.
- (7) C. Vázquez-Vázquez, B. Vaz, V. Giannini, M. Pérez-Lorenzo, R. A. Alvarez-Puebla and M. A. Correa-Duarte, *J. Am. Chem. Soc.*, 2013, **135**, 13616–13619.
- (8) R. Arenal, F. de la Peña, O. Stéphan, M. Walls, M. Tencé, A. Loiseau and C. Colliex, *Ultramicroscopy*, 2008, **109**, 32–38.
- (9) P. R. Van Rheeën, M. J. McKelvy and W. S. Glaunsinger, *J. Solid State Chem.*, 1987, **67**, 151–169.

