

Robust, ultrasmall organosilica nanoparticles without silica shells

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Abstract

Traditionally, organosilica nanoparticles have been prepared inside micelles with an external silica shell for mechanical support. Here, we compare these hybrid core-shell particles with new organosilica particles that are robust enough to be produced both inside micelles and alone in a sol-gel process. These particles form from ODTMS (octadecyltrimethoxy silane) as silica source either in microemulsions, resulting in water-dispersible particles with a hydrophobic core, or precipitate from an aqueous mixture to form particles with both hydrophobic core and surface. We examine size and morphology of the particles by dynamic light scattering and transmission electron microscopy and show that the particles consist of Si-O-Si networks pervaded by alkyl chains using nuclear magnetic resonance, infra-red spectroscopy and thermogravimetric analysis.

Keywords: Nanoparticle synthesis, Stöber process, organosilica, micelles

Introduction

Stable suspensions of hydrophobic silica nanoparticles in apolar solvents have found application in many areas including paints and coatings (Douce, Boilot et al. 2004; Jalili, Moradian et al. 2007), sensors (Qhobosheane, Santra et al. 2001), and catalysis (Reetz, Zonta et al. 1995; Reetz, Zonta et al. 1996; Reetz, Zonta et al. 1996) and have been shown to enhance physical and mechanical properties of nano-composites (Philipse and Vrij 1989;

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Bourgeat-Lami and Lang 1998; Bourgeat-Lami and Lang 1999; Zou, Wu et al. 2008). These nanomaterials have generally been produced by the synthesis of pristine, hydrophilic silica nanoparticles and their subsequent organic modification with hydrophobic silane moieties.

A promising alternative synthetic route uses oil-in-water microemulsions of oil droplets stabilized by surfactants. Such emulsion systems have been used to produce cores of hydrophobic silica/surfactant micelles with hydrophilic silica shells and have shown potential as materials for biomedical drug delivery and biodetoxification (Couvreur, Dubernet et al. 1995; Muller, Mader et al. 2000). In addition, the presence of a hydrophobic core with a hydrophilic surfactant layer makes organosilica produced in micelles an interesting material to host hydrophobic moieties in an aqueous environment. It has been shown that the organosilica core can be used as a host for the hydrophobic compounds, while the pure silica shell possesses inherent stability, biocompatibility and the potential to be modified with biomolecules (Lai, Garino et al. 2002; Underhill, Jovanovic et al. 2002; Jovanovic, Underhill et al. 2005; Sharma, Brown et al. 2006). It has been reported that the ODTMS combines with TEOS resulting in a hydrophilic pure silica shell that provides stiffness to a hydrophobic core that remains liquid. However, recent electron microscopy suggests that the cores of these particles are more solid and robust than previously supposed (Chavez, Wong et al. 2008). We show here that organosilica particles similar to those previously prepared as cores can be synthesized as free particles, casting further doubt on the liquid core theory. Previous studies have shown that alkylsilanes can self-assemble into thin films composed of ordered layers and bilayers, but to the best of our knowledge, dispersed nanoparticles have not been produced (Shimajima and Kuroda 2006).

In this paper, we examine particles produced both with a surfactant in a micellar system and without any surfactant in a sol-gel route. We show that stable organosilica particles, hydrophobic both in the bulk and on the surface, can be synthesized without micelles and

analyze the structures of these particles and compare them to hybrid organosilica/silica materials.

Experimental

Materials: All chemicals were used as purchased without further purification. Hexane, toluene, methanol, ammonium hydroxide (25 wt%), ethanol and tetraethylorthosilicate (TEOS), all puriss p.a. grade, were purchased from Fluka. Octadecyltrimethoxysilane (ODTMS tech. grade) and Triton X-100 were obtained from Aldrich. Deionised Millipore water (>18 m Ω) was used in all preparations.

Preparation:

Hydrophobic organosilica nanoparticles – Hydrophobic organosilica nanoparticles were synthesised by replacing the TEOS in the standard synthetic route developed by Stöber (Stober, Fink et al. 1968) with ODTMS as the single silica source (Murray, Born et al. 2010). In a standard synthesis, aqueous ammonia (25 % w/w, 0.8 ml) was mixed with 25 ml of ethanol and stirred vigorously at ambient temperature. After 20 minutes, 0.1 ml of ODTMS was added and stirring was continued overnight, after which time the organosilica had precipitated. The sample was filtered through a 200 nm membrane filter to remove any crosslinked bulk material, washed and resuspended in a suitable non-polar solvent using ultrasonication. Note that in all cases the sonication time has been chosen such that the solution became clear and opalescent and longer sonication did not affect the particle size.

Organosilica nanoparticles from oil-in-water emulsions – Water-dispersible organosilica nanoparticles were synthesised using Triton X-100 as a surfactant in an oil-in-water nanoemulsion. In a typical synthesis, 25 ml of a 1 % w/w aqueous Triton X-100 solution was pre-sonicated and 0.3 ml of a 1:1 hexane:ODTMS mixture was added and vigorously stirred at room temperature for 2 hours. The cloudy solution was filtered through an 800 nm membrane filter to remove crosslinked silane, sonicated for 2 hours, 0.2 ml aqueous NH₃

solution (25 %) was added with further sonication and the mixture was left to stir overnight. Following the reaction, the solution was again filtered (800 nm then 200nm filter), sonicated for 3-4 hours and dialysed against millipore water to remove excess surfactant and reactants.

Silica-coated organosilica nanoparticles ($SiO_2@organosilica$) – Organosilica/silica hybrid materials were synthesised using the micellar organosilica produced in the last step. An amount of 0.3 ml of TEOS was added to the dialysed and sonicated organosilica emulsion and the mixture was left to stir at room temperature for 2 hours. Following addition of 0.2 ml of aq. ammonia and overnight reaction the solution was filtered, dialysed and sonicated for 3-4 hours. The emulsion was broken by the addition of 20 ml of ethanol and the surfactant removed by a number of sequential washing steps with water:ethanol and ethanol. The material could then be resuspended in ethanol.

Hydrophilic silica nanoparticles – Hydrophilic silica nanoparticles were also synthesised using a variation of the standard synthetic route developed by Stöber (Stober, Fink et al. 1968) under sonication, as we have previously reported (Murray, Born et al. 2010)

Analytical Methods: Transmission electron microscopy (TEM) was performed using a Philips CM 200 TEM operating at 200 keV with a point-to-point resolution of 0.24 nm and a lattice resolution of 0.14 nm. For particle characterisation, copper TEM grids with carbon coating were dipped into the suspension and were dried in an oven at 105 °C.

Dynamic light scattering (DLS) analysis was performed using a Wyatt Technology DynaPro Titan operating at a wavelength of 831.2 nm to measure the hydrodynamic radius and standard deviation in the dispersity of the particles in suspension. Samples for DLS were prepared by suspending a small concentration of particles in a good solvent under sonication and filtration through a 500 nm membrane filter. The autocorrelation data was fit using Wyatts' Dynamics software, which uses a proprietary non-negative least-squares algorithm based

on an inverse Laplace transformation, and the subsequent distributions are given here in percent mass.

^{29}Si cross-polarized magic angle spinning nuclear magnetic resonance (CP/MAS-NMR) spectra were recorded in a Bruker AC-200 with 8000 scans at 39.733 MHz. Solid, powdered samples were prepared by overnight drying in a vacuum oven at reduced pressure at 35 °C after thorough washing to remove residual reactants or surfactants.

Thermal analysis (TGA-DSC-MS) was also performed using the same powders on a Netsch STA 449 C thermogravimeter coupled to a Netzsch QMS 403 C mass spectrometer. The dried sample was placed in aluminium pans under nitrogen and heated from 35-800 °C at 10 °C/min.

Infra-red spectroscopy was performed in the solid state on a Bruker Tensor 27 with a single reflection attenuated total reflection golden gate.

Results and Discussion

Synthesis of nanoparticles- particle size

The hydrophobic organosilica particles obtained from ODTMS as the single silica source in an ethanol/ammonia solution were between 2 and 10 nm in average radius (depending on the batch) and exhibited less than 10 % polydispersity by DLS. (figure 1) Varying the concentrations of reactants resulted in changes in particle size and particles up to 20 nm could be produced. However, the highly hydrophobic nature of these particles necessitates extremely careful work-up and washing procedures and leads to very low yield (<10 %wt of dispersed nanoparticles). The organosilica nanoparticles produced in surfactant micelles were between 5 and 10 nm in radius (depending on the batch) with less than 10% polydispersity. The micelles provided better control over size and dispersity than the sol-gel route. However, despite their hydrophobic core these particles retain a hydrophilic surface due to the presence of the surfactant. Addition of controlled amounts of TEOS to the micelle system to form a

silica/organosilica hybrid resulted in particles with increased particle radius of 10-12 nm when redispersed in a polar solvent, such as ethanol. (figure 1)

Long-chain alkylsilanes have been shown to produce self-assembled multilayers in thin films due to their amphiphilic nature. It is reasonable to assume that they may also form bilayer micellar structures. However, DLS and TEM showed that, unlike in previous reports, the micellar particles without a silica shell were robust enough to be observable dispersed in solution and also in solid state even after degassing in a TEM. Similarly, and more tellingly, the particles produced without the use of micelles also survived high vacuum and were observable by DLS when dispersed in a solution with an appropriate solvent.

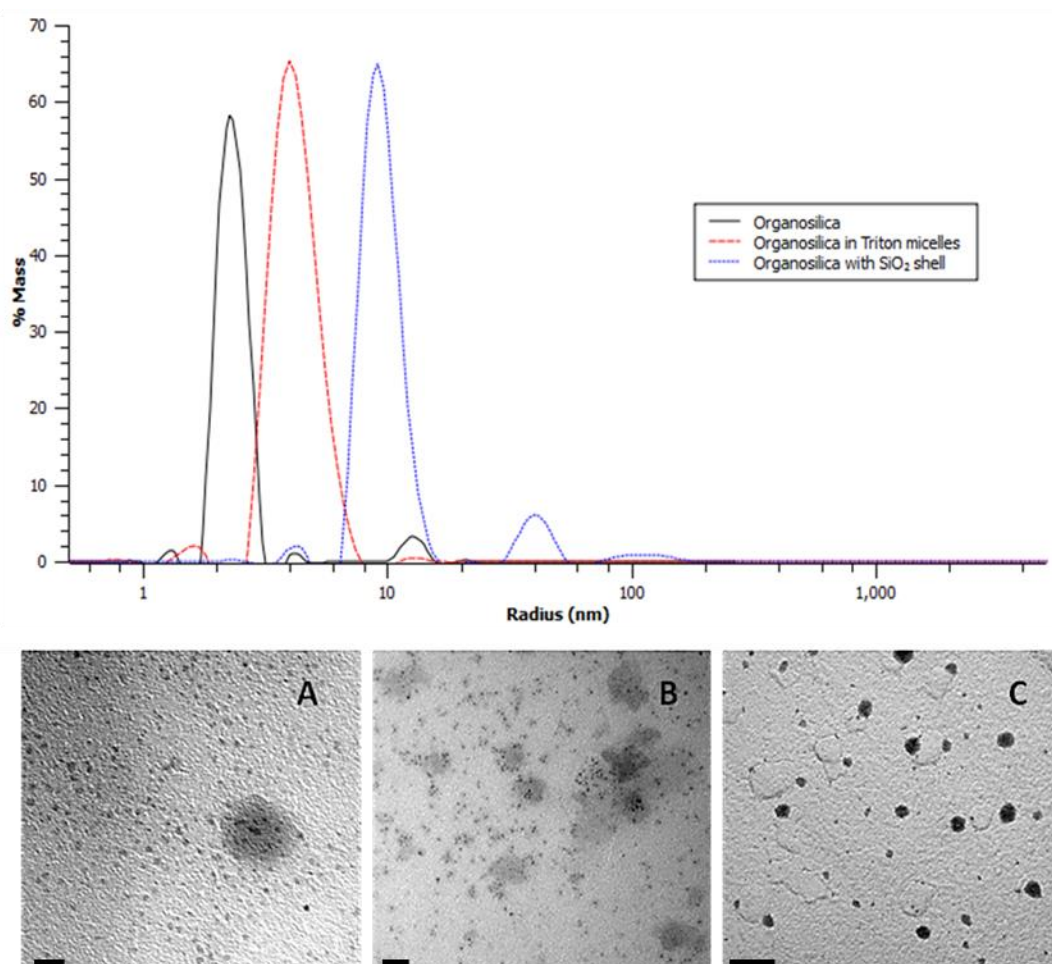


Figure 1. Dynamic light scattering data and representative TEM images for (A) organosilica nanoparticles (-), (B) organosilica particles grown in triton micelles (---) and (C) organosilica/silica core-shell nanoparticles (...). The scale bars are 20 nm in A and B and 50 nm in C.

Particle composition

^{29}Si CP/MAS NMR Solid state silica NMR of hydrophobic silica nanoparticles (SiO_2) showed the expected peaks (~96-112 ppm) corresponding to geminal silanol groups (Q2 97.5 ppm), single silanol groups (Q3 102.3 ppm) and siloxane groups (Q4 112.6 ppm) (Mijatovic, Binder et al. 2000) (figure 2).

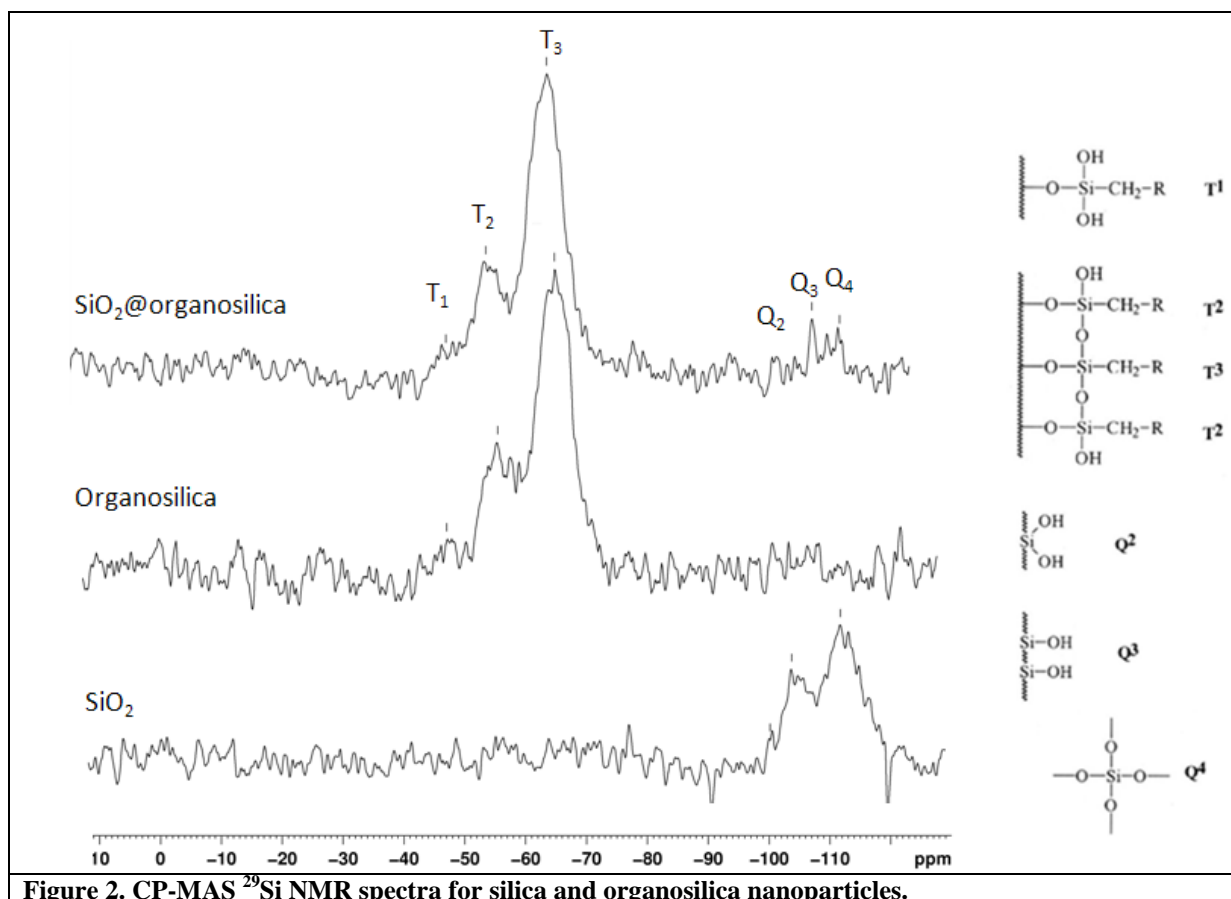


Figure 2. CP-MAS ^{29}Si NMR spectra for silica and organosilica nanoparticles.

The NMR spectra of organosilica nanoparticles without silica shells synthesised both in EtOH solution and in the micellar system do not exhibit these peaks. Instead, their spectra show geminal alkylsilanol groups (T_1 49.7 ppm), single alkylsilanol groups (T_2 58.0 ppm) and alkylsiloxane groups (T_3 67.3 ppm). (figure 2) The relative peak intensities are indicative of relative populations of silica species either on the surface or in the particle bulk. An approximate quantification by integration of the peaks showed T^3 species far in excess of T^1 or T^2 , indicative of an extensive $-\text{Si-O-Si}-$ framework with hydrophobic alkyl chains either as

a stabilising external layer or folded around the framework throughout the nanoparticle. The spectrum of organosilica particles with a thin silica shell (SiO_2 @organosilica) shows both T and Q peaks indicating the presence of surface Si-OH groups.

Infra-red spectroscopy – Pure silica nanoparticles exhibit characteristic peaks at 796 (-Si-O-Si- vibration), 950 (-Si-O-Si-OH vibration) and 1065 cm^{-1} (-Si-O-Si-) and a broad, weak peak between 3100 and 3600 cm^{-1} indicative of exchangeable protons from surface OH groups.

The spectra of organosilica particles (figure 3) synthesised both in solution and in a micellar system are similar to each other but very different to the coated silica. The broad OH peak is missing as is the Si-OH group at 950 cm^{-1} indicating a lack of free exchangeable OH surface sites. Two new peaks at 2850 and 2920 cm^{-1} characteristic of both terminal methyl and in-chain methylene groups are observed and a peak at 1110 cm^{-1} is observed corresponding to silica-carbon vibrations. Crucially, however, the peaks at 790 and 1060 cm^{-1} from Si-O-Si, while reduced, are still strongly present and suggest a pervading Si-O-Si network. Interestingly, there is a series of small, equally spaced peaks between 1180 and 1240 cm^{-1} which can be attributed to the relaxation oscillation of the interaction of the methylene groups of the alkyl chain (Hediger 1971). These vibrations have previously only been seen in long-chain molecules where one free end is interacting with a polar group in a crystalline state, such as an Si-O-Si group. This suggests that the particles are a network of alkyl chains interacting with an Si-O-Si framework.

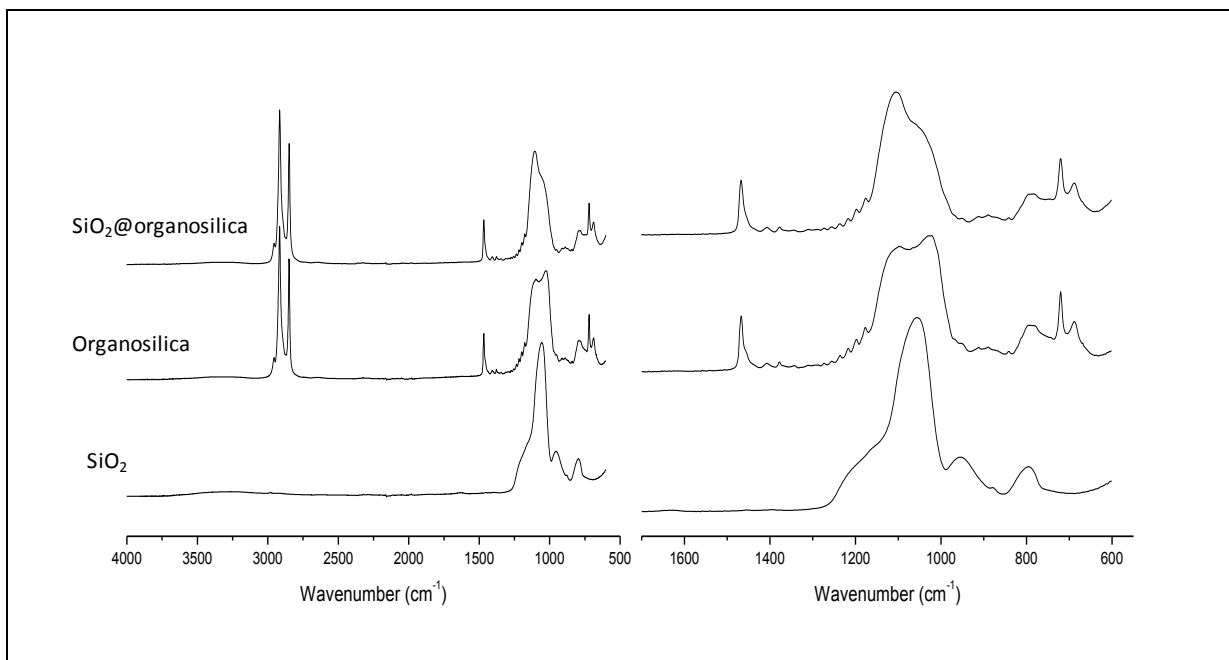


Figure 3. Infra red spectra of silica, organosilica and silica-organosilica materials.

Thermal analysis – Thermogravimetric analysis (TGA) of hydrophilic unmodified silica nanoparticles showed only very minor weight loss between 150 and 700 °C and differential scanning calorimetry showed no thermal events above 100 °C. (figure 4)

TGA showed 75% weight loss for organosilica samples in the same temperature regime. Infra-red and mass spectrometry of the vent gas (data not shown) again confirmed this weight loss as alkyl fragments suggesting that the thermal event was due to the removal of the alkyl chains from the Si-O-Si framework. The 75% weight loss implies that the organic loading in the nanoparticle was extremely high. DSC showed a double endotherm with the first maximum at 470 °C and the second at 495 °C, indicative of two separate populations of alkyl chains – one unhindered on the surface and the other entangled in the bulk of the particle requiring more energy to remove. DSC of hydrophilic silica particles surface modified with ODTMS (hydrophilic core with a hydrophobic shell) showed only one such endotherm. (see supporting informations).

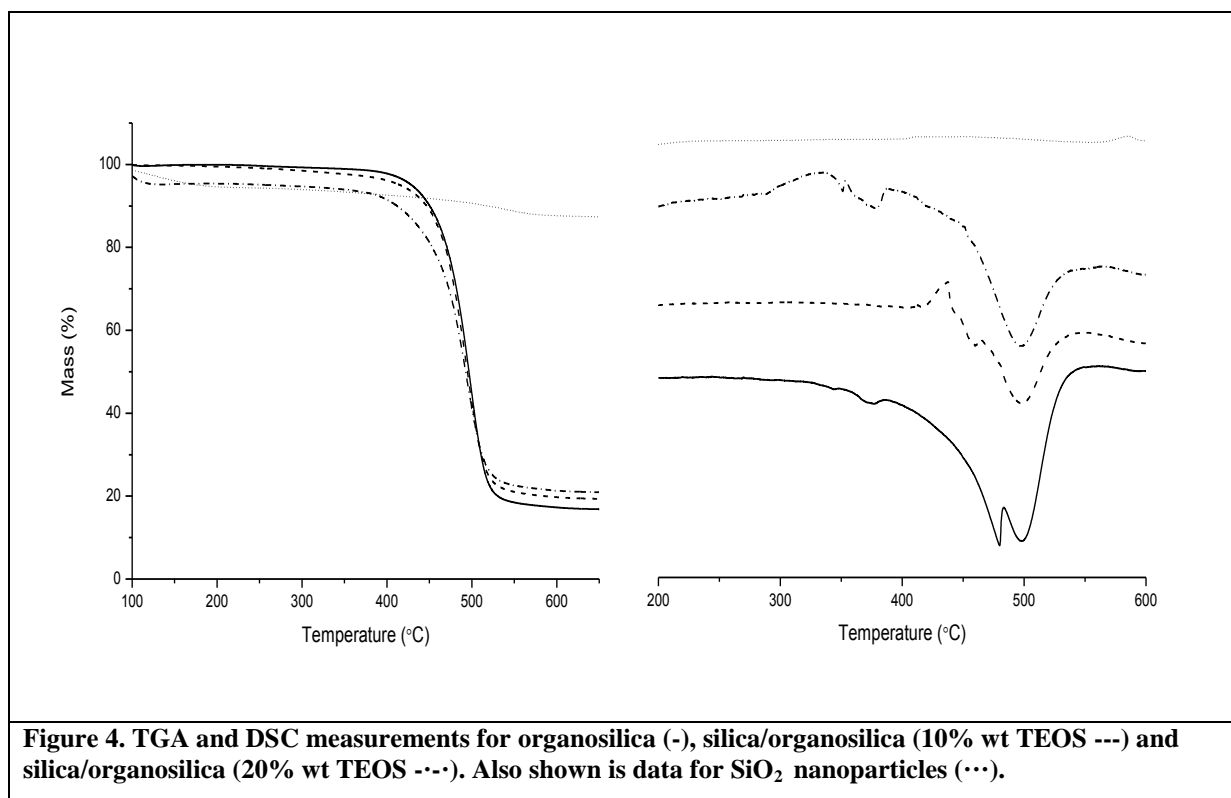


Figure 4. TGA and DSC measurements for organosilica (-), silica/organosilica (10% wt TEOS ---) and silica/organosilica (20% wt TEOS -·-·). Also shown is data for SiO₂ nanoparticles (···).

Hybrid organosilica/silica nanoparticles showed a weight loss between 460 and 510 °C, too. The weight loss was reduced when increasing the ratio of silica to organosilica by adding more TEOS to the organosilica micellar system and subsequent hydrolysis to SiO₂. The weight loss decreased from ~80% in an unmodified organosilica system to ~70% in a TEOS-containing system, indicating increased residual silica. The addition of silica also changed the proportion of peaks observed in DSC. Increasing the extent of the silica shell in the hybrid particles reduced the transition at 470 °C, suggesting that the new silica network forms a shell hindering the thermally activated removal of the surface alkyl groups.

Conclusion

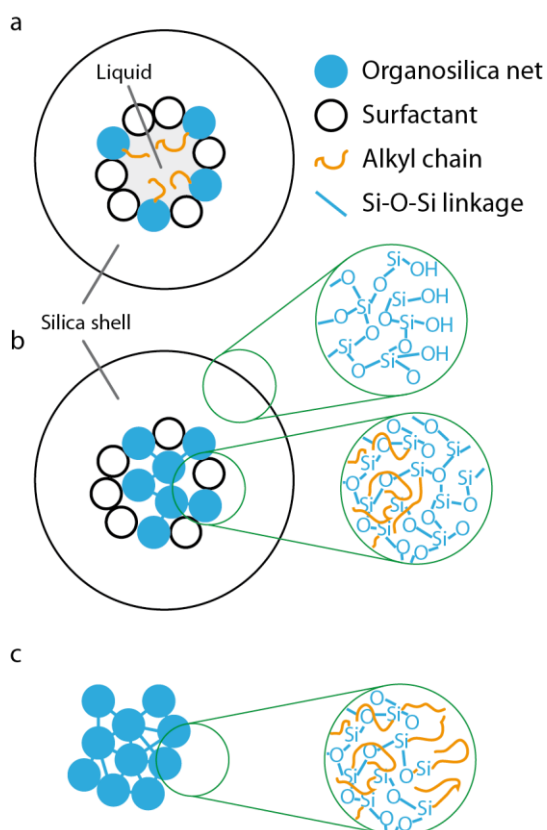


Figure 6. Possible structures of organosilica-containing nanoparticles. (a) shows the traditional view [14] of organosilica/silica particles with the organosilane and surfactant particles forming a micelle around a liquid core, all surrounded by a stiff silica shell, (b) shows our interpretation of the same particle with a hydrophobic organosilica Si-O-Si solid network core in a standard surfactant micelle surrounded by a silica shell. The organosilica core of these particles can also be produced in solution without a surfactant micelle (c), resulting in an Si-O-Si network with entangled alkyl chains providing a hydrophobic surface and core.

Our results prove that organosilica nanoparticles are solid objects that can exist as a suspension in apolar solvents. Their pervading silica network is strong enough to maintain integrity despite the large fraction of alkyl chains that render the particle strongly hydrophobic both in core and interface. This is in contrast to previous studies (Lai, Garino et al. 2002; Sharma, Brown et al. 2006; Chavez, Wong et al. 2008) that described the organosilica component as “oil” that needed to be encapsulated in a silica shell.

The organosilica particles were produced both in surfactant micelles and in a sol-gel system without surfactants. Extensive characterization showed that they are chemically identical to

the core of traditional core-shell organosilica-silica nanoparticles and consist of a solid network of alkyl chains entangled around an -Si-O-Si- framework. (figure 6)

“Naked” organosilica particles are a promising complement to their core-shell derivate. In the absence of a shell, solvents and solutes can directly interact with their organosilica network. Dyes and other compounds are thus taken up and released rapidly. (figure S2) Alkylsilanes are available with a variety of ω -functionalities that provide chemical reactivity inside the particles. This is a logical step ahead from the conventional, surface-bound functionalization of silica nanoparticles that have proven immensely useful in the past: in organosilica particles, the entire volume is accessible for adsorption and reaction.

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Supporting information – *Journal of Nanoparticle Research*

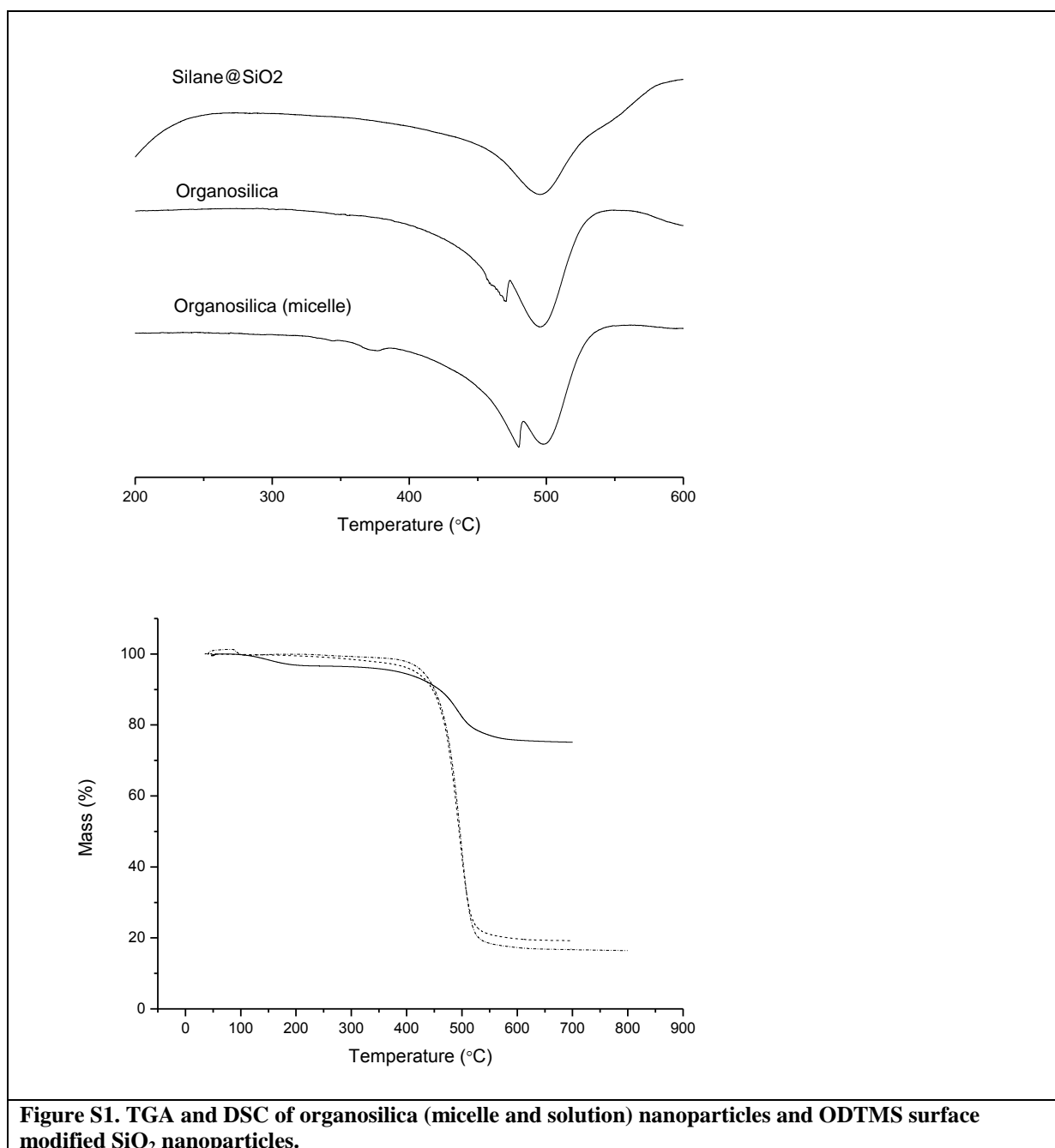
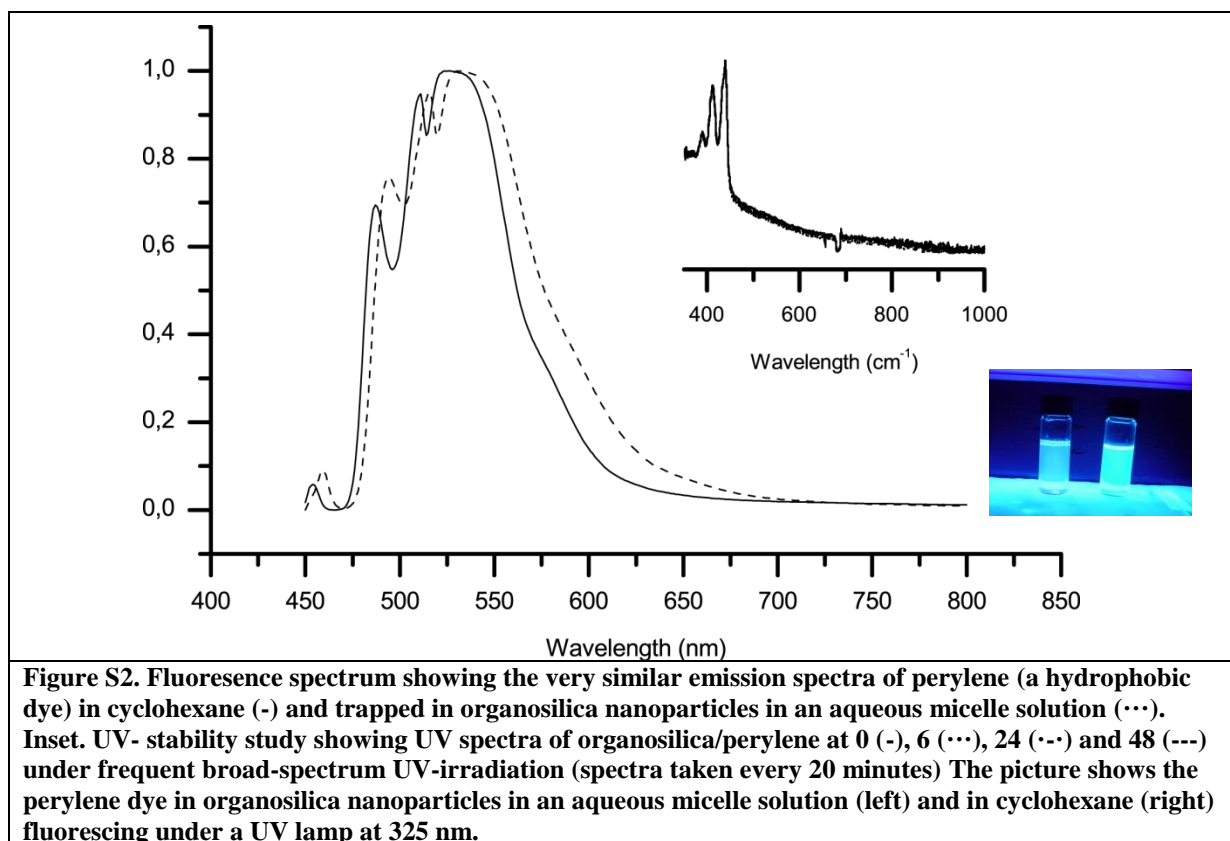


Figure S1. TGA and DSC of organosilica (micelle and solution) nanoparticles and ODTMS surface modified SiO₂ nanoparticles.

When SiO₂ nanoparticles are made hydrophobic by surface-modification with ODTMS a weight loss of ~20 % occurs between 470 and 500 °C which infra-red and mass spectrometry

prove to be due to alkyl fragments removed from the surface of the nanoparticle. Organosilica particles show weight losses of greater than 80% in the same temperature range. Differential scanning calorimetry (DSC) showed this transition to be a single endotherm with a maximum at 485 °C as opposed to the double endotherm of the organosilica materials.



Hydrophobic host - The presence of a hydrophobic core with a hydrophilic surfactant layer makes organosilica produced in micelles an interesting material to host hydrophobic moieties in an aqueous environment. Perylene is a blue fluorescing, aromatic hydrocarbon dye with a high molar absorptivity and extremely low water solubility. Initial tests with the addition of a very small amount to an aqueous solution of the micellar organosilica nanoparticles resulted in very stable UV absorbance and fluorescence similar to that of the dye in an organic solvent. (figure S2)