



Organosilicate nanoparticles - a familiar material in new shape

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Introduction

Silica nanoparticles have been commonly used as nanoscale components in hybrid systems for many years. For example, polydispersed nanoscale silica is used as a transparent filler in polymers, modifies the flow properties of emulsions and improves the properties of construction materials. Since Stöber et al developed a low-cost, facile synthetic route to highly monodispersed silica nanospheres, they have become the cornerstone of many facets of nanoparticulate research. When produced with a narrow size distribution, silica nanoparticles can introduce nanoscale regularity on surfaces or in bulk materials either as a component of the final material or as an etch mask in further processing steps. As such, assembly of monodispersed silica nanoparticles into regular superstructures is a promising route to materials with rationally designed microstructures. However, in all cases, the particle-matrix compatibility and composite behavior depend on the surface chemistry of the particles.

A commonly-used method to change and improve the properties of existing hybrid materials and to broaden the range of possible composite materials is to alter the surface chemistry of silica particles. Functionalization of the particle surface using organic modifiers can reduce aggregation, improve matrix compatibility or change the physical properties of a composite material. Functionalized silica nanoparticles have found application in many areas including paints and coatings [1; 2], sensors [3], catalysis [4; 5] and

drug delivery methodologies [6; 7]. For example, in previous projects at INM, silica nanoparticles have been coated with methylalkoxysilanes which resulted in weak bonding between the particles forming a soft network of binder molecules in a flexible gel, which prevented cracking of the otherwise brittle systems [23; 24].

Modification of particle surfaces using organic moieties can also produce hydrophobic particles. Hydrophobic silica nanoparticles interact strongly with the constituent molecules of apolar polymer matrices and have been shown to enhance their physical and mechanical properties in polymeric nano-composites [8; 13]. Stable suspensions of hydrophobic silica nanoparticles in apolar solvents are also good model systems for studying the equilibrium and transport properties of colloidal dispersions; their refractive index matches that of some apolar solvents, minimizing multiple scattering in light scattering experiments [9-11].

Two methods are presented here to produce two very different types of hydrophobic silica nanoparticles. The first approach is based on the commonly applied hydrolysis and condensation of tetraalkyl orthosilicates by a strong base as originally developed by Stöber [12]. The resulting hydrophilic particles were then modified by the grafting of organosilicate compounds onto their surfaces or by the co-hydrolysis of a tetraorthosilicate with the required functional organosilane. Using these techniques, silica nanoparticles were previously

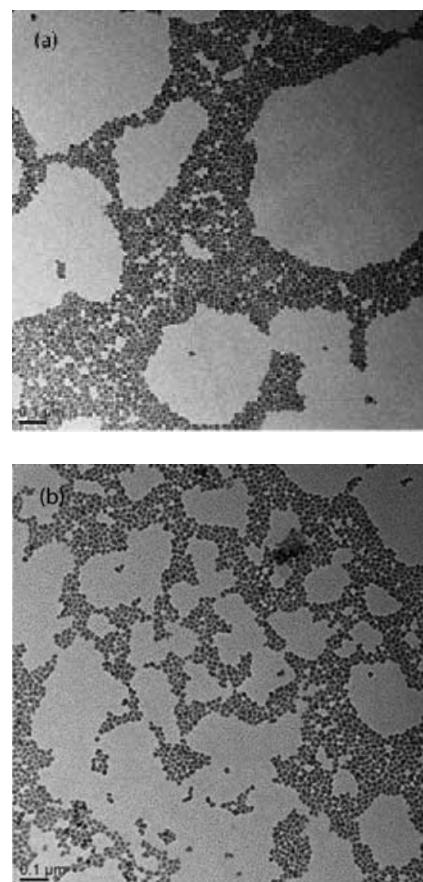


Figure 1: Transmission electron microscopy images of octadecyl coated silica nanoparticles synthesized using the modified Stöber route at ambient temperature, (a) with silane addition after the reaction and (b) during the reaction. Scale bars are 100 nm.

coated with a number of functional groups including vinyl, carboxylate, thiol, mercaptopropyl and amine [14; 15; 19; 20] and a variety of biomolecules [3; 21]. The surface of particles from the Stöber synthesis were also made hydrophobic by the esterification of the surface hydroxyl groups using octadecanol [9; 10; 14]. The resulting so-called octadecylsilica is a popular model system for hard-sphere colloids. In this work monodispersed colloidal SiO_2 particles with diameters of 15 to 25 nm were prepared via the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) by aqueous ammonia in ethanol. The surfaces of these particles were rendered hydrophobic with octadecyltrimethoxysilane (ODTMS) after the reaction or, more conveniently, by addition towards the end of the growth phase.

The second route departs from the core-shell structure to produce uniformly hydrophobic particles. Instead of using two different silanes, only one of which carries the desired surface functionality, synthesis is done starting solely from the alkylsilane. The resulting organosilica particles are inherently hydrophobic and carry organic moieties not only on their surface, but also throughout their core, which can thus host suitable dyes or other apolar agents [18]. In this case pure octadecyltrimethoxy silane (ODTMS) was hydrolyzed with ammonia to directly yield hydrophobic organosilicate particles.

Results and discussion

The hydrophilic particles obtained by Stöber's synthetic route were found, by

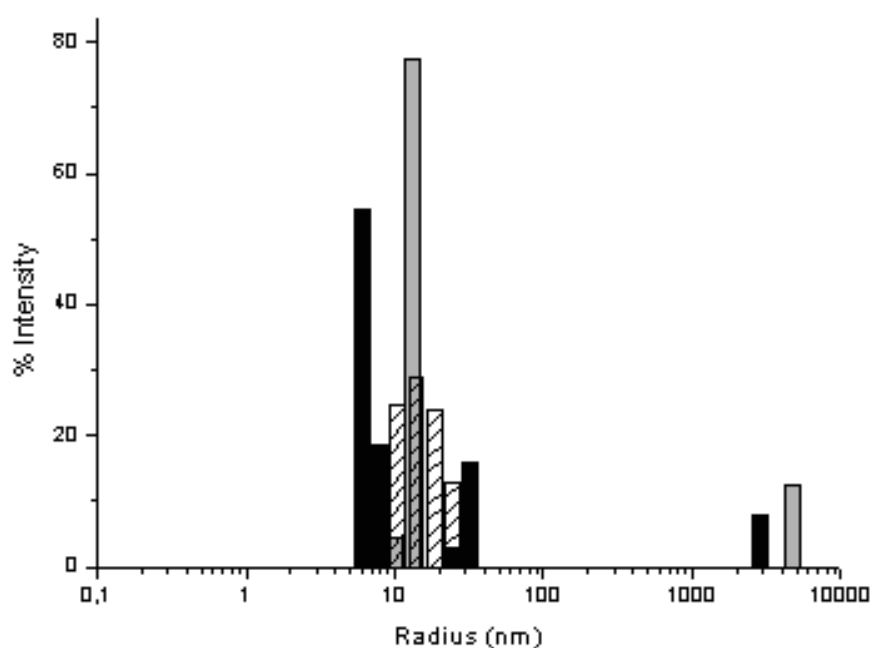


Figure 2: Particle size distribution from dynamic light scattering (DLS) of silane modified hydrophobic silica in heptane, produced using the Stöber synthesis with addition of octadecylsilane after the reaction (light) and during the reaction (dark) compared to the size distribution of the uncoated particles in ethanol from a similar Stöber synthesis (striped). The unmodified particles exhibit a slightly broadened size distribution while the modified particles contain a small fraction of large agglomerates. Note that the agglomerates scatter light strongly, but their fraction of the total particle mass is below 0.1 %.

both transmission electron microscopy (TEM) and dynamic light scattering (DLS) size distribution measurements, to have diameters in the range of 15 to 25 nm with a polydispersity (by DLS) of approximately 10 to 15 % (Figure 1). These particles were subsequently modified and made hydrophobic by the addition of ODTMS without significant increase in either the size of the particles or their polydispersity. Similarly modified particles were produced by *in situ* coating with ODTMS added during the hydrolysis reaction. These particles showed a slight increase in DLS polydispersity over both the bare silica in ethanol and



post-reaction modified silica in heptane (Figure 2).

While the synthetic route detailed above yields hydrophobic silica nanoparticles with acceptable quality, they are not useful in the preparation of very small (< 15 nm), spherical particles. There are limitations to the silica nanoparticles attainable using variations of the Stöber process. While narrow size distributions can be achieved for larger particles (> 200 nm), smaller particles generally exhibit more irregular shapes and sizes. Indeed, to our knowledge, the smallest useable particles that have been produced using the Stöber process are approximately 15 to 20 nm and have a polydispersity of 10-20 % [16; 17]. To obtain smaller, monodispersed particles, we resorted to a route that was again similar to the Stöber synthesis, but used ODTMS as the single silica source in an ethanol/ammonia solution. In this synthesis, the size of the organosilica nanoparticles could be controlled by varying the concentration of the reactants.

At low reactant concentrations and ambient temperatures, from DLS results the resulting particles were smaller than 10 nm and exhibited below 10 % polydispersity but at high reactant concentrations the particles were 20 to 40 nm in diameter, with polydispersities above 25 % (Figure 3). This reaction appears to be a quick and facile route to hydrophobic silica nanoparticles with size and shape dispersity comparable to or better than those produced by the Stöber routes. However, the TEM images revealed a fundamental dif-

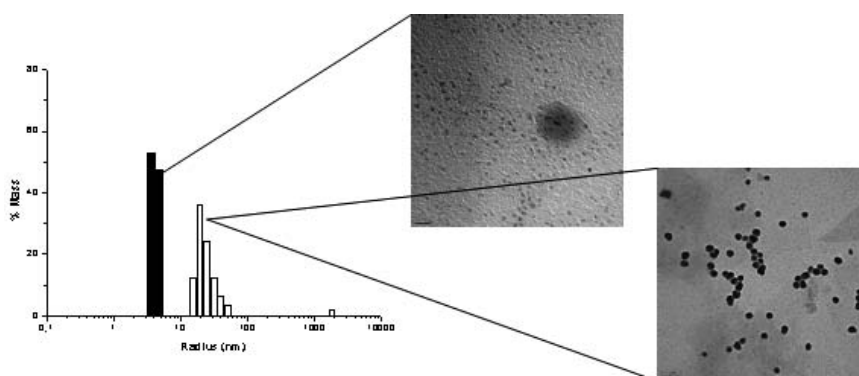


Figure 3: Particle size distribution from DLS of organosilica in heptane produced with low reactant concentrations (light) shows a very narrow particle size distribution with a minimum of large aggregates while the particles produced using higher concentrations show a broader distribution (dark). The corresponding transmission electron microscopy images are also presented showing the very low-density of the smaller particles.

ference with the particles produced using this method: The particles produced are of extremely low density due to the fact that, unlike those produced from method one, they do not have a surface modified SiO_2 core, but a $-\text{Si}-\text{O}-\text{Si}-$ framework supporting an amorphous network of organic chains. These chains are a 15-20 Å long when stretched so that a sub-10 nm particle can only contain a small number of $\text{C}_{18}-\text{Si}-\text{O}$ molecules. In stark contrast to those produced using conventional Stöber routes using TEOS, the resulting particles are porous and the core is inherently hydrophobic resulting in particles that can possibly be used as hosts for hydrophobic agents such as dyes.

Thermal analyses were performed to assess the fraction of the organic component in the organosilica particles and the degree of surface coverage of the Stöber particles with ODTMS modifier (Figure 4). Differential scanning calorimetry (DSC)

showed an endothermic peak at ~ 495 °C, which was identified via mass spectrometry (MS) as alkyl chain fragments formed during the desorption of the alkyl chains from the surface of the particles. The associated weight loss from thermal gravimetry analysis (TGA) was ~ 20 %, indicating the removal of organic modifiers from the silica particle surface. The DSC of the organosilica particles showed a double alkyl peak at ~ 495 °C, again identified by MS as alkyl chain fragments, likely from the decomposition of the particle's organic components. However, in this case the associated weight loss was close to 70 %, indicating that the decomposition affected both alkyl chains from the surface and from the organosilica core network that forms the bulk.

Conclusion

In summary a synthetic route to a novel type of hydrophobic silica nanoparticles has been developed and compared to conventional particles produced using a proven route based on the Stöber synthesis. In the standard synthetic route, nanoparticles in the diameter range of 15 to 25 nm with polydispersity below 15 % were prepared via hydrolysis of TEOS by ammonia under sonication and then modified with ODTMS to yield high coverage hydrophobic surfaces. We also developed a synthetic route, parting with the dual precursor concept, that led to the production of silica particles whose surface chemistry is similar to those produced using standard methods but which exhibit very different physical charac-

teristics. The synthesis of hydrophobic organosilica particles from ODTMS as the single silica source in a mixture of ethanol and ammonia yielded very small nanoparticles from 5 to 50 nm with polydispersities between 8 and 25 %. These particles contain 70 % by weight organic moieties in an organosilica network that make up a low density, porous hydrophobic core. As such, the surface chemistry of these particles is similar to those produced by regular synthetic routes but they are likely to exhibit disparate physical properties, such as the bulk absorption of molecules, different mechanical and optical properties and, possibly, weaker interparticulate attraction. The particles are promising candidates as host systems for hydrophobic moieties, such as dyes or additives or as low-k component in hybrid materials.

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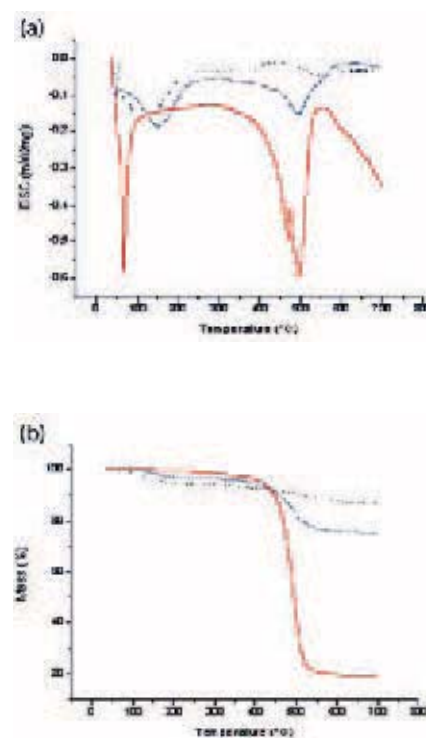


Figure 4. (a) Differential scanning calorimetry and (b) thermal gravimetry analysis results from hydrophilic unmodified Stöber particles (black \cdots), hydrophobic Stöber particles modified with ODTMS (blue $---$) and hydrophobic organosilica particles (red —). The DSC peaks between 70 °C and 100 °C in all three samples are due to residual solvents (ethanol in the case of the hydrophilic particles and heptane for the hydrophobic particles – the associated weight loss is less than 3 % in all cases). The weight-loss associated with the endothermic peaks at 495 °C was less than 3 % for unmodified Stöber particles (residual unreacted TEOS), 20 % for modified Stöber particles and over 70 % for the organosilica particles.



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