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COMMUNICATION

A Facile Route for the Synthesis of Sub-Micron Sized Hollow and Multiporous Organosilica Spheres

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We present a facile route for the synthesis of sub-micron sized hollow and multiporous organosilica spheres, which is based on an oil-in-water emulsion and merely uses one organosilica precursor - phenyl trimethoxysilane - that serves as monomer, precursor for a surface active species and oil phase.

Sub-micron sized hollow and multiporous spheres are applied to realize specific functional properties in coatings or bulk materials.¹ Examples for the utilisation of hollow particles are low refractive index quarter wavelength anti-reflective coatings,² materials with a low thermal conductivity for advanced thermal insulation,³ and coatings or materials that scatter UV or visible light.⁴ Multiporous particles are typically applied for advanced filtration processes,⁵ as support for heterogeneous catalysts,⁶ and for encapsulation and release of active agents.⁷ In most cases, the properties of the functional coatings or bulk materials comprising hollow spheres directly depend on the outer diameter of the sphere and the size of the void. Yet efficient synthesis routes that are suitable for scale up and stringent control of the size distribution, the outer diameter, and the void size remain a challenge.

Here we present a facile route for the synthesis of sub-micron sized hollow organosilica spheres, which is based on an oil-in-water emulsion and merely uses one organosilica precursor – phenyl trimethoxysilane (Ph-TMS) – that serves as monomer, precursor for a surface active species and oil phase. This route allows independent tailoring of outer diameter and void size. Additionally, we demonstrate that through addition of inert solvents to the oil phase, we can apply the same synthesis route for the production of sub-micron sized, multiporous spheres.

For the synthesis of sub-micron sized hollow spheres, we added Ph-TMS directly to an aqueous ammonia solution of pH 11 at 60°C (volume ratio oil:water = 1:118). We performed the synthesis in a standard emulsion reactor (see ESI) and observed emulsion formation after 3 to 6 minutes reaction time. Hollow spheres resulted when the hydrolytic conversion of Ph-TMS was stopped after 1 hour

reaction time and the unreacted monomer and low molecular weight core material was extracted with ethanol. Figure 1a depicts the hollow organosilica spheres with an average outer diameter D_{av} of 616 nm (standard deviation $\sigma = 22$ nm) and a size distribution (σ/D_{av}) of 0.036. The average shell thickness of the formed particles, t_{av} , was 107 nm.⁸ Most of the shells were dented. After 3 hours reaction time and subsequent extraction with ethanol, we obtained hollow particles with a D_{av} of 630 nm, a size distribution of 0.027 and a t_{av} of 139 nm (Figure 1b). In this case, the shells of the particles were not dented. After 5 hours reaction time, we observed the formation of particles with a D_{av} of 546 nm and a size distribution of 0.038 (Figure 1c). The particles had a distinct outer shell of a significantly higher density than the core, which comprises multiple pores in the size range of 10 to 200 nm. Figures 1d and 1e show the X-ray diffractogram and FT-IR spectrum, respectively, of the particles formed after 1 hour reaction time. The relatively sharp peak in the X-ray diffractogram at 7.3° and the broad peak at 18.2° confirm the presence of phenylsilsesquioxane(s) in the particle shell.⁹ They represent the chain to chain and intrachain distances of 1.21 nm and 0.49 nm, respectively.¹⁰ In the FT-IR spectrum, the OH functionality is represented by the absorption at 3618 cm⁻¹. The peaks in the region between 1200 cm⁻¹ and 1000 cm⁻¹ correspond to Si-O-Si stretching vibrations. The distinct absorption maximum at 1128 cm⁻¹ is indicative for the presence of the so-called T10 phenylsilsesquioxane.^{9, 11} The X-ray diffractogram and FT-IR spectrum of the particles formed after 5 h reaction time are similar to the diffractogram and spectrum of the particles formed after 1 h reaction time indicating a similar composition of the phenylsiloxane material (see ESI).

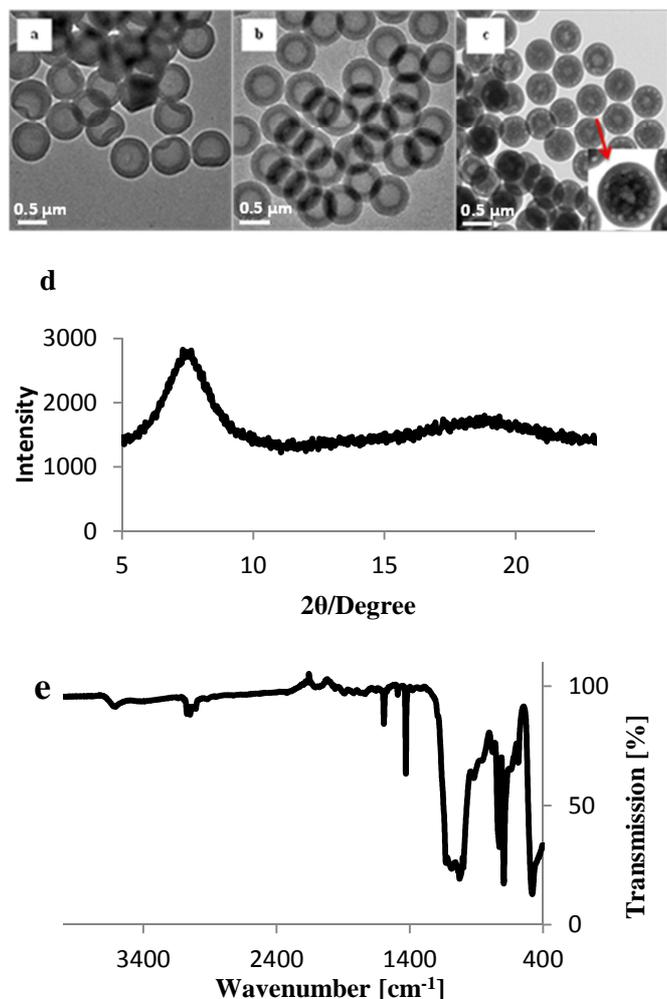


Figure 1. SEM images of particles formed after 1 (a), 3 (b) and 5 hours (c) reaction time and subsequent extraction with ethanol; (d) X-ray diffractogram and (e) FT-IR spectrum of the particles formed after 1 h (for the assignment of all main absorptions in the FT-IR spectrum, see ESI).

Since after 3 to 6 minutes, emulsion formation occurs in the reaction mixture consisting merely of aqueous ammonia of pH 11 and Ph-TMS, a surface active species derived from Ph-TMS must form. To confirm this, we performed pendant drop experiments analysing the change in shape of a droplet of aqueous ammonia (pH=11) in a 1:1 volume mixture of Ph-TMS and toluene (for more details, see ESI). The evolution of the droplet shape in this experiment directly relates to the evolution of the interfacial tension (IFT, Figure 2).

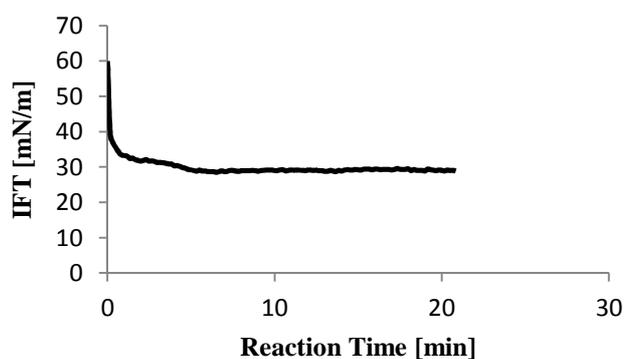


Figure 2. Evolution of the interfacial tension.

The IFT sharply drops to a final value of $29 \text{ mN}\cdot\text{m}^{-1}$ in the first 5 minutes of the experiment, which explains the rapid emulsion formation. In the course of the pendant drop experiment, we also observed the formation of a shell on the outside of the droplet.

The particles formed after 1 and 3 hours reaction time display a similar D_{av} (616 and 630 nm, respectively), a narrow size distribution (0.036 vs. 0.027) and differ only with respect to t_{av} (107 vs. 139 nm). Cryo-TEM analysis of the particles extracted with ethanol after 1 hour reaction time indicated that the particles collapsed during drying (Figure 3) and that the dents in the particle shells were not formed during the extraction process.

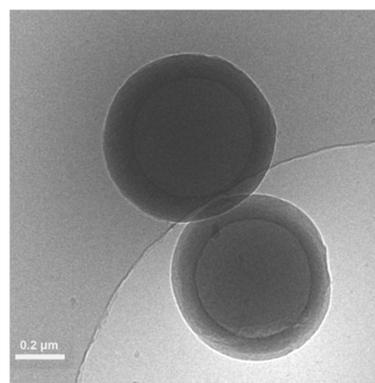


Figure 3. Cryo-TEM image of hollow particles after 1 hour reaction time. The particles lie on a copper grid covered with a carbon film with holes. This film is visible in the background of the image.

In order to mechanically stabilize the particles with a shell thickness of 107 nm or less, we added tetraethyl orthosilicate (TEOS) postulating that this would increase the density in the silica shell. Through substitution of 10 vol-% Ph-TMS by TEOS keeping all other reaction parameters constant, we obtained hollow particles with a D_{av} of 427 nm and a t_{av} of 96 nm after 1 hour reaction time (Figure 4). These particles displayed no dents. Similar results were obtained with tetramethyl orthosilicate (see ESI). A disadvantage of this method, however, was the increase in size distribution from about 0.04 to 0.17.

The particles formed after 5 hours reaction time have a D_{av} of 546 nm and a narrow size distribution, both similar to the particles formed after 1 and 3 hours. In contrast to the particles formed after 1

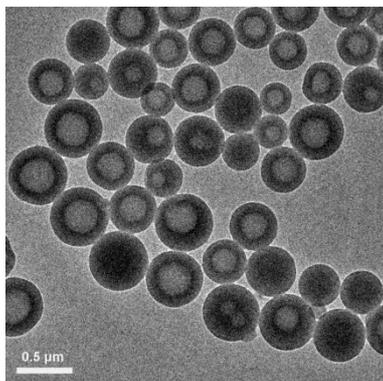


Figure 4. Particles obtained through substitution of 10 vol-% Ph-TMS with TEOS (1 hour reaction time).

and 3 hours, however, these particles have a core that comprises multiple pores instead of a single large void.

Systematic variation of D_{av} was achieved through variation of the volume ratio oil to water keeping all other reaction parameters constant (1 hour reaction time). Increase of the volume ratio from the standard 1:118 to 1:39 resulted in an increase in D_{av} from 616 to 1020 nm whilst retaining a narrow size distribution (0.055, Figure 5a). The t_{av} of these particles was 171 nm. Decrease of the volume ratio from 1:118 to 1:236 resulted in particles with a smaller D_{av} of 445 nm and a narrow size distribution (0.083, Figure 5b). The t_{av} of these particles was 95 nm.

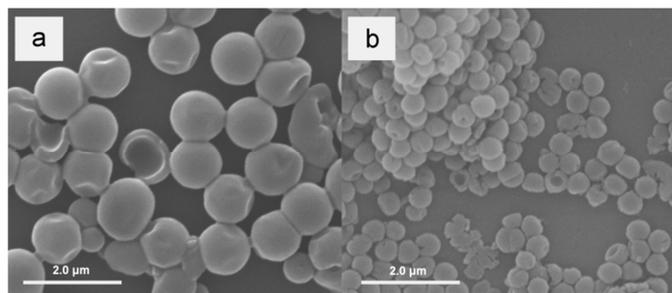


Figure 5. Particles obtained with a volume ratio oil to water of 1:39 (a) and 1:236 (b) (particles are crushed before analysis).

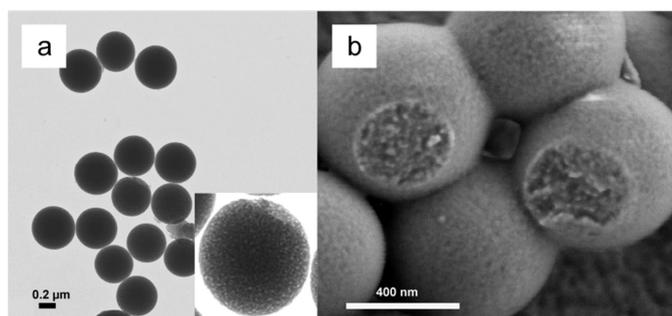


Figure 6. Multiporous organosilica particles obtained through substitution of 50 vol-% Ph-TMS with toluene (1 hour reaction time), observed using TEM (a) and STEM (b).

Through addition of inert solvents to the oil phase, whilst keeping all other reaction parameters constant (reaction time of 1 hour), we managed to synthesize sub-micron sized multiporous spheres. By

substitution of 50 vol-% Ph-TMS with toluene, we prepared multiporous organosilica particles with an average outer diameter D_{av} of 493 nm and a narrow size distribution (0.077, Figure 6). Through XRD and FT-IR analysis, we confirmed the presence of phenylsilsesquioxane(s). The composition is similar to the composition of the hollow and multiporous spheres presented above (see ESI). The pores in these particles were smaller than 10 nm and homogeneously distributed. Similar results were obtained with *o*-xylene, mesitylene, 1,2-dichlorobenzene and cyclohexane (see ESI).

Our observations confirm earlier reports from Hah *et al.*¹² and Wang *et al.*¹³ indicating that the shell growth proceeds from the outside of the particle inwards and that, consequently, D_{av} is fixed in an early stage of the reaction (see Figure 7).

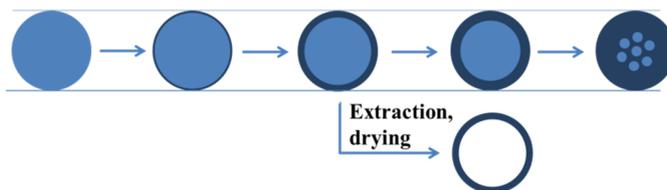


Figure 7. Schematic representation of the formation mechanism of the hollow and multiporous particles in the procedure without inert solvent.

Hence, the resulting structures are kinetically controlled, *i.e.* by the growth dynamics. Initially an organosilica barrier is formed between the water and oil phase which may cause local gradients in pH and concentration of water and Ph-TMS. Consequently, shell thickness and core size can be tuned by changing the reaction time. Furthermore, local gradients in pH will cause changes in the mechanism for the organosilica segregation.¹⁴ Relative variations of the nucleation and growth rates can explain the formation of the sponge like pore structure in the core of the particles after reaching a specific shell thickness. Only recently, Noorduin, Aizenberg *et al.* have demonstrated the extraordinary extent of structural control that can be achieved in silica deposition by local pH variations.¹⁵

Addition of an inert solvent to the oil phase, obviously affects the transport of water molecules inside the droplets and evolution of local pH-gradients substantially. It prevents the formation of a barrier at the surface of the organosilica droplets, that retards the hydrolysis inside the droplet. Multiple nucleation yields the homogeneous multiporous structure throughout the entire particle.

Conclusions

We have identified a facile route for the synthesis of hollow and multiporous organosilica spheres. This route involves merely one organosilica precursor, Ph-TMS, that serves as monomer, precursor for a surface active species and oil phase. We have progressed beyond the work from Hah *et al.*¹² and Wang *et al.*¹³ by providing quantitative information on the time needed to form the surface active species and the strength of the surface active species formed during this process. Furthermore, we demonstrated for the first time that this synthetic approach can yield hollow particles of different sizes with a narrow size distribution, and well-defined multiporous spheres, which significantly broadens the scope for potential applications. Both

the hollow and the multiporous spheres comprise phenylsilsesquioxane(s).

We managed to prepare hollow organosilica spheres with a D_{av} between 445 and 1020 nm and a narrow size distribution (0.036 – 0.083), simply by varying the volume ratio oil to water. As the particles grow from the outside inwards, the average outer diameter is fixed in an early stage of the reaction. Shell thickness and core size could be tuned through variation of the reaction time. If required, the mechanical stability of the shell can be improved through addition of tetrafunctional silica precursors. Addition of toluene results in the formation of multiporous organosilica particles with a D_{av} of 493 nm and a narrow size distribution of 0.077. The pores in these particles were smaller than 10 nm and homogeneously distributed. Similar results were obtained with other inert solvents. Currently, further studies are ongoing in our laboratories to elucidate the mechanism of formation of both types of particles. We anticipate that the outcome of these studies will enable the use of this system for rational design of hollow spheres, multiporous particles and other types of complex, hierarchical nano- and microspheres.

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Notes and references

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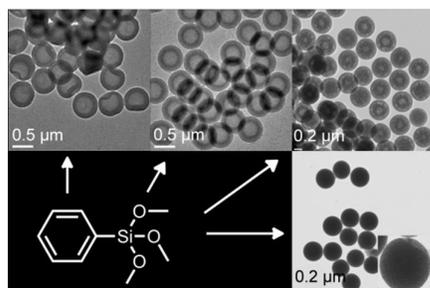
Electronic Supplementary Information (ESI) available: 1) Equipment; 2) Emulsion Formation; 3) Pendant Drop Experiments; 4) Particles obtained through substitution of 10 vol-% Ph-TMS with TMOS or TEOS; 5) Particles obtained through addition of inert solvents to the oil phase; 6) X-ray diffraction (XRD) analysis; 7) BET analysis; 8) FT-IR spectroscopy; 9) Thermogravimetric Analysis (TGA); 10) Experimental; 11) Electron Microscopy. See DOI: 10.1039/c000000x/

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Table of contents entry

A Facile Route for the Synthesis of Sub-Micron Sized Hollow and Multiporous Organosilica Spheres

Margot Segers, Nanning Arfsten, Pascal Buskens,* Martin Möller*



A synthesis yielding hollow and multiporous spheres with stringent control over outer diameter, size distribution and void size is presented.