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Encapsulation of emulsion droplets by organo–silica shells

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Abstract

Surfactant-stabilized emulsion droplets were used as templates for the synthesis of hollow colloidal particles. Monodisperse silicone oil droplets were prepared by hydrolysis and polymerization of dimethyldiethoxysiloxane monomer, in the presence of surfactant: sodium dodecyl sulphate (SDS, anionic) or Triton X-100 (non-ionic). A sharp decrease in the average droplet radius with increasing surfactant concentration was found, with a linear dependence of the droplet radius on the logarithm of the surfactant concentration. The surfactant-stabilized oil droplets were then encapsulated with a solid shell using tetraethoxysilane, and hollow particles were obtained by exchange of the liquid core. The size and polydispersity of the oil droplets and the thickness of the shell were determined using static light scattering, and hollow particles were characterized by electron microscopy. Details on the composition of the shell material were obtained from energy-dispersive X-ray analysis. In the case of sodium dodecyl sulphate, the resulting shells were relatively thin and rough, while when Triton X-100 was used, smooth shells were obtained which could be varied in thickness from very thick (≈150 nm) to very thin shells (≈17 nm). Finally, hexane droplets were encapsulated using the same procedure, showing that our method can in principle be extended to a wide range of emulsions.

Keywords: Hollow particles; Colloids; Emulsion templating; Surfactants; Encapsulation; Microspheres; Organo–silica

1. Introduction

In recent years, considerable effort has been devoted to the design and controlled fabrication of nano- and micro-structured materials with functional properties. The interest in these materials stems from the fact that their properties are a function of their size, composition and structural order. One approach to such materials is through self-assembly of colloidal building blocks. In this respect, over the last years, there have been immense efforts to fabricate core–shell colloidal particles with tailored structural, optical and surface properties, as precursor for such materials.

Colloidal particles with a hollow interior represent a special class of core–shell particles. The fabrication of uniformly-sized hollow spheres with controllable size and shape, has been the subject of many articles [1,2]. They often exhibit properties that are substantially different from those of other particles (e.g., their low density, large specific surface area, stability and surface permeability), thus making them attractive from both scientific and technological viewpoint. Hollow particles represent a distinct class of materials which are of interest in the fields of medicine, pharmaceutics, materials science and the paint industry. They find diverse applications, including encapsulation of products (for the controlled-release of drugs, cosmetics, inks and dyes), protection of sensitive components (as enzymes and proteins), ultrasound-contrast agents, catalysts, coatings, composite materials, artificial cells and fillers [3]. Additionally, they can be used to fabricate highly porous structures with applications in light-weight materials, adsorption, insulation and as filters [4–6]. Porous materials with ordered pores, are also predicted to have useful properties as optical devices [7–9].

The physicochemical characteristics of the hollow particles have to fulfill a large variety of requirements, depending on the specific applications, such as shell permeability, stability, biocompatibility, adsorptive/reflective properties, etc. Very often, these properties can be directly adjusted by careful selection of the preparation techniques. A variety of chemical and physico-

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chemical methods, including heterophase polymerization combined with a sol–gel process [10,11], emulsion polymerization strategies [12], spray-drying methods [13,14], surface polymerization processes [15] and colloidal templating [16–18] have been employed to prepare hollow spheres. Among these, a templating approach represents one of the most versatile techniques, which is based on the synthesis of core–shell particles and subsequent removal of the core by dissolution in a suitable solvent or by heating (calcination). Although it can be used to prepare hollow particles from very diverse materials, both organic and inorganic, starting with a variety of templating agents, this technique often encounters limitations related to the polydispersity of the template and/or the resulting particles, the coating procedure or the removal of the core without affecting the shell properties.

We recently developed a facile method for preparing monodisperse hollow colloidal particles, based on an emulsion templating technique [19,20], which allows the core to be removed under benign conditions. In our method, we first prepared highly uniform *surfactant-free* silicone oil-in-water emulsion droplets, starting with a di-functional silane monomer, after which a solid shell was grown around them by copolymerization between the remaining initial monomer and a tetra-functional silane monomer. We found that by tuning the ratio between the shell thickness and the template radius, three types of hollow spheres can be obtained. Based on the way they collapsed upon drying, they were designated as microspheres, microcapsules and microballoons. The microspheres maintain their spherical shape after drying, the microcapsules form hemispherical caps, while the microballoons have a crumpled appearance. The thickness of the coating was strongly influenced by the amount of hydrolyzed dimethyldiethoxysilane (DMDES) present in the sample at the beginning of the coating step, as a result of the copolymerization between the latter and the added tetra-functional silane monomer [19,20].

Because in general, when dealing with emulsions, surfactants are a necessary additive to impart stability, in the present work, we extended our method to surfactant-stabilized emulsions. This makes our encapsulation technique applicable to a wider range of emulsions. As will be shown, it also provides more control over the particle size. The surfactants used were sodium dodecyl sulphate (SDS, anionic) and Triton X-100 (non-ionic). The cationic surfactant hexadecyltrimethylammonium bromide (CTAB) was also tried, but did not lead to stable colloids.

2. Experimental

2.1. Materials

Dimethyldiethoxysilane (DMDES, ⩾97.0%) and tetraethoxysilane (TEOS, ⩾98.0%) were obtained from Fluka. The surfactants, sodium dodecyl sulphate (SDS, ⩾99.0%) and Triton X-100 (TX100) were purchased from Aldrich, and ammonia (29.7% w/w NH_3) and ethanol (absolute alcohol, analytical grade) from Merck. Hexane (⩾98.5%) was supplied by Aldrich. All chemicals were used as received. De-mineralized water was used in all described reactions and for the cleaning of glassware.

2.2. Synthesis of surfactant-stabilized emulsions

The silicone oil-in-water emulsions were prepared by the hydrolysis and polymerization of DMDES in the presence of one of the two surfactants, one anionic (SDS) and one non-ionic (TX100). The recipe follows that given by Vincent and coworkers [21]. In a typical run, a stock solution of the surfactant was prepared by dissolving 10 mg of SDS in 1000 mL de-mineralized water (for a concentration of $1 \times 10^{-3}\%$ w/w SDS). Typically, the total volume of the emulsions was 10 mL. For 1% v/v ammonia and 1% v/v of DMDES, 9.8 mL of the surfactant stock solution and 0.1 mL concentrated ammonia solution were added and mixed together in the reaction vial. 0.1 mL DMDES was then added to this solution, immediately followed by vigorous mixing for 0.5 or 1 min with a lab-minishaker (MS2 minishaker from IKA) at 2500 rpm. After shaking, a clear solution was obtained which indicated hydrolysis of the monomer, since the un-hydrolyzed DMDES is insoluble in water. Within ≈10 min, the solution started to become turbid, indicating the formation of the droplets. They were allowed to grow for at least 24 h before starting the coating step, except for the cases where the growth of the oil droplets was followed in time, or when mentioned otherwise. The emulsions were left without stirring during droplet growth. We varied the concentration of SDS used to prepare the PDMS emulsions in the range from 1×10^{-3} to 0.26% w/w. We also used various concentrations of DMDES (1, 2 and 3% v/v), and ammonia solutions (1, 2, 3 and 4% v/v). In the case of TX100, the concentration range was from 2×10^{-4} to 0.03% w/w, for the same concentrations of DMDES and ammonia solution as before.

2.3. Preparation of hollow particles

The encapsulation of the surfactant-stabilized PDMS oil droplets with a solid shell was achieved by adding TEOS to the as prepared PDMS emulsions, after 24 h, except for cases where a different time interval is mentioned. Typically for 10 mL volume of emulsion, various amounts of TEOS were added, from 0.038 to 0.173 g, producing final concentrations in the range of 0.018–0.08 M. The TEOS addition was made under stirring, either in one single step, four or five steps (5 min between steps), or by dissolving it first in an aqueous solution containing the same concentration of ammonia as the emulsion to be coated. The shells were then allowed to grow from 3 to 10 days, after which they were centrifuged and re-suspended in ethanol. This dissolves the PDMS droplets, leaving only the ethanol-filled solid shell. The centrifugation/redispersion procedure was repeated several times in order to clean the samples.

A second shell was coated on some of the samples, using the shells previously prepared as seeds for further growth [22]. The synthesis was carried out using small volumes of hollow shells dispersed in ethanol (≈1–3 mL dispersion), to which ammonia solution and then TEOS were added; the final concentrations used were: 1.5 M NH_3, 0.030 M TEOS and 3.4 M H_2O. The dispersions were stirred for 1–2 h and left for 2–3 days before isolation of the shells, after which the samples were cleaned by repeated centrifugation and changing of the solvent.

2.4. Encapsulation of hexane droplets with solid shells

The emulsions used in these experiments were prepared in 10 mL total volume of a solution of de-mineralized water containing Triton X-100 ($2 \times 10^{-3}\%$ w/w) and 5% v/v hexane (9.5 mL aqueous solution of Triton X-100 and 0.5 mL hexane). The samples were mixed with the minishaker (2500 rpm) for 1 min, followed by 1 min of sonication to emulsify the hexane. For the encapsulation step, a mixture was first prepared of 2.7 mL de-mineralized water, 0.15 mL DMDES and 0.15 mL concentrated ammonia solution. This mixture was vigorously shaken for 30 s so that a clear solution was formed. This solution, together with 0.053 mL TEOS (final concentration 0.018 M), was added to the freshly prepared emulsions (right after preparation), during stirring, which was continued for ≈20 h.

2.5. Characterization

The size and polydispersity of the oil droplets and the thickness of the coating were determined with static light scattering (SLS), which was performed with home-built equipment using a He–Ne laser as a light source (632.8 nm, 10 mW). The angular distribution of the scattered light was measured at scattering angles from 19° to 135° relative to the transmitted beam using a photomultiplier tube mounted on a turntable goniometer. The data were plotted against the scattering vector $k = 4\pi n \sin(\theta/2)/\lambda$, where n is the solvent refractive index, θ is the scattering angle, and λ the wavelength in vacuum. The SLS profiles were compared with the theoretical ones calculated with the full Mie solution for the scattering form factor [23], from which the radius and polydispersity were determined. The presence of scattering minima makes the determination of the radius very precise. We estimate the uncertainty at about 5 nm. The minima in the scattering curves shift to the left with increasing in size of the particles, therefore, by assuming the core size to be the same as before coating, the locations of these minima make possible a detailed comparison with theory, which allows us to obtain the thickness of the shell. Usually in a SLS curve, the first minimum (at low value of the scattering vector k) fills up faster than the next ones, due to multiple scattering, which is more severe at low angles. Therefore, the polydispersity is approximated by fitting the depth of the last minima in the scattering profile. However, for the case of surfactant-stabilized emulsions, due to the small size of the oil droplets, most of the SLS curves contain only one minimum, which makes it difficult to determine accurate values for the polydispersity. The values given must therefore be considered upper bounds.

The hollow shells obtained after encapsulation of the droplets and removal of the cores were analyzed with transmission electron microscopy (TEM), on a Philips Tecnai 12 transmission electron microscope, with an accelerating voltage of 120 keV. Samples were prepared by dipping copper 300 mesh-carrier grids, covered with Formvar films, in the as prepared suspension. The elemental microanalysis of the shell material was obtained from energy dispersive X-ray spectroscopy (EDX), carried out on a Philips Tecnai 20F transmission electron microscope. The accelerating voltage was 200 keV, and the same types of samples were used as for the TEM. The hexane droplets coated with solid shells were observed using a confocal microscope operated in transmission mode.

3. Results and discussion

3.1. SDS-stabilized PDMS emulsions

Fig. 1a presents the average droplet size for two series of emulsions as a function of surfactant concentration. The values for the radius and polydispersity of the droplets were measured with SLS, 24 h after emulsion preparation. For the emulsions prepared from 1% v/v DMDES, we observed a significant reduction in the average droplet size as the concentration of surfactant is increased, up to 0.1% w/w SDS (Fig. 1a). After that,

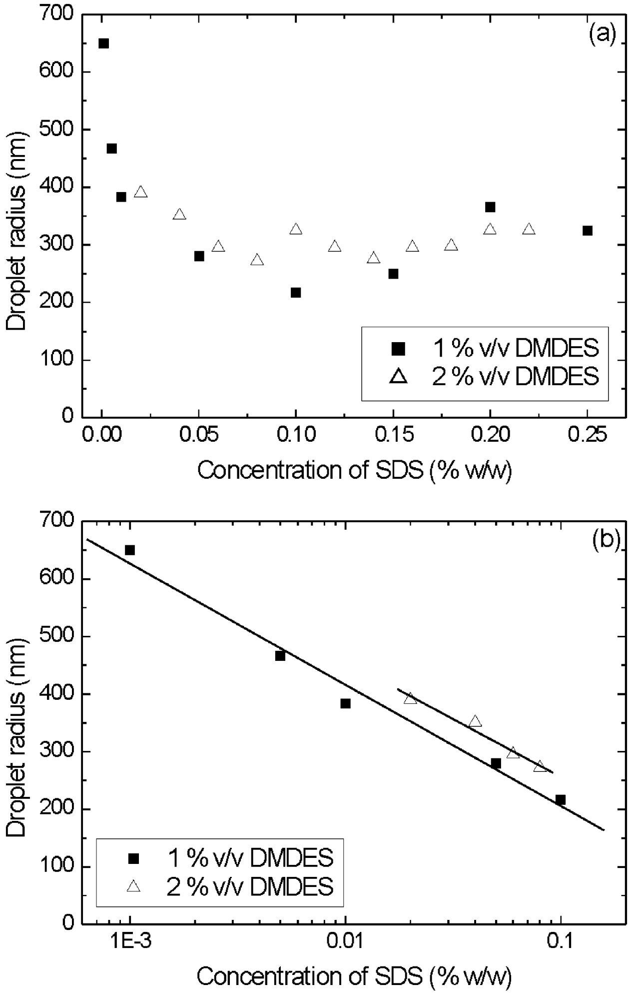

Fig. 1. (a) Radius of PDMS droplets as a function of SDS concentration, for emulsions prepared from 1 and 2% v/v DMDES and 4% v/v ammonia. (b) The same as (a), but using a logarithmic scale for the SDS concentration.

it slowly increases again. The same behavior was observed for the emulsions prepared from 2% v/v DMDES. However, in the latter case, the concentration of SDS up to which the droplet radius decreases, shifted to a slightly lower value (0.08% w/w SDS). In the region where the droplet radius decreases, there is a linear relation between the droplet size and the logarithm of the SDS concentration, as represented by Fig. 1b. This is in agreement with earlier investigations of surfactant stabilized PDMS droplets [21], and also consistent with the assumption that SDS mainly influences the droplets through a reduction in interfacial tension of the oil/water interface. According to the Gibbs equation [24], the interfacial tension decreases with the logarithm of the surfactant concentration. A lower interfacial tension gives a lower activation energy for homogeneous nucleation, leading to more nuclei; assuming that the number of droplets remains constant during growth, the same volume of oil is formed, but is divided over more droplets.

Usually, the radius of the droplets in surfactant-stabilized emulsions decreases with increasing surfactant concentration until the critical micelle concentration (CMC) is reached [25]. For SDS, the CMC corresponds to a concentration of 0.23% w/w [26]. Therefore we would expect a minimum in the average droplet size around this value. However, this is found at lower concentrations, as is seen in Fig. 1a: at 0.1% w/w for emulsions with 1% v/v DMDES and at 0.08% w/w for emulsions with 2% v/v DMDES. Above these values, the size of the droplets fluctuates, increasing and decreasing alternately, which makes it difficult to interpret as a sign that the CMC has been reached. However, the fact that deviations occur at lower concentrations than the CMC might indicate a reduction of the CMC due to the presence of ions (ammonia) and ethanol (hydrolysis of DMDES). It is known that the addition of small amounts of ethanol [27] or ions [28] can decrease the CMC considerably. In our emulsions, the 4% v/v of ammonia solution corresponds to an ionic strength of ≈3.3 mM. Moreover, a small amount of ethanol is formed in the condensation reaction of DMDES, from one mole of DMDES, two moles of ethanol are formed. This leads in our case (1 and 2% v/v DMDES) to 0.116 and 0.232 M ethanol, respectively, considering full conversion of DMDES into PDMS. The shift of the minimum in droplet size to a lower concentration for higher DMDES concentration is consistent with this interpretation, although the magnitude of the shift is not fully explained by it.

We also investigated the growth in time of the oil droplets, by preparing several emulsions with 1, 2 and 3% v/v DMDES and ammonia respectively, and SDS concentrations in the range 0.02–0.1% w/w. The emulsions were prepared as described in the synthesis section. The radius of the droplets was followed in time with SLS, and the results are plotted in (Fig. 2). Although the droplets are stabilized by SDS and their average size is smaller than in the case of surfactant-free emulsions [20], their growth shows the same behavior in time. The data can be fitted well by the same relation used in Ref. [20]:

$$R(t)^3 = R_f^3\left[1 - \exp\left(-\frac{t}{t_1}\right)\right] \tag{1}$$

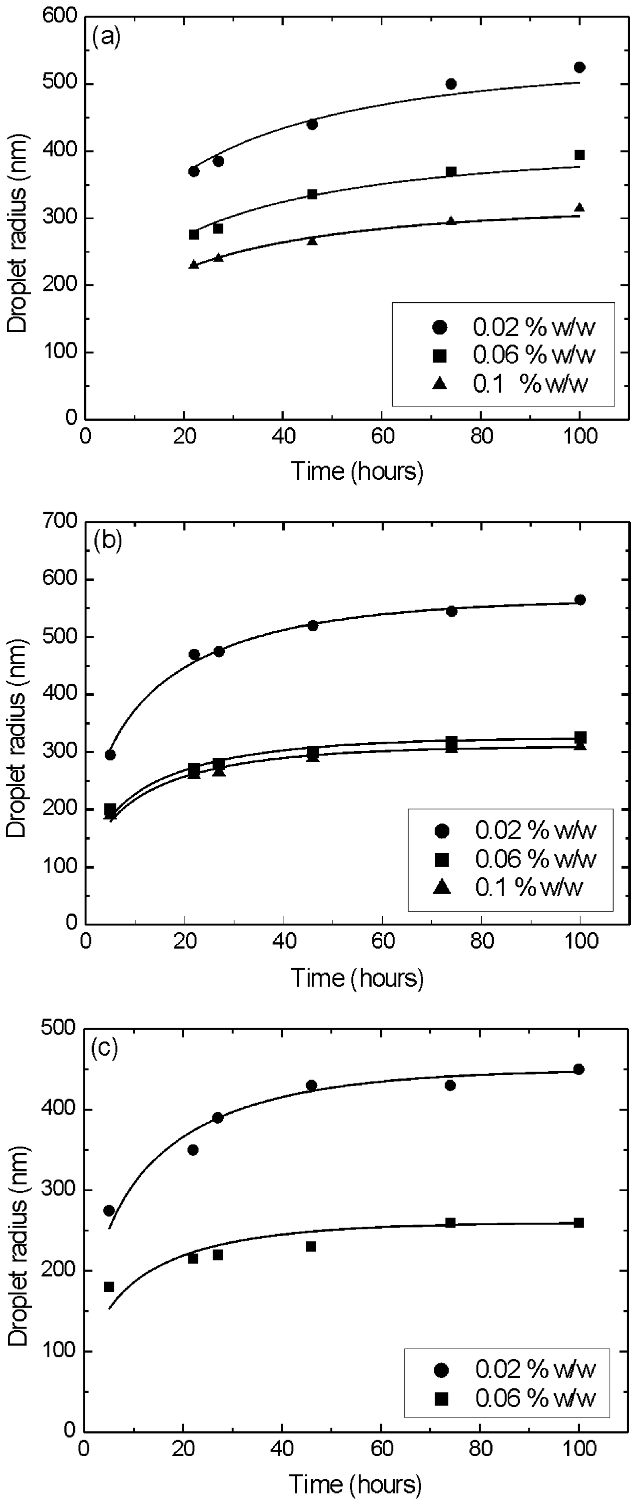

Fig. 2. Average droplet radius as a function of time, followed with SLS, for different SDS concentrations, shown in the legend. These emulsions were prepared from: (a) 1% v/v DMDES, 1% v/v ammonia solution, (b) 2% v/v DMDES, 2% v/v ammonia solution and (c) 3% v/v DMDES, 3% v/v ammonia solution; lines are drawn according to Eq. (1).

where R_f is the final droplet radius. The growth rate of the oil droplets was given by $1/t_1$, where t_1 was used as a fitting parameter. The value for t_1 was found to be 26 ± 2 h for 2 and 3% v/v DMDES, while for 1% v/v, it was 47 ± 2 h. These values

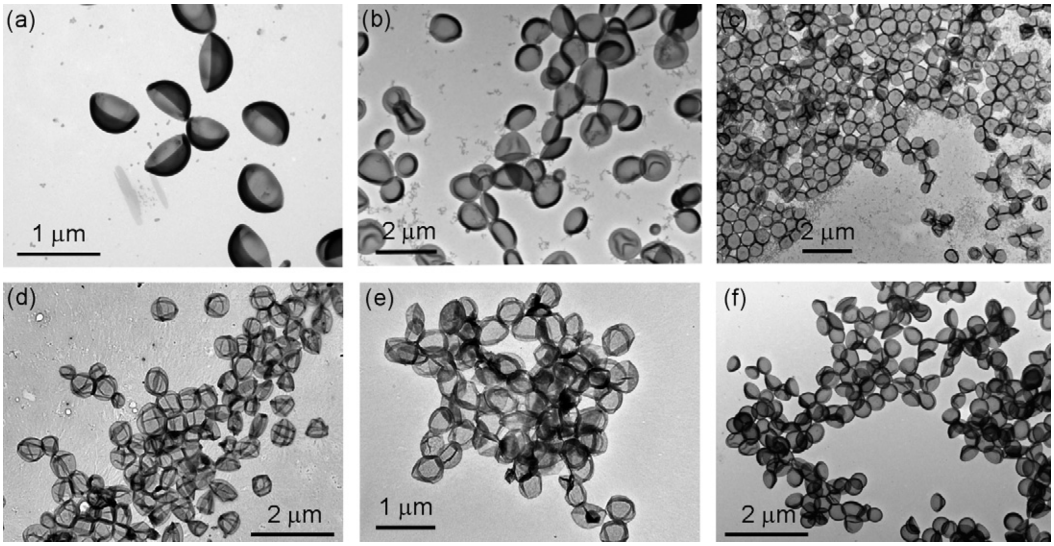

Fig. 3. TEM micrographs of hollow shells formed by templating of SDS-stabilized droplets: (a) core radius 310 nm, shell thickness 40 nm, 7% polydispersity ($S_{1,SDS}$), (b) core radius 272 nm, shell thickness 25 nm, 10% polydispersity ($S_{2,SDS}$), (c) core radius 262 nm, shell thickness 15 nm, 12% polydispersity ($S_{3,SDS}$), (d) core radius 237 nm, shell thickness 12 nm, 9% polydispersity ($S_{4,SDS}$), (e) core radius 242 nm, shell thickness 12 nm, 9% polydispersity ($S_{5,SDS}$), (f) core radius 229 nm, shell thickness 17 nm, 9% polydispersity ($S_{6,SDS}$). Size and polydispersity obtained from SLS.

are nearly the same as for emulsions prepared without surfactant [20].

From these results we conclude that even in the presence of SDS, at concentrations below the CMC, the oil droplets are formed by the same reaction mechanism, with a rate limiting step in the condensation reaction as observed in the absence of surfactant. By using SDS in the preparation of PDMS emulsions, we obtained smaller droplets sizes, with polydispersities in the range 6–10%. Although droplets with similar sizes were obtained also in the surfactant-free emulsions in the first hours of the reaction [20], their polydispersity was relatively high; by using surfactant, the polydispersity of the smaller droplets is improved, and consequently, their potential use for encapsulation.

3.2. *Hollow particles from SDS-stabilized oil droplets*

The silicone oil droplets described in the previous section were used as templates for encapsulation with solid shells. The formation of the shell is based on a copolymerization between the hydrolyzed DMDES still left in the sample and the added TEOS. For surfactant-free emulsions [19,20], we have shown that the shell thickness is mainly determined by the amount of un-polymerized DMDES at the time of TEOS addition. This holds also for surfactant-stabilized emulsions. However, to determine the influence on the resulting hollow shells, we varied the amount of TEOS used and the addition method. Table 1 and Fig. 3 represent an overview of the hollow particles obtained by coating SDS-stabilized oil droplets with solid shells. We emphasize that the polydispersities reported in Table 1 and in the caption of Fig. 3 must be considered upper bounds, as explained in the experimental section.

In one series of experiments, we used 0.018 M TEOS, which was added in four steps to emulsions that had been prepared 24 h earlier. The samples were stirred for three days, after which the coated droplets were transferred to ethanol to remove the PDMS cores. The droplets used as templates for these experiments were prepared from 1% v/v DMDES, 1% v/v ammonia and 0.02% w/w SDS (see Table 1, sample $S_{1,SDS}$). The hollow shells obtained after dissolution of the core can be seen in Fig. 3a. Although the shells were allowed to grow for three days, the final thickness was relatively small compared with the values obtained after three days in the case of surfactant-free emulsions (typically >100 nm). This indicates that the presence of SDS somehow limits the shell growth. Due to the thin shell compared to the total radius, the particles deformed when dried. Also, we found evidence of small secondary particles which have not been completely removed by centrifugation.

Even thinner shells were obtained when more SDS was used (0.04% w/w). The emulsion was prepared from 1% v/v DMDES and 4% v/v ammonia and after 24 h, TEOS was added to this mixture during stirring (sample $S_{2,SDS}$). The re-

Table 1
Particles obtained from encapsulation of SDS-stabilized droplets

Sample	SDS (% w/w)	R_d[a] (nm)	δ[b] (%)	TEOS (M)	d[c] (nm)
$S_{1,SDS}$	0.02	310	7	0.018	40
$S_{2,SDS}$	0.04	272	10	0.02	25
$S_{3,SDS}$	0.06	262	12	0.04	15
$S_{4,SDS}$	0.06	237	9	0.04	12
$S_{5,SDS}$	0.06	242	9	0.05	12
$S_{6,SDS}$	0.06	229	9	0.06	17

Note. The oil droplets were prepared from 1% v/v DMDES (samples $S_{1,SDS}$–$S_{3,SDS}$) and 2% v/v (samples $S_{4,SDS}$–$S_{6,SDS}$), respectively.

[a] R_d—radius of the droplets used as templates.

[b] δ—polydispersity.

[c] d—shell thickness, obtained by using various amounts of TEOS, which was added 24 h after the emulsion preparation for all samples, except sample $S_{4,SDS}$ when the time interval was 48 h.

sulting shells, after they were transferred to ethanol are shown in Fig. 3b.

As we already mentioned, the shell thickness is influenced mainly by the amount of DMDES which is not yet polymerized in the samples. Therefore, in some experiments, we added TEOS 48 h after the emulsion preparation. An emulsion was prepared (sample $S_{3,SDS}$) using 1% v/v DMDES, 4% v/v ammonia and 0.06% w/w SDS. TEOS was dissolved in an aqueous solution containing ammonia, prior to addition (final TEOS concentration 0.04 M). After 4 days, the coated droplets were transferred to ethanol and the hollow shells are shown in Fig. 3c. Similar shell thicknesses were obtained as before, which means that the growth of the shell is influenced also by the presence of SDS, and not only by DMDES.

To investigate the influence of the TEOS concentration on the shell thickness, several emulsions were prepared from 2% v/v DMDES, 4% v/v ammonia and 0.06% w/w SDS. TEOS was added again by dissolving it first in water/ammonia solution. The final concentrations of TEOS in the samples were 0.04, 0.05, 0.06 and 0.08 M, respectively. After three days, the particles were transferred to ethanol and cleaned by centrifugation and changing the solvent. For the first three TEOS concentrations we obtained very thin shells: 12, 12 and 17 nm, respectively. The hollow shells are shown in Figs. 3d–3f (samples $S_{4,SDS}$–$S_{6,SDS}$ from Table 1). For 0.08 M TEOS, no particles were obtained, only big aggregates, which indicates that 0.06 M is the concentration limit for the added TEOS for which stable particles can be obtained. Apparently, the amount of added TEOS does not influence the shell thickness significantly. This was also found for the surfactant-free emulsions [20]. Moreover, even when the shells are allowed to grow for several days and TEOS is added already after 24 h, their thickness does not exceed ≈40 nm, which is completely different from the surfactant-free case.

We conclude that from the encapsulation of SDS-stabilized oil droplets we can only obtain microballoon-like particles and microcapsules. The relative shell thicknesses for these shapes correspond with those found in Ref. [19]. When SDS-stabilized oil droplets are used for encapsulation with solid shells, apparently a part of the TEOS/DMDES goes into the formation of secondary particles. It is possible that SDS promotes the formation of new nuclei by stabilizing them. This is a likely mechanism through which SDS interferes with the shell growth. Moreover, the higher the SDS concentration, the thinner the shell.

3.3. *EDX analysis of the hollow shells*

To obtain information about the chemical composition of the shell material, we performed EDX elemental microanalysis on hollow shells obtained by coating SDS-stabilized emulsion droplets. The oil from the core was removed prior to the measurements by washing with ethanol and drying. A typical EDX spectrum is presented in Fig. 4. We found the same composition as for the shells obtained by templating surfactant-free emulsions [20], namely silicon, oxygen and carbon. We could not detect the presence of surfactant in the shell material, but this does not exclude the possibility that the shell does contain a small amount of SDS. If this would be the case, the S and Na signals would be very low considering the small weight percentage of surfactant used in the first place, and as a consequence, very difficult to detect. However, the presence of a significant amount of carbon is an indication that the hydrolyzed DMDES contributes to the shell formation.

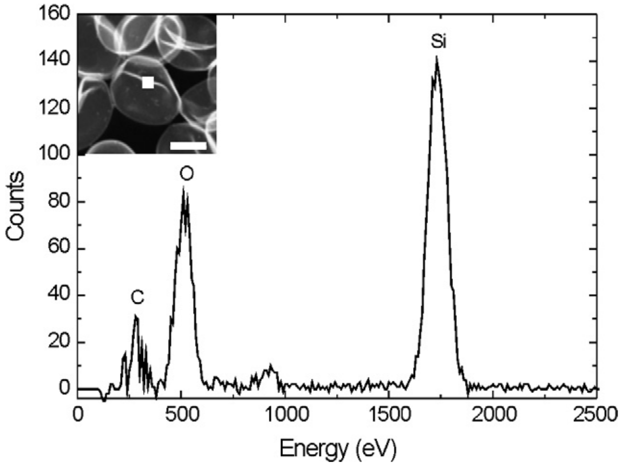

Fig. 4. EDX spectrum recorded in the middle of a hollow shell, in the point indicated by the white square from the inset. Inset: TEM dark field image, scale bar 200 nm.

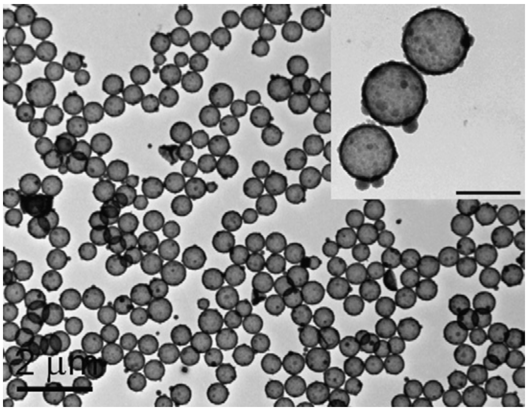

Fig. 5. TEM images of particles after the second shell growth. Scale bar of the inset: 0.5 μm.

3.4. *Second shell growth*

The encapsulation of SDS-stabilized oil droplets leads to a relatively thin shell thickness. Therefore, in order to obtain thicker shells, we tried to grow an extra silica shell by a regular seeded Stöber growth [22,29].

The second shell growth was carried out using hollow shells dispersed in ethanol, as described in the experimental part. TEM images of the particles obtained from the second growth step are shown in Fig. 5. Although the particles appear to have a thicker shell and did not collapse as they did before the second coating (Fig. 3d), they have a very rough surface. The sample also contained somewhat smaller particles which seemed to be secondary nucleation. This same type of shell was obtained in all samples used for second coating.

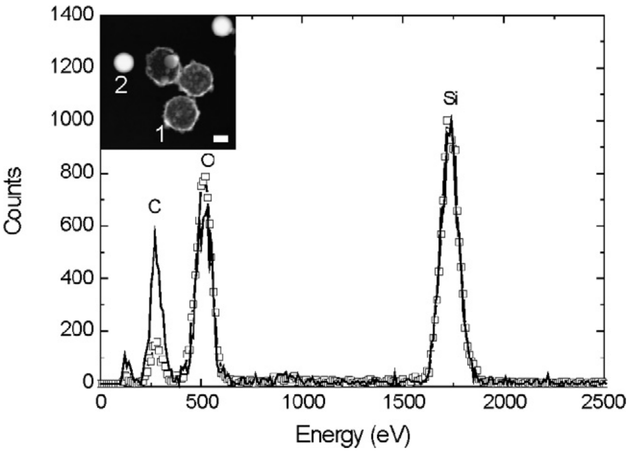

Fig. 6. EDX spectra recorded after second shell growth: (—) EDX in the middle of particle 1 and (—, □) EDX on the particle 2 (secondary nucleation). Inset: TEM dark field image, scale bar 200 nm.

EDX analysis (Fig. 6) performed on these samples shows the same shell composition as for particles after the first shell growth. By comparing the shell composition with that of a particle which is part of the secondary nucleation, it is obvious that the secondary particle has a lower carbon content (the small amount comes from the carbon-coated grid, since no background correction was applied), making it more similar to pure silica.

We concluded that a shell (with the same composition) thick enough to resist deformation can be formed in this way, but unfortunately, these shells are very rough. This might be a consequence of SDS which might have been adsorbed at the surface of the shells during the encapsulation step.

3.5. Triton X-100-stabilized PDMS emulsions

We also prepared PDMS emulsions in the presence of the non-ionic surfactant, Triton X-100, using 2% v/v DMDES and 2% v/v ammonia in 10 mL total volume of emulsion, with surfactant concentrations from 2×10^{-4} to 0.01% w/w. The samples were prepared by mixing the reagents for 1 min, and after 20 h the size of the oil droplets was measured with SLS. Also in the presence of Triton X-100, the average droplet radius decreases with increasing surfactant concentration up to 0.01% w/w. However, the concentrations for which Triton X-100 effectively influences the size of the oil droplets are considerably lower than for SDS due to the fact that it has a much lower CMC of 0.019% w/w [30]. Also for Triton X-100, the effective concentration range stopped below the CMC (not shown in the graph due to the very low concentrations), an effect which might be explained by a reduction of the CMC due to the same factors as discussed for SDS. Similar to the SDS-stabilized emulsions, we found a linear dependence of the final droplet radius on the logarithm of the concentration (Fig. 7), indicating that the presence of Triton X-100 influences the droplet size through a decrease in the interfacial tension of the oil/water interface.

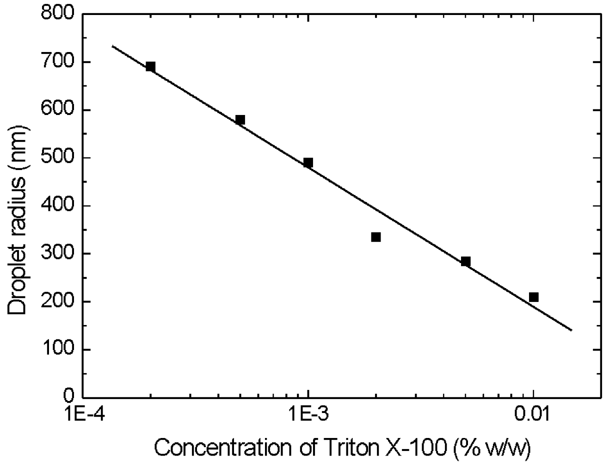

Fig. 7. Radius of PDMS droplets as a function of Triton X-100 concentration, for emulsions prepared from 2% v/v DMDES and 2% v/v ammonia, using a logarithmic scale for the surfactant concentration. The values for the radius were determined by SLS.

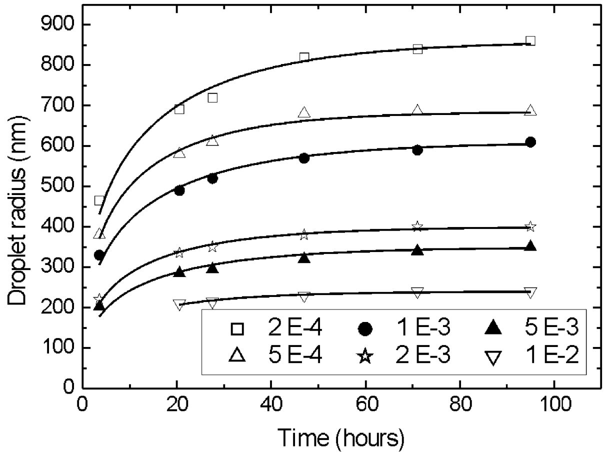

Fig. 8. Average droplet radius as a function of time, followed with SLS, for different Triton X-100 concentrations, shown in the legend. These emulsions were prepared from 2% v/v DMDES and 2% v/v ammonia solution; (—) are fits to Eq. (1).

The growth in time of the Triton X-100 stabilized oil droplets was investigated for a series of emulsions prepared from 2% v/v DMDES, 2% v/v ammonia and various TX100 concentrations. The size and polydispersity of the oil droplets were followed in time with SLS. The average droplet radius vs time is plotted in Fig. 8. By fitting the data with Eq. (1) as before, we obtained values for the growth rate $1/t_1$ quite similar to those found for both surfactant-free [20] and SDS-stabilized emulsions. The value for the fitting parameter t_1 was found to be $\approx 23.2 \pm 1.7$ h. Therefore we can conclude that, independent of the presence or the type of surfactant used to stabilize the PDMS droplets prepared through hydrolysis and condensation of DMDES, the reaction mechanism remains the same and can be described by a first order process due to a rate limiting step in the condensation reaction.

The influence of Triton X-100 does not differ substantially from that of SDS, as we observed also in this case a decrease in the average size of the droplets as we increased the surfactant concentration. However, the polydispersities obtained for the Triton-stabilized emulsions are somewhat lower than for SDS-

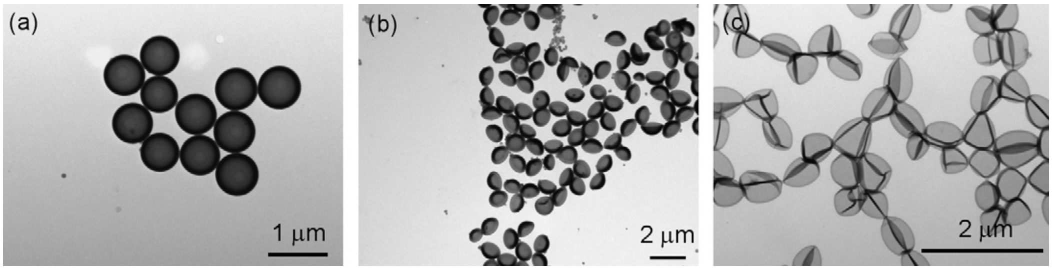

Fig. 9. TEM micrographs of hollow shells formed by templating Triton X-100-stabilized droplets: (a) sample prepared from 1% v/v DMDES, 4% v/v ammonia and 0.002% w/w Triton X-100, to which 0.02 M TEOS was added; core radius 320 nm, shell thickness 95 nm, 7% polydispersity (sample $S_{1,TX100}$); (b) sample prepared from 2% v/v DMDES, 2% v/v ammonia and 0.001% w/w Triton X-100, to which 0.02 M TEOS was added 20 h after preparation; core radius 500 nm, shell thickness 170 nm, 4% polydispersity (sample $S_{2,TX100}$); (c) sample prepared from 2% v/v DMDES, 2% v/v ammonia and 0.002% w/w Triton X-100, to which 0.02 M TEOS was added 20 h after preparation; core radius 265 nm, shell thickness 17.5 nm, 9% polydispersity (sample $S_{3,TX100}$). Size and polydispersity obtained from SLS.

Table 2
Particles obtained from encapsulation of Triton X-100-stabilized droplets

Sample	TX100 (% w/w)	R_d[a] (nm)	δ[b] (%)	TEOS (M)	d[c] (nm)
$S_{1,TX100}$	0.002	320	7	0.02	95
$S_{2,TX100}$	0.001	500	4	0.02	170
$S_{3,TX100}$	0.002	265	9	0.02	17.5

Note. The oil droplets were prepared from 1% v/v DMDES for sample $S_{1,TX100}$ and from 2% v/v DMDES for the rest of the samples. TEOS was added 24 h after the emulsion preparation in samples $S_{1,TX100}$ and $S_{2,TX100}$ and in sample $S_{3,TX100}$ after 20 h. For sample $S_{3,TX100}$, the growth of the shell was stopped by dialysis against de-mineralized water.

[a] R_d—radius of the droplets used as templates.

[b] δ—polydispersity.

[c] d—shell thickness.

stabilized emulsions, with typical values of 4–8% after 20 h. Additionally, much lower concentrations of Triton X-100 are needed to stabilize the PDMS droplets, which might have important consequences for the encapsulation step.

3.6. Hollow particles from Triton X-100-stabilized oil droplets

PDMS oil droplets prepared from 1% v/v DMDES and 4% v/v ammonia or 2% v/v DMDES and 2% v/v ammonia and stabilized with different Triton X-100 concentrations, were used as templates for encapsulation experiments. 24 h after their preparation, 0.02 M TEOS was added in 4 steps (3 min between steps), under stirring, which continued for one hour. After three days, the cores were removed by washing several times with ethanol. The TEM images of the resulting hollow shells are presented in Fig. 9, and Table 2 shows an overview of the particle size and polydispersity.

It is very interesting to notice that in contrast to the case of SDS, Triton X-100 allows the growth of thick shells in one single growth step. Hollow microspheres that do not collapse can be formed. Also the amount of secondary nucleation is much less. The TEOS was added after 24 h, following the same procedure described for the previous samples. Except for thick shells, also microballoon-like particles can be obtained if the shell growth is stopped earlier, as is shown in Fig. 9c (sample $S_{3,TX100}$ from Table 2. The thin shells were obtained by interrupting the shell growth after 3 h, by dialysis against demineralized water for two days, after which the samples were washed several times with ethanol.

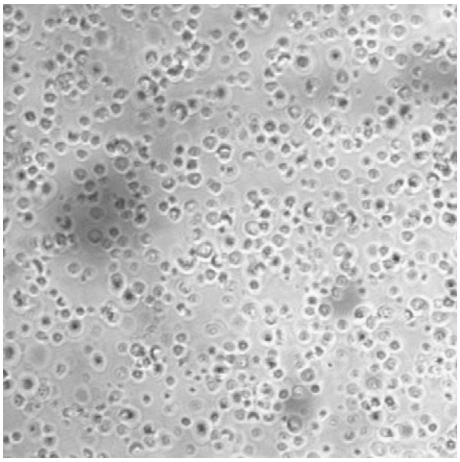

Fig. 10. Coated hexane droplets in water showing buckling (transmission mode). Image size: 73 μm × 73 μm.

The encapsulation experiments involving Triton X-100-stabilized oil droplets as templates show that this surfactant is more suitable for coating purposes. By varying the shell thickness, we can obtain different types of hollow shells, just as without surfactant. The advantage of using Triton X-100 is that it allows us to reduce considerably the size of the particles.

3.7. Coating hexane droplets with solid shells

We preliminarily investigated the possibility of coating other surfactant-stabilized oil droplets with solid shells, following the same procedure of copolymerization of TEOS with hydrolyzed DMDES. This would greatly expand the usefulness of our technique. The Triton X-100-stabilized hexane droplets in water, were coated with a solid shell, following the method described in the experimental section and after ≈20 h after the coating, the core–shell particles were investigated with confocal microscopy in transmission mode. The shells are too thin to resolve. However, they show a pronounced buckling (Fig. 10), probably due to evaporation of the volatile hexane. The presence of buckled shells is a clear evidence that the oil droplets are encapsulated by solid shells.

We conclude that our method to encapsulate PDMS oil droplets with a silica/siloxane shell can be extended to different oils, but more research is required to optimize the procedure.

4. Conclusions

We have shown that monodisperse, micrometer-sized hollow particles can be prepared using an emulsion templating approach where the templates consist of surfactant-stabilized oil droplets. This is important because it allows us to decrease the final size of the particles, maintaining at the same time reasonably good polydispersities. The oil droplets prepared in the first step of the synthesis were then encapsulated in a solid silica/siloxane shell, followed by dissolution of the core.

Monodisperse PDMS oil droplets can be prepared also using surfactants to stabilize them. Both surfactants used (SDS and Triton X-100) cause a decrease in the average radius of the oil droplets, but they are effective in different concentrations ranges, due to their different CMC. However, the highest concentration for which we still observed an influence of the surfactants were somewhat lower than their corresponding CMC's. We interpreted this effect as a reduction in the CMC value due to the presence of ions and ethanol resulting from the condensation reaction of DMDES. Moreover, in both cases, we found a linear dependence of the droplet radius on the logarithm of the surfactant concentration, indicating that the surfactant mainly influences the oil droplets through a reduction in interfacial tension of the oil/water interface. The formation reaction of the oil droplets in the presence of surfactants was found to take place at the same rate as for the surfactant-free emulsions, with the same growth rates in the average droplet size.

During the encapsulation step, the growth of the shell is limited by the presence of SDS; as a result, by using SDS-stabilized emulsions, we obtained only relatively thin shells which fall into the categories of microballoons and microcapsules. Although we were not able to detect the presence of SDS in the EDX spectrum, it is still likely that SDS is present on the surface of the shells and prevents the growth of silica to take place. However, the EDX elemental composition indicates that the shells consist of a siloxane/silica copolymer. Attempts to increase the shell thickness in a second growth step resulted in a thicker shell, but it was extremely rough and inhomogeneous. On the other hand, the presence of Triton X-100 does not seem to disturb the shell growth. By adding TEOS to Triton X-100-stabilized droplets, we can obtain hollow particles of different shell thicknesses, ranging from a few nanometers up to $\approx$150 nm in one growth step. It is possible that this difference originates in the lower amount of Triton X-100 needed to reduce the droplet size.

Moreover, preliminary experiments show that the procedure of coating PDMS droplets with solid shells based on copolymerization of hydrolyzed DMDES and TEOS can be extended also to other types of oil droplets stabilized by surfactants, but more systematic investigations need to be made.

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References

[1] E. Bourgeat-Lami, in: A. Elaissari (Ed.), Colloidal Polymers, in: Surfact. Sci. Ser., vol. 115, Marcel Dekker, New York, 2003.
[2] F. Caruso, Chem. Eur. J. 6 (2000) 413.
[3] D.L. Wilkox, M. Berg, T. Bernat, D. Kellerman, J.K. Cochran Jr., Hollow and Solid Spheres and Microspheres: Science and Technology Associated with Their Fabrication and Application, in: Materials Research Society Proceedings, Pittsburgh, vol. 372, 1995.
[4] D.J. Green, P. Colombo, MRS Bull. April (2003) 296.
[5] J. Banhart, M. Ashby, N. Fleck, Metal Foams and Porous Metal Structures, MIT-Verlag, Bremen, 1999.
[6] L. Gibson, M. Ashby, Cellular Solids: Structure and Properties, second ed., Cambridge Univ. Press, Cambridge, 1997.
[7] J.D. Joannopoulos, P.R. Villeneuve, F. Shanhui, Nature 386 (1997) 143.
[8] X. Xu, S.A. Asher, J. Am. Chem. Soc. 126 (2004) 7940.
[9] Y. Yin, Y. Lu, B. Gates, Y. Xia, Chem. Mater. 13 (2001) 1146.
[10] I. Tissot, J.P. Reymond, F. Lefebre, E. Bourgeat-Lami, Chem. Mater. 14 (2002) 1325.
[11] S. Schacht, Q. Hou, I.G. Voigt-Martin, G.D. Stucky, F. Schuth, Science 273 (1996) 768.
[12] C.E. Fowler, D. Khushalani, S. Mann, Chem. Commun. (2001) 2028.
[13] P.J. Bruinsma, A.Y. Kim, J. Liu, S. Baskaran, Chem. Mater. 9 (1997) 2507.
[14] M. Iida, T. Sasaki, M. Watanabe, Chem. Mater. 10 (1998) 3780.
[15] O. Emmerich, N. Hugenberg, M. Schmidt, S.S. Sheiko, F. Baumann, B. Deubzer, J. Weis, J. Ebenhoch, Adv. Mater. 11 (1999) 1299.
[16] A. Imhof, Langmuir 17 (2001) 3579.
[17] C. Graf, A. van Blaaderen, Langmuir 18 (2002) 524.
[18] S.M. Marinakos, J.P. Novak, L.C. Brousseau, A.B. House, E.M. Edeki, J.C. Feldhaus, D.L. Feldheim, J. Am. Chem. Soc. 121 (1999) 8518.
[19] C.I. Zoldesi, A. Imhof, Adv. Mater. 17 (2005) 924.
[20] C.I. Zoldesi, C.A. van Walree, A. Imhof, Langmuir 22 (2006) 4343.
[21] K.R. Anderson, T.M. Obey, B. Vincent, Langmuir 10 (1994) 2493.
[22] G.H. Bogush, M.A. Tracy, C.F. Zukoski IV, J. Non-Cryst. Solids 104 (1988) 95.
[23] C.F. Bohren, D.R. Huffman, Absorbtion and Scattering of Light by Small Particles, Wiley, New York, 1983.
[24] D.F. Evans, H. Wennerstrom, The Colloidal Domain—Where Physics, Chemistry, Biology, and Technology Meet, second ed., Wiley–VCH, New York, 1999.
[25] S.G. Oh, D.O. Shah, J. Phys. Chem. 97 (1993) 284.
[26] C.-E. Lin, J. Chromatogr. A 1037 (2004) 467.
[27] H. Onori, A. Santucci, J. Mol. Liq. 69 (1996) 161.
[28] R.J. Hunter, Foundations of Colloid Science, Oxford Univ. Press, Oxford, 1986.
[29] W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
[30] M. Li, Y. Rharbi, X. Huang, M.A. Winnik, J. Colloid Interface Sci. 230 (2000) 135.