Silica Hollow Spheres by Templating of Catanionic Vesicles

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A simple and effective means for obtaining hollow silica particles of controlled diameter from about 60 to 120 nm is presented. The synthesis utilizes equilibrium vesicles as templates for the directed growth of silica. Two different surfactant systems are used to form the vesicular templates: (a) mixtures of cetyltrimethylammonium bromide (CTAB) and sodium perfluorooctanoate (F127) and (b) mixtures of cetyltrimethylammonium tosylate (CTAT) and sodium dodecylbenzenesulfonate (SDBS). These templates were chosen because these mixtures of surfactants in water form unilamellar vesicles spontaneously that appear stable in the chemical environment required for silica synthesis. Tetramethoxysilane (TMOS) is added to the vesicular templates as a precursor for silica formation via acid-catalyzed hydrolysis and polycondensation. The morphology of the silica products as observed with transmission electron microscopy (TEM), quasi-elastic light scattering (QELS), and small-angle neutron scattering (SANS) is consistent with silica deposition at the vesicle surface, creating hollow silica particles with a 1–2-nm-thick shell and with a core diameter identical to that of the template. TEM reveals under different conditions either discrete hollow particles or networks of linked or aggregated hollow silica shells.

I. Introduction

The synthesis of materials structured on a nanometer scale is an intense and rapidly developing field of research. Nanostructured materials are potentially useful in a variety of applications such as catalysis, separations, and drug delivery. An effective and simple approach to preparing nanostructured materials involves template synthesis.1–3 Here, a usually nanostructured template directs the reaction of precursors toward the final product. A variety of different templating mechanisms have been described. In a transcriptive templating process, the reactants form products at the template interface, creating a cast of the template morphology. The template and the precursor may also cooperatively determine the product structure in a synergistic templating process. Finally, controlled demixing of template and product can also lead to well-organized, complex morphologies in a so-called reconstructive morphosynthesis.

Hollow, spherical nanoparticles represent a class of materials that can be synthesized by template syntheses. Potential applications for such particles are in encapsulation, drug release, controlled drug delivery, or the manufacture of “nanofoams”. Hollow particles have been prepared from many templates, such as polyelectrolyte nanoparticles4, emulsion droplets,5 lyotropic phases exhibiting a multilamellar vesicular structure,6 or vesicular solutions.7,9

So far, only multilamellar7 and kinetically stabilized unilamellar vesicles8,10 have been used as templates for silica synthesis. Pinnavaia et al. reported the template synthesis of multilamellar silica hollow spheres within vesicular solutions of gemini surfactants and their functionalization by incorporation of catalytic metal ion centers.7 Silica templating within mesophases of ionic block copolymers yields mesoporous morphologies that include vesicular structure elements,8 while kinetically stabilized unilamellar vesicles produced under shear have been used to create hollow silica particles.8 In the latter case, TEM images suggest a transcriptive silica deposition mechanism; however, a flattening of the vesicles also occurs that was attributed to alcohol formation during the synthesis.

The success of templating schemes depends particularly on the stability of the template. In addition to being inherently stable, equilibrium vesicles are both simple and inexpensive to prepare. In contrast to most vesicular systems which form only when shear or other mechanical energy is applied, equilibrium vesicles form spontaneously in solutions of certain cationic and anionic surfactants.11 The vesicles are unilamellar and attain an equilibrium size for a given surfactant ratio and concentration.12 No change in equilibrium size and unilamellar morphology is observed on the time scale of years and the size is recovered after shear. Hollow organic polymer particles can be synthesized from an equilibrium vesicle template.
formed by cationic and anionic surfactant mixtures. The polymer particles were formed by the cross-linking of an unsaturated monomer (such as divinyl benzene) present in the vesicle bilayer. The initial vesicle size is reproduced in the final polymer product and the hollow particles could be completely dried and resuspended in water without any loss of structure.

Here, we enlarge the scope of our templating approach to inorganic (silica) nanoparticles. Such particles are potentially suited for use as catalysts, hosts for chemical reactions, coatings, and many other applications. Two different thermodynamically stabilized vesicle templates of cationic and anionic surfactants are investigated in this study: (a) cetyltrimethylammonium bromide (CTAB) and sodium perfluorooctanoate (FC7) and (b) cetyltrimethylammonium tosylate (CTAT) and sodium dodecylbenzenesulfonate (SDBS). In such catanionic mixtures, strong electrostatic interactions between the oppositely charged headgroups initiate bilayer formation. Additionally, the combination of hydrocarbon and fluorocarbon chains in the vesicle bilayer of the CTAB/FC7 system leads to a high elastic constant for the bilayer; in turn, this leads to remarkably monodisperse vesicles. The vesicle bilayer in the CTAT/SDBS system consists only of hydrocarbon chains and are thus more flexible than in the CTAB/FC7 template.

The vesicular templates used for this study are capable of directing silica growth. Hollow silica nanoparticles are formed in each case by deposition of silica on the vesicles. These particles are characterized by quasi-elastic light scattering (QELS), small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), and transmission electron microscopy (TEM). Variations in silica morphology with the type and composition of the template are discussed to illustrate the scope and limitations of this approach.

II. Experimental Section

II.1 Preparation of Equilibrium Vesicles. The surfactants cetyltrimethylammonium bromide (CTAB, Aldrich), cetyltrimethylammonium tosylate (CTAT, Aldrich), sodium dodecylbenzenesulfonate (SDBS, TCI America), and sodium perfluorooctanoate (FC7, Lancaster) were used as supplied. Vesicular solutions were prepared from surfactant stock solutions in 0.01 M hydrochloric acid. Samples obtained by mixing appropriate amounts of the stock solutions were stirred in a 100-mL round-bottom flask at room temperature for 14 days to achieve equilibrium size, as monitored by dynamic light scattering. The composition of the catanionic surfactant solution is given by the equilibrium size, as monitored by dynamic light scattering. The vesicle bilayer of the CTAB/FC7 system leads to a high elastic constant for the bilayer; in turn, this leads to remarkably monodisperse vesicles. The vesicle bilayer in the CTAT/SDBS system consists only of hydrocarbon chains and is thus more flexible than in the CTAB/FC7 template.

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3. The spectrum displays a $q^{-2}$ dependence of the scattered intensity, which is a signature of scattering from bilayers and membranes. The spectra are thus qualitatively consistent with the presence of vesicles in solution. Fitting the spectra to the core−shell model yields a core diameter of 41.4 nm, a shell (bilayer) thickness of 2.2 nm, and a polydispersity of 0.25. These are in good agreement with the previously published results of 42.0 nm, 2.8 nm, and 0.22, respectively, for a CTAB/FC₇ sample of similar composition but without added acid.¹⁶

Following the fourteen day equilibration period, TMOS was added to each vesicular solution at a weight ratio 1:1 with respect to the total surfactant concentration. The solution immediately became slightly turbid on addition of the hydrophobic precursor. After stirring for 15 min, a transparent solution again emerged, and this was kept without further agitation at room temperature to complete the reaction. As the sol−gel reaction proceeds, there is an increase in the intensity of light scattered from the sample, as observed during QLS experiments (as a result of an increasing optical density by silica formation). However, only small changes in hydrodynamic diameter are observed during the course of the reaction (Figure 4).

Triton X-100, a nonionic surfactant that can micellize vesicles and destroy membranes, was added to the solutions as a qualitative test for changes due to reaction. In all cases, the vesicular template is easily destroyed at low concentrations (<1 g/l) of Triton X-100 whereas the templated silica particles remain in stable dispersion. Addition of Triton X-100 to the templated silica causes a

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small increase in the hydrodynamic diameter, as measured by QLS, which is consistent with the adsorption of Triton X-100 onto the surface of the hollow silica particles.

TEM images confirm the formation of hollow silica particles in the final product (Figure 5 and Table 1). Here, a drop of reacted solution was applied on the TEM grid without any further purification or staining. Following drying, hollow particles of templated silica are visible. Because of the formation of an unstructured surfactant film during drying, the observed contours are not sharp. The particles also appear to aggregate during the drying process. It is evident from the images that the silica is deposited on the surfactant bilayers. Attempts were also made to isolate the silica free of surfactant by repeated washing with methanol followed by centrifugation (Figure 6). Although most of the hollow structures collapsed or fused because of the centrifugal forces, TEM did reveal the existence of single hollow particles, an example of which is also shown in the CTAT/SDBS templated silica (Figure 7). Silica deposition on the vesicle is particularly evident in this image and the nonuniform shell thickness is similar to that observed by Hubert et al.9

SANS was also used to characterize the vesicle-templated silica particles in dispersion in D2O (Figure 3). The composition of the vesicle template was \( \gamma = 1.67\% \) and \( \delta = 0.80 \) at pH 3. To this solution, 1.67% TMOS was then added, corresponding to 1:1 (TMOS: surfactant) by weight. After the silica synthesis, the product was diluted with D2O by a factor of 4. The scattering from this product also shows a \( q^{-2} \) dependence and is qualitatively similar to that of the original template. This suggests that hollow particles with thin shells exist, that is, the vesicular structure is preserved. The concentration of scatterers in the templated product is lower because of the dilution, which is why the scattered intensity is lower. Fitting the SANS spectra from the hollow silica product to the core-shell model gives an overall shell thickness of 3.3 nm, which includes both silica layers and the surfactant bilayer. In turn, this suggests that about 1.1 nm of the shell is due to the silica network.

Templated silica dispersions prepared with a TMOS to surfactant weight ratio of 1:1 were stable for several weeks. For higher TMOS concentrations, solid silica particles are formed in the aqueous phase in addition to silica hollow spheres. In these cases, the particles appear to aggregate into branched networks causing a macroscopic gelation of the sample. Some aggregation was always observed in the CTAT/SDBS system over long periods of time. The hydrodynamic diameter of these samples remains unchanged for the first 12 h of the reaction, but eventually the dispersions phase separate and a strong increase in size is observed (QLS results not shown). During the initial part of the reaction (after 2 h), silica can be isolated by washing the solution with methanol to remove the surfactant followed by centrifugation. The longer term aggregation may be due to several reasons. First, methanol is generated during the reaction and this could affect the stability of the vesicle bilayers, thereby causing a loss of the tightly bound silica structure. Also, the silica surface charge is a function of pH, which drops as the reaction proceeds, thus influencing colloidal stability. Finally, with excess hydrophobic TMOS, the bilayer could swell ap-
precipitously causing microstructure perturbations or even a shift toward a flat lamellar architecture. Similar phase separation and gelation of the silica product were reported by Hubert et al. in vesicle templating studies for samples with high TMOS:surfactant ratios, and those authors suggest that the lowering of the pH was the prime driver for the observed silica aggregation.

Template synthesis is not only a powerful means for materials synthesis, but it can also contribute to the determination and analysis of self-organized morphologies. For instance, cubic, lamellar, hexagonal, and transition morphologies of mesophases have been directly visualized by TEM after synergistic templating of lyotropic amphiphilic block copolymer mesophases. The retention of structure was confirmed by polarized light microscopy, SAXS, and SANS, and in these cases comparisons of silica templated in the non-cross-linked mesophase with that of the cross-linked system revealed that no changes in morphology occurred during silica synthesis. Thus, by direct imaging of the templated material it is possible to gain structural information that is difficult to obtain from characterization of lyotropic mesophases by other techniques (e.g., cryo-TEM or freeze-fracturing). True one-to-one templating by sol–gel processes with retention of the parental order has also been observed for several other systems.

In addition to silica morphologies templated in equilibrated vesicular phases, silicate reactions were also carried out in the biphasic lamellar/vesicular region of the CTAB/FC phase diagram ($\lambda = 0.44$ and $\gamma = 2$ wt %, Figure 1) during equilibration. This is possible because the equilibration times of catanionic surfactant systems can range from days to weeks, so that the templating reactions are rapid compared to the time to reach equilibrium. Immediately after mixing the surfactant solutions, the sample appears transparent and has a low viscosity. Within 1 day the solution becomes more viscous and opaque and exhibits a Maltese-cross texture when observed with a polarized light microscope. To examine the different silica morphologies formed during this equilibration process, TMOS was added to the freshly prepared solution of surfactants. After both 12 and 24 h, samples were drawn and the silica isolated by centrifugation and subsequent washing with methanol. Transmission electron micrographs show different morphologies in both silica fractions, namely, small hollow spheres, layerlike structures, and multilamellar

Figure 8. TEM micrographs of silica templated in the biphasic $L_\text{v}/vesicle phase of CTAB/FC$_{2}$/water ($\lambda = 0.44$ and $\gamma = 2$ wt%).

(a) Silica isolated after 24 h: only small vesicular and layerlike structures are observed. (b) Silica isolated after 48 h: multilamellar and giant vesicular structures are observed.

morphologies (Figure 8). Whereas the silica isolated after 12 h shows only small hollow spheres and some sheetlike structures (Figure 8a), the sample isolated after 24 h also contains replicas of giant vesicles and multilamellar structures in addition to smaller hollow spheres (Figure 8b).

Of course, these results alone may not shed light on how the lamellar phase forms because changes in morphology induced by the templating process cannot be excluded. Nonetheless, these results do hint at a sensible morphological evolution of the lamellar phase starting from small unilamellar vesicles and progressing to giant and multilamellar vesicular structures. The latter can be seen as an intermediate state between discrete vesicles and L_α-mesophases.

**IV. Conclusion and Outlook**

Silica hollow particles were synthesized in equilibrium vesicle solutions by sol−gel synthesis. Templating catanionic vesicles formed by CTAB and FC_7 leads to a 1:1 casting of the vesicle structure by the formed silica matrix. The silica hollow spheres formed are typically stable for weeks. Unishell silica hollow spheres were observed by TEM and also characterized by QLS and SANS. Similar results were observed for templating in a second catanionic system (CTAT/SDBS), although the silica particles appear to be less stable in this case. The sizes of the hollow silica particles obtained are consistent with the sizes of equilibrium vesicle used for templating, ranging from about 60 to 120 nm. Hollow silica particles of desired size can thus be gained by tuning the size of the surfactant vesicles by changing the surfactant ratio or concentration.

<table>
<thead>
<tr>
<th>sample</th>
<th>m(CTAB/FC_7)/m(TMOS)</th>
<th>silica morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVT1</td>
<td>0.8 1.9 0.5</td>
<td>hollow spheres</td>
</tr>
<tr>
<td>SVT2</td>
<td>0.8 1.9 1</td>
<td>hollow spheres</td>
</tr>
<tr>
<td>SVT3</td>
<td>0.8 1.9 2</td>
<td>gelation</td>
</tr>
<tr>
<td>SVT4</td>
<td>0.85 2 1</td>
<td>hollow spheres</td>
</tr>
<tr>
<td>SVT5</td>
<td>0.85 3 1</td>
<td>hollow spheres</td>
</tr>
<tr>
<td>SVT6</td>
<td>0.85 3.5 1</td>
<td>hollow spheres</td>
</tr>
<tr>
<td>SVT7</td>
<td>0.44 2 1</td>
<td>multilamellar structures</td>
</tr>
</tbody>
</table>

Templating within the biphasic region of the CTAB/FC_7 phase diagram resulted in more complex morphologies. Reactions carried out during equilibration of the lamellar/vesicular phase reveal initially the presence of hollow silica nanospheres, followed at later times by the formation of much larger and multilamellar structures that are perhaps intermediate states encountered during the formation of the lamellar mesophase.

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