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Fabrication of perforated sub-micron silica shells

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Abstract

A new synthetic approach for fabrication of perforated hollow silica morphologies using colloidal template assemblies is demonstrated. As proof-of-principle, the polystyrene/silver colloidal assemblies had chemically modified surfaces. The template dissolution resulted in the fabrication of the submicron perforated hollow silica shells. The morphologies are characterized by transmission electron microscopy, energy dispersive spectroscopy and plasmon light extinction spectrophotometry.

Keywords

Silica shells; Hollow silica shells; Colloidal assemblies; Colloidal templates

In the last decade, there have been multiple reports describing the fabrication of hollow silica microshells [1-5]. Hollow silica shells of sub-micron size have multiple applications in the life sciences due to their stability and morphological similarities with liposomes, cells or organelles. These applications include drug delivery, chromatography and modeling of biological structures [1,2]. Hollow silica shells are usually prepared through silica polycondensation on the surface of template particles followed by the template's destruction. These methods provide simple silica shells without any additional structural features. Fabrication of silica shells with perforations in the walls is more challenging, and existing approaches provide limited control on the size and surface properties of the perforations [6].

In this work, the fabrication of silica shells with custom-size wall perforations is described. Assemblies of sub-micron particles with different surface properties are used as templates, directing silica polycondensation towards the designated parts of the template (Fig. 1).

These perforated shells may offer new possibilities in the separation of macromolecules and in drug delivery because the transport of molecules in and out of the shells could be regulated by custom-designing the size, charge and polarity of these perforations. Additionally, it is envisioned that these custom shell perforations could host functional transmembrane proteins, thereby making these shells useful to mimic functional organelles.

Commercially available polystyrene microspheres were chosen as the core of the template assembly since they are monodisperse and available in a wide size range. Commonly, pure polystyrene templates are not used for the fabrication of the silica shell due to the lack of polar groups on the polystyrene's surface; more popular polystyrene templates are made with

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copolymers, such as styrene-2 (methacryloyl) ethyltrimethylammonium chloride [5], or covalently modified particles that have an increased number of polar groups on the surface [7]. We took a different approach – modification of the surface of commercial polystyrene microspheres by physisorption of a positively charged polymer. Incubation of these microspheres in polylysine or polyethyleneimine solutions modified their surface, making it suitable for growing a silica layer using a modified Stober process [8,9] (Fig. 2A and B) and for immobilizing auxiliary particles (Fig. 2C). The polylysine treatment produced a more homogeneous coating and was used in all subsequent procedures.

Auxiliary particles must meet two requirements: (i) they must be easily immobilized onto the core surface; and (ii) they must be a poor substrate for silica growth. Both silver and gold particles meet the first requirement when using polylysine-modified core particles; immobilization occurs by simply mixing a suspension of the core particles with colloidal auxiliary particles (Fig. 2D). At the same time, silica can grow on these particles and completely cover the template assembly (Fig. 2E). Thus, in order to meet the second requirement, the template assemblies with immobilized particles were treated by octadecylthiol. This treatment produced a self-assembled monolayer (SAM) on the exposed metal surface (Fig. 1, step 3). One drawback of the auxiliary gold particles, immobilized on the amino-modified surface of the core, is that they can desorb during the treatment, likely due to the substitution of the amino–gold bonds by the stronger thiol–gold bonds. On the other hand, the silver particles are less prone to desorption, so in the subsequent experiments we used only silver as auxiliary particles.

The template assemblies with SAM-coated auxiliary particles, produced in Step 3, were then exposed to an isopropanol solution of tetraethoxysilane (TEOS) in the presence of ammonia, which resulted in silica growth only on the amino-modified surface. This selective silica growth was confirmed by a selective dissolution of the cores, which provides a good visualization of the uncoated auxiliary particles in the silica matrix (Fig. 2F). Additionally, the TEM with energy dispersive spectroscopy confirmed an elemental composition of the morphologies, and the template assemblies (see supporting materials, part 6).

On the final step of the synthetic approach the template assemblies have to be dissolved. The dissolution of components of the template assemblies can be performed simultaneously, or the components can be dissolved separately, opening possibilities for selective modification of the inner surface of the perforations or the surface of the main cavity.

The polystyrene component of the template was dissolved by incubation of the morphologies in toluene for 1 h at ~20°C. Surprisingly, the preliminary dissolution of the auxiliary particles was not necessary – the fresh silica shell is permeable enough to allow polystyrene chains to escape (Fig. 2B and C). In the same time, aging or thermal treatment of the shells strongly decreases their permeability and protects the polystyrene cores from dissolution.

The silver component of the template can be dissolved by any oxidative acid, such as nitric acid or acetic acid, in aerobic conditions. If milder conditions are desired, the mixture of EDTA and H₂O₂ works well. We found that even very diluted water solutions, such as 0.005% EDTA plus 0.05% H₂O₂, effectively dissolve the silver particles. The dissolution was monitored by decrease in UV-Vis light extinction spectroscopy (supporting materials, parts 4 and 5).

The final silica morphologies, obtained after dissolution of the template assemblies, are shown in Figure 3A and B.

In conclusion, this report shows the proof-of-principle of using template assemblies for the fabrication of perforated silica shells of submicrometer dimensions. Morphology of the resulting structures can be tailored, since morphology of the templates and dimensions of its components are very flexible: the core diameter could vary from tenths of nanometers to

microns, the auxiliary particles' diameters could vary from nanometers to hundreds of nanometers, and the shapes of the cores are not limited to spherical.

For selective modification of different surface areas of the morphologies, such as the outer or inner surface of the shell, or the inner surface of the perforations, selective exposure of the desired regions is necessary. The demonstrated selective dissociation of the template components provides a method for such exposure.

Furthermore, the suggested synthetic approach allows entirely flexible fabrication of the structures, which we envision to be employed in the separations of macromolecules, drug delivery and modeling of biological membrane-defined vessels with functional transmembrane proteins. On the other hand, this synthetic approach still needs further optimization of the reaction conditions that are required to minimize aggregation and prevent fusion of freshly prepared shells.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Synthesis of perforated silica shells. The template is assembled from a polystyrene core and auxiliary silver particles. The core is surface-modified (step 1) to be suitable for auxiliary particle immobilization (step 2) and subsequent silica growth (step 4). The auxiliary particles are modified (step 3) to prevent silica growth. The template assembly is dissolved (step 5).

Figure 2.

Validation of the synthetic process. (A) Encapsulation of 200 nm diameter polystyrene microspheres with silica. (B) Visualization of thin silica shells after partial dissolution of the template, 750 nm diameter polystyrene microspheres. (C) Visualization of thin silica shells after complete dissolution of the same template as in (B). (D) Auxiliary silver colloidal particles (diameter ~50 nm) immobilized on a 750 nm diameter template core. (E) Without modification of the auxiliary particles the silica covers both the core and the auxiliary particles. (F) Silica shell after dissolution of the core, but not of the auxiliary particles. All images are obtained by transmission electron microscopy (TEM).

Figure 3.
Perforated silica morphologies. TEM. (A) Partially fused perforated silica shells. (B)
Perforated silica shell with large crack, demonstrating inner cavity and holes on the rear wall.