

Oligosilsesquioxanes as Versatile Building Blocks for the Preparation of Self-Assembled Thin Films

Thierry Cassagneau and Frank Caruso*

Contribution from the Max Planck Institute of Colloids and Interfaces,
D-14424 Potsdam, Germany

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Abstract: A self-assembly approach to the preparation of nanocomposite siliceous thin films by using oligosilsesquioxanes as building blocks is presented. Poly(styrene-4-sulfonate), PSS, and octa(3-aminopropyl)silsesquioxane, NSi₈, were layer-by-layer (LbL) assembled onto planar substrates and polystyrene (PS) particles, thus forming composite multilayers. We have clarified the binding properties of NSi₈ to PSS by examining the pH influence on film buildup by microelectrophoresis (ζ -potential) and quartz crystal microgravimetry (QCM). The regular growth of PSS/NSi₈ multilayers on planar supports was confirmed by surface plasmon resonance (SPR) spectroscopy and QCM. By applying the LbL coating procedure to spherical templates, we prepared compact, microporous hollow silica spheres by calcining PS spheres coated with (poly(allylamine hydrochloride) (PAH)/PSS)₂/(NSi₈/PSS)_n (n varying from 3 to 12), at 750 °C, because of sintering of the octameric clusters (NSi₈). Hollow spheres derived from coatings with $n = 3$ drastically altered in size (relative to the template core), depending on the size of the PS particles used. The novelty of this method for the nanofabrication of siliceous films stems from the use of well-defined and discrete building blocks, such as NSi₈, leading to homogeneous organic-silica composite films as well as individual siliceous particles of variable size and shape.

Introduction

The development of novel approaches that permit the construction of functional, ultrathin composite films and coatings with tailored properties is a rapidly emerging area of research that has attracted considerable interest over the past decade.^{1–5} Self-assembly processes have been widely utilized and continue to be at the forefront of such research, as they allow the formation of novel and complex materials with a range of designed and unique properties. To this end, the layer-by-layer (LbL) self-assembly technique has been proven to be a suitable, versatile, and inexpensive means for nanostructured film preparation. It permits the sequential assembly of multiple layers of oppositely charged materials (e.g., preformed particles) on planar substrates^{1,2a} and spherical supports,^{3,4} using polyelectrolytes as electrostatic binders. Ultrathin, composite particle-containing films with unique electroactive,⁵ catalytic,³ magnetic,²

or optical properties⁶ have been prepared by the LbL method. In addition, the integration of particles in polymer-based thin films is useful both to introduce reactive (i.e., catalytically active) surfaces within the film as well as to control porosity and/or permeability.

Polymers have extensively been used as molecular “glues” in the preparation of composite films containing inorganic species, including silica. For example, composite organic–inorganic multilayers comprising silicate have been recently prepared by continuous self-assembly on planar substrates from silica–surfactant–monomer species spontaneously organizing into lyotropic mesophases partitioning the organic and inorganic precursors within a laminated structure, mimicking the nacre.⁷ The affinity of layered silicate compounds (especially montmorillonites and hectorites) for polymers has also been exploited to form composite thin film assemblies, which are interesting because of their stiffness, strength, and barrier properties.⁸ These silicates spontaneously delaminate in water, and as a result the negatively charged silicate sheets are ideal candidates to be restacked on planar surfaces by LbL adsorption with polycations.⁹ Silica particles have also been employed as building blocks in the LbL technique to form multilayered composite films on planar substrates.¹⁰ In this case, provided that the silica dispersion is at a pH above the isoelectric point of the silica

* To whom correspondence should be addressed. Fax: +49 331 567 9202. E-mail: frank.caruso@mpikg-golm.mpg.de.

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particles, a film can be simply grown by the alternate adsorption of a polycation (typically poly(diallyldimethylammonium chloride), PDDA) and silica particles.

In addition to composite films on planar supports, the preparation of inorganic coated and hollow colloids with controllable wall thickness and diameter is an important aspect of colloid synthesis, largely because of the proportional relationship between surface area and surface activity of particles. Such colloids are of technological interest in catalysis, separation processes, as fillers and pigments, etc.⁴ Two main approaches have been developed to obtain silica coatings on spherical particles. One method consists of allowing the silica shell to continuously grow from an appropriate silicate precursor (i.e., tetraethoxysilane (TEOS)) solution by a concomitant hydrolysis and condensation reaction. As the polycondensation reaction of the precursor is often difficult to control once it begins, the thickness of a coating is usually regulated by the relative amount of supporting particles and source of silica.^{11,12} The second approach favors the use of preformed building blocks (e.g., silica nanoparticles) to grow a film with a sequentially deposited binder (typically, polymer^{4,13} or vesicles¹⁴) on larger core particles (LbL method). A subsequent step can be applied to sinter the adsorbed particles and create a cohesive silica shell, leading to hollow spheres when polystyrene (PS) particles are used as a removable support.^{4,13} In this procedure, as with films prepared on planar supports, control of the uniformity and porosity of the shell is limited by the nanoparticle type and size. Additional control has been recently achieved using a colloidal-assisted self-assembly process involving the use of PS beads as a template onto which silicate species and surfactant micelles were electrostatically held together prior to calcination.¹⁵

One major limitation of previous studies in relation to using large siliceous compounds (e.g., clays) and particles as components when constructing ultrathin films is that the thickness resolution of the films as well as film porosity, stiffness, and strength are largely defined by the size and stability of the silica species or preformed building blocks utilized. Although control at the nanometer scale of the thickness (and hence properties) of silica films can be achieved from a soluble silica source (silicates, TEOS) using liquid crystals¹⁶ (ionic or nonionic) or micelles¹⁷ as a structure-directing template to form mesoporous materials under hydrothermal or very acidic conditions,¹⁸ or on metallic nanoparticles as templates,¹¹ the self-assembly of preformed nanobuilding blocks offers an alternative and versatile

route that is independent of chemical reactions (and organic solvents) to modulate the layer thickness.⁴ For optimum control, this strategy should also allow fine-tuning, at the nanoscale level (~1 nm), of the film properties. One solution would consist of using smaller building blocks; however, when preformed silica nanoparticles are desired to be used as components, problems arise from the limited stability of silica sols containing particles of size below 5 nm.¹⁹ The use of silica clusters stabilized with organic molecules, for example, could help overcome this limitation. One simple approach to this consists of synthesizing polyhedral oligosilsesquioxanes (POSS) as nanosized building blocks to obtain silica clusters.²⁰ Under appropriate conditions, a silane of general formula $XSiY_3$ (Y refers to a hydrolyzable moiety) bearing one organic moiety, X, which is stable toward hydrolysis can lead to the formation of POSS with each silicon atom covalently bound to the organic moiety X. Such a molecule offers the advantage of being potentially functionalizable with a range of organic groups (by varying the nature of X) and represents an attractive nanobuilding block for self-assembly to create thin films. Such silsesquioxanes have been of great interest over the past decade because of their applications in materials science (e.g., precursors for ceramics) and catalysis (supported catalysts, etc.).

In this study, octa(3-aminopropyl)silsesquioxane, NSi8, has been self-assembled in alternation with a polyanion, poly(styrene-4-sulfonate), PSS, to study and control its binding properties to form thin films on planar and spherical supports. Because of the presence of amine groups surrounding the molecule, it was possible to promote an acid–base interaction with the sulfonate groups of the polyanion. The acid–base interaction was chosen by analogy with the intercalation chemistry of alkylamines²¹ and amine-bearing organometallic molecules²² into layered Brønsted acid type compounds such as α -M(IV)(HPO₄)₂·H₂O (with M(IV) = Zr, Ti, Sn, etc.), HTiNbO₅, or HTaWO₆·nH₂O to sequentially build up films. Control over the film thickness is, in our case, only limited by the lateral dimensions of the silica core of NSi8, which is about 6 Å (including the van der Waals radius of the oxygen atoms). We introduce a method of nanofabrication of siliceous films by self-assembly from discrete and well-defined oligosilsesquioxane clusters (NSi8), leading to organic–inorganic composite films on planar substrates that are of potential interest for designing porous ceramic membranes (upon calcination on an

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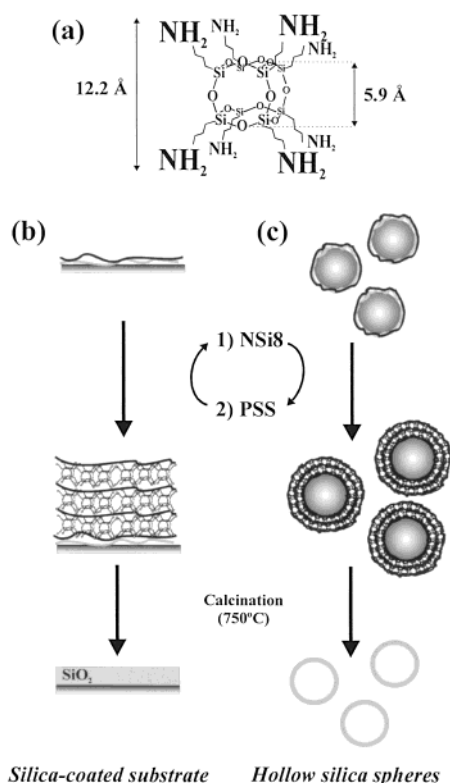


Figure 1. Schematic diagrams of the LbL assembly of NSi8 molecules (a) with PSS on planar substrates (b) and on PS particles (c). Subsequent calcination results in supported thin silica films (b) or hollow silica spheres (c).

appropriate support) as well as robust siliceous capsular colloids of different size (and variable shape) when spherical supports are used (Figure 1).

Experimental Section

Materials. Poly(allylamine hydrochloride), PAH ($M_w = 70\,000$), poly(sodium-4-styrenesulfonate), PSS ($M_w = 70\,000$), poly(diallyldimethylammonium chloride), 20 wt % water ($M_w \approx 100\,000$ – $200\,000$), 2-mercaptoethylamine hydrochloride (MEA), 98%, and (3-aminopropyl)triethoxysilane, 99%, were purchased from Aldrich and used as received. Sulfonated polystyrene (PS) particles (925 nm, 10 wt %; 640 nm, 5 wt %) were purchased from Microparticles GmbH. Deionized water (18.2 M Ω cm) was obtained from a Millipore Milli-Q Plus 185 purification system. The 9 MHz gold-coated quartz piezoelectric crystals (electrode area 16 mm²) were purchased from Kyushu Dentsu, Japan. Octa(3-aminopropyl)silsesquioxane (NSi8) was prepared according to a procedure previously reported by mixing, under stirring, (3-aminopropyl)triethoxysilane, ethanol, and water, leading to a 0.47 M NSi8 solution (ethanol/H₂O, v/v = 14:1) and was directly used in the LbL assembly.^{22c,f} NSi8 does not refer to a pure solution of condensed octamers,²³ but rather a mixture of oligosilsesquioxanes in which octamers (completely and incompletely condensed)^{22f,g} are the dominant species.

PSS/NSi8 Film Preparation. (a) LbL Assembly on Planar Substrates. LbL assembly was accomplished by first depositing a polycationic layer onto a gold substrate previously derivatized with mercaptoethylamine (MEA) or a clean quartz substrate from a 1 wt % solution (pH = 6.5) of poly(diallyldimethylammonium chloride) (PDDA) or poly(allylamine hydrochloride) (PAH), followed by the

sequential adsorption of poly(sodium-4-styrenesulfonate) (PSS, 0.02 M, pH = 2.0) and NSi8 (0.47 M, pH = 11.9). Typical dipping times were 10 min for the polyelectrolytes and 1 h for NSi8. After deposition of the PSS layers, they were thoroughly rinsed with water (pH = 2) and then dried with a gentle stream of nitrogen. (Rinsing the PSS layers at pH = 2 was essential to promote multilayer growth – see Results and Discussion section.) The deposited NSi8 layers were washed with deionized water (pH \approx 5.6), ethanol, and water, and then dried with nitrogen. Note that all dipping solutions did not contain added salt and that 0.1 M HCl was used to change the pH of the solutions.

(b) LbL Colloid Templating. For the LbL assembly of polyelectrolytes, 5.8 mM PSS (pH = 2, without added salt) and 10.7 mM PAH (0.5 M NaCl, pH = 6) solutions were used. The priming PAH layer was adsorbed by first adding and mixing 20 μ L of a 10 wt % PS particle (925 nm diameter) dispersion to 1.5 mL of the PAH (1 wt %) solution, shaking for 10 min, centrifuging (6900g, 7 min) and washing (2 mL of water) at least four times. Similarly, the next PSS layer was adsorbed by redispersing the coated particles in 1.5 mL of PSS solution (0.02 M, pH \approx 5–6) and following the same procedure used for the preceding PAH layers, with the exception that the outermost layer of PSS was washed finally with water at pH = 2. The (PAH/PSS)₂-coated PS spheres were then used as supports to deposit NSi8/PSS multilayers by first exposing the particles to 1.5 mL of the NSi8 solution (0.47 M, pH = 11.9) for 1 h with shaking, followed by centrifugation and four washing cycles (2 \times 2 mL) with water at pH = 5.6. (Monitoring the adsorption of NSi8 onto PSS by QCM indicated that no further NSi8 adsorbed beyond about 70 min of dipping.) Next, 1.5 mL of the PSS solution (0.02 M, pH = 2.0) was added to the coated particles and allowed to adsorb for 10 min prior to centrifugation, followed by washing four times with water at pH = 2. This procedure was repeated n times to obtain PS-(PAH/PSS)₂/(NSi8/PSS) _{n} (typically, n varying from 3 to 12) particles. Identical coating procedures and conditions were used for the smaller PS particles (640 nm in diameter), except that the centrifugation speed was set to 7500g for 10 min after each adsorption and washing cycle.

Hollow Sphere Fabrication. To prepare hollow silica spheres, the NSi8/PSS-coated particles were diluted with water prior to air-drying (room temperature) on a crucible. Calcination was performed by heating (4.3 K min⁻¹) at 500 °C under nitrogen for 5 h and at 750 °C (or lower in some cases, see the Results and Discussion section) under oxygen for another 6 h. Under these conditions, the organic matter (core included) was burnt off.

Measurements. Surface plasmon resonance (SPR) spectroscopy was carried out on a home-built instrument using chromium (1 nm)/gold (\sim 48 nm)-coated glass slides. Measurements were performed as previously reported.²⁴ Experimental data were fit to theoretical reflectivity curves, calculated from the Fresnel equations, allowing determination of the thicknesses and refractive indices (real and imaginary parts) for each adsorbed layer. Ellipsometric measurements were performed by null ellipsometry, using a Multiskop instrument (Optrel, GmbH; 2 mW HeNe laser; $\lambda = 632.8$ nm; angle of incidence = 70°). The refractive index of the silicon wafer was 3.8858–0.020*i*, and the silica top layer had a refractive index of 1.4598 (the imaginary part was assumed to be zero). Electrophoretic mobilities of the coated particles were measured with a Malvern Zetasizer 4 by taking the average of five measurements at the stationary level. The mobility u was converted to a ζ -potential by using the Smoluchowski relation ($\zeta = u\eta/\epsilon$; η and ϵ being the viscosity and permittivity of the solution, respectively). Deionized water with an appropriate pH (no buffer) was used to study the pH influence on the mobility. Scanning electron microscopy (SEM) images were obtained with a Zeiss DSM 940 instrument operating at 20 kV using gold-sputtered samples dried on glass pieces. Transmission electron microscopy (TEM) images were taken with a Zeiss EM 912 Omega instrument with an accelerating

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voltage of 120 kV. High-resolution TEM imaging was performed using a Philips CM12 microscope operating at 120 kV. Atomic force microscopy (AFM) images were recorded with a Nanoscope IIIa multimode microscope (Digital Instruments Inc., Santa Barbara, CA) operating in tapping mode by using silicon tips (Nanosensors, Wetzlar) characterized with a resonance frequency of 300 Hz and a spring constant of 32–41 N/m. A homemade QCM cell was used, and the QCM frequency changes were monitored by using a universal counter (Agilent). The adsorbed mass was determined from the Sauerbrey equation.²⁵

Results and Discussion

Binding Behavior of NSi8 to PSS. The lateral dimension of NSi8 used in this study is 12.2 Å from one –NH₂ group to the other, considering fully extended alkyl chains in an isotropic medium (Figure 1a). The inorganic core is formed by a silica cluster occupying a volume of 97 Å³, taking into account the van der Waals radius of the oxygen atoms. Eight organic groups spreading out from the silicon atoms allow the octamer to undergo deformations when constrained into a layered structure, for instance.

It was expected that the presence of sulfonate groups in the PSS layer would favor a strong interaction with the amine moieties of the octamer (acid–base interaction), by analogy with the intercalation processes observed with layered α-ZrP.²² The electrostatic interaction between –SO₃[–] (from PSS) and –NH₃⁺ (from NSi8) (Figure 1) adsorbed on a surface was dependent on the pH and the ionic strength of the dipping and rinsing solutions used in the LbL self-assembly process. The pH of the rinsing solutions was found to be critical in controlling the coverage of NSi8 on PSS after its adsorption (rinsing with water of pH < 4 could promote adsorption of NSi8, see later). The data for the PAH/PSS-coated particles followed a sigmoidal shape, with the ζ-potential shifting to negative values as the pH was raised, reflecting an increase in the deprotonation of the sulfonate groups of PSS (Figure 2). For the PAH/PSS/NSi8-coated particles (with an outermost NSi8 layer), two consecutive interfaces are pH-sensitive, PSS–NSi8 and NSi8–solution. The ζ-potential can originate from the charges at the PSS–solution (when NSi8 desorbs, even partially) and NSi8–solution interfaces. As the pH of the surrounding medium becomes higher than the isoelectric point of the adsorbed PSS (5.6), NSi8 starts to desorb because of the loss of protons shared at the PSS–NSi8 interface (Figure 2B). However, from pH = 5.6 to 6.3, the number of NSi8 molecules desorbed is still not high enough to reverse the ζ-potential to a negative value (Figure 2A). The charge (from NSi8) partially compensates that originating from the PSS–solution interface to give an overall positive ζ-potential. NSi8 exhibits a pK_a value of 9.96 in solution. Assuming that NSi8 has an approximately similar pK_a when adsorbed (i.e., at the interface), we found that the majority of amine groups would remain protonated below pH = 10; for example, at pH = 8 about 99% of the amine groups would be protonated at the NSi8–solution interface. Taking into account that the ζ-potential of the PSS–solution interface plateaus at about –56 mV at high pH (Figure 2A) and assuming that the water content in the Stern layer is similar for both the PAH/PSS/NSi8-coated and the PAH/PSS-coated particles, we found that the respective (percentage) coverage of NSi8, *B*, and PSS, *A*, on the surface can be estimated using the following set of equations at pH values higher than

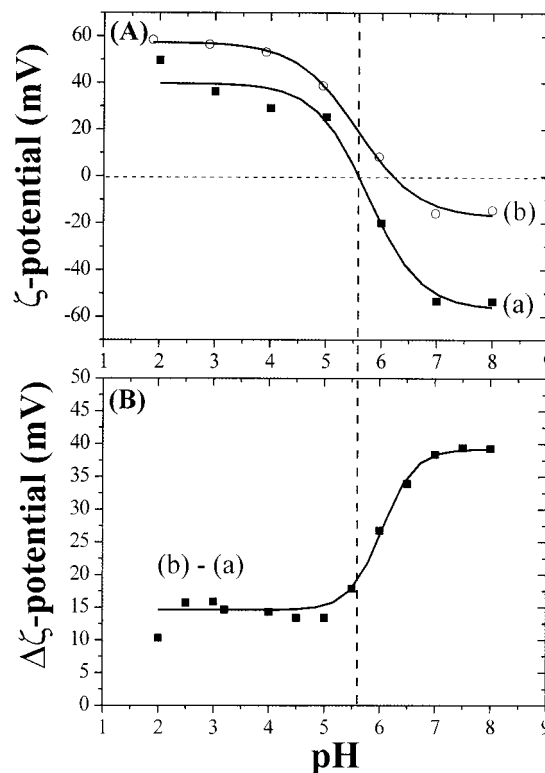


Figure 2. ζ-potential measurements of 925 nm PS particles coated with PAH/PSS (PSS outermost layer) (a) and PAH/PSS/NSi8 (NSi8 outermost layer) (b) as a function of pH (A). In (B), curve a is subtracted from curve b, revealing the influence of the pH on the interaction between PSS and NSi8 at the interface PSS–NSi8. Each curve represents a series of experiments of the same sample measured at different pH. Each value represents the average of five measurements.

the isoelectric point of adsorbed PSS onto PAH-coated PS particles (pH = 5.6):

$$A = \frac{1}{2} \left(100 + \frac{\zeta_{\text{pH}}^{\text{PSS/NSi8}} \cdot 100}{|\zeta_{\text{plateau}(-)}^{\text{PSS}}|} \right) \quad (1)$$

$$B = 100 - A \quad (2)$$

where $\zeta_{\text{pH}}^{\text{PSS/NSi8}}$ corresponds to the ζ-potential measured for PAH/PSS/NSi8-coated particles at a given pH (>5.6), and $\zeta_{\text{plateau}(-)}^{\text{PSS}}$ corresponds to the ζ-potential measured for PAH/PSS-coated particles at the high pH plateau (–56 mV). These relations are obtained by assuming that the NSi8–solution interface remains entirely protonated within the range of pH 2–8. They also satisfy the following equation, which is deduced by treating both pH-sensitive interfaces independently (i.e., the NSi8–solution interface bearing a constant positive charge, the PSS–solution interface a negative charge), leading to a ζ-potential resulting from a net charge averaged over these two interfaces:

$$\zeta_{\text{pH}}^{\text{PSS/NSi8}} = \frac{A \cdot \zeta_{\text{pH}}^{\text{PSS}} + B \cdot \zeta_{\text{plateau}(+)}^{\text{PSS/NSi8}}}{100} \quad (3)$$

where $\zeta_{\text{plateau}(+)}^{\text{PSS/NSi8}}$ is the low pH plateau value of the ζ-potential for PAH/PSS/NSi8-coated particles (58 mV). Note that this equation is only valid at pH values higher than 5.6.

Using eqs 1 and 2, we calculated that at pH = 8 about 66% of NSi8 molecules are desorbed. At this pH, the measured

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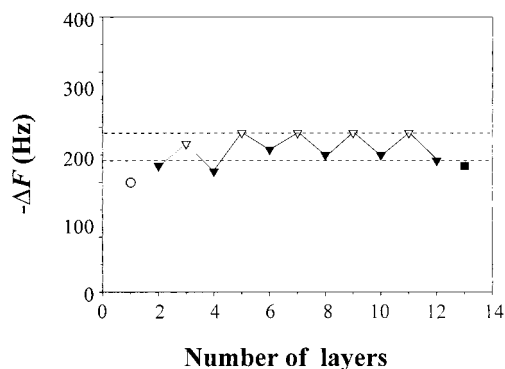


Figure 3. QCM frequency shifts measured from a PDDA-primed gold substrate (○), alternately coated with PSS (0.5 M NaCl, pH = 2) (▼) and NSi8 (0.47 M, pH = 11.9, no added salt) (▽), followed by a final washing at pH = 12.5 (■).

ζ -potential is approximately -18 mV, as compared with the -56 mV measured for the PAH/PSS-coated particles. This indicates that NSi8 at the NSi8–solution interface (covering 34% of the surface) is protonated, partially compensating the negative net charge at the PSS–solution interface. Therefore, the measured ζ -potential should result from the average potential of a surface covered 34% with NSi8 (ζ -potential = 58 mV) and 66% with PSS (-56 mV). Indeed, the value calculated from eq 3, -17 mV, is similar to that experimentally measured (-18 mV). The above supports the assumption that the NSi8 is actually protonated at pH 8 and below at the NSi8–solution interface.

The effect of salt concentration of the PSS solution used during the coating process was also studied, showing that NSi8 molecules were systematically desorbed from PSS upon contact with a 0.5 M NaCl PSS solution (even at pH = 2, Figure 3). Lowering the salt concentration down to 0.01 M still prevented the film from growing regularly after a few adsorption cycles (not shown). To circumvent this effect, the ionic strength was kept to a minimum, the only possible source of ions resulting from the pH adjustment of PSS solutions to 2 (with HCl). The adsorption of a polyelectrolyte layer onto an oppositely charged surface is induced by the cumulative effect of numerous binding pairs, each ionic pair $\text{NH}_3^+/\text{SO}_3^-$ involving an energy of only 2.48 kJ/mol.²⁶ The charge overcompensation results from the fact that 20–56% of the PSS monomers form ion pairs when adsorbed on a poly(allylamine hydrochloride), PAH, layer.²⁷ When ionizable binding sites are concentrated in a small volume (i.e., on oligomers), high layer coverage on a charged surface is expected at low ionic strength (to avoid charge screening). Not surprisingly, the binding of NSi8 (comparable to a PAH oligomer) to PSS is best achieved by minimizing the ionic strength of the solution. Washing the PSS layer with low pH water (pH = 2), allowing displacement of sodium ions with protons, was found to be essential to the binding. These conditions established for the binding of NSi8 to PSS (and vice versa) were used to construct NSi8/PSS multilayer films.

LbL Assembly of NSi8 with PSS. Self-assembled multilayers consisted of PSS alternately deposited with NSi8 on planar or spherical substrates (Figure 1). To study film growth, the

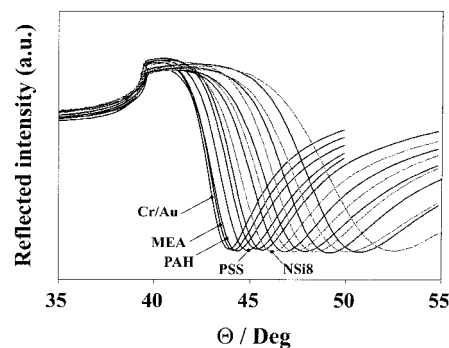


Figure 4. SPR curves indicative of regular film growth with an increasing number of adsorbed NSi8/PSS bilayers.

Table 1. Thickness Determination of Self-Assembled Layers on Au-Modified Quartz Slides, As Determined by SPR and QCM

outermost layer	SPR			QCM
	ϵ_r	ϵ_i	d (Å)	d (Å)
mercaptoethylamine (MEA) (onto Au)	2.6900	0.6650	11 ± 1	
poly(allylamine hydrochloride), PAH (onto MEA)	2.1370	0.6090	10 ± 1	
PSS (onto PAH) at pH = 2.0	1.8900	0.0000	21 ± 3	
PSS (onto PAH) at pH = 6.0	1.8900	0.0000	55 ± 3	
NSi8 (onto PSS adsorbed at pH = 2.0)	2.7860	0.0890	20 ± 2	20 ± 1
NSi8 (onto PSS adsorbed at pH = 6.0)	2.7860	0.0890	21 ± 2	

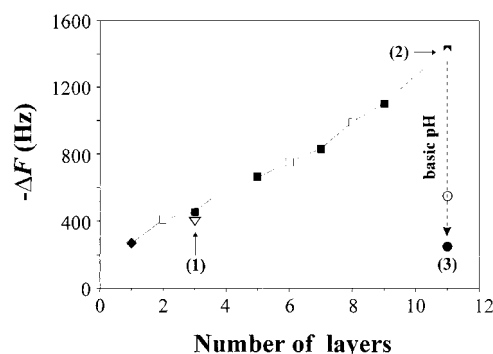


Figure 5. QCM frequency shifts measured for the consecutive adsorption of NSi8 and PSS under different conditions of rinsing pH at a gold electrode surface primed with mercaptoethylamine and PDDA (◆). PSS (□) and NSi8 (■) were consecutively adsorbed and rinsed with water at pH = 2 and deionized water (pH = 5.6), respectively. Arrow 1 indicates the frequency measured after washing PSS with deionized water prior to exposure to NSi8 (▽). Arrow 2 indicates that no frequency change (i.e., no loss of material) was observed when the outermost NSi8 layer was rinsed with water at pH = 2 (◇). On the other hand, rinsing the electrode with 1 mL of water at pH = 12.5 (○) and an additional 1 mL of water at pH = 12.5 (●) could delaminate the entire (PSS/NSi8)₅ film as indicated by arrow 3, demonstrating the importance of acid–base interactions in the assembly process.

consecutive adsorption of PSS and NSi8 was followed by SPR spectroscopy (Figure 4). The adsorption of NSi8 on a PSS layer was performed at pH = 2 (see Experimental Section) and was found to plateau at about 70 min of adsorption time. Each PSS layer contributed a thickness of 21 ± 3 Å, and each NSi8 layer contributed a thickness of 20 ± 2 Å (see Table 1). Regular growth of the multilayers was also observed from QCM measurements (Figure 5). The average frequency change associated with the adsorption of one NSi8 layer was -48 ± 5 Hz, and -77 ± 6 Hz for a PSS layer. The NSi8/PSS multilayers formed could be completely disassembled by raising the pH,

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(27) (a) Lowack, K.; Helm, C. A. *Macromolecules* **1998**, *31*, 823. (b) Caruso, F.; Lichtenfeld, H.; Donath, E.; Möhwald, H. *Macromolecules* **1999**, *32*, 2317.

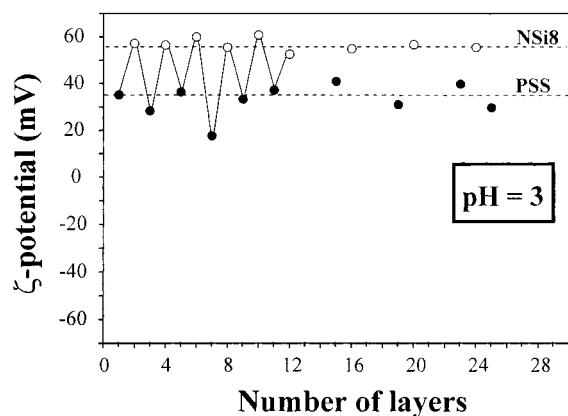


Figure 6. ζ -potential measurements of PDDA-precoated PS particles alternately coated with NSi8 and PSS at pH = 3.

because deprotonation influences the acid–base interaction between the layers. This phenomenon was also followed by QCM (Figure 5), which shows a pH-dependent film stability upon varying the pH of the rinsing solutions. In particular, it was found that rinsing the PSS layer at pH = 12.5 totally disassembled the film. The LbL growth of NSi8 and PSS was also undertaken on spherical PS particles and was followed by measuring the ζ -potential of particles alternately coated with NSi8 and PSS at a fixed pH (Figure 6). Typically, 20 mV accounted for the difference in electrophoretic mobility of the particles coated at pH = 3 with different outermost layers. The enhanced mobility of particles coated with an outermost layer of NSi8 is because of the protonated nature of the amine groups of NSi8. The coated particles were stable in air-equilibrated water for at least 3 weeks.

Simple consideration of the size of a NSi8 molecule (12.2 Å) cannot account for the measured thickness by SPR (20 Å). As control experiments did not reveal any infiltration of NSi8 into the PSS layer (see Supporting Information), this mismatch could originate from the polyelectrolyte coating itself. The topology of a PDDA/PSS/NSi8 film prepared on a mica substrate was examined by atomic force microscopy (AFM) (Figure 7). The film exhibited a root-mean-squared roughness of 0.46 nm with a peak-to-valley distance varying from 10 to 18 Å. The granular surface, with clusters clearly identifiable, indicated that NSi8 molecules do not form a compact monolayer as suggested by the SPR and QCM data (see Supporting Information), but a layer roughened by the polymer chains capable of extending their loops above the cluster height. Overall, the resulting layer “seen” spectroscopically (i.e., SPR) is as one made of interdigitated clusters. We have used this simplistic description to conveniently quantify the adsorption processes (see below).

The composite inorganic–organic films were converted into silica films by calcining at 570 °C (see Experimental Section). Calcining films comprising three PSS/NSi8 bilayers with an outermost PSS layer (seven layers total) deposited on PDDA-modified silicon substrates yielded ultrathin silica films (thickness of 13 Å), as determined by ellipsometry. (A bare silicon substrate was calcined and used as a reference.) This thickness is only marginally lower than the calculated length for three [SiO_{1.5}]₈ clusters (17.7 Å), indicating the formation of good quality initial composite films.

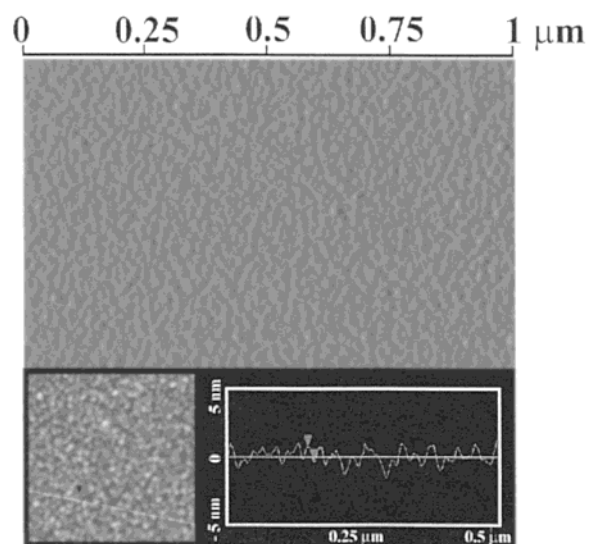


Figure 7. AFM image of NSi8 molecules adsorbed on a mica substrate precoated with PDDA and PSS. The peak to valley height shown in the inset corresponds to 10.8 Å. The schematic drawing represents the PSS/NSi8 interface.

Sacrificial Colloid Templating. The NSi8 nanobuilding blocks were also used for the preparation of hollow silica spheres. Depending on the number of PSS/NSi8 bilayers adsorbed on the PS particles, a dramatic shrinkage of the resulting spheres could be induced. Upon using 925 nm PS particles as a support, we found that approximately 75% shrinkage of the initial template volume occurred, leading to spherical hollow silica spheres of ~250 nm (Figure 8). (The spheres, deliberately broken, were confirmed to be hollow by scanning electron microscopy (not shown).) This phenomenon was observed when three PSS/NSi8 bilayers covered the template particle and a sintering temperature of 750 °C was employed (see Experimental Section). Attempts to stabilize hollow spheres at a lower temperature (i.e., 570 °C) were not successful (broken spheres were observed). Representing the NSi8 molecule as a sphere of 12.2 Å in diameter with an inorganic silsesquioxane core of 5.9 Å (taking into account the van der Waals radius of oxygen atoms), 49% of a coating surface would be covered with inorganic clusters at 50% interdigitation of the organic moieties, with the rest of the surface being coated with aminopropyl moieties. This large spacing between inorganic clusters is responsible for some unusual properties observed during template removal.

Using the geometrical model introduced earlier (see the section on LbL Assembly of NSi8 with PSS) describing the distribution of NSi8 molecules onto PSS, we estimated that the volume fraction, $V[\text{SiO}_{1.5}]$, of silsesquioxanes initially present on the template is $2.43 \times 10^{-21} \text{ m}^3$ (taking into account the

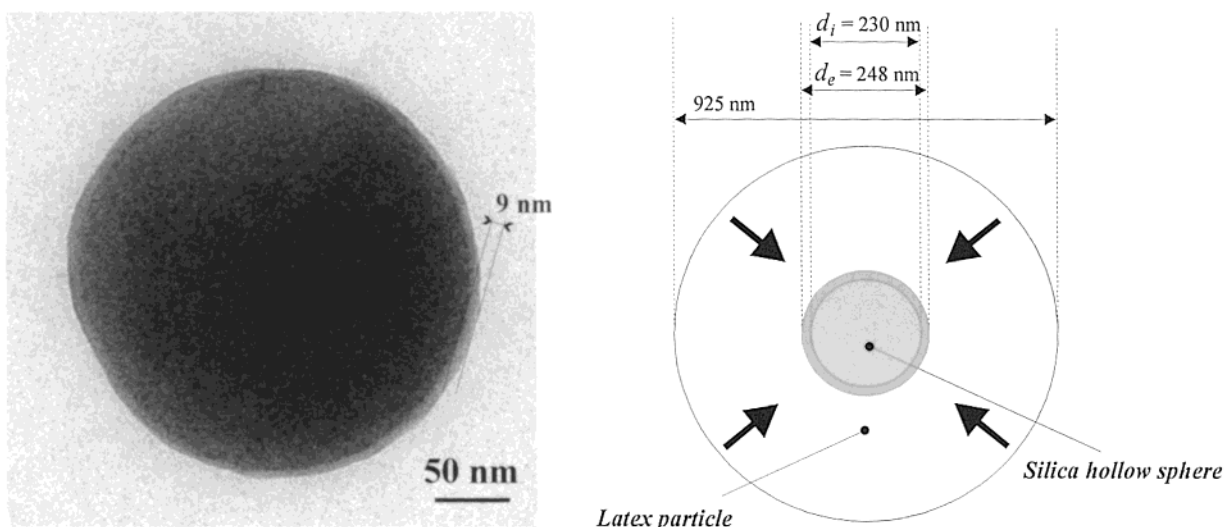


Figure 8. TEM image of a ~ 250 nm hollow silica sphere obtained by calcining 925 nm PS particles coated with PDDA/(PSS/NSi8)₃ at 750 °C. The drawing (to scale) shows the dramatic volume decrease observed relative to the template size.

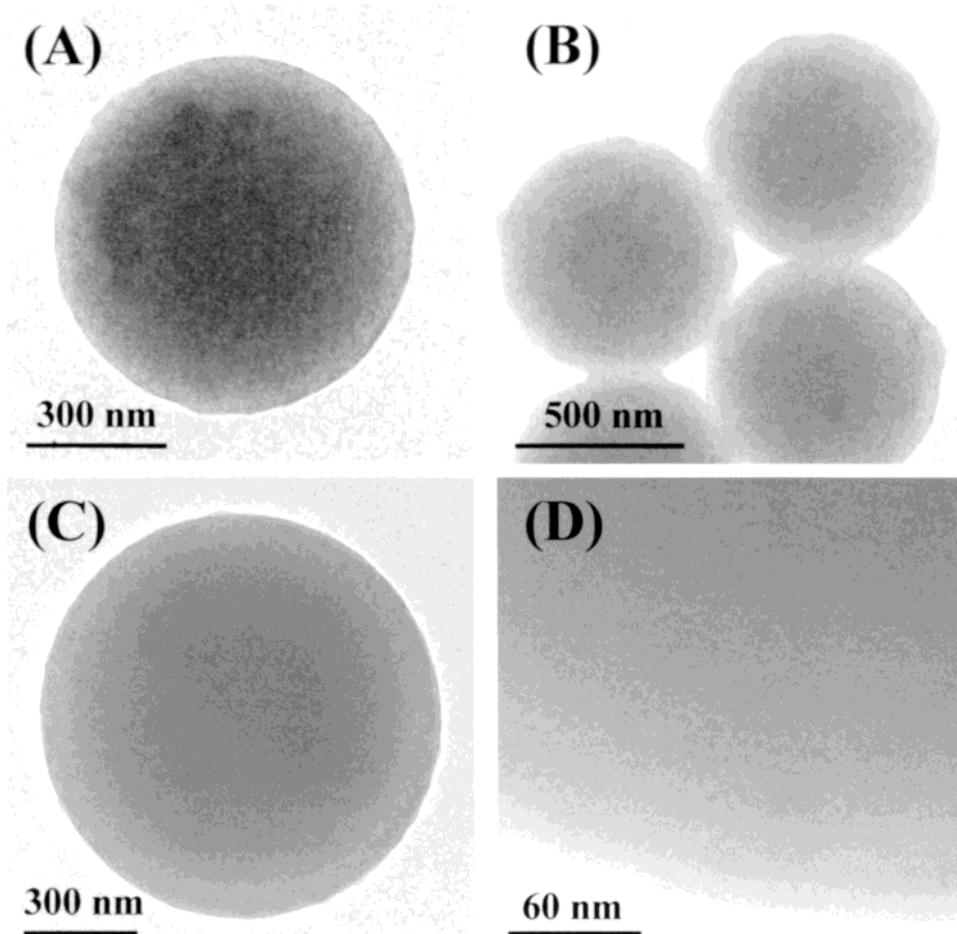


Figure 9. 640 nm PS particles coated with PDDA/(PSS/NSi8)₃ (A) and PDDA/(PSS/NSi8)₆ (B); 925 nm PS particle coated with PDDA/PSS/NSi8 (C), with a close view of the edge morphology (D).

increase of diameter after each adsorption cycle). The diameter of the hollow sphere experimentally measured from the inner shell is $d_i = 230$ nm, corresponding to an inner volume, V_i , of 6.37×10^{-21} m³. Knowing the volume of silsesquioxanes initially adsorbed on a 925 nm PS particle and the final inner diameter of the hollow sphere, we deduced the shell thickness

from the following equations:

$$S(m) = \left(\frac{d_i^3}{8} + \frac{3}{4\pi} V[\text{SiO}_{1.5}] \right)^{1/3} - \frac{d_i}{2} \quad (4)$$

or, if the image contrast does not allow visualization of a ring,

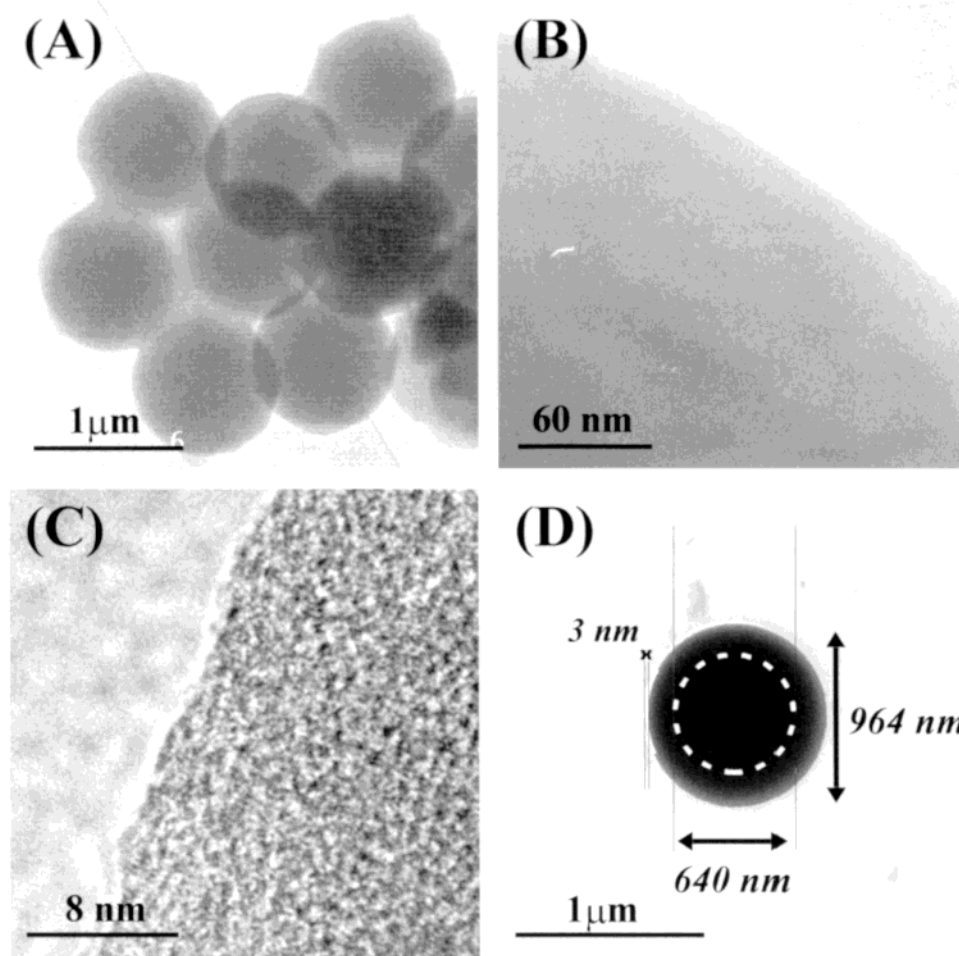


Figure 10. 925 nm PS particles coated with PDDA/(PSS/NSi8)₁₂ and calcined at 750 °C (A), showing a smooth surface (B), with no apparent crystallinity (C); 640 nm PS particle coated with PDDA/(PSS/NSi8)₆ after calcination at 750 °C (D). The white dashed line indicates the initial template size, while the white outlined arc gives an indication of the resulting shell thickness.

from the knowledge of the value of the outer diameter:

$$S(m) = -\left(\frac{d_o^3}{8} - \frac{3}{4\pi}V[\text{SiO}_{1.5}]\right)^{1/3} + \frac{d_o}{2} \quad (5)$$

where d_o is the outer diameter of the hollow sphere (as measured from TEM) and is related to d_i according to $d_o = d_i + 2S$.

The shell thickness, S , was estimated to be 13 nm from eq 4, differing from the experimentally measured value, 9 nm. This difference is likely because of the ideal hexagonal packing model (assuming half interdigitated alkyl chains) used to make this calculation. This estimated value drops to 7 nm if no interdigitation is assumed and if the porosity of the shell itself is not taken into account. The corresponding calculated diameter of the hollow sphere is 256 nm, which is in good agreement with the measured value (248 ± 5 nm), and is indirectly indicative of both the high NSi8 layer quality and the compactness of the shell. Increasing the number of bilayers PSS/NSi8 to six or more limited the shrinking, after calcination, to about 10% of the initial template volume. It should be noted that hollow gyroids could also be obtained by calcining at 570 °C (see Supporting Information). As their occurrence was low (ca. 5% content), we assume that a variation in the temperature gradient within the oven and/or the crucibles may account for their formation. This is an important observation, as it shows that under certain

conditions, the hollow spheres undergo an anisotropic stress that forces them to minimize the surface tension by forming faceted objects (fitting into a circle).

To gain a better understanding of the parameters that determine the final diameter of the hollow spheres (e.g., the sintering temperature, template diameter, the PSS/NSi8 film thickness, etc.), a similar experiment was conducted by using 640 nm template PS particles coated with three and six PSS/NSi8 bilayers (Figure 9A and B). When calcined at 750 °C, diameter increases to 960 ± 5 and 965 ± 5 nm were measured for the three- and six-bilayer coated PS templates, respectively. This corresponds to a 3.4-fold increase of volume relative to the template (Figure 10D). Using eq 5 to estimate the shell thickness after volume expansion reveals that such a shell would be only a few angstroms thick if the adsorbed amount of NSi8 molecules was the same as that previously found on planar substrates and larger (925 nm) spheres. The mismatch with the measured values indicated that many more NSi8 molecules were initially present on the PSS layers. Little is known about polyelectrolyte coating on spheres in a salt-free environment; however, the influence of the sphere size is critical, as the polyelectrolyte flexibility is assisted by the ionic strength.²⁸ In our experiments, it appears that the polymer tended to form

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flattened coated domains with small protuberances at the junction of these domains (Figure 9B). This effect could be because of the partial wrapping or the tangential adsorption of polymers with tails extended in opposite directions^{28b} and is more pronounced upon increasing the number of adsorbed bilayers (see Supporting Information). The shell thickness of a sphere coated with three PSS/NSi8 bilayers is about 260 Å (Figure 9A), corresponding to an average bilayer thickness increment of 87 Å; this value is more than twice that measured on planar substrates or larger spheres (41 Å) for the same number of bilayers deposited under identical conditions. This indicates that the amount of NSi8 adsorbed is higher on 640 nm spheres, as compared with the 925 nm spheres. The shell thickness of a calcined six-bilayer coated sphere was in the range of 30 Å (Figure 10D).

The above data indicate that by using molecular clusters of silica instead of large silica particles, the calcination conditions determine both the shape and the volume of the hollow colloids. A high-resolution image of the shell (Figure 10C) shows the homogeneity and microporosity of the shell; pores of a maximum size of 7.5 Å can be seen on the surface, which is comparable to the size of the silsesquioxane core, 5.9 Å. For larger template spheres, the thickness of the coating was found to be critical to form hollow spheres; three bilayers were required, as a lower number of layers led to broken spheres. The drastic size reduction is likely because of the initial low amount of silica clusters on the template, which are unable to coalesce and keep the original template size. Another important parameter is the porosity of the silica shell *as it forms*. The diameter of the template has a strong influence on the shell porosity because of the influence of coating the layers in the absence of salt. Using 640 nm PS particles, we observed an expansion of the hollow silica spheres. The existence of a pressure gradient between the inner volume of the shells and the outer medium may account for the large size variations observed in this study (including reshaping of the particles, see Supporting Information). These data bring new insights to the preparation of hollow inorganic spheres, showing how the size of the starting building blocks incorporated into the shell, the heating profile, and the core size impacts the formation of hollow siliceous particles.

Conclusions

We have demonstrated the self-assembly of oligosilsesquioxane, in alternation with polyelectrolyte, to prepare nanocomposite siliceous ultrathin films. By adjusting the pH conditions for the assembly processes, we found that NSi8 molecules can adsorb onto a PSS-coated surface by acid–base interaction. This property has been exploited to prepare multilayers of defined composition and thickness on both planar and spherical supports.²⁹ Subsequent calcination of the films yields ultrathin silica coatings and hollow silica spheres, respectively. The formation of the hollow spheres was found to be sensitive to the thickness of the coating, the diameter of the template core, and the calcination temperature. Changing these parameters yielded particles with different sizes and shapes relative to the initial template. This approach constitutes a novel alternative to the fabrication of planar silica films and microporous hollow silica spheres, with pore sizes below 1 nm. Further studies will be devoted to controlling and characterizing the pore structures achieved by using this approach with preformed silsesquioxane nanobuilding blocks.

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Supporting Information Available: Details of NSi8 infiltration experiments, NSi8 packing on PSS, absorption spectra of NSi8-coated primed quartz substrates, TEM images of 640 nm PS particles coated with PDDA/(PSS/NSi8)_n (*n* = 3 or 6), and hollow gyroids obtained by calcining PS particles coated with PDDA/(PSS/NSi8)₃ at 750 °C (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) Recently, we reported the formation of metalodielectric spheres with novel optical properties by alternately depositing NSi8-stabilized silver nanoparticles and PSS onto PS particles (Cassagneau, T.; Caruso, F. *Adv. Mater.* **2002**, *14*, 732).