

# Sol-gel preparation of macroporous silica films by templating with polystyrene microspheres

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**Polystyrene microspheres have been used as templating entities to fabricate thin macroporous silicate films with controllable porosity for catalysis and chemical sensing-related applications.**

The fabrication of microporous and mesoporous silica has received considerable attention due to the need to develop more efficient and stable materials for applications in catalysis, separations, coatings and chemical sensing.<sup>1,2</sup> Among various strategies for the preparation of porous materials, template-based sol-gel processing has rapidly gained popularity.<sup>1</sup> In this approach, the silicate matrix is assembled around a suitable template. Upon removal of the template, cavities with a specific size and shape remain in the cross-linked host.<sup>1</sup>

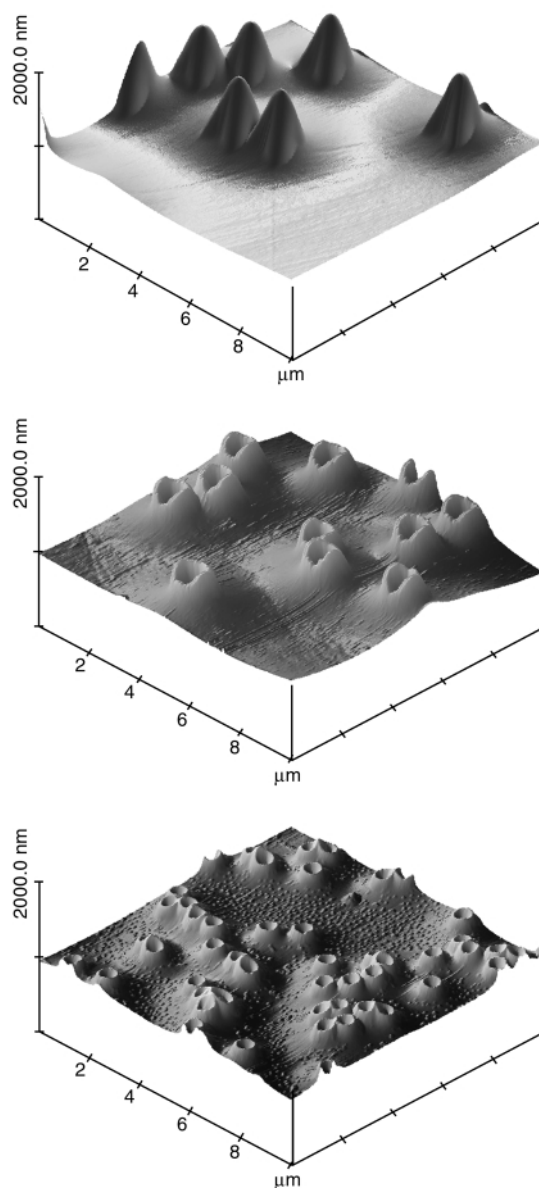
A wide variety of templates has been used to prepare materials with pore sizes that range from a few nanometers to several microns.<sup>1,2</sup> Examples used in the fabrication of porous silica materials include organic molecules,<sup>3,4</sup> latex spheres,<sup>5,6</sup> organic ligands,<sup>7,8</sup> bridged template ligands,<sup>9-11</sup> emulsion droplets,<sup>12</sup> and surfactants.<sup>13-18</sup> To date, most investigations have focused on the formation of *micropores* ( $d < 2$  nm) or *mesopores* ( $2 < d < 50$  nm) into bulk silica solids or thick membranes with a specific focus on the preparation of 3D arrays. Relatively little attention has been focused on the generation of *macroporosity* ( $d > 50$  nm) in thin films, particularly those that allow for easy transport through the film.

In chemical sensing, thin films (typically  $< 1$   $\mu\text{m}$ ) prepared using sol-gel technology are most often utilized due to their short path length for diffusion that decreases response times and improves recovery rates.<sup>19,20</sup> Sol-gel-derived thin films, however, are inherently much less porous than corresponding silica monoliths as gelation and evaporation occur simultaneously.<sup>21,22</sup> The ability to engineer porosity into these materials will clearly improve their performance in analytical science.

In this work, a new approach is described for the preparation of macroporous thin silica films whose pores are open on both sides and enable efficient transport of reagents through the film. This approach utilizes polystyrene microspheres as the templating entities to fabricate thin *macroporous* sol-gel-derived films with controllable porosity. A mild chemical treatment is used to completely remove the polystyrene template without destruction of the film. The morphology and properties of the templated silica films have been examined using a combination of microscopic, spectroscopic and electrochemical methods.

In these experiments, the silica sol was prepared by mixing tetramethoxysilane (TMOS) with water and 0.1 M hydrochloric acid followed by stirring for 5–10 min. The mole ratio of Si:H<sub>2</sub>O:HCl was 1:9:0.003. The original aqueous suspension of polystyrene microspheres (PSMS, Interfacial Dynamics, 8% wt/v surfactant-free, sulfated) was sonicated for 5 min prior to use. The sample solutions of PSMS suspension were prepared by mixing the original suspension with water and 10 mM sodium dodecyl sulfate followed by sonication for 2 min. The aged (3 days) silica sol was then added to a PSMS suspension in a ratio of 1:2 (v/v). The final mixture was vigorously stirred and again sonicated for 1 min and the resultant suspension was cast

on the surface of a glassy carbon electrode or on a silicon substrate at *ca.* 7000 rpm using an in-house built rotator. The thin films were allowed to dry overnight under room conditions (45–55% RH, ambient temperature). The polystyrene microspheres were removed from the dense silica framework by soaking the film in chloroform for two hours.



**Fig. 1** 10  $\mu\text{m} \times 10 \mu\text{m}$  AFM images of silicate films prepared from a sol containing 1.0  $\mu\text{m}$  polystyrene microspheres, 1.3% wt/v before (top) and after (middle) chloroform treatment. (Bottom) macroporous silica film formed after removal of polystyrene microspheres from the composite film prepared with a sol containing 2.5% wt/v of 0.5  $\mu\text{m}$  polystyrene microspheres.

Fig. 1 (top and middle) shows AFM images of the composite silica films prepared with 1  $\mu\text{m}$  diameter PSMS particles before and after chloroform treatment. As can be seen in the top panel of Fig. 1, the polystyrene particles embedded within the silicate film appear as the 'hills' randomly distributed through the topography of the film. Evaluation of the height of the embedded particles gives a value close to the diameter of the bare particle whereas the width is estimated to be approximately twice that of the particle. Upon formation of the film, the silica likely pulls away from the polystyrene microsphere exposing the top of the particle and building up around the sides.

After exposure to chloroform for two hours, the AFM images show craters that are visibly open with an inside top diameter close to the width of the polystyrene particle, Fig. 1 (middle). A blow up of the cross-section of a cavity formed from a 0.5  $\mu\text{m}$  polystyrene microsphere is shown in Fig. 2. As can be seen, the shape of the cavity mimics the shape of the bottom half of the polystyrene particle. Part of the electrode underneath the polystyrene microsphere becomes exposed after removal of the particle. The size of the cavity can be changed by changing the diameter of the polystyrene microsphere template. Likewise, the number density of the cavities in the film can be increased *via* changes in the amount of polystyrene particles added to the sol. Fig. 1 (bottom) shows an AFM image of a templated film prepared from a sol containing 2.5% of 0.5  $\mu\text{m}$  polystyrene microspheres. As can be seen, there are significantly more cavities in the films with an inner diameter close to the size of the polystyrene particle.

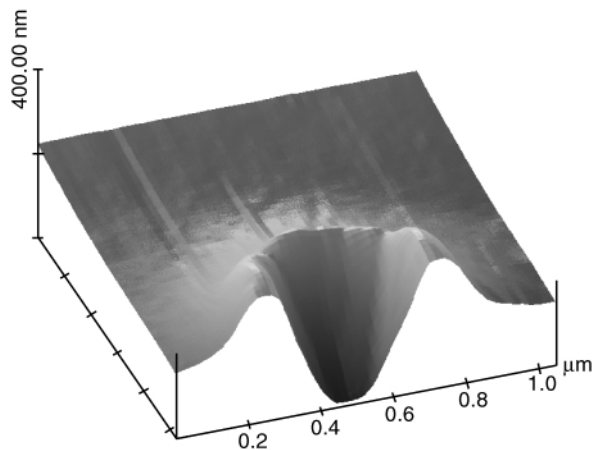


Fig. 2 Cross-section AFM image of an individual hole formed from a 0.5  $\mu\text{m}$  polystyrene microsphere.

In order to verify that the films are open on both sides and allow for easy transport of reagents, electrochemical probe experiments were conducted. In these experiments, the silicate film cast on an electrode surface is placed in a solution containing an electroactive 'probe' molecule. If the probe molecule is able to reach the underlying electrode surface *via* diffusion through a defect site or a template induced cavity, Faradaic current will be observed. Fig. 3 shows the cyclic voltammograms of 1 mM ruthenium hexaammine  $[\text{Ru}(\text{NH}_3)_6^{3+}]$  at the silicate film both before and after template removal. Prior to treatment in chloroform, no Faradaic current can be seen with any of the electroactive probes. This is consistent with our prior work that has shown that films fabricated with a silica sol prepared *via* the acid-catalyzed hydrolysis of tetramethoxysilane are compact and essentially defect-free.<sup>23</sup> After the polystyrene spheres are removed from the dense matrix, however, sigmoidal shaped CVs are obtained for  $\text{Ru}(\text{NH}_3)_6^{3+}$  due to electron transfer at the electrode-solution interface produced by the template. The magnitude of the Faradaic current increases upon increasing the number density of cavities within the film.

In summary, a relatively simple approach is described to engineer porosity in otherwise dense silica films. The size and number density of the pores thus produced can be easily varied over a large range *via* judicious selection of the size of the

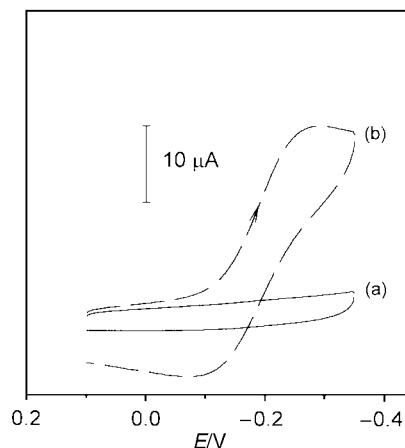


Fig. 3 Cyclic voltammograms of 1 mM ruthenium hexaammine in 0.1 M  $\text{KNO}_3$  at a polystyrene templated film (a) before and (b) after chloroform treatment. Films were prepared from a silica sol containing 0.5  $\mu\text{m}$  polystyrene microspheres, 1.3% wt/v. Scan rate 100  $\text{mV s}^{-1}$ .

polystyrene microsphere template and its concentration in the sol. The template is removed *via* chemical means, otherwise temperature sensitive reagents can also be entrapped within the silicate framework. It is envisioned that this approach can be utilized to prepare more porous sol-gel-derived materials for chemical sensing- and catalysis-related applications or serve as a unique way to fabricate ultra-small reaction vessels for small volume chemistry related applications.

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