

# Surface Patterning of Silica Nanostructures Using Bio-Inspired Templates and Directed Synthesis

Elizabeth A. Coffman,<sup>†</sup> Anatoli V. Melechko,<sup>‡,§</sup> David P. Allison,<sup>†,§</sup>  
Michael L. Simpson,<sup>‡,§</sup> and Mitchel J. Doktycz<sup>\*,†,‡</sup>

*Life Sciences Division and Condensed Matter Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6123, Oak Ridge, Tennessee 37831 and University of Tennessee, Knoxville, TN 37996*

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Natural systems excel in directing the synthesis of inorganic materials for various functional purposes. One of the best-studied systems is silica synthesis, as occurs in diatoms and marine sponges. Various biological and synthetic polymers have been shown to template and catalyze silica formation from silicic acid precursors. Here, we describe the use of poly-L-lysine to promote the synthesis of silica in neutral, aqueous solution and when immobilized onto a silicon support structure under similar conditions. Either reagent jetting or conventional photolithography techniques can be used to pattern the templating polymer. Spots created by reagent jetting led to the creation of silica structures in the shape of a ring that may be a result of the spotting process. Photolithographically defined poly-L-lysine spots led to thin laminate structures after exposure to a dilute aqueous silicic acid solution. The laminate structures were nanostructured and highly interconnected. Photolithographic patterning of (3-aminopropyl)trimethoxysilane, a reagent that mimics the lysine functional group, led to similar silica coatings even though low-molecular-weight materials do not rapidly promote silica synthesis in solution. This result highlights the importance of functional-group arrangement for templating and promoting the synthesis of inorganic materials. The described surface-patterning techniques offer a route to integrate conventional silicon-patterning technologies with biologically based material synthesis. Such combined fabrication techniques enable controlled assembly over multiple length scales and an approach to understanding interfacial silica synthesis, as occurs in natural systems.

## Introduction

Recent years have seen remarkable advances in understanding and mimicking biological routes to the synthesis of inorganic materials. Peptide sequences important in the recognition and assembly of inorganic materials, such as gold,<sup>1</sup> silver,<sup>2</sup> hydroxyapatite,<sup>3</sup> and semiconducting nanocrystals,<sup>4</sup> have been identified. Some of these sequences have been based on naturally occurring proteins; others have been discovered by combinatorial techniques. These discoveries are enabling the directed synthesis of inorganic nanostructures under relatively mild conditions of temperature and pressure. Particularly noteworthy is the discovery of the proteins and molecular mechanisms that direct silica synthesis in biological systems.<sup>5–7</sup> Natural silica structures exhibit diverse and intricately designed shapes. The silica architecture derives from biomolecular structure and, ultimately, genetic-based directions. Understanding the chemical structure, spatial positioning, and temporal expression of the templating organic molecule in relation to the resultant inorganic structure will reveal the rules for effectively designing synthetic structures.

Enabling this possibility is work by Morse and co-workers who have identified “silicateins” that catalyze the formation of silica spicules in a shallow-water sponge, *Tethya aurantia*.<sup>8,9</sup> Not only do silicateins catalyze the formation of silica from silicon alkoxide monomers at neutral pH but they also spatially direct the formation of silica structures. Additionally, “silaffin” proteins in marine diatoms have been identified.<sup>10,11</sup> Silaffins contain repeated peptide sequences that are rich in basic amino acids (lysine and arginine) and unusual alkylamine posttranslational modifications. Silaffins assist in the formation of the silica wall that encompasses the diatom. These proteins become incorporated into the cell wall and synthetic versions of these molecules show similar nanoscale morphologies.<sup>12</sup> Studies of silicateins and silaffins have highlighted the importance of carefully positioning functional groups to form hydrogen bonds, to create electrostatic interactions, and to serve as catalytic agents to template and catalyze silica formation.

Coincident with the description of silaffins and silicateins is the identification of natural and synthetic polymers that also template and catalyze the formation of silica from soluble precursors. Homopolymers of lysine,<sup>13–15</sup> arginine,<sup>13,14,16</sup> and allylamine<sup>13,17</sup> have all been shown to polymerize silicic acid by acting as both a

\* Author to whom correspondence should be addressed. E-mail: doktyczmj@ornl.gov.

<sup>†</sup> Life Sciences Division, Oak Ridge National Lab.

<sup>‡</sup> Condensed Matter Sciences Division, Oak Ridge National Lab.

<sup>§</sup> University of Tennessee.

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template and a catalyst. The size and morphology of the resulting silica structure can be controlled by the molecular weight of the polymer and the reaction conditions.<sup>18–20</sup> Block copolypeptides of lysine and cysteine that self-assemble into spheres and other structures have been shown to template and catalyze silica formation from silicon alkoxide precursors.<sup>21</sup> Templating methods present a promising approach to controlling inorganic synthesis for the creation of desired shapes.<sup>15,22,23</sup>

Here, we demonstrate the combination of a bio-inspired molecular-scale template and catalyst with conventional surface patterning techniques to control the growth of silica structures on planar surfaces. Poly-L-lysine (PLL) was patterned onto silicon surfaces using either photolithography or ink-jet-based deposition. Additionally, a functional analogue of surface immobilized poly-L-lysine, (3-aminopropyl)trimethoxysilane, was lithographically patterned. The surface-immobilized molecules are shown to direct silica formation from silicic acid precursor molecules. The use of conventional lithographic approaches enables specific arrangements of inorganic materials and nanostructures onto larger, wafer-scale structures, while the mild reaction conditions allow compatibility with biological reagents. These features may enable advanced technological devices suitable for biomedical applications. Further, refinements in surface chemistry that allow for control of functional group placement may also aid in elucidating the basic mechanisms of controlled synthesis on the nanoscale and the organization of nanostructures on longer length scales. Such developments may lead to the synthesis of inorganic structures with defined, nanoscale morphologies.

## Materials and Methods

**Reagents.** Sodium orthosilicate ( $\text{Na}_4\text{SiO}_4$ ) was obtained from Gelest, Inc. (Tullytown, PA). Poly-L-lysine with a molecular weight of 150 000–300 000 g/mol, (3-aminopropyl)trimethoxysilane, and buffer reagents were obtained from Sigma-Aldrich (St. Louis, MO). Silicon wafers (100 mm, N-type (Sb), 0.005–0.02 Ohm cm) were obtained from Silicon Quest International.

**Lithographic Patterning.** Two different patterning techniques were investigated. The first approach patterned PLL using a reagent-jet dispensing system while the second used conventional photolithography. Reagent-jet-based patterning of the PLL was accomplished using a custom dispensing system that incorporates solenoid-based reagent jets with a Hamilton Microlab 2200 liquid-dispensing robot. Details of the dispensing system can be found elsewhere.<sup>24</sup> The reagent jetting approach allows contactless dispensing of volumes down to a few nanoliters by rapidly actuating a valve that controls the flow of a pressurized fluid. For the experiments described here, a 1 mg/mL aqueous solution of PLL was dispensed onto small pieces of a silicon wafer ( $\sim 1 \text{ cm}^2$ ) on 750  $\mu\text{m}$  centers using a valve opening time of 300  $\mu\text{s}$  and a head pressure of 6 psi. The resulting dispensed volume is on the order of 5 nL. The dispensed spots were allowed to dry before subsequent treatments.

Photolithographic patterning was performed on 100 mm silicon wafers that were vapor primed with hexamethyldisilazane (90 °C, 30 min). The photoresist Shipley SPR955-0.7 (Microchem) was spun at 6000 rpm, resulting in a 0.7  $\mu\text{m}$  thick layer, and baked at 90 °C for 90 s. The central 5 cm  $\times$  5 cm area of a wafer was exposed with a pattern of 0.7  $\mu\text{m}$  diameter circles on a 5  $\mu\text{m}$  spacing using a GCA AutoStep200. The postexposure bake was performed at 120 °C for 90 s. The pattern was then developed in CD-26 developer. After development, the wafer was washed in water and dried with  $\text{N}_2$ . Finally, resist residue inside the patterned areas was removed by exposing the wafer to an oxygen-reactive ion etch (Orion, Trion Inc.) for 30 s.

For experiments involving photolithographically defined spots, the chip was soaked in 1 mg/mL PLL for five minutes. The structure was then rinsed with acetone to remove the photoresist and then washed thoroughly with water.

An alternate approach used (3-aminopropyl)trimethoxysilane to direct the formation of silica. For this method, the patterned chip was soaked in a 2% aqueous solution of the silane for 10 min. The structure was then washed with water, rinsed with acetone, and washed with water again. The chip was then placed in an oven at 75 °C for 20 min.

**Silica Synthesis.** A 10 mM solution of sodium orthosilicate was freshly prepared for each experiment by dissolving an appropriate amount in either borate buffer (50 mM, pH 8.5) or sodium phosphate buffer (50 mM, pH 7.0). For experiments describing silica synthesis in solution, 200  $\mu\text{L}$  of the silicic acid solution was added to 50  $\mu\text{L}$  of a 1 mg/mL aqueous solution of PLL in the desired buffer. The reaction was carried out in a 1.5 mL polypropylene centrifuge tube and was immediately noticeable. After the reaction was allowed to proceed for the designated amount of time, the precipitate was spun to the bottom of the tube using a microcentrifuge at 2000  $\times$  g. The solution was decanted and the precipitate rinsed with distilled, deionized  $\text{H}_2\text{O}$  and re-pelleted using the microcentrifuge. This washing procedure was repeated three times before re-suspending the silica precipitate in 50  $\mu\text{L}$  of  $\text{H}_2\text{O}$ .

For synthesis on PLL- or (3-aminopropyl)trimethoxysilane-treated surfaces, the silicon structure was placed in a freshly prepared solution of sodium orthosilicate for the designated amount of time. It was then rinsed with distilled, deionized  $\text{H}_2\text{O}$  and dried.

**Electron Microscopy.** The samples were imaged using a high-resolution cold cathode field emission scanning electron microscope Hitachi S4700 equipped with two secondary electron detectors. The lower detector is located inside the specimen chamber and allows electron collection in a wide energy range. While this leads to some loss in resolution, it also reduces the challenge of imaging insulating samples. In addition, it is possible to reduce surface charging by selecting the accelerating voltage of the incident electron beam. Metal coating of the samples was not used to avoid obscuring resultant nanostructures. Thus, thick silica structures initially prepared from solution and subsequently deposited were imaged at 2 kV using the lower detector. The upper detector in the Hitachi S4700 is located above the last lens and collects only elastically scattered electrons. The ultrahigh-resolution images were acquired at 30 kV using the upper detector. The images were acquired with beam incident normal to the surface.

## Results and Discussion

The ability of PLL to serve as both a template and a catalyst for silica formation from silicic acid is shown in Figure 1. Upon the PLL solution being mixed with a dilute solution of sodium orthosilicate, a precipitate is immediately observed. Although silicic acid solutions can eventually gel, the dilute solutions used here remained clear in the absence of PLL. Reactions that were allowed to proceed for 10 min are shown in Figure 1. Longer reaction times led to similar structures but with increased overall yield. No differences were apparent when the reactions were carried out at pH 7 or 8.5. In general, highly interconnected spherical structures are observed. The spheres are on the order of 100 nm in diameter. These

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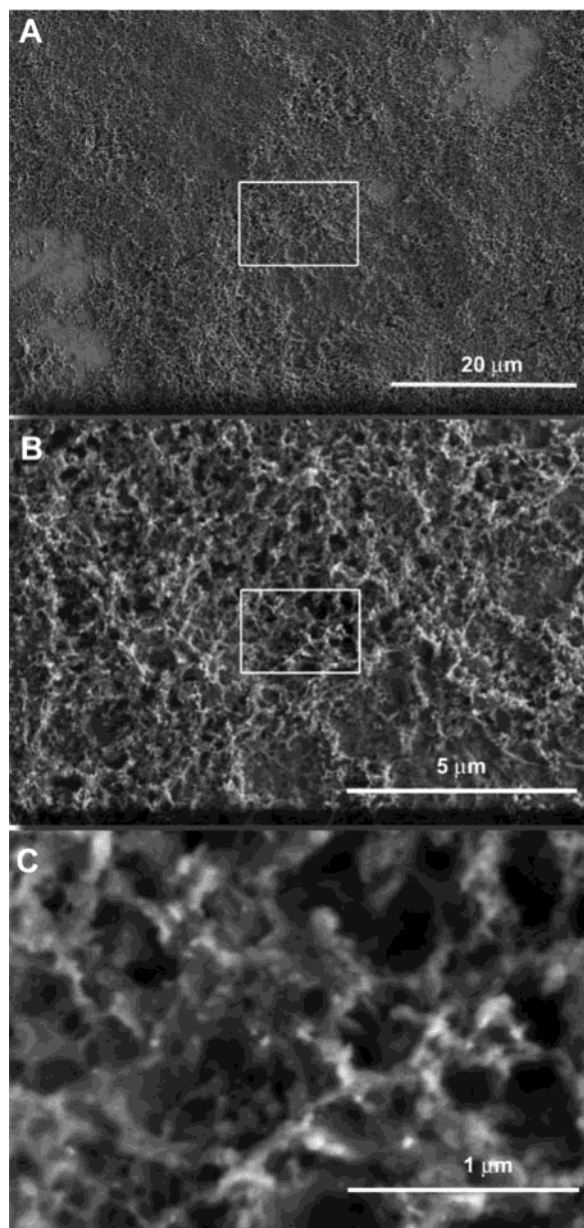
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**Figure 1.** SEM images of silica synthesized in solution. The silica structures were prepared using PLL and a dilute solution of silicic acid at pH 7. The images were acquired at 2 kV using the lower detector (see text). Shown are three different magnifications with the enlarged area indicated by the white rectangle.

reactions were carried out at approximately 1:5 molar ratio of polymer unit to sodium orthosilicate. The high-molecular-weight PLL (150 000–300 000 MW) used in these studies is critical for facilitating rapid precipitation of silica. Lower-molecular-weight polymers (4 000–150 000 MW) also precipitated sodium orthosilicate solutions, however, at a much slower rate or not at all (data not shown). Typically, overnight incubation was necessary for noticeable formation of silica when using low-molecular-weight polymers. No precipitation was observed when high-molecular-weight PLL was used with tetraethoxysilane.

These observations are consistent with those of others.<sup>14,15</sup> Previous studies have described the catalytic ability of amino acids and peptides to facilitate silica formation via condensation of silanol groups.<sup>13,14</sup> Although the silicic acid concentration is reduced due to polymerization, precipitation does not occur. Higher-molecular-

weight amine-containing polymers enable templating of the negatively charged silicic acid, leading to the precipitation of nanostructured silica. The spatial distribution of charged side groups is essential and assists in bringing reactive species and small particles together for condensation.<sup>14,18</sup> In general, random structures composed of interconnected silica spheres that contain the organic template are observed. The importance of spatial orientation is further supported by the observation that shear forces can lead to altered morphologies,<sup>20,25</sup> presumably by changing the conformation of the templating molecule. Collectively, the observed molecular-weight dependence, the requirement for hydrogen- and ionic-bonding functional groups, and the effects of flow and shear forces on product formation highlight the importance of the orientation and distribution of functional groups for facilitating silica synthesis. However, overall silica morphology is still largely uncontrolled when using polymers in solution.

To further understand the importance of functional-group orientation and distribution in defining silica morphology, PLL was patterned onto planar surfaces. This approach constrains the location of the templating molecules to the surface and limits the growth of the silica structure to the patterned location. Amine-containing polymers are known to strongly physisorb to silicon and glass surfaces.<sup>26</sup> For example, poly-L-lysine forms a monolayer coating and is often used for immobilizing biomolecules.<sup>27</sup>

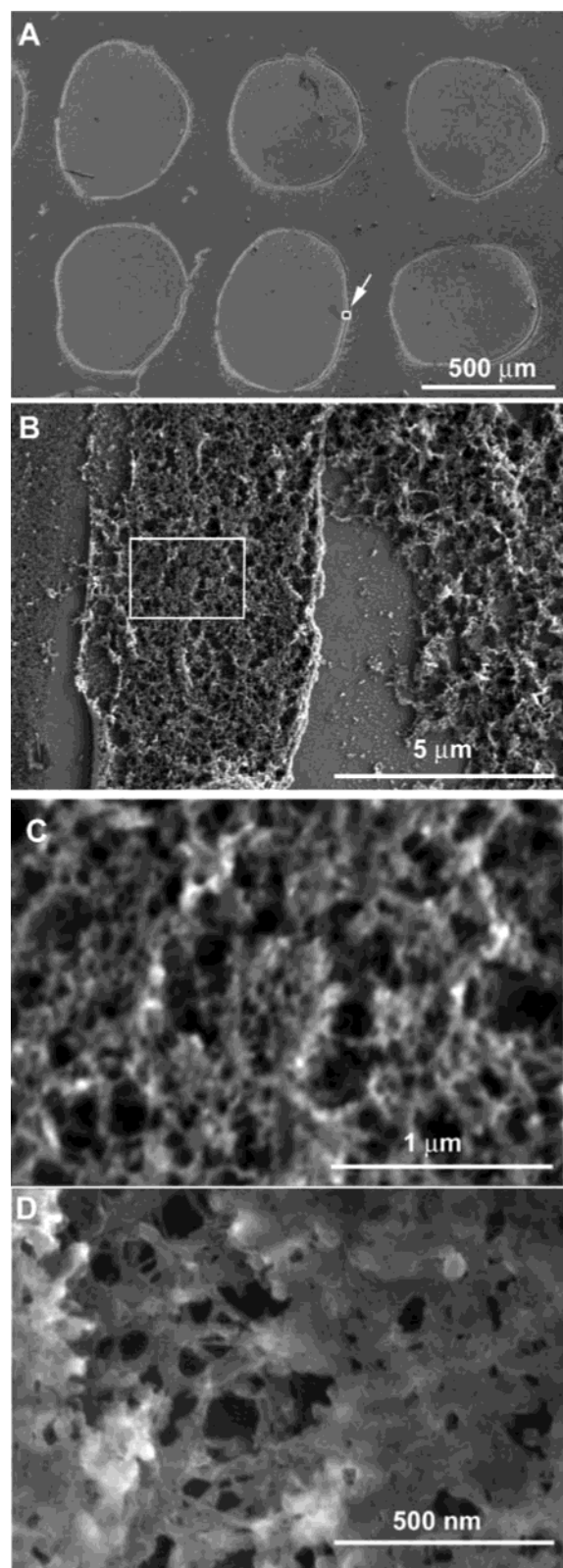
To pattern PLL, a reagent-jetting technique was used to deposit small droplets of the reagent onto silicon supports. Reagent jetting is a fairly gentle patterning technique, relative to photolithography, in that it does not expose the reagents to adverse solvent conditions. However, the dispensed volume can limit feature size. Using a solenoid-based reagent-jetting system, a pattern of approximately 5 nL spots of PLL was dispensed, yielding spot sizes on the order of 500  $\mu\text{m}$ . After drying, the spotted structure was subsequently washed and exposed to a 10 mM solution of sodium orthosilicate at either pH 7 or 8.5. Electron micrographs of the resulting structures are shown in Figure 2. Rings of silica are observed in the location of dispensed PLL spots. Ring patterns are often observed when microspotting due to the build-up of solute at the edges of the drying droplet.<sup>28</sup> The build-up of PLL at the spot edge leads to increased formation of silica relative to the center of the spot. The morphology of the silica at these edges closely resembles the morphology of the silica produced in solution (Figure 1). No differences were observed between structures prepared at pH 7 and 8.5. Exposure to the silicic acid solution was typically for 10 min. Longer exposures led to similar structures.

Although the ring formation that results from reagent jetting the template could be exploited for patterning, the uneven coating prevents clear interpretation of the effect of constraining the template polymer. To obtain an even surface coating of PLL, a lithographically defined pattern of spots was created in photoresist. After treatment with PLL and removal of the photoresist, the structure was exposed to a dilute solution of sodium orthosilicate. Figure 3 displays electron micrographs of the structures after exposure for 1 h. Flat, disk-shaped structures, larger than the original  $\sim 0.7 \mu\text{m}$  diameter templates, are observed.

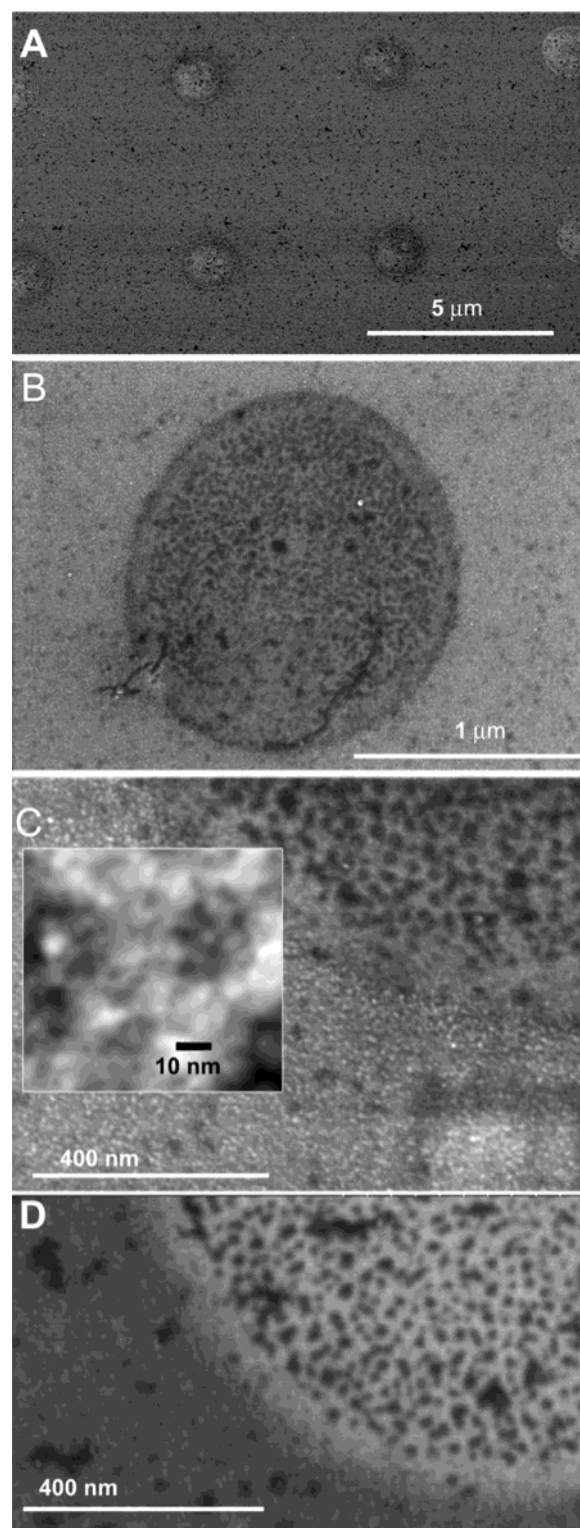
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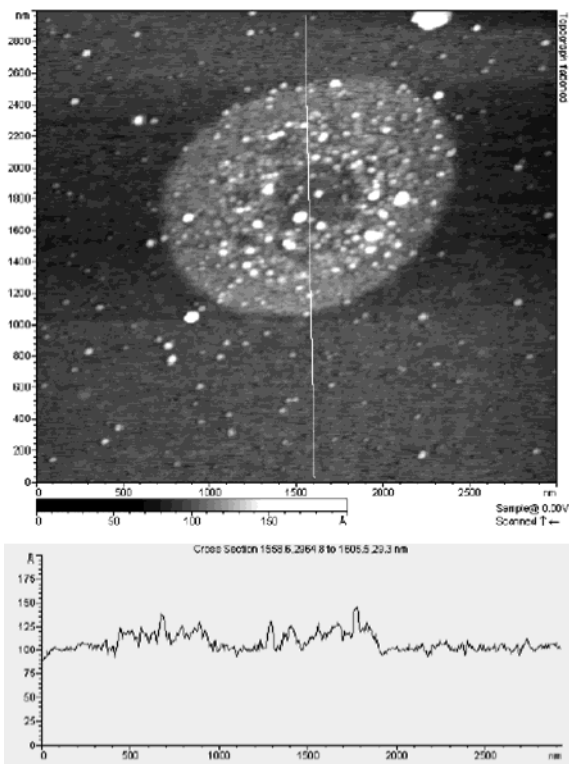
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**Figure 2.** SEM images of silica structures derived from reagent-jet patterning of PLL. The array of  $\sim 500 \mu\text{m}$  diameter spots (A) was obtained by dispensing  $\sim 5 \text{ nL}$  of 10 mM PLL at pH 7. Magnification of a portion of the image, indicated by the white rectangle, shows that the silica builds up at the spot edge (B). Greater magnification of the indicated area (C, D) shows that the structure is morphologically similar to silica formed in solution from a soluble PLL template (Figure 1). Electron micrographs A, B, and C were acquired at 2 kV using the lower detector (see text). Micrograph D is a high-resolution image obtained at 30 kV using the upper detector (see text).



**Figure 3.** SEM images of silica structures derived from photolithographically patterned PLL. A pattern of  $\sim 700 \text{ nm}$  diameter spots of PLL was exposed to a dilute solution of silicic acid for 1 h (A). Magnification of a representative spot shows highly interconnected silica nanostructures (B, C, D). Individual spots are somewhat larger than the initially patterned structure. This may be due to lifting of the resist at the spot edges or due to the growth of the silica structure. The images were obtained at 30 kV using the upper detector. Note the 5 nm particles overlaying larger 30 nm structures in the inset in C. These smaller particles are seen covering the entire surface of the silicon wafer. D is obtained after a 5 s reactive-ion etching process using a  $\text{CHF}_3/\text{O}_2$ -based plasma ( $\text{SiO}_2$  etch rate 25 nm/min). The etching process removed the 5 nm particles enabling observation of the nanoporous structure.

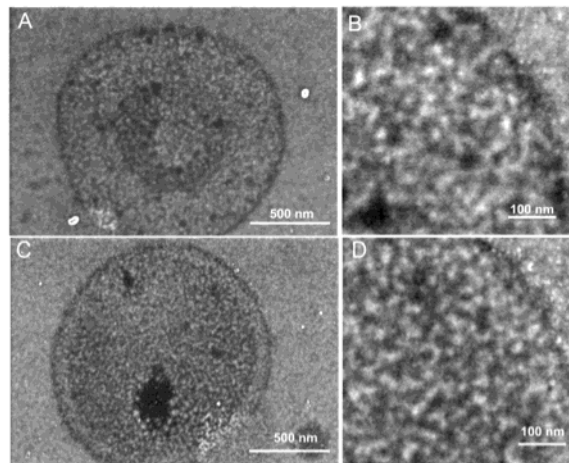


**Figure 4.** Atomic force microscopy image and height profile of a silica structure derived from photolithographically patterned PLL. The near vertical line overlaid onto the topographic image indicates the location where the height profile was taken. The image was collected using a Pico Plus atomic force microscope (Molecular Imaging Inc., Tempe, AZ).

As opposed to the structures derived from reagent jetting of the PLL, the photolithography-derived structures are fairly uniform across the entire spot and show highly interconnected silica particles on the order of 30 nm across. The even coating is consistent with an even coating of the polymer; however, longer exposures (Figure 3) show a rim around the spot that is not apparent with shorter exposure times. Further, a littering of 5 nm particles is seen throughout the structure. These smaller structures may form in solution and simply settle on the surface. Brief exposure to a reactive ion etch removes these features (Figure 3c and d).

The laminate structures formed from photolithographically patterned PLL do not appear to possess any measurable height when analyzed by electron microscopy. Atomic force microscopy of the structures indicates that the coating is on the order of 3–5 nm in height (Figure 4). Although the PLL appears to form a monolayer on the surface, it is possible that portions of the high-molecular-weight polymer are not constrained to the surface and could be instrumental in controlling silica synthesis. To rule out this possibility and to further understand surface templating of silica, a low-molecular-weight functional analogue of lysine was patterned. Low-molecular-weight polymers and amino acids of lysine do not lead to rapid silica precipitation in solution.<sup>13,14</sup> However, if an appropriate number of functional groups are co-localized, as they are in higher-molecular-weight polymers, then precipitation should be facilitated.

To test this hypothesis, (3-aminopropyl)trimethoxysilane was patterned using a similar photolithographic procedure as that used for PLL patterning. Electron micrographs of silica structures resulting from patterned (3-aminopropyl)trimethoxysilane are shown in Figure 5.



**Figure 5.** SEM images of silica structures derived from photolithographically patterned (3-aminopropyl)trimethoxysilane. Shown are individual spots of an array created using the same lithography masks as for Figure 3. The (3-aminopropyl)trimethoxysilane contains an amine functional group similar to the PLL. Co-localization of this functional group on the surface mimics the spatial templating achieved by the high-molecular-weight polymers. Electron micrographs A and B display different magnifications of silica nanostructures after 10 min exposure to silicic acid. Interconnected silica nanostructures are observed, though the degree of connectivity is lower than that observed when using a PLL template. Electron micrographs C and D display the silica nanostructures after 60 min of exposure. The degree of connectivity appears to be similar, although there appears to be a filling-in along the rim of the spot. Delamination from the surface is believed to cause the dark spot seen in C. Random sites such as these are seen across the surface and are believed to result from surface stresses upon drying. The images were obtained at a 30 kV accelerating voltage using the upper detector.

With brief exposure to sodium orthosilicate (Figure 5A and B), the silica extends to the limits of the patterned spots and an interconnected network of particles is observed. The particle sizes are again on the order of 30 nm; however, the degree of connectivity appears lower when compared to structures formed from PLL (Figure 3). Longer exposures to sodium orthosilicate (Figure 5C and D) led to a filling in of the rim of the spot but not an increase in the connectivity. It is possible that nanoscale surface heterogeneities prevent higher-order structures when using the low-molecular-weight compound. Alternatively, the reduced dynamic flexibility of the short-chain amine, compared to the high-molecular-weight polymer, constrains the growth process and reduces the connectivity.

The use of (3-aminopropyl)trimethoxysilane highlights the importance of the amine functionality in templating silica synthesis. Further, it demonstrates that the arrangement of these amine groups is critical for facilitating silica formation. When free in solution, higher-molecular-weight polymers are needed to rapidly nucleate and template silica structures. Catalysis and formation on a surface is possible with low-molecular-weight materials if the functional groups are co-localized, effectively mimicking features of the polymer. Previous reported attempts to facilitate silica formation on surfaces using amine-containing polymers were unsuccessful.<sup>29</sup> The immobilization techniques used in these previous studies were significantly different in that they exploited multilayer formation and charge pairing to immobilize the amine-containing polymer. Apparently, the availability of the amine-containing functional groups is critical for facilitating silica formation.

### Conclusions

Planar immobilized PLL and a functional analogue, propylamine, are effective in promoting the synthesis of silica from a silicic acid precursor under neutral, aqueous conditions. The resulting structures show silica particles on the order of 30 nm across that eventually fuse to form an interconnected coating. The degree of connectivity is higher when using PLL. The coated structures possess some similarity to silica structures produced in solution from PLL, but their growth is limited to the location of the surface patterned template. The described approach incorporates the use of conventional, microscale lithographies with molecular templates to enable the synthesis of planar silica structures of defined shape. This allows the fabrication of microscale structures with nanometer-scale features and integration of biologically based material synthesis approaches with commonly used microfabrication techniques. Reagent jetting of the catalytic molecule leads to an uneven, donut-shaped silica coating

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that replicates the pattern of the template. The photolithography-based patterning leads to evenly coated surfaces and disc-shaped laminate structures. The mechanism of silica growth requires further investigation; however, these initial studies show that nanoscale features may arise when the area of synthesis is constrained. Additional control of surface patterning and chemistry will aid in understanding the formation of these features and in understanding biological routes to the synthesis of inorganic materials.

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