



Effects of surface water on organosilane nanostructure fabrication using particle lithography



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ABSTRACT

Patterned organosilane self-assembled monolayers serve as molecular platforms for electronic, optical, and sensing applications. Among the numerous strategies to pattern organosilane monolayers, particle lithography offers a high throughput means to fabricate arrays of organosilane nanopatterns across large areas. Herein, we demonstrate that the utility of particle lithography for generating nanostructures can be further controlled by changes in sample preparation. Our systematic study of various drying conditions demonstrates a correlation between sample preparation and surface water and uses these findings to form nanopores, pillars, and rings within organosilane monolayers. Silica mesospheres deposited on Si substrates that are subjected to less rigorous drying conditions (3 h at room temperature) prior to organosilane deposition yield nanopores within decyltrichlorosilane monolayers that are significantly smaller than those produced on Si substrates that are prepared under more forcing conditions (12 h at room temperature and 2 h at 140 °C). This disparity in nanopore diameter can be rationalized by the presence or absence of water between the silica mesospheres and Si substrate. Sequential deposition of two organosilanes offers further evidence for the presence or absence of water beneath the silica mesospheres. For samples that are less rigorously dried, complete organosilane pillars are observed, and for samples that are more rigorously dried, organosilane rings are observed where the inner diameter is defined by the mesosphere-substrate contact geometry. The ability to produce varied organosilane nanostructures provides valuable insights about the water that is present on the surface and within the silica mesosphere template. These insights into the surface water and the effects of sample preparation on organosilane nanostructures enable greater hierarchical control over the fabrication process.

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1. Introduction

Self-assembled monolayers (SAMs) of organosilanes have been employed as versatile molecular architectures for electronic, optical, and sensing platforms [1–4]. Among the reasons for interest in these SAMs are the rich chemical functionalities and range of substrates (Si, glass, mica, Au, etc.) that can be utilized to produce novel surfaces with well-defined properties [5–12]. Further, organosilane SAMs are thermally and chemically robust due to the covalent bonds formed between the organosilane molecules and underlying substrates. There are many well established methods that are routinely utilized for patterning organosilane SAMs, including photolithography, electron-beam lithography, contact-printing lithography, and scanning probe lithography [13–21]. Another patterning technique, known as particle lithography, is a high throughput method that creates registered organosilane nanopatterns across large areas [22–31]. This method

utilizes aqueous dispersions of mesospheres that are cast onto substrates and organize into close-packed arrays with regular interpattern two-dimensional geometries as the water evaporates [32]. These arrays then serve as physical templates that facilitate the formation of organosilane films around the mesospheres. The periodicity and features sizes of the organosilane nanopatterns can be tailored by changing the diameter of the mesospheres that are used [22–24,26,27,30,31].

There has been significant interest in investigating the underlying factors required to generate densely-packed organosilane SAMs using both solution immersion and vapor deposition techniques in conjunction with particle lithography [22–24,27,33]. Of these factors, the residual water from the mesosphere organization process, is of particular interest as water is necessary for the hydrolysis reaction that forms the covalent linkage between the organosilane molecules and underlying substrate [23]. Further, the quality of the organosilane SAMs is greatly influenced by the amount and location of the water on the substrate [22]. Too much surface water leads to polymerization and agglomeration of the organosilane molecules in the bulk solvent, while too little water yields incomplete organosilane SAMs. Therefore, careful control of surface water is crucial to produce high-quality organosilane nanopatterns.

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The utility of particle lithography with organosilanes has been previously demonstrated through the fabrication of nanoscale surface structures, such as nanopores within organosilane SAMs and rings of organosilane molecules, where the fabrication is mediated by the water surrounding the mesospheres [23,26,33]. In addition, multicomponent nanopatterns of organosilanes have been fabricated by a three-step process that requires the formation of an organosilane SAM using a mesosphere template, followed by mechanical removal of the mesospheres, and subsequent exposure of the unmasked regions to a second organosilane [24]. We have recently reported that changes in solvent composition used in the deposition process can also influence the feature size thus providing even greater control over the organosilane nanopatterns [30]. Given the utility of particle lithography for generating organosilane nanostructures, we set out to better understand the factors that influence surface water coverage and to utilize these findings to enhance organosilane nanostructure fabrication. Herein, we report findings that show a correlation between sample preparation and surface water coverage and use these findings to tailor nanopore size and to form pillars and rings within organosilane SAMs.

2. Experimental details

2.1. Materials and reagents

Boron-doped, polished Si(111) substrates were purchased from Ted Pella (Redding, CA). These substrates were precut to lateral dimensions of 5 mm × 5 mm. Silica mesospheres in aqueous suspensions (500 nm in diameter, 8000 Series) were purchased from Thermo Scientific (Waltham, MA). Octadecyltrichlorosilane (OTS, >90%) was purchased from Sigma-Aldrich (St. Louis, MO), and decyltrichlorosilane (DTS) was purchased from Gelest (Morrisville, PA). Anhydrous toluene (ACS Grade), bicyclohexyl (>99.0%), hydrogen peroxide (30% aqueous solution), and sulfuric acid (ACS Grade) were purchased from VWR International (Randor, PA). Absolute ethanol was purchased from Pharmco-Aaper (Bookfield, CT). All reagents were used as received. Water (18 M Ω) was generated using a Milli-Q system (Q-GARD 2, Millipore, Billerica, MA).

2.2. Preparation of Si substrates

Si substrates were cleaned by immersing in piranha solution (3:1 by volume of sulfuric acid/30% hydrogen peroxide) for 1 h, followed by rinsing with copious amounts of 18 M Ω water [3,34]. The Si substrates were dried under a stream of N₂ prior to use in organosilane nanostructure fabrication. *Caution: piranha is a vigorous oxidant and should be used with extreme care!*

2.3. Preparation of silica mesospheres

An aliquot of the stock 500 nm silica mesosphere suspension (2% by weight) was pipetted into a microcentrifuge tube and subjected to centrifugation (9200 rpm) for 10 min. The supernatant was removed, and the pellet was resuspended in 18 M Ω water, using a vortex mixer, to a concentration of 4% by weight. This suspension was subjected to centrifugation and resuspension three more times prior to use in organosilane nanostructure generation.

2.4. Fabrication of nanostructures within DTS SAMs using particle lithography

Nanopores, OTS pillars, and OTS rings within DTS SAMs on Si substrates were fabricated using the two particle lithography strategies depicted in Fig. 1. For both procedures, 10 μ L aliquots of the silica mesosphere suspension (4% by weight) were deposited across Si substrates and allowed to dry in a humidity controlled environment (67 \pm 2%)

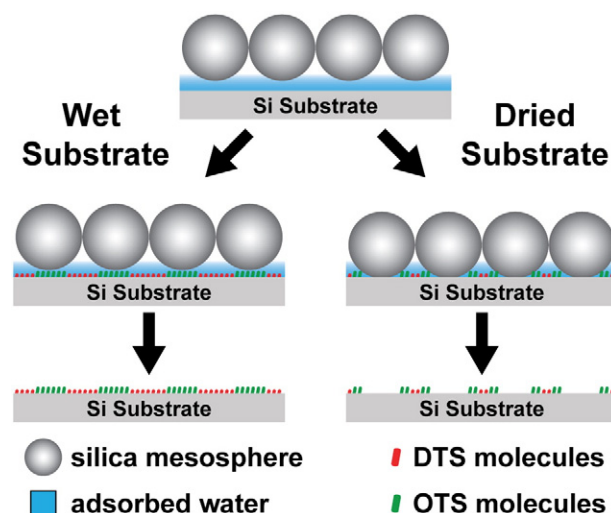


Fig. 1. Key steps for the fabrication of nanopores, OTS pillars, and OTS rings within DTS SAMs on Si substrates. *Wet substrate.* Silica mesospheres are cast across a Si substrate and are dried for 3 h prior to immersion into bicyclohexyl solutions of DTS for 5 min and OTS for 2 h. The silica mesospheres are removed via sonication in ethanol revealing the periodic arrangement of the organosilane nanostructures. *Dried substrate.* Silica mesospheres are cast across a Si substrate and are dried for 12 h at room temperature and 2 h in an oven prior to immersion into bicyclohexyl solutions of DTS for 5 min and OTS for 2 h. The silica mesospheres are removed via sonication in ethanol revealing the periodic arrangement of the organosilane nanostructures.

at room temperature (21 \pm 1 $^{\circ}$ C). The humidity was controlled by bubbling nitrogen through water into an acrylic desiccator cabinet (Thermo Scientific, Waltham, MA). These conditions yielded closed-packed silica mesosphere templates consistent with previous reports [20,23,24,32, 35–38]. For the first strategy, which produced nanopores and OTS pillars within a DTS SAM, the Si substrates with the silica mesosphere templates were dried for 3 h in the humidity controlled environment prior to immersion into piranha-cleaned glass V-vials filled with 5 mM bicyclohexyl solutions of DTS for 5 min. For the second strategy, which produced nanopores and OTS rings within a DTS SAM, the Si substrates with the silica mesosphere templates were dried for 12 h in the humidity controlled environment, dried in an oven at 140 $^{\circ}$ C for 2 h, and placed in the humidity controlled environment for 1 h prior to immersion into piranha-cleaned glass V-vials filled with 5 mM bicyclohexyl solutions of DTS for 5 min. To produce nanopores, the Si substrates with the silica mesosphere templates were rinsed with toluene, dried under a stream of N₂, rinsed with absolute ethanol, and dried under a stream of N₂. The silica mesosphere templates were removed from the Si substrates via sonication in absolute ethanol for 10 min, and the Si substrates were rinsed with absolute ethanol, dried under a stream of N₂, rinsed with toluene, and dried under a stream of N₂. To produce OTS pillars and OTS rings, the Si substrates were rinsed with bicyclohexyl and immersed into piranha-cleaned glass V-vials filled with 5 mM bicyclohexyl solutions of OTS for 2 h. Subsequently, the Si substrates with the silica mesosphere templates were rinsed with toluene, dried under a stream of N₂, rinsed with absolute ethanol, and dried under a stream of N₂. The silica mesosphere templates were removed from the Si substrates via sonication in absolute ethanol for 10 min, and the Si substrates were rinsed with absolute ethanol, dried under a stream of N₂, rinsed with toluene, and dried under a stream of N₂.

2.5. Atomic force microscopy characterization and analysis of nanopores within OTS SAMs

Tapping-mode (AC-mode) atomic force microscopy (AFM) images were acquired using an Agilent 5420 scanning probe microscope with OLTESPA Si cantilevers (Bruker AFM probes, Santa Barbara, CA) with nominal force constants of 2 N/m. The Si cantilevers were cleaned

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