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Communications

Mussel- and Diatom-Inspired Micropattern Generation of Silica on a Solid Substrate

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Biosilicification in diatoms[1] and sponges[2] potentially promises physiological, mild reaction conditions for controlling silica structures at the nanometer scale. Since Sumper *et al.* had isolated catalytic peptides (*i.e.*, silaffins) from diatoms,[3] a number of polymers bearing tertiary amine or ammonium groups have been used as a counterpart of silaffins to biomimetically synthesize silica structures.[4,5] This biomimetic silicification has several advantages over conventional chemical methods. For instance, biomimetic silicification provides relatively uniform films over large areas under physiological reaction conditions without special equipment. Moreover, this method can be simply incorporated into conventional processes.[6] As a result, recent years have witnessed a growing interest in the applications of biomimetic silicification, such as surface coating and patterning,[7,8] sensors,[9] (bio)-catalysis,[10,11] nanohybrids,[12,13] and biotechnology.[14,15]

Especially, micropattern generation through biomimetic silicification has been of interest due to its potential applications in microelectronics.[16] For example, Stone *et al.* generated sub-micrometer sized silica patterns by holographic two-photon-induced photopolymerization.[8a] In addition, Choi *et al.* reported the controlled pattern generation of silica on a solid substrate through atom-transfer radical polymerization and silicification.[8b] However, previous examples were performed on the limited kinds of materials due to the lack of versatility, and thus a versatile method of silica pattern generation has been required for wider applications. Very recently, a material-independent silica coating method was investigated by a combination of mussel-inspired polydopamine coating and subsequent diatom-inspired silicification.[17] This method enabled us to achieve the silica coating of many diverse materials. Furthermore, it was successfully applied to the preparation of thermally stable silica/polyethylene separators utilized in Li-ion batteries.[18]

The mussel- and diatom-inspired silica coating method has another advantage to use. It can be easily combined with a micromolding in capillaries (MIMIC) technique, which is a soft lithographic technique.[19] In MIMIC technique, microchannels of poly(dimethylsiloxane) (PDMS) are filled with a solution, and the solution is then incubated for interfacial reaction onto surfaces. In the same manner, as the alkaline solution of dopamine is injected into the microchannels, polydopamine films are selectively deposited on the surface.[20] Herein, we demonstrate a procedure for generating silica patterns by the above-mentioned method. Figure 1 shows the schematic description of the procedure. Briefly, MIMIC

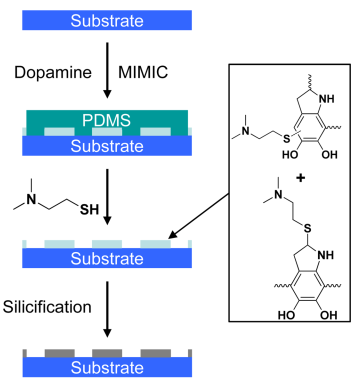

Figure 1. A schematic description of the silica micropattern generation on a solid substrate.

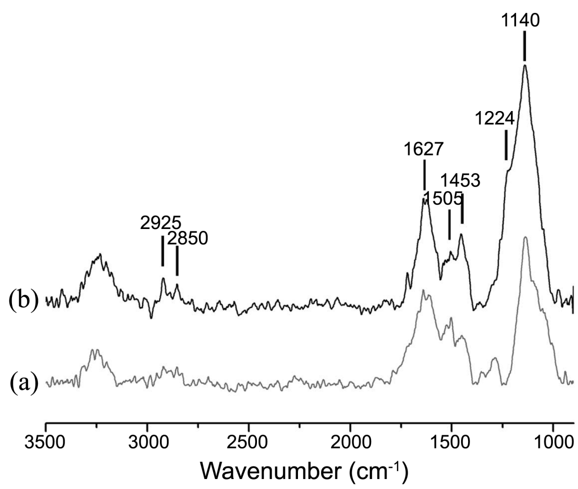

Figure 2. FT-IR spectra of (a) polydopamine-coated and (b) silica-coated substrates.

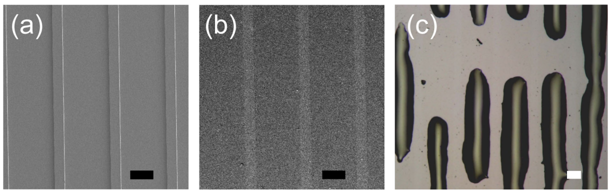

Figure 3. SEM images of (a) PDMS microchannels (200 μm in width) and (b) the silica-patterned substrate. (c) An optical micrograph of patterned water on silica microlines. The scale bar is 100 μm.

technique with dopamine solution generates polydopamine-based micropatterns. Subsequently, polydopamine layers are functionalized by 2-dimethylaminoethane-thiol (10 mM) at room temperature for 5 h in order to introduce tertiary amine groups onto polydopamine layers.[18] Finally, the resulting substrate is immersed into a monosilicic acid solution to form a silica micropattern on the surface.

FT-IR characterization showed a successful formation of amine-functionalized polydopamine and silica, respectively. Amine-functionalized polydopamine afforded characteristic peaks; for example, 1453 cm^{-1} (CH_2 scissors vibration), 1505 cm^{-1} (ring stretching from benzene), 1627 cm^{-1} (NH_2 deformation), 2925 and 2850 cm^{-1} (CH antisymmetric and symmetric stretching, respectively), and in the range of 1040-1140 cm^{-1} (C-O and C-N stretching), 3100-3300 cm^{-1} (NH and OH stretching) (Figure 2a). Upon the silicification, we observed a new peak at 1224 cm^{-1} and the increased peak intensity in the range of 1000-1250 cm^{-1} (Si-O-Si asymmetric stretching) (Figure 2b). Furthermore, all peaks from polydopamine were also monitored due to the coexistence of both polydopamine and silica (Figure 2b). Therefore, these peak assignments and changes indicate the successful silicification along the polydopamine layers.

Micropatterns generated by 200-μm-channels (Figure 3a) were characterized by scanning electron microscopy (SEM). SEM analysis displayed a formation of 200-μm-width silica-patterns on the substrate (Figure 3b). Moreover, the patterns were confirmed by dropping water droplets onto the surface. The water confined in the 200-μm-lines was observed along the silica-patterned region (Figure 3c). The phenomenon is caused by the selective change of the surface wettability through polydopamine coating and silicification. Thus, these results would develop a novel application of the silica-patterned surface such as a water-guiding device with a design of directions.

In summary, we demonstrated a micropattern generation of silica on the solid substrate by a mussel- and diatom-inspired approach combined with a soft lithography. This method shows several advantages to apply for a wide range of materials without harsh reaction conditions. Moreover, it could allow us to give proper functionalities on silica layers *via* well-defined organosilane chemistry.

Supporting Information. Experimental details.

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