FABRICATION AND EVALUATION OF HIERARCHICAL SUPERHYDROPHOBIC AND SALVINIA SURFACES

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ABSTRACT

We report an effective process to fabricate high-performance hierarchical superhydrophobic (SHPo) surfaces and a simple additional process to turn them into hierarchical Salvinia surfaces. The hierarchical roughness is obtained by creating microstructures, coating them conformally with alumina, and converting the coated alumina into nano-grass. The hierarchical roughness becomes SHPo after coating a fluorosilane self-assembled monolayer. Additionally, if desired, the hierarchical SHPo surface can be converted to a hierarchical Salvinia surface by applying polydopamine only to the top regions of the microstructures. Using a camera system designed to directly visualize the menisci on cleaved surfaces in water, we confirmed an increased plastron stability under negative hydrostatic pressure on the converted Salvinia surface compared to the SHPo surface with the same hierarchical roughness.

KEYWORDS

Superhydrophobic surface; polydopamine; Salvinia surface; plastron stability

INTRODUCTION

Most of the major applications of SHPo surface (e.g., drag reduction, antibiofouling) rely on an air layer trapped on the surface (called plastrons) in water. While the main challenge has been to retain the plastron under high hydrostatic pressure, negative pressure can also wither the plastron by making the neighboring air pockets merge and leave as bubbles. A natural solution for the negative pressure was found on the Salvinia leaves, where hydrophilic tips on otherwise SHPo microstructures would pin the meniscus and prevent the air-pocket merging [1]. Although multiple methods have been reported to fabricate Salvinia surfaces, they were either complex [2-4] or not confirmed under negative pressure condition [5]. Here, we report an advanced fabrication process to make high-performance hierarchical SHPo surfaces and a simple method to turn them into hierarchical Salvinia surfaces. A new camera setup and a pressure chamber were developed to evaluate the plastron stability on the SHPo and Salvinia surfaces under fluctuating hydrostatic pressure, for which confocal microscopy is unsuitable.

SAMPLE FABRICATION

The hierarchical structure used for this study was micro-trenches decorated with nano-grass (NG). Micro-trenches were created by regular MEMS fabrication processes (figure 1), starting with a 4 inch silicon wafer delivered with a layer of thermal oxide (1 μm thick) (figure 1a). The oxide layer was patterned using photolithography

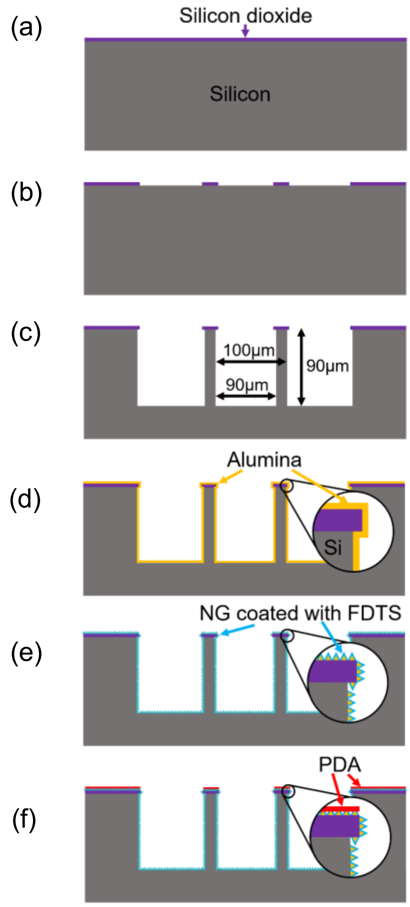

Figure 1: Process flow of the hierarchical Salvinia surface. (a, b) Pattern thermal oxide by RIE; (c) Create micro-trenches by silicon deep RIE; (d) Deposit alumina by ALD; (e) Form alumina nano-grass (NG) and coat FDTS to create SHPo surface; (f) After a KOH dip, coat PDA only on the grating top to create Salvinia surface.

and reactive ion etching (RIE) (figure 1b), followed by deep RIE (DRIE) to create micro-trenches (figure 1c). The trenches are 100 μm in pitch (i.e., periodicity), ~90 μm in width (i.e., ~10 μm in grating width), and ~90 μm in depth, The oxide layer, which formed re-entrant tips on the grating tops by the etch undercut during DRIE, was left in place. A 100 nm thick alumina layer was then coated conformally by atomic layer deposition (ALD) (figure 1d). After a 10 minutes immersion in 62°C hot water, the ALD alumina was roughened to form a 200-300 nm thick NG [6]. Taking advantage of the excellent conformality of ALD, NG covered the entire surface, including the bottom side of the re-entrant tip of the micro-trench (figure 2a). Since alumina is hydrophilic, the hierarchical surface of NG-decorated micro-trench was superhydrophilic (SHPi). To transform the hierarchical SHPi surface into a hierarchical SHPo surface, a self-assembled monolayer (SAM) of 1h,1h,2h,2h-perfluorodecyltrichlorosilane (FDTS) was coated by vapor deposition. Since SAM was also highly conformal, all the surfaces of NG became SHPo (figure 1e). The combination of microstructure with re-entrant tip, highly conformal NG on the microstructure, and the highly hydrophobic and conformal FDTS on the NG, led to a nearly ideal SHPo surface. The high performance of this SHPo surface was demonstrated by maintaining the plastron even under a speeding motorboat (up to 14 knots) in the harsh environment of ocean water for the first time [7].

Additionally, the hierarchical SHPo surface can be further transformed into a hierarchical Salvinia surface by coating a hydrophilic polymer only on the grating top (figure 1f). This was achieved by simple dopamine solution immersion. Coating a material on a highly hydrophobic surface, such as Teflon or FDTS SAM, was difficult until the advent of polydopamine (PDA) [8]. Indeed, PDA was coated on the eggbeater-like pillars by immersing the sample in a dopamine solution to fabricate Salvinia surfaces [3]. However, because the effective surface energy of the FDTS-coated NG was only a fraction of that the FDTS-coated smooth surface for the dopamine solution, even PDA could not be coated on the grating top. Note one cannot apply a pressure to let the dopamine solution penetrate the NG because it would penetrate the micro-trench first. Instead, we chose to dip the sample in 1% potassium hydroxide (KOH) solution for 30 s before the PDA coating. Since KOH etches alumina, it disrupted the extreme hydrophobicity of the FDTS-coated alumina NG and enabled PDA adhesion. Note the KOH and dopamine solutions contacted only the NG on the grating top, leaving all the FDTS-coated NG inside the trench unaffected. Since the PDA coating took about 8 hours and polymerization of dopamine consumed dissolved oxygen [9], only a half of the SHPo surface was immersed at a time so that the micro-trenches were replenished with air and not wetted. After the first coating (see figure 2b, which also show no PDA inside the trench), the sample was flipped and immersed again to coat the other half.

After hierarchical SHPo and Salvinia surfaces were made, the samples were cleaved perpendicular to the grating direction to reveal the cross-sections of micro-gratings and micro-trenches. Made to allow a direct visualization of the menisci of the plastron, the cross-sectioned surfaces of the microstructures were bare silicon with no NG.

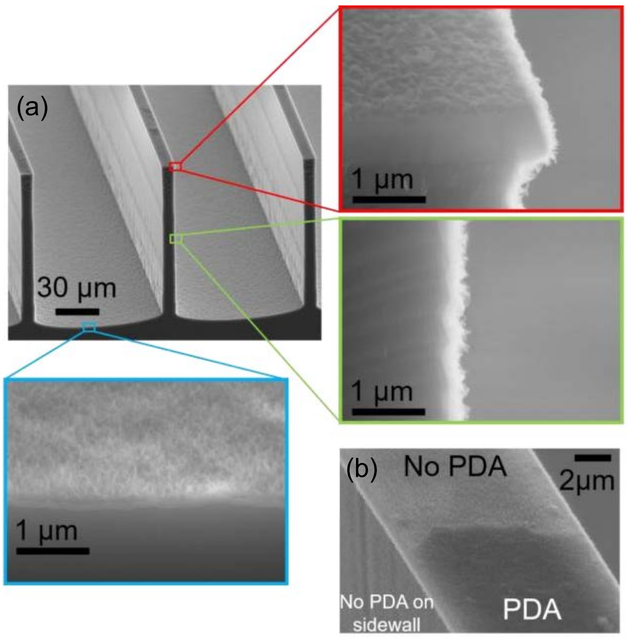

Figure 2: SEM pictures of the hierarchical Salvinia surface. (a) A cleaved sample to reveal the cross section of micro-trenches. (b) Top of one grating shows one half of it covered by PDA after one coating.

EXPERIMENTAL SETUP

To evaluate the plastron status in fluctuating hydrostatic pressure, we built a small pressure chamber (figure 3). The pressure fluctuation was created manually with a syringe and monitored by a manometer. The pressure chamber was made with a transparent rectangular plastic container so that samples can be inspected from outside the chamber with minimal optical distortion.

To enable a cross-sectional view of the menisci on the gratings of the cleaved silicon sample, we developed a bidirectional illumination approach (figure 3). One light illuminated the menisci from behind the sample, and the other illuminated the cross section of the gratings from the front. Visualization of the menisci relied on the total internal reflection of the air-water interface. Quality visualization of the gratings required a well-cleaved sample as well as optimal lighting angles. The orientations of the sample, lights and the camera were carefully tuned so that the cross sections of both menisci and gratings were visible simultaneously. A zoom lens and a CCD camera were used to inspect the menisci during experiments.

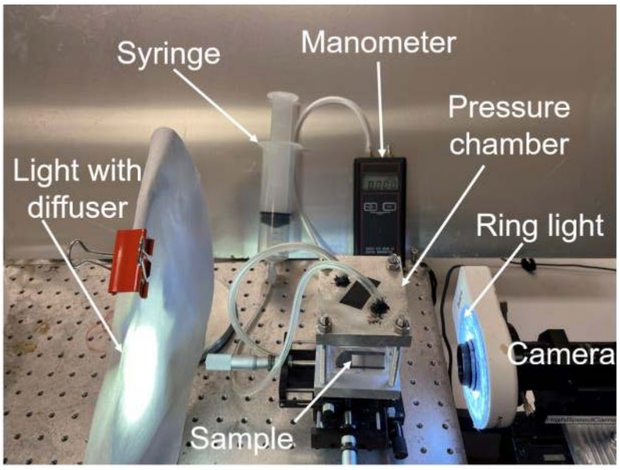

Figure 3: Visualization setup. The sample immersed in a transparent pressure chamber was illuminated by a bidirectional illumination system, which was developed to make the air-water interfaces (in a 100 μm periodicity) visible with a zoom lens and a CCD camera. The light on the left of the sample (i.e., the opposite side from the camera) shines up the meniscus. The ring light on the right of the sample (i.e., surrounding the camera lens) shines up the cleaved sidewall of the silicon substrate.

VISUALIZATION RESULTS

Hierarchical SHPo surface (i.e., without PDA) and hierarchical Salvinia surface (i.e., with PDA) were immersed in water and exposed to hydrostatic pressure fluctuating between positive and negative values compared with the atmospheric pressure. In figure 4a, two samples were immersed in air-saturated water under atmospheric pressure (0 kPa gauge pressure). Menisci on both samples were approximately flat, as expected. When exposed to a positive pressure, menisci on both samples bent down (into the trench). Figure 4b shows the shape of bent down menisci when the chamber was pressurized to positive ~20 kPa gauge pressure. A higher positive pressure would cause the menisci to depin and make the trenches wetted on both the SHPo and Salvinia surfaces. Since the cleaved surface does not have the re-entrant tip, which increases the resistant to wetting, the menisci on the cleaved samples were depinned from the cleaved end of trenches rather than from the grating top. Since the SHPo surface and the Salvinia surface had an identical cleaved end, they were wetted at the same positive pressure, as expected. Note the maximum positive pressure the surfaces can withstand,

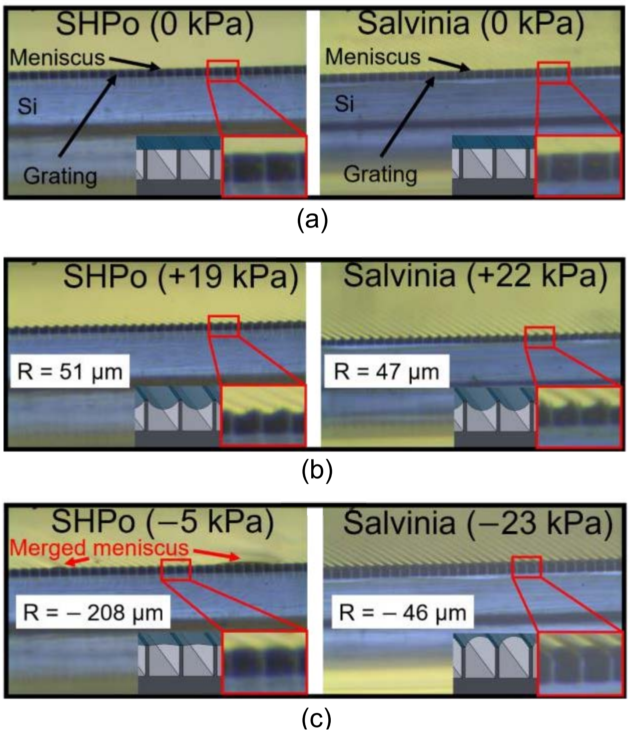

Figure 4: Cross-sectional views of the cleaved samples, revealing the air-water interface (menisci) formed on trenches across gratings. 3D schematics of the menisci are shown alongside the zoomed in pictures. (a) In atmospheric pressure (0 kPa gauge pressure), menisci were essentially flat for both; (b) In pressurized chamber (~20 kPa), menisci were concave for both; (c) In depressurized chamber, menisci were convex for both. Left: After some menisci on the SHPo surface started to merge at only -2 kPa, the merged bubbles grew with increasing negative pressure (-5 kPa shown). Right: In contrast, menisci on the Salvinia surface were intact even as they became highly convex under large negative pressure (-23 kPa shown). The radius of meniscus curvature was measured and presented as R (positive for concave; negative for convex).

which is higher than the values reported in this manuscript using the cleaved surfaces, can be measured with an un-cleaved sample if desired. However, it is not our main interest here because the maximum hydrostatic pressure on SHPo and Salvinia surfaces are the same and easily predictable.

In figure 4c (our main interest), negative pressure was applied to the samples. While the air pockets on the SHPo surface started to merge and form large air bubbles even under small negative pressure, the ones on the Salvinia surface remained intact even when the menisci were highly deformed by large negative pressure. Compared to the SHPo surface, the Salvinia surface withstood a ten times higher negative pressure before the plastron was deteriorated by bubble merging. The experimental data is summarized in table 1.

Table 1: Measured gauge pressure when the menisci depinned downward to start trench wetting (i.e., maximum positive pressure allowed for pinned plastron) and depinned out of trenches to grow bubbles (i.e., maximum negative pressure allowed for pinned plastron).

Sample type	**Maximum positive pressure**	**Maximum negative pressure**
SHPo	+19 kPa	-2 kPa
Salvinia	+22 kPa	-23 kPa

Note, under negative hydrostatic pressure, the menisci merged only on the top surface and never on the cleaved surface for both SHPo and Salvinia samples. This was because the cleaved surface was hydrophilic bare silicon (i.e., no NG or FDTS). The hydrophilic surface resisted the spreading of air under negative pressure, preventing the neighboring air pockets from merging on the cleaved end of trenches.

CONCLUSION

We have developed an effective fabrication process to make high-performance hierarchical SHPo surfaces, which consist of microstructures decorated with highly conformal and hydrophobic NG. We have additionally developed a simple PDA coating method to convert the hierarchical SHPo surfaces into hierarchical Salvinia surfaces. A newly developed camera system with bidirectional illumination directly visualized the shape of menisci on both types of surfaces. The result demonstrated a significantly enhanced plastron stability of the hierarchical Salvinia surface compared to the hierarchical SHPo surface in the negative pressure, which may be encountered in the fluctuating, natural environment.

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