TRANSFERRING SOFT DOUBLY RE-ENTRANT MICROSTRUCTURES FOR MECHANICALLY RESILIENT OMNIPHOBIC SURFACES

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ABSTRACT

Omniphobic surfaces, capable of repelling all types of liquids, are fundamentally reliant on the micro/nano doubly re-entrant structures, these overhanging structures, however, are prone to break under mechanical loading. Here, we report a robust technique to faithfully transfer an array of soft doubly re-entrant microstructures onto a target substrate, circumventing the limitation of demolding soft overhang structures, to realize a resilient omniphobic surface for the first time. The resulting surface not only exhibits omniphobic property, but also robust durability after substantial normal and shear mechanical stresses. The side view of the deformation and recovery of the structures against mechanical loads was captured under a microscope to help reveal the underlying mechanism. The innovative method presented in this study is scalable for the production of mechanically robust, omniphobic surfaces on a large scale. Such advancement facilitates the large-scale manufacturing of durable micro- and nanoscale surface textures, making them viable for practical applications.

KEYWORDS

Omniphobic surface, resilient surface, soft material, PDMS, doubly re-entrant, surface structures.

INTRODUCTION

Surface wettability is a crucial property of materials, it is affected by both the chemical composition and the physical topography. To enable super repellency to any liquids, it has been found that surface topography should be made doubly re-entrant [1]. So far, these delicate structures require MEMS fabrication that commonly involves multiple cycles of etching and deposition on a silicon-based substrate [1]–[3]. While the proof-of-concept of omniphobic surfaces based purely on surface structures has been shown, the production of such structures is constrained by the scalability of MEMS processes. Furthermore, the application of doubly re-entrant topography to create super-repellent surfaces has been limited because, following the physics of rigid materials, these delicate surface structures are prone to damage under mechanical stress. To improve mechanical resilience, we have previously reported a strategy where the pillar structure and the doubly re-entrant cap were fabricated separately and combined at a later stage [4]. This method enhanced the mechanical robustness of the superomniphobic surfaces, allowing a flexible material selection for the pillars and the caps. However, the fabrication complexity arises from the use of two different materials for the pillar and the cap, making both the alignment and the interfacial bonding strength critical yet challenging aspects of the process. Recent research has used soft lithography with polydimethylsiloxane (PDMS) molding into the reverse patterns of the upside-down doubly re-entrant structures [5], [6]. The molding process, however, is intrinsically challenging due to the existence of the overhangs in the mold, as explained in Figure 1. In contrast to the demolding of preferred pyramidal shapes from a mold (Figure 1a), the removal of overhanging structures demands the stretching of PDMS to enable the larger overhangs to pass through the narrower openings of the mold. This procedure often entails substantial necking and compression, potentially leading to PDMS tearing and the entrapment of residue within the mold (Figure 1b).

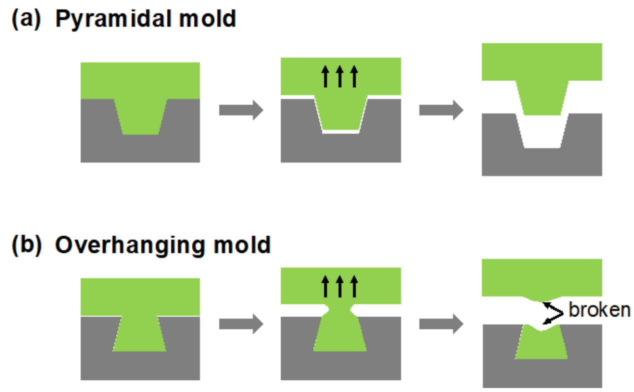

Figure 1: Comparison of demolding from different types of molds. (a) A soft structure (green) can be easily demolded from a mold with a pyramidal shape (gray). (b) A soft structure tends to be trapped in a mold with an overhanging shape. Successful demolding requires soft material with a larger size to be squeezed through a smaller opening.

Here we reported a novel fabrication method that molds the right-side-up doubly re-entrant structures and transfers them to a target substrate. The new mold eliminates overhangs, thus preventing the PDMS from getting stuck during the demolding process. We will first present a scalable MEMS fabrication process to realize our design. Second, we will visually verify the topology of the resulting microstructures. Finally, we will characterize the fabricated substrate with liquid repellency and mechanical compression and abrasion.

METHODS

The fabrication process flow to realize our design is shown in Figure 2. First, following our previous report [7], a special silicon mold with drainage wells was fabricated using general multi-step lithography and DRIE but with the reverse patterns of the right-side-up doubly re-entrant structures (Figure 2a). Next, we adopted the general procedure of soft lithography to prepare the PDMS pre-polymer (i.e., Sylgard 184, with a 10:1 ratio between the base prepolymer solution and the curing agent). The pre-polymer was thoroughly mixed and degassed in a vacuum chamber to remove all the bubbles. We then poured the uncured PDMS into the silicon mold and pressed it against a glass with ~8 MPa pressure to acquire the isolated structures (Figure 2b). Next, these surface structures were picked up by another layer of PDMS (aka. transfer buffer) with a hydrophobic silane treatment in between so that we could separate them in the final step. The structures were then placed on the target substrate which was coated with a partially cured PDMS layer (Figure 2c). Finally, after the PDMS layer was fully cured (Figure 2d), we removed the transfer buffer and obtained a soft surface with doubly re-entrant surface structures (Figure 2e).

Figure 3 demonstrates the fabricated doubly structures on our surface under SEM. The images reveal a well-defined array of microstructures on the substrate. The unique doubly re-entrant shapes were transferred with high fidelity, as confirmed in the angled bottom view (Figure 3b) and the cross-section (Figure 3c).

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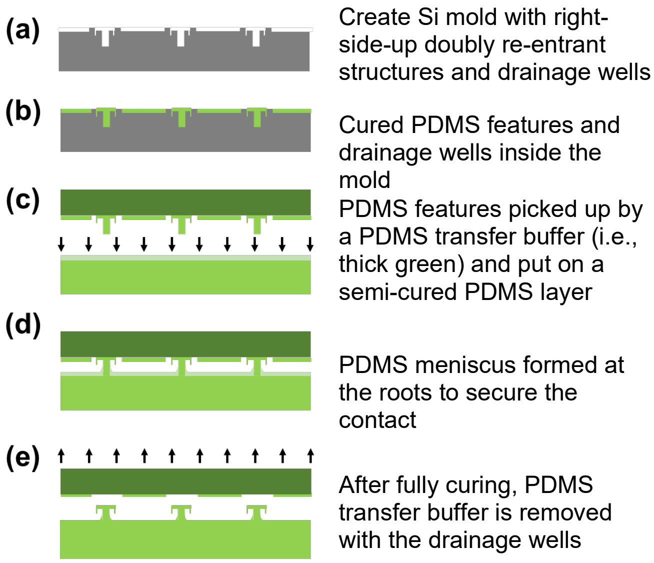

Figure 2. Schematic of the process flow.

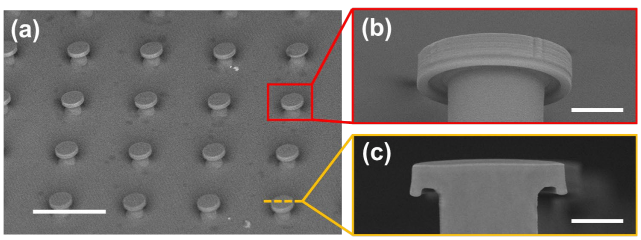

Figure 3. SEM micrograph of the fabricated surface. (a) Angled top view shows an array of doubly re-entrant structures. The scale bar is 100 µm. (b-c) Confirmation of high-fidelity doubly re-entrant structures from our process. *(b) Angled bottom view, and (c) Cross-section view of a single unit. The scale bars in (b) and (c) are 10 µm.*

EXPERIMENT

Contact Angle Measurement

Surfaces with doubly re-entrant surface structures have previously been shown to be super-repellent to any liquid [1]. Thus, we performed the contact angle measurements to verify whether our fabricated soft surfaces is super-repellent. The contact angles were measured at room temperature (~20°C) using an in-house built goniometer. To verify superomniphobicity, three different liquids with distinct surface tensions (γ) were selected: deionized water (DI water, γ = 72.8 mN/m), methanol (γ = 22.5 mN/m), and FC-72 (10.0 mN/m, i.e., lowest known [1]). The droplet was gently deposited by a syringe on the substrate. The static contact angles were measured to evaluate the repellency performance.

Mechanical Tests

To demonstrate the mechanical resilience to compression and abrasion, we built a testing setup to compress the units precisely on the doubly re-entrant units while we can monitor the mechanical loading and surface responses with a high-magnification microscopic observation. The setup apparatus is shown in Figure 4. The setup includes three parts: (1) linear stages movement control in X, Y, Z directions as well as rotating and tilting stages for better align the sample with the loading direction and visualization direction, (2) the testing surface was mounted on the rotating stage, facing to (3) the testing tip (i.e., a steel ball with a diameter of 2 mm). The microscope focuses on the top row of the surface structures, monitoring the testing tip approaching, compressing, and shearing the doubly re-entrant structures. Both vertical and horizontal loads were applied together to simulate a loaded abrasion test. The response of the microstructures was captured by a CCD camera.

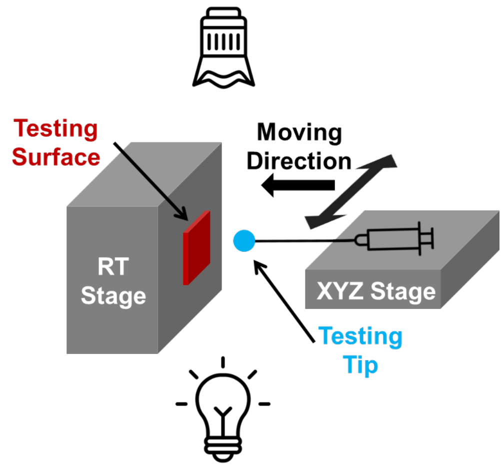

Figure 4. Mechanical testing setup is composed of (1) directional stages (X, Y, Z, Rotate, Tilt); (2) Testing surface to be observed and (3) Testing tip suspended by a fixed syringe. In this study, a steel ball was equipped to compress and shear the sample surface with the indicated moving direction. The dimensions are not to scale.

RESULTS AND DISCUSSION

We evaluated the liquid repellency using DI water, methanol, and FC-72. The contact angle results are shown in Figure 5. The surface enabled a static contact angle of 150° to DI water (Figure 5a), 135° to methanol (Figure 5b), and 121° to FC-72 (Figure 5c). The successful repulsion of FC-72 by our surface, which has the lowest surface tension on record, confirms the superomniphobic nature of the fabricated surface. This universal repellency serves as compelling evidence of the fabrication process's 100% yield, since even a single defective microstructure without the requisite doubly re-entrant topography would fail to repel FC-72.

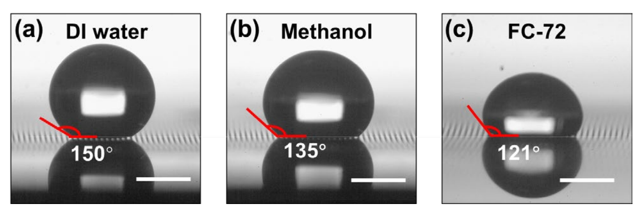

Figure 5. Liquid repellency tests on the fabricated surface using representative fluids covering the full spectrum of surface tensions. (a) DI water (γ = 72.8 mN/m), (b) methanol (γ = 22.5 mN/m), and (c) FC-72 (γ = 10.0 mN/m). The scale bars are 1 mm. These Cassie state (i.e., fakir) droplets with large contact angles confirm the superomniphobicity of the fabricated surface.

We studied the mechanical robustness of our surface by subjecting it to controlled stress along with microscopic observation. We used a steel ball to apply normal stress and shear stress. For normal stress (Figure 6a), the steel ball compressed the surface so that the doubly re-entrant surface structures were pushed flat against their base (0.0s – 5.8s). When the force was unloaded, the microstructures recovered to their original shape (5.8s – 8.8s). The yellow arrow indicates the loading direction. For shear stress (Figure

6b), the steel ball was dragged sideways across the microstructures before returning to shape. The green arrow indicates the abrasing direction. Figure 6c shows the close-up view of the notable recovery of a microstructure between 4.2s and 5.6s. As shown in the zoomed-in region, the doubly re-entrant structures were able to recover to their original shape even when the cap was folded and pushed into the soft substrate. These experiments demonstrated the elasticity and durability of the soft doubly re-entrant structures, resulting in the first-ever mechanically resilient omniphobic surface.

after normal stress was applied, causing them to bend and flatten

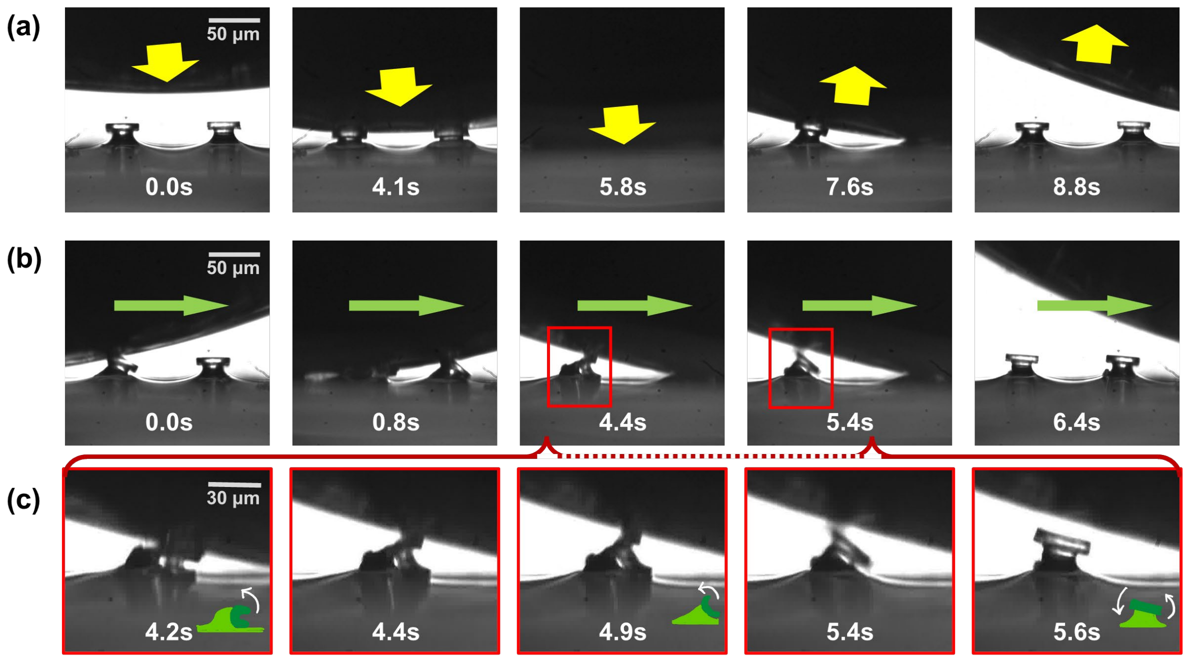

Figure 6. Mechanical tests of the microstructures with timestamps. (a) Normal stress (compression) was applied by using a steel ball that presses down in a nearly vertical direction, causing the collapse of the soft, doubly re-entrant structures. Yet, these structures rebounded to their original form upon release of the pressure. The trajectory of the steel ball is indicated by a yellow arrow. (b) Shear stress was induced by sliding the steel ball across the structures, leading to their bending, folding, and compression against the base. The direction of the ball's movement is denoted by a green arrow. (c) A zoomed-in close-up sequence of the microstructure's elastic recovery in (b). The inset drawings depict the recovery of the overhanging cap (dark green) and the support (shallow green). The white arrows indicate recovery directions.

CONCLUSIONS

In this paper, we reported a novel fabrication method that molds the right-side-up doubly re-entrant structures and transfers them to a target substrate to enable a durable omniphobic surface for the first time. Our method overcomes the challenges associated with soft lithography that uses molds with overhanging structures. The resultant surface demonstrated omniphobic properties by repelling the liquid with the lowest known surface tension and exhibited mechanical resilience under significant compression and abrasion. We anticipate this work to enable the manufacturing of surfaces with complex surface microstructures.

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