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Wetting and Active Dewetting Processes of Hierarchically Constructed Superhydrophobic Surfaces Fully Immersed in Water

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Abstract— When a superhydrophobic (SHPo) surface is fully submerged under water, the surface becomes wetted eventually and cannot recover the SHPo state naturally. In this article, we fabricate hydrophobic microposts on a hydrophobic nanostructured substrate, i.e., hierarchically structured SHPo surfaces, and investigate their wetting and dewetting processes while immersed under the water. All the micropost surfaces get wetted, with the conditions of the water only affecting the speed of wetting. All the nanopost surfaces get wetted over time after all the microposts on them are wetted. We demonstrate various active means (saturating air in the water; bridging the surface to the outside air; and gas generation on the substrate) that can dewet the already wetted microposts as far as the substrate nanoposts remained nonwetted. Particularly, the SHPo surfaces with the recently developed electrolytic recovery mechanism are shown to maintain a SHPo state even under previously irreconcilable conditions, such as surface defects and high liquid pressure, indefinitely.

Index Terms— Superhydrophobic, hierarchical surface, surface engineering, surface texture, dewetting

I. INTRODUCTION

Superhydrophobic surfaces

Inspired by the unique properties of lotus leaves [1] and encouraged by the possibility of engineering similar surfaces with microfabrication techniques [2], superhydrophobic (SHPo) surfaces have been the object of intensive research interests in various disciplines spanning chemistry, material science, and engineering [3]-[6]. Most of the early studies were to understand how a water droplet interacts with SHPo surfaces [7] and to fabricate them with different functionalities, e.g., a large sample area [8], optical transparency [9], or mechanical robustness [10]. In addition to the scientific interests with droplets, the recent studies have shown that the SHPo surfaces can also be useful for underwater applications (i.e., involving a continuous flow) by reducing frictional drag [11]-[18], promoting interfacial transport phenomena [19], and suppressing biofouling [20],

[21]. For instance, a giant liquid slip – large enough to affect even regular-scale fluidic systems – was obtained on optimally designed microstructures [14]-[16] and drag reduction by the surface slip was reported to be even higher for turbulent flows (~50% of reduction) [17]. Also, it was shown that biofouling activity could be suppressed on SHPo surfaces due to the reduced areas of contact with water [21].

Wetting of SHPo surface under water

Despite the above desirable properties for underwater applications, no SHPo surface was shown to demonstrate the nonwetting properties under water in realistic conditions. The SHPo surfaces with structural pitch in micrometers [11], [14], [15] would stay nonwetted only under low liquid pressure (e.g., < 2 kPa above ambient) for a limited time – valid only for laboratory tests. Those with structural pitch in nanometers [12], [13] may stay nonwetted under reasonable liquid pressures (e.g., > 10 kPa above ambient) but still for a limited time (< several hours). Under the water, the air layer held in between surface structures becomes unstable immediately by the liquid pressure or over time by gas diffusion, leading to the collapse of the air layer and the filling of the surrounding water in between the surface structures (i.e., wetting transition) [14], [22], [26]. While the wetting transition has been widely studied with droplets and puddles of liquids in air [27], it has rarely been studied under water, i.e., while completely submerged in the water, until recently. Although either thermodynamic energy minimum [28], [29] or force balance [30] can be applied to both the cases of in air and under water, the wetting transition under water is more complicated. For example, while the wetting transition in air was influenced primarily by the liquid pressure, the transition under water was highly influenced by the concentration of the dissolved gas in the surrounding liquid [25] and the dynamic condition (e.g., the liquid velocity) [24] as well as the liquid pressure [25], [26]. It is worth noting that hierarchical structures, which frequently exhibited extreme SHPo state against droplets in air, did not necessarily help prevent the wetting transition under the water. For example, a lotus leaf, known for its hierarchical morphology, became immediately wetted at mere 20 cm under the water and remained wetted even after it was taken out of the water [23].

Importance of liquid pressure for wetting

The systematic studies of the wetting transition under the

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water were recently conducted on several types of SHPo surfaces [25,26]. Without exception, the liquid pressure was shown to be a critically important factor for the occurrence of the wetting transition. Theoretically, the collapse pressure at which the wetting transition occurs is inversely proportional to the pitch of surface structures [30] ($\Delta P \sim \gamma / L$, ΔP : differential pressure of the liquid over the gas, γ : surface tension, L : structural pitch). In agreement with theoretical prediction, it was shown that the wetting transition occurred at the varying liquid pressure ranging from 5 kPa to 30 kPa above the ambient depending on microstructures [26]. It needs to be noted that most underwater applications (e.g., vessels, submarine) involve a much higher liquid pressure (e.g., > 100 kPa above ambient) than what have normally been tested under the laboratory conditions, implying that it would be more challenging to preserve a stable air layer in real applications. Even though the wetting transition by the high liquid pressure can be prevented by reducing the pitch of the structures down to nanometer scale [12], [13], the defense will be only temporary; the gas will be lost to the surrounding liquid by diffusion eventually, leading to the wetting of surface structures. In this diffusional wetting, the liquid pressure still plays a critical role, because a higher liquid pressure generally leads to the faster decay of air layer on SHPo surfaces [25]. Even though *Salvinia* leaves can hold a gas layer for a relatively long time (up to several weeks) [31], they normally reside in shallow water under a low liquid pressure (much less than 1 kPa above ambient), where the gas loss by diffusion was expected to be much slower than most underwater conditions.

Recovery of SHPo state under water

To date no SHPo surface has been reported to stay SHPo under water for an extended period (e.g., days) in practical conditions (e.g., a liquid pressure higher than 50 kPa above ambient). It is further suspected that such an ideal surface cannot even exist, because the loss of trapped gas to the surrounding liquid by diffusion is inevitable. Rather, practical approaches would be to actively replenish the gas as it is diffused out from the SHPo surface. The active approach would be more robust if also the surface can be dewetted, i.e., recover the SHPo state, even after it gets wetted, and it would be practical if the implementation of the approach is not too costly and does not consume too much energy.

Methods to recover the SHPo state under water have been reported most recently through an active means. By designing surface structures that make the gas spread on (rather than bubble off) the surface and implementing electrodes on the bottom surface, Lee and Kim [32] replenished the lost gas with an electrolytically generated gas. Such surfaces recovered the SHPo state from a fully wetted condition or withstood high water pressure (as high as 7 times the ambient pressure, i.e., 6 atm above ambient) indefinitely.

Consideration for drag reduction

Considered the most exciting underwater application of the SHPo surfaces has been reduction of skin friction. However, the drag reduction has never been proven in a realistic condition, because it requires that the surface maintains a SHPo state in the first place. For a structured hydrophobic surface to resist the wetting transition even for a short time, the surface structures need to be dense enough to withstand the liquid pressure. For a liquid pressure higher than 0.5 atm (~50 kPa or ~5 m of water) above ambient – a pressure commonly found in many applications, surface structures of a submicron pitch is needed [12], [13]. Unfortunately, while the resistance against wetting is inversely proportional to the pitch [30] ($\Delta P \sim \gamma / L$, ΔP), the slip length is proportional to the pitch ($\delta \sim L$) [33]. As a result, the surface structures with a submicron pitch – necessary to stay SHPo against a pressure – would induce a slip length around 200 nm [13], which is not large enough to benefit regular-scale flow systems. This dilemma can be overcome if the surface structures are built in a hierarchical way and an active means of gas recovery is used, as follows. Consider hydrophobic microstructures (i.e., primary structures) constructed on a substrate covered with hydrophobic nanostructures (i.e., secondary structures). After the primary structures get wetted under a liquid pressure, the secondary structures on the bottom surface can hold a gas layer against the pressure due to their small pitches and remain SHPo. The SHPo bottom surface will assist dewetting of the primary structures during the subsequent recovery phase. Meanwhile, the slippage effect depends only on the microstructures, as long as they are nonwetted; the nanostructures do not affect the amount of slip over the microstructures. Therefore, if a method of gas recovery is provisioned to a SHPo surface of hierarchical construction, the surface may possess both the resistance against liquid pressure and a large slippage effect.

The current study

In this article, we investigate the wetting and dewetting characteristics of hierarchical SHPo structures, built in the aforementioned way and proven capable of recovering the SHPo state under water [32]. Different ways to dewet a wetted surface are introduced: e.g., changing the environment outside the surface and generating gases inside structured surfaces. After presenting the fabrication of the hierarchically constructed surface structures integrated with patterned electrodes on the substrate and the rationales for the hierarchically constructed surfaces structures, wetting and dewetting of the surfaces are studied. We further show that our surface is functional even in two adverse conditions expected in engineering practices (i.e., high liquid pressure, defective surface).

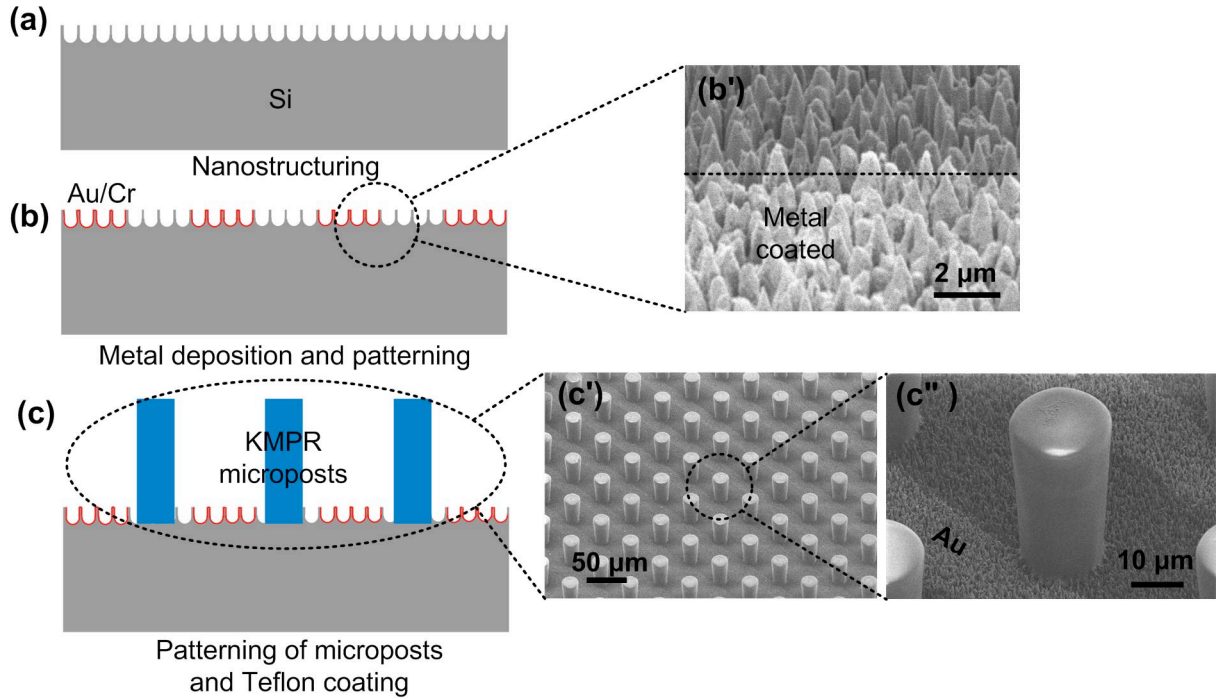


Fig. 1. Fabrication process of the hierarchical SHPo surfaces tested for underwater applications. (a) Nanoposts are formed on the silicon surface; (b) Au/Cr layer is deposited and patterned as electrodes for electrolysis; (b') SEM image shows the patterned metal electrodes on nanoposts; (c) Microposts are built on the nanostructured substrate out of a negative photoresist (KMPR), and all the surfaces are coated with a thin layer of Teflon AF; (c') SEM image of the completed hierarchical structures before Teflon coating; (c'') Magnified SEM image showing one micropost and the bottom surface.

II. EXPERIMENTAL DETAILS

Sample fabrication

To study dewetting, i.e., recovery of the SHPo state, under water, one has to supply a gas to the already wetted surfaces under the water. Although such a supplied gas has a strong tendency to form bubbles and leave off the microstructured surface, it can indeed form a stable gas layer if the microstructures satisfy certain geometric criteria [32]. For a square array of circular microposts, the geometric criteria can be expressed as the following [32]:

$$\frac{-\cos \theta_{h,rec}}{[2 \sin \theta_{p,rec} (1 - \sqrt{\pi(1-\phi)/\phi})]} > H/L > \frac{\sqrt{2} - 2\sqrt{(1-\phi)/\pi}(-1 + \sin \theta_{p,adv})}{2 \cos \theta_{p,adv}} \quad (1)$$

Here, ϕ , H , L , θ are the air fraction (i.e., $1 - \pi D^2 / 4$, where D is the diameter of post), height and pitch (i.e., center-to-center distance between posts) of the posts, and contact angle (CA), respectively. For the CA θ , the subscript *adv* and *rec* mean advancing and receding, and subscript p and b mean on the surface of the posts and on the bottom surface between the posts, all respectively. The above criteria are derived based on two conditions. The first condition is that the resistance against the spreading of gases in between microposts should be smaller than that against the growth of gases over the top surface of microposts (left inequality). The second condition is that there should be no premature destabilization of a gas film, i.e., the liquid-gas interface should not touch the bottom surface (right inequality).

Our target surface in this report consists of a square array of hydrophobic microposts, whose geometry (i.e., pitch, height and gas fraction) meets the above criteria, on a substrate covered with a random or square array of hydrophobic nanoposts. An overall fabrication process is shown in Fig. 1. First, in Fig. 1(a), we generated nanoposts on 4 in. Si wafer using two different methods: black silicon method and interference lithography. The black silicon method formed sharp nanoposts of random distribution with a typical height ranging between 1-5 μm and a typical pitch ranging between 0.5-1 μm . The process followed a specifically tuned recipe [2] to etch a blank Si substrate in deep reactive ion etcher (DRIE) for 40 min. The interference lithography and a subsequent DRIE process [8] generated a square array of nanoposts with ~ 250 nm height and 250 nm pitch. Due to its relative simplicity in fabrication, the black silicon method was used to fabricate most of the samples in the present study, while the interference lithography was used to prepare some of the samples tested for high liquid pressure, to be explained later.

After generating nanoposts on a silicon substrate, the electrodes for electrolysis were fabricated in Fig. 1(b), first by depositing 10 nm-thick Cr and 200 nm-thick Au layers successively on the substrate by electron-beam evaporator. Despite the high aspect ratio of the nanoposts, a positively tapered sidewall of nanoposts helped the coating as confirmed by SEM image in Fig. 1 (b') and conductivity measurement. Then, 8 μm -thick AZ 4620 photoresist was spin-coated and defined in the form of parallel lines by photolithography. The Cr/Au was then wet-etched to form a set of metal lines of 20 μm in width and 50 μm in pitch. The metal layer was patterned, anticipating that both the anode and cathode for

electrolysis may eventually be placed on the surface. The remaining photoresist was removed by acetone, methanol, deionized water rinsing, and O₂ plasma. Construction of microposts on the substrate full of Si nanoposts is depicted in Fig. 1(c). A negative photoresist (KMPR 1050, Microchem) was spin-coated and defined using photolithography. The photoresist became the final micropost structures of a fixed height (50 μm) and varying pitches (50 and 100 μm) and gas fractions (85, 90, 95, and 98%), as shown in Fig. 1(c') and Fig. 1(c''). To make all the surfaces hydrophobic, 2% Teflon AF (Dupont) solution was spin-coated on the wafer (thickness expected on the order of 200 nm on the flat surface), followed by a thorough rinsing with Perfluoro-compound FC-40TM (Acros Organics) to remove the excess Teflon especially on nanostructures. The thickness of Teflon was estimated to be 20-40 nm, based on an AFM study of identically processed Teflon on a flat surface. Most of the tests in this report used a sample cleaved out of the above-processed wafer to be 1.8 cm on a side.

Wetting experiments

The wetting and dewetting experiments were conducted using tap water without purification. In the present study, two different approaches were used to induce the wetting transition, i.e., nonwetting-to-wetting or Cassie-to-Wenzel transition, on the SHPo surfaces prepared above. The first approach was to subject the experimental setup to a moderate vacuum (1-2 kPa below ambient). Wetting was dependent on the resident time inside the vacuum environment, as expected. Once the vacuum (1-2 kPa below ambient) was applied, the microposts (used: 50 and 100 μm pitch and varying air fractions of 85, 90, 95, and 98%) started to get wetted immediately (and completed wetting the entire surface in 2-3 minutes), and the nanoposts (0.5-1 μm pitch and nominal air fraction over 95%) started to get wetted soon (~3 minute) after all the microposts were wetted (and completed wetting the entire surface in 3-4 minutes). Please note that the nanostructures started to be wetted only after the microposts were completely wetted. Once wetted, the surfaces did not recover the nonwetted state by removing the vacuum. In the present experiment, the resident time inside the vacuum environment was limited to less than 3 minutes to ensure that the microstructures were wetted but not the nanostructures. Similarly, it was possible to induce the wetting by placing the SHPo surface in water that had already been degassed, e.g., by vacuum over 3 minutes.

The second approach to wet the SHPo surfaces was to pressurize the surrounding liquid. The sample was placed inside a custom-made pressure chamber, which was filled with water and connected to a nitrogen tank. The liquid pressure was controlled in the range between 1 atm (i.e., ambient pressure) and 7 atm by regulating the pressure of the nitrogen gas above the water. The fact that one can wet the SHPo surface by either vacuuming or pressurizing indicates the frailness of the SHPo state under the water.

Dewetting experiments

Most of dewetting experiments, i.e., wetting-to-nonwetting or Wenzel-to-Cassie recovery, were conducted on a vibration isolation table under a 50-200x optical microscope connected to a video recorder. When electrolysis was used to generate the gas for dewetting, the Au electrodes on the nanostructured bottom surface and covered with a thin layer of Teflon were used as cathode generating H₂ gases, while a copper wire placed ~1 cm above the sample surface was used as anode. The operating voltage for electrolysis was fixed at 10 V, most of which was to overcome the resistance across the thin Teflon and through the electrical arrangement between the sample and the instruments.

III. RESULTS AND DISCUSSION

Wetting by gas diffusion

For all the experiments in this study, the samples were placed at the bottom of a laboratory beaker filled with a few centimeters of water. Under this small hydraulic pressure (much lower than 1 kPa above ambient), all the microposts on the SHPo surfaces remained nonwetted. However, the microposts (tested: 50 μm pitch, 90% air fraction) started to get wetted after several hours (and completely wetted in several days), as the trapped air was diffused out to the surrounding water, and the nanoposts at the bottom started to get wetted after the microposts were completely wetted. It is worth noting that, if the water had been degassed before the test, the wetting started much sooner: several seconds for the microposts (completed in several minutes) and several minutes for the nanoposts.

After the surface (microposts) was wetted, we were able to recover the nonwetted state by adding fresh tap (aerated) water to the degassed water, as far as the addition was done before the nanoposts got wetted, as shown in Fig. 2. The above experiments indicate that the wetting transition by gas diffusion is a direct manifestation of thermodynamic imbalance between the gas layer on the SHPo surfaces and the gas dissolved, usually not saturated, in the liquid. Numerous examples of wetting transition but almost no example of dewetting transition on SHPo surfaces under water support the natural tendency to lose the SHPo state and difficulty of recovering it. It may be possible to prevent the diffusional gas loss by controlling the gas concentration in the surrounding water, which is unfortunately impractical in most real applications.

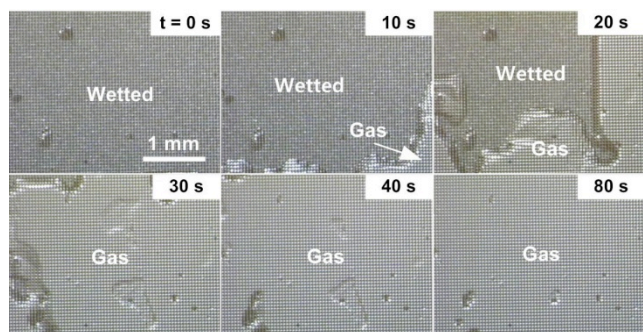


Fig. 2. Wetting and dewetting of the hierarchical surface (tested microposts: 50 μm pitch, 90% gas fraction) under water by gas diffusion. The sample had first been placed in degassed water, letting the air on the surface diffuse away and wetting all the microposts (entire surface) in two minutes. At 0 s, fresh (aerated) water was added to the beaker. With the air concentration of the water increased, dewetting has ensued, as shown, apparently because gas started to diffuse back into the surface structures.

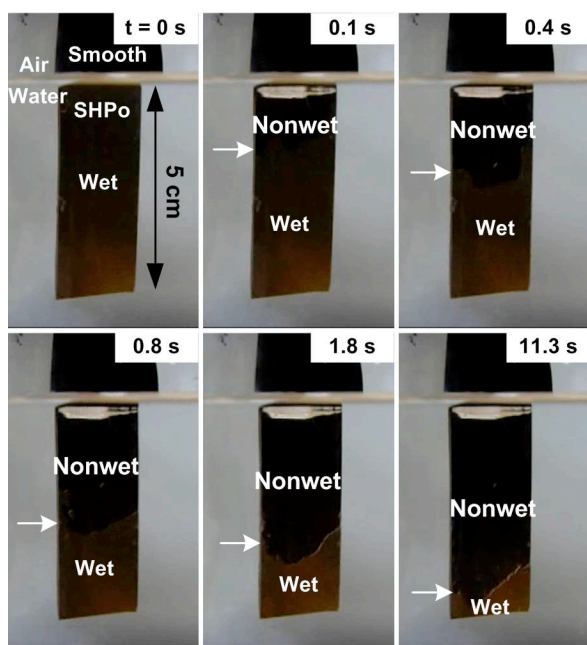


Fig. 3. Dewetting of the wetted hierarchical surface under water by entraining the outside air (tested microposts: 50 μm pitch, 90% gas fraction). The top part of the sample has a smooth surface, and the structured surface starts slightly below the water level. After making the surface structures wetted by subjecting the setup to a moderate vacuum, the sample was slowly raised. As soon as the top end of the structured region (wetted) was exposed to the air above water (between 0 and 0.1 s), air was entrained into the surface structures, initiating the dewetting. A thick silvery line on the SHPo surface right below the water surface (after 0.1 s) indicates an air-water interface connecting the outside air to the surface structures. The white arrows indicate the location of the advancing air front on the sample surface. Note the advancing is fast at beginning and slows down as the air front propagates deeper in the water.

Dewetting by breathing

Dewetting can be achieved, if there is a passage between the surface microstructures and an air source, e.g., the air outside liquid, as demonstrated in Fig. 3. For the sample in Fig. 3 (microposts: 50 μm pitch, 90% air fraction), the surface above the water was smooth, and the structured surface started

slightly below the water level. Note the entire structured area was submerged under the water before the test started. First, the SHPo surface was made wetted by subjecting the experimental setup to a vacuum. However, as soon as a part of the structured area was exposed to the outside air while pulling the sample up, air was suddenly entrained onto the structured surface (i.e., the microposts were dewetted) and started to propagate downward. It needs to be noted that, when the structured surface was exposed to the air (0.1 s in Fig. 4), a curved air-water interface (connecting the air outside the water to the surface structures) appeared as a thick silvery line on the sample surface right below the water surface. It was instructive that the dewetting slowed down as the gas film advanced deeper into the water and the hydrostatic pressure increased. How deep would the dewetting propagate by this breathing approach depends on the geometry of the microstructures.

In our test, the dewetting did not propagate deeper than 5 cm, which is consistent with the liquid pressure calculated to induce a wetting transition on the microposts (50 μm high, 50 μm pitch, 90% air fraction), i.e., ~ 0.5 kPa above the ambient. In any case, the above test suggests that it is possible to design indefinite SHPo surfaces for shallow-water applications.

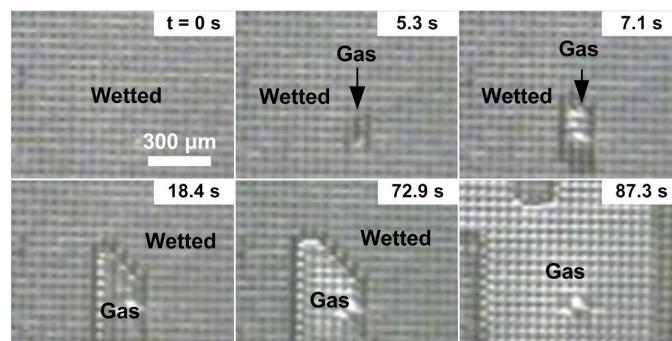


Fig. 4. Formation of a gas layer by electrolysis (microposts: 50 μm pitch, 85% gas fraction). Dewetting began with the nucleation of a gas (5.3 s), followed by the propagation of gas film into the surrounding area.

Gas generation

Unless the water is saturated with air, a gas needs to be actively provided to the surface in order to prevent the wetting by gas diffusion or recover an already wetted surface. Generally, gases can be made available by thermal, chemical, electrochemical, and pneumatic methods, among which we deemed the electrochemical the most suitable for our goal. As described in the experimental section, we could easily pattern electrodes on the substrate of the microposts. Compared with pneumatic methods, which would require a pump, feeding lines, and a source of gas, for example [34], generation of gases by electrolysis using the built-in electrodes and the surrounding water is much simpler. Compared with chemical methods, which would require specific combinations of materials that would be consumed, for example [35], the electrolytic method would be more practical. While thermal methods generate vapors, which would not only consume

significant energy [37] but also collapse as soon as the heat is removed, e.g., in a fraction of a second, the electrolysis generates gases, which would be dissolved into the water in hours [36]. Regarding the potential degradation of the metal electrodes for electrolysis under a corrosive environment (e.g., seawater), we note that electrodes will be protected from the corrosive environment by the gas layer most of the times. Moreover, electrolysis has been widely employed as a preferred gas generation method for drag reduction by microbubble injection [38]-[40] without any serious safety issues due to the generated gases.

Dewetting by electrolysis

After the microposts on the surface (but not the nanoposts on the bottom) were wetted inside the vacuum, 10 V was applied across two electrodes (cathode on the bottom surface, and anode inside the liquid pool) to initiate the electrolysis.

The dewetting process began with gas nucleation at random locations on the sample surface (microposts: 50 μm pitch, 85% air fraction), one of which is shown over time in Fig. 4. The nucleated gas (at 5.3 s) started to expand to the surrounding areas as a film by absorbing the generated gases from them, until it merged to the neighboring patches of gas films. This mode of gas film formation (i.e., preferential growth of a single large gas bubble) is due to the fact that gases on the surface are connected to each other via a residual gas layer on nanostructures. When a gas bubble is connected to smaller gas bubbles through a residual gas layer, gases inside smaller bubbles are transported to a larger bubble due to the pressure difference, resulting in the continuous growth of a single large bubble.

Time sequential images in Figs. 5 and 6 show the gradual propagation of a gas film on all the hydrophobic hierarchical surfaces fabricated for this report, starting with a wetted state over the entire surfaces and completing when the entire surfaces were dewetted. Fig. 5 shows the tests on the microposts with a fixed pitch of 50 μm and varying gas fractions of 85, 90, 95, and 98%. Fig. 6 shows the tests on the microposts with a fixed pitch of 100 μm and the same varying gas fractions. In both cases, dewetting was generally completed within several minutes. The process variation in the black silicon method caused the different color of each sample and probably also contributed to the difference in the total time required for dewetting. As a result, no direct correlation between the total time needed for dewetting and the gas fraction (i.e., the space to fill with a gas) was observed in the present study. During dewetting, the fluctuation of the liquid-gas interface on the microposts resulted in the color and darkness variation in the reflection, as shown best in Fig. 6(a).

A role of the nanostructured bottom

The above dewetting tests of Figs. 4-6 started after the entire area of the samples was wetted; they were the worst-case scenarios. It would take less time and energy to complete dewetting, if less area were wetted. During the wetting transition, usually the wetting starts on small regions

and propagates to the surrounding area.

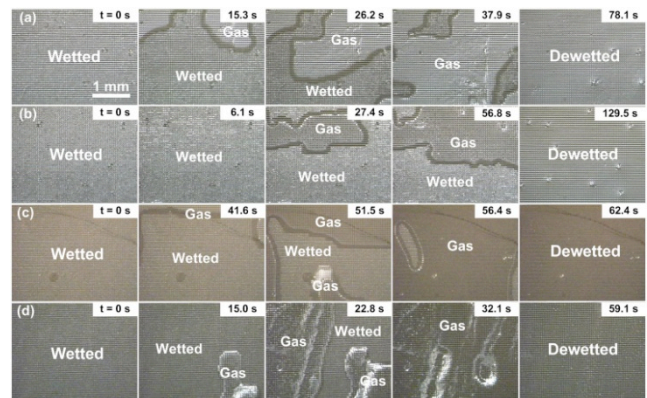


Fig. 5. Dewetting by electrolysis of microposts with a pitch of 50 μm and gas fractions of (a) 85%, (b) 90%, (c) 95%, and (d) 98%.

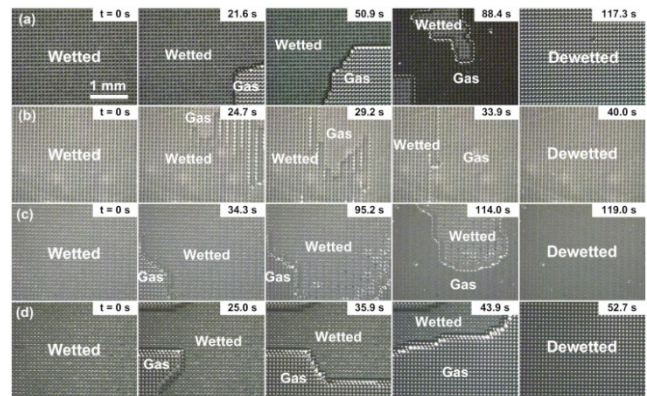


Fig. 6. Dewetting by electrolysis of microposts with a pitch of 100 μm and gas fractions of (a) 85%, (b) 90%, (c) 95%, and (d) 98%.

It would help if we can minimize the propagation when some spots get wetted perhaps accidentally. To test how wetting propagates on our hierarchically structured surface, we created a local wetting, as shown in Fig. 7(a), by jetting water onto the surface in a SHPo state with a syringe while immersed in water. While the jetted spot became wetted, the SHPo bottom surface resisted propagation of the wetting, and the wetted area did not increase over time. The same microposts on a smooth bottom would have seen the wetting propagate to the entire sample area. The confined wetted area easily recovered a nonwetted state by electrolysis within 20 seconds in Fig. 7(b), compared with the 60 seconds on the same geometry in Fig. 5(c). In addition to directing the gas to grow laterally between microposts for them to recover the nonwetted state (i.e., SHPo state) under water [32], the nonwetting nature of the nanostructured bottom (thus, SHPo on its own) prevented the wetting propagation across the microposts when wetting occurred locally.

Power consumption

Electrolysis on the reported surface is self-controlled, i.e., the electrolysis occurs only when the gas layer needs

additional gas without any external or feedback control.

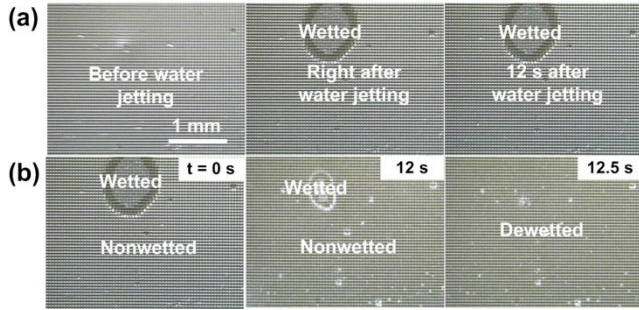


Fig. 7. The hierarchical surface resists against wetting propagation when locally wetted, rendering dewetting easier. (a) For the testing (microposts: 50 μm pitch, 95% gas fraction), the local wetting was induced by jetting water from a syringe under the water. The wetted area remained unchanged over time, as the SHPo bottom surface confined the wetted area from spreading. (b) When the electrolysis was initiated ($t = 0$ s), the small wetted area was subsequently dewetted.

If water wets any microposts and contacts the bottom surface under them, electrochemical circuits close and a gas is generated at the contact by electrolysis; when the gas covers the electrode, the circuit becomes open and the electrolysis stops. While this self-limiting, i.e., self-activating and self-terminating, electrolysis worked in principle, there was a leakage current through the substrate even after the surface restored the nonwetted state. The leakage current was significantly reduced by covering most of the substrate area outside the structured region with an adhesive tape to prevent the contact with the water, but the leakage was not completely eliminated in our current experiments. Although the electric current during the dewetting decreased (from 3 mA to less than 1 mA after the above passivation of the non-structured region), the leakage was still non-negligible (between ~ 0.1 mA and 1 mA). This corresponds to 2-8 mW input power per 1 cm^2 for dewetting process, and 0.2-2 mW additional power consumption 1 cm^2 due to the leakage. While the leakage calls for an improvement of experimental setup and procedure to accurately assess the power needed for the electrolytic recovery, it suggests the net power needed for the electrolytic dewetting is much smaller than the current measurement. Theoretically, i.e., based on Faraday's law of electrolysis, 40-50 mC (less than 1 mA when dewetting is completed in one minute) is needed to recover 1 cm^2 of the current sample surfaces from a wetted to a nonwetted state, corresponding to ~ 1 mW power consumption per 1 cm^2 when an activation voltage of 1.25 V is used for calculation.

Defective SHPo surfaces

To explore the implications of the electrolysis-assisted underwater SHPo surfaces in practical applications, we further tested dewetting under two simulated unfavorable conditions: defective surface and high hydraulic pressure. First, we artificially created defected areas, each 0.5 mm by 0.5 mm, by removing microposts in the area, as shown in Fig. 8. As some of the many foreign objects in the water will collide onto the

SHPo surface in applications and dense objects may cause damages, the SHPo recovery should reliably work in the presence of defects or at least the wetting on the defects should not propagate to the undamaged areas.

While the surface inside the defective area of missing posts gets wetted immediately under any liquid pressure, the wetting did not propagate to the adjacent non-defective area due to the SHPo bottom surface. The second image in Fig. 8, taken 5 s after the first image, shows no propagation of wetting. When electrolysis was initiated ($t = 0$ s), the defective region was covered with a gas layer, demonstrating the effectiveness of the electrolysis-based approach to overcome the surface defects. Of course, the defective areas will draw electric current continuously to remain covered with a gas.

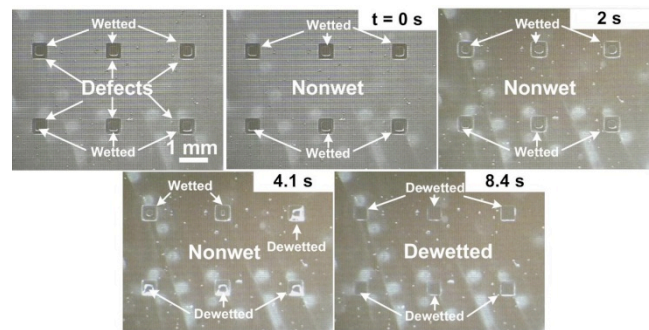


Fig. 8. Dewetting in the presence of defects (microposts: 50 μm pitch, 85% gas fraction), The wetted areas were confined to the defected areas due to the SHPo nature of the nanostructured bottom surface and did not spread to the surrounding area over time. The second image was taken 5 s after the first image and there was no noticeable change in the wetted area. When the voltage was applied ($t = 0$ s), the wetted area was easily dewetted by electrolysis.

Dewetting under pressure

The main disjoint between almost all the drag reduction research by the SHPo surfaces and the implementation to applications has been the existence of large hydrostatic pressure in most realistic situations. Here we elaborate how the electrolysis-based hierarchical surfaces, first presented by Lee and Kim [32], restore a gas layer under realistic liquid pressures. The approach was effective as long as the bottom surface remained SHPo, i.e., the nanostructures on the bottom was maintained nonwetting. In most of the current report (i.e., liquid pressure at 0-1 kPa above ambient) the nanoposts remained nonwetted after the microposts were wetted (the microposts began wetting at ~ 0.5 kPa above ambient). However, the nanoposts could be wetted too by pressurizing the liquid to 1.5-2 atm (i.e., 500-1000 kPa above ambient). Once the nanoposts were wetted, increasing $\theta_{b,rec}$ in Eq. 1 and tightening the recovery criteria, at activation of electrolysis spherical gas bubbles were formed instead of the desired gas film, as shown in Fig. 9, failing to dewet the surface. We have performed the dewetting tests under the highest pressures we could apply that wetted the microposts but not the nanoposts: between 1.4 atm and 1.7 atm. As the liquid pressure was

increased, the wetting occurred on some locations and started to propagate. Note that only the microposts became wetted during the experiment. When the power was turned on to start the electrolysis, the surface was dewetted in much the same way as Figs. 5 and 6 over 2-4 minutes, slower because more gas has to be generated to fill the same volume under a higher pressure. In addition, we have tested the same microposts on the nanoposts made by the interference lithography (Fig. 1(a-2)), which have an exact pitch of 0.25 μm . Since these nanoposts were more stable due to their smaller pitches, we were able to apply higher pressures to wet the microposts without wetting the nanoposts: between 3 atm and 4 atm. We have obtained the same success with this sample in dewetting the wetted microposts although even slower (more than 5 minutes) due to the higher compression.

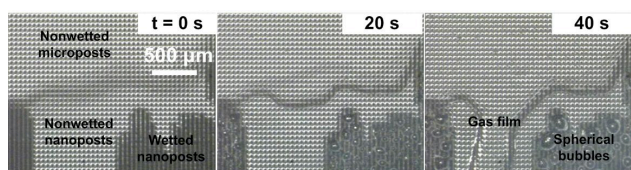


Fig. 9. Gas generation by electrolysis when some of the nanoposts are wetted (by an intentional liquid pressure of 700 kPa above ambient, i.e., 1.7 atm). While a gas film was formed on nonwetted nanoposts, spherical bubbles were formed on the wetted nanoposts.

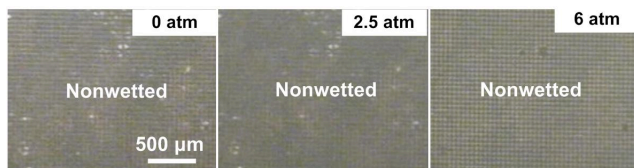


Fig. 10 The developed SHPo surface remained nonwetted under the water of an increasingly high pressure, when the voltage was kept on - tested up to 7 atm.

Staying SHPo under a high pressure

So far, we have considered rather pessimistic situations, i.e., recovering the nonwetting state after the microposts were already wetted, to be conservative in evaluating the developed SHPo surfaces. However, a more common scenario would be the surfaces maintaining a SHPo state most of the times and encountering problems (e.g., surface damage) occasionally on some spots. Under this condition of no intentional wetting, the microposts would recover the SHPo state by the electrolysis as soon as they get wetted, and the nanoposts on the bottom would not encounter the danger of getting wetted. This much-relaxed condition allowed us to test much higher liquid pressures, as shown in Fig. 10. Note that, even if there was no loss of mass, the gas on the SHPo surface was compressed when the liquid pressure increased. The resulting reduction of gas volume was continuously replenished by the electrolytically-generated new gas. Since the gas generation continued until the gas pressure balanced with the increasing liquid pressure, the surface remained SHPo under liquid pressures much higher than all the tests so far. Fig. 10 shows the surface remaining nonwetted at very high liquid pressures

(up to 7 atm, only limited by the maximum pressure of the nitrogen gas used). Note the nanoposts (made by the black silicon method) could not have withstood such high liquid pressures if the microposts were wetted. Incidentally, we could not observe the wetting and recovery cycles, perhaps because the cycles were too fast to visualize or electrolysis occurred through the moisture inside the gas layer, calling for future studies. As expected, this approach was effective only when the gas generation could catch up with the volume loss by the increasing pressure (0.5 atm/min in the present case). When the pressure was increased too fast (e.g., more than 1 atm/min), the wetting ensued on the surface.

IV. CONCLUSIONS

We have investigated the wetting and dewetting processes of the hydrophobic hierarchical surface structures (microposts on nanoposts) fabricated to meet the recently reported criteria for a gas recovery under water. While the wetting occurs naturally, the dewetting was obtained by active means. In the given configuration of surface structures, the nanoposts on the bottom confer the high contact angle and resistance against the wetting under the liquid pressure – the two properties required to dewet the wetted microposts, while the microposts provide a large slippage effect, which is crucial for drag-reduction application. On the tested surfaces, dewetting could be achieved by various active means, such as: increasing air concentration in the water; bridging the structured surface to the air outside the water; and generating gases from the bottom surface using electrolysis. In particular, with electrolysis, it was possible to maintain the SHPo state in near-real environment such as defected surfaces and high liquid pressure. Still, there are several issues to be addressed for practical SHPo surfaces. First, with electrolysis, the SHPo surface was found degrading after several hours of operation, such as the Teflon on nanostructures getting delaminated. Also, there still remain the practical issues such as the manufacturability of the presented surface on a large scale and the effective placement of both electrodes on the surface. We present our findings to help ameliorate the design of SHPo surfaces for underwater applications and bring the potentials of SHPo surfaces to reality. Our results suggest that it is feasible to design structured surfaces that can retain the SHPo state for a long time even under the challenging underwater conditions.

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