Substrate-Independent, Fast, and Reversible Switching between Underwater Superaerophobicity and Aerophilicity on the Femtosecond Laser-Induced Superhydrophobic Surfaces for Selectively Repelling or Capturing Bubbles in Water

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ABSTRACT: In this paper, the reversible switching between underwater (super-) aerophilicity and superaerophobicity was achieved on various femtosecond (fs) laser-induced superhydrophobic surfaces. A range of materials including Al, stainless steel, Cu, Ni, Si, poly(tetrafluoroethylene), and polydimethylsiloxane were first transformed to superhydrophobic after the formation of surface microstructures through fs laser treatment. These surfaces showed (super-) aerophilicity when immersed in water. In contrast, if the surface was prewetted with ethanol and then dipped into water, the surfaces showed superaerophobicity in water. The underwater aerophilicity of the superhydrophobic substrates could easily recover by drying. The switching between the underwater aerophilicity and superaerophobicity can be fast repeated many cycles and is substrate-independent in stark contrast to common wettability-switchable surfaces based on stimuli-responsive chemistry. Therefore, the as-prepared superhydrophobic surfaces can capture or repel air bubbles in water by selectively switching between underwater superaerophobicity and aerophilicity. Finally, we demonstrated that the underwater bubbles could pass through an underwater aerophilic porous sheet but were intercepted by an underwater superaerophobic porous sheet. The selective passage of the underwater bubbles was achieved by the reversible switching between the underwater aerophilicity and superaerophobicity. We believe that this substrate-independent and fast method of switching air wettability has important applications in controlling air behavior in water.

KEYWORDS: bubble wettability, underwater superaerophobicity, underwater superaerophilicity, switchable wettability, femtosecond laser

1. INTRODUCTION

Recently, smart surfaces with switchable wettability have attracted broad interest because they can selectively exhibit different and even inverted superwetting states.1–4 Such materials can reversibly switch their static and dynamic wettabilities by responding to different external stimulations, such as temperature,5–10 light,11–18 pH,19–23 electrical potential,24–29 and magnetic field.27–29 The wettability-switchable surfaces are generally prepared by modifying rough microstructures with stimuli-responsive molecules or directly generating surface microstructures on stimuli-responsive materials.3–5 For example, Sun et al. grafted the thermoresponsive poly(N-isopropylacrylamide) molecules onto a micro/nanostructured silicon substrate.5 When the ambient temperature increased from 25 to 40 °C, the wettability of the resultant surface could change from superhydrophilicity to superhydrophobicity. Cheng et al. prepared hierarchical microstructures on a copper sheet through chemical corrosion.23 The rough surface was modified by –CH3 and –COOH groups. Carboxyl group can respond to the pH of the aqueous solution, so the underwater oil wettability of the sample surface could be switched by the alteration of the water pH. The surface showed superoleophobicity in alkaline water and superoleophilicity in acidic water. Stratakis et al. grafted pH-responsive poly(2-(diisopropylamino)ethyl methacrylate) brushes onto the laser-structured rough substrate using surface-initiated atom transfer radical polymerization.30 The resultant surfaces showed superhydrophilicity following the immersion in solution at pH 2.5 and superhydrophobicity following the immersion at pH 8.5. Feng et al. observed the reversible transformation between superhydrophobicity and superhydrophilicity on the arranged ZnO nanorods array.31 The water
droplets on the structured surface had the contact angle (CA) of 161.2°, whereas the CA decreased to 0° after UV irradiation for 2 h. When the UV-irradiated sample was stored in a dark environment for 7 d, the surface could reobtain the superhydrophobicity. Our group achieved switchable underwater superoleophobicity—superoleophilicity on the laser-structured TiO2 surface through alternate UV irradiation and dark storage.12 Jiao et al. created multiscale TiO2 square micropillars on a titanium surface by femtosecond (fs) laser treatment.32 The original sample showed superaerophobicity in water, whereas it became underwater superaerophilic after heating in a dark environment for 0.5 h. After irradiated by UV light for 1 h, the sample could recover its underwater superaerophobicity. Such switchable bubble wettability is ascribed to the chemical conversion between Ti−OH and Ti−O. Shi et al. prepared different minigenerators and achieved electricity generation by reversible change of air bubbles.33,34 Although a large number of wettability-switchable surfaces have been developed, their switching ability mainly depends on the stimuli-responsive chemistry of the inherent substrates or the extra coatings.1−3 That is, the switchable wettability can only be achieved on some special stimuli-responsive substrates. For a common surface without stimuli-responsive chemistry, it cannot change surface wettability by responding to external stimulation (e.g., temperature, light, pH, electrical potential, and magnetic field). In addition, the wettability-switching cycle of those reported smart surfaces usually needs a long time (even several days). The substrate-dependent drawback and the slow response greatly limit the practical applications of those wettability-switchable surfaces based on the stimuli-responsive chemistry. Taking into account the widely practical applications, developing a substrate-independent and fast method for achieving switchable wettability remains a major challenge.

In this paper, the reversible switching between underwater (super-) aerophilicity and superaerophobicity was achieved on the fs laser-induced superhydrophobic substrates. After the formation of surface microstructures, different kinds of substrates were transformed to ultralow adhesive superhydrophobicity. These surfaces originally showed (super-) aerophilicity in water. By contrast, if the surfaces were prewetted with ethanol, the surfaces would turn to superaerophobicity after immersion in water. The fast switching between underwater (super-) aerophilicity and superaerophobicity is reversible and substrate-independent through alternate prewetting and drying treatments. We further demonstrated that underwater bubbles could pass through an underwater aerophilic porous sheet. On the contrary, the bubbles were intercepted by an underwater superaerophobic porous sheet. Finally, a strategy for removing bubbles in a water pipe was proposed.

2. EXPERIMENTAL SECTION

2.1. Laser Treatment. Fs laser treatment was used to prepare surface microstructures on different substrates. The substrate materials (including Al, stainless steel, Cu, Ni, Si, poly(tetrafluoroethylene) (PTFE) and polydimethylsiloxane (PDMS)) were fixed on a mobile platform. The fs laser beam (center wavelength = 800 nm, pulse width = 67 fs, and repetition rate = 1 kHz) was focused on the sample surfaces through a plano-convex lens (focal length = 250 mm). The samples were ablated by both the horizontal and vertical line-by-line scanning. The laser power was set at 500 mW, the scanning speed was 1 mm/s, and the space of the scanning lines was 100 μm. After laser treatment, the samples were carefully cleaned with ethanol and distilled water.

2.2. Reducing the Surface Free Energy. Superhydrophobicity can be directly obtained on the hydrophobic poly(tetrafluoroethylene) (PTFE) and polydimethylsiloxane (PDMS) surfaces by the fs laser treatment. Regarding the inherently hydrophilic substrates (Al, stainless steel, Cu, Ni, and Si), they need to further reduce the surface free energy to achieve superhydrophobicity after laser ablation. The typical fluoroalkylsilane modification was adopted here. The laser-ablated samples were immersed in a 1% fluoroalkylsilane (1H,1H,2H,2H-perfluorodecyltriethoxysilane) solution (in ethanol) for 1 day. Then, the samples were rinsed with ethanol to remove the excess fluoroalkylsilane molecules and heated at 100 °C for 1 h.

2.3. Characterization. The surface microstructures of the fs laser-treated substrates were observed by a scanning electron microscope (SEM, S-4100, Hitachi, Japan). The water and underwater bubble wettabilities of the resultant surfaces were investigated via a contact-angle measurement (SL2000KB, Kino). Regarding the underwater bubble wettability, the samples were fixed in a homemade container filled with water in advance. The average contact angles and sliding angles were measured in at least three different positions on a sample surface. The drying treatment was performed by blowing the samples with a high-pressure air duster (CompuCleaner 2.0, EasyGo).

3. RESULTS AND DISCUSSION

The features such as the extremely short pulse width and the ultrahigh peak intensity enable the fs laser pulses to ablate various kinds of materials and then directly build microstructures on different substrates.35−38 Figure 1a−d shows the surface morphology of an Al sheet after fs laser processing. The surface presents a micro/nanoscale hierarchical structure. There are many uniform microscale caves and wavy ridges on the resultant surface (Figure 1a,b). The top of every ridge is

Figure 1. Surface microstructure and water wettability of the fs laser-ablated Al surface. (a−d) SEM images of the Al surface after laser processing. (e) Water droplet on the superhydrophobic Al surface. (f) Water droplet rolling off a 6.5° tilted surface.
characterized by coral-shaped microstructures (Figure 1c). The coral is about several micrometers in size, and its surface is further covered by abundant nanoparticles with the diameter of tens of nanometer (Figure 1d). After the fluoroalkylsilane modification, the as-prepared Al surface became superhydrophobic. The water droplet on the surface had a water CA (WCA) of 157 ± 1.5° (Figure 1e). In addition, the water droplet could roll off as the substrate was tilted at 6.5 ± 1.5°, indicating ultralow adhesion between the droplet and the superhydrophobic Al surface (Figure 1f and Movie S1 in the Supporting Information).

The underwater bubble/air wettability of the fs laser-induced superhydrophobic Al surfaces was measured through immersing the samples in water and dispensing a small bubble onto the sample surfaces. In water, as a bubble came in contact with the resultant Al surface, the bubble would rapidly spread out on the sample surface (Movie S2, Supporting Information). The bubble CA (BCA) was finally only 6 ± 2.4°, so the original superhydrophobic Al surface showed underwater superaerophilicity (Figure 2a). Interestingly, the bubble wettability can be simply switched from underwater superaerophilicity to superaerophobicity. The superhydrophobic Al surface needs to be prewetted by ethanol before immersion in water. A mirror-like reflective interface could be observed when the original superhydrophobic Al surface was submerged in water, demonstrating that a trapped air layer existed between the water and the sample surface (Figure 2e). However, no mirror-like reflection appeared when the ethanol-wetted superhydrophobic surface was put in water because the surface microstructure was completely wetted by water (Figure 2f). The prewetting treatment was performed by dripping some ethanol droplets onto the laser-ablated area (Figure 2b). Then, the sample was put in water, and a bubble was released onto the sample surface after 1−2 min. As shown in Figure 2c, the bubble kept a sphere shape with the BCA of 154.9 ± 1.4°. If the surface was slightly vibrated or tilted to 1.8 ± 0.3°, the bubble would roll off easily (Figure 2g and Movie S3 in the Supporting Information). At present, the as-prepared surface exhibited superaerophobicity and extremely low adhesion to the bubbles in water. The sample surfaces can always remain the underwater superaerophobicity as long as it is stored in water.

The superhydrophobicity of the structured Al surface could recover if the wetted sample was taken out of water and dried by the high-pressure gas (Figure 2d). The drying process only need about 3 min. At present, once the surface was submerged in water again, it could reobtain underwater superaerophilicity (Figure 2a). Therefore, the switching between underwater (super-) aerophilicity and superaerophobicity on the laser-induced superhydrophobic Al surface is reversible. Such

Figure 2. Reversible switching between underwater superaerophilicity and superaerophobicity on the laser-structured superhydrophobic Al surface. (a) Underwater bubble on the as-prepared surface. (b) Prewetting the sample surface with ethanol droplets. (c) Underwater bubble on the prewetted surface. (d) Water droplet on the as-prepared surface after being taken out of the water and dried by the high-pressure gas. (e, f) Photos of the samples in water: (e) the original superhydrophobic surface and (f) the ethanol-pre-wetted surface. (g) Process of a bubble rolling off the underwater superaerophobic surface.
switching can be repeated many cycles by the alternant prewetting and drying treatments, as shown in Figure 3. A cycle of the switching between underwater (super-) aerophilicity and superaerophobicity needs no more than 5 min, which is much shorter than that of Wu’s work (~1.5 h).\textsuperscript{32} It should be noted that the underwater superaerophilicity could not perfectly recover by just short-time drying treatment after two switching cycles, because the water deep-inside the surface microstructure is difficult to be completely removed by the high-pressure wind. Alternatively, the bubble wettability can restore the aerophilic state with the BCA smaller than 30° (Figure 3). Such level of aerophilicity is enough for the substrate to absorb bubbles. The underwater superaerophobic surface has the ability to repel bubbles, whereas the underwater aerophilic surface can capture bubbles in water. As a result, the as-prepared superhydrophobic surface has both functions of the repelling or capturing bubbles by selectively switching underwater superaerophobicity and aerophilicity.

The alternant prewetting and drying treatments are important for the switchable bubble wettability. The original resultant surface shows ultralow adhesive superhydrophobicity. The touch between the water droplet and the sample microstructure is the Cassie contact state.\textsuperscript{48} As shown in Figure 4a, the water droplet only touches the top part of the microstructure, and a layer of air is formed underneath the droplet. As the superhydrophobic surface is dipped into water, the water is unable to wet the surface microstructure. As a result, a layer of air remains between the surface microstructure and the water (Figures 2e and 4c). If an underwater bubble is in contact with the sample, the gas in the bubble will easily

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**Figure 3.** Reversibility and repeatability of the switching between the underwater (super-) aerophilicity and superaerophobicity.

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**Figure 4.** Mechanism of the switching between the underwater superaerophilicity and superaerophobicity. (a) Water droplet on the superhydrophobic microstructure. (b) Prewetting the surface microstructure with ethanol droplets. (c, e, g) Formation of the underwater superaerophilicity of the superhydrophobic microstructure: (c) the superhydrophobic microstructure in water, (e) dispensing a bubble onto the microstructure, and (g) after some time. (d, f, h) Formation of the underwater superaerophobicity of the prewetted microstructure: (d) the prewetted microstructure in water, (f) dispensing a bubble onto the microstructure, and (h) after some time.
enter into the air layer around the laser-structured area (Figure 4e). As the gas in the bubble spreads out along the space between the surface microstructure, the gases in the trapped air layer and in the bubble finally merge together. The bubble looks like being absorbed by the superhydrophobic surface. Therefore, the surface shows superaerophilicity in water.

Conversely, once the surface is prewetted with ethanol before dipping into water, the space of the surface microstructure is occupied by ethanol in advance (Figure 4b). When the sample is instantly submerged into water, the ethanol layer will disperse in water in a short time (1−2 min). The ethanol layer is replaced by the water, and the surface

Figure 5. Switchable underwater (super-) aerophilicity and superaerophobicity on different laser-induced superhydrophobic substrates: (a) stainless steel, (b) Cu, (c) Ni, (d) Si, (e) PTFE, and (f) PDMS. First column: the SEM images of the laser-ablated substrates; second column: water droplets on the sample surfaces in air; third column: bubbles on the as-prepared superhydrophobic surfaces in water; fourth column: bubbles on the prewetted surfaces in water.
microstructure is fully wetted by water (Figure 4d). In this case, the underwater bubble that is placed on the sample surface is repelled by the trapped water filled in the surface microstructure (Figure 4f). The incompatibility between air and water leads to such repulsive force. The bubble contacts just the peak of the surface microstructure, agreeing well with the underwater version of the Cassie contact state (Figure 4f).48 The bubble has to maintain a spherical shape ever after some time (Figure 4h). Therefore, the ethanol-pre-wetted superhydrophobic surface exhibits underwater superaerophobicity. As long as the prewetted superhydrophobic surface is stored underwater, the trapped water layer will not disappear, so the surface always has underwater superaerophobicity in water. By taking the sample out of water and drying treatment, the sample is able to reobtain its original superhydrophobicity (Figure 4a) as well as the underwater superaerophicity (Figure 4g).

Ethanol was used to prewet the laser-induced superhydrophobic microstructures in this experiment, because it is a common liquid in lab and in our daily life with low cost and nontoxic. Furthermore, it has a very low surface tension and can easily dissolve in water. Besides ethanol, a variety of other liquids (e.g., some common organic solvents (acetone, methanol, isopropanol, etc.)) are also able to prewet the sample surface and switch the surface to underwater (super-) aerophobicity after immersion in water. Those prewetting liquids must have two properties: (a) extremely low surface tension and (b) soluble in water. Extremely low surface tension allows the liquid to wet the superhydrophobic microstructures in air. The space between the surface microstructures of the prewetted sample is occupied by such liquid. When the sample is further immersed in water, the prewetting liquid layer will gradually dissolve in water, and the original location of the prewetting liquid layer will be replaced by water. Finally, the space between the surface microstructures is occupied by water. It looks like that the superhydrophobic microstructures are fully “wetted” by water in a water medium, so the prewetted superhydrophobic surfaces exhibit underwater (super-) aerophobicity.

The reported method for achieving switchable underwater superaerophobicity—aerophilicity is independent of the stimuli-responsive chemistry of the substrates. As shown in the first column of Figure 5, rough surface microstructures can be created on the surfaces of different materials by the same fs laser treatment, such as stainless steel, Cu, Ni, Si, PTFE, and PDMS. All of these as-prepared surfaces have superhydrophobicity and ultralow water adhesion (see second column in Figure 5). If the surfaces were directly dipped into water, the surfaces would show underwater superaerophilicity or aerophilicity (third column in Figure 5). By contrast, when the surfaces were prewetted with ethanol and then immersed in water, the substrates became superaerophobic in water (fourth column in Figure 5). Regarding the as-prepared superhydrophobic Cu, Ni, Si, and PTFE surfaces, the prewetting treatments were performed by immersing the samples in ethanol assisting with an ultrasonic process, because

Figure 6. Selective passage of bubbles through the superhydrophobic porous sheet in water. (a–c) SEM images of the laser-ablated porous sheet. (d) Bubbles passage of the underwater superaerophilic porous sheet. (e) Schematic diagram of the bubbles-passage ability. (f) Bubbles interception of the underwater superaerophobic porous sheet. (g) Schematic diagram of the bubbles-intercepting ability.
After further being modi-
slightly tilted, the bubbles could roll o
sample surfaces were larger than 150
Strategy of removing bubbles in a water pipe by combining the underwater superaerophilic and superaerophobic porous sheets.

Figure 7. Strategy of removing bubbles in a water pipe by combining the underwater superaerophilic and superaerophobic porous sheets.

By combining with the through-holes microstructures, the fast and reversible switching between the underwater (super-) aerophilicity and superaerophobicity can be utilized for controlling the passage of the underwater bubbles. For example, both sides of a porous stainless steel sheet with through microholes (diameter of 0.4 mm) array were ablated by fs laser to form rough surface microstructures (Figure 6a–c). After further being modified with fluoroalkylsiline, the surfaces of the porous sheet had superhydrophobicity. Figure 6d shows the process of continuously dispensing gas bubbles below the resultant superhydrophobic porous sheet in water. Because of the underwater superaerophilicity, the bubbles were easily absorbed by the structured porous sheet as the bubbles reached to the lower surface of the sheet. Then, the bubble was able to bulge from the upper surface of the porous sheet. With absorbing bubbles, the air bulge growth gradually until its buoyancy could overcome the adhesion caused from the sheet. Finally, the air bulge detached from the porous sheet, rising up as a new big bubble. As a result, the bubbles easily passed through the underwater superaerophilic porous sheet (Movie S4, Supporting Information). The principle of bubble passage is schematically depicted in Figure 6e. Since the sheet is superhydrophobic, air is trapped in the surface microstructures of both sides of the sheet after immersing it into water. Such air layer connects the lower and the upper side of the sheet through the microholes. When a bubble rises up and touches the lower side of the sheet, the air in the bubble can enter into this trapped air layer freely due to the underwater superaerophilicity; that is, the porous sheet can absorb this bubble. With more and more bubbles being absorbed by the sheet, the pressure of the air layer increases and can lift the water from the sheet’s upper side at some point. Therefore, an air bulge appears on the upper side of the sheet, and its volume is increasing with bubbles reaching to the porous sheet. Finally, the buoyancy of the air bulge is higher than the adhesive force between the air bulge and the sheet, so the air bubble leaves the porous sheet and rises up. The underwater (super-) aerophilic porous sheets can allow all of the bubbles to pass through.

The superhydrophobic porous sheet can allow underwater bubbles to pass through because of the continuous air layer trapped on the porous sheet in a water medium. The stability of the trapped air film is greatly influenced by the pore diameter of the sheet, the submergence depth in water, the surface wettability, and the surface tension of the aqueous media. It is revealed that the intrusion pressure of the superhydrophobic pores in water increases with the decrease of the pores diameter.49 Smaller diameter of the micropores results in a higher intrusion pressure, enabling the superhydrophobic porous sheet to have a large depth of submergence and high stability.

The superhydrophobic porous sheet was underwater superaerophobic when it was prewetted with ethanol and then dipped into water. The underwater superaerophobic porous sheet has the bubble-intercepting ability in water. When the bubbles that were dispensed below the sheet reached to the lower side of the underwater superaerophobic porous sheet, all of the bubbles were intercepted, and no one could pass through the sheet successfully (Figure 6f and Movie S5 in the Supporting Information). The bubbles could only contact with each other and merge into a bigger one on the lower side of the sheet. The bubble-intercepting ability is caused by the underwater superaerophobicity of the porous sheet. As shown in Figure 6g, the prewetted porous sheet is completely wetted by water in a water medium. No matter the space between the surface microstructures or the through microholes are filled with water. The water filling in the microholes is able to block the bubbles from passing through the microholes. Therefore, the bubbles are unable to pass through the sheet because of the gas repellency of the underwater superaerophobic sheet.

The selective passage of bubbles through the as-prepared underwater superaerophilic–superaerophobic porous membrane can be used to exclude bubbles from the water pipes or microfluidics system. The bubbles in those systems will potentially cause local resistance, big fluid frictional loss, and even blockage. Figure 7 shows a proof-of-concept strategy of removing bubbles from the water flow in a pipe. The as-prepared porous sheet that is prewetted and then exhibits underwater superaerophobicity is perpendicularly fixed inside the pipe. The microholes are wetted by water and filled with water, so water is able to flow through the microholes. By contrast, the underwater superaerophobicity does not allow the bubbles in the water flow to penetrate through the porous sheet. The bubbles are stopped by the sheet. On the other
hand, a big through hole is made on the wall of the pipe, and the hole is covered by a porous sheet with both superhydrophobicity and underwater superaerophobicity. Water in the pipe cannot leak out of the pipe due to the superhydrophobicity of the sheet. Interestingly, the intercepted gas is able to cross the superaerophilic porous sheet. As a result, the bubbles in the water flow are removed by the combination of the underwater superaerophilic and superaerophobic porous sheets.

4. CONCLUSIONS

A substrate-independent method to achieve reversible switching between underwater (super-) aerophilicity and superaerophobicity on the laser-structured superhydrophobic surfaces is reported. After laser processing and subsequent fluoroalkylsilane modification, the resultant Al surface possessed ultralow adhesive superhydrophobicity. When such surface was immersed in water, the surface showed superaerophobicity with the BCA of 6 ± 2.4°. The underwater superaerophobic surfaces are able to capture bubbles in water. In contrast, the as-prepared superhydrophobic surface showed underwater superaerophobicity with the BCA of 154.9 ± 1.4° if it was prewetted by ethanol and then dipped into water. The underwater superaerophobic surfaces have the bubble-repellent ability. After taking out of water and drying treatment, the sample could recover to its original superhydrophobicity and underwater (super-) aerophilicity. Such reversible switching between underwater (super-) aerophilicity and superaerophobicity could be repeated many cycles by alternating prewetting and drying treatments. A cycle of the switching needs no more than 5 min. The laser-induced superhydrophobic surfaces can selectively exhibit underwater superaerophobicity or aerophilicity. With the same method, the switchable bubble wettability was also achieved on other laser-Induce superhydrophobic surfaces (e.g., stainless steel, Cu, Ni, Si, PTFE, and PDMS). Therefore, such switchable bubble wettability is substrate-independent, in stark contrast to the reported wettability-switchable surfaces that all depend on the stimuli-responsive chemistry of the substrates. We demonstrated that the passage of bubbles through a superhydrophobic porous sheet could be turned on and off by the selective aerophilicity and superaerophobicity in water. The underwater bubbles could pass through the underwater (super-) aerophilic porous sheet but were intercepted by the underwater superaerophobic porous sheet. A strategy for removing bubbles in a water pipe by using the underwater superaerophilic–superaerophobic porous sheets is also proposed. The switchable underwater aerophilicity–superaerophobicity will have significant applications in controlling the behavior of underwater air bubbles, such as avoiding the bubble-induced hazards and the collection of useful submarine gas.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b21465.

- Process of a water droplet rolling on the superhydrophobic Al surface (Movie S1) (AVI)
- Process of a bubble spreading out on the superhydrophobic Al surface in water (Movie S2) (AVI)
- Process of a bubble rolling off the underwater superaerophobic surface (Movie S3) (AVI)

- Bubbles passage of the underwater superaerophilic porous sheet (Movie S4) (AVI)
- Bubbles interception of the underwater superaerophobic porous sheet (Movie S5) (AVI)

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Notes

The authors declare no competing financial interest.

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