Switchable Underwater Bubble Wettability on Laser-Induced Titanium Multiscale Micro-/Nanostructures by Vertically Crossed Scanning

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ABSTRACT: We present here a kind of novel multiscale TiO2 square micropillar arrays on titanium sheets through vertically crossed scanning of femtosecond laser. This multiscale micro-/nanostructure is ascribed to the combination of laser ablation/shock compression/debris self-deposition, which shows superaerophobicity in water with a very small sliding angle. The laser-induced sample displays switchable bubble wettability in water via heating in a dark environment and ultraviolet (UV) irradiation in alcohol. After heating in a dark environment (0.5 h), the ablated titanium surface shows superaerophobicity in water with a bubble contact angle (BCA) of ~4°, which has a great ability of capturing bubbles in water. After UV irradiation in alcohol (1 h), the sample recovered its superaerophobicity in water and the BCA turns into 156°. The mechanism of reversible switching is believed as the chemical conversion between Ti–OH and Ti–O. It is worth noting that our proposed switching strategy is time-saving and the switch wetting cycle costs only 1.5 h. Then we repeat five switching cycles on the reversibility and the method shows excellent reproducibility and stability. Moreover, laser-induced samples with different scanning spacing (50−120 μm) are fabricated and all of them show switchable underwater bubble wettability via the above tunable methods. Finally, we fabricate hybrid-patterned microstructures to show different patterned bubbles in water on the heated samples. We believe the original works will provide some new insights to researchers in bubble manipulation and gas collection fields.

KEYWORDS: underwater bubble wettability, multiscale micropillar arrays, switchable superaerophobicity−superaerophilicity, femtosecond laser, bubble manipulation

1. INTRODUCTION

Underwater bubble wettability has attracted considerable attention because of its significant involvements in industrial manufacture and daily life, such as water treatment, enhancing the recovery of minerals particles from ores and improving heat transfer in the ocean. Understanding the bubble’s behaviors and realizing the controllable bubbles manipulation in a liquid medium are fascinating in various phenomena and applications. As a kind of smart materials, titanium dioxide with reversible wettability has become a hot issue because of their great potential in the fields of microfluidic devices, biosensors, and smart membranes. Inspired by its photosensitivity, a large number of experimental and theoretical attempts have been made by researchers with the purpose of achieving tunable in-air wettability and underwater−oil wettability. For example, Sakai et al. studied the kinetics on the photoresponsive hydrophilic conversion processes of titanium surface. It was indicated that the photoresponsive hydrophilic conversion competed with photocatalytic oxidation process under UV irradiation. Sun and co-workers fabricated a kind of nanocomposite intelligent films with TiO2 nano-particles, which exhibited excellent reversibility between superhydrophilicity and superhydrophobicity under UV light and heat. Yong et al. presented a simple way to achieve reversible switching between underwater superoleophobicity and underwater superoleophilicity on laser-ablated titanium materials, but the superhydrophilic sample needs to be placed in the dark for 48 h to recover superhydrophobicity. Recently, they achieved six different superwettabilities on the PDMS surfaces by utilizing laser direct-writing technology, which may expand their potential values in tuning underwater bubble wettability. Yu and co-workers presented for the first time the use of ethanol to switch underwater wettability of the TiO2 surface. It is worth noting that abundant studies have been conducted in the past 2 decades to reveal the mechanism of reversible wettability on the micro-/nanostructured surfaces. However, all current studies mainly focus on in-air and underwater oil tunable wettability. There are no reports on...
switchable underwater bubble wettability and corresponding theory is still not systematic enough. In addition, the current tunable method of finishing a wetting switching circle is time-consuming (mostly exceeds 48 h), which may largely decrease their potential applications in underwater bubble manipulation and gas collection. It is highly desirable to find a more time-saving solution for rapidly realizing switchable bubble wettability on the smart materials.

Here, we fabricate a kind of multiscale micropillar arrays on titanium sheets with a one-step femtosecond laser-induced method. Every multiscale square micropillar is mainly composed of four microcones and random smaller nanoparticles. The formation of the multilevel structures is the result of three effects: laser ablation, shock compression, and debris self-deposition. The modified titanium surface shows super-aerophobicity in water and has a great antibubble ability with a small sliding angle. Furthermore, we investigate the switchable underwater bubble wettability on the laser-modified titanium surface by heating in the dark (0.5 h) and UV irradiation in alcohol (1 h). The reversible wetting method proposed in the present study is time-efficient and the wetting switching cycle only costs 1.5 h. However, 48 h were needed to finish a wetting switching cycle in the other reported studies.22,23 Additionally, we fabricate a hybrid-patterned titanium surface like five-pointed star, triangle, circle, and square for obtaining different patterned bubbles via switchable underwater bubble wettability. The present study provides new insights into switchable bubble wettability in water, which should provide significant guidance to researchers and engineers to control well bubbles’ behavior on the smart materials in a water medium.

2. EXPERIMENTAL DETAILS

Materials. The Ti sheet (99.5% purity, 0.2 mm thick) was purchased from New Metal Material Tech. Co., Ltd., Beijing, China, and was cut into small pieces (2 × 2 cm) for laser processing. Before manufacturing, the Ti piece was cleaned ultrasonically in acetone. The distilled water (H2O, 1 g/cm3 density) and NPT (normal pressure and temperature) air (20 ºC, 1 atm, 1.205 × 10−3 g/cm3 density) were served as test material in the in-air and underwater contact angle measurement.

Micro-/Nanostructure Fabrication. The Ti piece was ablated by vertically crossed line-by-line femtosecond laser scanning. The laser beam (104 fs pulses) with a repetition rate of 1 kHz at a central wavelength of 800 nm from a regenerative amplified Ti:sapphire femtosecond laser system (Legend Elite-1K-HE, Coherent, USA) was employed for ablation. The laser beam was guided onto the titanium surface through a galvanometric scanning system (SCANLAB, Germany), which was equipped with a 63 mm telecentric fθ lens to make the laser beam focus and scan along the x/y coordinate direction. The schematic of the femtosecond laser system and scanning path is shown in Figure 1a. The scanning spacing between two adjacent lines ranged from 50 to 120 μm in both x and y coordinates direction. The laser processed area is 8 × 8 mm and scanning speed is 1 mm/s.

Instrument and Characterization. Scanning electron microscopy (SEM) photos were utilized to analyze the surface topography of laser-modified Ti pieces via use of a field-emission scanning electron microscope (JSM-6700F, JEOL, Japan). The contact angles of water in-air and bubble underwater were measured on the as-prepared Ti surfaces with a contact-angle system (CA100C, Innuo, China) by a sessile drop method. The volume of water droplet and air bubble is set to be 4 μL. The average values were obtained by measuring five drops at different locations on the same surface. Furthermore, to measure the sliding angle of the air bubble in water, the Ti pieces were slowly titled with an increment of 1° until the air bubble started to slide. Continuous photos were taken every 200 ms by the contact-angle system with a computer-controlled charge-coupled device (CCD) camera to display the sliding behavior of the air bubble on the as-prepared Ti surfaces in water. All the contact angle measurements.
were conducted under 10% humidity and 20 °C temperature, respectively.

Switchable Wetting Strategy. The laser-induced sample equipped with opaque aluminum foil was heated for 30 min at 200 °C on a heating plate (Lab Tech, EH35A plus). For UV light irradiation, the samples were immersed in a transparent box with adequate alcohol for 60 min. A 36 W UV lamp with a wavelength of 365 nm was placed above the heat-treated surface at a distance ~8 cm as the light source. The reversible switching of underwater bubble wettability between superaerophobicity and superaerophilicity was verified in cycle tests (five cycles) by using the proposed strategy. Different hybrid-patterned titanium surfaces were fabricated for obtaining different patterned bubbles via switchable underwater bubble wettability.

3. RESULTS AND DISCUSSION

Titanium surface with regular square micropillar arrays were fabricated by vertically crossed femtosecond laser scanning (Figure 1b) with laser power of ~450 mW and scanning interspace ~80 μm. From the low-resolution SEM image (Figure 1c), we can see that square micropillar arrays (~80 μm in length) are distributed regularly on the modified titanium surface. Every square micropillar (Figure 1d) is composed of four microcones with 25−30 μm in height and 25−40 μm in diameter. In addition, nanoparticles with 20−300 nm size are randomly located on the microcones (Figure 1e). To show the formation mechanism of the multiscale structure, SEM images of the scanning process were obtained on the modified titanium surface (Figure 1f−g). The initial groove arrays with the spacing of ~80 μm formed on the surface along the x-axis direction after the first horizontal scanning (Figure 1f). Then the square micropillar arrays were obtained by the second vertical laser scanning along the y-axis direction (Figure 1g). During the laser-ablating process, microcones and nanoparticles were induced on both sides of the pits under the combined effect of laser shock compression and debris deposition (Figure 1h).

Therefore, we concluded that the multiscale structures were achieved by the combination of laser ablation, shock compression, and debris self-deposition from the processed region to the unprocessed region. The height of the micropillars and microcones increases with the laser power and scanning times.

To study the water wettability in air and the bubble wettability in water, contact angle measurements were employed on the original and laser-modified surfaces, respectively. Before laser manufacturing, the unprocessed area showed hydrophilicity with a water contact angle (WCA) of ~152°. After laser manufacturing, the processed area (Figure 2b) showed superhydrophilicity with a WCA of ~156° (Figure 2c). Moreover, the original surface showed high adhesive force of the bubbles. Even when the surface was tilted at an angle of 90°, the air bubble could not roll (Figure 2a). While the bubble on the laser-induced surface shows lower adhesive force with a sliding angle (BSA) of ~3°, the sliding behavior of the bubble was recorded every 200 ms by the contact-angle system with a CCD camera (Figure 2c).

The laser-fabricated surface displays switchable water wettability in air and bubble wettability in water via heat in the dark and UV irradiation in alcohol. After being heated in a dark environment (0.5 h), the laser-induced superhydrophilic sample became superhydrophobic in air with a WCA of ~152° (Figure 3a). In contrast, the bubble wettability in water changed from superaerophobicity with a BCA of ~156° to superaerophilicity with a BCA of ~4°. After UV irradiation in alcohol (1 h), the sample recovered its superhydrophilicity in air and the WCA turned into only 5°. Therefore, the laser-modified sample finished a wetting switching circle between superhydrophobicity and superhydrophilicity. The underlying mechanism is mainly related to the conversion between Ti−OH and Ti−O (Figure 3b). On the basis of the previous theoretical studies, it can be concluded that the photoexcitation would contribute to the formation of oxygen vacancies on the titanium surface where ambient H2O could favorably compete with O2 for dissociative adsorption. When the original sample was modified by laser ablation, besides from the wettability amplification effect of rough surface microstructure, there was a large amount of hydrophilic hydroxyl.
groups (−OH) on the laser-induced sample. Hence, the obtained sample shows stable superhydrophilicity in air and ultralow bubble adhesive in water. However, the chemical bond Ti−OH would be easily replaced by Ti−O when the as-prepared sample was heated in a dark environment. The ambient O₂ rapidly replaced the −OH groups and formed more stable oxygen absorption on the heat-treated surface which endows the sample with stable superhydrophilicity. After the sample was irradiated by UV light, unstable oxygen vacancies formed on the titanium surface. These oxygen vacancies showed a stronger propensity for dissociative adsorption of −OH supplied by alcohol. The UV-treated sample recovered its superhydrophilicity because of the high surface energy of the chemical bond Ti−OH.

Moreover, the switching trend of bubble wettability in water reveals that the bubble wettability in water intensively depends on the water wettability in air. As shown in Figure 3c, the titanium surface after laser scanning was superhydrophilic in air. Following the Wenzel model, when the laser-induced sample was immersed in water, the water rapidly filled into the
microstructures and formed a water layer so that the surface had a great antibubble ability and displayed superaerophobicity in water. We speculated that the air bubble stayed on the peaks of the microstructure, leaving the water trapped in the pits. After being heated in a dark environment, the sample exhibited superhydrophobicity and ultralow water adhesive. Shown in Figure 3c was the water droplet staying at the bottom of the rough microcones, leaving the air trapped in the pits which was satisfied with the Cassie–Baxter model. When such a sample was immersed in water, the surface exhibited superaerophilicity. Therefore, it is revealed that superhydrophilic surface in air generally shows superaerophobicity in water and has a great antibubble ability.

Parts (c) and (d) of Figure 3 respectively showed the evolution of the WCA and BCA with time under heating in a dark environment and UV irradiation in alcohol. While the heating time increases from 0 to 30 min, the WCA gradually increased from 3° to 152°, indicating that the sample switched from superhydrophilic to superhydrophobic states. In contrast, the bubble wettability in water changed from superaerophobicity to superaerophilicity. To demonstrate the excellent reproducibility and stability of the proposed reversible method, we have repeated five switching cycles on the reversibility (Figure 3f). In addition, time consumption of different reversible wetting methods was compared (Figure 3g) and the switching wetting cycle cost only 1.5 h by heating in the dark and UV in alcohol. It is worth noting that the tunable time from superhydrophilicity to superhydrophobicity needed only 0.5 h by heating in a dark environment, which was far less than that shown in existing reports, needing 48 h longer to recover its superhydrophobicity in air.22,24

Finally, we studied the effect of scanning spacing on the wetting switching cycle of the femtosecond laser-modified rough titanium surface. As shown in Figure 4a, with the increase of scanning spacing, the micropillars induced by crossed laser ablation became more and more obvious. Multiscale micropillars (microcone, nanoripple) on the ablated sample with spacing of ~120 μm were observed in the high-resolution SEM image (Figure 4a). The reversible wetting results indicated that the laser-induced samples with different scanning spacing all exhibited switchable in-air and underwater wettability via the above switchable methods (Figure 4b). Additionally, we designed and fabricated different hybrid-patterned titanium surface-like five-pointed star, triangle, circle, and square to display a patterned bubble in water via heating in a dark environment. As shown in Figure 4c, the laser-ablated area with different patterns showed superhydrophobicity in air and superhydrophilicity in water by heating in a dark environment. The water droplets looked like a ball and seated on the heated surface in air. While the samples were immersed in water, different patterned bubbles formed on the superaerophilic areas because of high adhesive force of the sample. To show the fabrication accuracy and controllability of the femtosecond laser micro-/nanofabrication, complex patterns were achieved without masking, such as airplane and bicycle (Figure 4d). These microstructures may exhibit switching wetting properties on the titanium materials via femtosecond laser manufacturing.

4. CONCLUSION

In summary, we report a novel multiscale micro-/nanostructure on the titanium surface induced by femtosecond laser vertically crossed scanning for the first time, which efficiently and rapidly achieves switchable water wettability in air and bubble wettability in water via heating in the dark (0.5 h) and UV irradiation in alcohol (1 h). The multiscale structure is realized by the combination of three effects: laser ablation/shock compression/debris self-deposition. Furthermore, the reversible wetting strategy proposed in the present study is time-saving and the switching time of finishing a wetting recycle between...
superaerophobicity and superaerophobicity needs only 1.5 h. It is also revealed that bubble wettability intensively depends on the water wettability, and the switching trend of bubble wettability in water is opposite to that of water wettability in air. The heated surface has a great ability of absorbing and capturing bubble in water medium. Finally, hybrid-patterned microstructures such as five-pointed star, triangle, circle, and square are fabricated to show different patterned gas bubbles on the heated sample. It is worth noting that the present work may provide new insights to researchers in capturing/manipulating bubble fields and gas collection under aqueous environments.

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**Notes**

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