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Three-level cobblestone-like TiO_2 micro/nanocones for dual-responsive water/oil reversible wetting without fluorination

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In this work, a kind of three-level cobblestone-like anatase TiO_2 microcone array was fabricated on titanium sheets by femtosecond laser-induced self-assembly. This three level structure consisted of cobblestone-like features (15–25 μm in height and 20–35 μm in diameter), $\sim$460 nm ripple-like features, and smaller particles (10–500 nm). The formation of microcone arrays can be ascribed to the interaction of alternant laser beam ablation. TiO_2 surfaces display dual-responsive water/oil reversible wetting via heat treatment and selective UV irradiation without fluorination. It is indicated that three-level scale surface roughness can amplify the wetting character of the Ti surface, and the mechanism for reversible switching between extreme wettabilities is caused by the conversion between Ti-OH and Ti-O. Moreover, the double-faced superhydrophobic and double-faced superhydrophilic Ti samples were constructed, which exhibited stable superhydrophobicity and underwater superoleophobicity in water-oil solution, respectively, even when strongly shaken. Finally, we present the hybrid-patterned TiO_2 surface and realized reversible switching pattern wettability. *Published by AIP Publishing.* https://doi.org/10.1063/1.4998297

Over the past few decades, significant efforts have been devoted to exploring photo-responsive wettability switching between superhydrophobicity and superhydrophilicity for its merits in the fields of smart membranes,[1] micro-fluidic devices,[2] biosensors,[3] and photoactive coatings.[4] TiO_2 is one of the most in-depth researched materials for its enticing photocatalytic activity upon UV illumination that gives it a remarkable capability of switching the surface chemistry between the hydrophobic oxygen group and the hydrophilic hydroxyl group.[5] Recent investigations demonstrated that fabricating rough TiO_2 microstructures could achieve reversible wetting transformation. For example, Wu *et al.*[6] reported a melted copolymer method for the fabrication of multi-responsive TiO_2/polymer films that can reversibly switch the wetting between superhydrophilicity and superhydrophobicity under UV light/heat or acid/base solutions. Wang and co-workers[7] prepared hybrid TiO_2 electrochemical sol on a cellulose substrate through sol-gel electrochemical deposition. TiO_2 sol expressed excellent superhydrophobicity with a water contact angle (WCA) of $\sim$166° and sensitive superhydrophobic-superhydrophilic smart conversion. Although both TiO_2 films show excellent reversible wettability switching properties, the fabricating process is complex and requires special chemical reagents, which will pollute the environment. In terms of functional applications, Kota *et al.*[8] fabricated tunable superomniphobic surfaces with flower-like TiO_2 nanostructures by hydrothermal synthesis. It is indicated that the superomniphobic surfaces can be fabricated in a short time and reused multiple times, which can sort droplets via surface tension. However, the reversible wettability depends on fluorination treatment. Chen *et al.*[9] fabricated rough micro-hole arrays through a femtosecond laser-treated approach to realize reversible switching between underwater superoleophobicity and underwater superoleophilicity. The surface is responsive not only to UV light but also to the He-Ne laser. However, the fabricated hole-like microstructures are a little simple. Moreover, the superhydrophilic sample needs to take a long dark storage time to recover its superhydrophobicity. Many other types of responsive materials have been reported, which show the properties for wettability control. For example, Hozumi *et al.*[10] fabricated polyalkyl methacrylate brush surfaces with different alky chain lengths by ARGET-ATRP, which showed dynamic hydrophobicity and air bubble repellency in a variety of organic liquids. They also synthesized pDMAEMA brush surfaces with underwater superoleophobicity based on ARGET-ATRP, whose wetting responded to three different external stimuli (PH, ionic strength, and temperature).[11] Sun *et al.*[12] reported the facile fabrication of underwater superoleophobic membranes by coating a layer of graphene oxide on wire meshes with tunable pore sizes. Therefore, it is interesting to develop strategy to realize special micronanostructures for functional applications.

In this work, we fabricated a kind of special three-level cobblestone-like anatase TiO_2 microcone array by utilizing the femtosecond laser-induced self-assembly method. It is indicated that three-level structures are composed of cobblestone-like TiO_2 microcone arrays, periodic nanoripples, and random nanoparticles. The formation of microcone arrays can be

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ascribed to the interaction of alternant laser beam ablation, which results in the uniform cobblestone-like cone arrays. Furthermore, we constructed double-faced superhydrophobic and double-faced superhydrophilic surfaces by heating treatment and selective UV irradiation (1 h) without fluorination, respectively. It is expected that samples exhibit stable superhydrophobicity and underwater superoleophobicity in the water-oil solution. Additionally, we presented the hybrid-patterned TiO_2 surface for reversibly switching wettability. This work provides an insight into dual-responsive water/oil reversible wettability, which will find potential applications in artificial smart surface, lab-on-a-chip systems, stimuli-responsive devices, and so on.

The three-level cobblestone-like TiO_2 microcone arrays [Fig. 1(b)] were prepared by line-by-line femtosecond laser (fs) scanning with the spacing between adjacent scanning lines of $\sim$25 μm and the incident laser pulse energy of $\sim$0.45 mJ. It is well known that TiO_2 exists three natural phases: rutile, anatase, and brookite. Every titanium ion is surrounded by six oxygens to form a TiO_6 octahedron in the modifications, but they have different networks composed of TiO_6 octahedra. In this experiment, some of TiO_2 rutile phase transformed into the anatase phase by the high pressure due to fs laser micro-explosions on the TiO_2 surface. We can see that uniform cobblestone-like cone arrays with a diameter in the range of 20–35 μm and a height in the range of 15–25 μm [Fig. 1(c)] are densely distributed on the Ti surface. From the high-resolution SEM image in Fig. 1(d), it can be clearly observed ripples with a period of $\sim$460 nm grown along the generatrix direction of cones. In addition, nanoparticles with size ranging from tens to hundreds nanometers randomly located on the microcones and ripples. As for the formation mechanism of the three-level cobblestone-like microcones, we speculated that ablation occurs at the center of the laser beam due to the high peak intensity of the fs laser, which exceeded the ablation threshold of the material. In order to research the detailed surface topography, four scanning lines with a pitch of 25 μm were used to treat Ti surfaces [Figs. 1(e)–1(h)]. The initial microcone arrays with smaller diameter (5–7 μm) appeared at the center of the laser beam when the first scanning line treating the Ti surface was conducted [Fig. 1(i)]. Increasing with different laser scanning lines [Figs. 1(j) and 1(k)], higher (8–15 μm) microcones were fabricated owing to the interaction of the alternant laser beam. The final mircrocone arrays (15–25 μm in height) were presented when the third scanning lines treated the Ti surface [Fig. 1(l)]. Then, the structures become stable because the size of the laser spot is about 70–80 μm. Meanwhile, a series of microcones of different heights and bottom sizes could be fabricated by regulating the laser pulse energy and adjacent scanning lines (Fig. S1 in the supplementary material). We also made the statistics about the heights and bottom sizes (Fig. S2 in the supplementary material). It was observed that the height of the microcones increased with the laser pulse energy.

Contact angle measurements were used to evaluate the water/oil wetting of three-level cobblestone-like cone arrays, as shown in the optical photograph of the laser-treated Ti surface [Fig. 2(a)]. Water rapidly spreads on the superhydrophilic surface with a water contact angle (WCA) of $\sim$6° in air. In contrast, when subjected to 200 °C heat treatment for 75 min, the superhydrophilic surface could turn into a superhydrophobic surface with a WCA of $\sim$153° [Fig. 2(b)]. Meanwhile, if the superhydrophobic sample was tilted at an angle of 90°, the water droplet could not roll, indicating high adhesive force [Fig. S3(a) in the supplementary material]. The process of water reversible wettability via heat treatment and UV irradiation is displayed in Fig. 2(c). The superhydrophobic sample could recover its initial superhydrophilicity by UV irradiation, which indicates that the laser-treated surface exhibits the excellent photocatalytic performance in air. Figure 2(d) presents the evolution of the WCA on the superhydrophilic surface via heat treatment. While the heat time increased to 75 min, the WCA immediately increases from

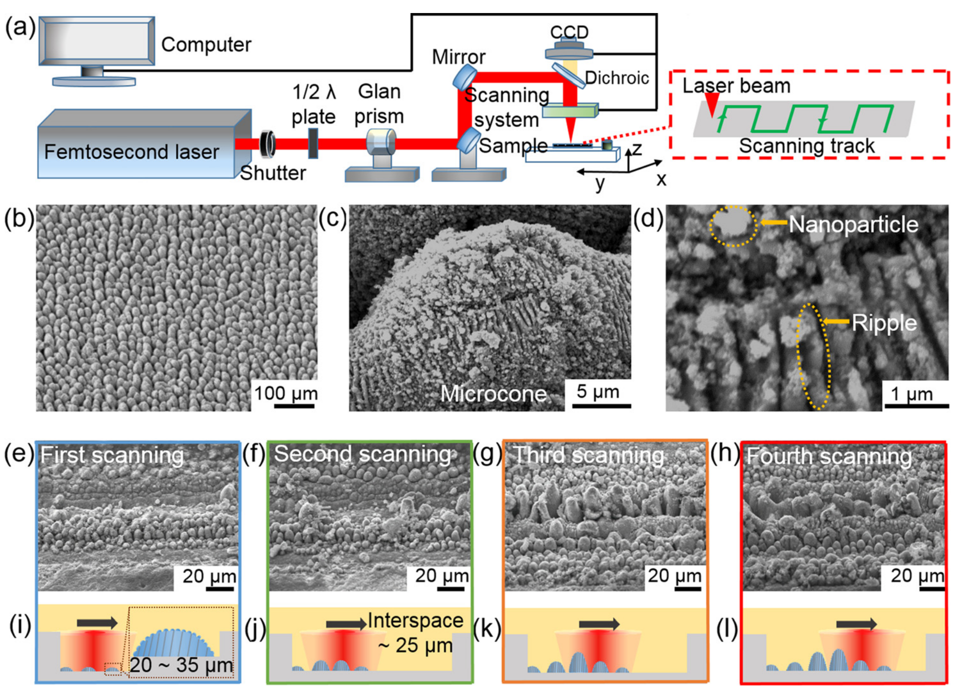

FIG. 1. The preparation and formation mechanism of three-level cobblestone-like TiO_2 micro/nanocones by femtosecond laser-treated titanium sheets. (a) The schematic diagram for the laser scanning process in air. (b)–(d) 45° tilted SEM images of the morphology of the laser-treated surfaces, demonstrating the presence of periodic stripes with rough nanoparticles together along the cobblestone-like microcones. The magnification is ×600, ×9600, ×38000, respectively. It is indicated that the size of microcones is in the range of 20–35 μm, and the average height is in the range of 15–25 μm. (e)–(h) Different numbers of scanning lines for demonstrating the formation of mircrocones. (i)–(l) The sketch for the formation mechanism of microcones.

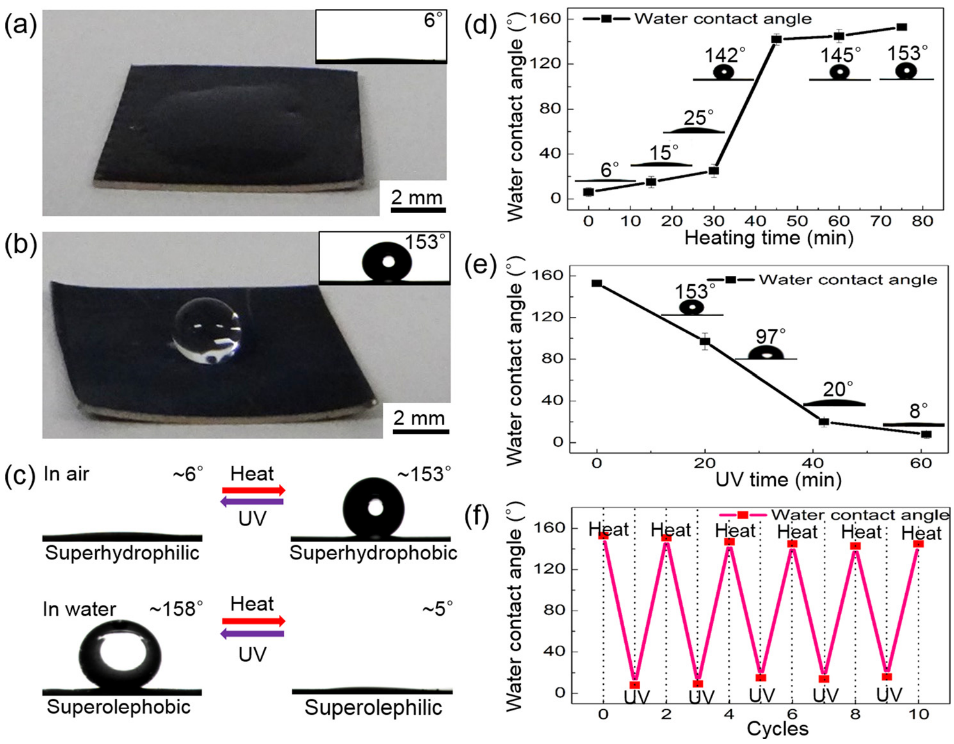

FIG. 2. Reversible switching between superhydrophobicity and superhydrophilicity by heat treatment and UV irradiation. (a) Water droplets on the laser-treated surface shows superhydrophilicity with a water contact angle (WCA) of 6°. (b) Water droplets on heat-treated surface exhibits superhydrophobicity with the WCA of 153°. (c) The specific process of switchable wettability of water or oil droplets via heat treatment and UV irradiation. (d) The laser-treated superhydrophilic Ti surfaces were heated at 200 °C for different times. (e) The superhydrophobic Ti surfaces exposed to UV irradiation for different times. (f) The six cycles were carried out to confirm the strong durability of tunable wettability.

6° to 153°. In contrast, the evolution of the WCA on the superhydrophobic surface subjected to UV irradiation is presented in Fig. 2(e). It is clearly seen that the WCA gradually decreased from 153° to 8° with UV irradiation for 1 h, indicating that the three-level cobblestone-like microcone structure exhibits the dual-responsive water reversible wetting without fluorination. The reversible wettability between superhydrophobicity and superhydrophilicity can be repeated for many times [Fig. 2(f)]. Additionally, we also researched the underwater oil wettability. The superoleophobic and superoleophilic surfaces exhibit oil contact angles (OCAs) of ∼158° and 5°, respectively. In water, the superhydrophilic surface shows extremely low oil adhesion for 1, 2-dichloroethane. The underwater oil droplet sliding angle (OSA) is as small as 6.1° [Fig. S3(b) in the supplementary material].

In order to explain this phenomenon, XPS analysis was carried out to confirm the chemical composition of untreated, laser-treated, and heat-treated samples. It can be seen that the related elements of C, Ti, and O were detected in fully scanned spectra [Fig. 3(a)]. The Ti 2p located at ∼460 eV was split into two peaks, agreeing well with a previous report.[13] The enhanced peak and subdued peak were assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively. After laser treating and heating treatment, both peaks became sharper due to the formation of high-valence titanium ions. The O 1s peak with ∼160 000 counts/s existed at ∼530 eV on the original Ti surface because the Ti sheets used in our experiment were oxidized slightly in air. The O 1s peak in laser-treated and heated-treated was ∼240 000 and ∼360 000 counts/s, respectively, indicating that both treated surfaces had a higher peak value than the original Ti surface [Figs. 3(b) and 3(c)]. The diagram of different water wetting on the cobblestone-like TiO_2 microcone arrays is described in Fig. 3(d). It can be seen clearly that the water droplet spreads rapidly along the surfaces through the subtle capillary force action with water displacing the trapped air.[14] Oppositely, a water droplet exists as a sphere shape on the heat-treated surface. In this experiment, the water droplet can slide on the surface with low adhesive force, so the superhydrophobic TiO_2 surface is in the Cassie state.

External stimulus is a decisive factor for tunable wetting, which can induce the change in chemical compositions. According to the previous theoretical studies,[15] we could speculate that band gap TiO_2 photoexcitation would result in the formation of surface defects (oxygen vacancies) where ambient H_2O could favorably compete with O_2 for dissociative adsorption. The underlying mechanism of reversible wettability switching between superhydrophilicity and superhydrophobicity was discussed in detail [Fig. 3(e)]. There are a large number of hydrophilic hydroxyl groups on the laser-treated Ti surface. So, the chemical bond between Ti and OH makes sure that the obtained surface exhibits stable superhydrophilicity. In contrast, oxygen vacancies could be formed and the ambient oxygen could replace them during heat treatment. This means that the chemical bond between Ti and O could replace Ti-OH, which endows the heat-treated surface with stable superhydrophobicity.[16] Meanwhile, oxygen vacancies would increase the probability of absorbing the ambient H_2O and enable the UV-treated sample to recover its initial superhydrophilicity.[17] Therefore, the reversible wettability switching can be attributed to the synergistic effect between the changeable chemical composition and the three-level cobblestone-like microcones. In our experiment, we presented three-level cobblestone-like microcone arrays and also realized the water/oil reversible wetting. Our superhydrophilic sample could recover its superhydrophobicity only for 75 min heat treatment, which has a faster dual-responsive speed and may be applied to diverse smart photo-responsive surfaces. However, two days were needed to realize switchable underwater superoleophobicity-superoleophilicity through UV irradiation and dark storage in the other previous report.[9]

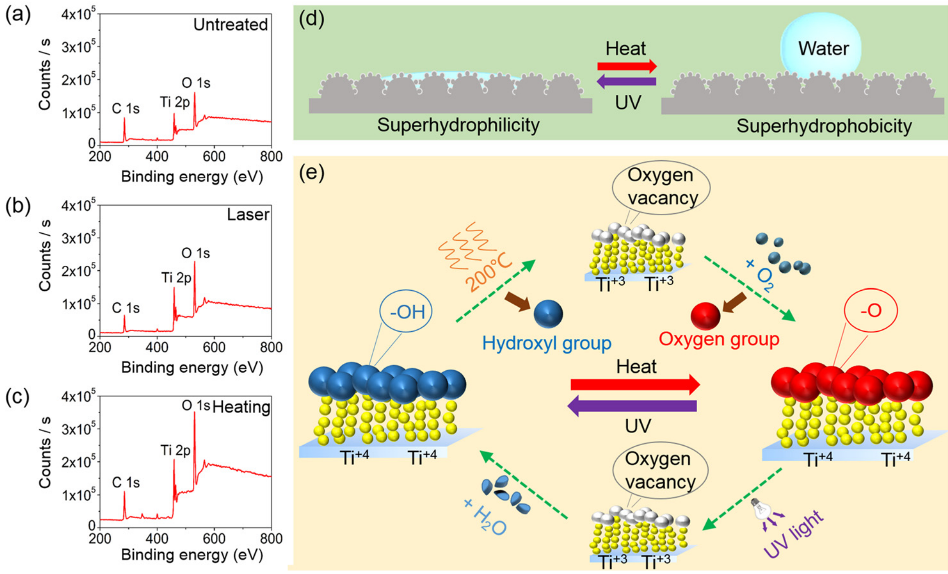

FIG. 3. Sketch of the mechanism for reversible wettability switching between superhydrophilicity and superhydrophobicity of the Ti surfaces. (a)–(c) XPS full spectra of the unprocessed, laser-treated, and heat-treated Ti surfaces, respectively. The O 1s peak in laser-treated and heated-treated was ~240 000 and ~360 000 counts/s, respectively, indicating that both the treated surfaces had a higher peak value than the original Ti surface. (d) The diagram of different water wetting on the three-level cobblestone-like TiO_2 micro/nanocones. (e) Dynamic transition of the hydrophobic oxygen groups and hydrophilic hydroxyl groups occurred on the Ti surface via heat treatment and UV irradiation.

The sensitive photocatalytic performance of TiO_2 has applications in anti-water coating and anti-oil coating. In order to explore its function, we produced three samples: the unprocessed surface (sample 1), double-faced superhydrophilic surface (sample 2) and double-faced superhydrophobic surface (sample 3), which are the three-level cobblestone-like microcones, respectively [Figs. 4(a)–4(c)]. Sample 1 is selected for the comparison. The stable superhydrophobicity and underwater superoleophobicity of the samples were evaluated by monitoring their underwater location after immersing them in water-oil solution and shaking the container. Three samples were successively immersed in the water-oil solution [Figs. 4(d)–4(g)]. Interestingly, it can be seen that sample 3 floats on the water surface due to its double-faced superhydrophobicity. In contrast, when Sample 2 is put on the water surface, it immediately sinks down and finally resides at the water/oil interface because of its double-faced superhydrophilicity. Meanwhile, sample 1 steadily sits on the bottom of the beaker for its density which is higher than that of water. Even when shaken strongly, three samples still stably maintain the unchangeable position [Movie S1 in the supplementary material].

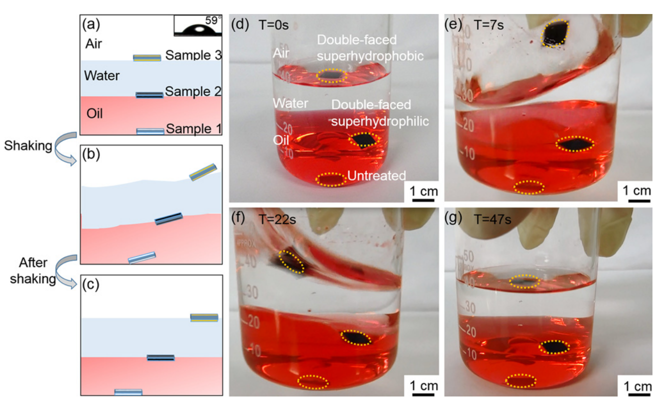

FIG. 4. Excellent superhydrophobicity and underwater superoleophobicity of the double-faced Ti samples in water-oil solution. (a)–(c) A small-scale model diagram was used to explain the process of shaking the container. The inset is the untreated sample with a WCA of ~59° (d)–(g) The unprocessed, laser-treated, and heat-treated Ti sample was successively placed in the container. It is clear to see that the three samples located at different positions owing to different wettabilities.

Furthermore, we designed the hybrid-patterned TiO_2 surfaces composed of three-level cobblestone-like microcones, which displayed superhydrophilicity and superhydrophobicity via heat treatment and selective UV irradiation [Fig. 5(a)]. The laser-treated Ti surfaces present superhydrophilicity on triangle and pentacle patterns. To get the superhydrophobic surfaces, the 200 °C heat treatment for 75 min is performed. It is shown that the water droplets sit on the heat-treated surface with a shape of nearly sphere [Fig. 5(b)]. In addition, the different positions of selective UV irradiation with the black tinfoils being used as the shelters are shown [Figs. 5(c) and 5(d)]. We realized the switching wettability of superhydrophobicity and superhydrophilicity by selective UV irradiation [Figs. 5(e) and 5(f)]. It is worth noting that due to the accuracy and controllability of the fs laser microfabrication, the multiple patterns can be prepared, such as USTC, panda, butterfly, and grating [Figs. 5(g)–5(j)]. Compared with the single wettability of the superhydrophilic or superhydrophobic surface, the hybrid-patterned surface of different wettabilities exhibits the advantage of controllable patterns and fast dual-responsive speed in the field of artificial smart photo-responsive surface, demonstrating its wide potential applications.

In summary, we reported the fabrication of the three-level cobblestone-like anatase TiO_2 micro/nanocones with water/oil reversible wettability by line-by-line scanning fs laser induced self-assembly, which is ascribed to the interaction of alternant laser beam ablation. Furthermore, the laser scanning technique enables a fine size and topological control of anatase TiO_2 surface features due to the high peak intensity of the fs laser. The superhydrophilic surfaces with a WCA of ~6° can be easily switched to superhydrophobicity with a WCA of 153° via heat treatment without fluorination. We also demonstrate that the surface chemistry of superhydrophobic surfaces can be tuned during UV irradiation. The mechanism for reversible wetting between two extreme wettabilities (many cycles >6) is believed as the conversion between Ti-OH and Ti-O. Meanwhile, double-faced superhydrophobic

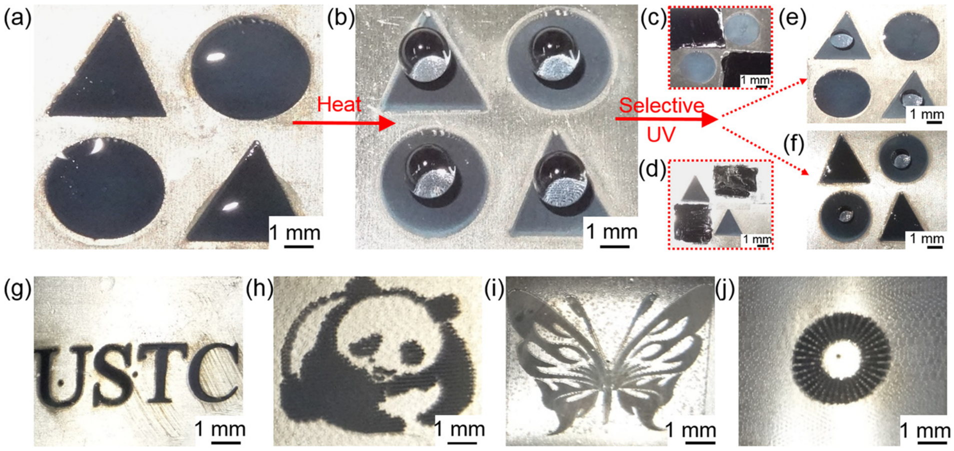

FIG. 5. The design of the hybrid-patterned Ti surface of different wettabilities between superhydrophobicity and superhydrophilicity. (a) The laser-treated superhydrophilic Ti surfaces. (b) The heat-treated superhydrophobic Ti surfaces. (c)–(d) The different positions of the selective UV irradiation with the black tinfoils being used as the shelters. (e)–(f) The switching wettability between superhydrophobicity and superhydrophilicity via selective UV irradiation. (g)–(j) The multiple patterns prepared by fs laser microfabrication, such as USTC, panda, butterfly, and grating. The scale bar is 1 mm.

and double-faced superhydrophilic surfaces show stable superhydrophobicity and underwater superoleophobicity in water-oil solution even when shaken strongly. Furthermore, hybrid-patterned TiO_2 surfaces of superhydrophobicity and superhydrophilicity were also demonstrated. Although the cost of preparation of the anatase TiO_2 surface by using the fs laser is very high, the TiO_2 surface can be prepared by using a high-speed galvoscanner system and a large-range mobile station for practical applications. Our work may provide an insight into potential applications in artificial smart surfaces, lab-on-a-chip systems, and stimuli-responsive devices.

See supplementary material for the complete structure and wetting of the studied TiO_2 surface.

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