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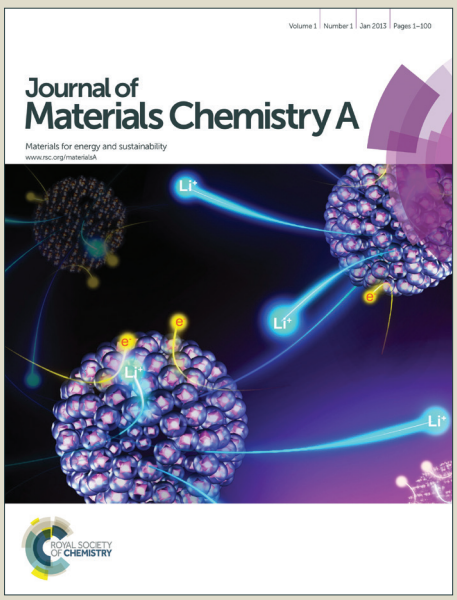

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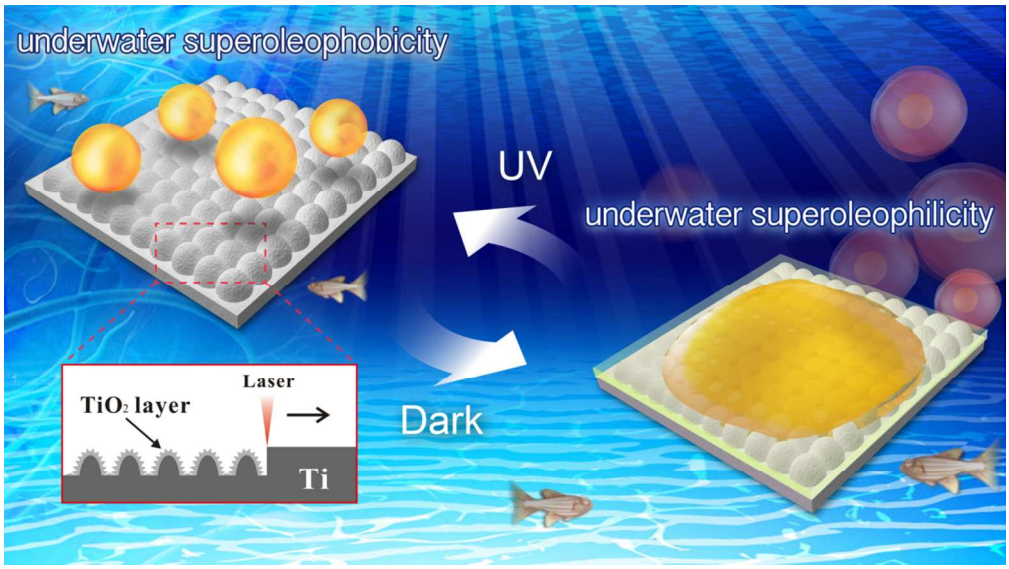

Graphical Abstract-1

Photoinduced Switchable Underwater Superoleophobicity-Superoleophilicity on Laser Modified Titanium Surfaces

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Abstract

Switchable underwater superoleophobicity-superoleophilicity achieving on femtosecond laser-induced rough TiO_2 surfaces by alternate UV irradiation and dark storage is demonstrated for the fist time. Femtosecond laser ablation not only forms a micro/nanoscale hierarchical rough structure but also oxidizes the Ti materials, resulting in a rough TiO_2 layer covering on the surface. The reversibly switching of underwater oil wettability is caused by photoinduced switching between superhydrophobic and superhydrophilic states in air. These rough TiO_2 surfaces even can respond to visible light. We believe this subtle switching method will be potentially applied in the biological and medical fields.

1. Introduction

Underwater oil wettability has recently emerged as a new research focus due to its importance in various phenomena and applications.[1] Two extreme states, underwater superoleophobicity and superhydrophilicity, are particularly fascinating.[2] In nature, the cooperation of the hydrophilic chemical composition and rough microstructure of fish scales,[3] clam shells,[4] and the lower side of lotus leaves[5] results in an underwater superoleophobicity with an oil contact angle (OCA) larger than 150°. This allows these biological surfaces to have remarkable oil-repellent abilities in water environments. Underwater superoleophobic surfaces inspired by nature have been fabricated through various methods to operate under a three phase (oil/water/solid) system.[1,2,6] These surfaces play a significant role in the fields of self-cleaning,[7]

submerged antifouling,[8] water/oil separation,[9] oil droplet manipulation,[10] anti-bioadhesion,[11] and microfluidics.[7] Additionally underwater superoleophilic surfaces (OCA lower than 10°) are of interest because of their excellent oil-adsorption properties, which are usually applied to oil collection and waste oil cleaning.[12] Recently, smart interfaces with tunable wettability have attracted considerable research interest and have been developed by forming rough surface microstructures on stimuli-responsive materials or modifying rough solid surfaces with stimuli-responsive molecular layers.[13] However, current strategies mainly target water wetting and water adhesion in air.[14] Finding a simple route to smart surfaces with switchable underwater superoleophobicity and superoleophilicity has remained challenging.

Here, we present a one-step strategy for constructing a micro/nanoscale hierarchical rough titanium dioxide (TiO_2) layer by femtosecond laser ablating a titanium (Ti) sheet. The femtosecond laser-induced TiO_2 surface shows not only hierarchical microstructure but also high oxygen content. The oil wettability of the as-prepared surfaces in water can be reversibly switched between underwater superoleophilicity and underwater superoleophobicity through UV irradiation and dark storage. This smart property is caused by photoinduced switching between superhydrophobic and superhydrophilic states in air. Oil can refer to lipid based materials such as cells, proteins, biological tissues, etc., which are often in aqueous media. Therefore, this switchable underwater oil wettability should have significant biomedical applications.

2. Experimental Section

The Ti sheets (1×1×0.1 cm^3) were ablated by a femtosecond laser using the typical line-by-line and serial scanning process. The laser beam (pulse duration: 50 fs; center wavelength: 800 nm; repetition: 1 kHz) coming from a regenerative amplified Ti:sapphire laser system (CoHerent, Libra-usp-1K-he-200) was focused on the sample using a microscope lens with NA of 0.45 (Nikon, Japan). The laser power was held constant at 15 mW. The scanning speed and the shift of adjacent laser scanning lines were set at 2 mm/s and 2 μm, respectively.

The microstructure was probed using a Quantan 250 FEG scanning electron microscope (FEI, America). The static and dynamic wettability was investigated by a JC2000D4 contact-angle system (Powereach, China). A droplet of 1,2-dichloroethane (8 μL) was mainly used as the test oil. UV light irradiation was carried out with a UV lamp with wavelength of 370 nm and power of 36 W. The distance between the light source and the samples was approximately 7 cm. For dark storage, the samples were placed into an opaque black box, and stored at a temperature of 150 °C to accelerate the recovery process. The reversible switching of underwater oil wettability was also verified by the He-Ne laser excitation at a wavelength of 633 nm and output power of 0.96 mW. The as-prepared samples were irradiated by the He-Ne laser for one day in an otherwise totally dark room. The spectral absorbance of the femtosecond laser induced TiO_2 surface was examined by a V-570 spectrophotometer (JASCO, Japan).

3. Results and Discussion

Ti and TiO_2 are widely used materials in industry, energy and environmental applications, agriculture, medicine, sports and other fields.[15] Besides its well-known photocatalysic properties, TiO_2 is capable of switching its wettability between hydrophilic and hydrophobic states by alternative UV irradiation and dark storage.[16] Combined with wettability amplification effects of rough surface microstructures, even the conversion from superhydrophobicity to superhydrophilicity can be realized. According to theoretical calculations, hydrophobic (hydrophilic) materials in air become oleophilic (oleophobic) once the sample is immersed in water.[17] This suggests that the photoinduced water wettability transition of a rough TiO_2 surface offers the opportunity to control underwater oil wettability.

Figure 1a-d shows typical scanning electron microscopy (SEM) images of femtosecond laser ablated Ti surfaces. There exist uniformly distributed rough micro-mountain arrays on the surfaces. The size of the features is several microns. The surface of each micro-mountain is covered by irregular protrusions ranging in size from tens to hundreds of nanometers (Figure 1d). The micro/nanoscale hierarchical rough structures result from laser ablation followed by the resolidification of ejected particles.[18] Figure 1e,f and Figure S1 show energy dispersive X-ray spectroscopy (EDXS) results for the Ti surface before and after femtosecond laser irradiation. It can be seen that the original material is primarily composed of Ti. Upon laser ablation, the atomic proportion of Ti decreases from 100% to 51.81% while the atomic proportion of oxygen increases to 48.19%. These results indicate that the laser ablated Ti surface is oxidized during the formation of the rough microstructures,

resulting in a rough TiO_2 layer on the surface. The EDXS results agree well with the fact that the color of the Ti sheet changed from yellowish to black upon femtosecond laser ablation (inset of Figure 1a). It has been recently demonstrated that black TiO_2 contains a high oxygen content which results in improved photocatalytic activity.[19]

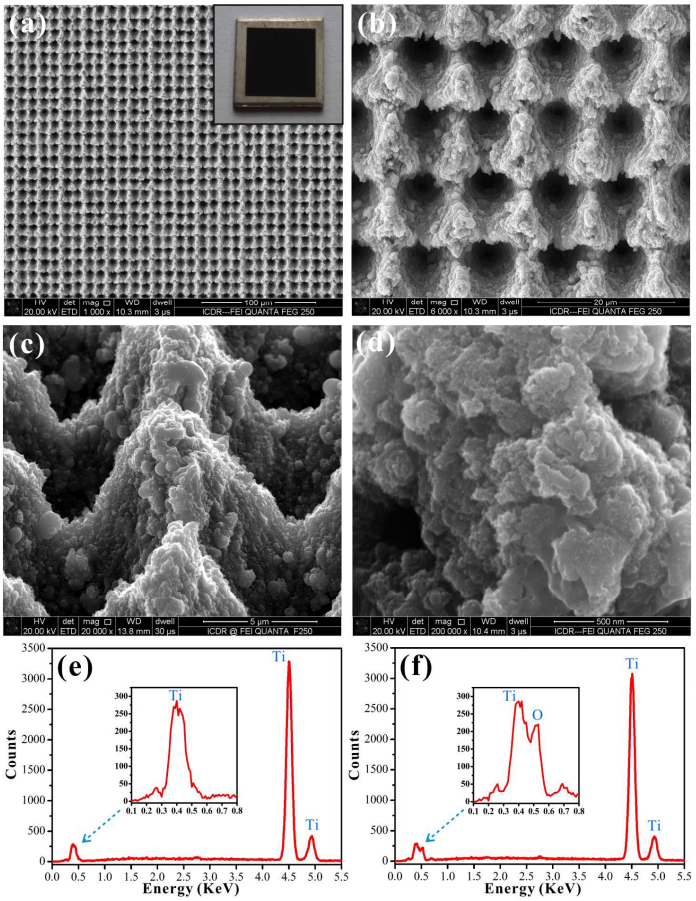

Figure 1. (a-d) SEM images of a femtosecond laser-ablated Ti surface. The sample in (c) is tilted 45°. The inset is a photograph of the laser-induced Ti sheet. (e,f) EDXS results of the Ti surface before (e) and after (f) femtosecond laser ablation.

Contact angle measurements were used to study the water wettability in air and oil wettability in water of the ablated Ti surfaces. Water droplets on the laser-induced surface showed superhydrophobicity with a water contact angle (WCA) of 154.5° ± 2.5° without any chemical modification (Figure 2a). When the sample was immersed in water, the laser-ablated region showed silver mirror like reflectance (Figure S2,

Supporting Information). This mirror-like interface is due to a trapped air layer between water and as-prepared surface suggesting that the laser-ablated Ti is a Cassie-Baxter surface.[20] After being irradiated by UV light for 40 min, the WCA was found to be only 2.5° (Figure 2b, Movie S1 in the Supporting Information); that is, the as-prepared surface was switched from superhydrophobic to superhydrophilic in air. Additionally the silver mirror did not appear with submerging the UV-exposed sample in water (Figure S2, Supporting Information). Interestingly, the sample can recover its superhydrophobicity after keeping it in dark for 2 days.

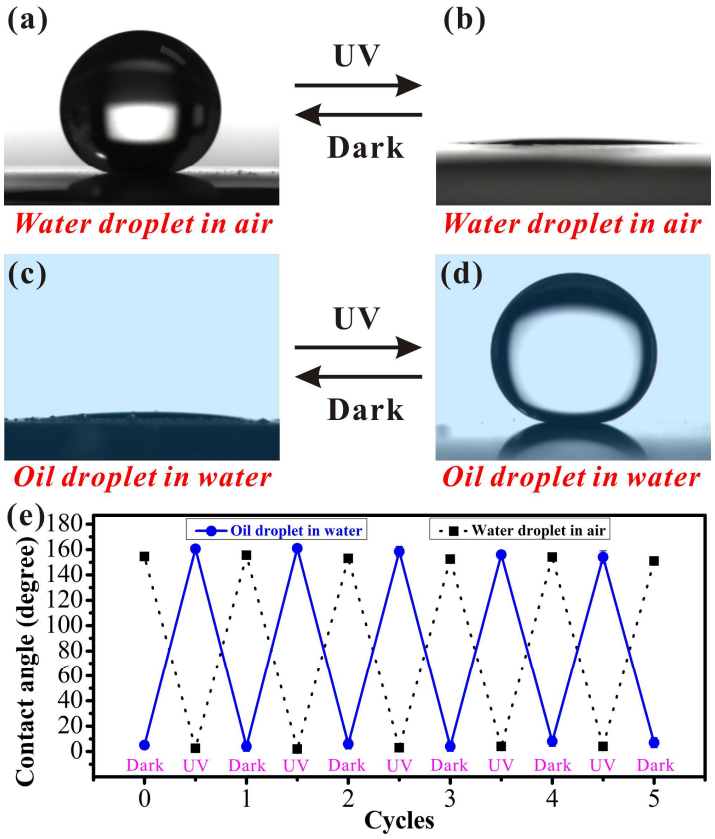

Figure 2. Reversible switching between underwater superoleophilicity and underwater superoleophobicity by alternate UV irradiation and dark storage. (a,b) Images of a water droplet on the femtosecond laser-ablated Ti surface after dark storage (a) and UV irradiation (b) in air. (c,d) Images of an oil droplet on the femtosecond laser-ablated Ti surface after dark storage (c) and UV irradiation (d) in water. (e) Reversibility of the oil wettability being switched between underwater superoleophilicity and underwater superoleophobicity.

The switching trend of underwater oil wettability is opposite that of water wettability in air. As demonstrated by the underwater oil repellency of fish scales, superhydrophilic solid surfaces become superoleophobic in water.[3] When an oil droplet approaches the submerged laser induced TiO_2 surface, the droplet spreads out quickly once it contacts the substrate, resulting in a very small OCA near 4°, as shown in Figure 2c and Movie S2 in the Supporting Information. Therefore, the as-prepared surface shows underwater superoleophilicity.[21] However, after being irradiated by UV light, the underwater oil wettability switches from superoleophilicity to superoleophobicity with OCA values reaching up to 160.5 ± 2°. Figure 2d shows the approximately spherical shape of an underwater oil droplet on the as-prepared surface. Additionally, the oil droplet can easily roll off the laser-ablated surface once it is tilted at an angle of 1°, indicating ultralow oil-adhesion in water medium (Figure S3 and Movie S3, Supporting Information). After dark storage for 2 days, the as-prepared sample can recover its underwater superoleophilicity (Figure 2c,d). Furthermore, this reversibility between underwater superoleophilicity and superoleophobicity can be repeated several times, demonstrating excellent reproducibility and stability (Figure 2e).

Figure 3a,b shows the evolution of the underwater OCA with time under UV irradiation and dark storage, respectively. While the UV irradiation time increases to 40 min, the OCA gradually increases from 4° to 160.5°, indicating that the wettability changes from underwater superoleophilic to underwater superoleophobic states. Upon dark storage, the OCA sharply decreases to 20° over the first day, and then slowly

recovers to its initial value of about 4° over the second day regaining underwater superoleophilicity. Interestingly, the femtosecond laser-induced TiO_2 surface is responsive not only to UV light but also to visible light. Figure S4a-d (Supporting Information) shows the reversible switching between underwater superoleophilic and underwater superoleophobic states after He-Ne laser (wavelength = 633 nm) irradiation and dark storage. The high absorption of visible light is further supported by UV-vis spectra measurement (Figure S4e, Supporting Information). Taking advantage of a broad absorption band, the as-prepared TiO_2 surfaces have the potential for sunlight induced switchability. Furthermore, the as-prepared surface also behaves switchable underwater oil wettability toward a wide range of oil liquids including petroleum ether, hexadecane, diesel, paraffin liquid, crude oil, and chloroform, as shown in Figure 3c.

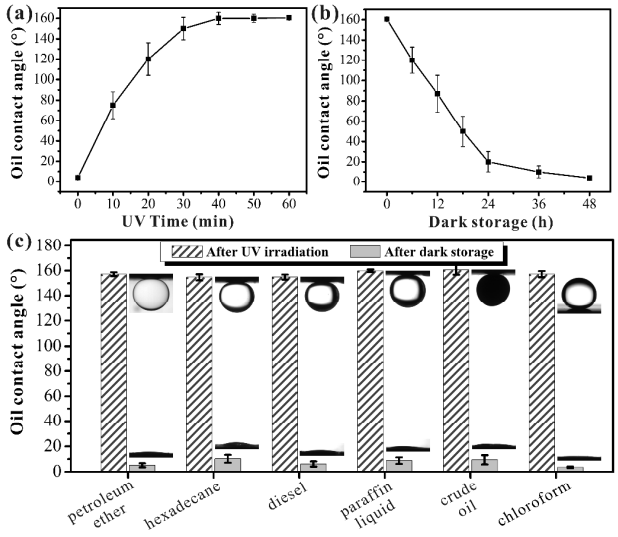

Figure 3. (a,b) Time dependent evolution of the underwater oil wettability on the femtosecond laser ablated Ti surface under UV irradiation and dark storage, respectively. (c) Switching between underwater superoleophobicity and underwater superoleophilicity for various oils.

Traditional smart surfaces often lose their wettable switchability after being oil fouled. However, TiO_2 materials are capable of photocatalytic degradation of organic compounds which can endow them with excellent antifouling performance.[22] To verify this property oleic acid, which has a low volatility, was chosen to pollute the as-prepared sample. As shown in Figure S5 of the Supporting Information, the WCA of the original UV-irradiated surface increases from 2.5° to 74°, and the underwater OCA decreases from 160.5° to 14° after being adhered by oleic acid. When this contaminated sample is irradiated by UV light for 5 h, the surface recovers its superhydrophilicity in air and superoleophobicity in water. This antifouling performance of femtosecond laser induced TiO_2 surfaces is important for repeated and long-term use.

The underlying mechanism of switching between underwater superoleophilicity and underwater superoleophobicity is depicted in Figure 4. As shown in Figure 4a, femtosecond laser ablation not only forms a micro/nanoscale hierarchical surface structure but also oxidizes the Ti material, resulting in a rough TiO_2 layer covering on the Ti surface. After ablation, the surface exhibits superhydrophobicity and ultralow water adhesion. Following the Cassie-Baxter model, the water droplet sits on the peaks of the microstructure leaving air trapped in the pores (Figure 4c).[23] If a large amount of water is poured on the as-prepared surface as opposed to a droplet or if the surface is completely submerged, the air cushion still exists. When an underwater oil droplet contacts the rough surface, the oil spreads along the gap between the water and microstructure surface under pressure and through capillary action with the

oil displacing the trapped air and filling the space between the rough surface and the water. This process can be observed directly, as shown in Figure S6 and Movie S2 in the Supporting Information. When an oil droplet contacts the as-prepared sample in water, air bubbles appear on the oil surface while the oil droplet spreads out. These air bubbles are believed to come mainly from the air cushion trapped between the water and the TiO_2 surface, which is pushed out when the oil droplet occupies that space. This mechanism is characteristic of the surface exhibiting underwater superoleophilicity (Figure 4e).

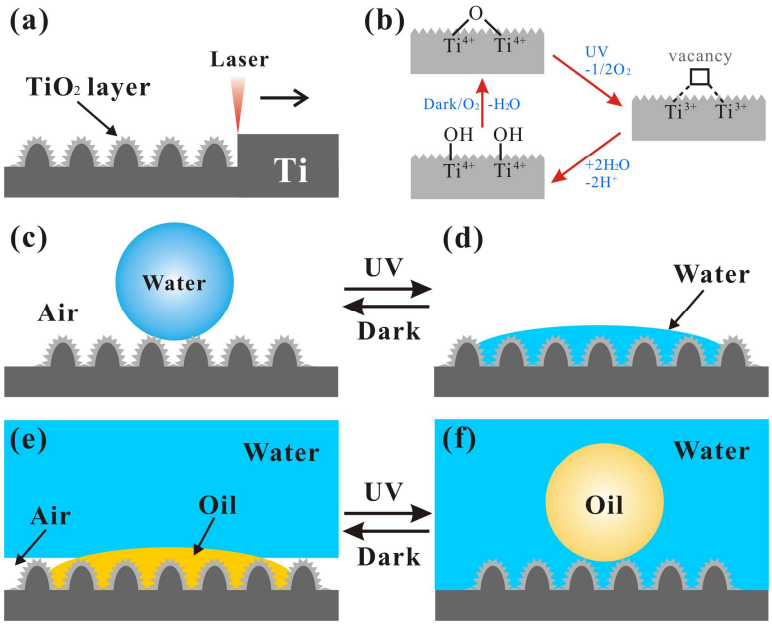

Figure 4. Schematic illustration of the switching between underwater superoleophilicity and underwater superoleophobicity.

TiO_2 is a well-known photo-responsive semiconducting oxide material.[16] After the structured surface is irradiated by UV light, photogenerated holes interact with lattice oxygen forming highly unstable oxygen vacancies form on the TiO_2 surface.[16] These oxygen vacancies possess a strong propensity for dissociative adsorption of

atmospheric water resulting in two adjacent Ti-OH groups per vacancy (Figure 4b). The hydroxyl groups have a high surface energy and endow the as-prepared surface with superhydrophilicity (Figure 4d). When such a sample is immersed in water, the rough surface is completely wetted, resulting in water occupying the interspace between the microstructures. When contacted by an oil droplet, a water cushion is formed between the oil droplet and the surface making the oil droplet sit on the peaks of the microstructure (Figure 4f). This oil wetting state follows the underwater version of Cassie-Baxter model, which is commonly used to describe the oil/water/solid three-phase system.[3] The water trapped in the hierarchical rough structure is a repulsive liquid phase to oil, giving rise to underwater superoleophobicity.[24] Interestingly, the underwater oil wettability returns to its initial superoleophilic state after 2 days of dark storage. During dark storage, ambient oxygen replaces the newly implanted hydroxyl moieties because oxygen adsorption is more stable thermodynamically.[16] As the hydrophobicity of the laser-induced surface increases, the surface recovers to its original superhydrophobic state as well as underwater superoleophilicity (Figure 4c,e). The reversible switching between underwater superoleophilicity and underwater superoleophobicity is ascribed to a combination of the controllable chemical composition and the hierarchical rough microstructure of femtosecond laser ablated Ti surfaces. The former switches the TiO_2 layer between hydrophobicity and hydrophilicity in air or oleophilicity and oleophobicity in water, and the latter strongly amplifies those wettability properties.

It is worth noting that the time of finishing a wetting switching cycle of the femtosecond laser induced rough TiO_2 surface is shorter than that of most other methods developed TiO_2 materials, which usually take several weeks.[25] This relatively fast switchability is a result of the laser ablated sample having a high level of oxygen content. This causes the oxygen vacancies and the implanted hydroxyl groups to form during UV irradiation more easily as well as to be removed by ambient oxygen under dark conditions. Additionally, our as-prepared surface exhibits micro/nanoscale hierarchical structure. The surface area of a multiscale structure is much larger than that of a single-scale structure, which allows the TiO_2 surface to absorb more photons during the UV irradiation process and contact more oxygen molecules during the dark storage process. The above-mentioned advantages endow the femtosecond laser-induced rough TiO_2 surface with faster response speed than traditional developed TiO_2 materials. Since TiO_2 materials are widely applied in solar cells, photocatalytic decomposition of water into hydrogen, and photodegradation of organic pollutants, highly oxygenated and multiscale microstructures may be a way to improve efficiency of those applications.[26]

In recent years, femtosecond laser microfabrication has proven to be a powerful and efficient way to control the wettability of a solid surface because it can not only form micro/nanoscale hierarchical structures via a one-step process, but it can also be applied to various materials.[27] Moreover, the processing position can be precisely controlled by a computer; thereby, complex structures can be designed without using expensive masks and clean rooms. Figure 5 shows some examples of different

patterns which can be realized by femtosecond laser microfabrication. Those heterogeneous structures may exhibit surprising wetting properties in combination with the photoinduced switchable wettability of TiO_2 materials.

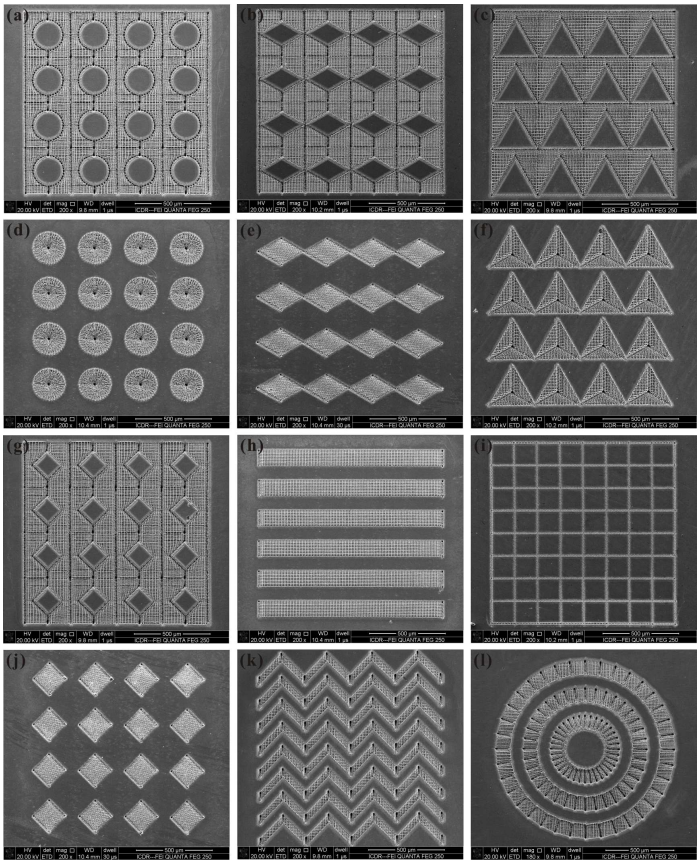

Figure 5. Various patterns prepared through femtosecond laser microfabrication.

4. Conclusions

In conclusion, a simple and effective way to achieve reversible switching between underwater superoleophobicity and underwater superoleophilicity of femtosecond laser ablated Ti material has been demonstrated for the fist time. Femtosecond laser ablation not only forms a micro/nanoscale hierarchical rough structure but also oxidizes the Ti materials, resulting in a rough TiO_2 layer on the surface. The as-prepared surface is superhydrophobic in air as well as superoleophilic in water.

However, after UV irradiation for 40 min, the surface becomes superoleophobic in water with the initial underwater superoleophilic state being recovered after 2 days of dark storage. Because of the hierarchical microstructure and high oxygen content, the femtosecond laser-induced TiO_2 surface performs shorter switching time of a single cycle than traditional developed TiO_2 materials. Furthermore, the TiO_2 surface is responsive not only to UV light but also to visible light. This subtle reversible switching of underwater oil wettability provides a new insight into smart surfaces, and we believe that the femtosecond laser ablated Ti surface will be potentially applied in the biological and medical fields.

Supporting Information

Supporting Information is available from the author.

Acknowledgements

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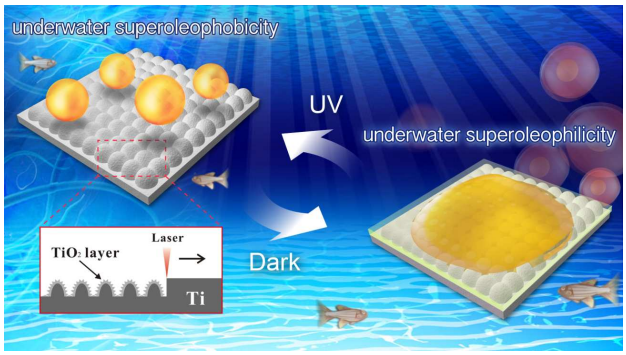

A table of contents entry

An one-step way to achieve smart reversible switching between underwater superoleophobicity and underwater superoleophilicity of femtosecond laser ablated Ti materials.