Controllable underwater anisotropic oil-wetting
Jiale Yong, Feng Chen, Qing Yang, Umar Farooq, Hao Bian, Guangqing Du, and Xun Hou

Citation: Applied Physics Letters 105, 071608 (2014); doi: 10.1063/1.4893945
View online: http://dx.doi.org/10.1063/1.4893945
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/105/7?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Wetting transparency of graphene in water

Effect of pore geometry and interfacial tension on water-oil displacement efficiency in oil-wet microfluidic porous media analogs
Phys. Fluids 26, 093102 (2014); 10.1063/1.4894071

Control of an electrowetting-based beam deflector
J. Appl. Phys. 107, 063101 (2010); 10.1063/1.3319649

A simple strategy to realize biomimetic surfaces with controlled anisotropic wetting
Appl. Phys. Lett. 96, 053704 (2010); 10.1063/1.3297881

Reactive spreading and recoil of oil on water
Phys. Fluids 18, 038105 (2006); 10.1063/1.2187068
Controllable underwater anisotropic oil-wetting

Jiale Yong, Feng Chen, Qing Yang, Umar Farooq, Hao Bian, Guangqing Du, and Xun Hou
State Key Laboratory for Manufacturing System Engineering & Key Laboratory of Photonics Technology for Information of Shaanxi Province, School of Electronics & Information Engineering, Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China

(Received 10 June 2014; accepted 13 August 2014; published online 21 August 2014)

This Letter demonstrates a simple method to achieve underwater anisotropic oil-wetting using silicon surfaces with a microgroove array produced by femtosecond laser ablation. The oil contact angles along the direction perpendicular to the grooves are consistently larger than those parallel to the microgroove arrays in water because the oil droplet is restricted by the energy barrier that exists between the non-irradiated domain and the trapped water in the laser-ablated microgrooves. This underwater anisotropic oil-wetting is able to be controlled, and the anisotropy can be tuned from 0° to ~20° by adjusting the period of the microgroove arrays. © 2014 AIP Publishing LLC.

Anisotropic wetting involves liquid contact angle variations along different directions and results in an elongated droplet, which has attracted tremendous scientific interest in fundamental research and practical applications such as microfluidics, self-cleaning coatings, liquid pumps, and smart device designs. Until now, anisotropic wetting has been achieved by various methods for a water droplet in an air environment. However, there are still significant challenges for organic liquids, which have an altogether different wetting behavior than water for lower surface tension. Recently, Jiang et al. reported the underlying principle that allows fish to swim freely under water and keep their scales clean even in the oil-polluted water. This discovery caused the wettability of underwater oil droplets to become a hot research field. Surfaces exhibiting underwater anisotropic oil-wetting create oil contact angles (OCAs) that are different when measured from different directions in water, which will find many applications in liquid manipulation for microfluidics and labs-on-chips. To meet the growing demand in these areas, a simple and effective method to produce a surface with underwater anisotropic oil-wetting is needed.

In this Letter, we report a simple way to generate a microgroove-array structure on a silicon surface using femtosecond laser ablation. The relationship between the parallel and perpendicular OCAs and the period (D) of the microgroove arrays are systematically investigated. The results show that the femtosecond laser-ablated microgroove arrays exhibit the property of underwater anisotropic oil-wetting, and the anisotropy exists as a consequence of the energy barrier difference between the two orthogonal directions. This production method is simple, rapid, and cost effective, and the oil-wetting anisotropy of these surfaces can be controlled by adjusting D.

The microgroove arrays were achieved using femtosecond laser ablation on a flat silicon surface through a line-by-line scanning process. Single-crystal p-type Si (100) wafers were scanned using a regenerative amplified Ti:sapphire laser system (Libra-USP-1 K-HE-200, Coherent) with a center wavelength of 800 nm, a pulse duration of 50 fs, and a repetition of 1 kHz. The laser beam was focused on the sample using a 20× microscope objective lens (Nikon) with a numerical aperture of 0.45. Each sample was fabricated with a constant average power of 25 mW and at a scanning speed of 2 mm/s. The period, or the average distance between adjacent microgrooves, was tuned by the interval of adjacent scanning lines. Following the irradiation process, the samples were successively cleaned for 10 min each in acetone, alcohol, and deionized water in an ultrasonic bath. For the detection of oil, 1,2-dichloroethane (8 μl) was used, and the OCAs were measured perpendicular to (OCA⊥) and parallel to (OCA∥) the direction of the microgrooves.

Figure 1 shows a typical scanning electron microscopy (SEM) image of the femtosecond laser-ablated silicon surface. The as-prepared surface is covered with rough periodic microgrooves ~8 μm wide and ~5 μm deep. The magnified SEM image reveals the many periodic micro-craters that are formed along the laser-ablated grooves (inset Fig. 1), and also shows the wall and outer rim of the microgrooves to be randomly decorated with many irregular particles with sizes

![FIG. 1. SEM image of a typical femtosecond laser-ablated microgroove array. (inset) The magnified image of a single microgroove.](Image)
ranging from several nanometers to nearly a micrometer. This micro/nanoscale hierarchical rough structure is caused by ablation under laser pulses, and by the recrystallization of ejected particles.\textsuperscript{17–19} As a result of this process, the rough microgroove array can be rapidly formed through a line-by-line scanning process.

The shape of an underwater oil droplet is greatly influenced by the presence of oriented micropatterns on the solid surface, and the contact angles along various directions are often different on anisotropic microstructures.\textsuperscript{20,21} In general, the anisotropic wetting property of groove-like surfaces is examined by measuring the perpendicular and parallel contact angles.\textsuperscript{22} Figures 2(a) and 2(b) show the shapes of an underwater oil droplet on the as-prepared surface along the parallel and perpendicular directions, respectively, with $D = 450 \mu m$. The OCA$||$ is $135.7^\circ \pm 1.5^\circ$, whereas the OCA$\perp$ is $155.5^\circ \pm 1.6^\circ$. The significantly smaller contact angle along the parallel direction indicates that the oil droplet preferentially spreads along the microgrooves. These two sets of OCA measurements are used to define the oil-wetting anisotropy such that OCA$\Delta = $OCA$\perp - $OCA$||$, whose value is as high as $19.8^\circ$ at $D = 450 \mu m$. Interestingly, the underwater anisotropic oil-wetting property is very stable, and the OCA$||$ and OCA$\perp$ values exhibit little change over 10 min. To some extent, this is because the oil droplet is in water and thereby avoids evaporation, unlike water droplets that exist in air.\textsuperscript{23}

Figure 3 shows the OCAs in the perpendicular and parallel directions on the as-prepared surfaces with the value of $D$ ranging from 2 to 600 $\mu m$. When $D$ is less than $100 \mu m$, there is no perceptible distinction between the OCA$\perp$ and OCA$||$ values, indicating that the anisotropy is not obvious although the microstructure is indeed anisotropic. However, when $D$ is greater than $100 \mu m$, the OCA values measured parallel to or perpendicular to the microgroove arrays show a distinct difference. In the perpendicular direction, an increase in $D$ causes a slow decrease in OCA$\perp$, with values decreasing as $159.8^\circ \pm 1.2^\circ$ ($D = 100 \mu m$), $159.4^\circ \pm 2^\circ$ ($D = 200 \mu m$), $156.7^\circ \pm 1.6^\circ$ ($D = 300 \mu m$), $156.1^\circ \pm 1.6^\circ$ ($D = 400 \mu m$), $152.4^\circ \pm 2.4^\circ$ ($D = 500 \mu m$), and $149^\circ \pm 1.6^\circ$ ($D = 600 \mu m$). However, a significant reduction in the OCA$\perp$ is seen with increasing $D$, with values decreasing as $159.7^\circ \pm 1.1^\circ$ ($D = 100 \mu m$), $155.8^\circ \pm 1.4^\circ$ ($D = 200 \mu m$), $145.6^\circ \pm 1^\circ$ ($D = 300 \mu m$), $139.2^\circ \pm 1.3^\circ$ ($D = 400 \mu m$), $132.9^\circ \pm 1.1^\circ$ ($D = 500 \mu m$), and $129^\circ \pm 1.2^\circ$ ($D = 600 \mu m$). The reduction of the OCA is caused by a decrease in the surface roughness owing to an increasing amount of flat non-structured domain with increasing $D$. Although the changes in the OCA$\perp$ and OCA$||$ have similar trends, the OCA$\perp$ is consistently larger than the OCA$||$, exhibiting underwater anisotropic oil-wetting in a wide parameter range.

The dependence curve between the oil-wetting anisotropy (OCA$\Delta$) and the period of the microgroove arrays ($D$) is also shown in Fig. 3. The OCA$\Delta$ gradually increases with increasing $D$, reaching a value of $20^\circ$ when $D$ is larger than $450 \mu m$. In addition, this underwater anisotropic oil-wetting is controllable, with an anisotropy that can be tuned from $0^\circ$ to $-20^\circ$ by adjusting the period of the microgroove arrays.

Femtosecond laser scanning is a simple and effective way to prepare underwater superoleophobic surfaces with OCA stabilization above $150^\circ$.\textsuperscript{24} The silicon surface is an intrinsic hydrophilic material in air, but becomes superhydrophilic after the introduction of a micro/nanoscale hierarchical rough structure by femtosecond laser ablation. When such surfaces are immersed in water, the water can easily enter into the rough microstructure and occupy the whole interspace between the microstructures on the surface. This means that an oil droplet placed on the surface will sit on the top of the rough microstructure, and water will be trapped below the oil.\textsuperscript{24} According to the Cassie-Baxter model, the oil droplet resides on a composite solid-water interface, forming an oil/water/solid three-phase system.\textsuperscript{10,25} The water trapped in the hierarchical rough structure is a repulsive liquid phase for oil, giving rise to a superoleophobic property. It can be clearly seen that the laser-ablated microgroove arrays exhibit underwater superoleophobicity when $D$ is less than $250 \mu m$ in the parallel direction, as shown in Fig. 3. In the perpendicular direction, the range of $D$ values which can realize superoleophobicity is much broader, and the underwater superoleophobicity can be obtained with $D$ less than $500 \mu m$. This emphasizes the fact that the underwater superoleophobicity is caused by the trapped water in laser-ablated microgrooves when the microgrooves are in close enough proximity to each other.

To better understand the underwater anisotropic oil-wetting of the microgroove-array surfaces, we discuss the potential mechanism influencing the shape and contact angle of underwater oil droplets. In fact, the as-prepared surfaces have a heterogeneous topographic structure including both
FIG. 4. Schematic demonstrating the underlying mechanism for anisotropic oil-wetting in water. The (a) side and (b) top views of an oil droplet (yellow) being restrained by an energy barrier between the trapped water (blue) in the laser-ablated microgrooves and the non-irradiated flat domains (grey).

superoleophobic microgrooves and ordinary oleophobic non-irradiated domains in water. According to our previous work, the femtosecond laser-ablated microgrooves exhibit a micro/nanoscale hierarchical structure and underwater superoleophobicity. The oil droplet has contact with only the peak of the micro/nanoscale hierarchical surface, leading to an extremely discontinuous three-phase contact line (TCL), and the interspace between the oil droplet and microgrooves is completely filled with water. The portion of the underwater oil droplet on the laser-irradiated microgrooves, therefore, belongs to the Cassie-Baxter state. The non-irradiated flat domain will have complete contact with the oil, however, because the detecting oil is heavier than water, and a continuous TCL will be formed in this region. This contact model can be considered an underwater Young state. Therefore, an oil droplet on the heterogeneous as-prepared surfaces in water is generally composed of both the Cassie-Baxter and Young contact states. It is known that an energy barrier can form between adjacent dissimilar chemical or morphologies with different apparent surface free energy values, according to Gibbs’ criterion. For our microgroove-array surfaces, when an underwater oil droplet spreads from the flat silicon domain (non-irradiated area between the microgrooves) to the laser-ablated microgroove, it needs to overcome the energy barrier between the flat domain and the trapped water in the laser-ablated microgrooves. The flat silicon domain initially contacts the oil droplet and generates a strong attraction, inducing the droplet to extend in a direction parallel to the microgrooves; while the trapped water in the microgrooves prevents the oil droplet from spreading in the perpendicular direction (Fig. 4). The restrictive effect can be directly observed in Figs. 2(c) and 2(d), which show the magnified contact state of an underwater oil droplet along the parallel and perpendicular directions on the as-prepared surface with \( D = 450 \mu m \). It can be clearly seen that the oil droplet is unconstrained in a direction parallel to the microgrooves, whereas it is restricted by two laser-ablated microgrooves in the perpendicular direction. Because of the restriction brought about by the energy barrier, the OCAs along the parallel direction are smaller than those along the perpendicular direction, exhibiting a controllable anisotropy.

In conclusion, we demonstrate a simple method to achieve underwater anisotropic oil-wetting using femtosecond laser-ablated microgroove-array surfaces. The OCAs along the perpendicular direction are consistently larger than those along the parallel direction on the as-prepared surfaces in water, showing stable underwater anisotropic oil-wetting. This anisotropic oil-wetting is controllable, and the anisotropy can be varied from 0 to 20° by adjusting the value of \( D \). The formation of the anisotropy comes about when the oil droplet is restricted by the energy barrier between the non-irradiated domain and the trapped water in the laser-ablated microgrooves. This developed approach can potentially have important applications in droplets/fluid manipulation, microfluidics, and fluid microreactors.

This work was supported by the National Science Foundation of China under the Grant Nos. 61275008 and 51335008, the special-funded programme on National Key Scientific Instruments and Equipment Development of China under the Grant No. 2012YQ12004706.