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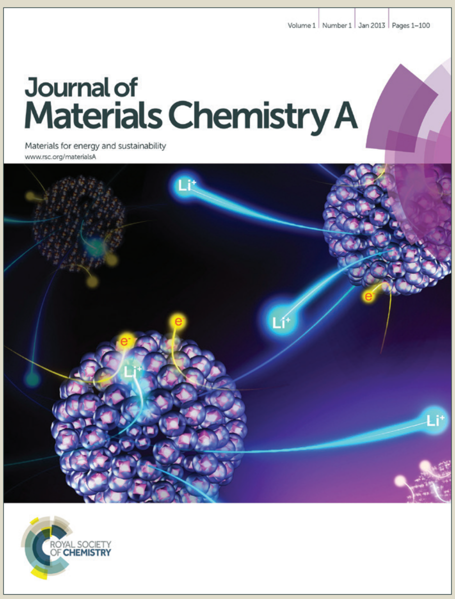

# Bioinspired Transparent Underwater Superoleophobic and Anti-Oil Surfaces

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**Abstract**

Reported here is a bioinspired fabrication of transparent underwater superoleophobic and anti-oil surfaces by means of femtosecond laser treatment. Rough nanoscale structures were readily created on silica glass surfaces by femtosecond laser-induced ablation. Underwater superoleophobicity and ultralow oil-adhesion can be obtained by the rough nanostructures with a wide variation of processing parameters, and the as-prepared surfaces exhibit high transparency in water. This is attributed to the presence of the water environment because scattering and refraction are effectively weakened. As a maskless and cost-effective method, femtosecond laser processing of transparent materials (glass) may open up a new method to create biomimetic transparent underwater surfaces, allowing for the development of novel underwater anti-oil optical devices.

## 1. Introduction

With billions of years of evolution, creatures develop almost perfect structures and exhibit various functions. Nature is the best school for human beings and inspires us to design advanced materials and to use new technology.[1-8] Recently, there has been growing interest in the design of underwater superoleophobic surfaces because of their importance in academia and industry, including such topics as submerged antifouling, oil/water separation, bioadhesion, and small oil-droplet manipulation.[9-17] In nature, water can be trapped in the rough microstructure of fish scales, thereby forming an oil-repellent layer.[18] The water cushion results in underwater superoleophobicity and ultralow oil-adhesion, endowing fish skin with anti-oil properties. Inspired by fish scales, various underwater superoleophobic surfaces have been artificially realized based on an oil/water/solid three-phase system using many techniques.[19-26] However, the reported underwater superoleophobic surfaces are usually opaque, which limits their applications in underwater optics, such as oil proof windows for underwater cameras, diving goggles, and even imageable substrates for biologically active cells or tissue. Therefore, finding a simple route for highly transparent superoleophobic surfaces in an aqueous medium is urgently needed and has remained challenging.

Building underwater superoleophobic substrates require hierarchical structures to improve surface roughness,[7,27] whereas rough surfaces constructed by various micro-nanostructures may be completely opaque because of the extensive light scattering effect. In nature, there is a fantastic phenomenon in which the petals of *Diphylleia grayi* turn from white to transparent in the rain, as shown in Figure 1.[28] In air, the petals of *Diphylleia grayi* appear to have a white color. The color does not come from a natural white pigment while results from the highly loose cell structure of the plant petals. The inner part of the petal comprises many lacunae and intercellular spaces that are filled with air. Diffuse reflection occurs in the interface between the trapped air and colorless cytolymphs on a sunny day, thereby endowing the petals with a white color. However, in the rain, water can enter the lacunae and intercellular spaces. The original air-liquid (air-cytolymph) interface is replaced by a liquid-liquid (water-cytolymph) interface. Because the cytolymph and water have comparable refractive indices, the light transmission is significantly increased. As a result, the petals appear transparent. This interesting phenomenon inspires us to a novel strategy for improving the transparency of rough interfaces; that is, the interspace of rough microstructures can be filled with water.


**Figure 1.** Petals of *Diphylleia grayi* becoming transparent. (a) In sunny day; (b) in the rain. [28]

In this paper, underwater ultralow oil-adhesive superoleophobicity is obtained on a silica glass surface through femtosecond laser ablation. The static and dynamic oil wettability in a water medium is systematically investigated at various average distances (*AD*s) of laser pulse ablated points and pH values of water solution. The results reveal that the as-prepared surfaces show underwater superoleophobicity and ultra-low oil-adhesion throughout a wide technology parameter range, and even in acid or alkaline aqueous solutions. Importantly, the as-prepared surfaces also possess transparent properties in water.

## 2. Experimental Section

Silica glass is widely applied in optical equipments and lab-on-chip devices for its good optical performance and biocompatibility. In our experiment, the silica glass sheets ($2 \times 2 \times 0.2$ cm$^3$) were ablated by a regenerative amplified Ti:sapphire laser system (CoHerent, Libra-usp-1K-he-200) that generates 50 fs pulses at repetition rate of 1 kHz with the center wavelength of 800 nm. The laser beam was focused on the silica glass surface using a microscope lens with numerical aperture (NA) of 0.45 (Nikon, Japan). A line-by-line and serial scanning process was used. Samples were ablated at a constant power of 20 mW with different *AD*s. *AD* is our mainly processing parameter which is determined by both the interval of adjacent laser scanning lines and the scanning speed. The detailed definition of *AD* is shown in Figure 2 and can refer to our previous work.[29,30] Since our laser system is a pulsed laser with a repetition rate of 1 kHz, the average distances of laser pulse ablated points in the $x$ direction, $AD_x$, is controlled by the scanning speed. In the $y$ direction, the $AD_y$ is directly dominated by the shift of adjacent laser scanning lines. We always make $AD_x$ approximately equal to $AD_y$ in the experiment, so that $AD \approx AD_x \approx AD_y$. For example, the as-prepared sample with $AD = 4$ μm is fabricated at scanning speed = 4000 μm/s and the interval of adjacent scanning lines = 4 μm.

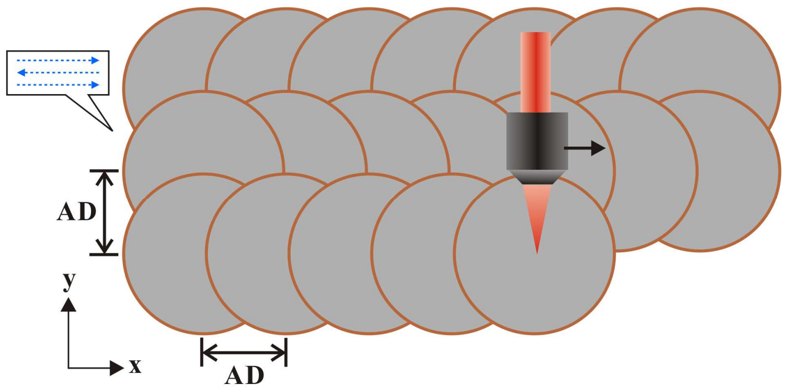


**Figure 2.** Schematic illustration of the scanning process and the detailed definition of *AD*.

The microstructure was observed by a Quantan 250 FEG scanning electron microscope (SEM, FEI, America). The static and dynamic wettability was investigated by a JC2000D2 contact-angle system (Powereach, China). The average values were obtained by measuring five different points on the same surface. 1,2-dichloroethane droplet (8 μL) was used as mainly test oil. The transmission spectra in the wavelength range of 200-900 nm were recorded using a UV 3010 spectrophotometer (Hitachi, Japan). The *AD*-dependent transmittance was obtained by measuring the light power before and after the pass through the silica glass. A He-Ne laser (wavelength = 633 nm, output power = 0.96 mW) was used as a light source. Water with different pH values were achieved by diluting sodium hydroxide and hydrochloric acid with deionized water, respectively, monitoring by a CT-6023 pH meter (Kedida, China).

### 3. Results and Discussion

Femtosecond laser processing has emerged as a new method to control wettability of solid surface.[30-34] Figure 3 presents the digital and SEM images of the femtosecond laser irradiated silica glass surface at *AD* = 4 μm. The surface is covered by abundant irregular particles with the size from tens to hundreds nanometer. Some particles pile up so that many holes and grooves are randomly on the as-prepared surface. High-temperature and high-pressure plasma can form above silica glass surface during the interaction between femtosecond laser and silica glass.[29,35] With the process of plasma expanding and bursting out of focal spot, the ablated materials are removed from the surface. On the other hand, ejected particles are in the molten state because of high temperature. When these ejected particles fall on the surfaces and instantly cool down, they will glue together with the silica glass substrate.[36] The ablation under laser pulses and the resolidification of ejected particles ultimately result in nanoscale rough microstructure.

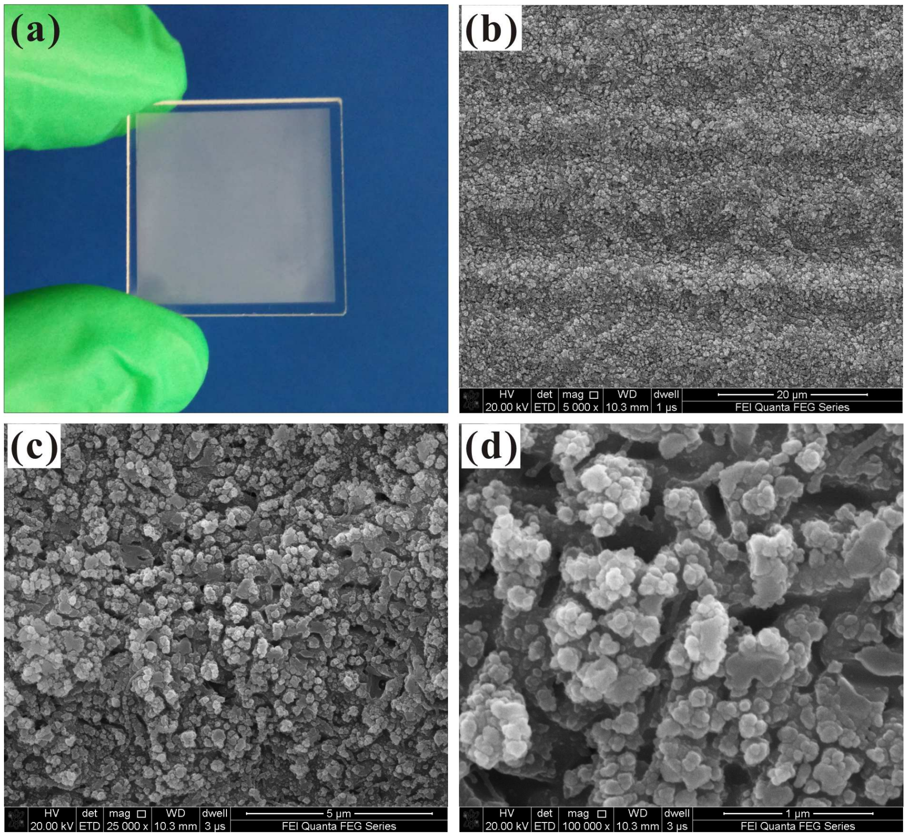


**Figure 3.** (a) Digital image of the femtosecond laser irradiated silica glass with the total size of 2×2 $cm^2$. (b-d) SEM images of laser-induced microstructure with different magnifications.

The underwater oil repellency of fish scales tells us that superhydrophilic solid surface will perform superoleophobicity in water.[9,10] Figure 4a depicts an oil droplet on the untreated flat silica glass surface in water medium. The surface exhibits weak oleophobicity with an intrinsic oil contact angle (OCA) of 125.5 ± 2°. After the sample being irradiated by femtosecond laser, nanoscale rough structure forms on the silica glass surface. If a water droplet is lowered down and contacted with the rough surface, the droplet will spread out quickly and cause a very small water contact angle (WCA) near 0° (Figure 4b). When the as-prepared surface is put into water, the wettability of the sample will switch from superhydrophilicity in air to underwater superoleophobicity. The oil droplet on the as-prepared surface keeps an approximately spherical shape with OCA of 160.2 ± 1° in a water medium, as shown in Figure 4c. In addition, underwater oil droplet can easily roll off on a 1° tilted as-prepared surface, revealing the oil sliding angle (OSA) lower than 1° (Figure 4d). This small value reveals that the femtosecond laser irradiated surface also has ultralow oil-adhesion.

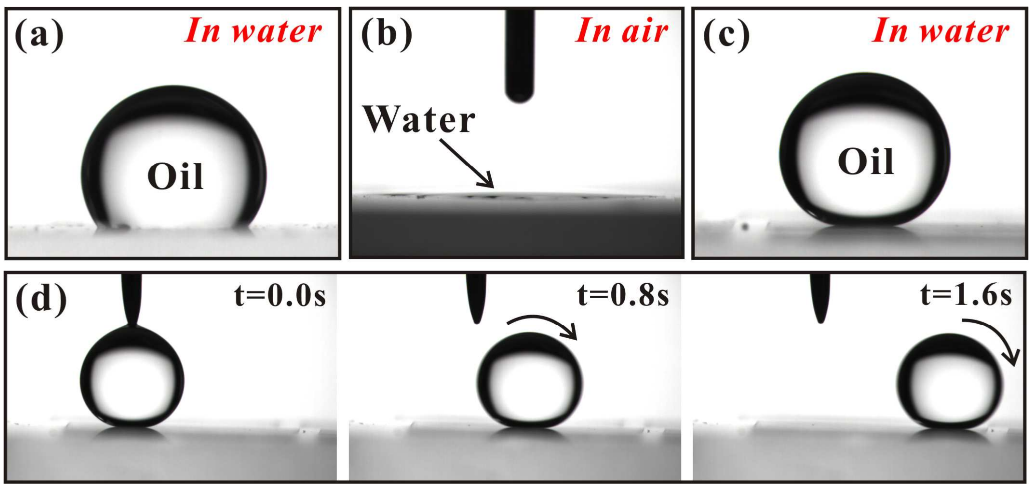


**Figure 4.** Wettability of the femtosecond laser irradiated silica glass (*AD* = 4 μm). (a) An oil droplet on the unstructured silica glass sample in water. (b) A water droplet spreading on the as-prepared rough surface in air medium. (c) Shape of an oil droplet on the laser-induced surface with OCA of 160.2 ± 1° in water medium. (d) An oil droplet rolling off on a 1° tilted sample.

Since the as-prepared surfaces have both underwater superoleophobicity and ultralow oil-adhesion, the wetting model of an oil droplet on the laser irradiated surface can consider at the underwater Cassie state.[9,10,18] Silica glass is intrinsically weak hydrophilic (WCA = 33.3 ± 0.5°) in air, and its wetting property can be significantly amplified to superhydrophilicity by the laser-induced rough microstructure (Figure 4b).[8,37] Once the as-prepared surface is immersed in water, the interspace between the rough microstructures will be entirely wetted and occupied by water, forming a water cushion between the substrate and the oil droplet. Therefore, the oil droplet indeed resides on a composite solid-water interface and only contacts the peak of the rough microstructure. The wetting phenomenon of this oil/water/solid three-phase system is often described by the underwater version of Cassie state.[9,10,38,39] Water is an optimal repulsive liquid phase for oil, so the trapped water cushion contributes to the underwater superoleophobicity of the laser-induced surfaces.[19,25] Because the trapped water layer hinders the oil droplet availably contact with the sample, the contact area between the silica glass surface and the oil droplet is dramatically reduced, endowing the laser irradiated surface with ultralow oil-adhesion.

The rough silica glass has a different transmittance in water medium by comparison to that in air. The femtosecond laser ablated silicon glass exhibits white in air that is close to the color of *Diphylleia grayi* petals (Figure 3a). When the as-prepared sample is put on a paper with black letters in air environment, it can be seen that the letters behind the sample is misty (Figure 5a). If an oil droplet (dyed with Sudan Ⅲ, red color) contacts with the laser-induced region, it will rapidly spread out, as shown in the upper-left area of the as-prepared surface in Figure 5a. In the contrary, the letters "XJTU" becomes very clear after putting the sample in water (Figure 5b). The dyed oil droplet always remains a small sphere on the substrate (inset of Figure 5b). The excellent readability of the letters reflects the high transparency of femtosecond laser ablated silica glass in water medium. The transmittance reaches up to 91.6% at $AD$ = 4 μm for the light with wavelength of 633 nm. The high optical transparency underwater is further supported by the UV-vis spectra measurement, as shown in Figure 4c. The rough sample exhibits poor transmittance in air but good transmittance in water. At visible wavelengths, the underwater transmittance of femtosecond laser ablated silica glass is very close to that of bare flat silica glass. Figure 5d describes the dependence of transmittance on *AD*. Clearly, the transmittance in water is consistently greater than that in air for every technology parameter. The difference is particularly evident when *AD* value is small. With increasing *AD*, the roughness of the sample decreases, and then an enhanced trend of the transmittance can be observed. The transmittance of the laser-induced silica glass surface fabricated at *AD* above 4 μm is more than 90% in water. The good transparency benefits from the presence of water environment.

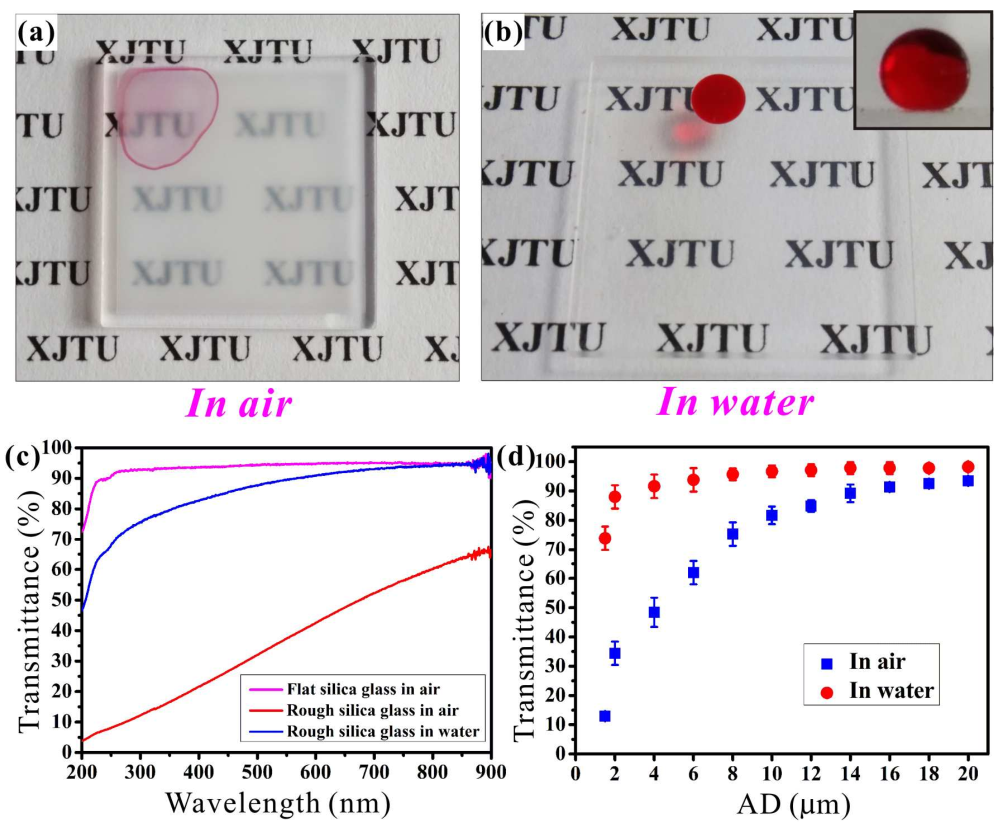

**Figure 5.** (a,b) Images of the as-prepared surface (*AD* = 4 μm) on a piece of paper in different medium: (a) in air; (b) in water. (c) UV-vis spectra of femtosecond laser ablated silica glass (*AD* = 4 μm). (d) Variation of transmittance of the femtosecond laser ablated silica glass with the average distance of laser pulse ablated point.

The laser-induced rough silica glass performs high transparency in water medium because the refractive index of silica glass is closer to that of water. The underlying mechanism is similar to the natural phenomenon that the petals of *Diphylleia grayi* become transparent in the rain. When the light beams pass through the interface between two different materials, smaller refraction occurs with those two materials having closer refractive indices. This principle agrees well with the fact that ground glass sheet will not be seen and seem "disappeared" when it is put into water. The interspace of rough microstructure is filled with water which has a closer refractive index with silica glass than that of air. Therefore, the degree of Mie scattering and refraction is effectively weakened for the existing of water environment, endowing the as-prepared rough materials with good transparency.[40,41]

Figure 6a shows the static and dynamic underwater oil-wettability of as-prepared surfaces with different average distances of laser pulse ablated point. Clearly, the OCAs keep higher than 150° as *AD* increases from 1.5 μm to 20 μm. At the same time, all the OSAs are lower that 10°. This result indicates that the underwater ultralow oil-adhesive superoleophobicity can be obtained with wide variation of processing parameters. Even being soaked in water for one month, the OCA and OSA of the laser-induced silica glass had no significant changes. Interestingly, the as-prepared surfaces still have the property of underwater superoleophobicity and ultralow oil-adhesion not only in water medium but also in acid or alkaline aqueous solutions. Figure 6b shows the dependences of the OCA/OSA on pH of water solution. When the pH is changed from 1 to 13, the OCAs maintain above 150°, while all the corresponding OSAs are very small and no more that 10°. One thing to note here is that the OCA value of pH = 13 is higher than the others because obtaining high pH water medium needs a large concentration of alkaline aqueous solution, thereby resulting in a relatively large buoyancy acting on the oil droplet.[20] The good chemical stability makes the as-prepared surfaces be applied more widely and more flexibly, especially in harsh water environments or in the chemical and biological applications.[17] Additionally, the as-prepared surfaces also behave underwater superoleophobicity with ultralow oil-adhesion for other oil droplets, such as hexadecane, petroleum ether, paraffin liquid, crude oil, sesame oil, and chloroform, as shown in Figure 7.

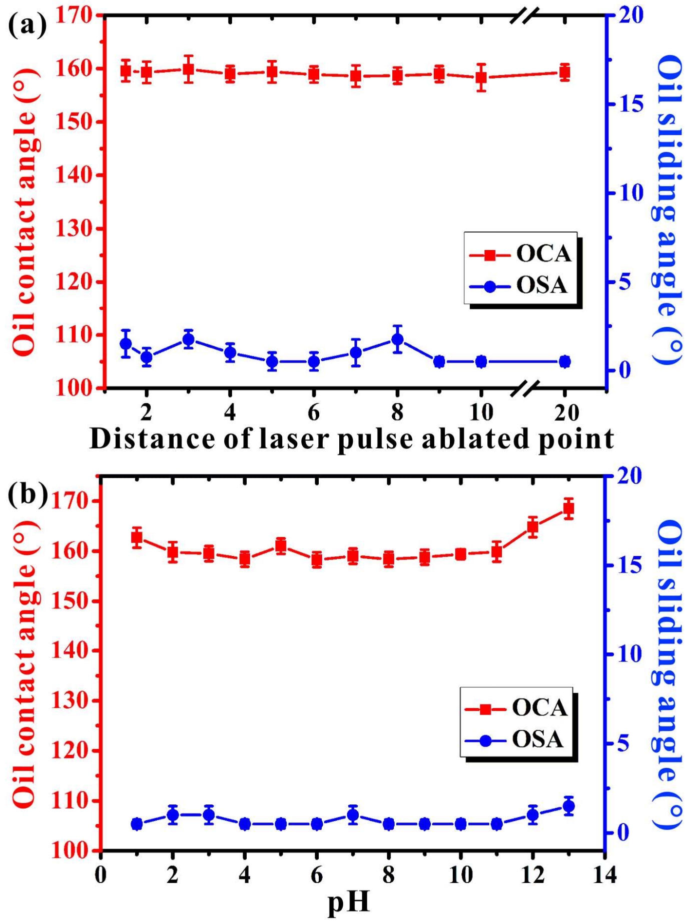


**Figure 6.** (a) Oil contact/sliding angles of underwater oil droplet on the as-prepared surface fabricating at different average distances of laser pulse ablated point. (b) Dependences of the oil contact/sliding angles on the pH of water solution.

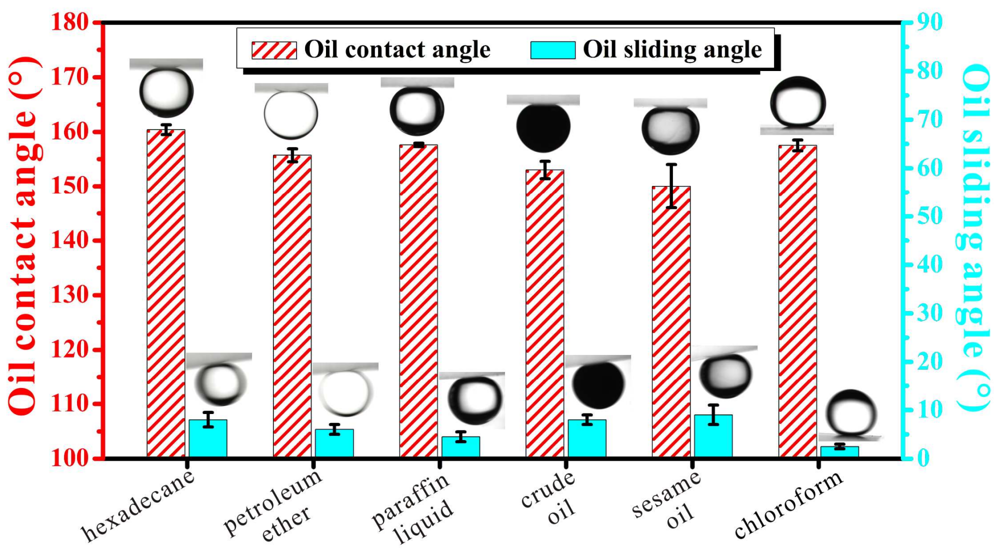

**Figure 7.** Underwater superoleophobicity and ultralow oil-adhesion of the femtosecond laser ablated silica glass surface (*AD* = 4 μm) for various oils in terms of their oil contact angles and oil sliding angles, respectively.

## 4. Conclusion

In summary, we have developed a one-step way to realize transparent underwater superoleophobic surface on silica glass by femtosecond laser ablation. Achieving underwater ultralow oil-adhesive superoleophobicity is inspired by fish scales while high transparency takes inspiration from *Diphylleia grayi* petals. The as-prepared surfaces exhibit underwater superoleophobicity and ultralow oil-adhesion in a wide technology parameter range (*AD* = 1.5 ~ 20 μm). Even in acid or alkaline aqueous solutions, the superoleophobicity shows no sign of abating. In addition, the rough silica glasses perform high transparency in water medium because the interspace of rough microstructures is filled with water and the refractive index of silica glass is closer to that of water. Scattering and refraction are effectively weakened. We believe that the underwater highly transparent, stable superoleophobic and ultralow oil-adhesive silica glass surfaces will have important potential applications in the underwater optics and biological imaging.

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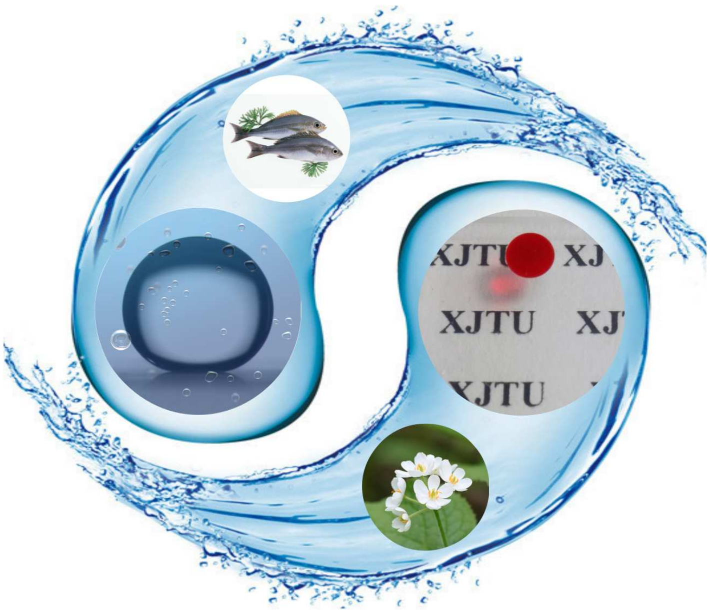


A table of contents entry

A bioinspired method to realize transparent underwater superoleophobic and anti-oil surfaces by femtosecond laser treatment.