Underwater Transparent Miniature “Mechanical Hand” Based on Femtosecond Laser-Induced Controllable Oil-Adhesive Patterned Glass for Oil Droplet Manipulation

Jinglan Huo,† Qing Yang,‡ Feng Chen,†* Jiale Yong,‡†§ Yao Fang,† Jingzhou Zhang,† Lin Liu,§ and Xun Hou †

†State Key Laboratory for Manufacturing System Engineering and Key Laboratory of Photonics Technology for Information of Shaanxi Province, School of Electronics & Information Engineering, ‡School of Mechanical Engineering, and §Department of Biological Science and Bioengineering, Key Laboratory of Biomedical Information Engineering of Ministry of Education, School of Life Science and Technology, Xi’an Jiaotong University, Xi’an 710049, PR China

ABSTRACT: Development of underwater superoleophobic surfaces has captured the imagination of researchers because of their applications; especially, oil manipulation based on such surfaces has attracted much attention. Here, we show a simple and effective way to fabricate an underwater transparent miniature “mechanical hand” based on controllable oil-adhesive patterned glass using a femtosecond laser. The underwater oil-adhesive force of the patterned glasses that compose the “mechanical hand” device can be controlled from ultralow to ultrahigh by adjusting the ratio of the untreated flat glass area to the laser-ablated rough area. These surfaces also showed favorable transparency in water. Various oils such as chloroform, hexadecane, n-dodecane, decane, liquid paraffin, and petroleum ether were tested, and their repellency against the as-prepared surfaces in water medium was confirmed. Moreover, the “mechanical hand” was used to implement oil transportation, fusion, and rapid capture, which can be applied in the construction of microfluidic devices, in situ detectors, and bioreactors.

1. INTRODUCTION

Over billions of years of evolution, creatures in the world have evolved various unique multifunctional biointerfaces to adapt to hostile environments.1−6 For example, fish scales with the property of resisting oil pollution in water are a tremendous fascination for researchers and have set off a tidal wave of research into underwater superoleophobic surfaces with an oil contact angle (OCA) greater than 150°.7−14 Jiang et al. first reported an underwater superoleophobic interface on Si substrates based on an oil/water/solid three-phase system inspired by the anti-oil behavior of fish scales.15 They revealed that the underwater superoleophobicity of fish scales is ascribed to both hydrophilic chemical components such as proteins and hierarchical rough structures on those surfaces. Underwater superoleophobic surfaces have many promising and practical applications such as self-cleaning surfaces,16−18 oil/water separation,19−27 tissue engineering,28−30 microfluidic chips,31,32 and micro-oil-droplet manipulation.33−37

In particular, in micro-oil-droplet manipulation, the oil microdroplet can be handled directly and precisely without any loss compared with traditional micro-oil-droplet manipulation technologies such as micropump, microvalve, and microchannel. These devices have the disadvantages of complex operation and oil loss during the manipulation.38−40

There are two kinds of approaches to manipulate an oil microdroplet in water based on underwater superoleophobic surfaces, that is, in situ transfer of the oil droplet by altering the ambient conditions in or around the surroundings of the liquid41−43 and oil droplet transportation by controllable oil adhesion on superoleophobic surfaces.44−52 Yong et al. reported a method for the in situ transfer of oil droplets in water based on inducing underwater superoleophobic surfaces with a femtosecond laser and switching the density of the water solution.41 An oil droplet could be picked up by simply adding sugar to a water environment and could be put down by adding water to dilute the sugar water by changing its buoyancy in water. However, this method lacks stability and practicability because the oil microdroplet easily rolls away when the underwater superoleophobic substrate shakes even gently. Another way of achieving oil droplet transfer is based on underwater superoleophobic surfaces with tunable oil adhesion ranging from ultralow (an oil droplet can roll down when the surface is tilted slightly) to ultrahigh (an oil droplet can be pinned on the surface even when the surface is upright or turned over). Generally, an ultrahigh adhesive surface is used as a “mechanical hand” to pick up an oil droplet from an ultralow adhesive surface to a flat surface with no volume loss. Underwater oil droplet adhesion is governed by both the
chemical composition of the surface of the materials and the surface roughness, and efforts have been made to develop methods for the fabrication of oil-adhesive controllable surfaces on various materials in recent years. Cheng et al. used the self-assembled monolayer technique to modify n-alkanoic acids with different chain lengths on the nanostructured copper films to prepare a series of underwater superoleophobic copper surfaces with controlled oil droplet adhesion, which could be used to transport an underwater oil droplet without volume loss.48 Zhang et al. fabricated underwater superoleophobic Ni/NiO surfaces with controllable morphologies on stainless steel through electrodeposition.49 By annealing at different temperatures, Ni/NiO surfaces with different microstructures were obtained, which resulted in underwater superoleophobicity with structure-dependent oil adhesion. The very high oil-adhesive surface could be regarded as a “mechanical hand” as well. By comparison, oil microdroplet manipulation based on surfaces with controllable adhesion yields higher stability. However, the above-mentioned methods for preparing controllable oil-adhesive surfaces need elevated temperatures, and the preparation procedures are complex. In addition, these underwater superoleophobic surfaces are usually adiaphanous, which may limit their application in underwater image formation, and the process has to be monitored accurately. All of these defects require that a transparent underwater adjustable oil-adhesive surface should be built via a simple and effective method.

Here, we demonstrate a simple way of realizing underwater transparent superoleophobic patterned glass surfaces with tunable oil adhesion using a femtosecond laser. These surfaces consist of a laser-induced hierarchical micro/nano rough structure and untreated flat glass, wherein the middle unstructured flat glass surface domain is round and surrounded by a structured rough surface domain. The fabricated surfaces show superoleophobicity in water, and their oil adhesion can be adjusted flexibly by changing the fraction of the untreated flat glass region to the laser-ablated rough region. Furthermore, the property endows the as-prepared surfaces with many practical applications for a miniature “mechanical hand” in the no-loss transportation, fusion, and capture of an oil microdroplet. Importantly, the as-prepared superoleophobic glass surface is proven to have a favorable transparency.

2. EXPERIMENTAL SECTION

2.1. Surface Laser Ablation. A regenerative amplified Ti:sapphire laser system (Coherent Libra-usp-He) that produces femtosecond laser pulses (pulse duration = 50 fs; central wavelength = 800 nm; and frequency = 1 kHz) was used for ablating the sample surfaces. The laser energy was modulated by an attenuator, and the laser beam was focused through a microscope objective lens (20×, NA = 0.45, Nikon) on the glass slide (Sail Brand) surface mounted on a motorized precise stage controlled by a computer. Through the design of specific assembly programs, the surface configuration composed of micro-/nanostructures on diverse scales was processed in one step.

2.2. Structured Center Circle Array. Figure 1 schematically shows the fabrication of the center circle array using a line-by-line scanning femtosecond laser on a glass slide. The gray domain demonstrates the structured area, on which the red and yellow lines with arrows indicate the scanning route of the focused laser beam. The speed of laser scanning was set at 2 mm/s under a constant average laser power of 15 mW; meanwhile, the interval between adjacent horizontal parallel lines was held unchanged at 2 μm. After femtosecond laser irradiation, the unstructured flat area took a circular shape (the blue domain in Figure 1) surrounded by laser-induced rough structures. Each machining unit that includes a center circle enclosed in a square has two crucial parameters, that is, the side length (SL) of the square and the diameter (D) of the center circle. To control the variables, SL was fixed at 200 μm. The size of the flat center circle was controlled by adjusting D through a computer program.

2.3. Morphology Analysis and Sample Characterization. The morphology of the laser-ablated pattern surfaces was observed using a Quanta FEG 250 scanning electron microscope (FEI, America). The transmission spectra with wavelength ranging from 300 to 900 nm were measured using a UV 3010 spectrophotometer (Hitachi, Japan). 1,2-Dichloroethane was chosen as the main tested oil in the experiment. The contact and sliding angles were measured using a JC2000D contact-angle system (Powereach, China), and the manipulation of oil droplets was observed using a charge-coupled device (CCD) camera system.

3. RESULTS AND DISCUSSION

Figure 2a shows the scanning electron microscopy (SEM) image of the entire laser-scanned glass surface (D = 0 μm).
After the laser irradiation, periodical hierarchical rough microislands with a size of approximately 10 μm were formed on the sample surface because of the overlap among the laser pulse-ablated craters. A further magnified SEM image shows that each microisland surface presents a loose and porous structure covered by hundreds of accumulated or sporadic nanograins formed from the ablation of laser pulses and the recrystallization of ejected particles (Figure 2b). When a water droplet is in touch with the as-prepared sample surface, it spreads out in a single second with a water contact angle (WCA) of just 15° (Figure 2d), which is very small in comparison with the WCA of 79° on a flat glass surface without any laser treatment (Figure 2c), demonstrating the quasi-superhydrophilicity of the femtosecond laser-scanned surface. Generally, a superhydrophilic substrate in air becomes superoleophobic in water. Once immersed in water, the OCA of a 1,2-dichloroethane oil droplet on the micro/nano rough surface augments from 100° for an untreated flat surface to 160 ± 1°, indicating the transition of the underwater surface from ordinary oleophobicity to superoleophobicity (Figure 2e,f). At the same time, the ultralow oil adhesion in water is also achieved so that an oil droplet could roll off easily even when the structured surface is tilted by only 1° (Figure 2g). The flat glass slide surface showed oleophobicity in water, whereas the femtosecond laser-induced rough microstructures could magnify the surface wettability to underwater superoleophobicity because of the formation of an underwater Cassie contact state.50 Water wetted the rough surface and was captured into the microstructures as soon as the sample was immersed in water, forming an oil-repellent trapped water layer. When an oil droplet was placed onto the sample surface in water, the droplet indeed sat on a solid/water composite interface and touched only the top of the nanograins. The OCA of an underwater oil droplet on such an interface, θ*, can be described as follows

\[ \cos \theta^* = f \cos \theta + f - 1 \]

where \( f \) is the area fraction of the rough solid surface that is in contact with the oil droplet and \( \theta \) is the OCA of an underwater oil droplet on the untreated flat glass surface. The measured \( \theta \) and \( \theta^* \) values are 100 and 160°, respectively, so the value of \( f \) is calculated to be 7.3%, verifying the very small contact area between the underwater oil droplet and the femtosecond laser-ablated substrate.

Furthermore, other oils having different values of surface tension were tested on the as-prepared sample with ultralow adhesion. The sample surface showed underwater superoleophobicity and ultralow oil adhesion toward all of those oils, including chloroform, hexadecane, n-dodecane, decane, liquid paraffin, and petroleum ether, as shown in Figure 3. These oil droplets could easily roll down when the surface was at a small angle, and their oil sliding angles (OSAs) were all less than 2°.

By changing the value of the parameter \( D \), the topographies of the sample surfaces can also be changed correspondingly. As shown in the SEM images of laser-irradiated periodic center circle arrays (Figure 4), the sample surfaces comprise an unprocessed flat circle and processed rough structures around the circle. The diameter \( D \) of the center circle is regarded as the paramount parameter having an effect not only on the patterning structures but also on the oil wettability and adhesion of the as-prepared surface. With the increase in \( D \), the center circle area increases, that is, on the premise of making SL constant, the flat-to-rough ratio increases as well (Figure 4a–d). Figure 4e,f shows the enlarged views of the laser-induced hierarchical rough microisland structures in the heterogeneous patterning systematization. This is the same as the entirely scanned rough structures (\( D = 0 \) μm) with which the surface shows underwater superoleophobicity and ultralow oil adhesion.

Figure 5 illustrates the relation between \( D \) and the static OCA and the dynamic OSA on the as-prepared surfaces. It could be easily seen that all of the samples demonstrate underwater superoleophobicity with the OCAs being approximately 160° and the oil droplet looking like a sphere. Taking two representative pattern surfaces as examples, the OCA of the surface with \( D = 0 \) μm reaches up to 160 ± 1° and that of the surface with \( D = 200 \) μm is still as high as 158 ± 2°. By contrast, the OSAs that enable characterization of the surface adhesion are quite different as the value of \( D \) is adjusted. When \( D \) ranges from 0 to 40 μm, the oil droplet can roll down easily when the surface is inclined at a small angle below 2° or even when shaken gently (insets in Figures 4a and 5), manifesting the ultralow adhesion of the surface to oil, as shown in area I in Figure 5. When the value of \( D \) increases from 40 to 180 μm, the OSA curve increases sharply as shown in area II in Figure 5. The inset in area II indicates the moment when the oil droplet starts rolling with an OSA of 48 ± 2° on the surface with \( D = 120 \) μm. The oil droplet, however dramatic, can be pinned on the surfaces (\( D = 180 \) and 200 μm) even when the surfaces are upright or upside down (insets in Figures 4d and 5), revealing an ultrahigh oil adhesion with OSAs being expressed via 180° in area III in Figure 5. It is obvious from the curve that the oil adhesion of the processed periodical center circular pattern of the sample is controllable, with the value of \( D \) ranging from 40 to 180 μm, which is ascribed to the proportion of the laser-induced micro-/nanostructure region to the unstructured region in the patterned substrates. In addition, the volume of the oil droplet also has an impact on the OCA of the oil microdroplet on the as-prepared surface. Generally, the larger the size of the oil droplet, the smaller is the OSA.51 Taking the patterned surface with \( D = 80 \) μm as an example, when the volume of the oil droplet is increased from 7 to 15 μL and then to 20 μL, the OSA decreases from 11 ± 2° to 7 ± 1° and then
to 2 ± 1°. It is found that with the increase in the volume of the oil droplet, the underwater OSA decreases accordingly.

The mechanism of tunable surface adhesion is discussed below. As is known, the liquid adhesiveness of a surface is governed by both the surface chemical composition and the surface morphological structure. Because the chemical composition of the glass surfaces change little after laser ablation, the latter factor is the foremost point in controlling the adhesion. In this work, the center circle array pattern of the laser-induced periodical surface consists of an unstructured flat domain and a structured rough domain. As for the former, the intrinsic hydrophilicity of the glass sheet results in its intrinsic ordinary underwater oleophobicity, giving rise to a large contact area between the oil droplet and the surface. This contact state can be regarded as the Young state (Figure 6c), in which the oil droplet fully wets the nonablated flat surface. The Young contact state not only facilitates the formation of the successive three-phase contact line (TCL) at the solid/oil/water interface but also expands the van der Waals force between the oil/solid molecules, resulting in an ultrahigh adhesion, with the oil droplet being adhered to the surface. With regard to the latter rough domain, the contact between the underwater oil and such a rough domain is at the Cassie contact state (Figure 6c). The oil droplet contacts only the tip of the rough microstructure and results in an inconsecutive TCL. The small contact area and the inconsecutive TCL rendered by the irregular distribution of nanograins diminish the van der Waals force. Therefore, such a laser-induced rough domain generates very small adhesion to the oil droplet. As is shown in the schematic diagram (Figure 6), by controlling the area fraction of the structured rough domain and the unstructured flat domain, the oil droplet adhesion can be adjusted from ultralow to ultrahigh.

The samples with tunable underwater oil adhesion can be used as a “mechanical hand” to manipulate an oil droplet in a water environment. Figure 7a shows the process of “no loss oil transition” from an ultralow adhesive surface to an ultrahigh one. The medial adhesion surface (M-surface in Figure 7a) with D of 160 μm and OSA of 65° serves as a “mechanical hand”, which can be moved up and down to pick up a 7 μL oil droplet from the ultralow adhesive surface (L-surface in Figure 7a) with D of 0 μm (OSA = 2°) and release it onto the ultrahigh adhesive surface (H-surface in Figure 7a) with D of 200 μm (OSA = 180°) without any loss. In a similar way, fusion of oil droplets can be achieved using the equipment whose...
The kinetic energy of the rushing oil droplet transformed into internal energy and then was consumed due to swing in situ. Finally, the oil droplet pinned onto the surface, realizing no-loss oil capture on a specific location (Figure 8h).

In addition, the good optical transparency of the femtosecond laser-structured slide glass in the water environment is verified using visible spectra, as shown in Figure 9. During the measurement, the transmittance of the flat glass surface in water is regarded as the reference standard with a value of 100%. At visible wavelengths, the transmittance of the laser-ablated patterned glass surface with various diameters nearly exceeds 80% except for the entirely scanning rough surface with ultralow oil adhesion whose transmittance in the visible spectra is between 75 and 90%. The insets in Figure 9 show the transparency images of the entire laser-ablated surface with D of 0 in air and in water. It can be seen that the letters beneath the as-prepared rough surface are misty in air. However, after dropping a drop of water and covering all of the rough region, the letters “xjt” become clear, which implies that the sample in water possesses a higher transparency compared with that in air. This is because the refractive index of glass is close to that of water. On immersing in water, the interface of the micro-/nanostructures is filled with water on account of its super-hydrophilicity, which effectively reduces the refraction and scattering of light when passing through the as-prepared sample. With the increase in D, the structured rough domain decreases, and the scattering and refraction of the light beams passing through the interface between the glass surface and water reduce accordingly, which gives rise to the enhancement of the transmittance. When D is equal to or greater than 80 μm, the transmittance curve tends to stabilize and practically approaches that of the flat glass surface. The favorable light-admitting quality endows the laser-induced glass samples with more potential applications in the underwater optics and biological observation field.

4. CONCLUSIONS

In conclusion, a simple and facile method was proposed to fabricate an underwater transparent miniature “mechanical hand” based on superoleophobic patterned glass surfaces with controllable oil adhesion ranging from ultralow to ultrahigh.
The surfaces consist of periodically arranged structured micro/ nano dual-scale rough domains with superoleophobicity and a nonstructured flat center circle domain with oleophobicity. By varying the area ratio of the two, that is, the diameter of the center circle specifically, the surface morphologies and the related adhesions could be tuned. The “mechanical hand”, based on the patterned surfaces, with this unique adhesive property was successfully applied in oil transportation, fusion, and rapid capture. Furthermore, the as-prepared glass “mechanical hand” exhibited favorable transparency. In addition, the underwater superoleophobicity was verified using various oils with different values of surface tension and density. Controlling the adhesion of oil on the underwater superoleophobic glass surface by changing the fraction of the different wettability areas has many potential applications in various fields such as antifoiling, droplet microreaction, microfluidic devices, and bioengineering.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: chenfeng@mail.xjtu.edu.cn (F.C.).
*E-mail: jlyong@xjtu.edu.cn (J.Y.).

AUTHOR CONTRIBUTIONS
F.C. directed and supervised the research. J.Y. proposed the main research idea and designed the experiments. J.H. and L.L. performed the experiments and wrote the manuscript. Other authors contributed toward significant discussions and revised the paper.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation of China under grant nos. 51335008 and 61475124, NSAF grant no. U1630111, Special-Funded Programme on National Key Scientific Instruments and Equipment Development of China under grant no. 2012YQ12004706, China Postdoctoral Science Foundation grant no. 2016M600786, the Collaborative Innovation Center of Suzhou Nano Science and Technology, and the International Joint Research Center for Micro/Nano Manufacturing and Measurement Technologies. The SEM work was done at International Center for Dielecctric Research (ICDR), Xi’an Jiaotong University.

REFERENCES


