Reducing Adhesion for Dispensing Tiny Water/Oil Droplets and Gas Bubbles by Femtosecond Laser-Treated Needle Nozzles: Superhydrophobicity, Superoleophobicity, and Superaerophobicity

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Abstract: Three-level microstructures were formed on the stainless-steel surfaces by simple femtosecond laser ablation. The structured surfaces exhibit superhydrophobicity in air and superoleophobicity/superaerophobicity in water. After further stearic acid modification, the surfaces turned to superhydrophobicity and underwater superoleophobicity/superaerophobicity. Through this technique, the nozzle of a needle is transformed to possess superwettabilities. When the nozzles were used to release liquid and gas, the sizes of the dispersed water and oil droplets and air bubbles were dramatically reduced. Particularly, we demonstrate that the underwater superaerophobic nozzle could dispense air bubbles in nanoliter volume without the need of reducing the nozzle diameter. The liquid retention at the opening of the needle was also effectively prevented. Therefore, the reduced droplet/bubble size and retention allow us to achieve a dramatically enhanced volume accuracy and resolution during manipulation and transport of aqueous solutions and gases. The femtosecond laser-induced super-wetting nozzles can be used in high-resolution liquid transport, inkjet printing, 3D printing, pipettes, medical devices, cell engineering, biological detection, microchemical reactor, and reducing industrial gas emission.

1. Introduction

Generation and manipulation of tiny liquid droplets (down to micro- or nanoliter scale) and fine bubbles have attracted an ever increasing amount of interest because of the broad applications, such as liquid transportation, inkjet printing, high-resolution three-dimensional (3D) printing, cell engineering, micro-reactor, bio-analysis, bio-sensing, energy production, chemical engineering, and environmental remediation.[1–10] Significant efforts have been devoted from scientific and industrial communities to produce smaller droplets by reducing the nozzle size or through assistance of special driving mechanisms (e.g., mechanical-, electrical-, and thermal-driven equipments) in the past.[11–18] However, the traditional nozzles and dispensing methods still face many limitations. For instance, the driving equipment usually makes the dispensing system become bulky and also increase the complexity of operation. In addition, it will be difficult to further decrease the volume of the dispersed droplets if the nozzle size of the needle is reduced to the limit given by current manufacturing technologies. In fact, the liquids adhesion and retention on the common nozzles are the most serious issues for many biomedical and chemical applications because they reduce the volumetric accuracy and increase the risk of cross contamination.[14–16] To overcome the above-mentioned problems, recently, superhydrophobic microstructures were coated onto the surface of the commercial syringe needles and could greatly improve the ability of the nozzle to dispense tiny water droplets.[17–19] For example, Dong et al. prepared superhydrophobic needle nozzle via the polymer/particles dip/coating process.[17] Wong et al. showed the nozzle of a hypodermic needle with superamphiphobicity by coating nanoparticles and rapid gas-phase nanotexturing method.[20] Those superhydrophobic nozzles were proven to effectively reduce the size of water droplets that could be separated from the syringe needles. However, the obtained superhydrophobic needles are unable to dispense tiny organic droplets and gas bubbles in a liquid medium.[18–20] Producing tiny oil droplets and bubbles in water also has many important applications (e.g., releasing cell/tissue into culture fluid, removing dust particles in the industrial burned gases by bubbling method), but the impact of the surface superwettability on the performance of a needle nozzle for dispensing underwater oil droplets and bubbles has not yet been reported.

In nature, the surfaces of many plants and animals show various special wettabilities.[11–20] Lotus leaf has great water repellence and ultralow adhesion to water droplets, allowing rain droplets and dewdrops to easily roll on its surface and take contaminations away (called “self-cleaning effect”).[21,22] Such superhydrophobicity is ascribed to the hierarchical rough papillae and the hydrophobic wax crystal layer covering on the...
The fish scale is characterized by oriented micropapillae with fine nano-pimples covering on their surface. Fish has the ability to swim in the oil-contaminated water freely with the strong ant-oil capability which resulted from the underwater superoleophobicity of fish scales. Recent research also indicates that fish scale can repel bubbles in water; that is, the fish scale is underwater superaerophobic. These natural phenomena inspire us to design special wettability on solid substrates by the combination of chemical composition and hierarchical surface micro/nanostructures and to reduce the adhesion between the needle nozzle and the water droplets/oil droplets/gas bubbles.

Here, we develop a simple method to achieve different superwettability on the surface of stainless steel sheets through femtosecond laser treatment, including superhydrophobicity and superhydrophilicity in air, and superoleophobicity, super-oleophilicity, superaerophobicity, and superaerophilicity in water. The influence of the surface superwettability of the stainless steel nozzles on the volume of the dispensed water droplet, underwater oil droplet, and underwater bubble is systematically investigated. We find that the laser-induced superhydrophobicity, underwater superoleophobicity, and underwater superaerophobicity are able to dramatically reduce the size of the water droplets, oil droplets, and bubbles separated from the structured nozzles and avoid the liquid retention at the opening of the needles.

2. Results and Discussion

A femtosecond laser was utilized to induce micro/nanostructures on the surface of stainless steel sheets and the nozzle of syringe needles. Figure S1a (Supporting Information) schematically shows the experimental setup of ablating a stainless steel sheet by the femtosecond laser beam. The stainless steel sheet (20 × 20 × 1 mm³) was fixed on a program-controlled translation stage. The femtosecond laser beam (pulse width = 67 fs, center wavelength = 800 nm, repetition rate = 1 kHz) was focused on the stainless steel surface by a plano-convex lens (focal length = 250 mm). The typical line-by-line laser scanning manner was used, which can be referred to our previous works.

In this experiment, the laser power and the scanning speed were set constantly at 500 mW and 1 mm s⁻¹, respectively. The space/interval, , of the laser scanning lines was tuned by a control program. The head surface of the needle nozzle (inner diameter = 250 μm and outer diameter = 700 μm) of a syringe could also be ablated by the femtosecond laser, as shown in Figure S1b (Supporting Information). After femtosecond laser treatment, the samples were immersed into a 0.01 M ethanol solution of stearic acid for 12 h to lower surface energy. In general, metal surfaces are easily oxidized during femtosecond laser ablation. The –COOH groups from the stearic acid can absorb onto the native oxide surface of the laser-ablated stainless steel, forming a self-assembled monolayer. For convenience, the original laser ablated stainless steel is defined as the “Rough surface”, and the rough surface that is further modified with stearic acid is defined as the “M-Rough surface” in this paper.

Femtosecond laser ablation made the color of the stainless steel surface change from silvery grey to grayish black (Figure 1a). Such a significant increase of optical absorption means that rough surface microstructures may be created on the sample surface under femtosecond laser treatment. Figure 1b–f shows the scanning electron microscopy (SEM) images of the surface of the laser-ablated stainless steel sheet at different solid/liquid/gas systems. Specifically, Figure 1c–g shows the cross-sectional characteristic possessed by laser irradiation and are known as the laser-induced periodic surface structure (LIPSS). LIPSS is generally ascribed to the interference between the incident laser pulse and the scattered tangential wave originated from the previous pulses. The period of the LIPSS was ~561 nm for the valley bottom and ~608 nm for the micro-spikes’ top. The laser-ablated stainless steel surface was measured to have a very low reflectance in the visible wavelengths, in comparison with the original bare flat surface (Figure 1h). The reflectance spectrum was also able to confirm that the laser-induced hierarchical microstructure was very rough.

Wettability is determined by the chemical composition and surface microstructure of a solid substrate. The wettabilities of the untreated stainless steel surface, the laser-structured rough surface, and the modified rough surface at different solid/liquid/gas systems were systematically investigated, respectively, including in-air water wettability, underwater oil wettability, and underwater bubble wettability. As shown in Figure 2a, the untreated stainless steel was intrinsically hydrophilic in air, with the water contact angle (WCA) of 78.9 ± 1.6° to a small water droplet. The wetting state between the water droplet and the flat substrate belongs to the Young wetting model (Figure 2b). When the stainless steel sheet was immersed in water and an oil droplet (chloroform) was put on the sample surface, the measured oil contact angle (OCA) of the oil droplet was 75.2 ± 6.7° (Figure 2c,d), revealing the underwater oleophilicity of the untreated stainless steel although most hydrophilic substrates will become oleophobic in water. Regarding an underwater bubble, it would adhere to the sample surface with the bubble contact angle (BCA) of 111.9 ± 4.6°, so the flat stainless steel showed underwater aerophobicity (Figure 2e,f).
All of the in-air water droplet, underwater oil droplet and bubble could firmly stick on the flat surface no matter the sample was tilted for any angle.

The surface wettability of the stainless steel was amplified by the femtosecond laser-induced microstructure. When a water droplet came in contact with the laser-treated area of the stainless steel surface in air, the droplet would spread out quickly and fully wet the rough microstructure (Figure 2g and Movie S1 in the Supporting Information). The WCA was as low as 1.5° to this water droplet. Therefore, the hydrophilicity of the stainless steel was enhanced to superhydrophilicity by the rough surface microstructure. Previously, the enhancement function of the hydrophilicity of different solid substrates (e.g., platinum, silicon, glass, and dentine surface) by the femtosecond laser-induced surface microstructures was already demonstrated by our group. Such superhydrophilicity can be explained by the Wenzel wetting state because the valley of the microstructure was completely wetted by water (Figure 2h). Interestingly, the laser-ablated surface had the great ability to repel oil droplets and air bubbles in water. The underwater oil droplet and bubble could hold spherical shapes on the rough stainless steel (Figure 2i and k). The measured OCA and BCA were 155.1° ± 1.1° and 152.4° ± 1.6°, respectively. Such high values indicated the laser-ablated surface was superoleophobic and superaerophobic underwater. Once the stainless steel sheet was slightly tilted at 1.5° ± 0.5°, the oil droplet would easily roll off on the stainless steel (Figure 2t and Movie S1 in the Supporting Information). Similarly, an underwater bubble could freely roll away on a 1.1° ± 0.9° tilted sample surface (Figure 2u and Movie S1 in the Supporting Information). The ultralow oil sliding angle (OSA) and bubble sliding angle (BSA) demonstrated that the laser-ablated surface also had ultralow adhesion to the oil droplets and bubbles, showing excellent oil/bubble repellence in water. As the rough stainless steel is dipped into water, superhydrophilicity will drive the water to fill in the space of the surface microstructures and completely wet the rough hierarchical microstructure. Water likes being trapped by the superhydrophilic rough texture. When an oil droplet or a bubble is dispensed onto the sample surface, the contact between the substrate and the oil droplet/bubble will be greatly prevented by the trapped water layer around the laser-induced microstructure (Figure 2j,l). Since the trapped water naturally repels oil and bubble, the oil droplet and the air bubble are allowed to contact with only the tip points of the surface microstructures. The contact between the substrate and the oil/bubble in water can be regarded as an underwater version of Cassie wetting state (Figure 2j,l). To reach a minimum free energy of the multi-phase system, the oil droplet and the bubble have to be approximately spherical on the rough substrate because they are surrounded by water. As a result, the surface exhibits underwater superoleophobicity and superaerophobicity.

Chemical modification is the most common way to change a solid substrate from hydrophilicity to hydrophobicity. When
the laser-ablated stainless steel surface was further modified with stearic acid, the resultant surface was switched to superhydrophobicity. Water droplet on the M-rough surfaces presented a spherical shape with the WCA of 156.3 ± 0.8° (Figure 2m) and could easily roll away with the water sliding angle (WSA) of 2.3 ± 0.3° (Figure 2s and Movie S2 in the Supporting Information). The contact angle hysteresis of a water droplet on the M-rough surfaces was measured to be 4.1 ± 0.4°. Such high WCA value and low WSA value revealed that the M-rough surface showed superhydrophobicity and extremely low adhesion to water droplets. The water droplet rolls more easily on the laser-induced three-level superhydrophobic microstructure than the double-scale stainless steel microstructure reported in Zhou’s work (WSA = 4.2 ± 1.0°).[50] The formation mechanism of the superhydrophobicity is the same as that of the lotus leaf surface, because the water droplet on the M-rough surface is at the Cassie state (Figure 2n).[43,49,51] As the sample was placed in water, a bright light reflection appeared on the laser-treated area, known as the “silver mirror effect.”[32,52] The mirror-like interface was a direct evidence of the formation of a trapped air layer between the substrate and the surrounding water. If an oil droplet was moved to touch the M-rough surface in water, the oil would rapidly spread out after just contacting the substrate and resulted in a very small OCA of 5.9 ± 0.9° (Figure 2o and Movie S2 in the Supporting Information). Similar to the behavior of the oil droplet, an underwater bubble would be completely absorbed by the M-rough surface as long as the bubble touched the sample (Figure 2q and Movie S2 in the Supporting Information). The measured BCA of this bubble was only 1 ± 1°. Therefore, the stainless steel surface had both underwater superoleophilicity and superaerophilicity after femtosecond laser treatment and subsequently lowing surface energy. The synergy between the laser-induced hierarchical rough microstructure and the low surface energy of the stearic acid monolayer gives rise to the superhydrophobicity of the M-rough stainless steel surface. According to the Cassie wetting state, a water droplet on such surface only touches the peaks of the surface microstructures, like sitting on the rough microstructures, as shown in Figure 2n. An air cushion exists underneath the water droplet, which remarkably reduces the contact area between the M-rough microstructure and the water droplet. Such extremely small contact area endows the surface with ultralow water adhesion as well as strong water repellence. The air cushion will develop to a layer of trapped air between the substrate and water as the stainless steel sheet is immersed into water. In this case, when an oil droplet is further placed onto the laser-treated domain, the oil will enter into this air layer and spread out along the thick gas space under the pressure and capillary action, resulting in a very small OCA (Figure 2p). As a result, the M-rough surface shows super-

Figure 2. Surface wettabilities and wetting states of in-air water droplet, underwater oil droplet, and underwater bubble on different stainless steel surfaces at different solid/liquid/gas systems. (a,b) Water droplet, (c,d) underwater oil droplet, and (e,f) underwater bubble on the untreated flat substrate. (g,h) Water droplet, (i,j) underwater oil droplet, and (k,l) underwater bubble on the laser-induced rough surface. (m,n) Water droplet, (o,p) underwater oil droplet, and (q,r) underwater bubble on the stearic acid-modified rough stainless steel surface. (s) Water droplet rolling on the M-rough stainless steel surface in air. (t) Underwater oil droplet and (u) underwater bubble rolling on the laser-ablated stainless steel sheet with rough surface.
oleophilicity to this oil droplet in water. Regarding the underwater bubble, when it is made in contact with the sample surface in water, the gas in the bubble is able to be merged by the trapped air layer (Figure 2r). The pressure drives the air in this bubble to enter into the trapped air layer rapidly, similar to the behavior of the underwater oil droplet. The bubble likes being absorbed by the resultant sample completely, so the underwater superaerophilicity is also exhibited by the M-rough surface.

The superhydrophobicity endows the stainless steel surface with excellent anti-water ability, while the underwater superoleophilicity and superaerophobicity lead to the anti-oil and anti-bubble abilities for the stainless steel in water. By contrast, the superhydrophilic, superoleophobic, and superaerophilic stainless steels can be used to absorb and capture water/oil/gas, respectively.

The experimental results and theoretical analyses reveal that the femtosecond laser-induced in-air superhydrophilic stainless steel surfaces will exhibit superoleophobicity and superaerophobicity in water, whereas the ultrawet adhesive superhydrophobic surfaces will show superoleophilicity and superaerophilicity in water. That is, the underwater oil superwettability and the bubble’s behavior have a close relationship with the water superwettability in air for the laser-treated stainless steel. The water wettability of the sample surface that was ablated by laser at different intervals (Λ) of the scanning lines was investigated, as shown in Figure 3. When the Λ was smaller than 200 μm, the laser ablated surfaces showed superhydrophilicity, with the measured WCAs of a water droplet on the rough stainless steel surfaces less than 10° (Figure 3a,b). As the Λ increased from 200 μm to 250 μm and then to 300 μm, the WCA increased from 5.5 ± 3.5° (Figure 3d) to 22.7 ± 2° (Figure 3f) and then to 34.7 ± 6° (Figure 3h). Such increase of the WCA values was caused by the increased area fraction of the non-ablated domain between the laser scanning lines. The WCA values were so small that the water droplets on the sample surface could not slide down. Regarding the stearic acid-modified textured stainless steel surfaces, they exhibited superhydrophobicity and ultrawet water adhesion with the WCA higher than 150° and the WSA smaller than 10° when Λ was no larger than 200 μm (Figure 3a,c). With continuing to increase Λ, the WCA decreases from 155.7 ± 0.3° (Λ = 200 μm, Figure 3e) to 151.1 ± 1° (Λ = 250 μm, Figure 3g) and then to 142.7 ± 0.8° (Λ = 300 μm, Figure 3i). As to that of the WSA, it increased from 2.9 ± 0.4° (Λ = 200 μm) to 26 ± 4° (Λ = 250 μm) and then to 55 ± 8° (Λ = 300 μm), as shown in Figure 3a. Therefore, excellent superhydrophilicity or superhydrophobicity can be obtained on the surfaces of stainless steel as long as the Λ was no more than 200 μm during femtosecond laser treatment.

Similar to the metal sheets, femtosecond laser can also be applied to treat the needle nozzle of a syringe. Figure 4 shows the SEM images of the nozzle surfaces of a pristine needle and the femtosecond laser-ablated needle. The pristine needle has a common texture which comes from metal fracture during industrial manufacture (Figure 4a,b). Such texture can be considered relatively smooth in comparison to the laser-treated nozzle. Femtosecond laser ablation leads to the formation of the dense microscale cone-shaped spikes on the surface of the needle nozzle (Figure 4c,d). The surface of the micro-spikes is decorated with LIPSS (Figure 4f). In addition, it is found that the side wall near the tip of the needle is also roughed by

![Figure 3](image-url). Wettability of the as-prepared rough stainless steel surfaces fabricated at different intervals of the laser scanning lines. (a) Relationship between the Λ and the WCA/WSA for the rough and the M-rough substrates. (b–i) Images of small water droplets on the resultant surfaces that fabricated at different Λ: (b,d,f,h) without stearic acid modification and (c,e,g,i) after stearic acid modification.

![Figure 4](image-url). SEM images of the nozzle surfaces of the pristine needle and the femtosecond laser-ablated needle. (a) Top view of the head of a pristine needle. (b) Large-magnified image of the untreated nozzle. (c) Top view of the head of the laser-ablated needle. (d) Large-magnified image of the laser-induced microstructure on the needle nozzle. (e) 45°-tilted view of the laser-treated nozzle. The yellow dotted line shows the boundary between the top surface and the side wall of the ablated needle nozzle. (f) Microstructure of the surface of the micro-spikes in (d).
femtosecond laser because the focal length of the used lens is relatively long (Figure 4e).

The effect of surface wettability on the liquid/bubble adhesion as well as the volume of the dispensed droplets/bubbles from a needle nozzle was carefully investigated by using the contact-angle measurement system. Liquid or gas was gradually ejected from the needle nozzles until the suspended droplets fell or the gas bubble risen up. The ejection speed of the water, oil, and gas was less than 0.3 μL/s. Because the dimensionless Weber number (\(\text{We} = \frac{\rho v^2 D}{\sigma}\)), where \(\rho\) is the density of the liquid, \(D\) is the diameter of the needle nozzle, \(v\) is the ejection speed, and \(\sigma\) is the liquid surface tension, was smaller than 10\(^{-5}\), so such low ejection speed has no impact on the volume of the dispensed droplets or bubbles.\(^{[1]}\) Figure 5a depicts the process of dispensing a water drop via the untreated nozzle. With gradually ejecting water out, the volume of the hanging droplet would increase. Until the volume reached 13.68 ± 0.1 μL, the water droplet would suddenly detach from the nozzle and drip down (Movie S3, Supporting Information). At this moment, the gravity of this droplet was just over the maximum adhesion force that the nozzle tip could provide. Regarding the superhydrophilic nozzle that was treated by femtosecond laser, the measured volume of the separated water droplet was 14.83 ± 0.27 μL (Figure 5b and Movie S3 in the Supporting Information), which was slightly higher than that was dispensed by a pristine syringe. Interestingly, as long as the volume of the suspended droplet growth to 6.44 ± 0.09 μL, the water droplet was able to detach from a superhydrophobic needle nozzle with M-rough surface (Figure 5c and Movie S3 in the Supporting Information). The size of the water droplet from the nozzle was greatly reduced by the superhydrophobic microstructure compared to the untreated or superhydrophilic needle. Force analysis was proposed to explain the size of the ejected water droplets. The minimum volume that allows a droplet to detach from the needle nozzle and drip down depends mostly on the competition between the hanging droplet’s gravity and the dragging force provided by the nozzle tip. In the case of the pristine needle (Figure 6a), there are three forces exerted on the suspended droplet, including the gravity (G), the adhesive force dragged by the liquid inside the needle (\(F_1\)), and the adhesive force dragged by the needle (\(F_2\)). \(F_1\) can be expressed as \(\pi r D \sin \theta\), which is influenced by the liquid surface tension, the diameter of the nozzle, and the detaching contact angle (\(\theta\)).\(^{[1,4]}\) When the G of the hanging water droplet was increased to higher than the sum of \(F_1\) and \(F_2\), the droplet finally separated from the needle nozzle. For the superhydrophobic needle, the laser-induced hierarchical microstructure distributes on both the head surface and the side wall of the needle near the tip (Figure 4e). Capillary force can drive water to climb to the outer wall of the superhydrophilic needle nozzle; that is, the ejected tiny droplet not only wet the head surface but also can slightly overflow the

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Dispensing water droplets in air, oil droplets in water, and bubbles in water by using different needle nozzles. (a–c) Process of gradually ejecting water from (a) an untreated nozzle, (b) the laser-induced rough nozzle, and (c) the nozzle with M-rough surface microstructures. (d–f) Process of gradually ejecting oil from (d) an untreated nozzle, (e) the laser-induced rough nozzle, and (f) the nozzle with M-rough surface microstructures in water. (g–i) Process of gradually ejecting gas from (g) an untreated nozzle, (h) the laser-induced rough nozzle, and (i) the nozzle with M-rough surface microstructures in water. (j–l) Enlarged images of before and after dispensing a water droplet in air by using the syringes with the (j) untreated nozzle, (k) laser-induced rough nozzle, and (l) stearic acid-modified rough nozzle. (m–o) Enlarged images of before and after dispensing an oil droplet underwater via the syringes with the (m) untreated nozzle, (n) laser-induced rough nozzle, and (o) stearic acid-modified rough nozzle.
Figure 6. Schematic diagram of dispensing water droplets in air, oil droplets in water, and underwater bubbles by using different needle nozzles. (a–c) Ejecting water from (a) an untreated nozzle, (b) the laser-induced rough nozzle, and (c) the nozzle with M-rough surface microstructures in air. (d–f) Ejecting oil from (d) an untreated nozzle, (e) the laser-induced rough nozzle, and (f) the nozzle with M-rough surface microstructures in water. (g–i) Ejecting gas from (g) an untreated nozzle, (h) the laser-induced rough nozzle, and (i) the nozzle with M-rough surface microstructures in water.

external surface of the needle, resulting in a serious adhesion of water droplet to the nozzle (Figure 6b). As a result, $F_{a}$ is larger than that in the case of an untreated hydrophilic nozzle, so the superhydrophobic needle dispenses a bigger water droplet. As far as the superhydrophobic needle, the laser-created superhydrophobic microstructures are able to prevent the suspended droplet from wetting the head and the external surface of the needle. The contact line is restricted in the inner edge of the nozzle, so the hanging drop is only pinned by the nozzle’s inner at the tip before detaching from the needle, as shown in Figure 6c. In addition, an air cushion is formed between the hanging droplet and the microstructures on the inner wall (near the tip) of the nozzle, giving rise to the small contact area and ultralow adhesion between the nozzle and the pendulous droplet. At present, $F_{a}$ closes to zero, so the volume of the water droplet separated from the superhydrophobic nozzle is dramatically reduced, which is only related to the liquid inside the nozzle (i.e., the inner diameter of the superhydrophobic nozzle).

Figure 5d–f shows the results of dispensing a tiny oil droplet in water by using different needle nozzles. With the growth of the ejected oil, the pendulous oil droplet suddenly dripped down from the pristine nozzle when the volume reached to 11.2 ± 0.09 μL (Figure 5d) and from the underwater superoleophobic nozzle when the volume reached to 11.1 ± 0.95 μL (Figure 5f), respectively (Movie 54, Supporting Information). The hanging oil droplet was more easily to wet the head surface of these nozzle tips, driven by the underwater oleophilicity (Figure 6d,f). The underwater superoleophobic nozzle, by contrast, could dispense a smaller oil droplet. As shown in Figure 5e and Movie 54 (Supporting Information), the oil droplet would detach from the superoleophobic nozzle once its volume reached to just 4.09 ± 0.47 μL. The average volume of the separated underwater oil droplets from the laser-induced superoleophobic nozzle was remarkably reduced to just about one third of that detached from the underwater (super-) oleophilic nozzles. The underwater superoleophobicity prevents the ejected oil from contacting the nozzle head, so the pendulous oil droplet only connects to the oil inside the nozzle channel, like hanging on the inner channel of the needle (Figure 6e). The inner wall of the nozzle near the tip also has extremely low adhesion to oil, thereby the adhesive force dragged by the needle is negligible. The gravity of the growing oil droplet just needs to overcome the buoyancy force and the adhesive force provided by the liquid inside the needle for detaching this droplet.

It is thus possible to dispense smaller tiny water and oil droplets from a commonly sized nozzle just by simple femtosecond laser treatment. Smaller dispersed droplets mean that the volume accuracy is remarkably increased during the manipulation and transport of aqueous solutions. Therefore, the superhydrophobic or the superoleophobic nozzles can have promising applications in liquids transport, inkjet printing devices, pipettes, medical devices, cell engineering, and achieving high-resolution 3D printing.

The generation of fine bubbles has a broad range of applications in aquaculture, environmental remediation, chemical engineering, and energy production. The size of the bubbles has a huge impact on the process efficiency in those applications. Fine bubbles can greatly increase the gas/liquid contact area, thereby improving the gas/liquid mass transfer. Until now, the influence of the superwettability on the process of dispensing tiny bubbles by the needle nozzle has still rarely been studied. Figure 5g shows the process of dispensing a gas bubble in water via a pristine nozzle. As the needle was dipped into water, the head surface of the nozzle firstly contacted with water. The inherent aerophobicity restricted the contact line of the ejected gas within the inner edge of the nozzle tip with increasing ejecting volume (Figure 6g). When the volume of the bubble was increased to 6.29 ± 0.55 μL, the bubble would detach from the nozzle and rise up, driven by the buoyancy (Figure 5g and Movie S5 in the Supporting Information). For the underwater superaerophobic needle, the bubble that could separate from the nozzle was much bigger than that dispensed by a pristine needle, because the head surface of the nozzle tip was in contact with the gas rather than the water (Figure 6i). The measured volume of the dispersed bubble was 13.77 ± 0.15 μL (Figure 5i and Movie S5 in the Supporting Information). Surprisingly, the underwater superaerophobic nozzle that was just treated by laser could generate fine bubbles with the volume being reduced down to 177 ± 10 nL (Figure 6h). The measured volume of the bubble detaching from (g) an untreated nozzle, (h) the laser-induced rough nozzle, and (i) the nozzle with M-rough surface microstructures in water. (g–i)
effectively touch the needle nozzle. On the one hand, the superhydrophilic and underwater superaerophobic nozzle had very low adhesion to the ejected bubble. On the other hand, the diameter of the inner hole of the nozzle allowing gas through seems to be greatly shrunken, because the water is driven by the superhydrophilic force and capillary action to inflow the inner wall of the needle (Figure 6h). The liquid ring near the nozzle is more easily to close so that the volume of the dispensed bubble can be as small as nanoliter scale, without the need of reducing the actual diameter of the needles. The capacity of releasing fine bubbles can be improved by parallelization of the needle nozzle array. A smaller bubble has the bigger ratio of surface area to volume, and fine bubbles can effectively extend the residency time in a liquid solution. That is, when a fixed amount of gas is divided into many bubbles in water, greater total liquid/gas contact area will be obtained in the case of smaller bubbles. The fabrication of underwater superaerophobic nozzles by a femtosecond laser is so simple that the resultant nozzle will have many potential applications in no matter the scientific research or the industrial production. For instance, in a chemical reaction between a gas phase and a liquid phase, the gas that is released into the liquid by the underwater superaerophobic nozzles is inclined to more fully contact with the reaction solution. The industrial burned gases contain lots of dust particles. Using underwater superaerophobic nozzles to blowing those gases into fine bubbles in a liquid medium can roughly remove most particles in the gas emissions.

The superhydrophobicity and underwater superoleophobicity can effectively reduce liquid retention at the opening when the laser-treated needles are used to disperse water droplets in air or oil droplets in water. After a water droplet being push out from a commercial needle nozzle (untreated nozzle) and falling down, a certain amount of water still stuck to the nozzle tip (Figure 5j). Such water retention would result in an inaccurate volume of the dispensed droplet. The water retention also appeared on the tip of the laser-induced rough nozzle (Figure 5k). Manipulating accurate volume of droplets and excluding liquid retention are still the thorny problems that constantly beset scientst and industrialists. Interestingly, we found that there was almost no water residual left on the tip of the superhydrophobic nozzle (M-rough nozzle, Figure 5l). Similarly, when an oil droplet freely fell from the tip of different needle nozzles in a water medium, no oil retention was observed on the underwater superoleophobic nozzle (Rough nozzle, Figure 5n) while a certain amount of oil residue stuck on the untreated and the M-rough nozzle tips (Figure 5m,o). There was no gas retention occurring when a bubble was dispensed by the untreated, the superaerophobic, or the superoleophobic nozzle in water. The reduced liquid retention caused by the superhydrophobicity and the underwater superoleophobicity are beneficial for the needles toward some practical applications, such as more accurate of manipulating liquid, increasing the accuracy of biological detection, saving expensive reagents, increasing the accuracy of the microchemical reactor, and reduced cross-contamination.

The laser-induced superhydrophobic surfaces (M-rough surfaces) are able to always remain their superwettability in air. By contrast, the superhydrophilic surfaces (Rough surfaces) must be stored in water, otherwise they will gradually lose superhydrophilicity in air because of absorbing environmental carbon contaminants. The superhydrophilicity, underwater superoleophobicity, and underwater superaerophobicity can be kept for a very long time by storing the rough surface in water. The stability of the superhydrophilicity (storing in water) and the superhydrophobicity of the laser-induced superwetting microstructures enable the femtosecond laser-treated needles to have a long-term practical service life (more than one month).

3. Conclusions

In conclusion, different superwettabilities were designed and achieved on the surfaces of stainless steel by femtosecond laser treatment. Femtosecond laser ablation resulted in the formation of three-level hierarchical microstructures which enhanced the sample surface from hydrophilicity to superhydrophilicity. The underwater oil droplets and bubbles had the contact angle higher than 150° on the rough superhydrophilic surface and could roll away easily, revealing the underwater superoleophobicity and superaerophobicity of the laser-ablated stainless steel. When the rough microstructure was further modified with stearic acid, the resultant surface became superhydrophobic in air and superoleophilic/superaerophilic in water. Femtosecond laser treatment could also endow the nozzle of a needle with superwettabilities, showing ultralow adhesion to water droplets, underwater oil droplets, and underwater bubbles. By using the superhydrophobic nozzle, underwater superoleophobic nozzle, and underwater superaerophobic nozzle to disperse water droplets in the air, oil droplets in water, and bubbles in water, respectively, it was found that the volume of the droplets/bubbles detached from the nozzle was dramatically reduced. 177 mL bubbles could even be separated from the underwater superaerophobic nozzle, without the need of shrinking the nozzle. The superhydrophobicity and underwater superoleophobicity also allowed the nozzles to effectively avoid the liquid retention at the opening of the needles. By taking advantages of the reduced droplet/bubble size and liquid retention, the volume accuracy during the manipulation and transport of aqueous solutions and gases is remarkably increased by using the superwetting nozzles. Such superwetting needle nozzles fabricated by femtosecond laser treatment have many potential applications, such as accurate liquids transport, inkjet printing devices, high-resolution 3D printing, pipettes, medical devices, cell engineering, biological detection, microchemical reactor, and the clean of industrial gas emissions.

Experimental Section

See Supporting Information in detail.
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Conflict of Interest

The authors declare no conflict of interest.

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