Fabrication of super-hydrophobic stainless steel needles and evaluation of their drag reduction properties

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Naturally, some living things have non-wettable super-hydrophobic surfaces that depend on surface roughness and surface chemistry. Mimicking such super-hydrophobic surfaces has applications for pain reduction and improving the functionality of needles used in health care. This study prepared a stainless steel needle with a super-hydrophobic surface using ultrasonic etching for microstructure fabrication and surface fluorination. The as-prepared stainless steel needle was super-hydrophobic, as evidenced by a water contact angle of 151.3°. Investigations into the effect of ultrasonic etch time on wettability indicated that microstructures on the surface of the stainless steel needle were important for developing super-hydrophobicity. Resistance properties of the as-prepared stainless steel needle were also governed by surface morphology. Super-hydrophobic stainless steel needles have self-cleaning and low adhesion properties and a drag reduction effect that may reduce pain during a puncture process. Simultaneously, the bionic needle with super-hydrophobic property has more applications in biological antibacterial, and reducing retention of expensive reagents. Furthermore, this method can also be applied to micropipette tips, and inkjet or bio-printer heads, which will make breakthroughs in small droplets manipulation, biometric, and inkjet printing equipment.

1. Introduction: Naturally, some living things have non-wettable super-hydrophobic surfaces that depend on surface roughness and surface chemistry. Mimicking such super-hydrophobic surfaces has applications for self-cleaning [1, 2] and anti-adhesion [3–5]. Currently, super-hydrophobic surfaces can be created using electrochemical technique [6], laser etching [7, 8], chemical vapour deposition [9, 10], post-treating [11], and sol–gel processing [12–14]. However, most of these methods are limited as they require a flat two-dimensional structure to generate a super-hydrophobic surface.

Curved stainless steel needles are commonly used as puncture instruments by health care providers for intravenous and intramuscular injections, biopsy sampling, and drug sensitivity tests. Patient satisfaction with health care is associated with pain [15] and may be increased by a reduction in injection pain. Injections may be rendered painless by altering pain perception in the nerves in the skin and/or by reducing the friction between the skin and the needle. Painless injections have been achieved using microneedle delivery, no-needle delivery, bionic-needle delivery, and surface microstructured needle delivery. In particular, the surface microstructured needle has been the topic of recent research. Wang [16] developed a drag reduction needle with a corrugated, serrated, and concave microstructure on its surface. Dong *et al.* [17] reported a super-hydrophobic hypodermic steel needle fabricated by a complex polymer/particle dip-coating approach. Qi *et al.* [18] prepared a super-hydrophobic stainless steel needle by hydrochloric acid etching and silver (Ag) nanoparticle deposition and studied the antibacterial property of the needle. However, these methods used to construct microstructures always involve the high cost, significant time, and complex process. In addition, studies on the surface microstructured needle with both super-hydrophobic and drag reduction properties used for painless injections are extremely limited.

In the current Letter, a surface microstructured stainless steel needle with both super-hydrophobic and drag reduction properties was obtained using a two-step preparation process that included ultrasonic etching and chemical modification. The etching process created an irregular microscale roughness on the surface of the stainless steel needle. Subsequently, the stainless steel needle surface was chemically modified with a low surface energy material. Super-hydrophobic stainless steel needles have self-cleaning and low adhesion properties and a drag reduction effect that may reduce pain during a puncture process. This Letter provides a new approach to the preparation of multifunctional puncture instruments for medical use.

2. Experimental section

2.1. Materials: Stainless steel needles (no. 12) were purchased from the Jiangxi Hongda Medical Equipment Group Co. Ltd. Acetone, alcohol, distilled water, hydrofluoric acid (HF), and 1H, 1H, 2H, 2H-perfluorodecyltriethoxy-silane (PFDTES, 97%) were used without further purification.

2.2. Methods: Stainless steel needles were cleaned with distilled water for 10 min. Conventional and ultrasonic etching methods were compared. For conventional etching, a stainless steel needle was placed directly into a beaker with 80 ml HF solution (60% in water) as the etchant. For ultrasonic etching, a beaker filled with 80 ml HF solution (60% in water) was placed in an ultrasonic cleaner, a stainless steel needle was set vertically into the etchant, and ultrasonic etching was initiated. Needles were ultrasonically etched for various times (range 1–8 min). Subsequently, the conventionally and ultrasonically etched stainless steel needles were washed in distilled water for 5 min to remove the residual solution and dried in an oven at 7°C for 30 min. Dried stainless steel needles were immersed in a solution of PFDTES and methanol (1:100) for 100 min and dried in the oven at 135°C for 2 h.

2.3. Characterisation: The surface morphology of the original and as-prepared stainless steel needles was observed using a scanning electron microscope (SEM, JMS-6700F). The hydrophobicity of the original and as-prepared stainless steel needles was determined from the static water contact angle (CA), which was measured using the OCA20 optical CA measuring instrument with a 2 µl water droplet. Water CA values from three different positions on the same needle were measured, and the mean was calculated. Surface chemical analysis of the original and as-prepared stainless steel needles was made using energy dispersive X-ray spectroscopy (Oxford X-Max80) and a substrate area of $\sim 200 \times 200\ \mu m^2$. Resistance to puncture of silica gel by the original and ultrasonically etched stainless steel needles was measured with a universal

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tester (WSN-500N) at 24°C and a puncture speed of 100 mm/min. The maximum displacement of the puncture was 25 mm, and the puncture test took 15 s to complete. Mean resistance from three stainless steel needles was calculated. Ultrasonically etched stainless steel needles that had undergone different etch times were used to investigate the role of roughness in surface wettability and resistance.

3. Results

3.1. Morphology and wettability: Stainless steel needles were prepared by microstructure fabrication (etching) and chemical modification with a low surface energy material (PFDTES) (Fig. 1). SEM images and the water CA were used to compare the surface morphology and wettability of the as-prepared stainless steel needles to an original stainless steel needle (Fig. 2). The surface of the original stainless steel needle that had been ultrasonically cleaned in distilled water for 15 min was relatively smooth (Fig. 2*a*). After modification with PFDTES, the water CA of the surface of the original stainless steel needle was 124.4° (Fig. 2*a*, inset). The surface of the stainless steel needle that had been conventionally etched for 5 min was sparsely covered with microstructures, each with a diameter of ∼100 µm (Fig. 2*b*). After modification with PFDTES, the water CA of the surface of the conventionally etched stainless steel needle was 141.4° (Fig. 2*b*, inset). The surface of the stainless steel needle that had been ultrasonically etched for 5 min was uniformly covered with many microstructures, each with a diameter of ∼50 µm (Fig. 2*c*). After modification with PFDTES, the water CA of the ultrasonically etched stainless steel needle was 151.3° (Fig. 2*c*, inset).

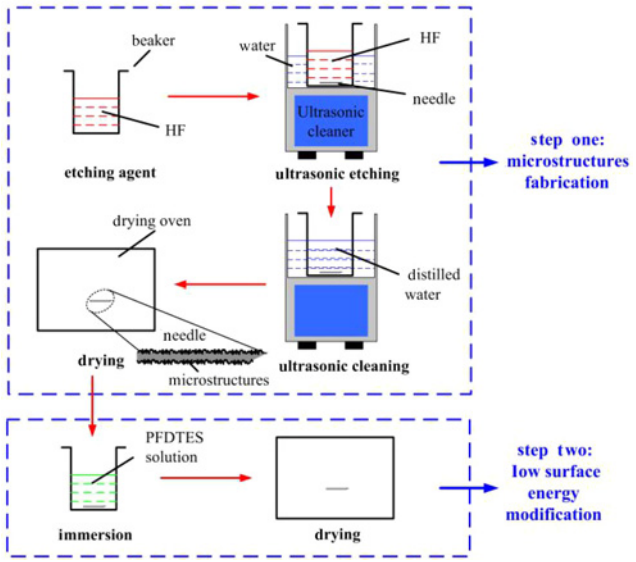


Fig. 1 *Schematic illustration of the preparation process of a stainless steel needle by ultrasonic etching*

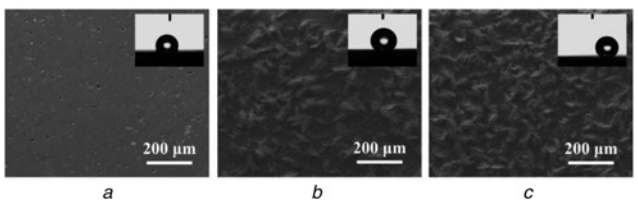


Fig. 2 *SEM images*
a Original stainless steel needle following ultrasonic cleaning in distilled water for 15 min
b Stainless steel needle obtained by conventional etching for 5 min
c Stainless steel needle obtained by ultrasonic etching for 5 min

The wettability of stainless steel needles ultrasonically etched for different times (1–8 min) was studied after subsequent fluorination using water CA measurements (Fig. 3). The surface of the chemically modified original stainless steel needle displayed a water CA of 124.4° (Fig. 2*a*, inset). After a 5 min etch time, the water CA was >150°, but it reached a maximum value of 153.8° after a 6 min etch time. There are two wetting states on rough solid surfaces, Cassie–Baxter's wetting state and Wenzel's wetting states. These wetting states are determined by the microstructure and the chemical composition of the surface. In Cassie–Baxter's state, trapped air pockets within the surface of the rough structure prevent liquid from penetrating; therefore, a liquid drop sits on the top of asperities on the surface maintaining a high CA and rolling off at small tilt angles [19]. In Wenzel's state, a liquid drop can easily penetrate and wet the rough structure resulting in high adhesion to the surface [20]. The stainless steel needle fabricated after 6 min of etching and fluorination corresponded to the Cassie–Baxter's state. As the etch time was extended, microstructures were destroyed, and the wetting state switched to Wenzel's state. SEM images obtained at different ultrasonic etch times are displayed in Fig. 4.

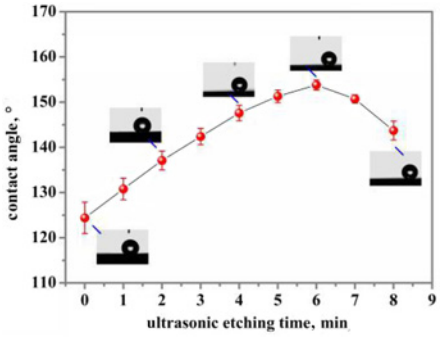


Fig. 3 *Water CA of the ultrasonically etched stainless steel needle and subsequent fluorination as a function of ultrasonic etch time*

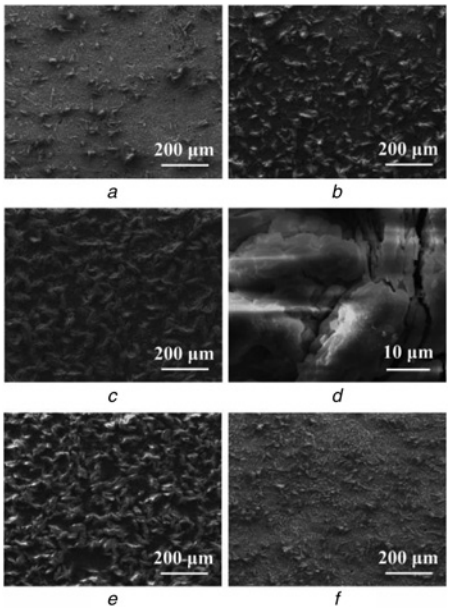


Fig. 4 *SEM images of stainless steel needle surfaces as a function of ultrasonic etch time*
a 1 min
b 3 min
c, *d* 5 min
e 6 min
f 8 min

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3.2. Analysis of surface wettability: Super-hydrophobicity is defined as water CA >150°. Therefore, in this Letter, a super-hydrophobic stainless steel needle was fabricated after ultrasonic etching for 6 min and chemical modification with PFDTES. The super-hydrophobic property of this stainless steel needle can be expressed as [19]

$$\cos\,\theta_C = f_1\,\cos\,\theta - f_2 \tag{1}$$

where θ_c is the water CA of the as-prepared super-hydrophobic stainless steel needle; θ is the water CA of the original stainless steel needle modified with PFDTES (124.4°); and f_1 and f_2 are the fractions of the solid/liquid and air/liquid interfaces ($f_1+f_2=1$). According to the equation ($\theta_c=153.8°$, $\theta=124.4°$), f_2 is 0.764; therefore, air occupies 76.4% of the contact area between a water droplet and the as-prepared stainless steel needle surface. Fig. 5*a* displays a schematic illustration of a water droplet on the surface of the super-hydrophobic stainless steel needle. The droplet of water is suspended on the surface of the stainless steel needle, and the trapped air prevents contact between the water and the surface.

3.3. Resistance test: A resistance test was used to investigate the drag reduction property of ultrasonically etched as-prepared stainless steel needles compared with the original stainless steel needle. The resistance value and mean maximum resistance of an original stainless steel needle and stainless steel needles prepared using different etch times measured using a universal tester (WSN-500N) are shown in Fig. 6. Resistance to puncture of silica gel was lower for all fabricated stainless steel needles compared with the original needle (18.2 N). When the ultrasonic etch time was 6 min, mean resistance was at a minimum, and the drag was reduced by a maximum of 55%. When the ultrasonic etch time was ≥7 min, mean resistance increased, and the drag reduction effect decreased.

It can be seen from the resistance test that the microstructured needle has a drag reducing effect because the resistance value F during the needle puncture is in accordance with the Coulomb formula, which can be expressed as [21]

$$F = \mathrm{CA} + N\,\tan\beta \tag{2}$$

where F is the resistance value during the needle puncture, C is the adhesion of the silica gel, A is the contact area between the needle and the silica gel, N is the positive pressure received during the needle puncture, and β is the friction angle between the needle and the silica gel. During the resistance test, the surface microstructures created during the 6 min etch minimised the contact area between the silica gel and the surface of the stainless steel needle, and the positive pressure N, the friction angle β, and the adhesion

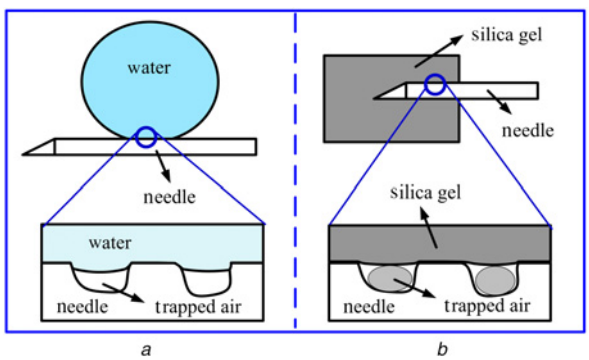


Fig. 5 *Schematic illustrations of super-hydrophobic and drag reduction properties*
a Water droplet on the surface of the super-hydrophobic stainless steel needle
b Contact state between the structured stainless steel needle and silica gel

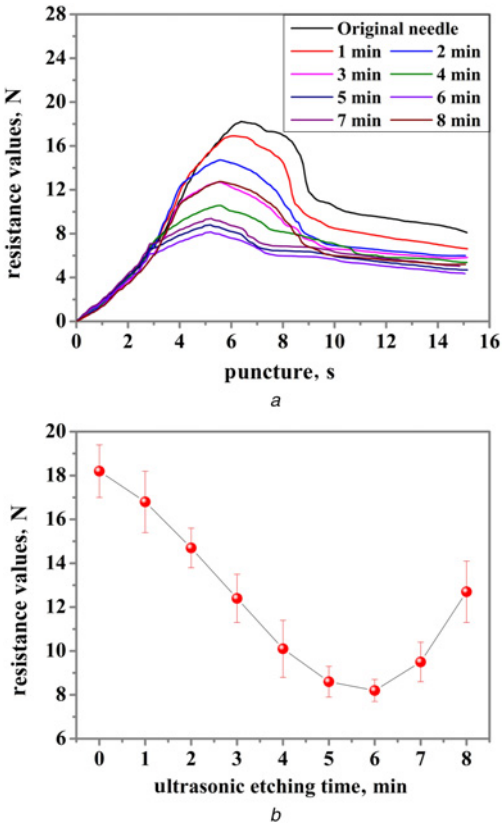


Fig. 6 *Resistance value and mean maximum resistance of an original stainless steel needle and stainless steel needles prepared using different etch times*
a Resistance values of the original and prepared stainless steel needle as a function of puncture time
b Mean maximum resistance values of the stainless steel needles as a function of ultrasonic etch time

force C of the needle were not affected by the microstructures; therefore, the resistance value F of the needle was reduced.

Besides, the microstructures allowed air to exist in the structural depression. In this case, the surface of the microstructured needle, the air, and the silica gel formed a rolling bearing model during the resistance test (Fig. 5*b*). Compared to the original needle, the resistance value of the microstructured needle was reduced under the sliding friction condition.

4. Discussion: Recent studies revealed that the super-hydrophobicity of certain biological surfaces is affected by surface roughness and low surface energy [22–24]. In this Letter, a super-hydrophobic stainless steel needle was fabricated using 6 min of ultrasonic etching and fluorination in PFDTES to create surface microstructures and achieve low surface energy. The as-prepared stainless steel needle was super-hydrophobic, with water CA >150°. The surface of the stainless steel needle was uniformly covered with microstructures with a diameter of ~50 μm. These microstructures can trap a large amount of air, which reduces the contact area between water and the stainless steel needle. The super-hydrophobic surface imparts both self-cleaning and low adhesion properties to the stainless steel needle. In clinical practise, this as-prepared stainless steel needle may enhance the needle's function and reduce injection-associated pain.

Previous studies confirm that surface roughness enhances super-hydrophobicity. Long *et al.* [8] fabricated a super-hydrophobic copper surface by picosecond laser nanostructuring and subsequent modification with triethoxyoctylsilane. The surface showed robust ripples with a large number of nanoscale structures, and the CA was 153.9°. Qi *et al.* [18] fabricated a super-hydrophobic bionic

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needle by an electroless replacement reaction process between an Ag nitrate solution and an activated stainless steel needle and subsequent surface modification with octadecanethiol. Ag micro-nanostructures were formed on the surface of the bionic needle, and a maximum CA of 152° was achieved. Wang [16] fabricated a bionic needle with corrugated, serrated, and concave micro-structures on its surface; however, the super-hydrophobicity of this stainless steel needle was not investigated.

Resistance properties of structures are also strongly governed by surface morphology [4, 10, 18]. In the current Letter, the super-hydrophobic stainless steel needle underwent a resistance test in which silica gel was used to simulate skin. The microstructures on the surface of the as-prepared stainless steel needle were filled with air. This minimised contact between the stainless steel needle and the simulated skin and reduced frictional effects. In an *in vivo* model, biological fluids could displace the air in the microstructures providing a lubricating effect during the puncture process. Furthermore, the microstructures will cause vibration perpendicular to the direction of the advancing stainless steel needle, which could increase the flow of biological fluids and the lubricating effect [16, 25].

5. Conclusions: In summary, a super-hydrophobic stainless steel needle was successfully fabricated using ultrasonic etching and surface modification. The super-hydrophobic surface of the stainless steel needle was attributed to the presence of microstructures and chemical modification with a low surface energy material. The as-prepared stainless steel needle had drag reduction properties which could reduce pain during a puncture process. This Letter provides a new approach to the preparation of multifunctional medical puncture instruments, and we hope the ultrasonic etching method can contribute to promoting small droplets manipulation and biometric and inkjet printing applications.

6. Acknowledgment: We thank Zhongxu Lian for measuring contact angles and resistance values.

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