

# Robust Superhydrophobic Conical Pillars from Syringe Needle Shape to Straight Conical Pillar Shape for Droplet Pancake Bouncing

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**ABSTRACT:** Superhydrophobic conical pillars have great industrial application potential in, for example, anti-icing of aircraft wings and protecting high voltage transmission lines from freezing rain because of their droplet pancake bouncing phenomenon which is recognized to furthest reduce the liquid-solid contact time. However, there are still no methods that can large-scale fabricate robust

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3 superhydrophobic conical pillars. Here, a mold replication technology was proposed to realize the large-  
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5 scale fabrication of superhydrophobic conical pillars with a high mechanical strength. An Al mold with  
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7 intensive conical holes decorated with micro/nanometer-scale structures was fabricated by nanosecond  
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9 laser drilling and HCl etching. The conical shape originated from a near Gaussian spatial distribution of  
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11 the energy and temperature in the radial direction in the laser drilling processes. Robust superhydrophobic  
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13 conical pillars from syringe needle shape to straight conical pillar shape were easily fabricated through  
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15 replication from the Al mold without any extra spray of superhydrophobic nanoparticles. It was also found  
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17 that although all superhydrophobic conical pillars with different shape could generate the droplet pancake  
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19 bouncing, the shape had a great influence on the critical bottom space and the critical Weber number ( $We$ )  
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21 to generate pancake bouncing. The pancake bouncing with the shortest contact time of a 68.5% reduction  
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23 appeared on superhydrophobic straight conical pillars with the shape angle of  $180^\circ$ . Overcoming the  
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25 difficulties in the large-scale fabrication and robustness of superhydrophobic conical pillars will promote  
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27 practical applications of the droplet pancake bouncing phenomenon.  
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34 **KEYWORDS:** conical pillars, superhydrophobic, pancake bouncing, large-scale, robust  
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## 37 1. INTRODUCTION

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40 Superhydrophobic surfaces which are inspired from the lotus leaf have been widely studied for more than  
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42 20 years. However, due to the continuous development of new application prospects, such as self-  
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44 cleaning<sup>1, 2</sup>, oil/water separation<sup>3</sup>, drag-reduction<sup>4-6</sup>, corrosion-resistance<sup>7</sup>, anti-bacterium<sup>8</sup>, anti-icing<sup>9-11</sup>,  
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46 fog-harvest<sup>12-14</sup>, pumpless transport of liquid<sup>15, 16</sup>, condensation-enhancement<sup>17-20</sup>, and biomedical  
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48 applications<sup>21-27</sup>, superhydrophobic surfaces still attract more and more attention from the academic  
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50 community. The number of papers about superhydrophobic surface increases every year with > 1670  
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52 papers indexed in the ISI Web of Science in 2018 (Figure S1). Hence, developments on superhydrophobic  
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54 surfaces will be of great interest to the academic community particularly where possibilities of widespread  
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3 application can be realized.  
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5 Superhydrophobic surface could effectively reduce the liquid-solid contact time compared with  
6 common hydrophilic or hydrophobic surface because of its  $>150^\circ$  contact angle and  $<10^\circ$  sliding angle.  
7 However, the liquid-solid contact time of a water droplet with a certain volume on a superhydrophobic  
8 flat surface is constant<sup>28</sup>. How to further reduce the contact time has fascinated many scientists and the  
9 investigations showed that superhydrophobic point-like macrotexture<sup>29</sup>, micrometer-scale ridge<sup>30-32</sup>,  
10 millimeter-scale ridge<sup>32, 33</sup> and submillimeter-scale conical pillars could effectively further reduce the  
11 liquid-solid contact time<sup>34</sup>. Among them, superhydrophobic submillimeter-scale conical pillars can  
12 produce a droplet pancake bouncing phenomenon which is recognized to furthest reduce the liquid-solid  
13 contact time. That is, the droplet pancake bouncing surface corresponds to the lowest liquid-solid contact  
14 time which can be worthy of further exploration. Additionally, only superhydrophobic submillimeter-scale  
15 conical pillars can ensure that all water droplets impacted on the solid surface detach quickly with a  
16 pancake shape from the substrate, showing great practical application potential at anti-icing from the  
17 freezing rains. How to fabricate superhydrophobic submillimeter-scale conical pillars is the key to the  
18 application of the droplet pancake bouncing phenomenon. Liu et al. developed a combined process  
19 composed of electric spark cutting, chemical oxidation, and fluoroalkylsilane modification to fabricate  
20 superhydrophobic submillimeter-scale conical pillars on a Cu substrate<sup>34</sup>. They first constructed conical  
21 pillars with diameter of 20-200  $\mu\text{m}$  and height of 800-1200  $\mu\text{m}$  and then constructed micro/nanometer-  
22 scale flower-like and needle-like structures and finally reduced the surface energy. Graeber et al.  
23 fabricated a polymer mold with conical holes by 3D printing, and then replicated submillimeter-scale  
24 conical polymeric pillars<sup>35</sup>. Since the surface of the pillars was too smooth, superhydrophobic PTFE  
25 nanoparticles were sprayed on top to render the submillimeter-scale conical polymeric pillars  
26 superhydrophobic. However, the aforementioned methods have certain deficiencies. The processing  
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3 efficiency of electric spark cutting is very low, resulting in a time consuming and costly fabrication  
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5 processes for a large-scale surface. Theoretically, mold replication technology is high efficiency, low cost,  
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7 and easy in operation. However, the non-metal mold obtained by 3D printing is easy to wear out and the  
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9 smooth replica needs extra spray treatment to acquire superhydrophobicity. In addition, the adhesive force  
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11 between the sprayed superhydrophobic nanoparticles and the replica is low, resulting in a low mechanical  
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13 strength. The reported method did not take advantage of mold replication technology and is still low  
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15 efficiency and high cost. It is still an unanswered question as to how to fabricate a metal mold with  
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17 intensive conical holes and how to cancel extra spray treatment but still acquire superhydrophobicity.  
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19 These are important questions to decide if the mold replication technology can fabricate large-scale  
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21 superhydrophobic conical pillars with high efficiency and low cost. Moreover, further exploration of  
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23 whether superhydrophobic conical pillars with a larger diameter besides submillimeter-scale can generate  
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25 the pancake bouncing is required.  
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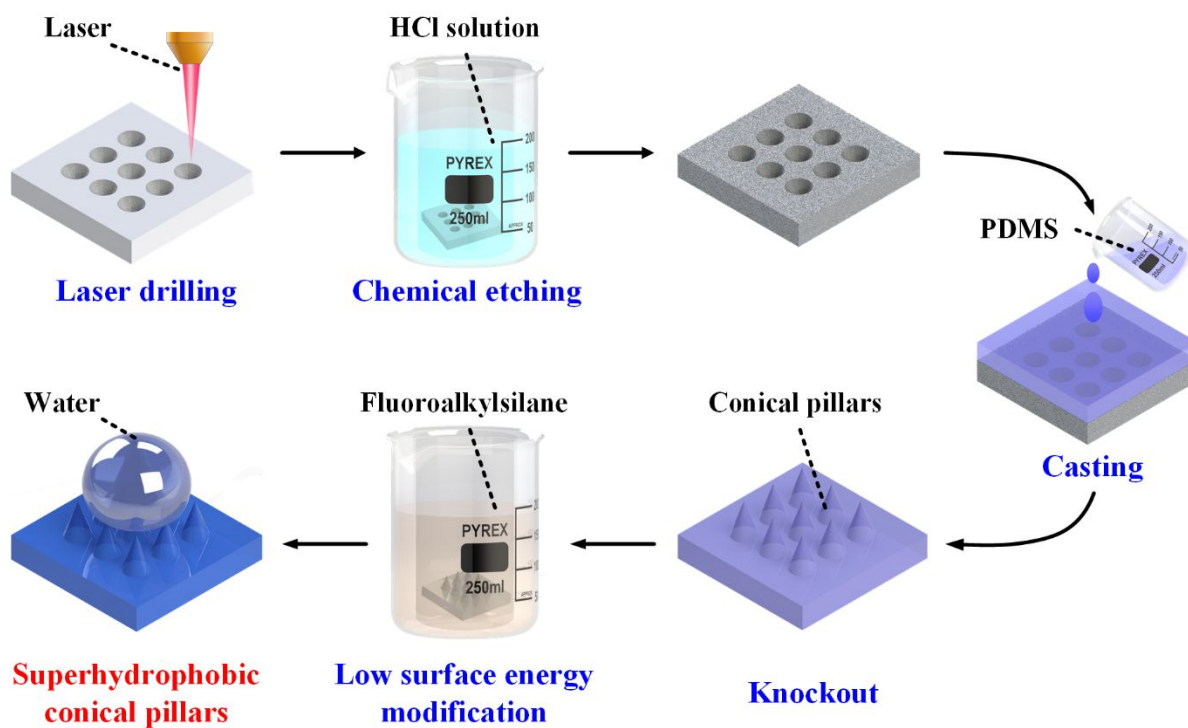
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31 Nanosecond laser is often used to drill holes on metal substrates because of its high efficiency and low  
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33 cost. However nanosecond laser with a near Gaussian spatial distribution of the energy and temperature  
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35 in the radial direction in the laser drilling processes has a fatal disadvantage for drilling holes with a high  
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37 depth-diameter ratio in that conical holes often occur, which is tried to be avoided in the industry. Here,  
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39 we made full use of the aforementioned disadvantages and drilled intensive conical holes on Al substrate  
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41 by nanosecond laser. After HCl etching to decorate micro/nanometer-scale structures on the inner wall of  
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43 the conical holes, the Al mold was obtained. Robust superhydrophobic conical pillars from syringe needle  
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45 shape to straight conical pillar shape were easily fabricated through replication from the Al mold without  
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47 any extra spray of superhydrophobic nanoparticles. Bouncing dynamics of an impacting water droplet  
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49 shows that the replicated superhydrophobic conical pillars with different shapes and bottom diameter from  
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51 submillimeter to millimeter could generate the pancake bouncing phenomenon. This developed method  
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3 makes full use of the advantages of mold replication technology to fabricate large-scale superhydrophobic  
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## 8 9 **2. EXPERIMENTAL**

### 10 11 **2.1 Fabrication of Superhydrophobic Conical Pillars**

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14 The fabrication processes of superhydrophobic conical pillars is shown in Figure 1. Prior to laser drilling,  
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16 an aluminum (Al, purity > 99%, Alighting Co., Shanghai) plate with thickness of 2 mm was ultrasonically  
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18 washed in deionized water and air-dried. Then, intensive conical holes with different shape and size  
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20 (diameter, height, and space) were drilled on the Al plate in ambient condition with humidity of 30-50%  
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22 and temperature of 20-25 °C by nanosecond laser (wavelength 1064 nm, pulse duration 100 ns, repetition  
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24 rate 20 kHz, spot size 100 μm). The scanning speed was 500 mm/s and the scanning times for each hole  
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26 was 60 times. After laser drilling, the Al plate was ultrasonically washed in deionized water and immersed  
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28 in the 0.4 mol/L aqueous HCl (Alighting Co., Shanghai) solution for 2 min to construct micro/nanometer-  
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30 scale structures on the inner wall of the conical holes. After another ultrasonic wash in deionized water,  
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32 the Al mold was obtained. Then, polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, Germany),  
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34 which was used as the representative casting body, was poured onto the Al mold and baked at 60°C for 3  
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36 h in a vacuum drying oven. The mass ratio of PDMS and cross-linker was 10:1. After knockout, the  
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38 intensive conical pillars were replicated. Finally, the replica was immersed in a 1.0 wt % ethanol solution  
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40 of FAS (fluoroalkylsilane, C<sub>8</sub>F<sub>13</sub>H<sub>4</sub>Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, Degussa Co., Germany) for 30 min and heated at 50 °C  
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42 for 10 min. Thus, superhydrophobic conical pillars were fabricated. It is worth noting that the Al mold  
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44 can be reused.  
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**Figure 1.** Schematics of the fabrication processes of superhydrophobic conical pillars.

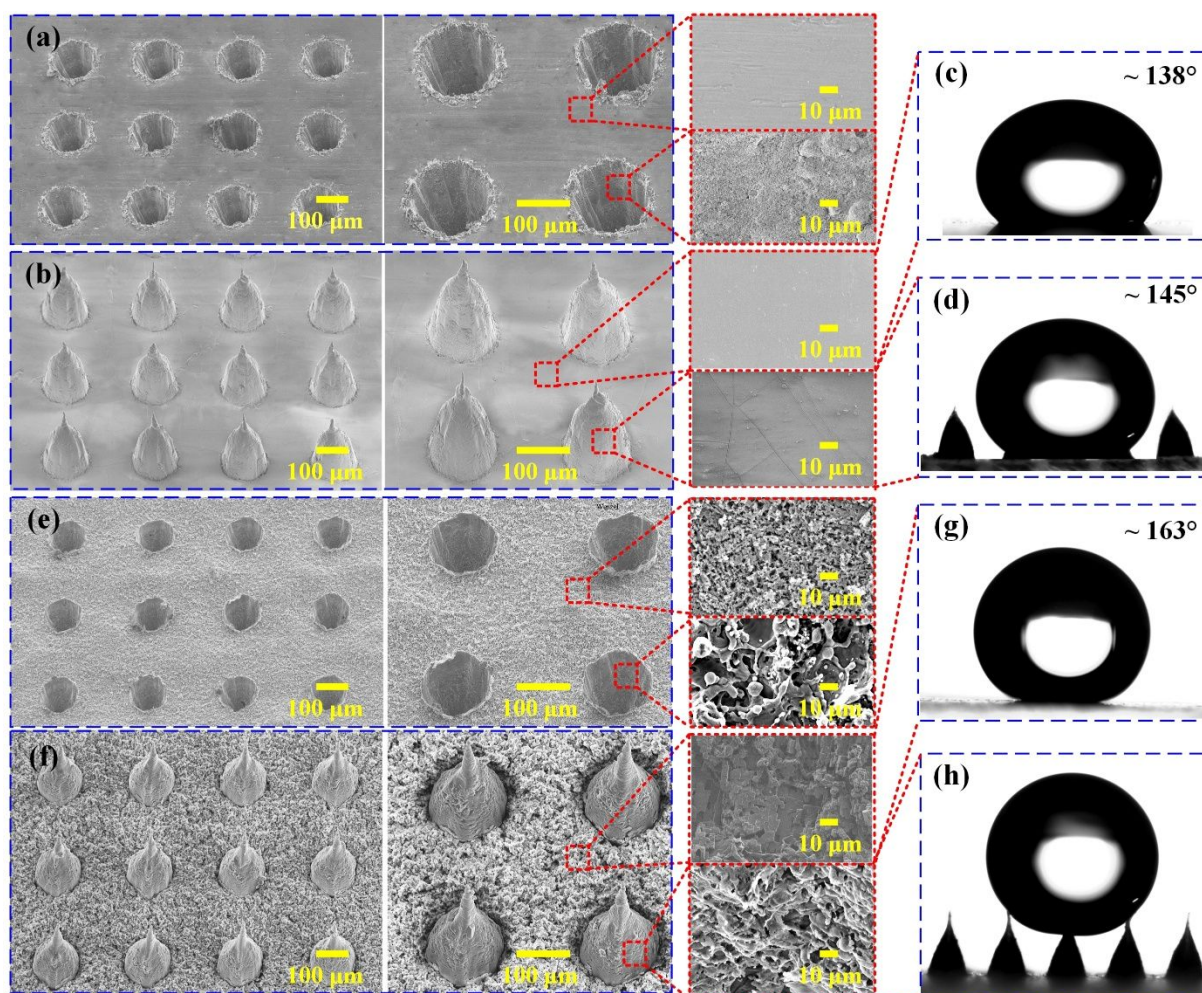
## 2.2 Characterization

The micro structures and surface morphology of the samples were characterized using a scanning electron microscope (SEM, SUPRA 55 SAPPHERE, Germany). The contact angle (CA) of a 5  $\mu\text{L}$  water droplet on the samples was measured using an optical contact angle meter (Krüss, DSA100, Germany). The dynamic bouncing processes of water droplets with volume of 21  $\mu\text{L}$  on the samples were characterized using a high speed camera (NAC, MEMRECAM HX-7S, Japan) at 10000 frame/s. For a water droplet, when the ratio ( $Q$ ) of the lateral extension diameter ( $d_{\text{jump}}$ ) at the detachment moment from the sample surface and the maximum lateral extension diameter ( $d_{\text{max}}$ ) in the jumping processes is larger than 0.8, that is  $Q = (d_{\text{jump}}/d_{\text{max}}) > 0.8$ , the pancake bouncing is obtained<sup>32</sup>, as shown in Figure S2. The Weber number  $We$  is defined as  $We = \rho v^2 r_0 / \gamma$ , where  $\rho$ ,  $v$ ,  $r_0$ , and  $\gamma$  relate to the density, impact velocity, radius, and surface tension of water droplets, respectively. The bottom diameter, height, and bottom space of the conical

pillars were defined as  $D$ ,  $H$ , and  $S$ , as shown in Figure S3.

### 3. RESULTS AND DISCUSSION

It is well known that surface micro/nanometer-scale structures and low surface energy are necessary for superhydrophobicity. Although the nanosecond laser could easily drill conical holes on an Al substrate, the substrate surface was rather smooth and the inner wall of the holes was not rough enough (Figure 2(a)), resulting in that the replica substrate surface and the external surface of the replicated conical pillars were also smooth (Figure 2(b)). Such a smooth surface cannot obtain superhydrophobicity even after FAS modification. For water droplet on the replica substrate surface, the contact angle was only  $138^\circ$  (Figure 2(c)). For water droplet on the replicated conical pillars, the water droplet penetrated into the voids between the conical pillars, showing a typical Wenzel hydrophobic state (Figure 2(d))<sup>36</sup>. In order to construct micro/nanometer-scale structures on the substrate surface and the inner wall of the conical holes, after laser drilling an HCl etching process was introduced, which effectively formed the micro structures required for superhydrophobicity<sup>37</sup>. Figure 2(e) shows the SEM image of the Al substrate after laser drilling and HCl etching. It can be seen that the substrate surface and the inner wall of the conical holes were rough and composed of micro/nanometer-scale pits and protuberances. After replication, the replica substrate surface and the external surface of the replicated conical pillars were also rough (Figure 2(f)). With further FAS modification, superhydrophobicity was obtained. Water droplet on the replica substrate surface showed a spherical shape with contact angle of  $163^\circ$  (Figure 2(g)). Water droplet on the replicated conical pillars also showed a spherical shape whose bottom has a composite contact region composed of liquid-solid contact region and liquid-air contact region (Figure 2(h)), showing Cassie-Baxter superhydrophobic state. Thus, superhydrophobic conical pillars were fabricated.

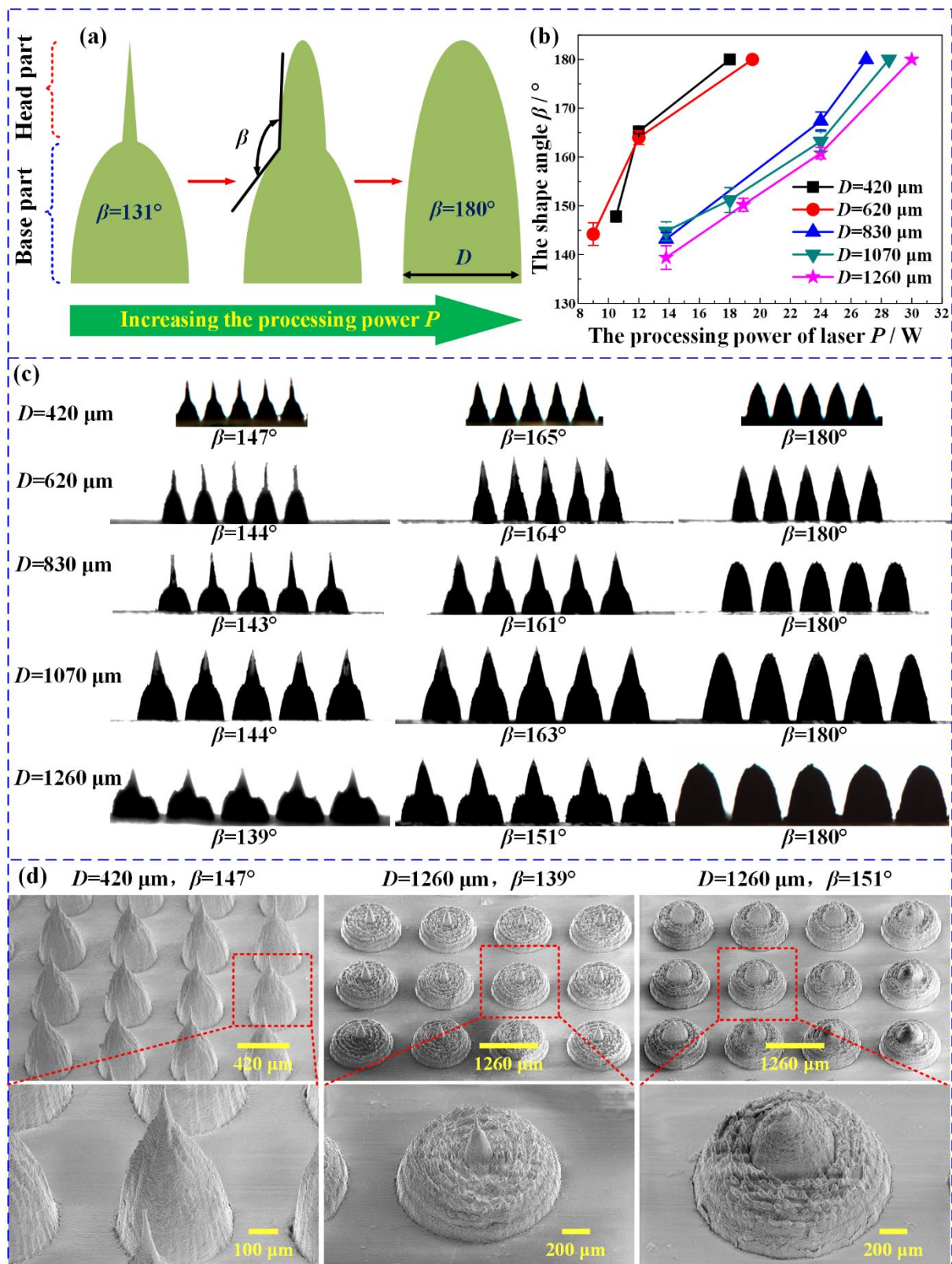


**Figure 2.** Surface morphology of the Al mold and the replica. (a) SEM images with different magnifications of the Al mold obtained by laser drilling. (b) SEM images with different magnifications of the conical pillars with  $D=210\ \mu\text{m}$ ,  $H=640\ \mu\text{m}$ , and  $S=180\ \mu\text{m}$  replicated from the Al mold obtained by laser drilling. (c) The replica substrate surface was smooth and had a water CA of  $138^\circ$ . (d) The surface of the replicated conical pillars was not rough enough and water droplet on it showed a Wenzel hydrophobic state. (e) SEM images with different magnifications of the Al mold obtained by laser drilling and HCl etching. (f) SEM images with different magnifications of the conical pillars with  $D=210\ \mu\text{m}$ ,  $H=640\ \mu\text{m}$ , and  $S=180\ \mu\text{m}$  replicated from the Al mold obtained by laser drilling and HCl etching. (g) The replica substrate surface was rough and had a water CA of  $163^\circ$ . (h) The surface of the replicated conical pillars was rough and water droplet on it showed a Cassie-Baxter superhydrophobic state. The processing



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3 power of nanosecond laser for the conical holes in (a) and (e) was 9 W.  
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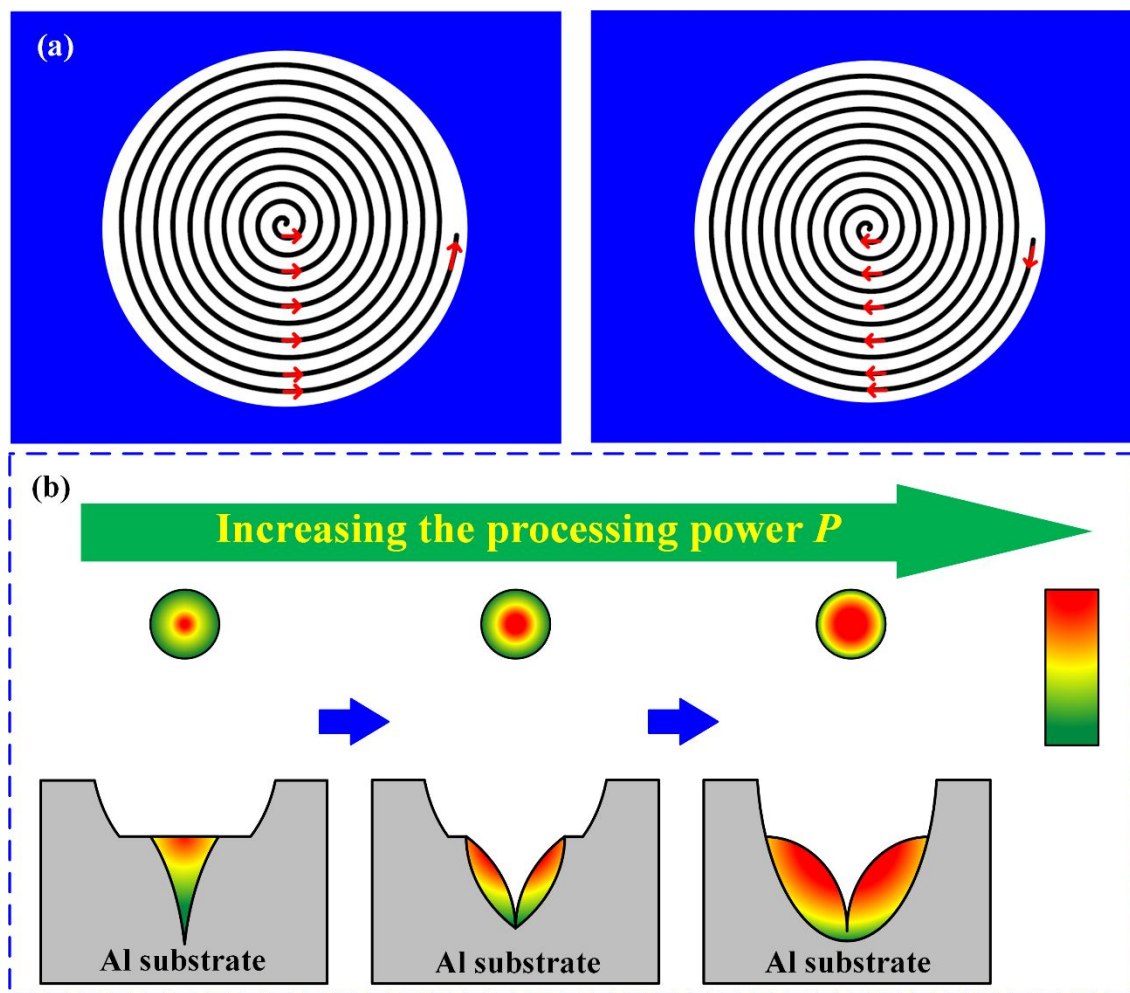
8 In the replication processes of the conical pillars by the Al mold, it was surprising to find that the conical  
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10 pillars with special shape were obtained besides the common straight conical pillars simply by adjusting  
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12 the processing power of the nanosecond laser. In order to describe the conical pillars more clearly, the  
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14 conical pillar was divided into two parts composed of head part and base part, as shown in Figure 3 (a). A  
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16 shape angle  $\beta$  was then defined, which is the angle between the tangent lines along conical pillars contour  
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18 at the cross point of head part and base part. The influence of the processing power  $P$  of the nanosecond  
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20 laser on the  $\beta$  at different bottom diameter is shown in Figure 3(b). It can be seen that the  $\beta$  at different  
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22 bottom diameter changes with the same trend that the  $\beta$  increased with the increase of the processing  
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24 power  $P$ . The conical pillar changed from syringe needle shape with the  $\beta$  of 139-147° to straight conical  
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26 pillar shape with the  $\beta$  of 180° with the increase of the  $\beta$ , as shown in Figure 3(c) and 3(d). It was also  
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28 observed that the required processing power for the straight conical pillar increased with the increase of  
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30 the bottom diameter. All the conical pillars with different shape replicated from the Al mold obtained by  
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32 laser drilling and HCl etching show superhydrophobicity with CA > 160°.  
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3 **Figure 3.** The influence of the processing power of the nanosecond laser on the shape of the replicated  
4 conical pillars. (a) The schematics of the evolution processes of the shape of the replicated conical pillars.  
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7 (b) The influence of the processing power  $P$  of the nanosecond laser on the  $\beta$  at different bottom diameters.  
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10 (c) The side view of the replicated conical pillars with different  $\beta$  at different bottom diameter. (d) SEM  
11 images with different magnifications of the replicated conical pillars with 3 typical shapes.  
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17 The conical pillar with different shape angle  $\beta$  was replicated from the conical hole with different shape  
18 angle  $\beta$ . Figure 4 provides an explanation for the conical hole with different shape angle  $\beta$ . Since the laser  
19 spot is often much smaller than the required hole diameter, the laser spot often performs spiral scanning  
20 from the inside to the outside and then from the outside to inside again for each scanning time, as shown  
21 in Figure 4(a). The total scanning times can be set by manipulator and was set at 60 times here. In the  
22 drilling processes, energy and temperature were a near Gaussian spatial distribution in the radial direction  
23 that is the energy and temperature presented a decreasing trend from the center to the edge of the hole<sup>38,</sup>  
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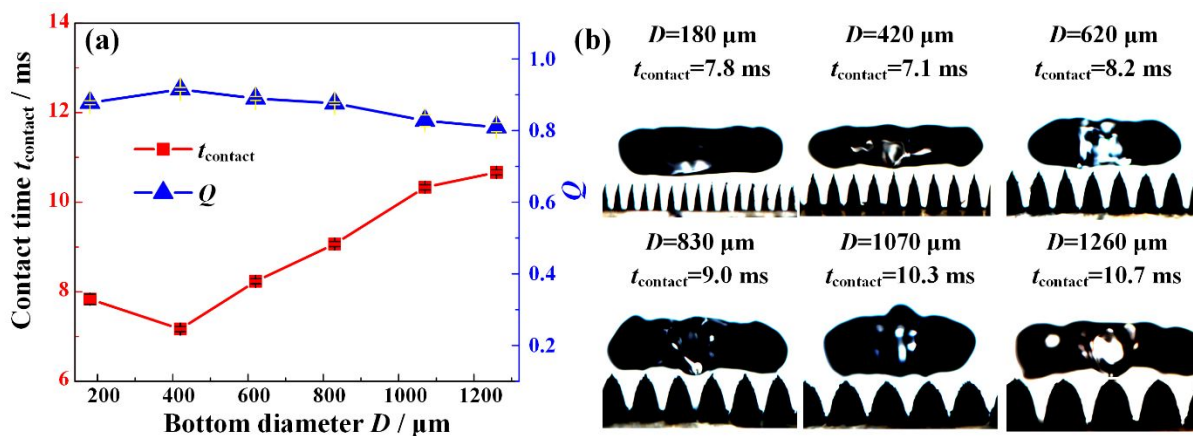
39. The higher energy and temperature indicate a faster removing velocity of the Al material. Thus, a conical hole was formed. For the low processing power, the area of high energy and temperature near the hole center is small, resulting in the syringe needle shape with the small  $\beta$ . With the increase of the processing power, the area of high energy and temperature near the hole center became larger gradually, resulting in a larger  $\beta$ . Thus the straight conical pillar with the  $\beta$  of  $180^\circ$  was eventually formed, as shown in Figure 4(b). Therefore, for the hole with certain diameter, the shape angle  $\beta$  was determined by the processing power. In addition, similar to  $\beta$ , the depth of the hole with certain diameter was also determined by the processing power, as shown in Figure S4.



**Figure 4.** The schematics of the trajectory of the laser spot for each scanning time (a) and the schematics of the variation of the area of high energy and temperature near the hole center with the processing power of the laser (b). The gradual change of the color from green to red indicates the increase of the temperature.

The dynamic behavior of an impacting water droplet on superhydrophobic conical pillars with different shape was then studied in order to explore if the pancake bouncing phenomenon could occur on superhydrophobic conical pillars replicated from Al mold. For a superhydrophobic flat surface, an impacting water droplet with volume of 21  $\mu\text{L}$  and  $We$  of 14 spread laterally first to a thin film, then recoiled, and finally detached from the substrate with an elongated shape, as shown in Figure S5 and Video S1. The total liquid-solid contact time was 22.7 ms. However, in contrast to superhydrophobic flat

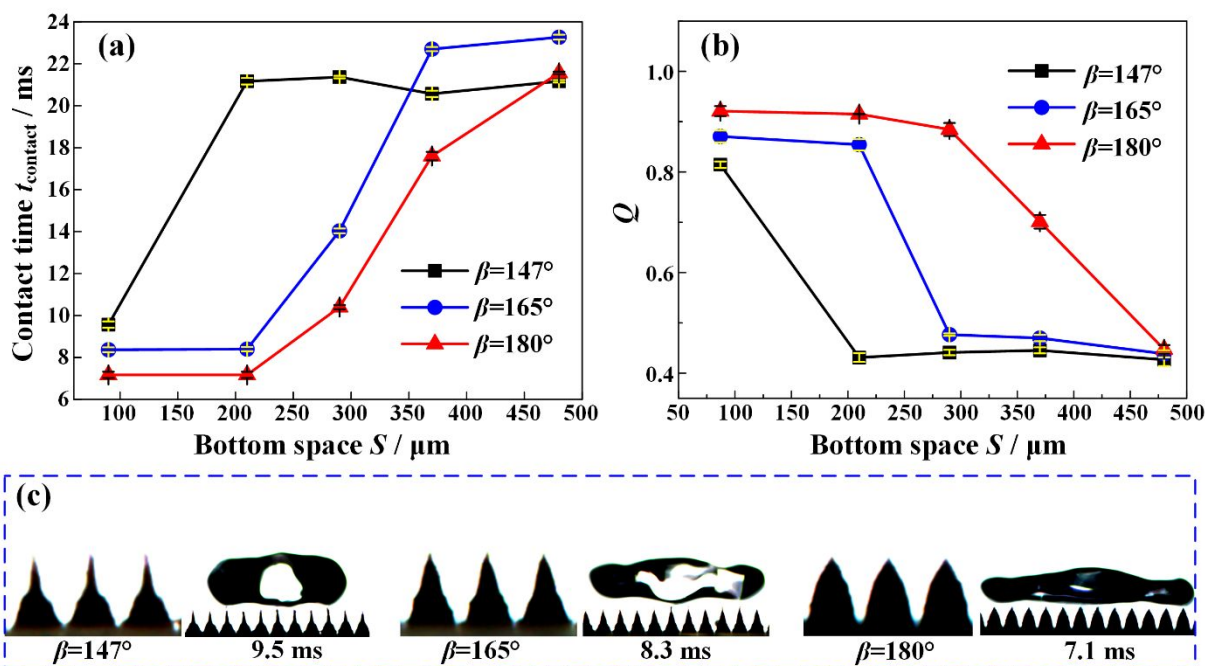
surface, the dynamic behavior of an impacting water droplet on superhydrophobic conical pillars was completely changed. Figure S6 and 5 shows the bouncing processes of water droplet with volume of 21  $\mu\text{L}$  on superhydrophobic conical pillars with different bottom diameter  $D$  ( $S=210 \mu\text{m}$  and  $\beta=180^\circ$ ) at  $We=14$ . The impacting water droplet also spread laterally first to a thin film, then recoiled, but finally detached from the substrate with a pancake shape and a reduced liquid-solid contact time. It is also worth noting that all superhydrophobic conical pillars with the bottom diameters from 180-1260  $\mu\text{m}$  could generate the pancake bouncing phenomenon with  $t_{\text{contact}}$  smaller than 10.7 ms and  $Q$  larger than 0.81. The pancake bouncing with the shortest contact time and a 68.5% reduction ( $t_{\text{contact}}=7.1 \text{ ms}$ ,  $Q=0.91$ ) in contact time compared with the conventional bouncing occurred at  $D=420 \mu\text{m}$  (Video S2).



**Figure 5.** Variations of the liquid-solid contact time  $t_{\text{contact}}$  and  $Q$  of a water droplet (21  $\mu\text{L}$ ) with the bottom diameter  $D$  of superhydrophobic conical pillars ( $S=210 \mu\text{m}$  and  $\beta=180^\circ$ ) at  $We=14$  (a) and the detachment moment of the water droplet impacting on superhydrophobic conical pillars with different  $D$  (b).

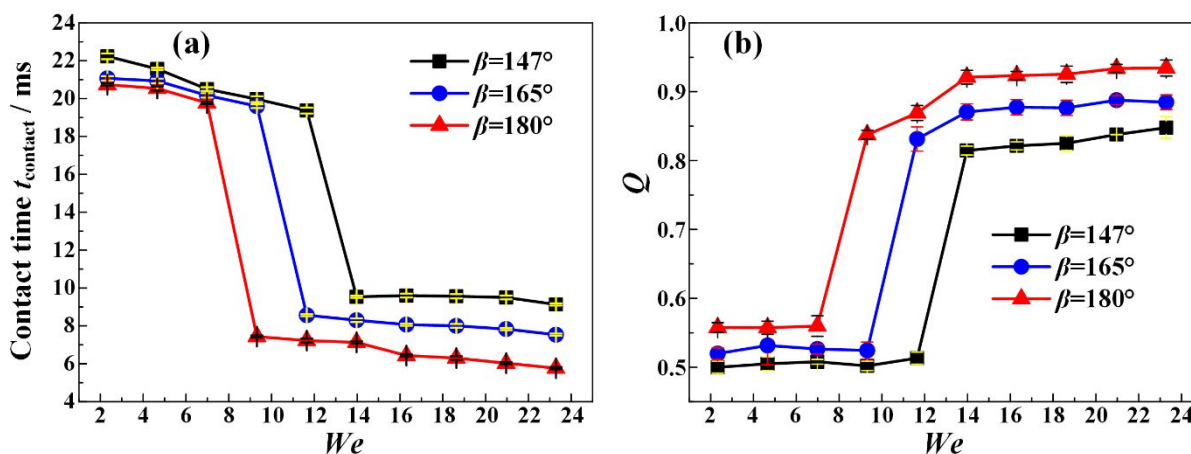
The influence of the bottom space  $S$  and shape angle  $\beta$  of superhydrophobic conical pillars on the liquid-solid contact time  $t_{\text{contact}}$  and  $Q$  was then studied. The bottom diameter  $D$ , volume of water droplet and  $We$ ,

were 420  $\mu\text{m}$ , 21  $\mu\text{L}$  and 14, respectively. As shown in Figures 6(a) and 6(b), when the bottom space  $S$  was small, all superhydrophobic conical pillars with different shape angle  $\beta$  generated the pancake bouncing phenomenon with a small  $t_{\text{contact}}$  and a large  $Q$ . With the increase of  $S$ , the bouncing dynamics on all superhydrophobic conical pillars with different shape angle  $\beta$  were transformed into the conventional bouncing. However, the critical bottom space  $S$  to generate the pancake bouncing was different for superhydrophobic conical pillars with different  $\beta$ . The larger  $\beta$  results in a larger critical  $S$  for the pancake bouncing. The critical  $S$  to generate the pancake bouncing for superhydrophobic conical pillars ( $D=420 \mu\text{m}$ ) with  $\beta$  of  $147^\circ$ ,  $165^\circ$ , and  $168^\circ$  were 90  $\mu\text{m}$ , 210  $\mu\text{m}$ , and 290  $\mu\text{m}$ , respectively. We also found that although all superhydrophobic conical pillars with different  $\beta$  can generate the pancake bouncing, the liquid-solid contact time  $t_{\text{contact}}$  decreased with the increase of  $\beta$ , while  $Q$  increased with the increase of  $\beta$ . As shown in Figure 6(c), for  $S=90 \mu\text{m}$ , the  $(t_{\text{contact}}, Q)$  for the  $\beta$  of  $147^\circ$ ,  $165^\circ$ , and  $168^\circ$  were (9.5 ms, 0.81), (8.3 ms, 0.87), and (7.1 ms, 0.92), respectively.



**Figure 6.** Variations of the liquid-solid contact time  $t_{\text{contact}}$  (a) and  $Q$  (b) of a water droplet (21  $\mu\text{L}$ ) with the bottom space  $S$  of superhydrophobic conical pillars with different  $\beta$  ( $D=420 \mu\text{m}$ ) at  $We=14$ . (c) The detachment moment of the water droplet impacting on superhydrophobic conical pillars with different  $\beta$ .

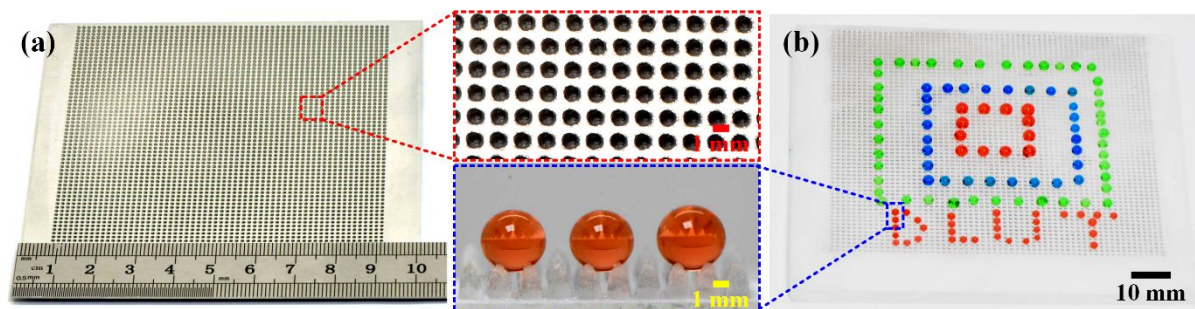
The influence of  $We$  on the liquid-solid contact time  $t_{\text{contact}}$  and  $Q$  for superhydrophobic conical pillars with different  $\beta$  was also studied. Figures 7(a) and 7(b) show the variation of  $t_{\text{contact}}$  and  $Q$  with  $We$  on superhydrophobic conical pillars with different  $\beta$ . The bottom diameter  $D$  was 420  $\mu\text{m}$ , the bottom space  $S$  was 90  $\mu\text{m}$ , and the volume of the water droplet was 21  $\mu\text{L}$ . We found a step-like variation of  $t_{\text{contact}}$  and  $Q$  with  $We$ . When the  $We$  was smaller than a critical value, a large  $t_{\text{contact}}$  and a small  $Q$  remained stable, indicating the conventional bouncing. When the  $We$  increased into the critical value, the  $t_{\text{contact}}$  decreased sharply and the  $Q$  increased sharply. The conventional bouncing was completely transferred into the pancake bouncing. With the further increase of  $We$ ,  $t_{\text{contact}}$  and  $Q$  remained stable. The critical  $We$  to generate the pancake bouncing decreased with the increase of the  $\beta$  and was 14, 11.6, and 9.3 for the  $\beta$  of 147°, 165°, and 180°, respectively. Further, in agreement with Figure 5, although all superhydrophobic conical pillars with different  $\beta$  can generate the pancake bouncing with  $We >$  the critical value, the  $t_{\text{contact}}$  decreased with the increase of the  $\beta$ , while  $Q$  increased with the increase of the  $\beta$ .



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3 **Figure 7.** Variations of the liquid-solid contact time  $t_{\text{contact}}$  (a) and  $Q$  (b) of a water droplet (21  $\mu\text{L}$ ) with  
4 the  $We$  on superhydrophobic conical pillars with different  $\beta$  ( $D=420\ \mu\text{m}$  and  $S=90\ \mu\text{m}$ ).  
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10 Apart from the observed pancake bouncing of droplet with room temperature ( $\sim 20^\circ\text{C}$ ), we have also  
11 tested the dynamic bouncing processes of cold and hot water droplets on superhydrophobic conical pillars.  
12 After all, anti-icing was one of the important application prospects of the droplet pancake bouncing surface.  
13 Figure S7 shows the bouncing processes of water droplets with temperature of  $2^\circ\text{C}$ ,  $5^\circ\text{C}$ ,  $20^\circ\text{C}$ ,  $50^\circ\text{C}$  and  
14  $70^\circ\text{C}$  on superhydrophobic conical pillars with  $D=420\ \mu\text{m}$ ,  $S=90\ \mu\text{m}$ , and  $\beta=180^\circ$  at  $We=19$ . All water  
15 droplets with low temperature as well as high temperature also showed a typical pancake bouncing with  
16  $t_{\text{contact}} \sim 4.9\ \text{ms}$ , indicating possible application in the freezing and high temperature environment.  
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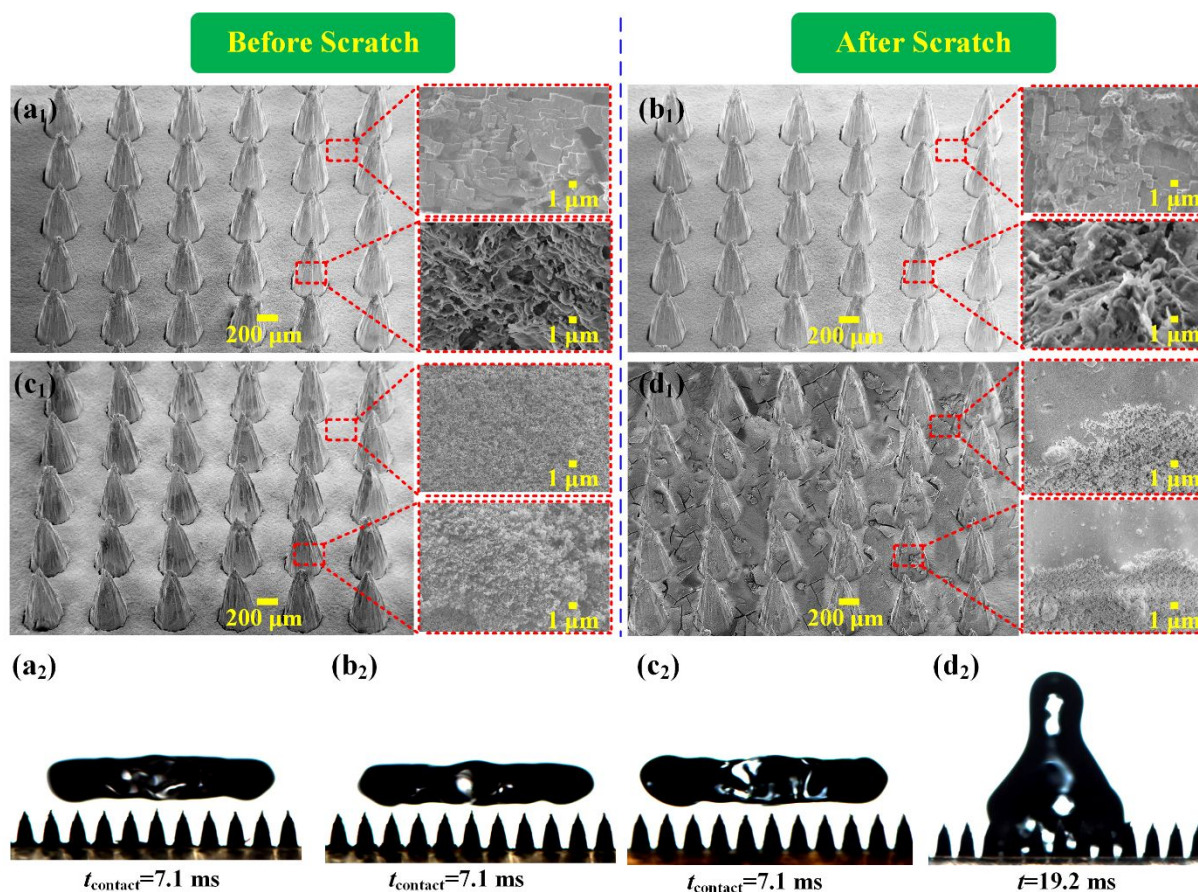
26 Since the pancake bouncing of a water droplet can occur on the replicated superhydrophobic conical  
27 pillars from the laser-drilled Al mold, we explored if the method developed here could be realized for the  
28 large-scale fabrication. We first drilled the intensive conical holes by laser on the Al substrate with an area  
29 of  $80\ \text{mm} \times 80\ \text{mm}$ . After chemical etching, the large-scale Al mold was obtained (Figure 8(a)). Then, the  
30 PDMS conical pillars ( $D=830\ \mu\text{m}$ ,  $S=90\ \mu\text{m}$ , and  $\beta=180^\circ$ ) with area of  $80\ \text{mm} \times 80\ \text{mm}$  were replicated.  
31 After FAS modification, superhydrophobic conical pillars with area of  $80\ \text{mm} \times 80\ \text{mm}$  were obtained, as  
32 shown in Figure 8(b).  
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3 **Figure 8.** Digital photo of the large-scale Al mold with intensive conical holes (a) and the replicated  
4 superhydrophobic conical pillars with  $D=830\ \mu\text{m}$ ,  $S=90\ \mu\text{m}$ , and  $\beta=180^\circ$  (b). The area of the mold and  
5 sample was  $80\ \text{mm} \times 80\ \text{mm}$ .  
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12 To show the higher mechanical strength and robustness of superhydrophobic conical pillars obtained  
13 by our method compared with that obtained by spraying superhydrophobic nanoparticles, we scratched  
14 two types of samples by steel ruler with thickness of  $200\ \mu\text{m}$ , as shown in Figure S8. Figures 9(a<sub>1</sub>) and  
15 9(b<sub>1</sub>) show the SEM images of superhydrophobic conical pillars replicated from the laser-drilled and HCl-  
16 etched Al mold before and after steel ruler scratch for 20 times. No changes was observed on the surface  
17 morphology and the impacting water droplets showed the pancake bouncing phenomenon both on  
18 superhydrophobic conical pillars before and after scratch, as shown in Figures 9(a<sub>2</sub>) and 9(b<sub>2</sub>). Figures  
19 9(c<sub>1</sub>) and 9(d<sub>1</sub>) show the SEM images of superhydrophobic conical pillars obtained by replication from  
20 the laser-drilled Al mold and spraying commercial *Never-wet* superhydrophobic nanoparticles before and  
21 after steel ruler scratch for 3 times. Before scratch, the replica substrate surface and the external surface  
22 of the replicated conical pillars were coated with nanoparticles and the impacting water droplet showed  
23 the pancake bouncing phenomenon (Figure 9(c<sub>2</sub>)). After scratch, the nanoparticles were scraped and left  
24 some smooth regions on the substrate surface. Superhydrophobicity and the pancake bouncing  
25 phenomenon were also lost and the impacting water droplets even could not detach from the scratched  
26 conical pillars, as shown in Figure 9(d<sub>2</sub>) and Video S3. The poor adhesive force between the sprayed  
27 superhydrophobic nanoparticles and the replica resulted in poor mechanical strength. Therefore, the cancel  
28 of extra spray treatment in our method greatly improve the mechanical strength and robustness of  
29 superhydrophobic conical pillars.  
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**Figure 9.** Surface morphology of superhydrophobic conical pillars and bouncing state of an impacting water droplet on them before and after scratch. (a<sub>1</sub>) SEM images with different magnifications of superhydrophobic conical pillars replicated from the laser-drilled and HCl-etched Al mold and (a<sub>2</sub>) the detachment moment of a water droplet (21 μL) impacting on them at  $We=14$ . (b<sub>1</sub>) SEM images with different magnifications of superhydrophobic conical pillars replicated from the laser-drilled and HCl-etched Al mold after scratch for 20 times and (b<sub>2</sub>) the detachment moment of a water droplet (21 μL) impacting on them at  $We=14$ . (c<sub>1</sub>) SEM images with different magnifications of superhydrophobic conical pillars obtained by replication from the laser-drilled Al mold and spraying commercial *Never-wet* superhydrophobic nanoparticles and (c<sub>2</sub>) the detachment moment of a water droplet (21 μL) impacting on them at  $We=14$ . (d<sub>1</sub>) SEM images with different magnifications of superhydrophobic conical pillars obtained by replication from the laser-drilled Al mold and spraying commercial *Never-wet*

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3 superhydrophobic nanoparticles after scratch for 3 times and ( $d_2$ ) an impacting water droplet (21  $\mu\text{L}$ ,  
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5  $We=14$ ) on them could not detach from the surface. The  $D$ ,  $H$ ,  $S$ , and  $\beta$  of superhydrophobic conical pillars  
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7 were 420  $\mu\text{m}$ , 830  $\mu\text{m}$ , 210  $\mu\text{m}$ , and  $180^\circ$ , respectively.  
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#### 10 11 **4. CONCLUSION**

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13 In summary, an Al mold with intensive conical holes decorated with micro/nanometer-scale structures  
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15 were fabricated by nanosecond laser drilling and HCl etching. Through the replication of the Al mold,  
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17 robust superhydrophobic conical pillars with different shapes ranging from syringe needle shape to  
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19 straight conical pillar shape were easily fabricated without requiring any spray of superhydrophobic  
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21 nanoparticles. The formation mechanism of the aforementioned different shape is attributed to the near  
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23 Gaussian spatial distribution of energy and temperature in the radial direction in the laser drilling processes,  
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25 which results in a shape that can be controlled by the processing power of the laser. We then systemically  
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27 studied the influence of bottom diameter, bottom space, shape angle, and Webber number ( $We$ ) on the  
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29 contact time and bouncing shape of the impacting water droplets. It was revealed that superhydrophobic  
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31 conical pillars with different shape and bottom diameter from submillimeter to millimeter could generate  
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33 the pancake bouncing phenomenon. However, the critical bottom space and the critical  $We$  to generate the  
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35 pancake bouncing was affected largely by the shape angle. The critical bottom space increased while the  
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37 critical  $We$  decreased with the increase of the shape angle. In addition, the liquid-solid contact time for the  
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39 pancake bouncing decreased with the increase of the shape angle and the shortest contact time with a 68.5%  
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41 reduction appeared on superhydrophobic straight conical pillars with the shape angle of  $180^\circ$ . This mold  
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43 replication technology is easily extended to large-scale fabrication of robust superhydrophobic conical  
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45 pillars, which will promote the practical applications of the droplet pancake bouncing phenomenon.  
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## Notes

The authors declare no competing financial interest.

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## SUPPORTING INFORMATION

The number of papers about superhydrophobic surface indexed in the ISI Web of Science; schematics of the bouncing processes of a water droplet on the superhydrophobic surface; schematics of superhydrophobic conical pillars; variations of the hole depth, shape angle  $\beta$  with the hole diameter and the processing power of the laser; selected snapshots of a water droplet impacting on superhydrophobic flat surface at  $We=14$ ; selected snapshots of a water droplet impacting on superhydrophobic conical pillars with different bottom diameter  $D$  at  $We=14$ ; selected snapshots of water droplets with different temperature impacting on superhydrophobic conical pillars; schematics of steel ruler scratch on superhydrophobic conical pillars (PDF)

The bouncing dynamics of a water droplet impacting on superhydrophobic flat surface at  $We=14$  (AVI)

The bouncing dynamics of a water droplet impacting on superhydrophobic conical pillars with  $D=420$   $\mu\text{m}$ ,  $S=210$   $\mu\text{m}$ ,  $H=830$   $\mu\text{m}$ , and  $\beta=180^\circ$  at  $We=14$  (AVI)

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3 The bouncing dynamics of a water droplet impacting on Never-wet spray coated superhydrophobic conical  
4 pillars before and after steel ruler scratch for 3 times (AVI)  
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