Bioinspired Ribbed Nanoneedles with Robust Superhydrophobicity

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The robustness of superhydrophobicity is a fundamental issue for the applications of water-repellent materials. Inspired by the hierarchical structures of water-strider legs, this work describes a new water-repellent material decorated with ribbed, conical nanoneedles, successfully achieved on the surface of copper and consisting of copper hydroxide nanoneedle arrays sculptured with nanogrooves. The behavior of water drops on an as-prepared surface under various external disturbances is investigated. It is shown in particular that squeezing and relaxing drops between two such surfaces leads to a fully reversible exploration of the solid surface by the liquid, which is distinct from other superhydrophobic surfaces. This unique character is attributed to the penetrating Cassie state that occurs at the ribbed, conical nanoneedles. The proprietary lateral nanogrooves can, not only vigorously support the enwrapped liquid-air interface when a force is applied to the drop, but also provide reliable contact lines for the easy depinning of the deformed interface when the force is released from the drop. The results confirm the exceptional ability of strider legs to repel water, and should help to further the design of robust water-repellent materials and miniaturized aquatic devices.

1. Introduction

The wettability of solid surfaces is a subject that has attracted great interest in the past decades. Water is likely to adhere to the surfaces of most materials due to its high surface energy, resulting in various problems, such as pollution, corrosion and fluidic drag. Adopting low-surface-energy materials and roughening the surface textures can enhance the surface water-repellency and reduce water adhesion, achieving “superhydrophobicity.” Recent work on water-repellent materials has often been inspired by natural examples, such as lotus leaves.[1–3] On these materials, hierarchical micro- and nanostructures can trap air beneath water droplets, forming solid-liquid-air composite interfaces, which provide superhydrophobicity with low contact-angle hysteresis. However, recent studies have also suggested that lotus leaves can become highly hysteretic and even hydrophilic-like when soaked in water or exposed to vapor.[4,5] More generally, the robustness of superhydrophobicity was raised through observations of droplet impalement induced by compression[6–8] or evaporation[9,10] on synthesized superhydrophobic surfaces. Under these conditions, the forming solid-liquid-air composite interfaces will be broken and the surfaces will lose their functions: water will be irreversibly impregnated into and subsequently wet the surface textures to achieve a Wenzel or wet-contact form on increasing the hydrostatic pressure. The wetted microstructures will, in return, provide large capillary forces and make the surface highly water-adhesive. The robustness of the superhydrophobicity leads to the intrinsic intensity of the surface superhydrophobicity, the stability of the formed solid-liquid-air composite interfaces, which is an essential issue for applications of water-repellent materials. Considering the presented limitations of micro-, nano-, and lotus-type micro-/nano composite structures, it is crucial to design and fabricate robust water-repellent materials, especially suitable for the fields of prolonged water contact or humid atmospheres, which can extend the application field of water-repellent materials and, more importantly, inspire new attention to material design and mechanism revolution.

The robustness of the superhydrophobicity is crucial for aquatic insects such as water striders, whose legs must remain dry while standing, moving and jumping on the surface of water.[11,12] These creatures provide a unique example of durable and robust superhydrophobicity, despite prolonged contact with the water and a humid atmosphere, and dramatic pressure disturbances.[12–14] Their legs exhibit a hierarchical structure made up of oriented setae and nanogrooves, which seems to enhance their water
resistance and provide a strong supporting force,\cite{13,14} and might give a cognitive model for robust superhydrophobicity. Some attempts have been made to mimic strider legs by adding rough nanostructures to metallic wires in a lotus-like fashion, but ignoring the potential interplay between the strider setae and grooves.\cite{15,16} Thus, it is necessary and significant to investigate the structure-property relationships of the hierarchical structures of the setae and grooves, which is helpful not only to understand the exceptional ability of strider legs to repel water, but also, further, to design and fabricate robust water-repellent materials and miniaturized aquatic devices.

In this manuscript, we describe a new material, decorated with ribbed, conical nanoneedles, successfully achieved on the surface of copper and consisting of copper hydroxide nanoneedle arrays sculptured with nanogrooves, which is similar to the unique structure of the setae of strider legs. The behavior of water drops on prepared surfaces under various external disturbances are investigated. It is shown in particular that squeezing and relaxing drops between two such surfaces leads to a fully reversible exploration of the solid surface by the liquid, which is distinct from other superhydrophobic surfaces. This unique character is attributed to the penetrating Cassie state that occurs at the ribbed, conical nanoneedles, where the nanogrooves prevent an intimate contact between the water and the needles. The proprietary lateral nanogrooves can, not only vigorously support the enwrapped liquid-air interface when a force is applied on the drop, but also provide reliable contact lines for the easy de-pinning of the deformed interface when a force is released from the drop. To the best of our knowledge, there have been no previous reports regarding the fully reversible exploration of the solid surface by water droplet under an external pressure in the squeezing and relaxing process.

2. Results and Discussion

2.1. Model Setup

Typical scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of strider setae are shown in Figure 1A–B. The sub-micrometer needle-shaped setae are long and thin (aspect ratio larger than 10, cone angle between 3° and 5°), and sculptured with oriented nanogrooves. These grooves are around 174 ± 29 nm in half-width and 89 ± 15 nm in depth. Such a unique structure, idealized in Figure 1C, offers two advantages: 1) conical needle shapes are likely to minimize the solid-liquid contact area, and their remarkable length should prevent contact between the leg and water;\cite{19} 2) the lateral nanogrooves can effectively trap air,\cite{17} and vigorously support the enwrapped liquid-air interface.\cite{18,19} This design thus favors both superhydrophobicity and the robustness of this state, which we try to demonstrate by fabricating ribbed nanoneedle arrays (RNNA), based on the structure idealized in Figure 1C.

2.2. Fabrication of Cu(OH)$_2$ RNNA Surface

The materials were prepared by a chemical-base deposition method. After immersing a fresh copper foil into a 0.03 M ammonia solution for 36 h at 5.0 °C,\cite{20} we obtained a uniformly blue film coating. As shown in Figure 2A–B, the surface was covered with a large number of Cu(OH)$_2$ needles roughly perpendicular to the substrate. The average length of the needles was ~5 μm and the diameters decreased from ~300 nm at the base down to ~40 nm at the tip, providing an aspect ratio larger than 10 and a cone angle α = 3°; both features are similar to the strider setae. Surprisingly, the lateral surface of the needles was also sculptured with nanogrooves in the longitudinal direction, and was actually constructed by crossed coaxial nanoribbons with a wall thickness of ~20 nm (Fig. S1). The number of grooves per needle was between 4 and 10, with a peak in the distribution around 8 (Fig. 2C).

This complex structure may be attributed to the hydrogen-bonding interactions of the copper hydroxide nanoribbons, which stack along the axial direction, form the bundled structure and eventually provide the nanogrooves.\cite{21,22} To confirm this process, we studied the effect of the reaction time, and monitored the corresponding surface-structure evolution. Figure 3 shows SEM images of Cu(OH)$_2$ nanoneedles prepared at the same
distribution is centered at around 8 grooves per needle. As the reaction time was increased to 24 h, the nanoneedles grew longer and denser; they could grow vertically and almost completely covered the substrate (Fig. 3B). Moreover, the nanoribbons not only grew in parallel but also vertically to the needle axis, so that the nanoneedles started to present a cone shape with more-clear lateral nanogrooves. As the reaction time was increased to 96 h, the tips of the nanoneedles became much larger, and the Cu(OH)$_2$ nanoneedles appeared to have a gear-like structure, rather than the previous cone shape (Fig. 3C). For a reaction time of 240 h, the nanogears grew much larger, and had a good alignment on the substrate. Moreover, the X-ray diffraction (XRD) spectrum indicates that these Cu(OH)$_2$ nanostructures were orthorhombic crystalline, and the growth of Cu(OH)$_2$ nanostructures was a gradual crystallization process (Fig. S1). This indicates that the nanoneedle/nanogear alignment was caused by the space-limited growth, and the evolution of the Cu(OH)$_2$ nanostructures (nanoneedles or nanogears) was dominated by the growth of the constructed nanoribbons.

2.3. Characterization and Analysis of the Superhydrophobic Robustness of the Cu(OH)$_2$ RNNA surfaces (as in Fig. 2, the nanoneedles of cone shape) were further modified with a self-assembling perfluoroalkylsilane (FAS) monolayer. While the contact angle $\theta$ of water on such a flat surface was $114^\circ \pm 3^\circ$, the apparent contact angle $\theta'$ on the textured surface was $162^\circ \pm 3^\circ$, with a (contact angle) hysteresis less than $3^\circ$. Since this material shares the main characteristics of the strider’s leg setae, we studied quantitatively the behavior of these surfaces when facing water, and designed an original test to quantify the robustness of the observed superhydrophobicity.$^{[21]}$

We firstly performed compression experiments on the drops. A 4 μL water droplet was placed between two identical substrates covered with the superhydrophobic Cu(OH)$_2$ RNA structures. The upper substrate was displaced, using a micrometric screw, allowing us to squeeze the drop by a distance of a few millimeters; then, the pressure was slowly relaxed, until the initial distance between the plates was restored (Fig. 4A). The whole process was recorded using a monitoring system consisting of an optical microscope lens and a charge-coupled-device (CCD) camera. As seen in the sequence of photos, the drop was flattened, and the advancing contact angle gradually decreased from $162^\circ \pm 2^\circ$ to $142^\circ \pm 3^\circ$ as the drop’s internal pressure increased from 100 to 300 Pa. Remarkably, the receding angles superimpose to the advancing ones all along the sequence (within the error bars), and the droplet recovered its original shape when the pressure was relaxed (Fig. 4A v–viii), demonstrating a robust nonstick behavior in this extended range of compression.

Since there is little hysteresis, the Cassie equation might apply along the whole sequence of compression.$^{[24]}$ The apparent contact angle $\theta'$ is an average between the Young contact angle, $\theta \approx 114^\circ$ (the angle on the same solid, yet flat) and $180^\circ$ (the angle on air), respectively weighted by the fraction of surface area contacting each phase and denoted as $\phi_S$ and $1 - \phi_S$.

$$\cos \theta' = -1 + \phi_S (\cos \theta + 1)$$

As is noted above, the contact angle at the beginning and end of the sequence (Fig. 4A i & viii) was $162^\circ \pm 2^\circ$, which yielded an effective solid/liquid contact on a fraction $\phi_S = 0.08 \pm 0.02$. During compression, the decrease of the apparent contact angle $\theta'$ can be interpreted as resulting from an increase of the solid-liquid fraction, $\phi_S$, up to $0.36 \pm 0.03$, as given by the Cassie equation. This

![Image](image-url)

Figure 2. A) SEM image of Cu(OH)$_2$ RNA: low-magnification top-view ($\times 3000$). B) SEM image of Cu(OH)$_2$ RNA: higher magnification ($\times 20,000$). C) Statistics of the number of nanogrooves per needle: the distribution is centered around 8 grooves per needle.

temperature for different time periods. Figure 3A–D are SEM images of the samples synthesized at 5.0 °C for 12, 24, 96 and 240 h, respectively. When the reaction time was short (12 h), the Cu(OH)$_2$ nanoneedles were sparse and lay down on the substrate (Fig. 3A). As shown in the enlarged view, the nanoneedles were constructed as tiny nanoribbons that had subtle nanogrooves. As the reaction time was increased to 24 h, the nanoneedles grew longer and denser; they could grow vertically and almost completely covered the substrate (Fig. 3B). Moreover, the nanoribbons not only grew in parallel but also vertically to the needle axis, so that the nanoneedles started to present a cone shape with more-clear lateral nanogrooves. As the reaction time was
The different surface energies are related to each other by the Young formula:

\[ \gamma_{SL} - \gamma_{SV} = \gamma \cos \theta \]  

(3)

It is unfavorable for the liquid to penetrate the cones (\( E > 0 \)) if \( \alpha \) is smaller than \( \alpha_c = -2 \cos \theta \), a condition that is largely fulfilled for our material, for which \( \alpha \approx 0.05 \) and \( \alpha_c \approx 0.8 \). Moreover, the solid/liquid surface area increases quadratically with the distance of penetration (instead of linearly for classical pillars), which also contributes to preserving the superhydrophobicity. An increase of \( H \) by about 30%, as suggested by the experiment in Figure 4, corresponds to a penetration distance of about twice the (local) cone radius, around 200 nm, much smaller than the cone height: far from a complete impalement of water inside the texture.

The recovery of the initial \( \theta \) after a cycle of compression and relaxation indicates that water easily detached from the needles. This sharply contrasts with nonrobust superhydrophobic states, for which similar pressures can induce an irreversible transition towards highly adhesive wetting situations.\(^{[5,25]}\) For the RNNA, the reversibility of the drop states in the compression/relaxation cycles and the absence of a measurable hysteresis implies negligible pinning along the cones and inside the grooves. If the liquid were to penetrate the nanogrooves, the resulting wet contact area would give rise to a strong adhesive force,\(^{[6,25]}\) and would prevent the drop from recovering its initial, highly nonwetting state at the end of the cycle.

Figure 3. SEM images of synthesized Cu(OH)$_2$ nanoneedles/nanogears at 5.0°C and for different durations: A) 12 h; B) 24 h; C) 96 h; D) 240 h. The top row shows low-magnification top-views (scale bar = 5 \( \mu \)m) of the surface topography, and the bottom row shows the corresponding higher magnification (scale bar = 500 nm).

This suggests that compression here creates a kind of penetrating Cassie state, where the nanogrooves prevent an intimate contact between the water and the needles. This feature is unusual. Even well-known textured materials (such as lotus leaves) do not exhibit such an ideal behavior (Fig. S2). To demonstrate this, we used a micro-electromechanical balance system to monitor the action of the effective curvature force on different substrates (including the RNNA), a new test for finely distinguishing between different superhydrophobic materials. A water droplet of volume \( V = 4 \mu \)L was deposited on the lower substrate, which was moved up at \( \nu = 10 \mu \)m s\(^{-1}\) towards the (static) upper substrate. The latter substrate was connected to a balance that was initially calibrated to zero. The force \( F \) was measured with a sampling rate of 30 Hz as a function of the displacement \( \delta \) of the lower substrate. As shown in Figure 5A, \( F \) gradually and smoothly increased as the droplet was squeezed between the RNNA substrates, and the forcedisplacement relationship was found to be reversible as the solids were separated. The force eventually recovered its initial null value, confirming that there was no water left on the upper substrate after detachment. Since the curvature force mainly results from the water surface tension and contact angles, this experiment emphasizes the absence of any measurable hysteresis all along the cycle of compression and relaxation (see also Fig. S3).

We first discuss the \( F(\delta) \) variation and focus on its non-linear behavior. We denote the drop thickness as: 

\[ h = H - \delta \]

(4)

In Equation (4), \( H \) is the initial height of the drop:

\[ H = R(1 - \cos \theta^2) \]

(5)

For small compressions (\( \delta \ll H \)), the contact radius \( l \) of a nonwetting drop\(^{[26]}\) is geometrically given by: \( l^2 \sim \delta R \). Since the pressure, \( \Delta P \), is the Laplace pressure inside the drop, which scales...
as $g/R$, we get a force $F \sim \Delta P \lambda^2 \sim g\delta$. This linear dependency is observed in Figure 5A for small $\delta$, with a slope of $35 \pm 15 \text{ mN m}^{-1}$ of the order of the water surface tension. For highly compressed drops ($h \ll H$), the force acting on the plate can be written $F \approx \frac{\gamma V}{2d} \cos\theta / (H - \delta)^2$. This force diverges as $\delta$ approaches $H$, as observed in Figure 4A. Its value at the maximum compression ($\delta \approx 1.2 \text{ mm}$, $\delta^\ast \approx 142^\circ$) is about $930 \mu\text{N}$, slightly smaller than the value reported in Figure 5A ($\sim 1200 \mu\text{N}$). The agreement becomes quantitative if we take into account the Laplace pressure arising from the equatorial curvature of the drop, which yields an additional force of $\gamma L \sim \gamma (\pi \Omega (H - \delta) \right)^{1/2}$, i.e., $\sim 300 \text{ Pa}$ at the maximum compression.

More importantly, we can comment on the smoothness of the curve $F(\delta)$. The force was measured at a frequency $f = 30 \text{ Hz}$, which corresponds to elementary vertical displacements of $\delta^\ast = \nu f = 0.3 \mu\text{m}$. If we assume a nonstick behavior (no pinning), the corresponding lateral displacement $\lambda^\ast$ is directly deduced from volume conservation: $\lambda^\ast = \beta^\ast / 2 \delta$, of the order

![Figure 4](image-url) Behavior of a 4 mL water droplet between two identical substrates covered by a superhydrophobic Cu(OH)$_2$ RNN structure: A) Sequential snapshots for a cycle of compression/relaxation. Image (iv) shows the maximum compression. In image (vii), the droplet detaches from the upper substrate without any visible elongation. The whole sequence appears to be reversible. B) Corresponding advancing angles (in the compression stage, solid squares) and receding angles (in the relaxing stage, open squares), as a function of the imposed pressure $\Delta P$. Both angles regularly decrease as $\Delta P$ increases, but the hysteresis remains negligible throughout the process.

![Figure 5](image-url) Compression forces on the RNN surface and other superhydrophobic surfaces. The force $F$ acting on a surface through pressing a water drop (volume $\Omega = 4 \mu\text{L}$) was recorded with a micro-electromechanical balance as a function of the displacement $\delta$ of the other plate. A) For RNN, the curve $F(\delta)$ is reversible, even at high compression. B) Data using lotus leaves as the contact surfaces. C) Data for silicon surfaces patterned with arrays of micrometric micropillars as the contact surfaces. The inserts in (A), (B), and (C) enlarge the curve at the position where the substrate leaves the droplet.
of 0.2 μm in this experiment. In the relaxing stage, the number of pillars left behind in this displacement is \(2π\frac{2}{3}n\), denoting \(n\) as the number of pillars per unit area (as seen in Fig. 2A, \(n\) is typically 100 per 10 μm² for the RNNA samples). Usually, the contact line will pin on each pillar of radius \(b\) (~100 nm for RNNA), with a pinning force of the order of \(2nb\).\(^{27,28}\) In such a case, the typical force fluctuations monitored in this experiment would be \(4π\frac{2}{3}nb\), approximately 10 μN. This force is much larger than the sensitivity of our capsort (~0.5 μN), demonstrating the absence of measurable pinning on these ribbed nanoneedles. In addition, stronger pinning would lead to avalanches in the relaxing stage – collective de-pinning instead of individual de-pinning – as assumed above. This, again, is not observed in Figure 5A.

The latter observations sharply contrast with what can be seen with other kinds of superhydrophobic materials, as shown in Figure 5B–C, which show similar experiments performed with lotus leaves (decorated by papillae of 12 μm surrounded by branch-like nanocrystals of 100–150 nm) and on silicon surfaces patterned with square micropillars (height 10 μm, diameter 7–10 μm, distance 30 μm). For the lotus leaves, we note a small hysteresis between the squeezing and relaxing curves. The hysteresis increased for \(\delta > 0.7\) mm (i.e., \(P > \sim 200\) Pa), which might correspond to penetration of the liquid into the array of the largest microtextures. Moreover, we observed a significant adhesive force of about 30 μN at the end of the cycle (insert in Fig. 5B), which was accompanied by visible distortions of the drop (Fig. 52). The force eventually came back to zero after the drop detachment, indicating that the superhydrophobic state of the lotus leaves was not totally broken\(^{22}\) in these experiments, which might be related to the nanostructures present on the leaves.\(^{29}\)

For the micropillar surface (Fig. 5C), the hysteresis was even larger (about 80 μN); in addition, a differential force of about 30 μN was measured at the end of the cycle, indicating that the droplet penetrated and adhered to the pillars (insert in Fig. 5C). Since we found that the force \(F(δ)\) can be written as \(F(δ)\cos(δ)\), hysteresis in the curve of \(F(δ)\) directly reflects a contact-angle hysteresis between the squeezing and relaxing stages, arising from a strong pinning of the contact line on/in the solid texture.\(^{30,31}\) This is confirmed by focusing on the roughness of the relaxing curve, \(F(δ)\), for both substrates. We observed "jumps" in the force curves, whose typical amplitudes (5 to 50 μN) correspond to the de-pinning of the contact line from the defects (as the drop retracts) or along the pillars (as the drop moves upwards when relaxing the pressure). This again highlights the remarkable properties of the RNNA surface when compared to "classical" superhydrophobic surfaces characterized by similar contact angles.

We interpret the RNNA surface properties as a consequence of the unique surface structure (Fig. S4). The reversibility observed in Figure 4A depends on the mobility of the water/air interface at the RNNA surface, as the liquid impregnates it. This reversibility is particularly crucial for water-strider legs, which constantly endure cycles of compression/relaxation comparable to those described here. There are two conditions to satisfy this reversibility: 1) the penetrating Cassie state must occur and be preserved despite external pressure; 2) the contact lines must not find pinning sites as they gradually sink along the nanogrooves, owing to the applied pressure. Thus, the deformed liquid can release the stored energy when the external pressure relaxes and restore to its initial state with little energy loss. The force method introduced here to distinguish the RNNA surfaces could be extended to all kinds of textured surfaces in order to provide finer classifications of their superhydrophobic properties.

3. Conclusions

We describe a new water-repellent material decorated with ribbed, conical nanoneedles, which was successfully achieved on the surface of copper and consisted of copper hydroxide nanoneedle arrays sculptured with nanogrooves. The as-prepared superhydrophobic surface was minimally water-adhesive, and shows little contact-angle hysteresis even under certain hydrostatic pressure. Squeezing and relaxing the drops between two such surfaces led to a fully reversible exploration of the solid surface by the liquid, which is distinct from other superhydrophobic surfaces. Analysis shows that this unique character is attributed to the penetrating Cassie state that occurs at the ribbed, conical nanoneedles. The proprietary lateral nanogrooves can, not only vigorously support the enwrapped liquid–air interface when a force is applied to the drop, but also provide reliable contact lines for the easy de-pinning of the deformed interface when the force is released from the drop. This work gives new insight to metastable Cassie states. It also implies that interfaces can be locally controlled by introducing lateral nanogrooves to a primary structure, which opens a new route to the design of robust superhydrophobic materials and miniaturized aquatic devices.

4. Experimental

Preparation of Ribbed Nanoneedle Arrays (RNNA): The copper foils (~7 × 7 mm²) were washed with a 1 M HCl aqueous solution for 10 min, and then rinsed three times with deionized water to remove surface impurities. 30 mL of a 0.03 M solution of ammonia (Aldrich) was prepared in a 70 mL glass bottle. The fresh copper foils were immersed into the solution and kept at 5.0 ± 0.1 °C. After a reaction time of 36 to 48 h, the samples were taken out of the solution, washed three times with deionized water, and dried in air. A blue film was obtained, uniformly covering the surface of copper foils.

Hydrophobization Treatment: The Cu(OH)₂ RNNA, as-prepared on the surface of the copper foils, were treated with a 1.0 wt% solution of hydroxylated heptadecanfluorodicytrimethoxysilane (FAS-17) (CF₃(CF₂)₇(CH₃)₃Si(OCH₃)₃) (Shin-Etsu chemical Co., Ltd., Tokyo, Japan) for 12 h at room temperature, and then taken out for drying in an oven at 50 °C.

Characterization: The SEM images were taken using a field-emission SEM (JSM-6700F, JEOL) at 3.0 kV. AFM images of single setae were obtained using tapping mode atomic force microscopy (SPI3800N, Seiko Instruments Inc., Japan). The water contact angles and contact-angle hysteresis on the FAS-modified RNNA were measured using a Dataphysics OCA20 contact-angle system at ambient temperature. The superhydrophobic robustness of the samples was characterized by compressing water droplets on the prepared surfaces. A substrate attached to a homemade micrometric screw was used to compress a 4 μL water droplet deposited on an identical substrate. Photographs were taken using a CCD camera at 24 frames per s under an optical microscope lens. The contact angles were deduced from the captured images. All of the experiments were repeated at least three times, and reproducible results were obtained, as shown by the error bars. The interaction force generated by the compressed drop on the RNNA was monitored by hanging the upper substrate onto a high-sensitivity micro-electromechanical balance (Dataphysics DCAT 11, Germany) and moving the lower substrate at a speed of 0.01 mm s⁻¹.
The experiments conducted on lotus leaves and patterned silicon pillar surfaces were performed in a similar way. The test conditions of the static contact angles and the compression measurements were restricted to a temperature of 25 °C and a relative humidity of 30%.

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[23] Data not shown: in fact, although the synthesized nanoneedle or nanogear surfaces in Figure 3 show high contact angles, only this Cu(OH)2 RNA surface of cone shapes has the best quality of superhydrophobicity.