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Regular Article

Understanding how surface chemistry and topography enhance fog harvesting based on the superwetting surface with patterned hemispherical bulges

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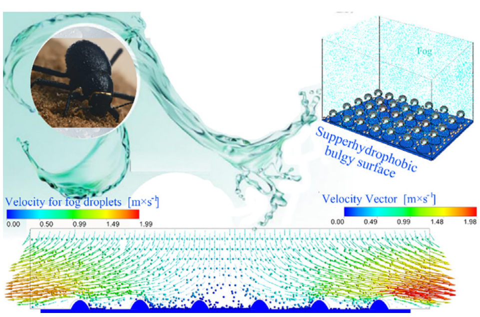
GRAPHICAL ABSTRACT



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ABSTRACT

The Namib Desert beetle-*Stenocara* can adapt to the arid environment by its fog harvesting ability. A series of samples with different topography and wettability that mimicked the elytra of the beetle were fabricated to study the effect of these factors on fog harvesting. The superhydrophobic bulgy sample harvested 1.5 times the amount of water than the sample with combinational pattern of hydrophilic bulgy/superhydrophobic surrounding and 2.83 times than the superhydrophobic surface without bulge. These bulges focused the droplets around them which endowed droplets with higher velocity and induced the highest dynamic pressure atop them. Superhydrophobicity was beneficial for the departure of harvested water on the surface of sample. The bulgy topography, together with surface wettability, dominated the process of water supply and water removal.

1. Introduction

It has been pointed out that more than one billion people who lived in arid regions will face the problem of grim water scarcity by 2025 [1,2]. What is more, climate change may lead to significant changes in water supply in many regions. Especially, it can increase water demand and decrease water availability [3,4]. In addition to rainfall, there are three main forms of 'non-rainfall' water that can be used in daily life: fog deposition, dew formation and water vapor adsorption [5]. In the arid regions, fog is the main source of water that can supply creatures [6–9]. Fog consists of floating water droplets whose diameter is usually up to a few 10 μm in the atmosphere [10]. In the Namib Desert, these Darkling Beetles

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can adapt to this arid environment by employing different strategies for obtaining the fog water [11]. The genus *Stenocara* has been reported to capture fog in the fog-laden winds by its hydrophilic/-superhydrophobic patterned elytra surface and the fog-basking behavior [12–14]. Other results showed that the elytra of the beetle is completely hydrophobic, moreover, stressed that fog-basking behavior itself is the main factor for the beetle harvesting water from fog [13].

From the point of wettability, the adaption behavior is attributed to the combinational pattern of wettability, hydrophilic bulges/ hydrophobic surrounding. Water droplets in fog are captured by the hydrophilic bulges and continue to grow until they fall down with the aid of these hydrophobic areas [12]. Many biomimetic materials have been developed and proven to have excellent fog harvesting ability based on the combinational superhydrophobic/ superhydrophilic patterns [15–22]. Among them, the superhydrophobic/superhydrophilic pattern with micro/nanoscale textures has been fabricated successfully, showing excellent fog harvesting ability [17–20,23]. From the point of surface topography, the differences between these biomimetic surfaces are notable at micro/nanoscale while ordinary at macroscale. Moreover, the surface topography nearly has no distinction when the size of superhydrophobic/superhydrophilic pattern reached millimeter-scale [15]. As for other biomimetic materials fabricated for fog harvesting, surface topography or structure plays a key role. *Cotula fallax* harvests fog by its hierarchical 3D structure (which endows it with the large surface area to volume ratio) [24]. The biomimetic PDMS film inspired by the rice leaf can facilitate the fog harvesting process by virtue of the three-level macrogrooves and micro/-nanostructures [25]. The fog harvesting ability of Polyethylene Terephthalate (PET) fibers is reported to be affected by its cross section and surface structure [26]. Therefore, the topography (bulges) of biomimetic surface has been underestimated when compared with special surface wettability pattern. Though inkjet printing, the superhydrophilic bulges (whose size is about 0.5 mm) were printed on the superhydrophobic surrounding to fabricate a surface with combinational wettability and it presented enhanced fog harvesting ability [17]. For example, Aizenberg et al. [27] confirmed that the specific surface topographies based on slippery surface can facilitate water condensation and proved that the discontinuities can enhance vapor diffusion flux [28]. Thereby, the effect of surface topography and wettability on fog harvesting is worthy of further studying.

To this end, a series of patterned bulgy surfaces were fabricated (These bulges are 0.5 mm in diameter and 1.2–3.65 mm apart, which is nearly identical to the elytra of *Stenocara*) to explore how the surface wettability and, especially the bulgy topography affects the water supply and water removal behavior of fog harvesting. During the fog harvesting experiments, superhydrophobic bulgy surfaces showed better performance in water supply and water removal than the others. The droplets that grow on superhydrophobic bulges is 13.8 times faster than that on the superhydrophobic flat. The superhydrophobic bulgy surface can harvest 6.17 times and 2.82 times the amount of water than the original copper foil and homogeneous superhydrophobic flat surface without bulges, respectively. The growth rates of droplets increased to the maximum and then decreased when the number of the bulges on the superhydrophobic surface increased from 35 to 160, which correspond to the amount of water harvested by these samples. Especially, the arrangements of bulges (with same number) influenced the amount of water harvested. Based on the Fluent software, the flow field analysis (CFD) clearly indicated that these bulges can change the dynamic pressure distribution above the surface and focused the flow (composed of micro-water droplets and air) around bulges. Thus, there are more micro-water droplets captured by these bulges. The growth rate of droplets on it can be enhanced greatly. The bulgy surface, together with surface superwettability, can improve the fog harvesting ability greatly. This outcome will be of great significance in designing more efficient fog harvesting materials by combining both special surface chemistry and surface topographies.

2. Experiments

2.1. Materials

Ethanol, sodium hydroxide (96%, NaOH) and Ammonium persulfate (98%, $(NH_4)_2S_2O_8$) were obtained from Tianjin Rionlon Pharmaceutical Science & Technology Development Co., Ltd. Copper foils (99%) and *n*-Octadecane thiol (96%, $C_{18}H_{38}S$) were obtained from Sinopharm Chemical Reagent Co. TiO_2 powders (Degussa p25, ca. 80% anatase, 20% rutile) were of analytical grade and used as received.

2.2. Sample preparation

Preparation of bulgy copper surface. Copper foils (30 mm $\times$ 20 mm $\times$ 0.25 mm) were settled in a model under the pressure of 15 M Pa to get the bulgy surface. Here five kinds of bulgy samples have been fabricated whose surface was covered with 5×7 (35), 10×10 (100), 10×12 (120), 10×14 (140) and 10×16 (160) hemispherical bulges (k^{-1} = 0.5 mm) respectively.

Fabrication of $Cu(OH)_2$ Nanoribbons by ammonia corrosion. Samples were ultrasonic washed in deionized water for 10 min and immersed in 0.1 M HCl for 1 min to remove the oxide layer. Samples were then cleaned with acetone/ethanol, rinsed with deionized water and dried with N_2 to remove the contamination. Then, we fabricate the nanoribbons-like structured $Cu(OH)_2$ by the ammonia corrosion. The surface of sample was settled flush with liquid level in a beaker filled with the mixtures of 1 M NaOH and 0.05 M $(NH_4)_2S_2O_8$. Reaction time is maintained in 40 min to get a higher density of $Cu(OH)_2$ nanoribbons. The mechanism of ammonia corrosion is listed as follow:

$$Cu+4NaOH+(NH_4)_2S_2O_8 \rightarrow Cu(OH)_2+2Na_2SO_4+2NH_3+2H_2O.$$

In this process, 6 kinds of samples, initial copper foils, copper foils with 35 (5×7), 100 (10×10), 120 (10×12), 140 (10×14) and 160 (10×16) hemispherical bulges were prepared for ammonia etching, respectively. When the ammonia corrosion finished, samples were rinsed with deionized water and dried in N_2 flow.

2.3. Surface modification

Surface with hydrophilic bulges and superhydrophobic surroundings. Combinational hydrophilic/superhydrophobic pattern was fabricated by the alternative modifications between $Cu(OH)_2$, TiO_2 and thiols [22,29]. As shown in Fig. S1, selective deposition of TiO2 nanoparticles on bulges can be realized by applying a mask. The surfaces were lay aside for 24 h to ensure that nanoparticles were attached to $Cu(OH)_2$ micro-needles. Then, these samples were immersed in 0.05 M *n*-Octadecyl thiol (96%)/ethanol for 10 min and the reaction follows equation:

$$Cu(OH)_2+2C_{18}H_{37}SH \rightarrow Cu(SC_{18}H_{37})_2+2H_2O.$$

After that, samples were washed with ethanol three times and dried in N_2 flow.

Surface with both superhydrophobic bulges and surroundings. These samples that were covered with $Cu(OH)_2$ nanoribbons were immersed in 0.05 M *n*-Octadecyl thiol (96%)/ethanol for 10 min. Then, the modified surfaces were washed with ethanol three times and dried in N_2 flow to obtain superhydrophobic bulgy sur-