

## Mist harvesting using bioinspired polydopamine coating and microfabrication technology

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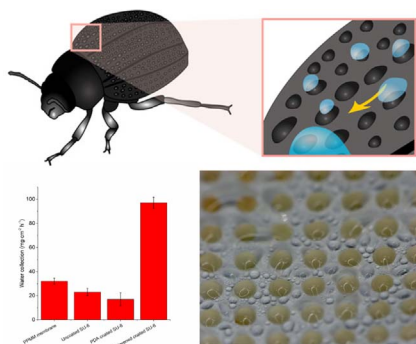
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### GRAPHICAL ABSTRACT



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### ABSTRACT

The fascinating biopolymer of polydopamine (PDA) and negative photolithography method was utilized to produce porous membrane surfaces with contrast wettabilities via creating hydrophilic patterns (nanoscale PDA coated SU-8 bumps) on the hydrophobic background of polypropylene (PP) membranes. The high rate of water collection ( $97 \text{ mg cm}^{-2} \text{ h}^{-1}$ ) highlighted the impact of hydrophilic patterns and wetting properties on mist-harvesting results. Modified samples exhibited droplet motion by coalescence rather than rolling which means created hydrophilic patterns also have a significant impact on the behavior of the droplets on these surfaces. Surface characterization including Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and contact angle as well as surface free energy measurement were performed to study the effect of topography and roughness on the system performance. This created structure has the great potential to be fabricated in large scale. Also, due to the porous nature of its hydrophobic background, water collection rate can be substantially increased by using vacuum pressure, makes it attractive for industry.

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## 1. Introduction

Clean water shortages affect approximately 900 million people in drought areas and desert regions worldwide. Although, water exists in the air, as water vapor form, it cannot be directly used for either drinking or agriculture; therefore, available fresh water is not equally distributed all around the world [1]. In fact, drinking water shortage has become one of a major growing and thorny global crises affecting all facets of human life, ecosystem, and industrial developments. Bio-desalination has recently attracted researcher attention for fresh water production. Biodesalination is defined as “utilizing living organisms or biological elements directly or indirectly, mimicking their structures and mechanisms, and borrowing concepts or inspiration from their desalination mechanisms for the production of sustainable freshwater” [2]. Industrial multi-stage flash distillation and reverse osmosis are widely used as current commercially main water desalination methods. Both multi-stage flash distillation and reverse osmosis approaches have many side effects including a great deal of heating energy consumption and chemical cleaning of the membrane as well as significant capital cost. Unfortunately, hundreds of thousands of people are living in villages and remote areas in developing countries with no or very limited access to healthy fresh water across the world. Therefore, providing those poor areas with an affordable green sustained technology is a continuing quest [3–5].

Atmospheric water, especially ocean fog represents an invaluable untapped source of fresh water in inhabited deserts and arid regions [6]. Years of evolution in some species of desert plants and animals have offered ingenious ways of collecting water in nature [7]. For instance, Hipster herbs is an obscure herb with leaves covered by ultra-hydrophobic hairs that collect the water moisture and retain it over an extended period of time [8]. *Cotula fallax* is a South African plant with uncanny wetting properties that can collect moisture due to its super-hydrophobic and 3D hierarchical structure of leaves [9,10]. Green tree frogs, Nimb grass, and Australian desert lizards are other species that show outstanding and interesting fog harvesting ability [10–12]. For Namib beetles (family Tenebrionidae) millions of years of evolutions are the secret to success in harsh conditions of African deserts with annual rainfall less than 13 mm (0.5 in.) [7]. This beetle is able to absorb the environments' humidity thanks to their very special wetting properties of their body surface [13]. The beetle's backside surface consists of hydrophobic and hydrophilic regions that serve the purpose of droplet formation and absorption [14]. Namib beetles collect water through both smooth and grooves of their backside surfaces in which water droplets disposed on the upper wing [14,15]. Then, droplets gather size until they combine and are guided to the beetle's mouth. A unique three-dimensional surface in fog collection to stores small water droplets and prevents them from being lost or evaporating before they can be collected by the deserts species [7,16–18].

As shown in Fig. 1, the beetles of Namib Desert serves as a source of inspiration for a significant amount of future research which has been devoted to the development of fog harvesting devices to achieve a substantial water-collecting surface for fresh water collection in a novel and functional way [7,14–16,19–21]. Through the use of biomimicry,

we have studied the beetles' skins to distill the principles and functions of their skins that have developed through recent decades and applied this knowledge to develop a novel and exciting measure to address water shortage crisis in the arid area [14].

Andrew R. Parker and Chris R. Lawrence [22] studied the Namib Desert beetles on a macroscopic scale. They observed that the elytra of the beetles are covered in a near-random array of bumps 0.5–1.5 mm apart, each about 0.5 mm in diameter. They also found at the microscopic level that bumps peaks are smooth and are not covered. But, the troughs, including their sloping sides, are covered by a microstructure coated in wax. They reported that the microstructure consists of flattened hemispheres, 10  $\mu\text{m}$  in diameter and arranged in a regular hexagonal array, which creates a superhydrophobic system reminiscent of the lotus leaf.

Biomimetic water-collecting materials inspired by nature have been recently reviewed by Zhu et al. [23]. In their review, a great number of bioinspired materials with the water collection ability have been developed. In addition, they simultaneously detailed water collection mechanisms and their corresponding bioinspired materials of natural animals and plants such as cactus, spider, desert beetles butterfly, shorebirds, wheat awns, green bristlegrass, *Cotula fallax* plant, Namib grass, green tree frogs and Australian desert lizards. General attempt is to develop a porous surface consist of at least two portions with different wettability properties [24,25]. Superhydrophilic region is responsible for fog absorption and forming the droplets while superhydrophobic portion transport the water droplets [14,26]. Guo group introduced a water-harvesting device with water collection rate (WCR) of 1309.9  $\text{mg h}^{-1} \text{cm}^{-2}$  by using  $\text{TiO}_2$  and Cu as hydrophilic areas and hydrophobic areas, respectively [27]. The same group has also been able to demonstrate a WCR of 1316.9  $\text{mg h}^{-1} \text{cm}^{-2}$  using a nano-needle to create two superhydrophobic circular patterns on a copper Cu  $(\text{OH})_2$  super hydrophilic surface [28]. White et al. [29] tested other samples (e.g. PTFE, Al, Ti, and SS-CNT) to better understand of the wetting properties of materials as well as the effect of pattern structure on the desert beetles' capability of collecting water. They found that, although there were slight differences in the coalescence and motion of the drops on the differently patterned surfaces, no direct influence of the type of pattern on the sample was found on its water collection ability [29]. Although the Guo's group's approach can create a reasonable high WCR, their approach is costly and seems difficult for large-scale production.

Dopamine has many amine and catechol functional groups and received large attention due to its unique properties such as self-polymerization, anchoring capability, reactivity, reductive ability, powerful adhesive capability, carbonizable feature, and special recognition [30]. The surface properties of virtually any material can be easily altered by the tightly adhesive hydrophilic PDA coating. More importantly, the PDA layer comprises active secondary reaction functional entities which could form covalent bonds with species containing primary amine or thiol groups. In addition, various metals, metal oxides, and semiconductors nanoparticles can be readily grown on the PDA coating owing to its reductive ability. This virtually unlimited variety provided by PDA layer will provide an opportunity to design and produce highly

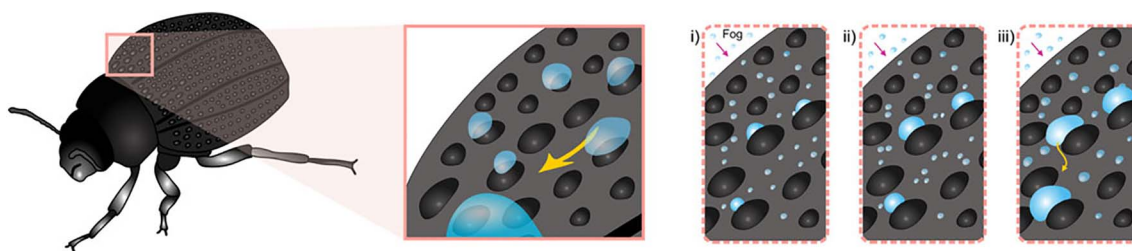


Fig. 1. Schematic of the fog-harvesting process in a desert beetle. Beetle' back side surface consists of a micro-sized bumpy super-hydrophilic structure that absorbs the fog and a hardened forewings which are superhydrophobic and helps collect and direct water droplets toward the beetle's awaiting mouth.

**Table 1**

Acid-base (Van-Oss) parameters used for calculating the surface free energy of samples including  $\gamma^{\text{TOT}}$  "Total Surface Tension (mN/m<sup>2</sup>)",  $\gamma^{\text{d}}$  "Dispersive Component (mN/m<sup>2</sup>)",  $\gamma^{\text{+}}$  "Acid Component (mN/m<sup>2</sup>)" and  $\gamma^{\text{-}}$  "Base Component (mN/m<sup>2</sup>)".

Liquid	$\gamma^{\text{TOT}}$ (mN/m <sup>2</sup> )	$\gamma^{\text{d}}$ (mN/m <sup>2</sup> )	$\gamma^{\text{+}}$ (mN/m <sup>2</sup> )	$\gamma^{\text{-}}$ (mN/m <sup>2</sup> )
Milli-Q water	72.8	21.8	25.5	25.5
Glycerol	64.0	34.0	3.92	57.4
Formamide	58.0	39.0	23.2	23.2

efficient micro-fabricated devices. In this study, using microfabrication techniques and the fascinating properties of dopamine, a flexible surface with two embedded portions with different wettability properties has been developed to closely mimic the morphology and structure of Namib desert beetle [16,31]. Hydrophilic patterns with well-controlled dimensions are achieved on the hydrophobic surfaces through the formation of polydopamine via in situ polymerization together with UV light exposure and negative photolithography method to enhance water collection efficiency compared to the related literature. The proposed water harvester is flexible and surface mountable is made of polypropylene MF porous membrane with a suitable pore size of 0.2  $\mu\text{m}$ . Furthermore, this sample exhibited an excellent repeatability after 10 times water collection without obvious variation in WCR.

## 2. Experimental section

### 2.1. Material

Hydrophobic Flat Membrane Type PP 2E HF (R/P) PPMM was purchased from Membrana GmbH (Germany). Positive photoresist AZ 1518 and negative photoresists AZ 125nXT and SU-8 2075 were purchased from MicroChemicals-Australia. Dopamine hydrochloride (DA), polypropyleneimine (PEI, Mw = 600 Da), Tris(hydroxymethyl) aminomethane, phosphate buffered saline (PBS) were provided from Sigma-Aldrich (USA).

### 2.2. Microscopy analysis

In order to study the effect of surface modification on the surface morphology and roughness in micron and nanoscale, the surface microstructure of samples was studied by scanning electron microscope. The samples were sputter coated with gold (EMITECH K550) and observed by SEM (Hitachi S-3400).

The AFM analysis has been done in 2 scan sizes;  $1 \times 1 \mu\text{m}^2$  and  $10 \times 10 \mu\text{m}^2$ . As the bump is about 100  $\mu\text{m}$ , we first measured the samples in the small scan and also did it with a bigger scan size of  $10 \times 10$ . To overcome any drift or sample movement, the samples were attached to the holder using different bonding methods (double-sided tape, glue, etc.). To accurately image the samples, firstly, the AFM probe (OTESPA-R3, supplied by Bruker AFM probes) was tuned slightly below the resonance frequency (5–8% offset), with an oscillation amplitude of around 20–25 nm. The modestly low amplitude was chosen because the SU-8 polymer is a relatively soft material and higher tapping amplitude may cause unwanted deformation to the surface. However, the tapping amplitude cannot be set too low as well, as the cantilever needs sufficient drive to overcome the adhesive force on the sample surface. Through experimentation, the ratio between the amplitude set point and the free air amplitude is set to about 0.8 to 0.85. The gains are adjusted slightly lower to avoid any oscillation noise. The measurements were done at least 5 times for each sample and we repeated the imaging experiment 3 times. In addition, after the measurement, we looked at the AFM probe using SEM. The probe was still very sharp even after 10 + scans. There was a minor amount of polymer contamination, but that is expected after so many scans. Surface roughness was calculated by analyzing the images using NanoScope

Analysis software (version 1.7) and Rq was reported as the roughness in nm.

### 2.3. Water contact angle (WCA) goniometry

The samples' wettability was studied using sessile drop technique in which the contact angle of a water droplet on the sample surface was measured. The water contact angle was determined using Amcap v3.0 software equipped with a video camera and a tilting stage. The mean static contact of 5  $\mu\text{l}$  droplets on the five randomly selected regions was reported.

### 2.4. Surface free energy (SFE) measurements

One of the most important applications of the contact angle measurement is the surface free energy (SFE) assessment of the surface. The contact angle itself also provides indications on the surface wetting properties and depends on the liquid used for the measurements. SFE is equivalent to the surface tension of the liquid and the unit is mN/m<sup>2</sup>. To study the effect of modification process on the surface free energy of the samples, acid-base (Van-Oss) method was used through three different liquids including water, glycerol, and formamide with known parameters [32] as shown in Table 1.

### 2.5. Water collection measurement

The samples' fog harvesting capabilities were evaluated using a homemade experimental setup built in the lab. The set up was designed based on the previously published works [23,33,34]. The setup consists of a closed chamber, a commercial humidifier, a digital balance thermometer and a humidity sensor as well as a small fan to generate an air flow (about 10 cm s<sup>-1</sup>) simulating the fog in nature. All prepared samples with uniform size ( $2.5 \times 2.5 \text{ cm}^2$ ) were placed on the sample holder and positioned vertically to the direction of fog flow at room temperature (24 °C) vertical to the direction of airflow. The distance between the humidifier and devices were kept constant at 10 cm. Thermometer and humidity sensor were placed in the chamber to monitor the temperature and humidity during the experiments. A container was placed under the sample and on the digital balance to collect the water droplets harvested by the surface. The fog-harvesting capacity of the samples was evaluated over a 60 min cycle. In all experiment, temperature and relative humidity of the chamber were maintained constant at 23 °C and 80–85%, respectively.

## 3. Results and discussion

### 3.1. Fabrication process

Microfabrication techniques were used to mimic Namib Desert beetle backside through the creation of hydrophilic SU-8 bumps modified by PDA on a hydrophobic PP background to render water repellency on the certain areas of the surface. The fabrication process involves four main steps: (i) polypropylene microfiltration membrane (PPMM) silicon wafer bonding, (ii) creating SU-8 bumps using microfabrication techniques, (iii) surface coating of the SU-8 bumps with PDA, and (iv) removing the sample from the silicon wafer. The fabrication process commenced by cutting the PPMM into a 4" circular shape. The sample was then bounded on a 4" silicon wafer using an approximately 1.2  $\mu\text{m}$  of AZ 1518 positive photoresist as an intermediate adhesion layer. The PPMM and silicon wafer exhibited good bonding with minimum buckling observed in the PPMM. The buckling has been attributed to a large mismatch between the coefficient of thermal expansion of silicon (3.2 ppm°C<sup>-1</sup>) compared to PPMM (20 ppm°C<sup>-1</sup>). To ensure no air bubbles in the interface, a uniform load was applied to press the PPMM to the silicon wafer. The sample was kept in an oven and temperature was slowly increased and maintained

at 65 °C for 10 min before increasing to 100 °C for five minutes for the baking process. This avoids abrupt change of temperature and reduced the buckling issue in PPMM after bonding. This step was followed by spin coating a thick layer of SU-8 2075 at 1500 rpm for the 30s to create an approximately 200 μm thick SU-8 layer on the PPMM surface. Since the PPMM surface is porous, SU-8 penetrates into the surface and form a thickness smaller than 200 μm. We observe almost 90 μm of SU-8 diffuses into the PPMM surface forming a final SU-8 layer with a height of 120 μm. The SU-8 surface is by nature hydrophobic with the contact angle of 90°. In order to make the SU-8 surface superhydrophilic, we used a polydopamine coating which reduces the surface free energy of the surface and creates an SU-8 surface with contact angle as low as 10° within 5 s. Based on our recently published PDA coating methodology [35], the coating was performed by immersing the SU-8 substrate in a freshly prepared solution (pH 8.5) containing dopamine hydrochloride (2 mg/ml) and polyethyleneimine (1000 MW, 2 mg/ml) for 4 h. The next step was to pattern the bump structures on the SU-8 surface using photolithography. Negative Photolithography process was used for transferring geometric shapes on a mask to the surface of the SU-8 photoresist. After photolithography and developing process, the sample was soaked in acetone to remove the PPMM from the silicon wafer. The steps involved in the fabrication scheme is illustrated pictorially in Fig. 2.

### 3.2. Surface morphology and topography

Fig. 3 shows the mimetic structure of the modified surfaces. As can be seen in the

SEM images (Fig. 3A, B and C) the created bumps on the PP membranes resemble Namib beetle's backside. The diameters of the circular bumps are around 200 μm, which can easily be changed during microfabrication process. The AFM images (Fig. 3D–F) reveals that PDA coating can significantly increase the roughness values of the bumps from around 2 nm to 19 nm. For more details of AFM analysis see Fig. S1 in Supporting Information. According to Wenzel theory (see next section), this increase in roughness plays an important role in changing the wettability of a surface toward extremes wettability modes of superhydrophilicity or superhydrophobicity [32].

### 3.3. Water contact angle and surface free energy

Wetting properties are important for technical applications as well as for fog-harvesting process. Surface chemistry and structure may be combined to create a variety of wetting effects [12]. Wetting properties are involved in the interactions between surfaces and moist in surrounding environment and also have a powerful impact on collecting

water trend. As mentioned earlier, the notable contrast between contact angle and surface free energy of pattern and background surfaces can enhance water collection rate. In Fig. 4 the water contact angle and surface free energy for three different samples i) PPMM membrane ii) SU-8 layer before surface treatment and iii) SU-8 layer after PDA coating was measured. Results indicate that the PPMM membrane substrates are hydrophobic with the water contact angle of 124° and surface free energy of 7.6 mN/m. Values of contact angle and surface free energy for SU-8 without surface treatment were 59° and 56.7 mN/m, respectively. Coating the SU-8 surface with PDA significantly reduced the contact angle and increased surface free energy to 14° and 87.9 mN/m which yields a hydrophilic surface for the bumps. This increase in the hydrophilicity after PDA coating is due to the chemical nature of PDA layer and also change in roughness.

It has been reported in our previous publication [35] that PH-induced PDA coating thickness can be reached a maximum of about 60 nm in a single reaction, which results in many quinone and catechol groups. A comprehensive XPS analysis using exactly our PDA coating recipe on 25 diverse materials was performed by Lee et al. [36]. They observed a little variation in the atomic composition of the coating, suggesting that the composition of the polymer coating was independent of the substrate composition. They also demonstrated that the nitrogen-to-carbon signal ratio (N/C) of 0.1 to 0.13 for the 25 substrates is similar to that of the theoretical value for dopamine (N/C = 0.125), which implies that the coating is derived from dopamine polymerization. The OH-groups on the PDA layer alters the surface chemistry of SU-8 such that its surface became hydrophilic. Increase in roughness (see Fig. 3F) can make the surface even more hydrophilic. The effect of surface chemistry and morphology on the water contact angle (WCA) was explained by the below equation which was introduced by Wenzel [37]:

$$\cos \theta = r \cos \theta^e \quad (1)$$

where  $\theta^e$  is the WCA on a flat surface,  $\theta$  is apparent contact angle and the roughness factor “ $r$ ” is the ratio of the actual solid/liquid contact area to its vertical projection. According to the model, the surface chemistry represents by  $\theta^e$  whilst morphology/surface structure lies within “ $r$ ” [38]. Increase in roughness raises the  $r$ -value and thus renders superhydrophilicity. It was observed that the PDA coating creates a high degree of fog adhesion to the SU-8 bumps leading to a better absorption of droplets to the bump surface. Therefore, having the PPMM membrane with hydrophobic properties in the background and PDA coated SU-8 bumps with strong hydrophilic properties will create a surface with different wetting properties. Such combination of hydrophobic background and hydrophilic pattern surface can closely mimic the water collection morphology in a Namib beetle.

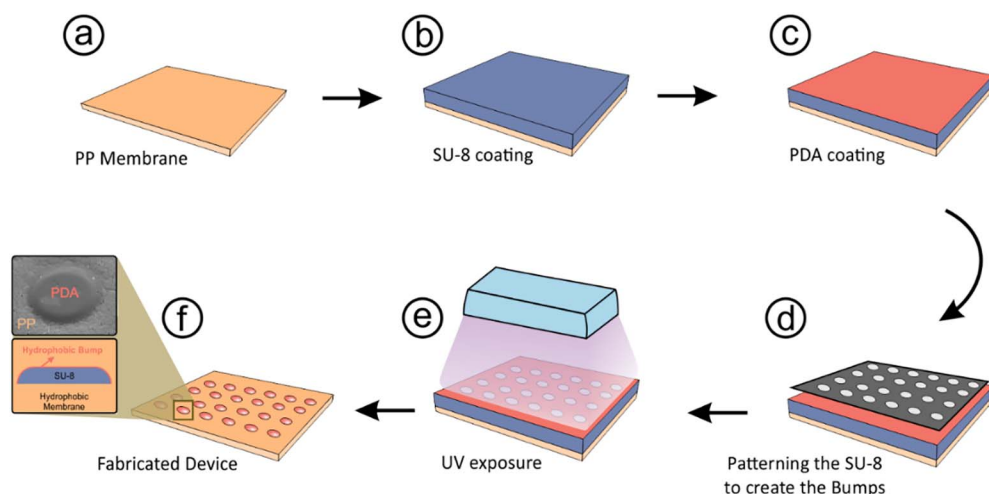


Fig. 2. Biomimetic water harvester device fabrication (a) PPMM membrane bonded on silicon wafer (b) SU-8 spin coating on PPMM surface (c) PDA coating to create a superhydrophilic SU-8 surface (d) SU-8 patterning (e) photolithography and SU-8 developing to form circular bumps on PPMM surface.

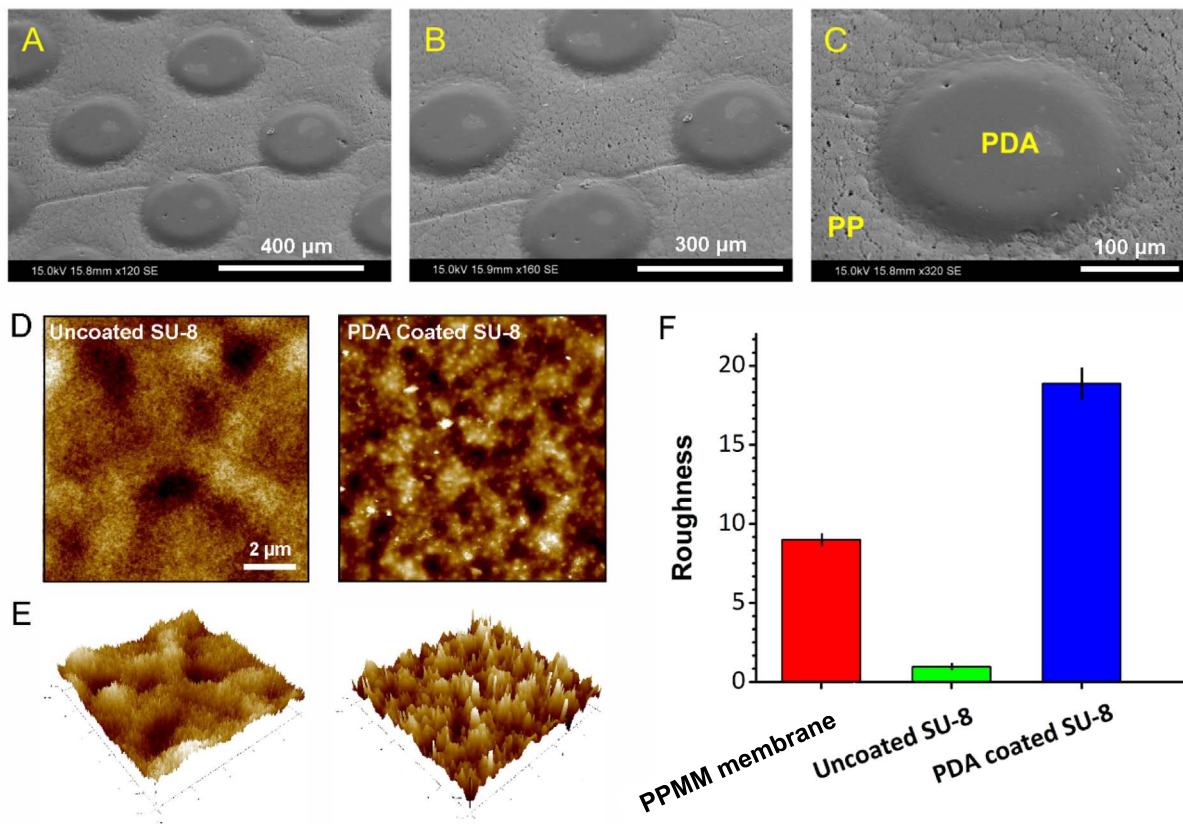


Fig. 3. Morphology of the hydrophilic bump surface and hydrophobic background shows the structure of samples in different magnifications. (a, b and c), images are taken by rotating the sample in 45°. The roughness and surface topography of the samples, namely silicon wafer (SU-8 photoresist) and created bumps on the background surface were studied by atomic force microscopy with two and three dimensions (D and E), and also average roughness (nm) of these samples were calculated (F).

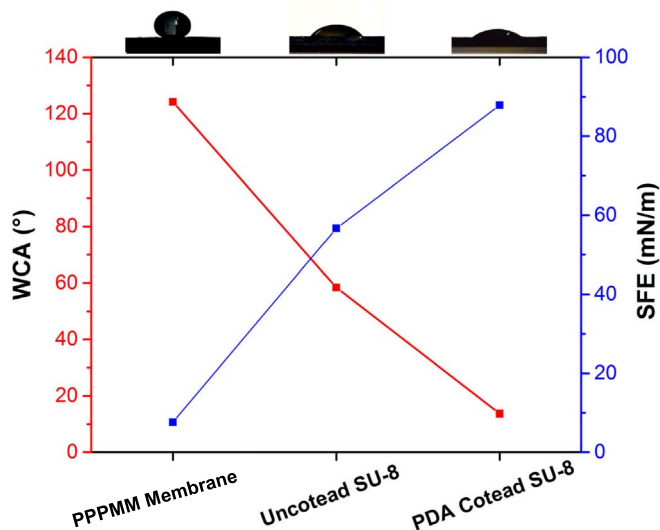


Fig. 4. Wetting properties of samples were studied by sessile drop technique, here hydrophilic bumps on the hydrophobic polypropylene membrane, SU-8, and universal polydopamine (PDA) coating, were created by negative photolithography approach, so that water contact angle (CA) and surface free energy (SFE) for (a) Membrane Matrix, (b) Uncoated SU-8 and (c) PDA coated SU-8 were shown.

### 3.4. Fog harvesting process

Having confirmed the successful micropatterning of the hydrophilic SU-8 coated surfaces, we then investigated the fog-harvesting

performance of different surfaces prepared by microfabrication technology. Fig. 5a shows the schematic setup for the fog-harvesting system. Control data were obtained by placing a container in the water-collecting system with no sample. The weight of the container was measured at 0.5 h intervals over a 5 h period. Fig. 5b compares the water collection efficiency of the different substrates: PPMM membrane; an uncoated SU-8 substrate; PDA coated SU-8 substrate; PDA coated SU-8 bumps on PPMM membrane with a pattern size of about 400 μm.

Among the four tested substrates, the PPMM membrane surface displayed the water collection efficiency of 32 mg cm<sup>-2</sup> h<sup>-1</sup>. The uncoated SU-8 hydrophobic surface reached the water collection efficiency of approximately 23 mg cm<sup>-2</sup> h<sup>-1</sup>. The low water collection efficiency of PPMM membrane and the uncoated SU-8 surface was predicted as they have a hydrophobic nature. Surprisingly this value for PDA coated SU-8 substrate was 17 mg cm<sup>-2</sup> h<sup>-1</sup>, although the PDA coated SU-8 is hydrophilic. This reduction of water collection is actually was predicted as the hydrophilic PDA layer holds the absorbed water molecules inside of its bulk rather than let them be collected. A sharp increase in the collection efficiency of 97 mg cm<sup>-2</sup> h<sup>-1</sup> (23.28 l/m<sup>2</sup> day) was observed for patterned coated SU-8 surface mimicking the fog-harvesting process of Namib desert beetle. The already available commercial Fog collection rates are typically 1–10 l/m<sup>2</sup> day [39,40], which is significantly lower than that of this work. Wang et al. prepared samples with different surface wettabilities and water collection rates: CuO-50-FPDT, CuO-FPDT-foil, PS, Cu-50-FPDT-PS-130, CuO-50-PS-130 and CuO-50-FPDT-PS-130 with water collection rates of 41, 67, 60, 67, 66, 55, and 159 mg cm<sup>-2</sup> h<sup>-1</sup>, respectively [33]. Bai et al., also created biomimetic fog harvester using superhydrophilic TiO<sub>2</sub> coating and ep-tadecafluorodecyl-trimethoxysilane (FAS) to change the wettability from superhydrophilic to superhydrophobic. Using the methodology,

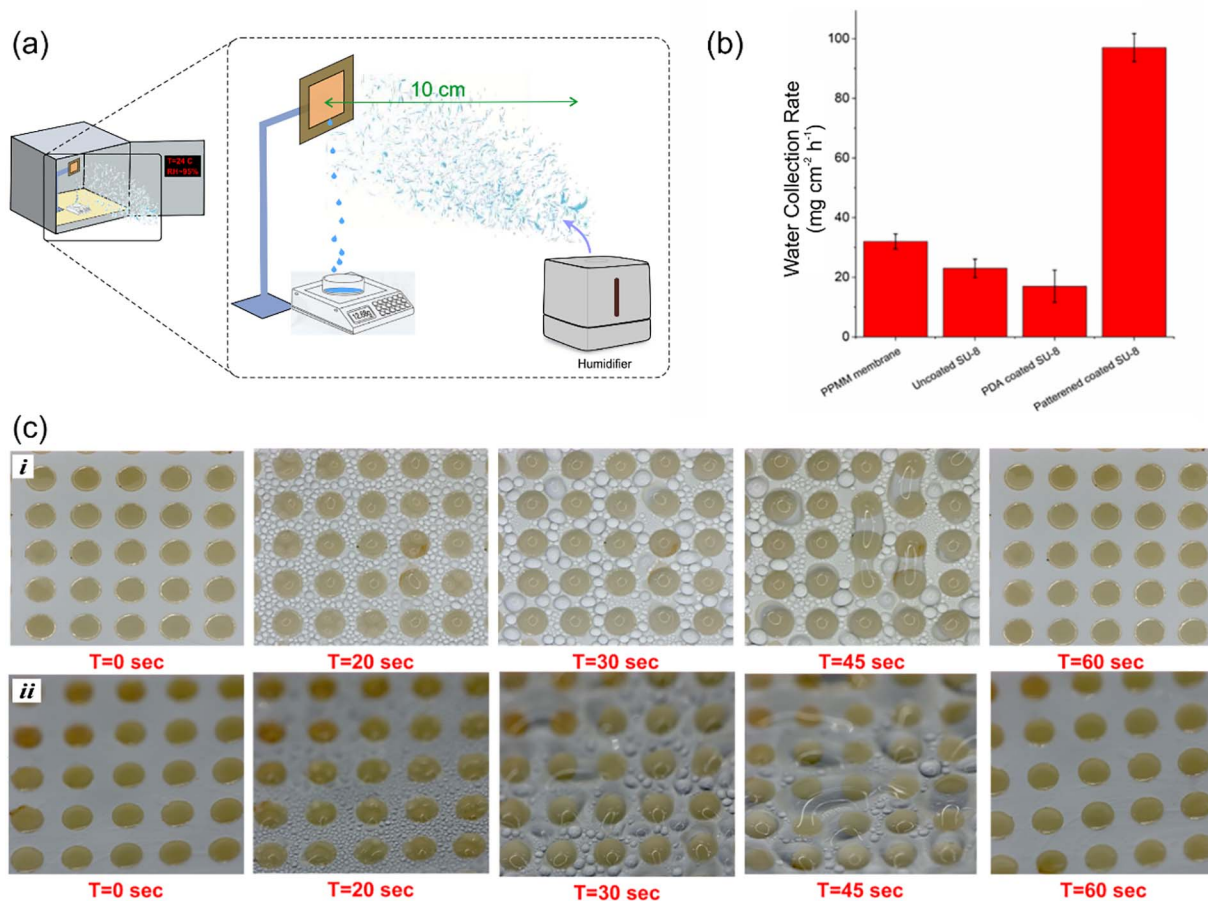


Fig. 5. Fog harvesting process, (a) experimental setup, (b) water collection rates on different surfaces and (c) snapshots of water collection which depicts the amount water that was achieved on the hydrophobic region during different times (sec), and then showing water channeling through coalescence on hydrophilic bumps on the surface: (i) straight samples (ii) tilted samples.

they prepared different shaped patterns i.e. circle, 4-pointed star, 5-pointed star, 6-pointed star, and 8-pointed star with water collection rates of around 1.6, 2, 2.7, 2.5 and 2.1 mg cm<sup>-2</sup> h<sup>-1</sup>, respectively [41]. These results confirm that our microstructure has a comparable water collection efficacy.

An optical microscope was used to collect images of the water collection processes. Insights from these images were used to understand the mechanism behind the fog-harvesting behavior of the hydrophilic-hydrophobic surfaces and are presented in Fig. 5Ci. The mechanism of water collection in the patterned surface is based on the slipping of unbound water from the surface of bumps down to the hydrophobic background, after the bond water completely saturated the PDA layer on the bumps. As can be seen in the figure, there is no free water droplet on the hydrophobic background of PP membranes until  $t = 20$ s at which point the PDA layer is saturated with bound water inside the three-dimensional network of the PDA layer. After the time, the free water began to appear on the surface until  $t = 45$  s when droplets coalesce and reach a threshold size at which point they become unstable. Gravity then forces the unstable droplets onto the hydrophobic surface which allows for the formation of new droplets on the recently freed hydrophilic PDA coated bump surface and the process repeats, thus enhancing water collection [42]. Tilting the pattern for 15° improved the water collection efficiency of our system (see Fig. 5C ii).

The reproducibility of the results was verified by examining the water collection on surface PPMM bump structure a number of times at 10-day intervals (Fig. 6a). The results show small variations water collection over time which has been attributed to the effects of

temperature, lighting, etc. Despite these small variations, the water collection limit and detection range remain approximately the same. The water collection rate of the Namib Desert beetles was simulated by varying the incline of the samples relative to the horizontal plane. Fig. 6b shows the effect of the different incline angles of 15°, 45° and 90° investigated. The most effective water collection efficiency was achieved at 90°.

As mentioned water scarcity is one of the major global crises, to overcome this issue, water conservation with bio-inspired wetting alteration can be employed by means of this approach toward achieving fresh water in a humid environment without consuming energy. It is hoped that the fabricated structures by current approach can be mass-produced because of having a great practical value in large-scale application due to its high efficiency.

#### 4. Conclusion

Multifunctional surfaces inspired from Namib Desert beetles and principles universal features of these surfaces were inspired to create biomimetic synthetic surfaces. Hydrophobic polypropylene membrane was used as a substrate. To alter wettability of the substrate, negative photolithography was utilized to create bumps on the surface together with polydopamine (PDA) solution coating to have hydrophilic bumps on the hydrophobic background as an innovative initiative approach to enhance fog-harvesting yield. The hydrophilic circular bump patterns on the hydrophobic background were fabricated via a simple, cost-effective, green and rapid method called, negative photolithography, to

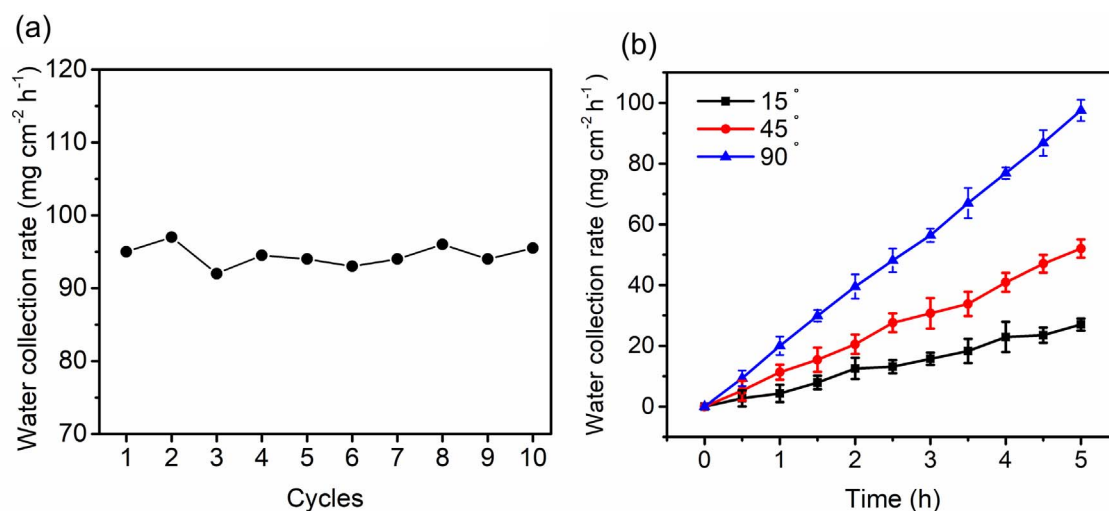


Fig. 6. Water collection rate of the sample (PDA coated SU-8 bumps on PPMM surface) (a) with intervals of 10 days between each experiment and (b) with the different inclined angle.

mimic fog harvesting properties of Namib Desert beetle with a high water collection rate (WCR). The produced samples in this study were characterized by SEM, AFM spectroscopy, contact angle, and surface free energy measurements. In conclusion, as mentioned water scarcity is one of the major global crises, to overcome this issue, water conservation with bio-inspired wetting alteration can be employed by means of this approach toward achieving fresh water in a humid environment without consuming energy. It is hoped that the fabricated structures by current approach can be mass-produced because of having a great practical value in large-scale application due to its high efficiency. Other potential applications of such structures include open-air microchannel devices, lab-on-chip devices, and controlled drug release coatings. Our future work will be in the testing and use of other novel efficient techniques to create a hierarchical structure using 3D-printing in order to scale up the mimic desert beetle's hierarchical surfaces. In addition tannic acid, as an alternative to polydopamine will be used to create the wettability patterning and mimicking desert beetle's back structure.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.desal.2017.12.023>.

## References

- [1] A. Razmjou, Q. Liu, G.P. Simon, H. Wang, Bifunctional polymer hydrogel layers as forward osmosis draw agents for continuous production of fresh water using solar energy, *Environ. Sci. Technol.* 47 (22) (2013) 13160–13166.
- [2] R. Taheri, A. Razmjou, G. Szekely, J. Hou, G.R. Ghezlbash, Biodesalination—On harnessing the potential of nature's desalination processes, *Bioinspir. Biomim.* 11 (4) (2016).
- [3] J.M. Amezcaga, et al., Biodesalination: a case study for applications of photo-synthetic bacteria in water treatment, *Plant Physiol.* 164 (4) (2014) 1661–1676.
- [4] S. Avlonitis, K. Kouroumbas, N. Vlachakis, Energy consumption and membrane replacement cost for seawater RO desalination plants, *Desalination* 157 (1) (2003) 151–158.
- [5] S.S. Al-Beaini, Biomimicry Using Nano-Engineered Enhanced Condensing Surfaces for Sustainable Fresh Water Technology, University of California, Berkeley, 2012.
- [6] P.H. Gleick, *Water in Crisis: A Guide to the World's Fresh Water Resources*, (1993).
- [7] A.R. Parker, C.R. Lawrence, Water capture by a desert beetle, *Nature* 414 (6859) (2001) 33–34.
- [8] H.G. Andrews, E.A. Eccles, W.C.E. Schofield, J.P.S. Badyal, Three-dimensional hierarchical structures for fog harvesting, *Langmuir* 27 (7) (Apr 2011) 3798–3802.
- [9] M. Santos, J. White, Theory and simulation of angular hysteresis on planar surfaces, *Langmuir* 27 (24) (2011) 14868–14875.
- [10] H. Zhu, Z.G. Guo, W.M. Liu, Biomimetic water-collecting materials inspired by nature, *Chem. Commun.* 52 (20) (2016) 3863–3879.
- [11] X. Liu, Y. Liang, F. Zhou, W. Liu, Extreme wettability and tunable adhesion: biomimicking beyond nature? *Soft Matter* 8 (7) (2012) 2070–2086.
- [12] A. Lee, M.-W. Moon, H. Lim, W.-D. Kim, H.-Y. Kim, Water harvest via dewing, *Langmuir* 28 (27) (2012) 10183–10191.
- [13] J. Sun, B. Bhushan, Structure and mechanical properties of beetle wings: a review, *RSC Adv.* 2 (33) (2012) 12606–12623.
- [14] L. Zhai, et al., Patterned superhydrophobic surfaces: toward a synthetic mimic of the Namib Desert beetle, *Nano Lett.* 6 (6) (2006) 1213–1217.
- [15] R. Garrod, et al., Mimicking a stenocara beetle's back for microcondensation using plasmachemical patterned superhydrophobic-superhydrophilic surfaces, *Langmuir* 23 (2) (2007) 689–693.
- [16] H. Andrews, E. Eccles, W. Schofield, J. Badyal, Three-dimensional hierarchical structures for fog harvesting, *Langmuir* 27 (7) (2011) 3798–3802.
- [17] J. Guadarrama-Cetina, et al., Dew condensation on desert beetle skin, *Eur. Phys. J. E* 37 (11) (2014) 1–6.
- [18] S. Vogel, U. Müller-Dobies, Desert geophytes under dew and fog: the “curly-whirlies” of Namaqualand (South Africa), *Flora Morphol. Distrib. Func. Ecol. Plants* 206 (1) (2011) 3–31.
- [19] C. Dorrer, J.R. Rühle, Mimicking the Stenocara beetle—dewetting of drops from a patterned superhydrophobic surface, *Langmuir* 24 (12) (2008) 6154–6158.
- [20] E. Ueda, P.A. Levkin, Emerging applications of superhydrophilic-superhydrophobic micropatterns, *Adv. Mater.* 25 (9) (2013) 1234–1247.
- [21] S. Wang, K. Liu, X. Yao, L. Jiang, Bioinspired surfaces with superwettability: new insight on theory, design, and applications, *Chem. Rev.* 115 (16) (2015) 8230–8293.
- [22] A.R. Parker, C.R. Lawrence, Water capture by a desert beetle, *Nature* 414 (2001) 33 (11/01/online).
- [23] Y. Wang, et al., Biomimetic water-collecting fabric with light-induced superhydrophilic bumps, *ACS Appl. Mater. Interfaces* 8 (5) (2016) 2950–2960 (2016/02/10).
- [24] K. Liu, X. Yao, L. Jiang, Recent developments in bio-inspired special wettability, *Chem. Soc. Rev.* 39 (8) (2010) 3240–3255.
- [25] K. Liu, Y. Tian, L. Jiang, Bio-inspired superoleophobic and smart materials: design, fabrication, and application, *Prog. Mater. Sci.* 58 (4) (2013) 503–564.
- [26] K.-C. Park, S.S. Chhatre, S. Srinivasan, R.E. Cohen, G.H. McKinley, Optimal design of permeable fiber network structures for fog harvesting, *Langmuir* 29 (43) (2013) 13269–13277.
- [27] H. Zhu, Z.G. Guo, Hybrid engineered materials with high water-collecting efficiency inspired by Namib Desert beetles, *Chem. Commun.* 52 (41) (2016) 6809–6812.
- [28] J. Ju, K. Xiao, X. Yao, H. Bai, L. Jiang, Bioinspired conical copper wire with gradient wettability for continuous and efficient fog collection, *Adv. Mater.* 25 (41) (2013) 5937–5942.
- [29] B. White, A. Sarkar, A.-M. Kietzig, Fog-harvesting inspired by the Stenocara beetle—an analysis of drop collection and removal from biomimetic samples with wetting contrast, *Appl. Surf. Sci.* 284 (2013) 826–836.
- [30] Y. Jiang, et al., Polydopamine-based photonic crystal structures, *J. Mater. Chem. C* 1 (38) (2013) 6136.
- [31] Z. Yu, et al., Desert beetle-inspired superwettable patterned surfaces for water harvesting, *Small* 13 (36) (2017).
- [32] A.R. Chaharmahali, The Effect of TiO<sub>2</sub> Nanoparticles on the Surface Chemistry, Structure and Fouling Performance of Polymeric Membranes, The University of New South Wales, Sydney, 2012.
- [33] Y. Wang, L. Zhang, J. Wu, M.N. Hedhili, P. Wang, A facile strategy for the fabrication of a bioinspired hydrophilic-superhydrophobic patterned surface for highly efficient fog-harvesting, *J. Mater. Chem. A* 3 (37) (2015) 18963–18969, <http://dx.doi.org/10.1039/C5TA04930J>.
- [34] X. Yang, J. Song, J. Liu, X. Liu, Z. Jin, A twice electrochemical-etching method to fabricate superhydrophobic-superhydrophilic patterns for biomimetic fog harvest, *Sci. Rep.* 7 (1) (2017) 8816 (2017/08/18).
- [35] A. Razmjou, et al., Preparation of iridescent 2D photonic crystals by using a mussel-inspired spatial patterning of ZIF-8 with potential applications in optical switch and chemical sensor, *ACS Appl. Mater. Interfaces* 9 (43) (2017) 38076–38080 (2017/11/01).
- [36] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface

- chemistry for multifunctional coatings, *Science* 318 (5849) (2007) 426–430 (2007-10-19 00:00:00).
- [37] F. Noorisafa, A. Razmjou, N. Emami, Z.-X. Low, A. Habibnejad Korayem, A. Abbasi Kajani, Surface modification of polyurethane via creating a biocompatible superhydrophilic nanostructured layer: role of surface chemistry and structure, *J. Exp. Nanosci.* (2016) 1–23.
- [38] P. Moazzam, A. Razmjou, M. Golabi, D. Shokri, A. Landarani-Isfahani, Investigating the BSA protein adsorption and bacterial adhesion of Al-alloy surfaces after creating a hierarchical (micro/nano) superhydrophobic structure, *J. Biomed. Mater. Res. A* 104 (9) (2016) 2220–2233.
- [39] R.S. Schemenauer, P. Cereceda, A proposed standard fog collector for use in high-elevation regions, *J. Appl. Meteorol.* 33 (11) (1994) 1313–1322.
- [40] M. Correggiari, G. Castelli, E. Bresci, F. Salbitano, Fog collection and participatory approach for water management and local development: practical reflections from case studies in the Atacama drylands, in: M. Ouassar, D. Gabriels, A. Tsunekawa, S. Evett (Eds.), *Water and Land Security in Drylands: Response to Climate Change*, Springer International Publishing, Cham, 2017, pp. 141–158.
- [41] H. Bai, L. Wang, J. Ju, R. Sun, Y. Zheng, L. Jiang, Efficient water collection on integrative bioinspired surfaces with star-shaped wettability patterns, *Adv. Mater.* 26 (29) (2014) 5025–5030.
- [42] N. Miljkovic, et al., Jumping-droplet-enhanced condensation on scalable superhydrophobic nanostructured surfaces, *Nano Lett.* 13 (1) (Jan 2013) 179–187.