A facile strategy for the fabrication of a bioinspired hydrophilic-superhydrophobic patterned surface for highly efficient fog-harvesting

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Fog water collection represents a meaningful effort in the places where regular water sources, including surface water and ground water, are scarce. Inspired by the amazing fog water collection capability of Stenocara beetles in the Namib Desert and based on the recent work in biomimetic water collection, this work reported a facile, easy-to-operate, and low-cost method for the fabrication of hydrophilic-superhydrophobic patterned hybrid surface toward highly efficient fog water collection. The essence of the method is incorporating a (super)hydrophobically modified metal-based gauze onto the surface of a hydrophilic polystyrene (PS) flat sheet by a simple lab oven-based thermal pressing procedure. The produced hybrid patterned surfaces consisted of PS patches sitting within the holes of the metal gauzes. The method allows for an easy control over the pattern dimension (e.g., patch size) by varying gauze mesh size and thermal pressing temperature, which is then translated to an easy optimization of the ultimate fog water collection efficiency. Given the low-cost and wide availability of both PS and metal gauze, this method has a great potential for scaling-up. The results showed that the hydrophilic-superhydrophobic patterned hybrid surfaces with a similar pattern size to Stenocara beetle’s back pattern produced significantly higher fog collection efficiency than the uniformly (super)hydrophilic or (super)hydrophobic surfaces. This work contributes to general effort in fabricating wettability patterned surfaces and to atmospheric water collection for direct portal use.

Introduction

Atmospheric water, especially fog, represents a significant but largely untapped fresh water source, especially in semi-arid, desert regions, land-scarce regions as well as countries with high economic activities.1, 2 In the past decade, research attention has been paid on learning from the nature and on biomimetically imitating the ways of capturing atmospheric water by some natural creatures, among which, Stenocara beetles, which survive in the Namib Desert, have inspired many scientists.3-6 It has been revealed that the great fog water collection capability of the beetles is resulted from the special structure on their back, which consists of an array of hydrophilic bumps distributed on a superhydrophobic background.7, 8 It is generally believed that the hydrophilic bumps are conducive to fog droplet capture and then coalescence while the hydrophobic background help clear the water droplets from the surface once they reach a certain size.9, 10

In producing such hydrophilic-hydrophobic patterned surfaces, three major strategies are generally utilized: (i) randomly disperse the hydrophilic glass spheres on a hydrophobic waxy substance;9 (ii) mask-based lithographic method;11-13 (iii) direct-patterning by inkjet printing,14-17 with the strategies (ii) and (iii) being capable of precisely producing pre-designed patterns, which is strategy (i) incapable of. However, the mask-based strategy consists of mask preparation, pattern transfer and pattern wettability adjustment, which is lengthy and multistep. While the inkjet printing method, which although is a one-step procedure, demands a special printer to print well-controlled patterns. Thus, it is still highly sought after a facile, simple and easy-to-operate method that is able to produce stable hydrophilic-hydrophobic patterned surface with low-cost.

On such a patterned surface, there are at least two portions with different wettability (hydrophilic versus hydrophobic), so one possibility would be to simply press together materials with different wettability so that they both appear to make a composite surface with pattern dimension suitable for fog collection. Following this new idea, the below requirements have to be met: (i) the two materials possess different wettability or are amicable to wettability modification, and (ii) one material has to be porous with suitable pore size and the other has to be made flexible so the two can come together by simple treatment to build a composite surface. This way, the porous material literally
serves as a mask in producing the patterned surface and the flexible one is then considered as molding material in the same process.

Gauzes are commonly seen in our daily life, such as mosquito screen, kitchen strainer and colander. They are made of polymeric materials (e.g., polypropylene), metal (e.g., copper, nickel, iron, titanium), or stainless steel and can have different mesh sizes, depending on their intended purposes.\textsuperscript{18–20} Among all these gauze materials, the metal gauzes attract our attention as a candidate for the mask material in producing the patterned surface, due to their amicability to surface chemical modification and their mechanical strength and long-term stability.\textsuperscript{21, 22} On the other hand, polystyrene (PS) is a kind of low-cost and widely used commercial wettable polymer with a contact angle generally less than 90° and it is thus considered a hydrophilic material.\textsuperscript{23} Additionally, PS has a relatively low processing temperature, with a glass transition temperature around 80-100 °C.\textsuperscript{24, 25} With the metal gauze being a mask material, PS can then be a suitable choice as a molding material to make the composite surface.\textsuperscript{26}

Herein, we develop a simple and controllable technique to fabricate a well-patterned composite surface for fog harvesting by combining two commonly available materials: copper gauze and PS plane sheet. The copper gauzes were modified to be superhydrophobic, which was then combined with the hydrophilic PS plane sheet directly by thermal-pressing to successfully achieve hydrophilic PS patches patterned superhydrophobic copper mesh surface. Our method is low-cost and easy-to-operate and allows for easy control of the mesh size and thus pattern size. The so-produced surface exhibits excellent fog collection efficiency, showing much better performance than uniformly hydrophilic and superhydrophobic surfaces. This work contributes to general effort in fabricating wettability patterned surfaces and to atmospheric water collection for direct portal use.

## Experimental

### 1. Materials

Copper gauzes with different mesh sizes (50 mesh with 0.23 mm wire diameter/270 µm × 270 µm pore size, 60 mesh with 0.19 mm wire diameter/250 µm × 250 µm pore size, 80 mesh with 0.14 mm wire diameter/180 µm × 180 µm pore size, and 100 mesh with 0.11 mm wire diameter/145 µm × 145 µm pore size) were purchased from Alfa Aesar (Karlsruhe, Germany). Copper foil with a thickness of 1.0 mm, hydrochloric acid (HCl, 37 %), absolute ethanol (≥99.8 %) and 1H,1H,2H,2H-perfluorodecanethiol (PFDT, 97 %) were obtained from Sigma-Aldrich (St Louis, MO, USA). Polystyrene (PS) plane sheet was purchased from Thermo Fisher Scientific (Waltham, MA, USA). As shown in Fig. S1 in Supporting Information, the water contact angle (CA) of PS sheet was about 76°, defined as a hydrophilic surface. All chemicals were used as received. De-ionized (DI) water purified in a Milli-Q (Millipore, Billerica, MA, USA) system was used in all experiments.

### 2. The preparation of superhydrophobic surface on copper gauzes

The preparation of hydrophilic-superhydrophobic patterned surface is schematically shown in Scheme 1. The copper gauzes were first immersed in a 4 M HCl aqueous solution for few seconds, and then washed with copious of ethanol and deionized water. The pre-cleaned copper gauzes were calcined at 400 °C for 3 h in an oven to form surface copper oxide nanostructures. To convert hydrophilic gauzes into hydrophobic ones, the gauzes with black copper oxide layer were immersed into a 1.0 % v/v PFDT ethanol solution for 20 minutes, followed by washing with ethanol and drying by nitrogen flow. The resultant samples were denoted as CuO-x-PFDT, with x being the gauze mesh size while PFDT being fluorine compound modification. While, the copper gauzes without calcinations (denoted as Cu-x-PFDT) and thus without metal oxide surface layer, were hydrophilically modified with the otherwise same procedure as CuO-x-PFDT and a uniformly superhydrophobic surface was fabricated on the copper foil via the otherwise same process, which was denoted as CuO-PFDT.

### 3. The preparation of composite samples

A piece of superhydrophobic CuO-x-PFDT with a dimension of 2.5 cm × 2.5 cm was placed on a same sized PS sheet and a fixed pressure was applied on top to keep the two pieces of materials together, which were then together transferred and heated in an oven at a pre-defined temperature (i.e., 120, 130, 140, 150, 160 °C) for 3 hours (Scheme 1). The resultant composite samples were indicated as CuO-x-PFDT-PS-y, where x represented mesh size of the copper gauze and y represented the thermal-treatment temperature. For comparison, the Cu-x-PFDT sample was thermally pressed with PS by the otherwise same method and the corresponding composite sample was denoted as Cu-x-PFDT-PS-y.

### 4. Material Characterization

Scanning electron microscopy (SEM) images were taken with a FEI Quanta 600 scanning electron microscope (FEI Co., Hillsboro, OR, USA). Contact angle and sliding angle data were obtained on a commercial contact angle system (OCA 35, Data-Physics, Filderstadt, Germany) at ambient temperature using a 5 µL droplet as the indicator. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer). X-ray photoelectron spectroscopy (XPS) measurements were made with an AXISNOVA instrument (Kratos Analytical Ltd, Manchester, UK) using a monochromatic Al Kα X-ray source (1486.6 eV). Digital photo was captured using a Canon EOS 7D.

### 5. Fog-harvesting measurements

A homemade test system was built in our lab to evaluate the fog-harvesting performance of our samples, which is schematically presented in Fig. 6a. The as-prepared samples (2.5 cm × 2.5 cm in size) were fixed on a holder at ambient condition. The sample was held so that its surface was perpendicular to the horizontal plane. A simulated flow of fog (about 12 cm s\textsuperscript{-1}) was generated by a commercial humidifier
and captured by the vertically placed sample surfaces. The distance between the fog generator and the sample was kept at 7 cm. The duration of one cycle measurement is four hours. The temperature and relative humidity around the samples were 22 °C and 90-95 %, respectively. Water droplets collected by the surfaces were drained by gravity into a container placed on top of a digital balance.

Results and Discussions

As shown in Scheme 1, a pre-cleaned copper gauze was first calcined to form a copper oxide (CuO) coating layer and the CuO-coated gauze was then modified by PFDT to render a superhydrophobic mesh surface. The PFDT-modified gauze was finally thermally pressed together with a hydrophilic PS sheet (contact angle 76°) to give rise to a hydrophilicity-patterned superhydrophobic hybrid surface. Due to the nature of the method, the produced composite surface assumed a three-dimensional concaving surface structure at micro-scale, with the hydrophilic PS patches sitting within the mesh holes and serving as the bottoms of the concaves. The image at the bottom of Scheme 1 is a digital photo of a hybrid circular material with a diameter of 12 cm produced by the current method, demonstrating its scalability. To facilitate discussion, from this point on, the samples prepared on 50# mesh gauzes were chosen for the focused discussion unless otherwise noted.

Fig. 1 presents SEM images of the samples prepared from 50# gauzes at different preparation stages: Cu (a, b), CuO (c-e), CuO-PFDT (f-h) and Cu-PFDT (i, j).

Scheme 1. The preparation procedure for the hydrophilic-superhydrophobic patterned composite surface: (i) calcination of copper gauze to form oxide surface coating layer; (ii) hydrophobic modification of the oxide coated copper gauze with PFDT; (iii) thermal- pressing of the PFDT modified gauze and PS sheet to form the composite surface with patterned wettability. The insert image presents some water droplets sitting on a composite sample surface.

Fig. 1 SEM images of the samples prepared from 50# gauzes at different preparation stages: Cu (a, b), CuO (c-e), CuO-PFDT (f-h) and Cu-PFDT (i, j).
the successful PFDT functionalization of the copper gauze. PFDT is a widely used surface hydrophobic modification reagent and it has been proved that it can easily react with many metals and metal oxides and form covalent bonds.\textsuperscript{29-32} More details could be obtained from the high-resolution photoelectron spectra of Cu 2p in Fig. 2e and 2f. For the CuO-50-PFDT surface, two different Cu 2p3/2 peaks were observed. One peak at 933.8 eV corresponded to Cu in copper oxides. The other peak at 931.4 eV occurred at the binding energy of Cu in Cu-S. It indicated that there was a covalent-like bonding between Cu (in surface) and S (in PFDT).\textsuperscript{33, 34} The covalent bonding between PFDT and Cu-S makes ensure that the obtained surface is a stable superhydrophobic surface. By carefully weighing the samples before and after PFDT modification, a slight weight increase of 0.026 wt% was recorded due to the PFDT surface grafting.

![Figure 2](image_url)

**Fig. 2.** XRD patterns of raw Cu gauze (50# mesh) (a) and CuO-50 (b). XPS spectra of CuO-50 (c), CuO-50-PFDT (d), and the Cu 2p spectra of CuO-50 (e), CuO-50-PFDT (f).

As shown in Fig. 3a and Table 1, the pre-cleaned copper gauze before calcination showed hydrophobicity with a static water contact angle about 109°. After the calcination, the uniform CuO coating layer with the nanowire structure drastically turned a hydrophobic surface to a superhydrophilic one with a water contact angle of 4°.\textsuperscript{38} A static water contact angle ≥ 150° and a water sliding angle ≤ 10° were obtained on the surface of the PFDT modified CuO gauzes, indicating a real superhydrophobic surfaces with Cassie’s wetting type. Beside hydrophobic PFDT functional groups on the surface, the surface wettability of CuO-PFDT can be ascribed to the inherent microscale mesh structure of the gauzes, and the surface CuO nanostructure on each thread of the gauzes. However, the PFDT modified Cu gauze (Cu-PFDT), namely the Cu gauze without calcination at 400 °C, although exhibited a highly hydrophobic property with a water contact angle of 147° (Fig. 3d), showed a high surface adhesion, suggesting that the surface had difficulty in removing water droplets from it. The high surface adhesion of Cu-PFDT may due to the small surface roughness caused by the lack of micro-structure on its surface.\textsuperscript{39} Such a hydrophobic surface with a high sliding angle would not be conducive to efficient fog water collection system in which a balance must be struck between fog droplet capture and clearance of the droplets off the surface.\textsuperscript{40} The rational comparison clearly demonstrates the necessity of the surface oxide layer by calcination, which gives rise to the ultimate superhydrophobic gauze after PFDT modification with Cassie wetting behavior. After the thermal pressing with PS, the wettability of the resulted hybrid patterned surface was similar to the gauze surface before the pressing (Fig. S3 in Supporting Information).

![Figure 3](image_url)

**Fig. 3.** The CA measurement images of the sample prepared from 50# gauze at different preparation stages, including (a) Cu, (b) CuO, (c) CuO-PFDT and (d) Cu-PFDT. The inset image was the water contact angle of Cu-PFDT with tilt angles of 90°. The water droplet volume in these images was all 5 µL.

| & Cu\(^{a}\) & CuO & CuO-PFDT & Cu-PFDT & PS\(^{c}\) |
|---|---|---|---|---|---|
| Water contact angle | 109±8° | <4° | 161±3° | 147±3° | 76±4° |
| Water sliding angle | NA\(^{b}\) | 8±1° | NA\(^{b}\) | NA\(^{b}\) | |

a All the water contact angle results are based on gauze with 50# mesh number.
b Liquid droplets were pinned on the surfaces with high adhesion, and no sliding behavior was observed during tilting of the substrates.
c The contact angle result of PS based on the commercial PS plane sheet obtained from petri dish of Thermo Fisher Scientific.

One of the attractive features of this method is that the pattern size can be easily and conveniently controlled by choosing gauze with different mesh number. Fig. 4 presents SEM images of hybrid surfaces composed of PS and PFDT modified CuO gauze with different mesh numbers. As can be clearly seen, uniform patterns of PS with different dimensions were successfully produced. For example, the PS domain’s
area could be adjusted from $7.3 \times 10^4 \, \mu m^2$ to $2.1 \times 10^4 \, \mu m^2$ with the mesh number increased from 50# to 100# respectively. The versatility in controlling the pattern size allows for an easy optimization of water collection efficiency later.

Fig. 4. The top view SEM images of the hybrid surfaces composed of the PS and PFDT modified CuO gauze with different mesh numbers (a) 50#, (b) 60#, (c) 80#, (d) 100#.

An added benefit of the thermal pressing in this work is that it permits an easy control over the height of the PS patches within the mesh holes of the gauzes. Fig. 5 presents cross-section SEM images of the PS patches with different thermal pressing temperatures to show the variation of the PS patch height as a function of the temperature. For the purpose of clear observation, the superhydrophobic CuO-PFDT gauzes were removed from the PS sheets in taking the SEM images. Due to its low glass transition temperature, the PS sheet is softer and moldable under higher temperature, leading to higher PS patch height under higher treatment temperature (Fig. 5 and S4 in Supporting Information). The PS patch height, a parameter which is generally overlooked, was later found a relevant parameter in fog collection efficiency.

Fig. 5. The SEM images of composite surfaces composed of the PS and PFDT modified CuO gauze with different mesh sizes prepared under different thermal treatment temperatures (a, d, g) and the SEM top view (b, e, h) and cross-section view (c, f, i) of the PS surface morphology (a, b, c at 120°C; d, e, f at 130°C; g, h, i at 140°C) with the gauzes being removed.

Fig. 6. (a) Schematic illustration of the homemade fog-harvesting system. (b) Water collection rates of different samples.

To verify the performance of the designed hydrophilic-superhydrophobic patterned composite surfaces, the fog-harvesting efficiencies of these surfaces were then investigated by a homemade fog-harvesting system, which is schematically presented in Fig. 6a. In brief, a commercial humidifier was used to generate a simulated fog flow and the prepared composite sample was held vertically. Fog water was collected onto the patterned composite surface at ambient conditions, drained by gravity and collected in a glass container placed on a digital balance which was connected to a computer. The water collection rates of six samples with different surface wettability were listed in Fig. 6b, which were CuO-50-PFDT-PS-130 (hydrophilic-superhydrophobic patterned surface), Cu-50-PS-130 (hydrophobic gauze without PFDT modification with PS), CuO-50-PS-130 (superhydrophilic gauze with PS), Cu-50-PFDT-PS-130 (highly hydrophobic gauze with high sliding angle with PS), flat PS sheet, and superhydrophobic CuO-PFDT foil. The hydrophilic-superhydrophobic hybrid surface on the CuO-50-PFDT-PS-130 exhibited a water collection rate of 159 mg cm$^{-2}$ h$^{-1}$, the highest among all six samples tested, whereas, in a sharp contrast, the water collection rates on the other five samples were all no better than 68 mg cm$^{-2}$ h$^{-1}$. Such a huge difference in water collection efficiency clearly demonstrates the great benefit of
having hydrophilic-superhydrophobic patterned surface for water collection. The water droplet condensing on the larger pattern can be more near to the rolling threshold. And larger superhydrophobic tracks are beneficial for the droplet departure. As the water droplets are removed from the patterned surface, new water droplets can form and grow on the PS patterns immediately. So larger holes (PS patterns) and wider superhydrophobic tracks (PFDT modified CuO wires) ensure the enhancement of water collection.

The uniformly superhydrophobic CuO-PFDT foil and uniformly hydrophilic PS sheet generated water collection rates of 67 and 60 mg cm⁻² h⁻¹, respectively, which are both far lower than the CuO-50-PFDT-PS-130 sample with hydrophilic-superhydrophobic patterned surface. The main difference among these three samples was the hydrophobic degree of the gauzes, demonstrating again the necessity of both surface CuO coating layer and PFDT modification for the optimized water collection performance. The water collection rates of the composite surfaces on the gauzes with different mesh numbers (i.e., 50#, 60#, 80# and 100#) are shown in Fig. 7a. The CuO-50-PFDT-PS-130 with a patterned PS patch size of about 7.3×10⁴ µm² and a separation distance of about 222 µm exhibited the highest efficiency among all samples, which, not surprisingly, was similar to the patch dimension on the back of the Stenocara beetles. Fig. 7b compares fog-harvesting performance of the composite surfaces with different concave heights prepared on 50# gauzes by using different thermal treatment temperatures, among which, the CuO-50-PFDT-PS-130 possessed the best performance. The result shows that the height of the PS hydrophilic patches within the mesh holes is not a trivial factor and the mechanism behind the relationship in Fig. 7b is currently under investigation in our group.

Conclusions

In summary, we developed a facile, easy-to-operate, and low-cost method for the fabrication of hydrophilic-superhydrophobic patterned hybrid surfaces, which provides excellent performance in fog water collection. The method is based on thermal pressing of a hydrophilic PS sheet with a superhydrophobic gauze. And the convenient control over the pattern size and the pattern height in the method allows for an easy optimization of fog water collection efficiency. We believe that the current method has a great practical value in large-scale application due to its high efficiency and scalability.

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References

1. Q. Schiermeier, Nature, 2014, 505, 10-11.
2. M. M. Pendergast and E. M. V. Hoek, Energy & Environmental Science, 2011, 4, 1946-1971.
3. A. R. Parker and C. R. Lawrence, Nature, 2001, 414, 33-34.
4. J. Ju, H. Bai, Y. Zheng, T. Zhao, R. Fang and L. Jiang, Nat Commun, 2012, 3, 1247.
