Fabrication of Bio-inspired Hydrophobic Self-Assembled Electrospun Nanofiber Based Hierarchical Structures

Manohar Kakunuri[a*], *Mudrika Khandelwal*[a], *Chandra S. Sharma*[b], *Stephen J. Eichhorn*[c]

[a]Department of Material Science and Metallurgical Engineering, Indian Institute of Technology Hyderabad, Kandi, Telangana 502285, India

[b]Creative & Advanced Research Based On Nanomaterials (CARBON) Laboratory, Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Kandi, Telangana 502285, India

[c]College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter, Devon, EX4 4QF, United Kingdom.

*****Email: manohar@iith.ac.in

Abstract

In this letter, we present a facile approach to fabricate hydrophobic surfaces based on electrostatic field assisted self-assembly of fibers onto conductive micropillars. Hydrophobic patterns fabricated in this work are inspired by an underwater fern *Salvinia molesta*. Hydrophilic cellulose acetate nanofibers were electrospun on a conducting micro-patterned surface to create a hierarchical structure. The water contact angle increased from just below 70° (hydrophilic) on the micro-patterned structures to ~140° (hydrophobic) for the hierarchical structures. Introduced hydrophobicity is due to the pinning of the water droplet to suspended hydrophilic nanofibers and a reduced solid-water interface.

Keywords: Self-assembly; Biomimetic; Interfaces; Hydrophobicity; Hierarchical structures; Salvinia.

1. Introduction

Nature has inspired the engineering of materials to provide a number of functionalities like superhydrophobicity, adhesiveness, antireflectivity, low drag and self-healing among others [1]. Of these, the fabrication of superhydrophobic surfaces has received intense attention due to a wide variety of potential applications. Among various superhydrophobic surfaces, air-retaining surfaces are of special interest for ship coatings, non-wettable swimwear, microfluidics and underwater applications where drag is a concern. However, most superhydrophobic surfaces which are fabricated by inducing roughness, are not suitable for underwater applications due to the transition from a Cassie to a Wenzel state when submerged [2]. In Nature, there are many examples of air-retaining insect surfaces and plant surfaces. Of these, *Salvinia molesta* is widely known due to its ability to pin water and retain air even in turbulence [3,4]. In contrast to air retaining hairy insect surfaces and superhydrophobic plant surfaces with a waxy layer, the *S. molesta* leaf is composed of hydrophobic eggbeater-shaped hairs with hydrophilic tips forming trichomes [3]. These hydrophilic tips pin the water droplets and oscillations of trichomes accommodate changes due to turbulence, thus stabilizing the air layer under the water for prolonged periods of time [5]. Recently, *Salvinia* inspired surfaces have been fabricated by 3D laser lithography and photolithography techniques [4,6]. Laser lithography has also been used to fabricate *Salvinia* like structures with smaller features. Hydrophobic micropillars with hydrophilic tops were also fabricated to mimic the *Salvinia* pinning behavior. However, these structures are rigid and missing resistance to turbulence. In this study, we aim to fabricate hierarchical structures with trapped air, water droplet pinning and also resistance to turbulence from electrospun fibers.

The most common approaches to the biomimicry of hierarchical structures have been to deposit platelets and tubules, plasma etching on micro-patterned structures and the deposition of electrospun nanofibers on micron scale structures or directly by micropatterning of electrospun nanofiber mats [7–10]. As far as the fabrication of hierarchical structures using electrospinning is concerned, nanofibers deposited are typically randomly oriented yielding a non-woven matrix due to the whipping motion from the Rayleigh instability of the fiber jet. The fabrication of suspended aligned nanofiber based hierarchical structures however requires a greater level of control of the electrospinning process. Controlled fiber deposition has been achieved in the literature by modifying the collector plate or by using near-field electrospinning [11,12]. In this study, we combine an electrostatic field assisted nanofibers self-assembly approach with photolithography to fabricate hierarchical hydrophobic surfaces by depositing hanging cellulose acetate (CA) electrospun nanofibers onto gold coated micropatterned structures. These hierarchical structures resemble the surface properties of *S. molesta* leaves' behavior by trapping the air into the gap areas. We further studied the role of surface conductivity and interpillar distance on the fiber alignment and therefore on controlling the wetting behavior.

2. Experimental

Figure 1 shows a schematic of the procedure used to fabricate the hierarchical structures. SU-8, an epoxy based negative photoresist was used as a precursor for micro-patterning. Detailed lithography process conditions are given in Table S1. Three different types of samples with pillar diameters and heights of 50 µm with spacings of 50, 100 and 150 µm respectively were fabricated. These samples were gold coated for ~10 s to make the surfaces of the micro-patterned pillars and silicon substrates conductive. These gold coated micro-patterned samples were then used as a collector in an electrospinning setup as shown in Figure S1. Electrospinning parameters used are described in Table S2.

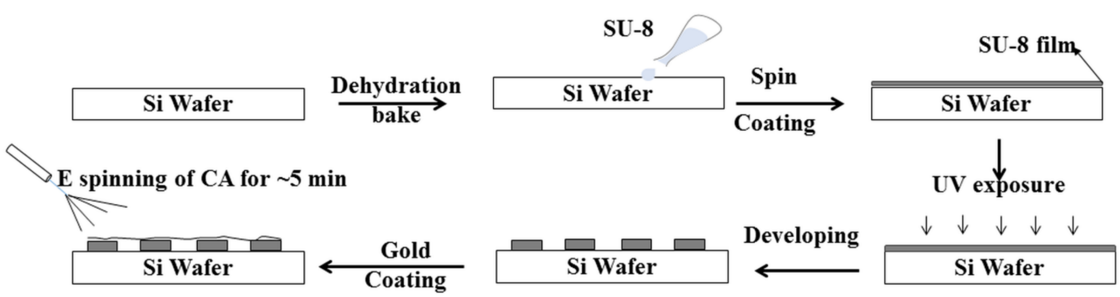

Figure 1. Schematic of the experimental procedure for fabricating self-assembled nanofiber based hierarchical structures.

3. Results and discussion

Figure 2 shows the FESEM images of the SU-8 micro-patterned array (Figure. 2a), and the hierarchical structure obtained after electrospinning the CA nanofibers onto this array (Figure. 2b and c). During the electrospinning process, electrostatic interactions as per the collector geometry and conductivity play a key role in the alignment of nanofibers. For a flat plate collector, the polymer jet ejected from the needle tip undergoes bending instabilities and the fibers deposit randomly over the flat collector due to a lack of a preferential direction to the electrostatic forces. However, for the micropatterned gold coated conductive surface as in this case, nanofibers are attracted towards the top of the conductive micro-patterned pillars, which are nearer to the source (syringe needle). This splitting of the electrostatic field between two adjacent pillars results in the stretching of the nanofibers [11] that ultimately results in their suspension and alignment between the micro-pillars as shown in Figure 2b. The effect of the gold coating on fiber alignment is discussed in the Supporting Information.

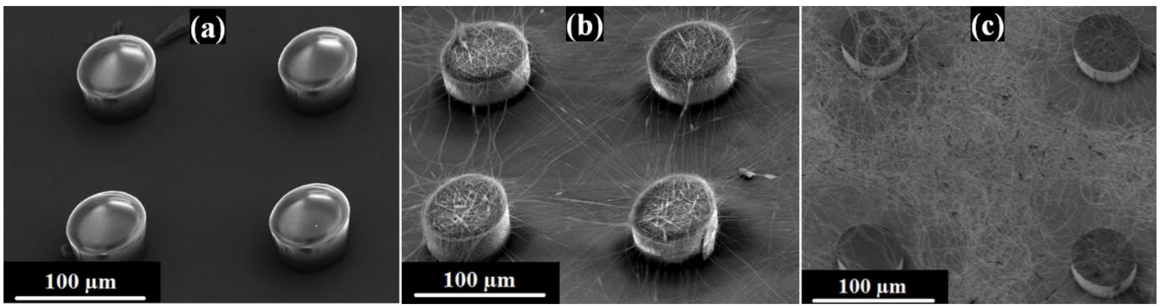

Figure 2. Typical SEM micrographs of (a) a micro-patterned, (b) a suspended nanofibrous hierarchical structure and (c) a micro-patterned surface with preferential random deposition of the nanofibers on a Si substrate (image taken at a 45° tilt angle).

Furthermore, to investigate the effect of the distance between pillars on the deposition of nanofibers, three different samples with varying pillar distances (50, 100 and 150 µm) were fabricated. For the samples with spacings of 50 and 100 µm, the fibers were aligned on the pillars as shown in Figure 2b. However for the sample with a 150 µm spacing, the fibers deposited on the pillars as well as a random deposition on the substrate without alignment as shown in Figure. 2c. This difference in deposition may be attributed to reduced Coulumbic interactions between the adjacent pillars (with a 150 µm spacing) compared to the narrower gap sizes [11].

Contact angle experiments were performed to investigate the effect of a reduced solid-liquid interface and the pinning behavior due to suspended nanofibers over the three-dimensional micro-patterned surfaces. These suspended nanofibers on the micro-patterned pillars prevent the Wenzel transition of water droplets by pinning them due to their hydrophilic nature. Figure 3 (a-f) shows images of micro-patterned and hierarchical surfaces while Figure 3 (a'-f') shows the water droplet images on the micro-patterned samples (without nanofiber deposition) and hierarchical surfaces with pillar to pillar spacings of 50, 100 and 150 µm respectively.

For patterned and hierarchical structures, in addition to surface roughness, capillary pressure also affects the wetting behavior. Capillary pressure is a non-wetting pressure which prevents the transition of a water droplet from a Wenzel to Cassie state. Capillary pressure increases with the reduced feature size and spacing between the features [13]. In addition, for hydrophilic samples, contact angle decreases with an increase in the roughness factor (actual surface area/projected surface area) according to Wenzel theory. In the present study, the contact angle values for the patterned samples decreased from ~88^o to ~68^o with an increasing distance between the pillars. In other words, the contact angle decreased with a decreasing roughness factor from 1.7 (for a 50 µm spacing) to 1.2 (for a 150 µm spacing). Calculations of the roughness factor are presented in the Supporting Information. The contact angle values for these micro-patterned surfaces are higher than for a planar film (Figure S3), and the trend is not in agreement with Wenzel theory. This can be attributed to an increasing capillary pressure due to air trapped around the pillars causing higher non-wetting pressure with a decreasing spacing between pillars [13,14].

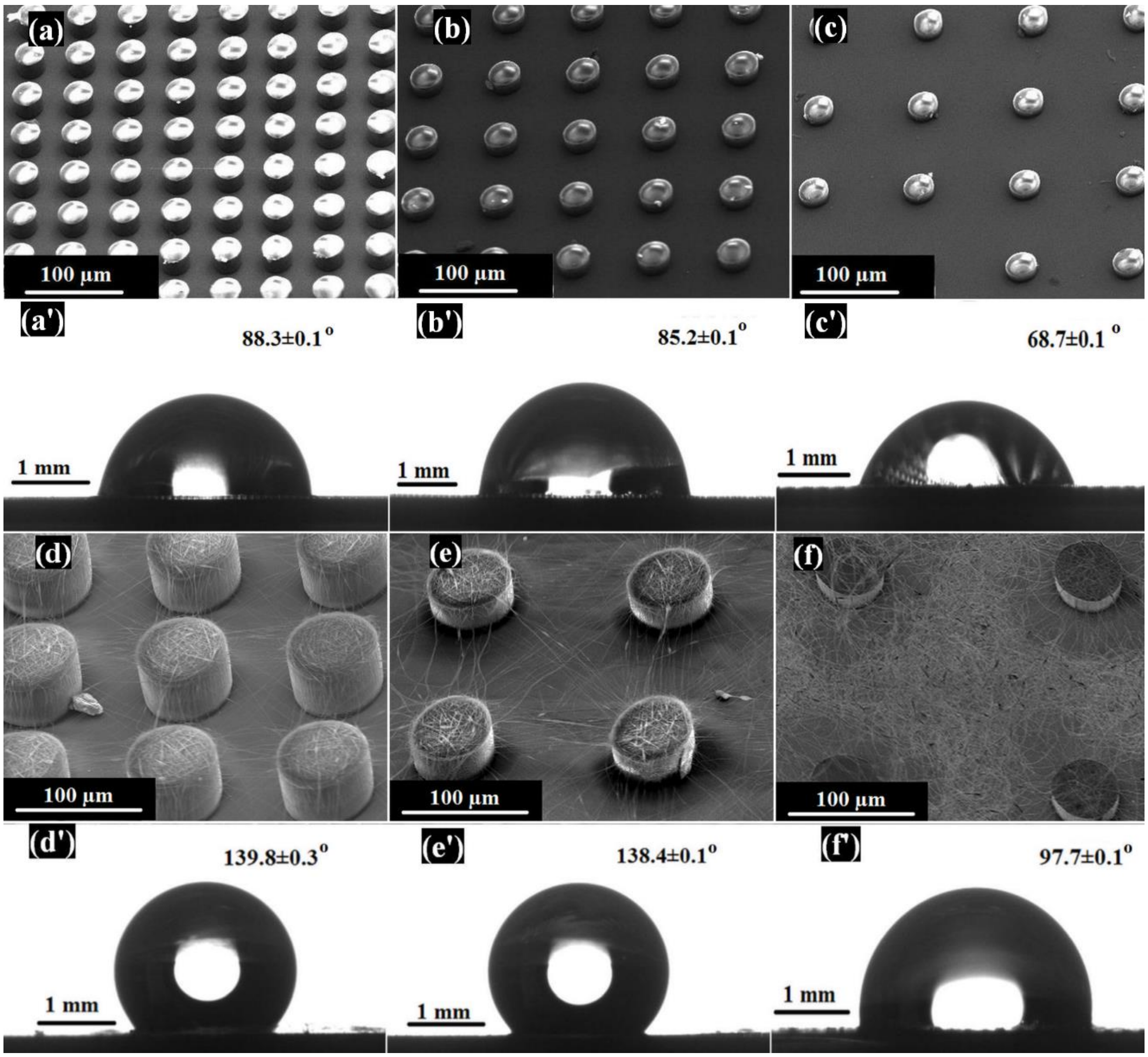

Figure 3. (a-c) Typical SEM images of micro-patterned SU-8 structures with pillar to pillar distances of 50 µm, 100 µm and 150 µm, (d-f) hierarchical structures with pillar to pillar distances of 50 µm, 100 µm and 150 µm taken at a 45° tilt angle; (a'-c') contact angle images of a water droplet on micro-patterned surfaces (a-c); (d'-f') contact angle images of a water droplet on hierarchical structures corresponding to (d-f)

For hierarchical structures, the contact angle decreased from ~139° to ~98° with an increasing pillar spacing from 50 to 150 µm. This decrease in contact angle can also be ascribed to a decrease in the non-wetting capillary pressure with an increasing spacing between pillars and pinning of the water droplet. The contact angles for hierarchical surfaces are noticeably higher than that for samples with micro-patterned structures only. Hanging nanofibers based hierarchical structures with 50 and 100 µm spacings exhibit a pronounced hydrophobic behavior compared to the hydrophilic micro-patterned surfaces. This enhanced hydrophobicity of the hierarchical structures may be attributed to the stabilization of an air layer under the water due to the pinning of the water droplet by the suspended nanofibers and an enhanced liquid-air interface area, where the air trapped below the water droplet acts as a cushion [3]. This behavior is similar to the water fern *S. molesta*; except for the presence of hydrophobic hairy supports below the hydrophilic tips for the plant leaves. In this case, hydrophilic fibers acting at the tips are supported by hair-like micro-patterned pillars. However, samples with 150 µm spacings show significantly lower contact angles after fiber deposition compared to suspended nanofiber samples. This wetting behavior could be due to the transition of a water droplet from a Cassie to a Wenzel state because of the absence of suspended hydrophilic nanofibers to pin the water droplet and lower capillary pressure.

4. Conclusions

We have successfully fabricated bio-inspired air retaining hydrophobic surfaces by aligning electrospun nanofibers over an array of micro-patterned surfaces. The morphology of the micro-textured pattern not only affects the fiber alignment process but also its wetting behavior. These aligned suspended nanofibers help to pin water droplet and stabilize the air-water interface. This approach may find applications in fabricating hydrophobic surfaces in underwater conditions. Further, the possibility to electrospin a large number of polymers makes this simple technique to fabricate complex hierarchical structures potentially generic and therefore opens up a wide variety of applications in fluid transport, ship coatings and other submersible conditions.

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