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# Mimicking a Stenocara Beetle's Back for Microcondensation Using Plasmachemical Patterned Superhydrophobic–Superhydrophilic Surfaces

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A simple two-step plasmachemical methodology is outlined for the fabrication of microcondensor surfaces. This comprises the creation of a superhydrophobic background followed by pulsed plasma deposition of a hydrophilic polymer array. Microcondensation efficiency has been explored in terms of the chemical nature of the hydrophilic pixels and their dimensions. These results are compared to the hydrophilic–hydrophobic pattern present on the Stenocara beetle's back, which is used by the insect to collect water in the desert. Potential applications include fog harvesting, microfluidics, and biomolecule immobilization.

## 1. Introduction

Hydrophilic–hydrophobic patterned surfaces offer a means for controlling the wetting behavior of aqueous media. This is important for a whole host of technological applications including: cell growth,<sup>1,2</sup> protein manipulation,<sup>3</sup> the spotting of biomolecules,<sup>4,5</sup> micro-fluidics (to control the location and movement of liquids),<sup>6–9</sup> and the formation of anti-dew/frost-free protective exteriors.<sup>10–14</sup> Hydrophilic–hydrophobic patterned surfaces are also found in nature. One example is the Stenocara beetle, which lives in arid desert conditions where the only available source of water is fog droplets (these range between 1 and 40  $\mu\text{m}$  in diameter, i.e., much smaller in size as compared to normal rain droplets). A random array of smooth hydrophilic bumps are present on the Stenocara beetle's back (0.5 mm in size, and arranged 0.5–1.5 mm apart).<sup>15</sup> These hydrophilic regions are surrounded by waxy areas comprising physical features (approximately 10  $\mu\text{m}$  in size), arranged in a hexagonal array. Water collection onto the nonwaxy hydrophilic regions occurs by the beetle tilting its back wings into the fog. Any fog vapor incident upon the waxy hydrophobic regions is blown along the surface until it reaches a nonwaxy hydrophilic region. The droplets

grow until they cover the entire hydrophilic bump, and then, under their own weight, they detach and roll downward into the beetle's mouth. This naturally occurring microcondensation surface has been previously mimicked in the laboratory using random and ordered arrays of 0.6 mm glass spheres on a waxy background.<sup>15</sup> It was found that an ordered array of spheres gave rise to optimum microcondensation. However, the functionality of the surface was limited to only glass (contact angle of  $\sim 20^\circ$ ) and a waxy hydrophobic background (contact angle of  $111^\circ$ ).<sup>16</sup> Clearly, the degree of hydrophilicity/hydrophobicity in the respective regions and their dimensions must play a pivotal role in determining the overall microcondensation efficiency.

In this Article, we evaluate the microcondensation efficiency of a variety of hydrophilic–hydrophobic patterned substrates with respect to their surface functionality and dimensional parameters. Two types of superhydrophobic background are employed, corresponding to plasma-fluorinated polybutadiene (advancing/receding water contact angle =  $154^\circ/152^\circ$ )<sup>17</sup> and plasma etched poly(tetrafluoroethylene) (advancing/receding water contact angle =  $152^\circ/151^\circ$ ),<sup>18–20</sup> Scheme 1. A range of hydrophilic plasma polymers has been patterned onto these superhydrophobic backgrounds, and their water microcondensation performances have been compared.

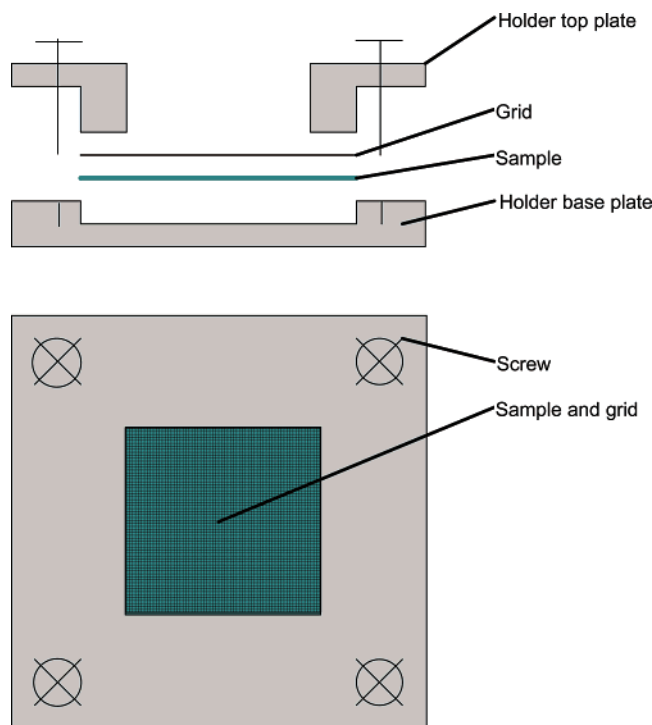
## 2. Experimental Section

Plasmachemical modification and deposition were carried out in a cylindrical glass reactor (5 cm diameter and 470 cm<sup>3</sup> volume) connected to a two-stage rotary pump via a liquid nitrogen cold trap at a base pressure of  $4 \times 10^{-3}$  mbar and a leak rate better than  $5 \times 10^{-9}$  mol s<sup>-1</sup>.<sup>21</sup> An L-C matching unit was used to minimize the standing wave ratio of the power transmitted from a 13.56 MHz radio frequency generator to a copper coil externally wound around the glass reactor. Prior to each plasma treatment, the chamber was scrubbed with detergent, rinsed in propan-2-ol, and further cleaned using a 50 W air plasma for 30 min. Samples were then placed into the center of the reactor, followed by evacuation to base pressure.

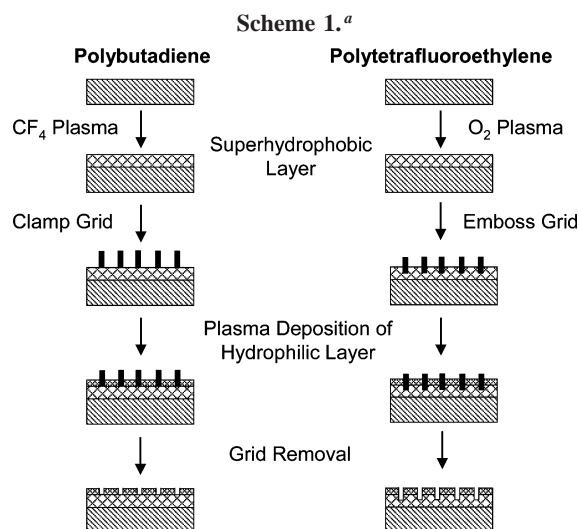
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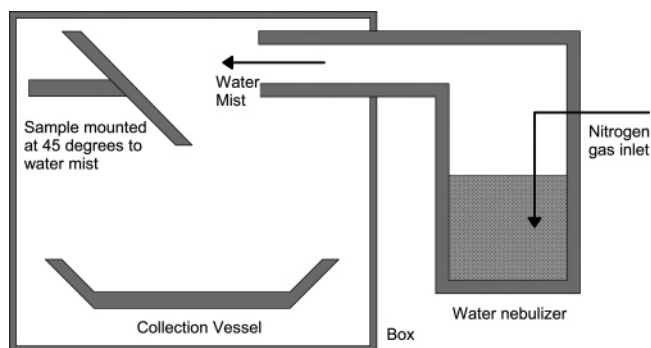
**Figure 1.** Side and top views of the holder used to clamp the grid in position on top of the sample.



<sup>a</sup> Micropatterning a hydrophilic plasma polymer onto a superhydrophobic background (created by either  $\text{CF}_4$  plasma fluorination of polybutadiene film, or oxygen plasma treatment of PTFE polymer film).

Next, the feed gas/monomer was admitted into the system via a control needle valve at a pressure of 0.2 mbar for 5 min, and the electrical discharge ignited for a selected duration. Upon completion of the surface treatment, the RF power supply was switched off and the feed gas/monomer was allowed to continue flowing through the chamber for a further 5 min.

Two types of superhydrophobic surface were prepared, Scheme 1. In one case, an 8% (w/v) solution of polybutadiene (Aldrich, MW = 420 000, *cis* 1,4-addition) in toluene (BDH, +99.5% purity) was spin-coated onto polished silicon wafers (MEMC Electronics Materials, 25 mm  $\times$  25 mm) using a photoresist spinner (Cammax Precima) operating at 2000 rpm for 60 s. These polymer films were subsequently vacuum annealed at 90  $^\circ\text{C}$  for 1 h to remove entrapped solvent. Plasma treatment with  $\text{CF}_4$  gas (99.7% purity, Air Products) at 50 W for 5 min yielded a superhydrophobic surface (advancing/



**Figure 2.** Apparatus for measurement of water microcondensation efficiency.

receding water contact angle = 154 $^\circ$ /152 $^\circ$ ).<sup>17</sup> The plasma-fluorinated polybutadiene-coated silicon wafers were then clamped screw-tight to a grid (0.1 mm thick brass sheet, machine-drilled with a regular square array of circular holes) mounted in an aluminum holder, Figure 1.

The other approach for creating a superhydrophobic background consisted of ultrasonic cleaning of 25 mm  $\times$  25 mm plaques of poly(tetrafluoroethylene) (Goodfellows, 0.1 mm thick film) for 10 min in propan-2-ol and cyclohexane (50/50 v/v) followed by  $\text{O}_2$  gas (99% purity, Air Products) plasma treatment at 50 W for 60 min (advancing/receding water contact angle = 152 $^\circ$ /151 $^\circ$ ).<sup>22</sup> These superhydrophobic substrates were then embossed with a grid (0.1 mm thick brass sheet, machine-drilled with a regular square array of circular holes) at a pressure of 400 MPa for 10 s using a mechanical press (Moores Press) and then mounted in the aluminum holder, Figure 1.

For both types of superhydrophobic substrate, the aluminum holder was then placed into the center of the plasma chamber ready for hydrophilic functionalization through the exposed array holes. Evacuation to base pressure was followed by monomer vapor introduction into the system via a fine needle control valve at a pressure of 0.2 mbar for 5 min prior to electrical discharge ignition. In the case of pulsed plasma deposition, a signal generator was used to trigger the RF power supply in combination with the respective monomer, Table 1.

Sessile drop contact angle measurements were made at 20  $^\circ\text{C}$  using a video capture apparatus (A.S.T. Products VCA 2500 XE) and 2  $\mu\text{L}$  of high purity water droplets (BS 3978 Grade 1). Advancing and receding contact angle values were determined by increasing or decreasing the probe liquid volume at the surface.<sup>23</sup>

Film thickness measurements were carried out using a spectrophotometer (Aquila Instruments Ltd., model nkd-6000). The obtained transmittance–reflectance curves (350–1000 nm wavelength range) were fitted to a Cauchy model for dielectric materials using a modified Levenburg–Marquardt method.<sup>24</sup>

XPS characterization of the functionalized surfaces was undertaken on a VG Escalab Mk II spectrometer equipped with an unmonochromated Mg K $\alpha$  X-ray source (1253.6 eV) and a concentric hemispherical analyzer. Photoemitted core level electrons were collected at a 23 $^\circ$  fixed takeoff angle with electron detection in constant analyzer energy (CAE) mode operating at 20 eV pass energy. Experimentally determined elemental sensitivity (multiplication) factors were taken as being C(1s):F(1s):O(1s):N(1s):Br(3d) = 1.00:0.29:0.46:0.69:0.29. No spectral deterioration due to X-ray radiation damage of the surface was observed during the time scale of the data acquisition.

Water microcondensation onto the functionalized substrates entailed exposure to a mist of high purity water (BS 3978 Grade 1)

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**Table 1. Optimum Duty Cycle and Peak Powers Employed during Pulsed Plasma Polymerization of Various Hydrophilic Monomers<sup>a</sup>**

monomer	time on / $\mu$ s	time off /ms	peak power /W	thickness /nm ( $\pm 5$ nm)
4-vinyl pyridine (4-VP)	100	4	40	70
maleic anhydride (MA)	20	1.2	4	63
glycidyl methacrylate (GMA)	20	20	40	104
bromoethyl-acrylate (BEA)	30	10	20	225
4-vinyl aniline (4-VA)	100	4	40	62
3-vinylbenzaldehyde (3-VBAL)	50	4	40	114

<sup>a</sup> The thickness value corresponds to deposition onto a flat silicon wafer placed adjacent to the patterned sample.

**Table 2. Surface Chemical Composition Measured by XPS**

surface	% carbon ( $\pm 1\%$ )	% fluorine ( $\pm 1\%$ )	% oxygen ( $\pm 1\%$ )	% nitrogen ( $\pm 1\%$ )	% bromine ( $\pm 1\%$ )
polybutadiene	99		1		
CF <sub>4</sub> plasma/polybutadiene	42	56	2		
poly(tetrafluoroethylene)	32	68			
O <sub>2</sub> plasma/poly(tetrafluoroethylene)	33	66	2		
poly(4-vinyl pyridine) theoretical	88			13	
pulsed plasma poly(4-vinyl pyridine)	85		3	12	
poly(maleic anhydride) theoretical	57		43		
pulsed plasma poly(maleic anhydride)	66		34		
poly(glycidyl methacrylate) theoretical	70		30		
pulsed plasma poly(glycidyl methacrylate)	71		30		
poly(bromo ethyl-acrylate) theoretical	63		25		13
pulsed plasma poly(bromo ethyl-acrylate)	64		24		12
poly(4-vinyl aniline) theoretical	89			11.1	
pulsed plasma poly(4-vinyl aniline)	85		4	11.2	
poly(vinylbenzaldehyde) theoretical	90		10		
pulsed plasma poly(vinylbenzaldehyde)	92		8		

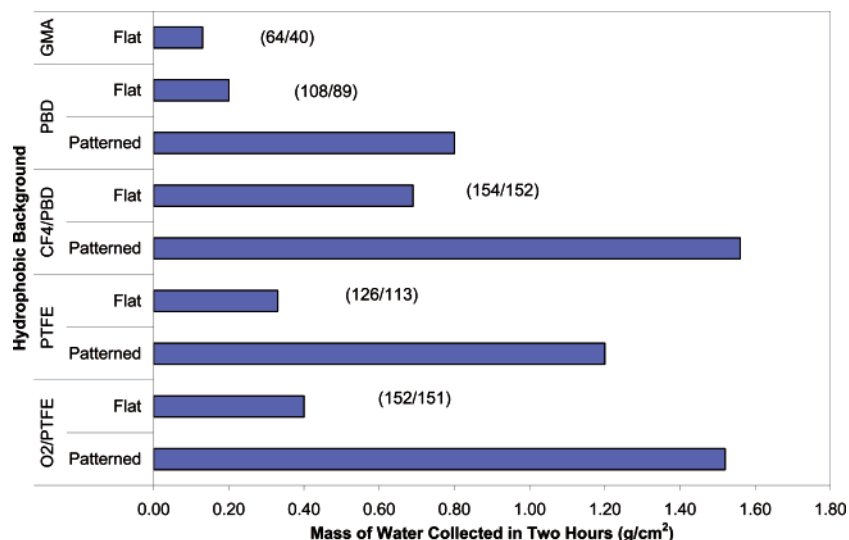
generated by a nebulizer set to a gas flow rate of 11 L min<sup>-1</sup> N<sub>2</sub> (99.7% purity, Air Products), Figure 2. The mass of water collected was measured in 30 min intervals over a period of 2 h.

To demonstrate the practical potential of these hydrophobic—hydrophilic arrays for chemical immobilization, the patterned substrates were immersed in a solution of water and drawn slowly out at an angle of 45°. This produced a uniform pattern of water droplets across the array of hydrophilic (poly(glycidyl methacrylate)) pixels. Aminomethyl polystyrene beads ( $\sim 50$   $\mu$ m mean diameter, Biosearch Technologies) were sprinkled as a fine dust above the surface, mounted at 45°. The sample was then gently blown with air from a pipet, left overnight at 42 °C in a humidity chamber, and finally the surface was washed with high purity water to remove any unbound polymer microspheres.

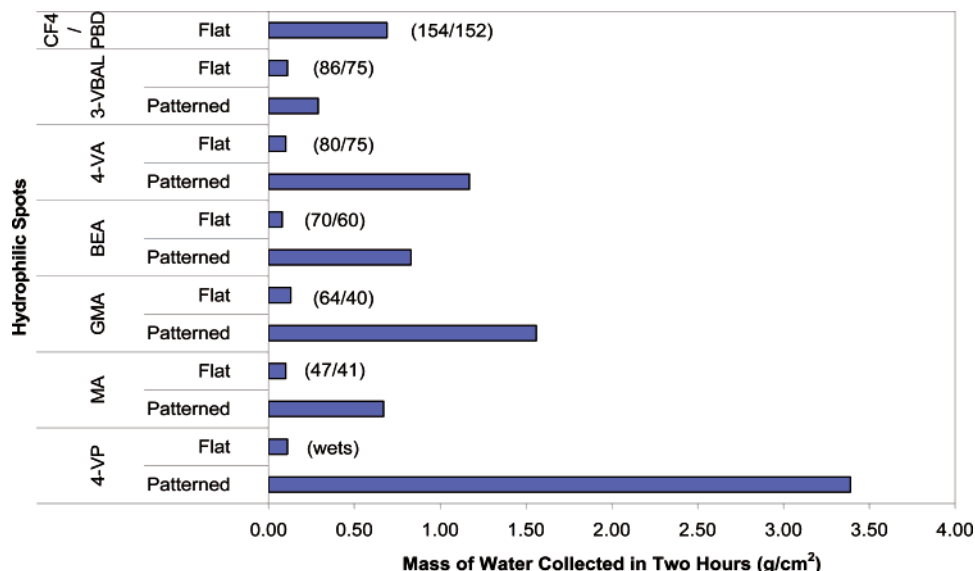
Optical images of the various patterned surfaces were taken with the mapping stage of an infrared microscope (Perkin-Elmer Spectrum One FTIR).

### 3. Results

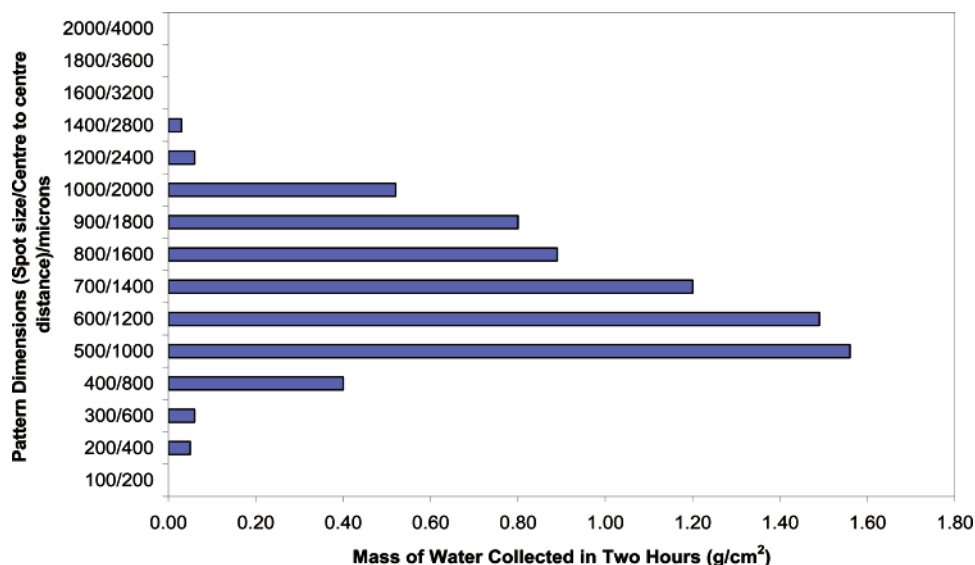
The chemical compositions of the functionalized surfaces as measured by XPS are in good agreement with theoretically predicted values (calculated on the premise of complete structural retention of the monomer structure), Table 2. The efficiency of these surfaces to perform as microcondensers was investigated by collecting water from a fine mist over a 2 h period, Figure 3. These studies clearly show that purely hydrophilic or



**Figure 3.** Water condensation study (mass of water collected over 2 h). Flat samples of each superhydrophobic polymer are compared to superhydrophobic samples patterned with a regular array of 500  $\mu$ m diameter spots of pulsed plasma-deposited hydrophilic poly(glycidyl methacrylate) arranged 1 mm center-to-center. (The numbers in brackets correspond to advancing/receding water contact angle values.)



**Figure 4.** Water condensation study (mass of water collected over 2 h). Hydrophilic plasma polymer coatings are compared to a regular array of 500  $\mu\text{m}$  diameter hydrophilic plasma polymer spots arranged, 1 mm center-to-center, on a superhydrophobic background (CF<sub>4</sub> plasma-fluorinated polybutadiene (PBD) in this case, although O<sub>2</sub> plasma etched PTFE shows a similar trend). (The numbers in brackets correspond to advancing/receding water contact angle values.)



**Figure 5.** Water condensation study for different sized arrays of pulsed plasma-deposited hydrophilic poly(glycidyl methacrylate) spots arranged in a regular array on a superhydrophobic CF<sub>4</sub> plasma-fluorinated polybutadiene substrate.

superhydrophobic surfaces do not collect significant volumes of water. Large bulbous drops were evident around the bottom edge of the nonpatterned hydrophilic surfaces (often they were insufficient in size to fall from the sample and be measured). The superhydrophobic surfaces were somewhat better at collecting water.

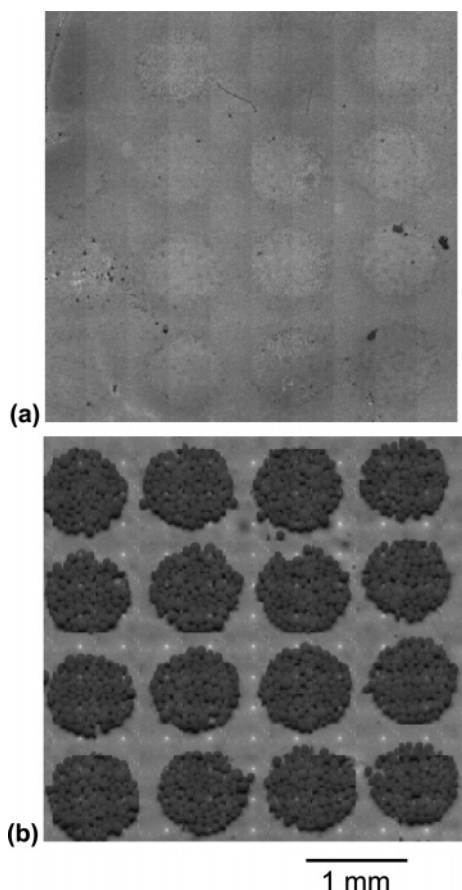
On the other hand, patterned hydrophilic—hydrophobic surfaces were found to be the most efficient for water microcondensation. In this case, any small water droplets that formed on the hydrophobic areas were blown across the surface until they reached a hydrophilic region. Here, the droplets combined with droplets already present on the hydrophilic region. These droplets continued to expand until they reached a critical droplet size, and then fell (due to gravity) at a steady rate into the collection vessel. The combination of a superhydrophobic background and a superhydrophilic poly(4-vinyl pyridine) array was found to outperform all of the other functional surfaces screened in this study, Figure 4. A similar trend was noted for both the plasma-fluorinated polybutadiene and the O<sub>2</sub> plasma etched PTFE

superhydrophobic backgrounds, Scheme 1. The slight difference in surface topography between these two fabrication methods was not found to affect the microcondensation behavior.

Beyond a threshold value of approximately 500  $\mu\text{m}$ , water condensation was observed to decrease with increasing hydrophilic spot size, Figure 5. Above 1200  $\mu\text{m}$  spot size, water collection became minimal. No variation in microcondensation behavior due to the hydrophilic layer film thickness was observed. Also, these coatings were stable for over one year.

These chemically patterned surfaces were also found to readily undergo derivatization reactions. For example, a poly(glycidyl methacrylate) micropatterned superhydrophobic polybutadiene surface selectively adsorbs amino-methyl-polystyrene beads via the microcondensation effect, Figure 6. These beads can then be chemically fixed into the regions of poly(glycidyl methacrylate) via the reaction between epoxide groups associated with the hydrophilic plasma polymer and amine groups present on the microspheres<sup>25</sup> by heating to 42 °C. Repeated washing in water





**Figure 6.** Optical micrographs showing: (a) pulsed plasma-deposited poly(glycidyl methacrylate) array onto CF<sub>4</sub> plasma-fluorinated poly(butadiene) surface; and (b) the same pattern reacted with 50  $\mu$ m amino-polystyrene microspheres. The spots of pulsed plasma-deposited poly(glycidyl methacrylate) are 500  $\mu$ m in diameter and 1 mm center-to-center.

confirmed that these immobilized amine-functionalized beads were chemically bound to the substrate.

#### 4. Discussion

Microcondensation can be an effective means for fog harvesting by utilizing vertically mounted mesh sheets in the air to collect the dew from trees.<sup>26</sup> Steam condensation is another potential application.<sup>27</sup> There is also scope for condensing organic vapors by combining oleophilic and oleophobic patterned surfaces.

In this study, pulsed plasma-deposited poly(4-vinyl pyridine) displays the lowest water contact angle of all of the functional coatings screened. The contact angle is sufficiently low that the surface can be designated superhydrophilic, or completely wettable<sup>28</sup> (water spreads out so rapidly that it becomes impossible to observe any meaningful contact angle). The greater hydrophilicity associated with the pyridine-based films can be attributed to the pK<sub>a</sub> of pyridine systems being approximately 5.2, while for instance aniline analogues have lower values around 4.6.<sup>29</sup> In the case of pyridine, the nitrogen lone pair is not delocalized (it is in fact perpendicular to the aromatic  $\pi$  system), but in aniline the N lone pair can be delocalized using resonance with

the adjacent  $\pi$  system. Hence, the nitrogen atom present in the pyridine ring is more readily able to form hydrogen bonding with water molecules. When combined with a superhydrophobic background, the micropatterned poly(4-vinyl pyridine) superhydrophilic plasma polymer outperforms the other hydrophilic—hydrophobic combinations. This can be attributed to the high wettability of the hydrophilic surface allowing the mist droplets to combine more readily and thus reaching the critical size for detachment sooner.

As well as the absolute contact angle, the sliding angle is also important (the angle at which a droplet begins to move down a surface). This angle,  $\alpha$ , is defined by:<sup>30</sup>

$$mg(\sin \alpha)/w = \beta_{LV}(\cos \theta_R - \cos \theta_A)$$

where L is liquid, V is vapor,  $\beta_{LV}$  is the surface tension,  $m$  is the mass of droplet,  $w$  is the width of the droplet (horizontal to the direction of drop movement), and  $g$  is gravity.  $\theta_R$  and  $\theta_A$  are the receding and advancing contact angles, respectively. The low contact angle hysteresis characteristic of the two superhydrophobic surfaces (oxygen-treated PTFE, and CF<sub>4</sub> plasma-treated polybutadiene) can help to explain the enhancement in microcondensation. Such ease of movement of a droplet on a surface is beneficial to microcondensation in two ways: the fog droplets are more easily blown into the hydrophilic regions, and when the critical size of droplet is reached within the hydrophilic regions, the detached droplets will readily roll down the hydrophobic surface.

It is also evident that the size of the hydrophilic spots has a large bearing on the surface's ability to collect water. Spots around 500  $\mu$ m were found to be optimal in the present study, whereas spots exceeding 1200  $\mu$ m showed little to no condensation. In the latter case, it was observed that a critical size for droplet detachment is never reached: the rate of water loss through processes such as evaporation exceeds the rate of fog droplet condensation. Effectively, hydrophilic domains are so large that they act in a way similar to that of purely hydrophilic surfaces. In addition, there is also a minimum hydrophilic spot diameter required to facilitate microcondensation: below 400  $\mu$ m, droplets were seen to form and quickly reach critical size. However, they lacked sufficient mass to overcome the surface tension, and thus remained attached to the surface. These results are consistent with the *Stenocara* beetle's back, which has spots approximately 600  $\mu$ m in diameter and 500  $\mu$ m to 1.5 mm apart.<sup>15</sup>

Plasmachemical patterned hydrophilic—hydrophobic surfaces offer scope for controlling the wetting behavior of aqueous media. This is potentially useful for the patterning of moieties dispersed within aqueous media (as exemplified by the amine-functionalized polystyrene microspheres, Figure 6).

#### 5. Conclusions

Microcondensor surfaces can be fabricated by the plasma-chemical arraying of hydrophilic pixels onto a superhydrophobic background. CF<sub>4</sub> plasma-fluorinated polybutadiene and O<sub>2</sub> plasma etched poly(tetrafluoroethylene) provide sufficient background superhydrophobicity, while superhydrophilic poly(4-vinyl pyridine) spots exhibit the greatest efficiency for microcondensation. The optimum hydrophilic pixel size/center-to-center distance of 500  $\mu$ m/1000  $\mu$ m compares favorably with the hydrophilic—hydrophobic patterned back of the *Stenocara* beetle used by the insect to collect water in the desert.

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