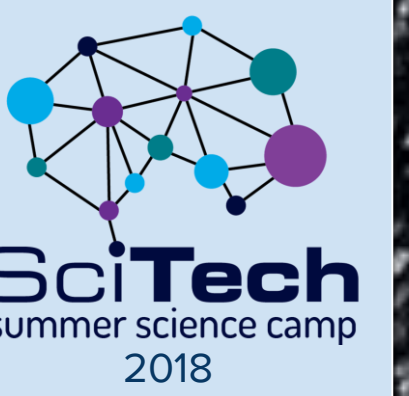


Utilising a Soft-lithography Technique for Fabricating Biomimetic Superhydrophobic Polymeric Surfaces



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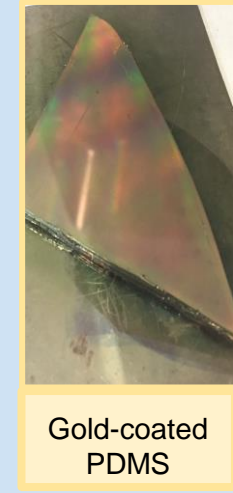


Abstract

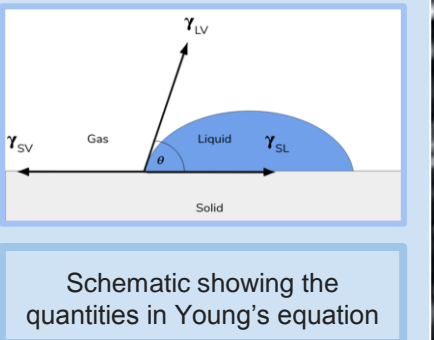


A myriad of natural examples exhibit nano and microstructures on the surface of plant leaves that give rise to superior superhydrophobic and self-cleaning properties. High-aspect-ratio nano and microfibers on the surface of lotus leaves and seta in gecko feet have inspired new material designs with enhanced superhydrophobicity [1]. From these biological examples, it is possible to learn how to artificially produce nanostructured surfaces in order to give the surface superior superhydrophobic properties.

Hydrophobic and hydrophilic surfaces are generally defined by the degree of the contact angle of a water droplet and a surface, or, inversely, the wetting ability of the surface [2]. A surface is classified as superhydrophobic when the contact angle exceeds 150 degrees [3]. Thomas Young related the surface energies of the states of matter surrounding the droplet with the equation: $\sigma_{sg} = \sigma_{sl} + \sigma_{lg} \cdot \cos\theta$. Nano- and microstructured materials will have less contact with water droplets due to their roughness. This, combined with hydrophobic chemistry, renders them superhydrophobic properties.



Silicon has been commonly used as a master surface to synthetically fabricate these biologically-inspired structures. However, its expensive fabrication and brittle properties hinder its direct usage and has inspired the concept of replication. In order to replicate micro-structures from Si surfaces onto a range of materials, we used a soft-lithography technique, which requires the formation of a PDMS negative replica, followed by casting of the desired polymer. The final polymer material possesses microstructures identical to that of the Si masters and combined with hydrophobic surface chemistry exhibits superior superhydrophobic and self-cleaning properties.



Experimental

We coated our nanostructured surfaces with wax crystals ($C_{24}F_{50}$) and self-assembled monolayers to increase the superhydrophobic properties. Gold was also coated onto our epoxy and PDMS in order to carry out SEM (Scanning Electron Microscopy).

A high-aspect ratio, silicon template was used as the master surface to fabricate identical nanostructures on varying materials. Furthermore, the nanostructures were tested with differing dimensions in order to identify the superior dimensions for a superhydrophobic surface.

Results

We compared the hydrophobicity of treated and untreated materials by measuring hysteresis and contact angles. Generally, we saw a trend of increased hydrophobicity with the use of nanostructures, however, structure alone did not render materials superhydrophobic.

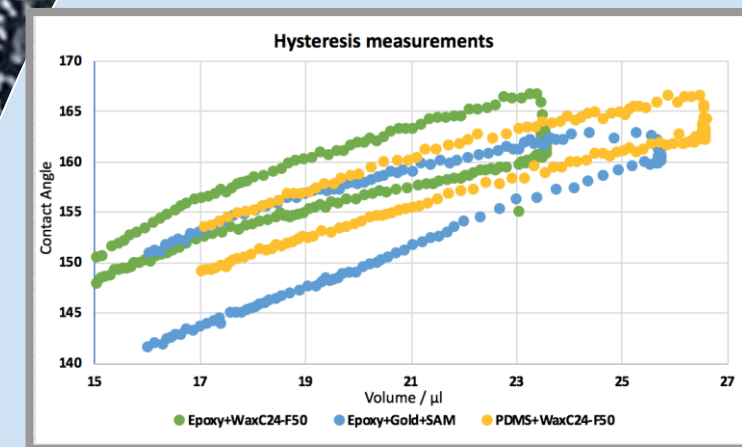


Figure 1: Hysteresis of Contact Angle on the Samples. The wax-coated PDMS displayed the lowest hysteresis while the epoxy coated with gold and SAM displayed the highest hysteresis (the lower the contact angle hysteresis, the more superior the superhydrophobic properties.)

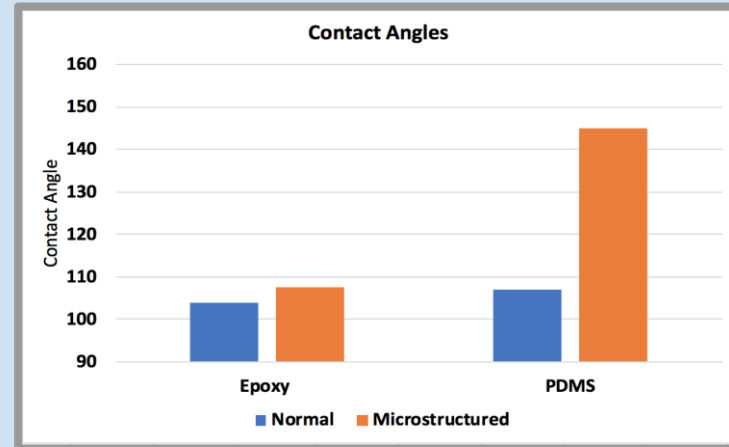


Figure 2: Contact angles of microstructured and flat surfaces. Microstructures on both the epoxy and PDMS surfaces increased the contact angles, rendering each surface more hydrophobic.

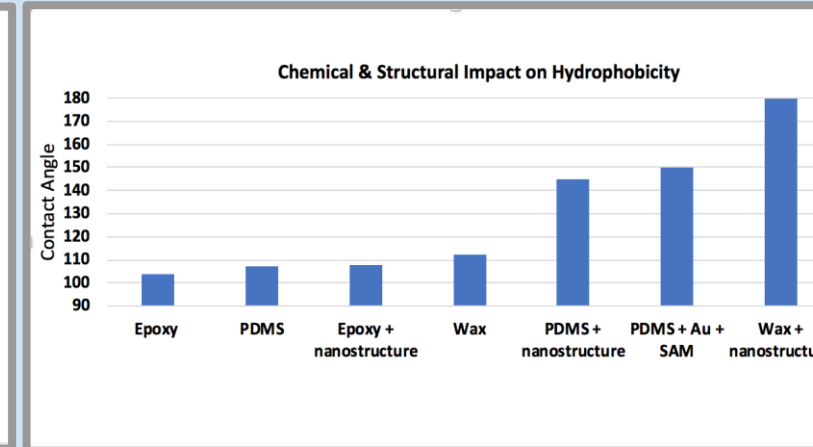
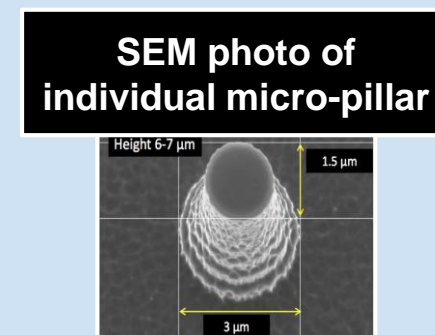


Figure 3: Contact angles of flat, nanostructured and wax-coated samples. The contact angles increased with the introduction of roughness (micro- and nanostructures) as well as the introduction of intrinsic hydrophobicity (for example, wax).

The epoxy was carefully peeled off of the PDMS, in order to avoid damaging the nanostructures, and studied using an optical microscope, confocal microscope and optical tensiometer. We were able to observe the pillars, identify their dimensions and measure the contact angle using each of these machines respectively.

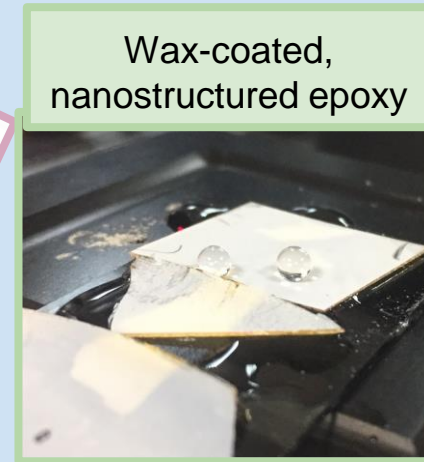
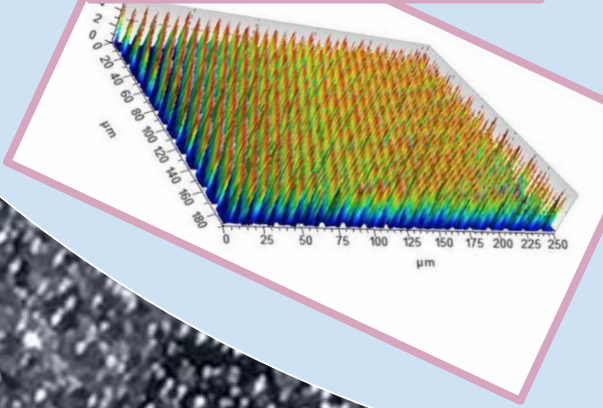
Using the Sylgard 184 kit, PDMS (Polydimethylsiloxane) was created to act as a negative mold for our double replication process. The mixture of the elastomer base with the curing agent at a specific ratio was essential in ensuring our subsequent success.

SEM image of Nanostructured pillars

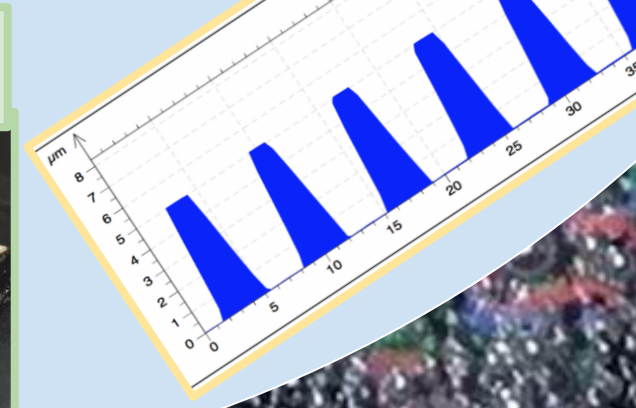


Gold coated epoxy with nanostructured pillars and SAM

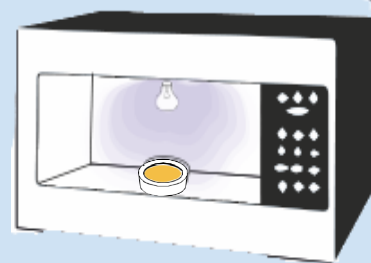
Confocal Leica DCM 3D



Profile view of micro-structures



Prolonged exposure to UV rays ensured the complete curing of the epoxy material.



PDMS was poured onto the original master surface, to create a negative mold.

Although different materials can be used, our project primarily involved epoxy, which was poured evenly onto the negative PDMS mold.



The PDMS mold was cured using a vacuum chamber and subsequently dried. Once it cured, the mold was carefully removed from the Silicon master surface using ethanol, which dries quickly and leaves little residue.



Conclusions

We have demonstrated a successful use of the soft-lithography technique to produce versatile high-aspect-ratio nanostructured surfaces inspired by the surface of the lotus leaf and seta in a gecko foot.

We have shown that soft-lithography is successful for a variety of materials, which makes this technique very useful for the production of smart materials and surfaces to be applied to a wide range of contexts. Furthermore, through observations of contact angle and hysteresis we have demonstrated the varying impacts of nano and microstructures in improving a material's superhydrophobicity.

Considering the multi-functional characteristics of these replicated surfaces — superior superhydrophobic and self-cleaning properties — this technique will find exciting applications to produce self-cleaning windows and other dynamic materials.

Acknowledgments

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Bibliography

- [1] B. Pokroy, A. K. Epstein, M. Persson-Gulda, and J. Aizenberg, 'Fabrication of Bioinspired Actuated Nanostructures with Arbitrary Geometry and Stiffness', *Adv. Mater.* **2009**, 21, 463
- [2] D. Quere, 'Wetting and Roughness', *Annu. Rev. Mater. Res.* **2008**, 38:71
- [3] K. Law 'Definitions for Hydrophilicity, Hydrophobicity, and Superhydrophobicity', *J. Phys. Chem. Lett.* **2014**, 5, 686