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Dual-scale roughness produces unusually water repellent surfaces

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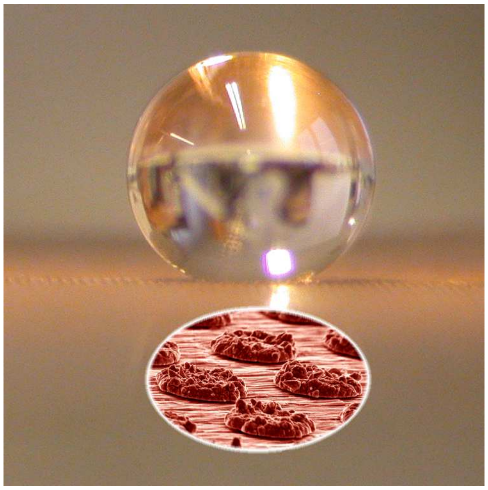
Super-hydrophobicity can be achieved on relatively smooth surfaces. Short, wide pillars on slightly rough surfaces are shown to produce super-hydrophobic surfaces (see Figure) where neither the pillars nor the slight roughness suffice alone. This use of two length scales to create super-hydrophobic surfaces directly mimics the mechanism used by some plants including the lotus.



Extreme water repellency (super-hydrophobicity) is commonly observable on plant leaves,[1] with some plants having surfaces from which water rolls off more effectively than from smooth PTFE. The surfaces of these leaves are also self-cleaning, as rolling drops of water collect and remove dust and other debris. Plants achieve super-hydrophobicity by creating a rough and hydrophobic surface so that topography enhances the effect of surface chemistry into super-hydrophobicity. In recent years, super-hydrophobic surfaces have been created in the laboratory using a wide variety of techniques including fractally rough wax surfaces,[2] lithographically fabricated surfaces[3,4] and sol-gel surfaces[5,6]. The common idea underlying all these approaches is to use a rough, patterned or porous surface on which there are methyl or fluorine terminal groups or to which a thin, hydrophobic layer can be applied.

When a drop of water is placed onto a surface it will spread or contract until the contact angle it makes with the surface reaches a certain value. The angle reached is determined by a balance between the relative interfacial contact areas so as to minimise the surface free energy[7,8]. Wenzel[9] showed that on a rough surface the solid-liquid and solid-vapour area contributions to the surface free energy are increased. Wenzel's equation predicts that the basic wetting behaviour of a surface will be enhanced by roughness or surface texture. The assumption in this type of enhancement of wetting behaviour is that the liquid remains in contact with the solid surface at all points within the projected contact area of the droplet.

If thin, deep channels are present on a hydrophobic surface, water will not enter the channels. On these surfaces a liquid drop effectively sits upon a composite surface of the solid protuberances and air. This situation is described by Cassie and Baxter's equation,[10] which assumes that a certain percentage of the liquid-solid interface is replaced with liquid-gas interface. The type of roughness or texture present on a given surface would be expected to influence whether full contact or partial contact occurs between a drop and a solid surface. Wenzel's equation calls for an increase in effective surface area, whereas Cassie's equation calls for sufficient aspect ratio that the fluid cannot penetrate. A pattern of tall, smooth pillars would be likely to behave as a composite Cassie surface whereas short squat pillars would be likely to behave as a Wenzel surface. In practice, for laboratory created hydrophobic surfaces, increasing roughness usually initially leads to Wenzel type enhancement of the contact angle followed by a sharp transition to a Cassie type super-hydrophobicity. [*11*]

The surface shown in Fig. 1 consists of short, squat pillars but behaves as if it were very rough. The pillars and the surface are rough on a smaller scale but neither the pillars nor the roughness of the surface alone could account for the water contact angles measured on it, around 160(±3)º. Indeed pillars of this height and separation usually have a negligible effect on contact angle as the area added to the surface is low. Similar surfaces with rough, squat pillars on a rough base were prepared and investigated to determine the cause of this effect.

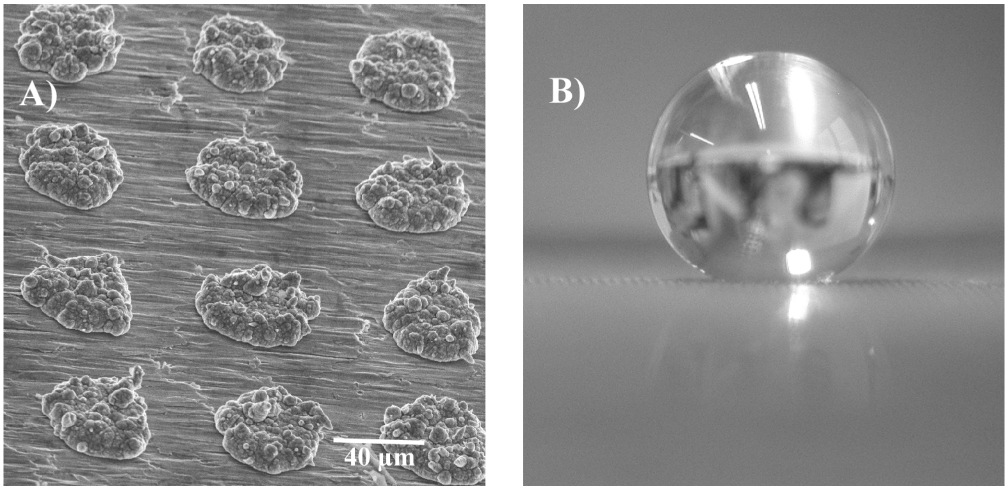


Figure 1 A) Electron micrograph of rolled copper surface with squat pillars, 40 µm diameter and separation and 4 µm in height. B) photograph of a water drop on hydrophobised copper surface in (A).

We electrodeposited copper from acidic copper sulfate solution onto flat copper to create surfaces of varying levels of roughness. Under diffusion-limited conditions, growth of copper by electrodeposition occurs preferentially on any protuberances, leading to dendritic and fractal growth.[*12*] In our experiments at lower currents globular rough surfaces were obtained. The deposited layers of copper were coated with a fluorocarbon hydrophobic layer; water drops on them then showed contact angles ranging from 115(±3)º to greater than 165º, depending upon the current density during deposition and therefore the degree of roughness of the surface. The concept of this study was to combine this random surface roughness with surface texture to produce two length scales: one due to a regular surface texture and the other due to surface roughness. A current density was chosen so that the resulting copper layer was only slightly rough (Fig. 2A) and produced a small amount of contact angle enhancement, from 110(±3)º up to 136(±3)º (Fig 2B). The specific surface area of the rough copper surfaces were measured by underpotential deposition of lead[13] and found to be 3.1 whereas the initial surfaces were found to have a specific surface area of 1.1. To combine surface texture with the controllable levels of roughness achieved by the current density, we then used S18-13 photoresist patterns to mask specific areas of surface and deposited more copper at the same current density in a regular pattern of discs. The photoresist was then removed and the surface hydrophobised. The resulting surfaces resembled “chocolate chip cookies” when observed using a scanning electron microscope (Fig. 2C). These rough, textured surfaces demonstrated strong contact angle enhancement to 160(±3)º (Fig. 2D). The aspect ratio of the copper discs was extremely low, down to less than 1/10, Fig. 2C shows 2 µm high by 15 µm diameter “cookies” with 15 µm separation); a level of roughness that would not be expected to produce significant contact angle enhancement. Their surface area could be estimated as the area of the sides of the rough cylinders plus the electrodeposition texture, giving an increase in specific surface area to 3.2. Copper electrodeposits without additional surface texture did not produce contact angles as high as 160º until their specific surface areas exceeded 10. This suggests that the combined effect of texture and roughness is far greater than the sum of the parts. The similarity between the samples produced and the leaves of some plants suggests that nature uses this mechanism to enhance non-wetting surfaces[14]. This has been commented upon in other publications[15, 16]. The results shown here indicate that two-level roughness has a strong effect on contact angle that can be observed on a micrometer scale.

Three further types of surface were created using short pillars (2 µm high by 15 µm diameter); growing the rough pillars on a smooth copper surface and using the negative of the photolithographic mask to create S 18-13 photoresist pillars on both smooth and rough copper. These techniques enabled us to create all combinations of rough and smooth pillars on rough and smooth surfaces.

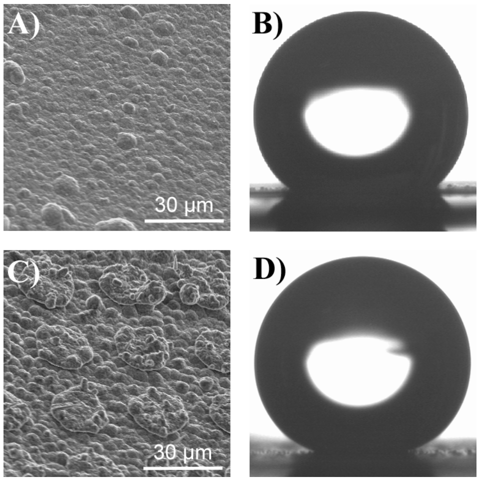


Figure 2 A) Scanning electron micrograph of electrodeposited copper. B) Drop of water on surface A, contact angle 136(±3)º. C) Scanning electron micrograph of electrodeposited copper with copper “chocolate chip cookies” . D) Drop of water on surface C, contact angle 160(±3)º. The electron micrographs were taken at an angle of 45º to emphasize roughness.

The contact angle of water on the hydrophobised, smooth pillars on a smooth base (Fig. 3A) was ~ 110(±3)º, approximately the same as that on a flat surface. Such short pillars are neither of sufficient aspect ratio to prevent the water from coming into contact with the base layer of smooth copper (the Cassie mechanism) nor of sufficient surface area for the Wenzel mechanism to be effective. The short, slightly rough, copper growths on smooth copper bases (Fig. 3B) showed a contact angle of 136(±3)º after hydrophobisation, which is similar to the contact angle on the slightly rough surface without the surface texture provided by the pillars. Smooth S18-13 photoresist pillars on rough copper (Fig. 3C) also showed no extra contact angle enhancement, suggesting that both levels of roughness are required on the tops of the pillars and at their bases to produce the high contact angles observed in Figures 1, 2D.

By increasing the height of the smooth pillars whilst maintaining the rough bases, we created surfaces with contact angle enhancement greater than that of either surface although the surface area of the composite surface was less than that of the electrodeposited copper. Contact angles of 146(±3)º were observed on the composite surfaces whereas the pillars alone produced angles of 130(±3)º (Fig. 3C). These experiments suggest that replacing a portion of a rough surface by a smooth protuberance can enhance the contact angle, even if the replacement reduces the overall area of the solid surface. We therefore suggest that the large scale, low aspect ratio surface projections combine with the small-scale roughness on the base surface to enhance the contact angle. The upward component of the surface tension between the columns allowing suspension of the drop on a surface of lower roughness (at the base of the pillars) than would otherwise be the case. Patterns of this type reach a maximum contact angle when the aspect ratio of the pattern exceeds 1[17]; when the contact angle on a pattern of tall SU-8 pillars (15 µm diameter and separation, 30 µm height) was measured the contact angle was the same as that observed on the pillars on a rough base (147(±3)º). For a pattern of smooth pillars, as the pillars grow in height, the influence of the base decreases until the drop is suspended solely by the pillars and the observed contact angle is independent of pillar height. By slightly roughening the base layer it appears that the same final value due to the pillars could be reached at lower heights of the pillars; an aspect ratio of 1/10 instead of 1. When the tops of the pillars themselves were also roughened the saturation value due to the pillars could also increase thus giving the super-hydrophobic effect in Fig. 2D.

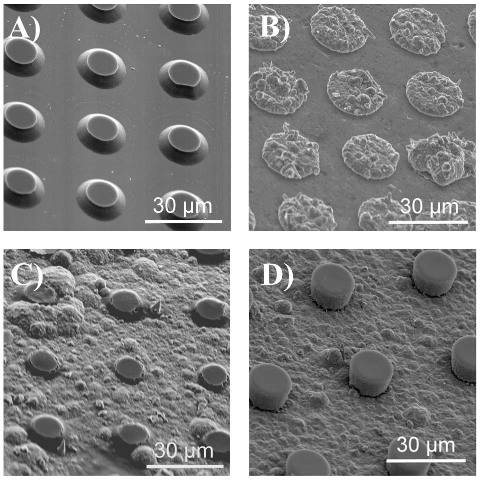


Figure 3 Scanning electron micrographs of combination rough-smooth-textured surfaces. A) Smooth photoresist pillars on smooth copper base surfaces. B) Rough copper pillars on smooth copper base surfaces. C) Smooth photoresist pillars on rough copper base surfaces. D) Smooth SU-8 pillars on rough copper, the water contact angle on these combines surfaces was increased from 136(±3)º on the copper, 130(±3)º on the SU-8 to 146(±3)º, close to the angle where very high pillars of this size and separation reach a maximum contact angle. The electron micrographs were taken at an angle of 45º to emphasize roughness.

Contact angle hysteresis is the difference between the contact angles at the front and rear of a sliding drop and determines how easily drops can be tipped off a surface. Some suggest that contact angle hysteresis can be used as a measure of whether a water drop is in full or partial contact with a hydrophobic surface. Quéré[18] has described the Wenzel superhydrophobic state as "sticky", and the Cassie-Baxter state as "slippery" as the contact angle hysteresis on surfaces where Wenzel's equation applies are generally higher than those where the Cassie-Baxter equation applies. When the contact angle hystereses of water on the different surfaces described in this article were measured, those on rough copper pillars on a smooth base and smooth pillars on a rough copper base Figures 2B, C were found to be similar; 102(±6)º and 108(±6)º respectively. The combined pattern of rough pillars on a rough base showed a contact angle hysteresis of just 16(±6)º. A flat surface coated with the same hydrophobic coating showed contact angle hysteresis of 47(±6)º. This supports the argument that combining the levels or roughness caused a transition from Wenzel "sticky hydrophobicity" to Cassie-Baxter "slippery hydrophobicity" at the bases of the pillars.

Grundmeier *et al.*[*19*] also noticed that coating a micro-rough surface with a nano-rough polymer produced higher contact angles than the polymer on a flat surface. Herminghaus[*15*] showed theoretically that small-scale roughness on the sides of larger roughness can reduce the steepness of the larger scale roughness required for drop suspension to occur. This behavior relies on the sides of the features being rough and may contribute to the larger effect observed with the copper "chocolate chip cookies". More recently Feng *et al.*[20] used a combination of roughness scales inspired by combining the Cassie-Baxter equation for large pillars with Wenzel's equation for the lower scale roughness on the tops of the peaks. They produced surfaces with micro- and nano-structures with high contact angles. Our results add a further case to this, where smaller scale roughness at the base of a larger pattern enhances super-hydrophobicity.

Cassie and Wenzel mechanisms have been demonstrated together on a single surface by Bico *et al*,[*11*] where water drops placed on silicon pillars showing high contact angles, corresponding to Cassie's equation could be switched to lower contact angles predicted by Wenzel's equation by pressing them onto the pattern. This suggests that the suspension of the drop can be a local minimum in energy with the lowest energy state being the unsuspended, Wenzel, condition.

Dual length scale roughness can be used to enhance contact angles at lower roughnesses than would be expected. It appeared that the upward component of the surface tension of a drop of water hanging between two short pillars could add to the effect of smaller scale roughness at the base of the pillars enabling suspension of the drop on the smaller scale roughness. This allowed surfaces to be produced with relatively low roughness but that showed very high contact angles. This effect could be used to enhance the toughness or effectiveness of water repellent coatings and gives insight into why plants produce surfaces of this type. The combination of a rough base with smooth pillars is a way of protecting rough surfaces against wear.

Acknowledgements

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Experimental

Flat copper surfaces were prepared by sputtering a thin layer of titanium onto glass coverslips and then sputtering copper on top.

S18-13 photoresist was patterned on to some of the copper on glass samples. The mask used was made up of tessellating squares with a circle of one half the side length in one corner being open. SU8 patterns were produced using the same mask. As SU8 is a thick, negative resist a pattern of circular pillars was produced after developing.

Copper growth was carried out using copper sulfate in sulfuric acid. Samples were masked off using clear nail varnish.

Hydrophobisation was carried out using a wash in solution designed for waterproofing breathable fabrics (Grangers Extreme Wash In). This treatment was found to coat this particular type of sample evenly, as far as could be detected by electron microscopy.

Contact angle measurements were made using a Krüss DSA10; 1μl of de-ionised water was dropped onto the sample from a hydrophobised needle on a microsyringe. The needle usually had to be tapped to get the drop to detach. A picture of the drop was taken a few seconds later, to avoid any problems relating to drying of the drop. The drop shapes were found to be often uneven, so tangent measurements were made and three images (6 angles) were taken to allow removal of the occasional rogue point, caused by contamination of the surface. Advancing and receding angles were measured by increasing the volume of water in the drop to measure advancing angles and decreasing it to measure receding angles. On surfaces with low contact angle hysteresis angles were measured on sliding drops.

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Figures

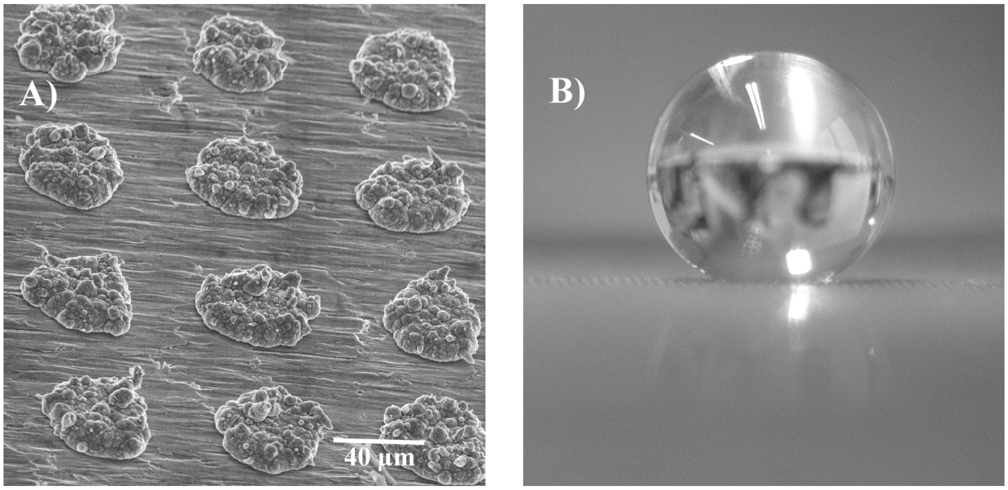


Figure 4 A) Electron micrograph of rolled copper surface with squat pillars, 40 µm diameter and separation and 4 µm in height. B) photograph of a water drop on hydrophobised copper surface in (A).

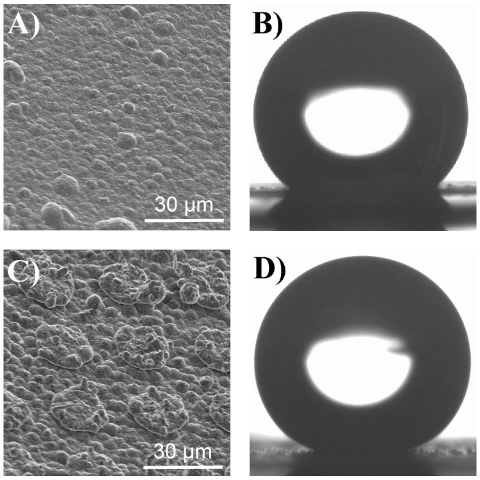
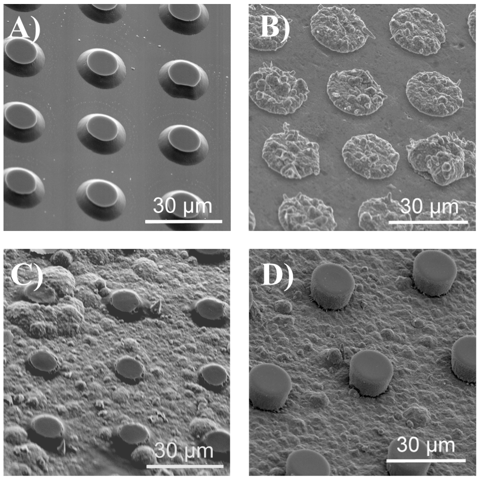


Figure 5 A) Scanning electron micrograph of electrodeposited copper. B) Drop of water on surface A, contact angle 136(±3)°. C) Scanning electron micrograph of electrodeposited copper with copper "chocolate chip cookies" . D) Drop of water on surface C, contact angle 160(±3)°. The electron micrographs were taken at an angle of 45° to emphasize roughness.



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