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Learning from Superhydrophobic Plants: The Use of Hydrophilic Areas on Superhydrophobic Surfaces for Droplet Control[†]

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In many countries, the mornings in spring are graced with spectacular displays of dew drops hanging on spiders' webs and on leaves. Some leaves, in particular, sport particularly large droplets that last well into the morning. In this paper, we study a group of plants that show this effect on their superhydrophobic leaves to try to discover how and why they do it. We describe the structures they use to gather droplets and suggest that these droplets are used as a damper to absorb kinetic energy allowing water to be redirected from sideways motion into vertical motion. Model surfaces in the shape of leaves and as more general flat sheets show that this principle can be used to manipulate water passively, such as on the covers of solar panels, and could also be used in parts of microfluidic devices. The mode of transport can be switched between rolling droplets and rivulets to maximize control.

1. Introduction

In the mornings, it is often possible to see large droplets of water attached to the leaves of some plants. These droplets make an excellent subject for photography and do not have an obvious purpose. Some of them, notably those on the leaves of Alchemilla sp. (Lady's Mantle) have been admired over the centuries with alchemists collecting the droplets as "the purest form of water" for their recipes for transmutation and the elixir of life.¹ The persistence of droplets of water on this plant long into the day has led many to consider whether these plants may exude water. A simple experiment with water-soluble dye reveals that this is not the case. However, the persistence of the droplet after other dew has evaporated is still remarkable. Many photographs, such as those in Figure 1, have been taken, showing how mesmerizing the droplets can be, particularly in the morning sun. On further investigation, the more spectacular droplets all appear to be found on plants whose leaves are superhydrophobic. However, some superhydrophobic leaves do not display these droplets at all. The superhydrophobic fruiting bodies of some lichen, for example, do not appear to collect water, even though they are bowl-shaped.

Superhydrophobicity in plant leaves has been known for some time. It is where a combination of topography and hydrophobicity generates an interface with such low interfacial interaction that droplets of water bounce and roll over the surface like rubber balls. Some leaves in particular are known for this, such as the lotus Nelumbo nucifera, after which the Lotus effect² is named, but many other examples are also known. Nelumbo nucifera is known for its purity, in part because the leaves always appear to be clean despite floating on muddy water. The superhydrophobic surface causes raindrops to bounce and roll off the leaves, carrying dirt with it; other plants may use superhydrophobicity for similar selfcleaning reasons. However, self-cleaning is only one possible reason nature has developed superhydrophobic surfaces. Lichens possessing superhydrophobic surfaces have been found to be particularly resistant to pollution, mainly because water they absorb has first been filtered through the ground,^{3,4} and some aquatic insects use a superhydrophobic surface, called a plastron, to extract oxygen from water without the need for a gill.^{5,6} It is therefore possible to speculate that the benefits of superhydrophobicity for plants will not be restricted simply to its self-cleaning properties.

Superhydrophobicity and superhydrophilicity can be produced in the laboratory and are available in some products, as described in recent reviews,⁷⁻⁹ and in other parts of this special issue. All that is required is that a suitable type of topography or roughness is combined with the correct type of surface chemistry; there are a huge number of possibilities of ordered and disordered structures over different and multiple length scales and using different materials and materials approaches. The exact definition of superhydrophobicity is the subject of debate,¹⁰ but a high contact angle and a low contact angle hysteresis, or slipperiness of the surface, are usually required, although the two are not always found together.¹¹ In a recent review, two of the authors of this article suggested surfaces often labeled "superhydrophobic" need to clearly differentiate between those that demonstrate a high contact angle and on which water droplets moves freely and those that have a high contact angle, but on which water droplets become attached.⁹ A point also previously emphasized by other authors in terms of superhydrophobicity and contact angle hysteresis.^{12–14} This is important in plants, as these display both types of surfaces; leaves can have superhydrophobic surfaces and

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Figure 1. Plants showing retained water droplets. (a) Lady's Mantle, (b) Echeveria, (c) Lupin, (d) Euphorbia.

easy roll-off¹⁵ properties, while petals can have high contact angle surfaces that are sticky.¹⁶

Topography and roughness do not necessarily lead to superhydrophobicity. When the surface chemistry tends toward complete wetting, the effect of roughness can be to produce superhydrophilicity, where the contact angle is decreased. The modification of wetting by topography or roughness is not limited to materials that when flat and smooth have partial wetting droplets. Materials with a surface chemistry that favors the formation of a film also have their wetting, and hence their adhesive, properties modified by roughness. This is important because some natural surfaces have a zero contact angle for water even when flat. The additional surface area for wetting from roughness enables the interaction area between a droplet and a surface to be increased thereby altering the balance of the different interfacial areas and the overall surface free energy, and this can have wide-ranging consequential effects, including superspreading.¹⁷ In particular, the experiments described in this report show

how plants can form rivulets (continuous streams) from separate droplets, guide and direct both rivulets and droplets, and trap large droplets of water, and why they adopt such strategies. We show that plants use a combination of roughness/topography and both superhydrophobicity and highly "sticky" states in a designed manner to achieve effective water collection. We use this bioinspiration to construct working model surfaces using superhydrophobicity and superhydrophilicity to show that it could be useful for liquid handling and water management outside the plant world.

2. Experimental Methods

One of the simpler superhydrophobic leaves is that of the Nasturtium (Tropaeolum spp.). This is an almost flat leaf with the stem junction near its center. In its normal habit, the leaves are inclined at an angle to the vertical and are entirely superhydrophobic. On damp mornings, they do not collect a large water droplet and any smaller droplets present have no obvious pattern. Similarly, Aquilegia (Columbine) leaves do not gather droplets, despite being superhydrophobic. Tropaeolum (Nasturtium), which do not retain conspicuous droplets, are native to moist subtropical areas of South America, and Aquilegia vulgaris (Columbine), which also does not, is native to moist grassland.

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Our observation is that the plants that collect droplets of water are mostly Xerophytes, Euphorbia (Spurge, e.g., Euphorbia polychroma) mostly living in arid climes, Echeveria schaviana (Mexican Hens, also called Hen and Chicks) and Echeveria elegans, which are succulents from Mexico; Alchemilla mollis (Lady's mantle) thrives in cracks in rocks (and more recently paving), so can live on limited resources; Lupin are widespread, but also originated in warmer areas of Europe, North, and South America.

If correct, this suggests that the retained water droplets might be part of a natural water management strategy. Our initial hypothesis was that the water droplets sit on grouped stomata, acting as an external humidity reservoir, so extending the period that the plant can photosynthesize in the morning with little or no water loss. To investigate how and why large droplets of water are formed and maintained, we investigated the wetting properties of several large droplet retaining plants: Euphorbia (Euphorbia polychroma), Lady's Mantle (Alchemilla mollis), Lupin (Lupin regalis), Red Clover (Trifolium pratense), and Echeveria schaviana, and two that do not: Nasturtium (Tropaeolum majus) and Aquilegia (Aquilegia vulgaris).

Water droplets collecting on leaves can be divided into two types. The first type occurs on leaves arranged around the stem in a bottle brush pattern; often the water collects at the bases of the leaves. Examples of these tested were the Echeveria schaviana and Euphorbia polychroma. The water droplets become trapped in the notch between the leaves and the stem; they persist for some time and can often be seen after a cold night. The second type is droplets found on plant leaves. They form at the junction of the bases of the leaves (leaflets) on plants such as the Lupin and Clover and are surprisingly persistent, given that they are smaller and more exposed than the other type of droplet.

Leaves from plants showing droplet retention properties and some that do not were flash-frozen in liquid nitrogen, freezedried, and then imaged using a scanning electron microscope (JEOL JSM 840A). The samples were sputter-coated with around 15 nm of gold to make them conductive and increase their secondary electron yields. Leaves from the same plants were sprayed with a fine mist of water while being filmed using a video camera. Fine sprays were generated using a gravity-fed, compressed air paint sprayer with cross jets (droplet diameter ca. 100 μ m); the air pressure used was relatively low to reduce wind at the leaf surface. The image sequences were viewed in slow motion to observe what happened to the water and how it gathered. Samples were then placed under a dripping nozzle composed of a pipet tip from a 200 μ L syringe fed with deionized water using a Harvard 11 plus syringe pump and filmed using a high-speed camera (Streamview SVSi, U.S.). The pipet tip produced droplets of ca. 2.1 and 4.6 mm diameter depending on whether the small or large end was used. Some of the water was colored using a blue food dye (erioglaucine from Fluka, U.K.).

For comparison, models were prepared using thin card, 3 mm extruded acrylic, copper wire, two-component epoxy adhesive, filter paper, WX2100 superhydrophobic spray paint (Cytonix, U.S.), and polyvinylphenol (average MW 8000, Aldrich, U.K.) 10% in isopropanol. The first type of model was an artificial leaf cut out of thin card and fixed to a copper wire stalk. The stalk was masked and the leaf painted with WX2100 before colored water droplets were applied using a syringe. The same leaf was modified by affixing a small piece of filter paper to the junction of the leaflets for further testing. A second model used a silicone hydrophobic spray (Scotchguard) to make the center area hydrophobic. The second type of model was flat panels of acrylic with WX2100 superhydrophobic coating on one side except for 4-mmwide channels arranged in a double chevron shape pointing down with another channel connecting the apexes and extending downward that were masked off using tape during spray painting. The channels on different samples were variously left blank, coated with polyvinylphenol using a paintbrush, incised with 5 parallel V shaped notches $300 \,\mu\text{m}$ wide and $750 \,\mu\text{m}$ deep along the length of the channels using a laser cutter, and both incised and coated. The coated samples were immersed in water for 30 min to render them more hydrophilic.

3. Observations and Experiments

3.1. Observations on Plants. Small droplets of dyed water were placed on the leaves and then tipped off. This revealed that the areas where the large droplets collect on Lupin (Lupin regalis) and Lady's Mantle (Alchemilla mollis), unlike those on Euphorbia or Echeveria, retained some water when the plant was inverted. Contact angle measurements on Lupin leaves showed a large difference in equilibrium contact angle between the superhydrophobic part of the leaf at around 160° and the central zone at around 25°. Error in these measurements is high, due to the curvature of the surface. The difference indicates that these parts have a different structure or surface chemistry from the rest of the leaf.

Either the surface roughness or the surface chemistry can be used to increase hysteresis and sticking.¹⁸ If the roughness is not very large, the surface behaves like petals,¹⁶ where the liquid more or less covers the whole surface and generates a Wenzel large contact angle sticky state. If the roughness contains cup-like structures, these can be closed by the meniscus and then act like suckers.¹⁹ The contiguity of the contact line can also affect hysteresis with pillared structures more slippery than equivalent meshes.²⁰ The surface chemistry can cause stickiness intrinsically or by using a mixture of chemicals to create domains of low and high contact angle; this can convert a normally low hysteresis surface into a high one without strongly affecting the advancing angle.21

Electron micrographs of different parts of different leaves were taken to assess the differences and similarities between the flat parts of the leaves. The parts observed in detail were the flat parts of the leaves, the stems, and the bases of the leaves (leaflets).

The electron micrographs revealed structures typical of superhydrophobic surfaces on the main areas (Figure 2). Waxes on the leaves have a micro-nano multilayered structure, and this roughness, combined with the chemical hydrophobicity of the waxes, explains the superhydrophobicity of all but the Lady's Mantle (Alchemilla mollis), the Red Clover (Trifolium pratense), and the Euphorbia polychroma. These plants use a slightly different system. Many trichomes (hairlike structures) are present on the leaves; these are somewhat flexible and wrap around the droplet slightly. This allows the droplet to be supported and the leaf surface to remain dry even though the hairs themselves are slightly hydrophilic (it is not known whether the Euphorbia trichomes are hydrophilic).²² The shapes of droplets on thin rods shows that the increased air-water surface area required to wet down the rod is large enough that a droplet will not spread down a hydrophilic rod if it is thin.²³⁻²⁵ Otten and Herminghaus²² also showed that this arrangement can lift a droplet that condenses on the leaf

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Figure 2. Electron micrographs of plant surfaces. a(i) *Echeveria schaviana* typical wax surface, a(ii) *Aquilegia* typical wax surface; b *Alchemilla mollis*, (i) main part of leaf, (ii) central patch; c Lupin, (i) main part of leaf, (ii) central patch.

surface, converting it into a mobile droplet that moves across the leaf.

The structures in the center of the Lady's Mantle (Alchemilla mollis), Lupin (Lupin regalis) and Red Clover (Trifolium pratense) leaves where the droplets are trapped differ considerably from the structures on the leaves themselves (Figure 2bi and 2bii, Figure 2ci and 2cii). The Lupin center is made up of densely packed, flattened trichomes lying at an angle to the surface much like a wild hairstyle (Figure 2cii). The Lady's Mantle central trichomes are more densely packed than those on the rest of the leaf, and they have bulbous structures near their ends much like a medieval mace (Figure 2.bii). On younger leaves, these bulbs are absent, but the density of trichomes in the central patch is greater, and some of them have a hook structure at the end where the trichome turns 90° to sit parallel to the surface. The Clover central zone is made up of stalk, which has sparse hairs, not sufficient to cause superhydrophobicity, and little other structure. Underneath the structures at the center of the Lupin leaf, there was no space for stomata; on the other plants, there was no evidence of increased density of stomata, meaning that the local humidity hypothesis (the water drop supplying the region with water vapor to allow the plant to photosynthesize without losing water) was not likely to be true. It should be noted that the Lady's Mantle leaves appear to go through stages as they age: young leaves have no central attachment areas, hooked trichomes appear, and then, the clubbed ones appear; eventually, very old leaves become hydrophilic. These changes are accompanied by changes in shape as the leaf unfolds.

The flat shape of the Lupin trichomes and the bulbous features and hooks of Lady's Mantle are probably functional and have something to do with the attachment of drops; plants such as the *Echeveria* do not retain their droplets when turned upside down, whereas Lupin and medium-age Lady's Mantle leaves do. This indicates that the structures increase the interfacial surface area and therefore the contact angle hysteresis, making water on these parts of the plants adhere. There has been considerable work in this area suggesting that the interfacial area and the continuity of the contact line influence hysteresis.^{26–29} This is important because the structures appear to be particularly suited to producing a suspended droplet that is pinned, or adhered to the spot. The bulbous parts of the Lady's Mantle, the bent-over hairs of the Lupin and the high areal density of trichomes on the central area of both are likely to have this effect, increasing interfacial area and, in the case of the Lupin, producing a relatively unbroken contact line. Some water insects use almost identical hooked hairs arranged so that the interfacial area is high to stabilize their plastrons.⁶ Clover leaves appear to trap a small droplet by having trichomes that are so sparse that the water wets between them to the stem, this arrangement also increasing interfacial contact area.

The droplet being suspended on the trichomes will have several important effects. First, the water is not in contact with the plant surface. As the trichomes are not living tissue, they are not as susceptible to fungal attack, which would be a serious problem if the plant trapped water next to its surface for lengthy periods. Second, as the water droplet begins to evaporate, the droplet will then cool and will remain cooler than a similar droplet on a normal surface because heat transfer along the trichomes will be low. This process has been described before³⁰ and might account for the long lifetimes of the water droplets that are not replenished by the plant. Finally, the flexible hairs will have an effect on the final state of the droplet. It has been shown that on a fixed superhydrophobic surface a droplet can eventually wet into the roughness during evaporation due increasing local curvature.³¹ This effect will be much reduced on a flexible hair surface; a droplet only needs a cross junction of hairs to be completely pinned at the junction until complete evaporation occurs. Despite this, we noted that the central portions of Lady's Mantle leaves

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Figure 3. Stills from videos of plants being sprayed with water showing (a) a Nasturtium leaf sheds water, (b) the droplets on a Lady's Mantle leaf gather to the center, and (c) droplets on a Clover leaf end up on the stem.

often had deposits of particulate material on them. This is probably left over from when the droplet evaporates.

The *Euphorbia* and *Echeveria* show little difference in structure between the main part of the leaf and the part where the water gathers; the droplets are retained in cupped parts of the plant on wholly superhydrophobic surfaces, which is why they do not adhere when the plant is inverted.

This would appear to explain how the plants retain water droplets, the droplets are retained on a suspended but "sticky" state by a high interfacial solid fraction made up of a high density of trichomes either flat to the drop or with bulging ends. This does not, however, explain whether they have a function. To address this question, water was sprayed onto plants using an air sprayer. The idea was to simulate a foggy, misty, or dew environment, but at greater speed, and to observe the behavior of the water under these conditions. The water collected on the nondroplet retaining leaves until it reached a critical size and then ran off them. Each small droplet collected other droplets as it traveled, becoming larger and eventually rolling off the edge of the leaf, shooting off in a trajectory determined by its momentum and traveling some distance from what would be the base of the plant, with larger drops traveling further. However, on the Echeveria and the Euphorbia the leaves acted like channels, steering the small droplets of water toward the midrib and then to the stem where they were trapped and large droplets were formed (Figure 1d). These overflowed as more water was added and ran down the stem of the plant to the soil at the roots. If the first drop was relatively large, it burst on collision with the stem and sprayed some water away from the plant, which would always occur if no drop were retained.

It is interesting to note that water is also collected on nonsuperhydrophobic leaves arranged in the same geometry. Indeed, some *Euphorbia* species, such as some types of *Euphorbia mellifera*, are not superhydrophobic, but appear to collect water in this way.

On the Lupin and Clover, the water gathered as on the *Euphorbia* and was channeled to the sticky patch where it became attached (Figure 3b). More water flowing in swelled this patch until it overflowed down the stem of the plant toward the roots (Figure 3c). Again, the shape and orientation of the leaves without the special patch would be sufficient for a nonsuperhydrophobic plant to gather water, although more of the water would remain on the plant surface and be lost to evaporation. Without the patch, the water would shoot away from the plant as on the first set of plants, so it would seem that the sticky patch slows the water sufficiently to allow it to fall vertically.

High-speed footage of larger droplets (not shown here) impacting the same surfaces showed that the Nasturtium leaves



Figure 4. An artificial leaf with a superhydrophobic coating (a) causes a drop of water to bounce away; (b) a hydrophobic center is not sufficient to halt the drop; (c) a trapped drop swells and drains down the stem.

a)

deflected the drops at an angle, but barely affected them otherwise. Heavier droplets caused the leaf and stem to sway away, protecting the leaf against damage and allowing the droplet to continue more directly downward.

The Lupin group showed the opposite behavior in selecting water droplets. Small droplets and "dew" were retained by the leaves and continued down to their stems and roots. Larger droplets split on impact with much of the volume being ejected at an angle and less of the water (proportionally) continuing down the stem. It was not possible to compare this statistically, as the leaves varied in size, inclination, and strength of superhydrophobicity.

This suggests that the structures in the centers of the leaves are present to gather water in fine rain and dewy conditions, with the droplet observed after the event being a byproduct. Where water was collected as a large droplet on a sticky patch, it appeared to act as a hydrodynamic damper, absorbing the momentum of other droplets flowing into it. In heavier rain, the leaves flex down and propel water away from the base of the plant. The *Euphorbia* type of arrangement was less selective, most of the water was collected regardless of the conditions.

Once again, it is important to note that not all of the leaves tested behaved in the same manner; small *Echeveria* retained far more water than necessary to buffer the momentum of the drops, and some Lupin and Lady's Mantle leaves retained so much it is likely that the stem would bend under the weight. Our theory cannot fully explain this behavior.

3.2. Bio-Inspired Test Surfaces. To investigate the effect of patterns of surface roughness and surface chemistry on water



there and push water out of the lowest point.

collection properties, model superhydrophobic leaves were prepared and droplets of colored water were placed on them using a syringe. The motion of the droplets was followed using a video camera.

When the center part of the artificial leaf is superhydrophobic, even though it is the lowest part of the leaf, droplets of water arriving at the "leaves" shoot off at high horizontal velocities (Figure 4a). With a flat and hydrophobic coating, the center

b



Figure 6. An artificial flat surface shows (a) water breaking out of channels on grooved acrylic; (b) a grooved and treated pattern maintains a nearly constant stream of water.

collects more water, but most of it is still lost, as many drops continue straight over this patch (Figure 4b). When a rough and hydrophilic piece of filter paper was placed in the center of the leaf, a large drop would still travel over it, but small drops were retained. Once a retained drop was formed, even large drops (still smaller than the retained drop) could not escape; the momentum of the incoming droplet was absorbed in the collision with the retained droplet into oscillations that were quickly damped. When it was sufficiently large, the droplet then overflowed, running down the stem of the artificial plant (Figure 4c). This shows that the retained droplet is acting as a hydrodynamic damper, absorbing the energy of the incoming droplets and allowing them to change direction. A water collection strategy that appears highly effective. This idea is shown in schematically in Figure 5a. This is likely to be what is happening on the real leaves.

A second set of models were prepared on flat surfaces to investigate the potential for use on flat surfaces. The models consisted of acrylic panels painted with WX2100 superhydrophobic paint (Cytonix, U.S.) except for a double-Y channel that was masked off and then treated in four different manners to investigate droplet capture, to redirect droplets, and to try to form permanent rivulets. Water was sprayed onto these surfaces, angled at 20° to the vertical. The results were filmed, with excerpts shown in Figure 6; the behavior is described more clearly in the schematic diagram in Figure 5b,c.

As shown in the Figure 6 and illustrated in Figure 5b,c, the more hydrophilic areas divert the droplet trajectories across the surface. The flat acrylic is not very effective, with many droplets missing entirely and those traveling along the bare strip only doing so for a short distance before continuing their normal path. The grooved acrylic and coated flat acrylic performed slightly better, with the droplets forming a rivulet (stream), but this did not extend the length of the pattern; some water was able to bounce or slide over gaps in the rivulet. The combination of hydrophilic coating and grooves generated a reasonably stable wetted line, in effect a water pipe with one side. This collected almost all of the water droplets that crossed its path and conducted them into its outlet. This system is different from common hydrophilic patterning techniques³² and the microfluidic system of Zhao et al.³³ in that an open wetted track is formed. The ones in our experiments were not perfect, but the surface could be made more effective by increasing their roughness.

4. Discussion

Superhydrophobic leaves can have the major disadvantage that water which would collect on a normal leaf is lost as it rolls as droplets away from the base of the plant. It is difficult to trap water with a superhydrophobic leaf surface, as water droplets rapidly gain momentum and therefore land away from the base of the plant. This is a problem for xerophytes, particularly those in rocky conditions where stem flow is highly important, so that there is a natural evolutionary advantage to solving this problem. In fact, a plant can gain water by being superhydrophobic because less water from a short shower or dew event will stay on the leaves and evaporate and more will make it to the ground. Large droplets of water appear to be retained at points on the plant surface where transport of water must change direction. These retained droplets absorb the momentum of incoming droplets and catch those that are skipping across the surfaces, as the droplet of water is large compared with the height of the jumps. The momentum appears to be absorbed in oscillation modes of the stationary drop. The droplet can then increase in size until it overflows down the stem with little sideways motion. Some plants use a strategy of upward pointing leaves that channel the water to the stem by gravity. This mechanism works well if the plants are not superhydrophobic, but if they are made superhydrophobic, the droplets hitting the stem junction will burst and some of the water will be lost. A retained droplet of water in a small well at the plant stem junction can absorb the energy. Some succulents have barrelshaped leaves, so any water retained is held between leaflets. Other plants have cup-shaped leaves or ones shaped like the palm of an upturned hand. In this case, water droplets transferring from the top surface of the leaf to the stalk have to negotiate an outside bend. Water does not maintain contact with superhydrophobic surfaces on outside bends where it becomes detached and continues in a ballistic path. To prevent this, some plants have a patch of high contact angle hysteresis surface that traps a droplet of water, again to absorb the momentum of following droplets.

It is possible to mimic the effect using superhydrophobic and superhydrophilic surfaces. This allows water to be channeled without any physical confinement and to compensate for some of the shortcomings of superhydrophobic surfaces, in that droplets can easily be made to move too fast and then escape the area they are intended to move over. By patterning the surface with different high and low hysteresis areas, this tendency can be controlled and used constructively to guide the transport of water.

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5. Conclusion

The spectacular droplets observed on some plant leaves in the mornings appear to be remnants of a system that channels water from the leaves to the roots. The retained droplets absorb the momentum of smaller droplets rolling down the leaves, allowing a change of direction at the intersection between leaf and stem without the droplet flying off at an angle or bursting on hitting a superhydrophobic wall. Models using this principle showed that water can negotiate an outside curve on a superhydrophobic surface provided that a stationary droplet is present at the junction and that open channels of water can be generated on a flat surface, and these can be used to collect and direct water with a simple chemical pattern on a rough surface.

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