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Pitcher plant

Photo: The Rocketeer, 2011 | Flickr cc

Case study

Return of the Swamp Thing

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Return of the Swamp Thing: the Wyss Institute Finds a New Inspiration for a Slicker World

Swamp Thing I: The Original Version

In Buddhist lore the sacred lotus is renowned for its ability to emerge unblemished from the dirtiest muck of Asian wetlands. Such is the messy nature of life on this earthly plane, the texts say, and we all should emulate the plant's ability to avoid having any of it stick to us.

The sacred lotus is an aquatic perennial that spreads by rhizomes. Its floating leaves can reach sizes of 60 centimeters in diameter while the overall plant can sprawl up to 3 meters. It has the ability to regulate the temperature of its flowers, apparently in order to be receptive to insect pollinators. Its seeds are also remarkably viable after long dormancy; successful germination of 1300-year-old seeds has been accomplished. The seeds, flowers, young leaves and roots are all edible and many parts are used in traditional medicine. It is the national flower of both India and Vietnam and, besides being forever linked with the Buddha, is associated with the Hindu gods Vishnu and Lakshmi.

While a hundred generations of devotees have puzzled over how to achieve the plant's non-attachment metaphorically, it wasn't until 1988 that a German botanist by the name of Wilhelm Barthlott wondered how he might do so literally. The Director of the Bonn Botanic Garden, Barthlott had had a long career investigating evolutionary development by comparing the anatomy of plants. He had become fascinated by the slippery nature of plant surfaces (cuticles) when he had realized in 1974 that some of his specimens never needed cleaning before being put under the microscope. He compared hundreds of species in a quest to find the slickest. His ultimate champion was the sacred lotus (Nelumbo nucifera).

Barthlott discovered something counter intuitive about the lotus: the surface of the plant, rather than being ultra-smooth as one would expect, was actually quite bumpy. Of course, one had to look closely to see the bumps, and Barthlott's discovery was enabled by a relatively new device, the scanning electron microscope (SEM) brought to market in 1965. Now scientists could see things at the micro and nano scale. The typical electron microscope could magnify specimens from 10 to 500,000 times and was not restricted by the power of an objective lens or the shortest wavelength of visible light (about 200 nanometers). One could now see the rough form of large molecular structures like ribosomes and the clear outlines and interiors of cells (1 mi-

Water

The nature of water itself is what makes both of our swamp solutions work. Water is a so-called polar molecule, meaning that its two atoms, oxygen and hydrogen, have opposite charges, positive and negative. They are joined by covalent bonds, meaning that they share an electron between them, and because oxygen attracts that negatively charged electron more strongly it takes on a negative charge while hydrogen assumes a positive charge.

Because of this, water molecules stick easily to each other, head to tail, so to speak, in weak bonds and to other surfaces with appropriately charged molecules. It is the reason why salt (sodium chloride) dissolves so easily in water, the positive sodium quickly bonding with the oxygen, and the negative chloride bonding with the hydrogen. It is also the reason why water can cling to the sides of a glass, or, more importantly in nature, to the walls of xylem in, say, a redwood tree.

In the case of the lotus, the polar attraction of water to itself is stronger than its attraction to the minimal surface of the plant. In the case of the Pitcher Plant, the water and the micro fibrous solid surface form a thin sheet in which the water molecules are held in place by both their attraction to each other and to the solid.

Lotus flower

Photo: tanakawho, 2007 | Flickr cc

crometer and above). This power revealed the structure of plant cuticles to Barthlott as an intricate topography of architectural shapes.

Here is what the new tool revealed: water molecules were beading up on the dimpled wax micro surface of the leaf, and, as the water rolled off, these individual beads were riding on the tops of the bumps. A layer of air, therefore, separated the water from the solid surface of the leaf at the base of the bumps. This buffer created a condition in which the attraction of the water to itself (cohesion) was stronger than its attraction to the leaf (adhesion). Hence, the beading up. With the water nicely balled up and skipping over the tops of the bumps, dirt and debris were sucked into the surface tension of the water beads and carried off the plant.

Barthlott realized later that the phenomenon was not unique to the tissue of the lotus, but was of a physical, and therefore universal, nature. Any micro surface so configured and made from a hydrophobic substance could produce this effect. It was then that the scientist became the technologist.

A one-man promotional machine, Barthlott spent the next decade trotting his slippery invention around to chemical manufacturers. Eventually, the breakthrough, known as the "Lotus-Effect®" was patented and presented to the public in 1997. It has made its way into many coating products, the best known being *Lotusan* paint, a liquid pigment containing silicone microchips that mimic the effect when spread on a surface. Its main advantage is its self-cleaning properties and the paints have been applied to both buildings and vehicles.

Drop on lotus leaf

Photo: Pison Jauji, 2011 | Flickr cc

The Lotus-Effect® is a great example of a passive structure doing work that might otherwise have cost a lot of energy. It is also emblematic of the adage that "scale matters". The micro topography of the surface works to advantage because it is appropriately scaled to the size of water molecules. It therefore influences and takes advantage of the phenomena associated with the polarity of those molecules (see sidebar).

While the Lotus-Effect® was a conceptual and technological breakthrough, it has had its application limits. Artificial lotus surfaces, relying on a cushion of trapped air between the micro bumps, do not repel all liquids, particularly those with a low surface tension such as oils. The surface plane has to be tilted quite a bit above horizontal to be effective (high contact angle hysteresis) and the treatment fails under pressure or physical damage to the surface: liquids can be pushed through into the air cushion by additional pressure and imperfections in the solid surface can afford places where droplets can adhere.

Manufacturing a relatively precise surface to prevent this is fairly costly, but it nevertheless does not guarantee that, over time, the wear and tear of use won't degrade or halt its performance. While the self-cleaning performance of the lotus leaf depends on physical structure rather than biological processes or material, the maintenance of the surface is very much in the realm of bio-miracles. The plant "breathes" its renewing wax coating up through the cuticle with exhaled gases where it self organizes into a fresh layer. Technological translations have yet to mimic this process.

Swamp Thing II: The New Inspiration

These limits had led a team at the Wyss Institute for Biologically Inspired Engineering at Harvard to search for a superior biological model for slickness. Their initial goal was to synthesize a material that was "omniphobic" and repelled everything. Their search brought them back to the swamp. There they found Nepenthes, the Pitcher Plant, a sly and devious character that lives throughout the Malay Archipelago. Nepenthes has more than one trick to play in the "red in tooth and claw" game.

Life is not easy for a bog plant. Despite the fecund character of the place, the soils are very acidic and nutrient poor. Moreover, because they are saturated with water they are often oxygen deprived or anoxic. Without oxygen, organic matter does not break down and nutrients are not made available. What's a plant to do? Many of them, the Pitcher Plant included, have evolved to put meat on the menu.

Being a plant presents several disadvantages in chasing down prey, however. If you are stationary and in a spot that you didn't choose, then you had better come up with a pretty good strategy to get your prey to come to you. The Pitcher Plant has just such a strategy to supplement its more traditional harvesting of soil nutrients.

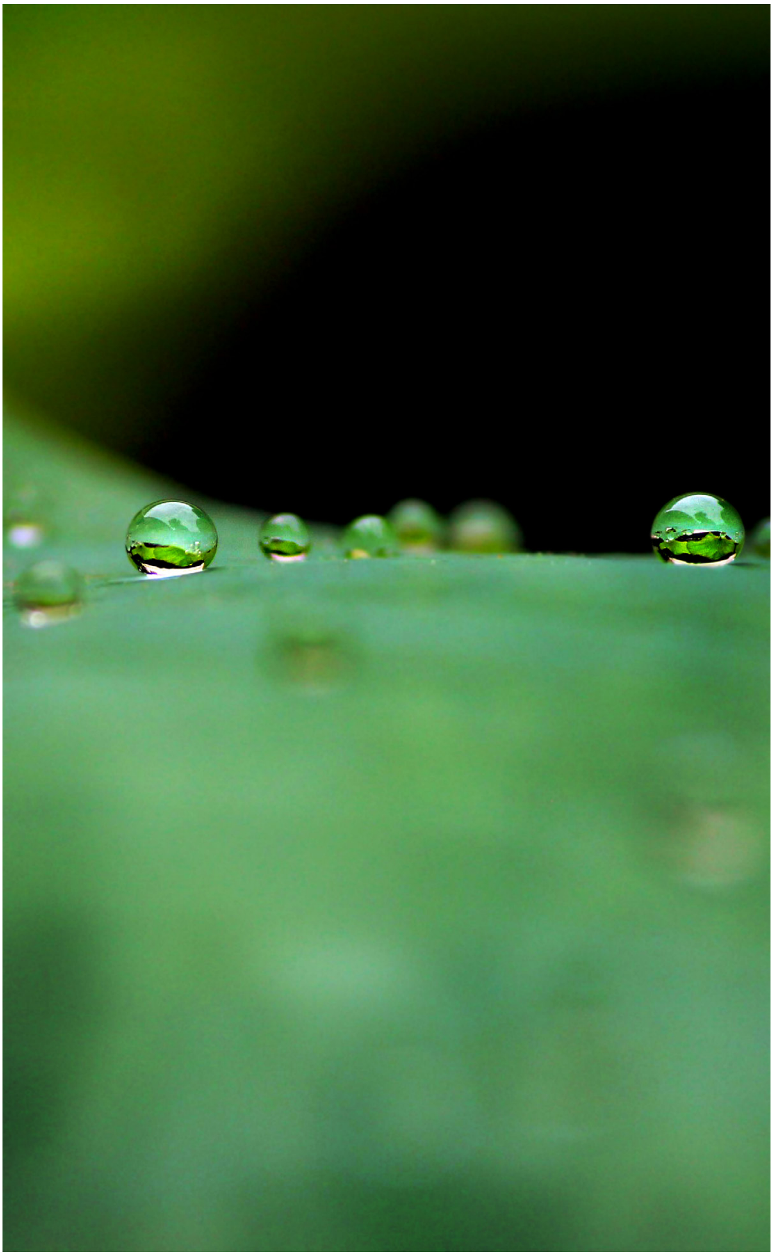
The plant lures animals, from insects to amphibians to rats and even birds, into a modified leaf that forms a bowl. It does this by a combination of color, nectar and scent. The color, usually red, is caused by anthocyanin pigments in its leaf walls and mimics the red found in meat. The nectar is usually laid down in a trail on the flange or flap of the bowl-shaped leaf, and the scent is either produced by the plant or is a result of the decaying victims already in the bowl. Within the bowl, water collects and contains viscoelastic polymers (read that "goo") that help further disable flying insects' wings.

The plant receives nitrogen and phosphorus from its decaying victims through several glands at the base of the bowl, and also hosts a variety of "boarders": insect larvae, spiders, mites, even crabs. While they feed every day on victims' parts, their patient landlord is actually just waiting for them to process the material and redeliver it as fertilizer in the form of defecations. There is one species, Nepenthes lowii, which has evolved a mutualistic relationship with a mammal, the tree shrew, by providing nectar in exchange for its droppings.

Research by Bohn and Federle in 2004 had revealed the unique properties of the plant's peristome, the rounded lip of the bowl. Overlapping wet cells formed anisotropic ridges in which an aqueous solution was held in surface tension as a thin film. The edge formed, in effect, a tiny Slip 'n Slide, and even ants, with their oiled footpads, could not get a grip on the surface and would aquaplane to their doom.

A Different Paradigm

The Pitcher Plant, as the Harvard team's top candidate for study, offered a completely different paradigm for liquid repellency performance. The material structure of the plant was more important for its voids than for its solid matrix, for it was the liquid that did the work of sliding insects to the waiting bowl. The matrix was there merely to hold this liquid in place. Once this became the contact material, the liquid medium brought additional characteristics: liquids typically organize themselves by molecular bond-



Drops on lotus leaf 2

Photo: tanakawho, 2012 | Flickr cc

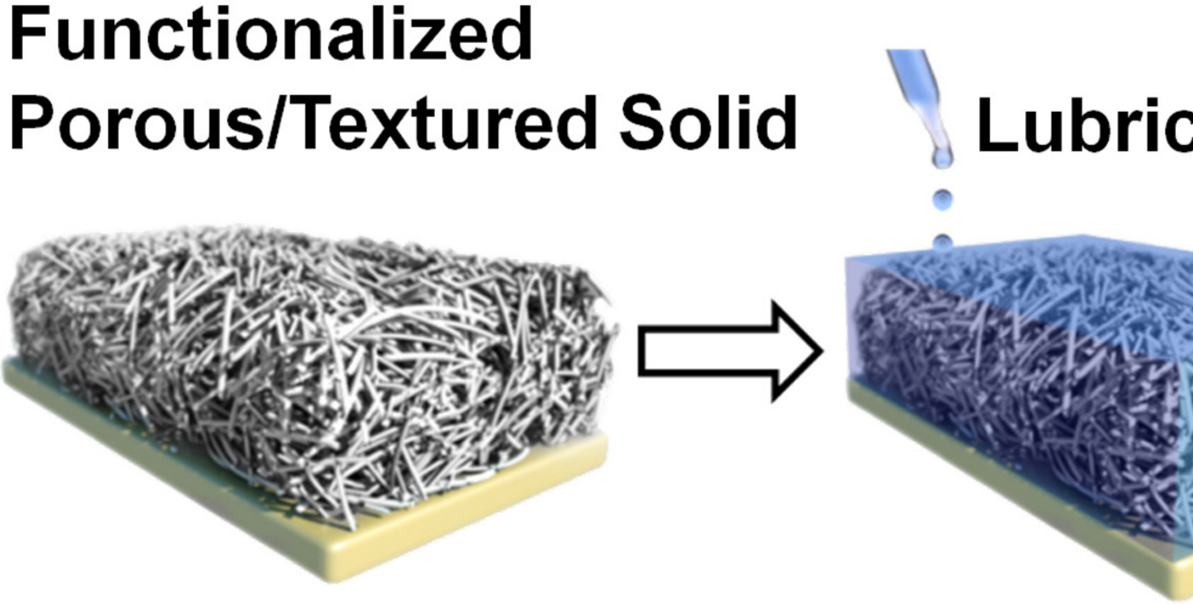
Wetlands

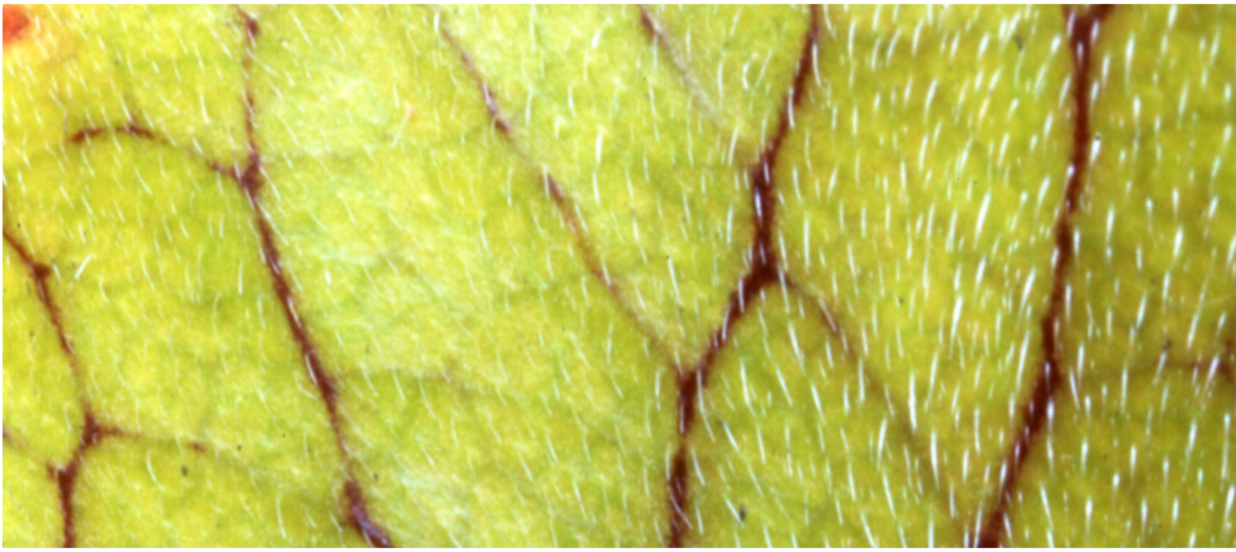
Both of the living inspirations for our slippery surface solutions live in wet ecosystems in Asia. Wetlands comprise about 6% of the world's land area (approximately 12.8 million square kilometers), yet account for a disproportionate share of biological diversity and productivity. Forty percent of all the world's species are estimated to live in wetlands, including 12% of all animals.

Wetland ecosystems, bogs, fens, swamps, marshes and open water perform many vital functions like flood and erosion control, fishery production, carbon sequestration and water supply. The World Wildlife Fund estimates that the economic value of wetlands could be as much as $70 billion per year.

In addition to having a functional value in regulation, production, and carrying capacity, wetlands are also a repository of information. The diverse organisms that are interrelated within these ecosystems have much to teach us. Mangroves, for example, are being studied for their method of desalination, an increasingly vital strategy in a water scarce world.

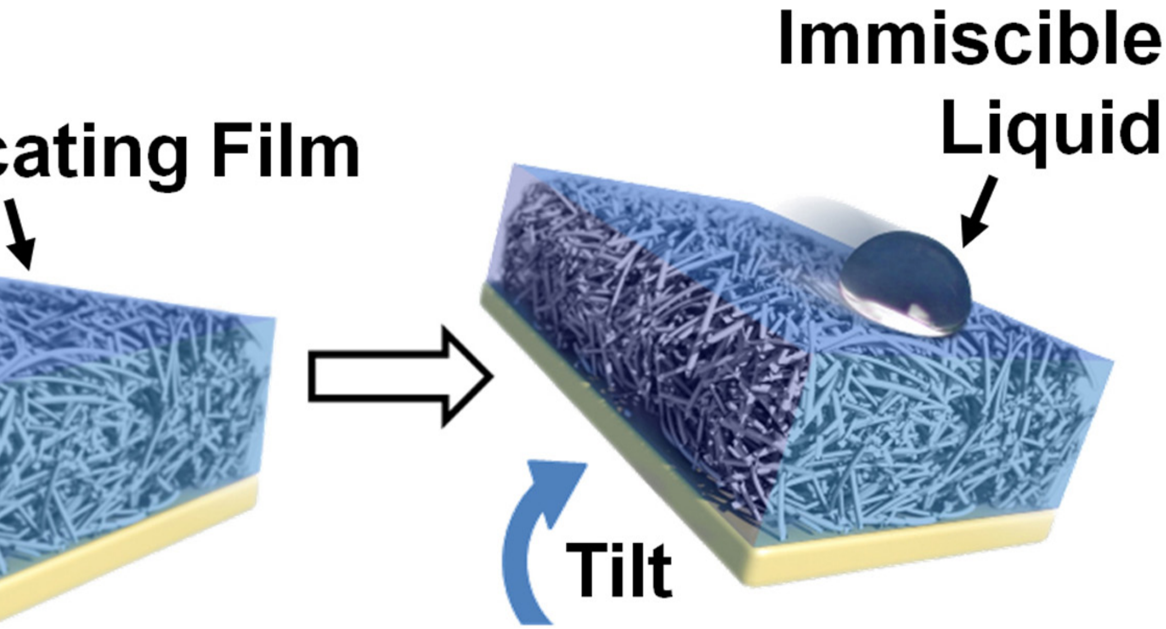
These lessons will be lost if the present rate of habitat destruction continues. It has been estimated that over half of the world's wetlands have disappeared since 1900.

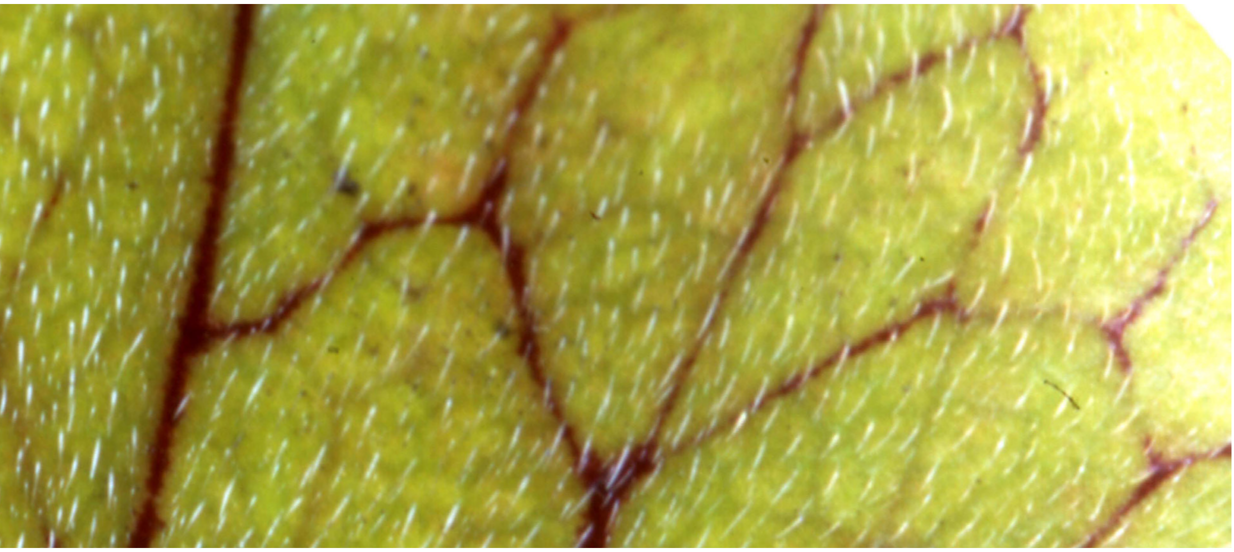




SLIPS structure

Image courtesy of Joanna Aizenberg, James C. Weaver, Tak-Sing Wong |
Wyss Institute at Harvard University





Detail of a Sarracenia (pitcher plant) leaf

Photo: Science and Plants for Schools, 2006 | Flickr cc ing, and they can fill gaps in solids automatically, thus adding the benefits of self-organization and self-healing.

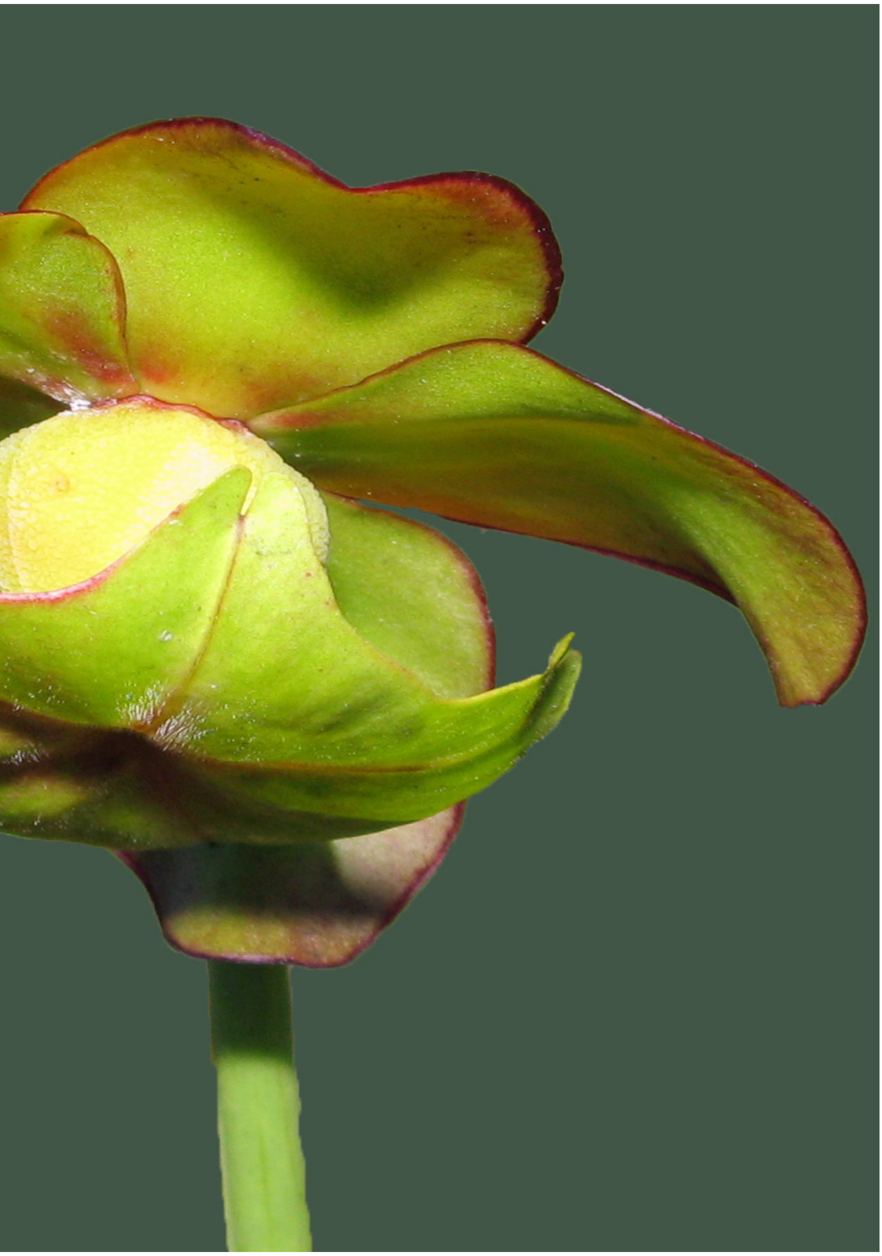
The Design Challenge

The Harvard team needed to produce a substrate that was fully wetted by lubricating liquid. This material must prefer to retain this liquid over any other that was poured on it. The lubricating liquid must be immiscible with other liquids, in other words, not able to be blended.

The team experimented with two general types of materials, a porous solid which was more or less a random matrix like the material of the pitcher plant's peristome, and a perfluorinated fluid which mimicked its aqueous solution. Perfluorinated compounds (PFC's) have unique properties to make materials stain, oil, and water resistant, and are widely used in diverse applications. Teflon, the best- known slippery material, is made from PFC's, and the 3M stain resistant coating product, Scotchgard, was also made from them. PFCs persist in the environment as persistent organic pollutants, but unlike PCBs (Polychlorinated biphenyls), they are not known to degrade by any natural processes due to the strength of their carbon–fluorine bond.

They used two types of porous solids: one made from Teflon nanofibrous membranes, and another made from epoxy-resin-based nanostructured surfaces molded from silicon masters. These solid materials were typically 60-80 micrometers thick with pore sizes of 200 nanometers, 300 nanometers, and 500 nanometers. For an idea of relative size, consider that the head of a pin is about 1-2 millimeters across. One millim-

Current loss rates are in the order of 24 hectares (60 acres) per hour globally. In the United States a majority (89%) of this loss is from conversion to agriculture. Global climate change is a relatively new and ominous threat to coastal wetlands, and the continued destruction of Asian peatlands (where Nepenthes lives) is, ironically, a major contributor to this condition. Peatland conversion accounts for 7% of all fossil fuel CO2 emissions. Protection of these habitats is fundamental to the ecological and economic health of the world. Protection will also give us a chance to learn more innovative techniques from organisms like the sacred lotus and the pitcher plant.



Pitcher plant flower

Photo: sandy richard, 2008 | Flickr cc

eter is equal to 1,000 micrometers or 1,000,000 nanometers. Human hair and red blood cells are in the micrometer range, about 60-120, and 7-8 micrometers across respectively, while DNA is in the nanometer range, about 2.5 nanometers in diameter.

For fluids, they tested 3M Fluorinert FC-70 as well as Dupont Krytox 100 and 103. When the team had matched the surface chemistry and roughness of the two materials, a known volume of the liquid was poured onto the substrate and capillary action achieved a uniform liquid surface level.

The Results

The random matrix of Teflon nanofibers that they filled with the low-tension perfluorinated proprietary liquid from 3M (Fluorinet FC-70) was a very slick success. They have called their product SLIPS (Slippery Liquid Infused Porous Surface), and it does, indeed, appear to repel everything: blood, oil, even ice cannot form on its surface. The researchers claim that their artificial surface outperforms its natural counterparts and all other liquid-repellent products in its capacity to repel water, hydrocarbons, crude oil and blood. Things slip off at a mere 2.5-degree angle and liquids that would stain other slippery surfaces completely exit the surface. Unlike current Lotus-Effect® surfaces, the new matrix functions at pressures up to 680 atmospheres, and is virtually unaffected by minor mechanical damage, being able to restore liquid-repellency within 1 second or less.

Reporting in Nature, the researchers highlighted the benefits of the new repellency method:

> *The premise for our design is that a liquid surface is intrinsically smooth and defect-free down to the molecular scale; provides immediate self-repair by wicking into damaged sites in the underlying substrate; is largely incompressible; and can be chosen to repel immiscible liquids of virtually any surface tension. We show that our SLIPS creates a smooth, stable interface that nearly eliminates pinning of the liquid contact line for both high- and low-surface-tension liquids, minimizes pressure-induced impalement into the porous structures, self-heals and retains its function following mechanical damage, and can be made optically transparent.*
>
> (Nature, Vol 477, Sept 22, 2011)

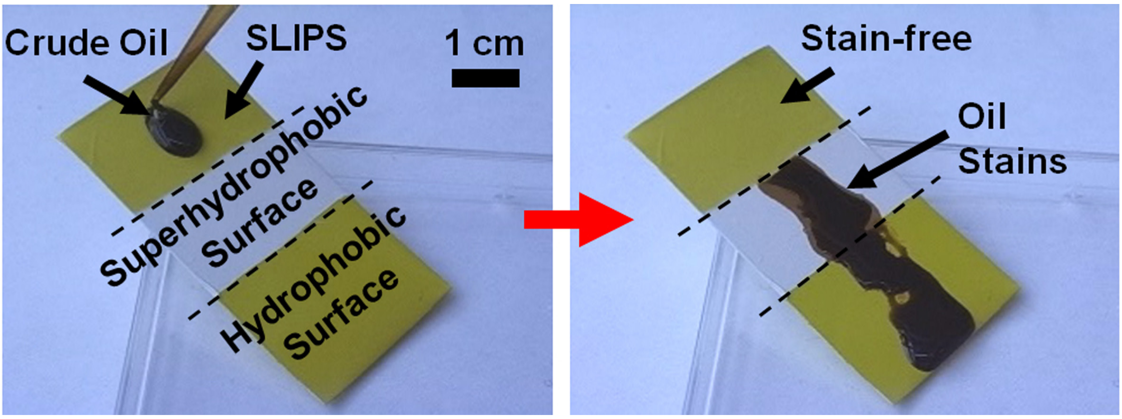
Applications

Lead researcher Dr Tak Sing Wong reports the new biomaterial has performed well at low temperatures and high pressures and he believes it to be more slippery than Teflon, the reigning slick solid of our industrial world. It would be useful for a range of biomedical, industrial and other applications, such as pipe coatings, self-cleaning public surfaces and de-icing applications. Not the least, its transparency potential and self-cleaning make it an excellent choice for lenses, sensors and solar cells.

> *No synthetic surface reported until now possesses all the unique characteristics of SLIPS: negligible contact angle hysteresis for low-surface-tension liquids and their complex mixtures, low sliding angles, instantaneous and repeatable self-healing, extreme pressure stability and optical transparency. Our bioin-*

Pitcher plant

Photo: John Guest, 2011 | Flickr cc

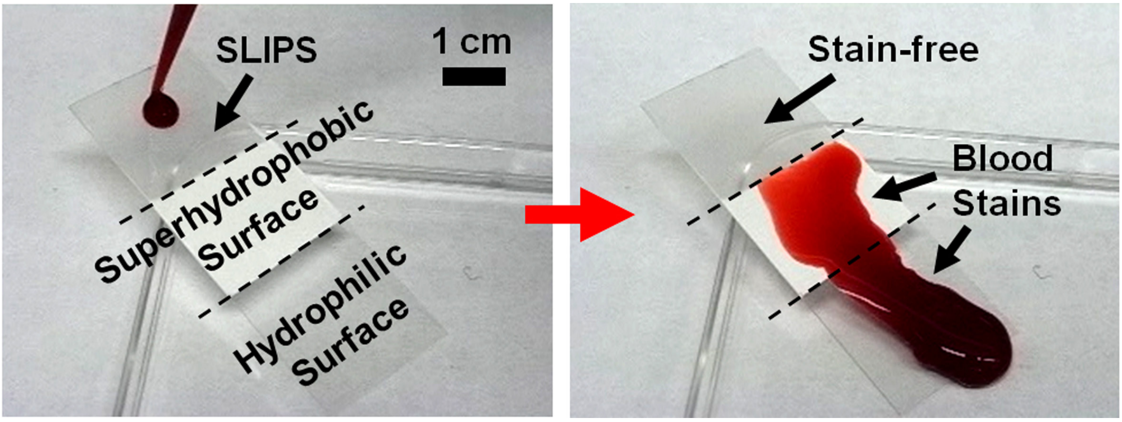


SLIPS surface

Image courtesy of Joanna Aizenberg and Tak-Sing Wong |
Wyss Institute at Harvard University

Pitcher plants

Photo: ggallice, 2008 | Flickr cc



SLIPS surface

Image courtesy of Joanna Aizenberg, Ben Hatton, Tak-Sing Wong | Wyss Institute at Harvard University

> *spired SLIPS, which are prepared simply by infiltrating low-surface-energy porous solids with lubricating liquids, provide a straightforward and versatile solution for liquid repellency and resistance to fouling.*

Implications

The SLIPS development has taken self-cleaning surface techniques from rolling beads of water (and the dirt that they collect) off a microscopically bumpy surface to sliding liquids and solids alike along a thin film. It has quite a few technical implications.

> *Because low-surface-energy porous solids are abundant and commercially available, and the structural details are irrelevant to the resulting performance, one can turn any of these solids into highly omniphobic surfaces without the need to access expensive fabrication facilities. Any liquid film is inherently smooth, self-healing and pressure resistant, so the lubricant can be chosen to be either biocompatible, index-matched with the substrate, optimized for extreme temperatures, or otherwise suitable for specific applications. With a broad variety of commercially available lubricants that possess a range of physical and chemical properties, we are currently exploring the limits of the performance of SLIPS for long-term operation and under extreme conditions, such as high flow, turbulence, and high- or low-temperature environments.*

Here are a few of the possible applications for this new technology:

- Biomedical Fluid Handling: nonabsorbent surfaces could save precious liquids, prevent spread of pathogens, avoid fouling of intravenous tubes and speed the delivery of medicine.
- Fuel transport: Reducing drag at the liquid/solid interface would mean increased flow and savings in the energy needed to move commodities like crude oil. Moving the liquids in heating and cooling (and perhaps hydraulic) systems in SLIPS lines might lead to improved efficiency or performance.
- Anti-fouling: prevention of biofilms on surfaces could mean energy savings in avoided mechanical or chemical cleanup of marine vessels and the prevention of infection sources on medical devices.
- Anti-icing: vehicles of all kinds might no longer need high pressure or chemical treatments to de-ice. Medical devices could operate in low temperature environments.
- Self-cleaning windows: could mean the end of expensive and sometimes hazardous manual washing, savings in the energy used for artificial lighting.
- Self-cleaning optical devices: could mean increased output for solar panels, avoided maintenance for sensors, increased accuracy and precision for field optics.

While it is early in the development of the SLIPS innovation, several factors suggest that it may take its place in the limited pantheon of biomimetic devices that have been distributed en masse.

Like Velcro, this material replaces one that needed more precision and effort to work and there-

Sarracenia Trumpet Pitcher Plant

Photo: Kate's Photo Diary, 2009 | Flickr cc

fore had a more limited range of applications. Consider the effort of tying a shoelace versus slapping a flap of fabric against another surface. Now think of the various surfaces, angles and situations in which a cloth ribbon laced through a row of holes simply does not work.

Like the Lotus-Effect®, another bona fide commercial success, the SLIPS device depends on its passive structure to take advantage of a universal physical dynamic in order to do work, in this case, capillary action and the immiscibility of certain liquids, among other processes. Passive structures that do this are said to "surf for free" and are critical to solving problems in a resource-limited world.

Finally, the wider range of applications, the potentially improved performance and greater dependability may actually come at a lower cost. Manufacture of this type of material, while having a significant environmental issue associated with persistent organic pollutants, appears cheaper than comparable processes, all because the new paradigm has leapt over the old. That's not bad for a lowly bog plant that eats bugs for a living.

References:

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