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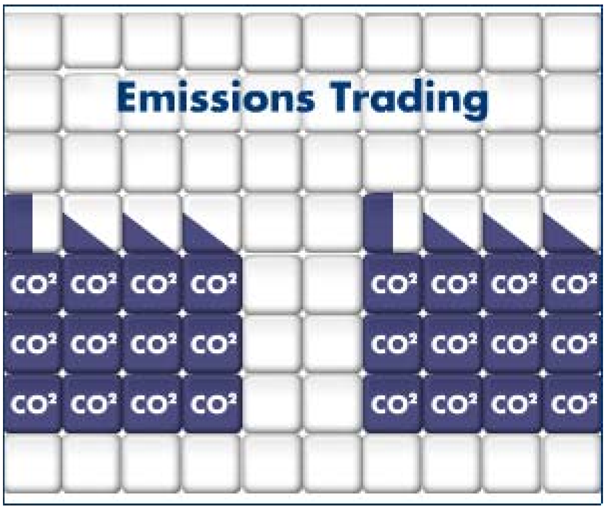
Self-Cleaning Materials: Lotus Leaf-Inspired Nanotechnology

The lotus plant's magnificent ability to repel dirt has inspired a range of self-cleaning and antibacterial technologies that may also help control microfluidic "lab-on-a-chip" devices

By Peter Forbes



Wilhelm Barthlott of the University of Bonn in Germany, discoverer and developer of the “lotus effect,” has a vision of a self-cleaning Manhattan, where a little rain washes the windows and walls of skyscrapers as clean as the immaculate lotus. Elsewhere, he sees tents and marquees using new textiles that stay equally spotless with no intervention from a human cleaner. He is not the only one with his sights set on a future populated with objects that rarely if ever need washing: in Japan, technologists are developing self-deodorizing and disinfectant surfaces for bathrooms and hospitals. Michael Rubner and Robert Cohen of the Massachusetts Institute of Technology envisage similar technologies keeping bathroom mirrors unfogged and controlling microfluidic “labs on a chip” (in which fluids move through microscopic pathways). Already with us are shirts, blouses, skirts and trousers that shrug off ketchup, mustard, red wine and coffee. A revolution in self-cleaning surfaces is under way.

The story of self-cleaning materials begins in nature with the sacred lotus (*Nelumbo nucifera*), a radiantly graceful aquatic perennial that has played an enormous role in the religions and cultures of India, Myanmar, China and Japan. The lotus is venerated because of its exceptional purity. It grows in muddy water, but its leaves, when they emerge, stand meters above the water and are seemingly never dirty. Drops of water on a lotus leaf have an unearthly sparkle, and rainwater washes dirt from that leaf more readily than from any other plant.

It is this last property that drew Barthlott’s attention. In the 1970s he became excited by the possibilities of the scanning electron microscope, which had become commercially available in 1965 and offered vivid images down to the nanometer realm. At that scale of magnification, specks of dirt can ruin the picture, and so the samples have to be cleaned. But Barthlott noticed that some plants never seemed to need washing, and the prince of these was the lotus.

Barthlott realized that the effect is caused by the combination of two features of the leaf surface: its waxiness and the microscopic bumps (a few microns in size) that cover it. He knew from basic physics that the waxiness alone should make the leaves hydrophobic, or water-hating. On such a material, drops of water sit up high to minimize their area of contact with the material. Water on a more hydrophilic, or water-loving, substance spreads across it to maximize the contact area. For a hydrophilic surface, the contact angle (where the droplet’s surface meets the material) is less than 30 degrees; a hydrophobic surface has a contact angle greater than 90 degrees.

In addition, he understood that the innumerable bumps take things a step further and cause the lotus surface to be superhydrophobic—the contact angle exceeds 150 degrees, and water on it forms nearly spherical droplets with very little surface contact that roll across it as easily as ball bearings would. The water sits on top of the bumps like a person lying on a bed of nails. Air trapped between the water and the leaf surface in the spaces around the bumps increases the contact angle, an effect that is described by the Cassie-Baxter equation, named after A.B.D. Cassie and S. Baxter, who first developed it in the 1940s.

Dirt, Barthlott saw, similarly touches only the peaks of the lotus leaf’s bumps. Raindrops easily wet the dirt and roll it off the leaf. This discovery that microscopic bumps enhance cleanliness is wonderfully paradoxical. I learned at my mother's apron that "nooks and crannies harbor dirt"—capturing the conventional folk wisdom that if you want to keep things clean, keep them smooth. But contemplation of the lotus showed that this homily is not entirely true.

First and foremost a botanist, Barthlott initially did not see commercial possibilities in his observation of how the minuscule bumps keep lotus leaves spotless. In the 1980s, though, he realized that if rough, waxy surfaces could be synthesized, an artificial lotus effect could have many applications. He later patented the idea of constructing surfaces with microscopic raised areas to make them self-cleaning and registered Lotus Effect as a trademark.

Engineering a superhydrophobic surface on an object by using the lotus effect was not easy—the nature of a hydrophobic material is to repel, but this stuff that repels everything has to be made to stick to the object itself. Nevertheless, by the early 1990s Barthlott had created the "honey spoon": a spoon with a homemade microscopically rough silicone surface that allows honey to roll off, leaving none behind. This product finally convinced some large chemical companies that the technique was viable, and their research muscle was soon finding more ways to exploit the effect. The leading application so far is StoLotusan facade paint for buildings, introduced in 1999 by the German multinational Sto AG and a huge success. "Lotus Effect" is now a household name in Germany; last October the journal *Wirtschaftswoche* named it as one of the 50 most significant German inventions of recent years.

No More Restaurant Disasters

Say "self-cleaning...," and many people would add "clothes" as the missing word. We do not clean the outside of our houses very often, but washing clothes is always with us. After a tentative start, self-cleaning fabrics are popping up all over. It began with Nano-Care.

Nano-Care is a finish applied to fabrics developed by inventor and entrepreneur David Soane, now made by his company Nano-Tex. Think of the fuzz on a peach; put the peach under the tap, and you will see the Nano-Care effect. Nano-Care's "fuzz" is made of minuscule whiskers and is attached to the cotton threads. The whiskers are so small—less than a thousandth of the height of lotus bumps—that the cotton threads are like great tree trunks in comparison.

Nano-Tex's rival is the Swiss firm Schoeller Textil AG, which calls its technology NanoSphere. The system has nanoscopic particles of silica or of a polymer on the clothing fibers, and these particles provide the lotuslike bumpy roughness.

Because many untested claims have been made to support nanotechnology products, standards institutions are beginning to set stringent tests for self-cleaning clothing that are based on these innovations. In October 2005 the German Hohenstein Research Institute, which offers tests and certifications to trade and industry around the world, announced that NanoSphere textiles were the first of such fabrics to pass a whole range of tests, including those examining water repellency and the ability of the fabric to maintain its performance after ordinary wash cycles and other wear and tear. In a test of my own, samples of NanoSphere showed an impressive ability to shrug off oily tomato sauces, coffee and red wine stains—some of the worst of the usual suspects.

Easy-clean clothes are becoming widely available, but buyers of marquees, awnings and sails are expected to constitute the biggest market (in terms of money spent) for lotus effect finishes. No one really wants to have to clean these large outside structures.

Superwettability

The exploration of the lotus effect began as an attempt to understand the self-cleaning powers of one type of surface—waxy ones with microscopic or even nanoscale structures. This research has now broadened into an entire new science of wettability, self-cleaning and disinfection. Researchers realized that there might be many ways to make superhydrophobic surfaces and that superhydrophobicity's reverse—superhydrophilicity—might also be interesting. The leading player in superhydrophilicity is the mineral titanium dioxide, or titania.

Titania's journey to stardom began more than four decades ago with a property that has nothing to do with wettability. In 1967 Akira Fujishima, then a graduate student at the University of Tokyo, discovered that when exposed to ultraviolet light, titania could split water into hydrogen and oxygen. The splitting of water powered by light, or photolysis, has long been something of a holy grail because if it could be made to work efficiently, it could generate hydrogen cheaply enough to make that gas a viable, carbon-free substitute for fossil fuels. Fujishima and other researchers pursued the idea vigorously, but eventually they realized that achieving a commercial yield was a very distant prospect.

The studies did reveal that thin films of titania (in the range of nanometers to microns thick) work more efficiently than do larger particles. And, in 1990, after Fujishima teamed up with Kazuhito Hashimoto of the University of Tokyo and Toshiya Watanabe of the sanitary equipment manufacturer TOTO, he and his colleagues discovered that nanoscale thin films of titania activated by ultraviolet light have a photocatalytic effect, breaking down organic compounds—including those in the cell walls of bacteria—to carbon dioxide and water.

Titania is photocatalytic because it is a semiconductor, meaning that a moderate amount of energy is needed to lift an electron from the mineral’s so-called valence band of filled energy levels across what is known as a band gap (composed of forbidden energy levels) into the empty “conduction band,” where electrons can flow and carry a current. In titania’s case, a photon of ultraviolet light with a wavelength of about 388 nanometers can do the trick, and in the process it produces two mobile charges: the electron that it hoists to the conduction band as well as the hole that is left behind in the valence band, which behaves much like a positively charged particle. While these two charges are on the loose, they can interact with water and oxygen at the surface of the titania, producing superoxide radical anions (O2–) and hydroxyl radicals (OH)—highly reactive chemical species that can then convert organic compounds to carbon dioxide and water.

In the mid-1990s the three Japanese researchers made another crucial discovery about titania when they prepared a thin film from an aqueous suspension of titania particles and annealed it at 500 degrees Celsius. After the scientists exposed the resulting transparent coating to ultraviolet light, it had the extraordinary property of complete wettability—a contact angle of zero degrees—for both oil and water. The ultraviolet light had removed some of the oxygen atoms from the surface of the titania, resulting in a patchwork of nanoscale domains where hydroxyl groups became adsorbed, which produced the superhydrophilicity. The areas not in those domains were responsible for the great affinity for oil. The effect remained for several days after the ultraviolet exposure, but the titania slowly reverted to its original state the longer it was kept in the dark.

Although it is the very opposite of the lotus leaf’s repulsion of water, titania’s superhydrophilicity turns out also to be good for self-cleaning: the water tends to spread across the whole surface, forming a sheet that can carry away dirt as it flows. The surface also resists fogging, because condensing water spreads out instead of becoming the thousands of tiny droplets that constitute a fog. The photocatalytic action of titania adds deodorizing and disinfection to the self-cleaning ability of coated items by breaking down organics and killing bacteria.

The titania-coating industry is now burgeoning. TOTO, for instance, produces a range of photocatalytic self-cleaning products, such as outdoor ceramic tiles, and it licenses the technology worldwide.

Because nanocoatings of titania are transparent, treated window glass was an obvious development. In 2001 Activ Glass, developed by Pilkington, the largest glass manufacturer in the U.K., became the first to hit the market. In general, glass is formed at about 1,600 degrees C on a bed of molten tin. To make Activ Glass, titanium tetrachloride vapor is passed over the glass at a later cooling stage, depositing a layer of titania finer than 20 nanometers thick. Activ Glass is fast becoming the glass of choice for conservatory roofs and vehicles’ side mirrors in the U.K.

Unfortunately, ordinary window glass blocks the ultraviolet wavelengths that drive titania’s photocatalytic activity, so titania nanolayers are less useful indoors than out. The answer is to “dope” the titania with other substances, just as silicon and other semiconductors are doped for electronics. Doping can decrease the material’s band gap, which means that the somewhat longer wavelengths of indoor lighting can activate photocatalysis. In 1985 Shinri Sato of Hokkaido University in Japan serendipitously discovered the benefit of doping titania with nitrogen. Silver can also be used to dope the titania. Only in recent years, however, have these approaches been translated into commercial processes.

The antibacterial and deodorizing properties of doped titania are expected to have wide applications in kitchens and bathrooms. Titania is also being used in self-cleaning textiles and offers the advantage of removing odors. Various techniques have been devised to attach it to fabrics, including via direct chemical bonds.

Convergence of Opposites

The lotus-inspired materials and the titania-based thin films can be seen as opposite extremes rarely found in our everyday world where, as English poet Philip Larkin said, "nothing's made / As new or washed quite clean." For a long time, the techniques and materials were entirely different, and studies of the superhydrophobic effect and photocatalytic superhydrophilicity were totally separate. More recently, a remarkable convergence has occurred, with investigators working on combining the two effects and on producing both of them with very similar materials. Researchers are even exploring ways to get the same structure to switch from being superhydrophobic to being superhydrophilic, and vice versa.

An early hint of the convergence came in 2000 from titania pioneers Fujishima, Watanabe and Hashimoto. They wanted to use titania to extend the life of lotus effect surfaces. At first blush, this approach sounds destined for failure: titania's photocatalytic activity would be expected to attack the hydrophobic, waxy coatings of lotus surfaces and destroy the effect. And indeed, such attacks do happen with large concentrations of titania. But the group found that adding just a tiny amount of titania could significantly prolong lotus effect activity without greatly changing the high contact angle needed for the strong repellency.

In 2003 Rubner and Cohen's laboratory at M.I.T. discovered how a minor change in construction could determine whether a superhydrophobic or superhydrophilic surface was produced. During a visit to China that year, Rubner recalls, he "got excited about some superhydrophobic structures" that were mentioned at a meeting. On his return, he directed some of his group's members to attempt to make such structures. His lab had developed a layer-by-layer technique for making thin films out of a class of compounds called polyelectrolytes. Ordinary electrolytes are substances that when dissolved in water split up into positively and negatively charged ions; common salt or sulfuric acid would be examples. Polyelectrolytes are organic polymers, plastic materials that, unlike most polymers, carry charge, either positive or negative. Rubner and Cohen stacked up alternating layers of positively charged poly(allylamine hydrochloride) and negatively charged silica particles. (In earlier work they had used coatings with silica particles to mimic the lotus's rough hydrophobic surface.)

To these multilayers, they added a final coating of silicone (a hydrophobic material), but along the way they noticed something intriguing: before they applied the silicone, the layer cake was actually superhydro*philic*. In Rubner and Cohen's experiments, the silica layers had created a vast warren of nanopores, forming a sponge that soaked up any surface water instantly, a phenomenon called nanowicking. The silica-polymer multilayers they developed will not fog even if held over steaming water. If the pores get saturated, water starts running off the edge. When the wet conditions abate, the water in the nanowicks slowly evaporates away.

Because glass itself is mostly silica, the multilayers are well suited for application to glass. The superhydrophilic coatings are not only transparent and antifogging but are also antireflective. Rubner's team is working with industrial partners to commercialize the discovery. Applications of this work include bathroom mirrors that never fog and car windshields that never need a blower on cold, wet winter mornings. Unlike titania, Rubner's surfaces work equally well in the light or dark.

Smart Beetles
Millions of years before scientists put together the lotus effect and superwettability for technological applications, a small beetle of the Namib Desert in southern Africa was busy applying the two effects to another end: collecting water for its own survival.
The Namib Desert is extremely inhospitable. The daytime temperatures can reach 50 degrees C (about 120 degrees Fahrenheit), and rain is very scarce. About the only source of moisture is thick morning fogs, typically driven by a stiff breeze. The beetle, *Stenocara* sp., has developed a way to harvest the water in those mists: it squats with its head down and its back up, facing the foggy wind. Water condenses on its back and trickles down into its mouth. The scientific rationale behind the *Stenocara* beetle's technique has inspired ideas for water-collecting technology in arid regions.

As so often happens, the beetle's mechanism was discovered by a researcher looking for something else. In 2001 zoologist Andrew R. Parker, then at the University of Oxford, came across a photograph of beetles eating a locust in the Namib Desert. The locust, which had been blown there by the region's strong winds, would have perished from the heat as soon as it hit the sand. Yet the beetles feasting on this literal windfall were obviously comfortable. Parker guessed that they must have sophisticated heat-reflection surfaces.

Indeed, *Stenocara* beetles do reflect heat, but when Parker examined their backs, he immediately suspected that some adaptation of the lotus effect was at work in their morning water-collection process. Most of the back of a Stenocara beetle is a bumpy, waxy, superhydrophobic surface. The tops of the bumps, though, are free of wax and are hydrophilic. Those hydrophilic spots capture water from the fog, forming droplets that quickly grow large enough for gravity and the surrounding superhydrophobic area to dislodge them. In lab experiments with glass slides, Parker found that this arrangement of regions is about twice as efficient as a smooth, uniform surface, regardless of whether it is hydrophilic or hydrophobic.

Parker has patented a design to imitate the beetle's process, and the U.K. defense contractor QinetiQ is developing it for fog harvesting in arid regions. Others are also trying to mimic *Stenocara*. In 2006 Rubner and Cohen's team created superhydrophilic spots of silica on superhydrophobic multilayers. This is one better than the beetles, whose spots are merely hydrophilic.

The new science of superwettability, as exemplified by the artificial *Stenocara* surfaces, makes it possible to control liquid flows at the microscale and the nanoscale, for use in applications that go well beyond that of keeping a surface clean. Rubner says: "Once you realize that textured surfaces can be either superhydrophobic or superhydrophilic depending on the top's surface chemistry, all sorts of possibilities open up." Of particular use would be switchable surfaces—ones whose wettability can be reversed at precise locations.

Such tunability might be achieved by many means: ultraviolet light, electricity, temperature, solvent and acidity. In 2006 a team led by Kilwon Cho of Pohang University of Science and Technology in South Korea achieved complete switchability by adding a compound based on the molecule azobenzene to the siliconized (superhydrophobic) surface of a silica-polyelectrolyte multilayer. The new surface is also superhydrophobic, but under ultraviolet light the azobenzene compound changes configuration and converts it to superhydrophilic.

Visible light reverses the change. This kind of control could have major applications in the field of microfluidics, such as the microarrays now used for drug screening and other biochemical tests [see "Big Lab on a Tiny Chip," by Charles Q. Choi; *Scientific American*, October 2007]. For instance, hydrophilic pathways could be closed or opened by switching parts of them to be hydrophobic or hydrophilic.

Staying Dry Underwater
It is one of the pleasant surprises of the 21st century that the radiance of the lotus is penetrating into previously unknown nooks and crannies, as well as beyond self-cleaning applications.

Barthlott, who saw the potential in a drop of water on a lotus leaf, now sees almost limitless vistas. But he warns those who want to translate from nature to technology that they are likely to encounter great skepticism, as he did. "Do trust your own eyes and *not* the textbooks, and if your observation is repeatedly confirmed, publish it," he advises. "But take a deep breath—expect rejections of your manuscript."

He is, not surprisingly, a passionate advocate for biodiversity, pointing out that many other plants and animals may have useful properties—possibly including species unknown to science and in danger of extinction. His current research involves superhydrophobicity underwater. After studying how plants such as the water lettuce *Pistia* and the floating fern *Salvinia* trap air on their leaf surfaces, Barthlott created fabrics that stay dry underwater for four days. An unwettable swimsuit is in prospect. The big prize would be to reduce the drag on ships' hulls. The lotus collects no dirt, but it is garnering an impressive string of patents.

Note: This story was originally published with the title, "Self-Cleaning Materials".

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