A model for materials scientists: Water runs off the surface of a lotus leaf without a trace. Researchers in Mainz use this concept to develop coatings that repel both water and oil.

A Slippery Slope for Every Drop

The research being undertaken by **Doris Vollmer** and **Hans-Jürgen Butt** could not only put an end to the annoying smears on window panes, it could also make it possible to produce self-cleaning solar panels or more effective heart-lung machines. The scientists from the **Max Planck Institute for Polymer Research** in Mainz are developing surfaces that are extremely water and blood repellent.

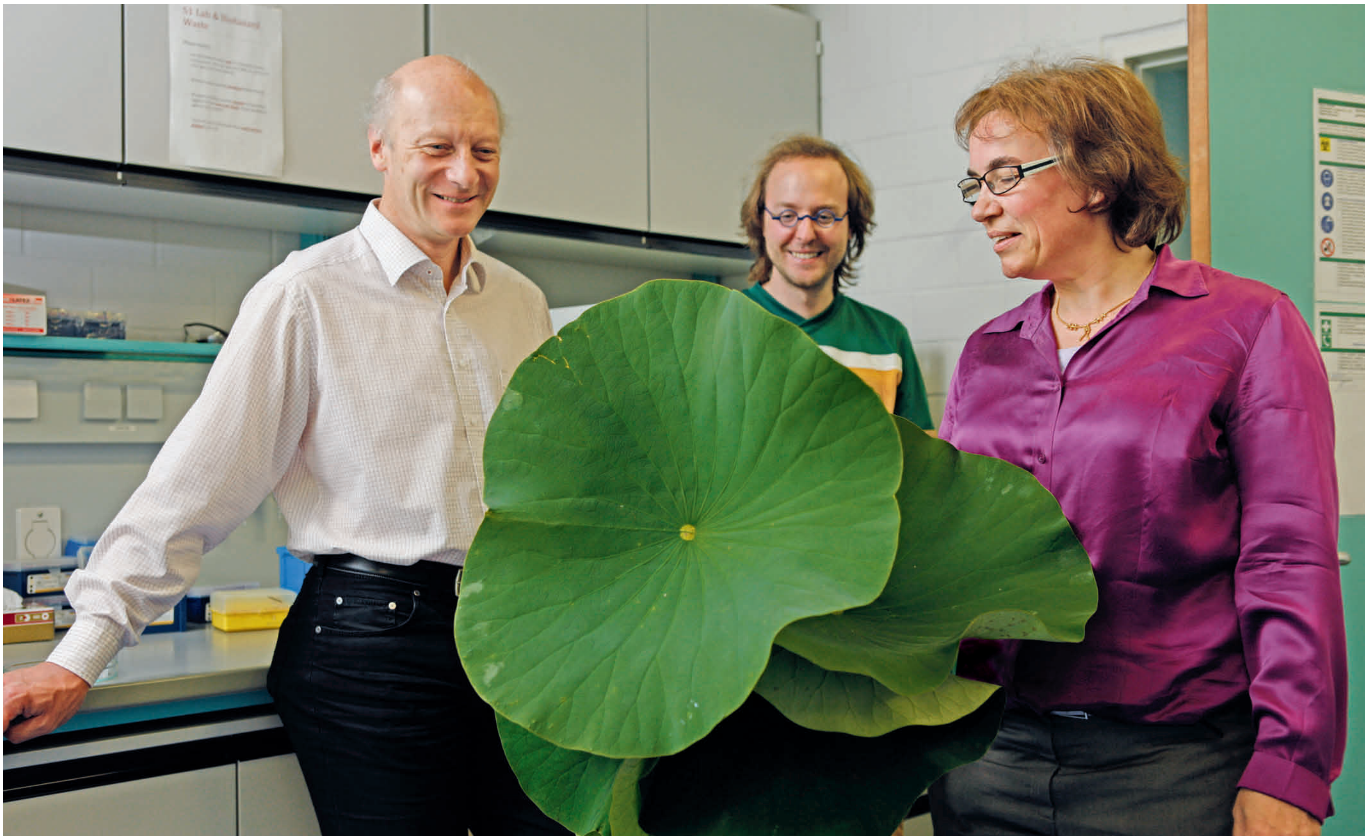
TEXT **ROLAND WENGENMAYR**

I just picked these lotus leaves from the botanical garden," says Doris Vollmer emphatically, as she proudly presents a fresh bunch of large leaves with long stalks. Vollmer is a group leader in the department of Hans-Jürgen Butt, a Director at the Max Planck Institute for Polymer Research in Mainz. The surfaces of the leaves shimmer mysteriously and indeed, evolution has given them a particularly sophisticated design.

Periklis Papadopoulos, a young postdoc in Vollmer's team, takes a lotus leaf and sprinkles a drop of water onto it. The drop briefly remains in a small indentation in the center of the leaf, as if slightly undecided. It then slides off the leaf like a miniature spherical hovercraft, without leaving a damp trace behind. It finally ends up on the Greek physicist's trousers. The wet spot on the denim creates an impressive contrast to the lotus leaf, which looks perfectly dry, as if no water drop had ever landed on it. The plant uses the lotus effect to keep its leaves, which float on the water, not only dry but, most importantly, clean. As the water runs off, it rinses away the dirt, which is why the lotus is held to be a symbol of purity in some cultures. This allows the plant to catch as much sunlight as possible. And it is precisely this ability to clean itself that has been fascinating scientists ever since the German botanist Wilhelm Barthlott first studied lotus leaves under an electron microscope in the 1970s.

A MICRO-FOREST MAKES SURFACES SUPERHYDROPHOBIC

The first coatings that apply the lotus effect are even available on the market. They haven't been very successful yet, because they still have too many disadvantages. Doris Vollmer's team is now using new ideas in the battle against the annoying smeary film that gets left behind. Reliably self-cleaning



Hans-Jürgen Butt, Frank Schellenberger and Doris Vollmer (from left) are investigating the conditions under which surfaces like those of a lotus leaf repel water and when they even repel oil. They use their findings to help them develop coatings from which nearly all liquids run off.

Photo: Axel Stephan

car windows, glass facades and solar panels would truly be significant progress. Just like lotus leaves, solar cells would no longer suffer from light loss as they get dirty.

The precise scientific term for extremely water-repellent surfaces is superhydrophobic. Superamphiphobic surfaces are an even greater challenge, explains Hans-Jürgen Butt, because they repel even oily substances without a trace. It's this second property that makes them a perfect anti-smear coating. However, for applications such as coating solar cells, they also have to be transparent, and the transparency presents a real challenge.

Superhydrophobic and superamphiphobic surfaces aren't perfectly smooth, as one might assume. Quite the contrary: Microscopy images of lotus leaves reveal a complex micro-forest of tree-like protuberances that measure roughly ten micrometers (thousandths of a millimeter) wide and high. At even greater magnification, one can see that they are covered with fine rods measuring a few dozen nanometers (millionths of a millimeter) in diameter and a few hundred nanometers in length. Vollmer points at them and says: "These are important in making the surface of the lotus leaves really superhydrophobic."

CANDLE SOOT AS A TEMPLATE FOR A SUPERAMPHIPHOBIC COATING

The lotus plant has been optimizing its water-repellent properties for many thousands of years. Since the middle of the 1990s, research has become better and better at imitating the lotus effect with artificial micro- and nanostructures. Doris Vollmer's computer contains a whole collection of electron microscope images of tiny pillars, raspberry-like micro-spheres with nanobumps, and other structures from the laboratory in Mainz, all of which are very good at repelling water.

The difficulty arises when these surfaces need to additionally repel oil, blood or soap solutions, because these liquids can wet many materials. "Until a few years ago, it was unclear whether superamphiphobic surfaces were possible at all," explains Vollmer. It wasn't until 2007 that American researchers succeeded in making a breakthrough with mushroom-shaped micro-structures. Since then, the physicist in Mainz, who obtained her German post-doctoral lecturing qualification in chemistry in the course of her career, has advanced the development of superamphiphobic materials.

Surfaces that even particularly low-viscosity oils can't wet are quite demanding from a scientific perspective. This makes the simple manufacturing process discovered by the Mainz-based researchers all the more surprising. And it is precisely this simplicity that could give rise to completely new technical applications. Hans-Jürgen Butt is working on a self-cleaning membrane that could enrich the blood of patients on heart-lung machines with oxygen much more efficiently than today's machines, for example.

But more on this later. First we will step into the lab. Here we find Periklis Papadopoulos, who demonstrates the surprising simplicity of the Mainz recipe for superamphiphobic coatings. The first step, at least, is simple enough to do at home. The physicist takes a thin glass plate and a candle. He lights the candle and then holds the glass

» Even low-viscosity hexadecane rolls off the superamphiphobic layer without a trace. Only a few years ago, many experts would hardly have believed it possible.

above it. It quickly becomes black with candle soot. And this layer of soot is very special.

Under the microscope one can see a conglomeration of tiny spheres of soot that are surprisingly uniform in size, but deposited one on top of another in quite a disorderly fashion. The layer is still pitch black, however, and can easily be wiped off. Further steps are necessary before a transparent and more wear-resistant coating is achieved, but these can be undertaken only in a well-equipped laboratory and require experimental skill.

The sponge-like structure of the spheres of soot provides only the template – that's the art of it. The researchers in Mainz now deposit a volatile, organic silicon compound onto the soot. The recipe also requires a pinch of ammonia. The two substances react chemically on the surface of the soot particles to form silicon dioxide – that is, glass. All the soot spheres are gradually coated with a thin, porous layer of glass. The researchers then heat the finished, glass-coated structure to 500 degrees Celsius and thus burn off the soot, which consists essentially of carbon, with oxygen.

What remains at the end are hollow glass spheres – colorless, nano-sized Christmas tree baubles that stick together. They are roughly 60 nanometers in diameter, making them about as tiny as many viruses. The sponge-like glass layer is now transparent. As the view through a microscope shows, the sponge of glass spheres features overhangs. These are necessary for the surface to repel water and oil. The Max Planck scientists finally coat the surface with a fluorinated silicon compound so that oil droplets are guaranteed not to wet the surface. "The surface then repels oil much better than a non-stick frying pan," explains Periklis Papadopoulos.

THE DROPLETS' RIDE ACROSS NANO-STUBBLE FIELDS

The postdoc presents some glass slides with the finished superamphiphobic glass coating. They still look slightly frosted. "We are working on improving the transparency," says the physicist. He sprinkles some water onto one of the glass slides and it rolls off as if it were on a perfect playground slide, even when the glass slide has only a slight inclination. This is the lotus effect. But even more impressive, at least for those in the know, is the demonstration with hexadecane. This low-viscosity oil is a component of, for example, heating and lubricating oils. Even the hexadecane rolls off without a trace. Only a few years ago, many experts would have hardly believed this to be possible.

The delicate sponge of glass spheres is still quite sensitive. Nevertheless, it still works after sand has been sprinkled onto it for a while from a height of 30 centimeters. "Although the top particles are gone, the thickness of the layer means there are still enough sitting on the surface," explains Papadopoulos. The group in Mainz is just working on an improved method that bakes the glass spheres to each other and makes the coating more wear resistant.

But why do such micro-landscapes repel drops of water or oil so perfectly? Vollmer and Papadopoulos turn to the computer to demonstrate at large magnification what happens to the drops of liquid. The researchers use a particularly high-resolution microscope, which scans the droplets on the surfaces with a very fine laser beam. The instrument is called a confocal microscope, and provides the researchers with complete,

A glass micro-forest that repels water and oil: The image from a scanning electron microscope (left) shows the spherical structures that make up the surface coating. Liquids form the same wetting angle on the spherical surfaces as on a plane surface of the material. With water, this angle can be up to 120 degrees, much less for oil, here 50 degrees. An oil-repellent surface thus requires overhanging structures. If the overhangs aren't pronounced enough for oil to assume the wetting angle, it sinks in through the pores.

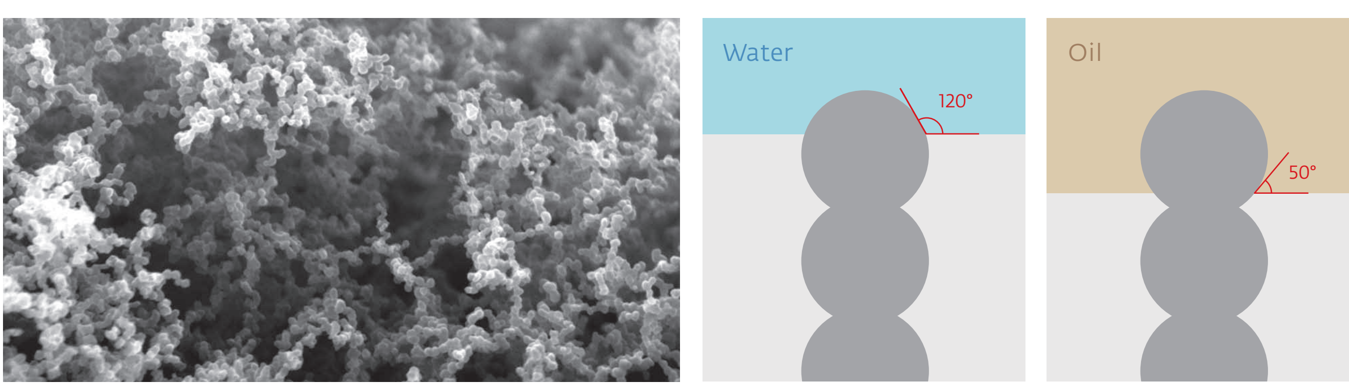
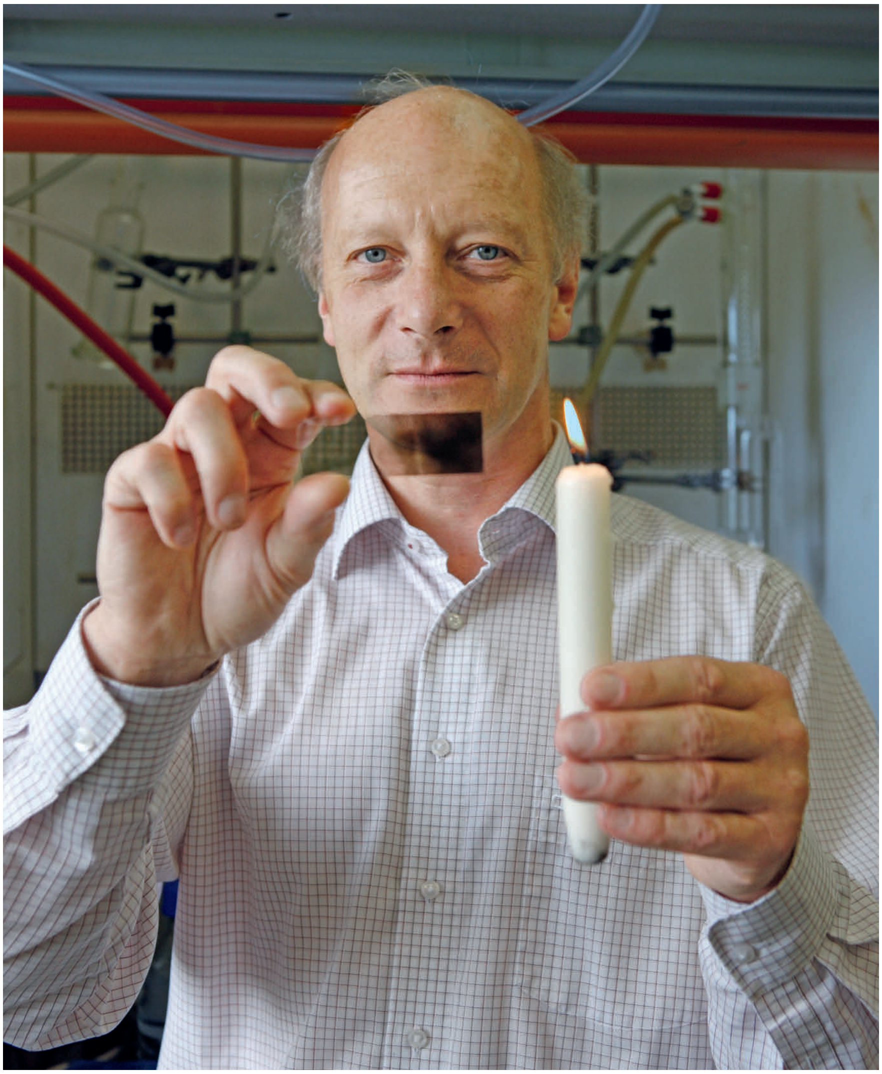


Photo and diagram: MPI for Polymer Research



It's that simple: Hans-Jürgen Butt demonstrates the first step to producing superamphiphobic coatings. He holds a glass slide into a candle flame so that soot deposits on it. The soot's porous structure of aggregated tiny spheres serves as the template for the subsequent steps.

Photo: Axel Stephan

three-dimensional information on the ride of the tiny droplets across micro-forests and nano-stubble fields.

The important thing is that the droplets lie only on top of the microscopic pillars, bumps or spheres. They roll off easily as long as they don't come into contact with the actual surface at the base of these structures and have the opportunity to wet them. The impression that the drop on the lotus leaf moves like a small hovercraft isn't far removed. On the microscopy images, the drops on the superhydrophobic micro-structures resemble tiny, spherical fakirs sitting on a bed of nails. And, in fact, this sitting on the very tips is called the fakir or Cassie state, because it was British researcher A. B. D. Cassie who first described it scientifically in 1944. Underneath the drop is mainly air, so it easily rolls off the surface.

There is one thing you wouldn't wish on a fakir: that he sinks into his bed of nails. Yet the researchers get their tiny water drops to slip through the micro-forest – and observe them as they do so. The superhydrophobic property then breaks down. Precisely what was happening on the microscopic level was previously a mystery. In order to find out, the Max Planck researchers put droplets measuring only a few hundred micrometers in diameter onto a grid of fine plastic pillars that they produced just for this purpose: the pillars were 10 micrometers thick and 23 micrometers high, for example, giving them a slightly stocky design. As long as the drop rested only on their upper, circular surfaces, the roofless hall of micro-pillars behaved superhydrophobically.

The researchers then made the droplet, and thus its contact surface, shrink on the grid of pillars. They did this by simply letting the droplet slowly dry up. The video – taken from below through the transparent floor of the micro-pillar hall – shows how the contact surface of the drop shrinks. At the receding edge, the water tries to wet the pillars at the top as long as possible. As the protrusions get longer and longer, the drop clings to the pillars before it is forced to let go. Eventually, these water threads tear off, and quite suddenly the drop becomes a dark spot. At that moment, the area of the pillar tips is no longer sufficient to keep the drop at the top. It sinks through to the bottom.

ONE POSSIBLE APPLICATION IS HEMODIALYSIS

As the lateral view shows, the bottom of a water drop hangs ever lower between the decreasing number of pillars. "It's as if someone were lying in a hammock and getting heavier and heavier," comments Doris Vollmer, narrating the images. With the aid of these high-resolution images, her group found out that some details of Cassie's original model need to be corrected.

"In contrast to the situation with a hammock, it's not gravity that causes the drop to sink in, but the so-called internal capillary pressure," says Hans-Jürgen Butt. The capillary pressure causes the drop to become rounded at the bottom as well. It can only do this if it penetrates between the pillars. "The capillary pressure increases when the drop shrinks, and the effect of the surface tension becomes larger and larger," explains the Max Planck Director. Computer simulations undertaken by the research group working with Stephan Herminghaus, a Director at the Max Planck Institute for Complex Systems in Göttingen, confirm these observations.

As soon as the drop spreads out on the bottom of the micro-pillar hall and

» One factor that influences whether a drop sinks through a porous structure is the ratio of the drop size to the fineness of the surface structure; the other is the chemical attraction between the liquid and the surface.

the super-water-repellent state has broken down, the drop is in a state named after Norbert Wenzel. In 1936, the German scientist was the first to describe the principle whereby a drop wets a rough surface.

The Mainz-based researchers' experiments therefore demonstrate the conditions under which a drop sinks through a porous surface structure. This depends, on the one hand, on the ratio of the drop size to the fineness of the surface structure or the size of the pores. It also depends on how the liquid and surface chemically attract or repel each other. The fluoridated coating of the superamphiphobic structure thus additionally repels the oil droplets. This causes them to lose all interest, so to speak, in settling down properly on the surface that is so unappealing to them.

After this excursion into the theory of the contact between drop and surface, the conversation with Hans-Jürgen Butt turns to possible applications. During his academic career, the physicist has moved from biophysics to the physics and chemistry of surfaces. Correspondingly unconventional are his thoughts on possible applications for the new superamphiphobic surface structure. "We came up with the idea of using this new structure to develop a new technology for hemodialysis," he recounts. Here, a liquid – blood – is in contact with another liquid, that is, the dialysis solution, via a membrane.

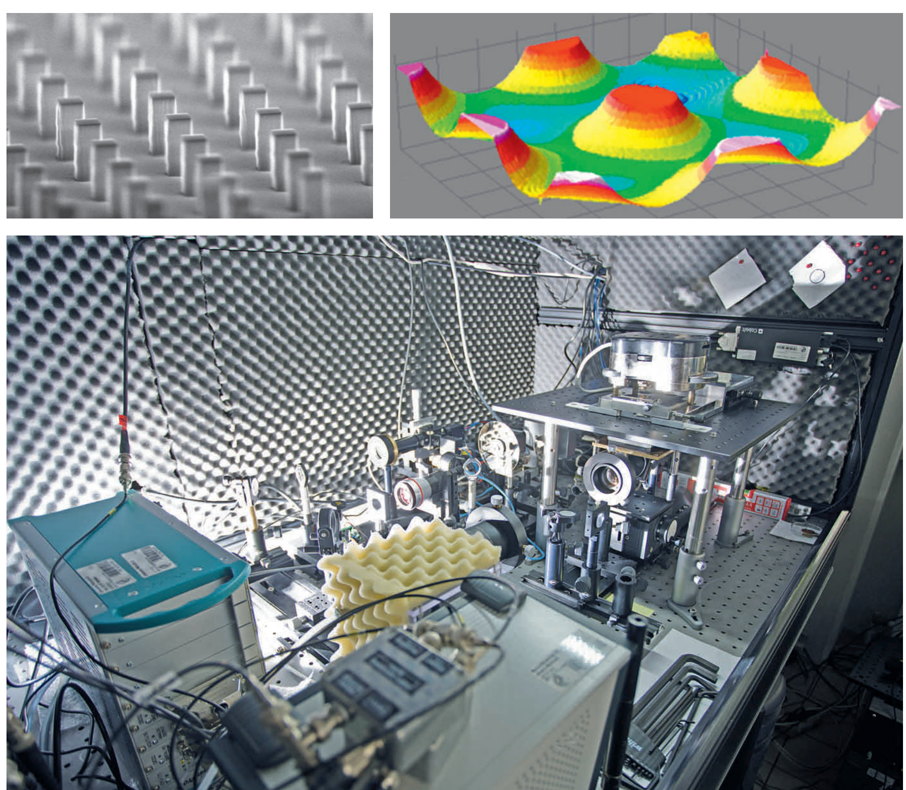
From here, it was but a short mental jump to the exchange of gas between blood and air, as occurs in lungs. In terms of surface technology, intensive contact between a liquid and a gas presents a certain challenge if the liquid is to remain locked in a container. This is the case for blood that comes into contact with pulmonary alveoli. For some time now, artificial lungs have been a well-established feature in heart-lung machines, otherwise known as life-support machines, such as those used in operating rooms. In the modern devices, synthetic membranes with tiny pores ensure that oxygen gets into the blood and carbon dioxide is removed from it.

However, conventional membranes have disadvantages. One consists in the fact that the liquid can penetrate into the membrane pores – in other words, it wets the membrane. This means that the boundary surface between the liquid and air shrinks, resulting in less gas being exchanged. Artificial lungs are thus much less efficient than our real lungs. Moreover, blood is a very special juice, as Goethe's Mephisto remarked. The blood platelets responsible for coagulation threaten to close the pores, for example. Clots can form, which break off and block the patient's blood vessels.

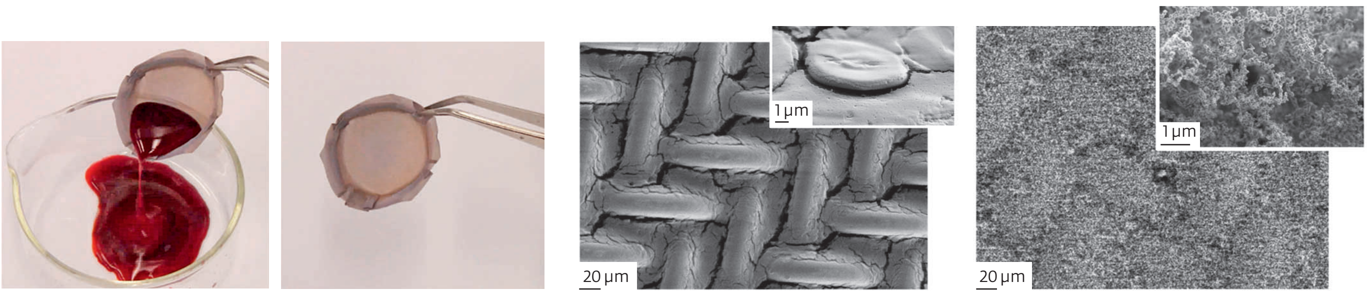
THE COMPLETELY NOVEL MEMBRANE WAS A TEAM IDEA

The Mainz-based researchers considered how the membranes could be improved with the aid of their superamphiphobic structures. "I think it's very important to provide a creative atmo-

Topography of wetting: The Mainz-based researchers use a confocal microscope (bottom) to investigate the conditions under which liquid wets a surface. Some of their model surfaces resemble microscopic halls of pillars without a roof (top left). With the aid of reflection measurements, they reconstruct how the bottom of a drop is curved when it lies on top of the pillars (top right). The false colors in this section show how far the drop sinks in.



Photos: MPI for Polymer Research (top, 2), Axel Stephan (bottom)



Blood leaves no trace on a membrane made of superamphiphobic material (left). Blood doesn't flow off a hydrophilic net without leaving something behind, so dried residues can be seen in the scanning electron microscope (second image from right). In contrast, the fine-pored structure of a superamphiphobic layer has no traces of blood (right).

Photos: MPI for Polymer Research

sphere for discussions," emphasizes Hans-Jürgen Butt. The team thus had the idea of developing a completely new type of membrane. The basic skeleton was an extremely fine lattice of stainless steel wire. These wires are around 30 micrometers thick – a human hair is roughly three times as thick.

HEART-LUNG MACHINES FOR PREMATURE BABIES

Equally tiny are the apertures in the steel mesh, which the researchers now coat on both sides with the superamphiphobic layer of glass spheres. This provides the crucial property of the new membrane: blood can no longer wet it. The blood remains on its own side, and the air can get to it almost unhindered through the membrane pores. Conversely, the blood can expel carbon dioxide very efficiently.

The Mainz-based researchers did, however, hit on one difficulty: How do you let your own blood if you don't have any medical training? "Fortunately, the husband of my colleague Katharina Landfester is a transplant surgeon, and time and again he has donated his own blood," says Butt, explaining, "a few milliliters are all we need." The membrane already works very well in the laboratory. "It's efficient," continues Butt, "but even more important is that no blood sticks to it."

The pieces of membrane produced in the laboratory are still small, but in principle they can easily be scaled up. But the researchers in Mainz still have a long way to go from pure basic research to medical application. "Comprehensive clinical tests will then be necessary," says the Max Planck Director. Butt is skeptical that the new membrane technology can supersede the well-established heart-lung machines for adult patients, though its much-improved properties mean it could save very small patients, who have very little blood. "For premature babies, such heart-lung machines would be much better," says the scientist.

The scientist is also thinking about quite different fields of application. In principle, similar membranes could also efficiently separate off carbon dioxide from power station emissions in the future. "Gas exchange is certainly the potentially greatest field of application," says Butt. In this way, the membranes from Mainz could also help protect the climate. ◂

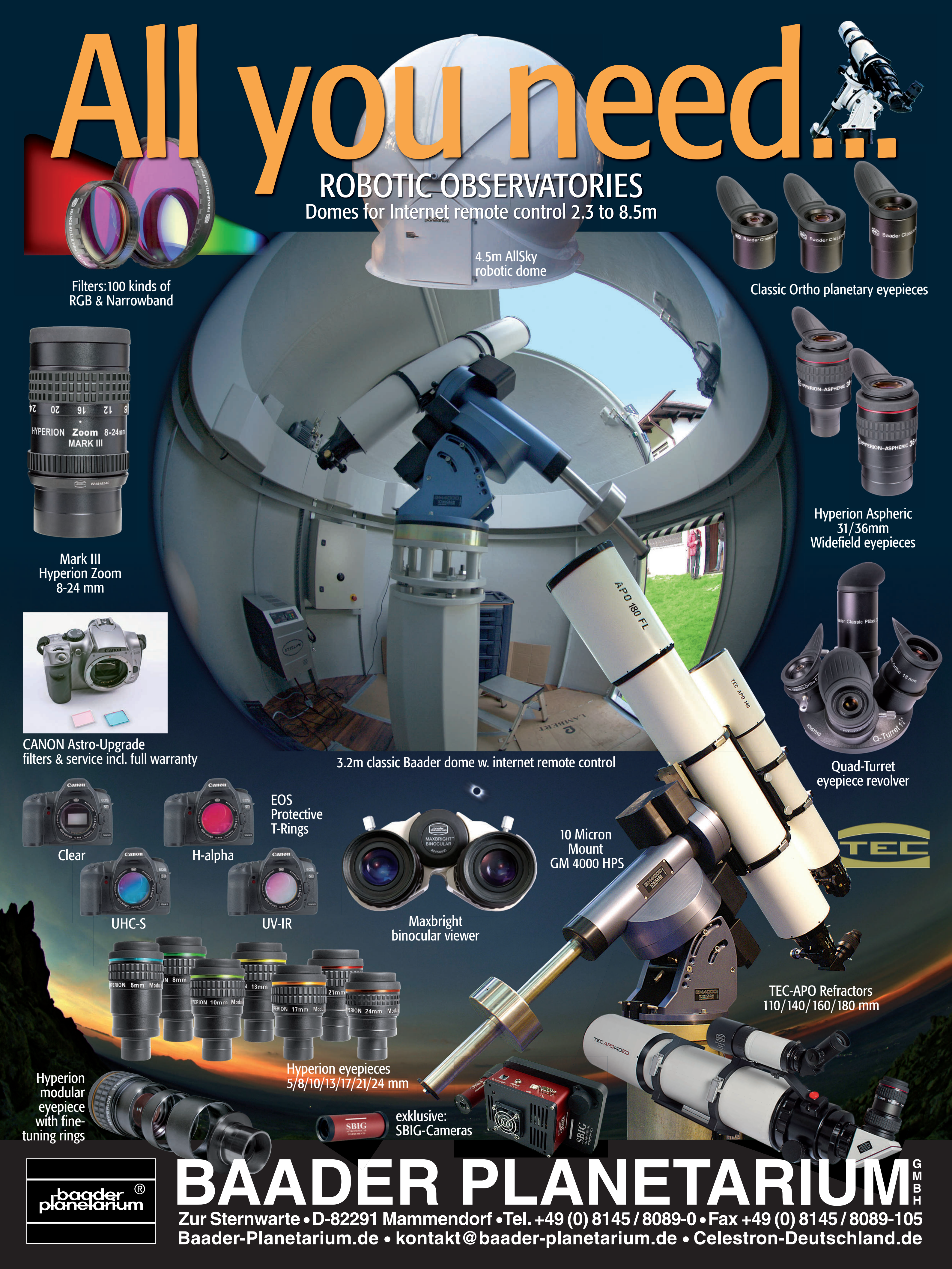
TO THE POINT

- **Superhydrophobic surfaces, such as lotus leaves, can't be wetted by water; superamphiphobic surfaces repel water, oil, blood and soap solutions.**
- **A porous structure of connected glass spheres produced with the aid of candle soot has superamphiphobic properties because it has microscopic overhangs. These keep the drop in a metastable state and prevent it from penetrating into the structure.**
- **Whether a drop wets a surface depends, on the one hand, on whether the liquid and the surface material chemically attract or repel each other. The ratio of the fineness of the surface structure and the pores to the drop size is also crucial. If the structure is too coarse or the drop too small, the capillary pressure in the drop makes it sink through the structure.**
- **Superamphiphobic layers may be used as the membrane in heart-lung machines or for purifying exhaust emissions.**

GLOSSARY

Capillary pressure: Due to surface tension, there is increased pressure inside a drop, similar to a balloon. This is known as capillary pressure. It is necessary in order to maintain the curvature of the surface.

Surface tension: The forces between the particles of a liquid cause the liquid to try to minimize its surface area. That's why water forms drops, even on water-repellent surfaces, but not on water-attracting surfaces.


All you need...
ROBOTIC OBSERVATORIES
Domes for Internet remote control 2.3 to 8.5m
4.5m AllSky robotic dome
Filters:100 kinds of RGB & Narrowband
Classic Ortho planetary eyepieces
HYPERION Zoom 8-24mm MARK III
Mark III Hyperion Zoom 8-24 mm
Hyperion Aspheric 31/36mm Widefield eyepieces
APO 180 FL
TEC APO 140
CANON Astro-Upgrade filters & service incl. full warranty
3.2m classic Baader dome w. internet remote control
Quad-Turret eyepiece revolver
EOS Protective T-Rings
Clear
H-alpha
UHC-S
UV-IR
10 Micron Mount GM 4000 HPS
Maxbright binocular viewer
TEC
TEC-APO Refractors 110/140/160/180 mm
Hyperion eyepieces 5/8/10/13/17/21/24 mm
Hyperion modular eyepiece with fine-tuning rings
exklusive: SBIG-Cameras
baader planetarium
BAADER PLANETARIUM GMBH
Zur Sternwarte • D-82291 Mammendorf • Tel. +49 (0) 8145 / 8089-0 • Fax +49 (0) 8145 / 8089-105
Baader-Planetarium.de • kontakt@baader-planetarium.de • Celestron-Deutschland.de