Water beads on the leaf of a lotus flower thanks to the texture of its surface. The leaf is covered with tiny bumps (1) which, under increasing magnification (2 and 3), are found to have a shaggy coating of waxy tubes. Water droplets stand on the points of the tubes and roll away.

Just about anyone who has spent time in an office has worked with temporary adhesives. The ubiquitous Post-It note is backed with tiny acrylic spheres that stick when they are tangent to a surface; that gives them enough hold to keep two pieces of paper together, but not enough to tear the pages when they are pulled apart. The adhesive's light touch enables it to be reused repeatedly.

When Post-Its first hit the market in the 1980s, they seemed like magic. But Nature had solved the problem of reusable adhesion millions of years earlier. Some lizards, including the gecko, have adhesive pads on their toes that enable them to run straight up walls.

Only in recent decades have researchers have been able to understand what makes gecko-foot adhesive—and any number of other biological surfaces with interesting properties—work. That's because the features themselves are structured at the nanoscale, and only since the early 1990s have the tools been available to characterize structures on that scale.

Understanding how naturally occurring surfaces function has inspired scientists and engineers to attempt to replicate those functions in engineered surfaces. That sort of biologically inspired design, is referred to as "biomimetics." The field of biomimetics is highly

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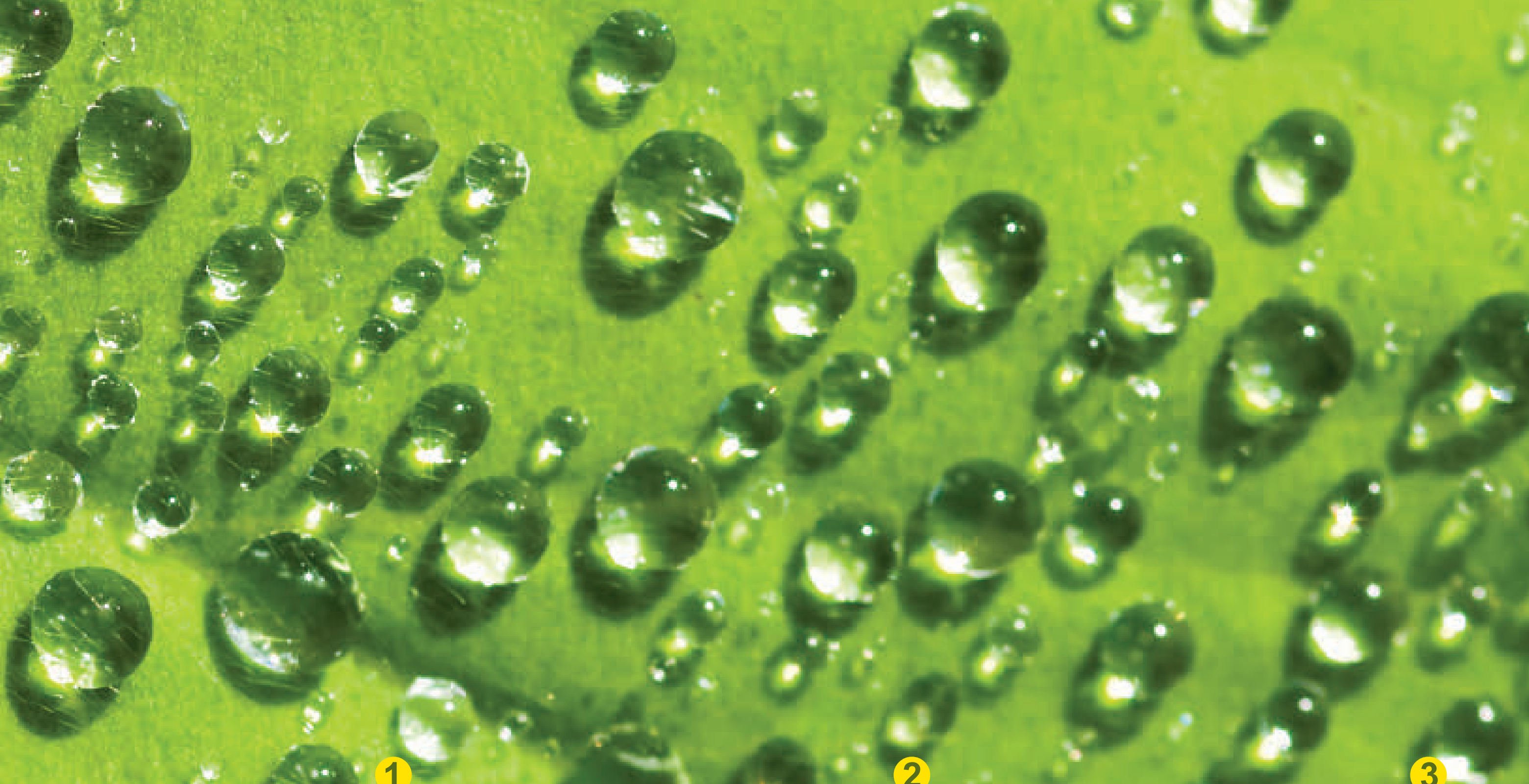
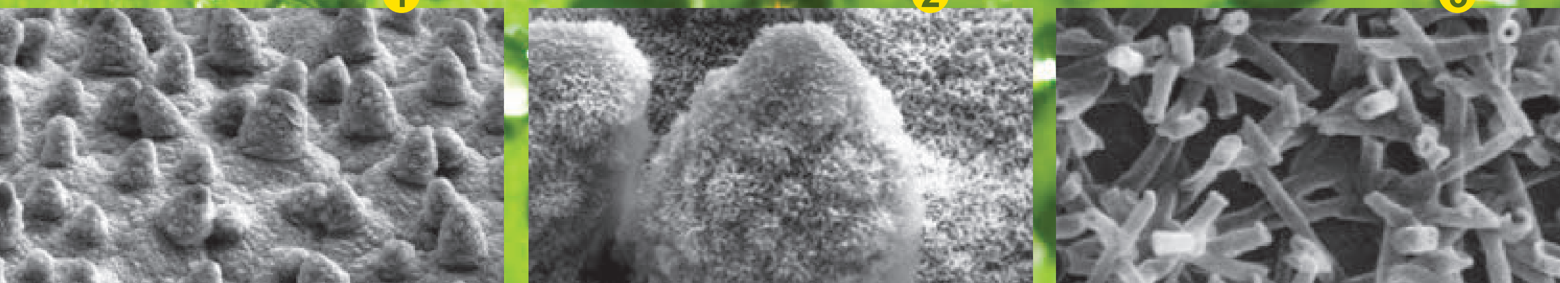
nature's nanotechnology

As engineers uncover the secrets of some of Nature's most amazing materials, they've found some startling similarities between surfaces that act radically different.

BY BHARAT BHUSHAN





interdisciplinary. It involves the understanding of biological functions, structures, and principles of various objects found in nature by biologists, physicists, chemists, and material scientists, and the design and fabrication of various materials and devices of commercial interest from bioinspiration.

Today, biomimetic materials are moving out of the laboratory and into industrial applications. As we get better at understanding how these natural surfaces work and how to replicate them artificially, more such materials—some with seemingly magical properties—will reach the market. Through biological evolution, Nature has conducted a 3.8 billion-year research and development program, and we find ourselves preparing to make commercial use of its discoveries.

I would like to talk about two well-known and seemingly unconnected surfaces we've studied in my lab—the water-shedding leaves of the lotus plant and the wall-gripping toes of the gecko. In trying to find a means to replicate those surfaces, we've discovered that they actually have a deep physical connection to each another.

The lotus leaf has long been the source of a paradox: its surface is rough, and yet it remains clean even as it grows in the muddiest of waters. Indeed, the effect is so pronounced that the lotus is a symbol of purity in Buddhism.

But it was only in the late 1990s that its secret was revealed through science. Wilhelm Barthlott and Christoph Neinhuis of the University of Bonn in Germany began examining extremely high resolution images of leaves captured using a scanning electron microscope. They discovered that lotus leaves weren't rough only at the macro scale but also at the micro- and nanoscale. The leaf surface is covered with minuscule waxy tubes that repel water droplets. Because the droplets sit atop the points of the tubes rather than along a flat, continuous surface, the droplets tend to roll off the leaves instead of wet them. The rolling water droplets carry away particles of dirt, cleaning the leaves.

The so-called lotus effect points toward one way to engineer manufactured surfaces so to make them shed water: increase the surface roughness. Studies of extremely hydrophobic surfaces have identified several factors that enable them to shed water. The surface needs to be rough on both the microscale and nanoscale, and it needs to have an overall convex shape. The tubes or needles on the surface should be high enough, relatively speaking, to resist the capillary waves, while nanobumps on those needles, or asperities, prevent nanodroplets of water from filing the valleys between them.

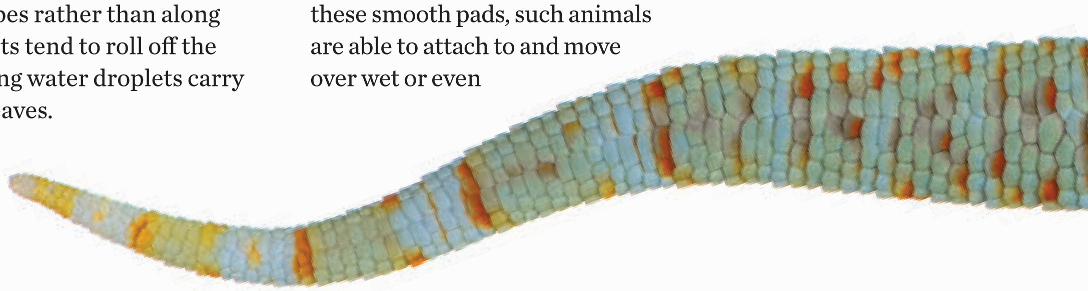
In my lab at Ohio State University, we have worked to replicate this effect artificially. One approach was to use composites of carbon nanotubes, which are long and narrow much like the asperities on a lotus leaf. The CNT composites were sprayed onto a flat epoxy resin and a microstructure to create both nanoscale and hierarchical structures. Graduate student Yong Chae Jung and I found that both nanoscale and hierarchical structures created with CNT showed superhydrophobicity and self-cleaning ability. They acted like lotus leaves.

These surfaces are also fairly robust. We conducted wear tests by pressing these CNT nanostructures with an atomic force microscope tipped with a borosilicate ball. The AFM tip raked across the surface with a force of 100 nN and then we checked for wear scars; none were found. We upped the force by a factor of 100, to 10 micronewtons, and repeated the test. Again, we couldn't find a wear scar, but we did find that the CNTs seemed to have bent or slid a bit from the force of the borosilicate ball, much as the bristles of a toothbrush deform against the pressure of a tooth.

It appears that the lotus effect can be created artificially using carbon nanotubes in the place of naturally occurring surface roughness. These manmade surfaces are durable enough to apply as coatings in industrial settings, where self-cleaning, superhydrophobic properties could have many uses.

Gecko feet, as mentioned earlier, also have some useful properties. It's not just geckos that can climb up walls, of course. The leg attachment pads of several animals, including many insects, spiders, and lizards, are capable of attaching to and detaching from a variety of surfaces and are used for locomotion, even on vertical walls or across ceilings. Biological evolution over many millions of years has led to the optimization of their leg attachment systems. This dynamic attachment ability is referred to as reversible adhesion or smart adhesion.

There are two kinds of attachment pads: relatively smooth and hairy. The relatively smooth pads, so-called arolia and euplantulae, are soft and deformable. They are found in some amphibians, such as tree frogs and torrent frogs, as well as cockroaches, grasshoppers, and other bugs. Using these smooth pads, such animals are able to attach to and move over wet or even flooded environments without falling.



Tree frog toe attachment pads consist of a hexagonal array of flat-topped epidermal cells about 10 micrometers across separated by approximately 1 micrometer wide mucus-filled channels; the flattened surface of each cell consists of a submicron array of nanopillars or pegs of approximately 100 to 400 nm diameter. The toe pads are made of an extremely soft, inhomogeneous material; the epithelium itself has an effective elastic modulus of about 15 MPa, equivalent to silicone rubber. The pads are permanently wetted by mucus secreted from glands that open into the channels between epidermal cells, and attach to mating surfaces by wet adhesion.

Frogs are capable of climbing on wet rocks even when water is flowing over the surface. Torrent frogs, for instance, can

1

The toe pads (1) of the Tokay gecko are made up of a hierarchical set of structures—flexible ridges covered with bristles which have branched tips that end in nanoscale spatula-shape structures. Researchers have been able to artificially replicate this structure using oriented polypropylene fibers (2, 3, and 4) that were 100 to 600 nanometers in diameter, and found that they had roughly the same adhesion. Larger diameter fibers (5) showed a lotus effect.

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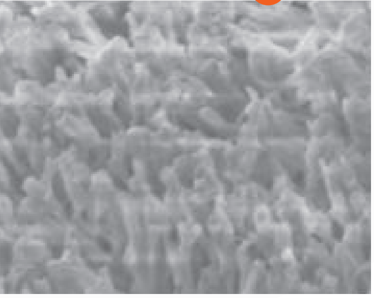

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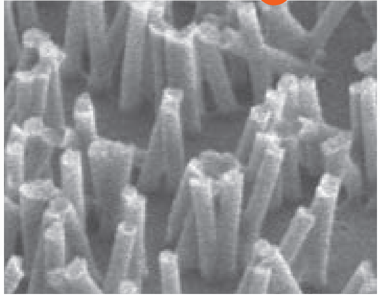

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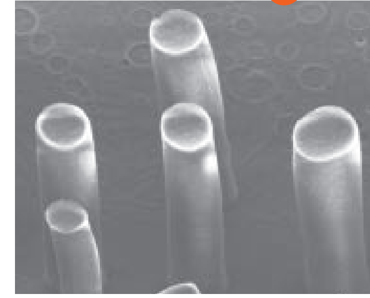

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resist sliding even on flooded surfaces. The surface of their toe pads is similar to that of tree frogs with some changes in the structure to handle the large flow of water.

Hairy attachment pads, conversely, consist of long deformable bristles, called setae, and are found in insects such as beetles and flies, as well as spiders and lizards. The microstructures used by beetles, flies, spiders, and geckos have similar structures. As the mass of the creature increases, the radius of the terminal attachment elements decreases. This allows a greater number of setae to be packed into an area, hence increasing the linear dimension of contact and the adhesion strength.

Because they have the highest body mass and exhibit the most versatile and effective adhesive known in nature, geckos have drawn the most attention from researchers studying reusable adhesion in animals. The research has found that the skin on gecko pads comprises a complex hierarchical structure of lamellae, setae, branches, and spatulae.

The lamellae are soft ridges one or two millimeters in length that are located on the toes; they compress easily so that contact can be established with rough bumpy surfaces. The setae are keratin bristles, each around 30 to 130 micrometers long, packed on the lamellae with densities as high as 14,000 per square millimeter. The end of each seta explodes into a spray of 100 to 1,000 branches that form the points of contact with the surface. And the tip of each branch flattens into a spatula, each only 10 nanometers thick.

The attachment pads on four feet of the Tokay gecko have an area of only about 220 square millimeters—around the area of a human fingernail. The approximately three million setae on their toes branch off into about three billion spatulae on four feet. Research led by Kellar Autumn at Lewis and Clark College in Portland, Ore., found that the divided points of contact served as a way to increase the van der Waals attraction between the toes and the surface of the gecko is climbing. (Typically, rough rigid surfaces have nanoscale areas of contact two to six orders of magnitude less than the apparent area of contact; this reduces the van der Waals attraction considerably.) Together, the three billion spatulae can resist a vertical force of 20 newtons trying to pull a gecko from a wall.

Although geckos are capable of producing large adhesion forces, they can remove their feet from an attachment surface at will. The adhesion force of gecko setae is dependent on the three-dimensional orientation as well as the preload applied during attachment. Due to this fact, geckos have developed a complex foot motion during walking: the toes are carefully uncurled during detachment so that the angle between the setae and the surface provides the maximum grip. The gecko is then able to peel its foot from surfaces one row of setae at a time by changing the angle at which its setae contact a surface. At an attachment angle greater than 30 degrees, the gecko will detach from the surface.

Because of the gecko's ability to detach and reattach its toes in mere milliseconds, the lizards can climb a ten-foot wall in just three seconds.

A nanostructured engineered material based on gecko-foot reusable adhesive would have a wide range of applications, from everyday objects such as adhesive tapes and fasteners to exotic items such as wall-climbing robots. But engineering such a material isn't straightforward. The design has to ensure that the fibrils are compliant enough to easily deform when pressed against a rough surface, but remain rigid enough not to collapse under their own weight. Spacing between the individual fibrils is also important: Too small, and adjacent fibrils can attract each other through intermolecular forces which will lead to bunching. The limits of current fabrication methods must be taken into account.

Hyungoo Lee and I discovered something in my lab when working on designing a lotus-effect superhydrophobic surface out of polypropylene, using a porous membrane as a template. By changing the density and diameter of the hierarchically structured nanofibers, you can turn a material that sheds water to one that, like the gecko toe pads, becomes adhesive.

The oriented fibers of 100 and 600 nm diameter exhibited gecko-effect adhesion due to their high fiber densities and large contact areas. When the diameter of the same type of oriented fiber was about an order of magnitude greater—between 5 and 14 micrometers—the material exhibited the lotus effect due to the smaller fiber density.

The emerging field of biomimetics is already gaining a foothold in the scientific and technical arena. Over billions of years of evolution, Nature has used basic material to provide a breathtaking array of functionality, and we're discovering that one means for doing this is the clever use of hierarchical structure.

As we understand the underlying mechanisms, we can begin to exploit them for commercial applications. Significant advancements in nanofabrication allow engineers to replicate structures of interest in biomimetics using smart materials. The commercial applications include nanomaterials, nanodevices, and processes that may enable self-cleaning surfaces or pads that hang pictures without hooks or wires. Some of these applications may at first seem magical, but they simply will be the result of applying science and engineering to uncovering the secrets of Nature. ■