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Laser structuring of water-repellent biomimetic surfaces

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A water-resistant surface inspired by the lotus leaf could enable applications in microfluidics, underwater coatings, and controlled deposition.

Manufactured water-repellent and self-cleaning surfaces, which shed debris or contaminants when sprayed, have many potential uses in daily life, agriculture, and industry. Mimicking nature has been a central strategy in this field, since biological species have many extraordinary wetting properties. One example is the lotus plant, *Nelumbo nucifera*. Revered as a symbol of purity in several ancient cultures, its leaves stay clean even though it grows in muddy lakes and ponds. The leaf is so water repellent that a droplet touching its surface instantly acquires a spherical shape, and even slight tilting causes it to roll off the leaf. Artificial surfaces exhibiting the lotus effect[1] could have many applications.

In order to create the lotus effect, it is important to understand how nature generates this property. Scanning electron microscope (SEM) images of water-repellent biosurfaces have revealed large structural diversity, with the common characteristic of roughness over two different length scales. As shown in Figure 1(a) and (b), the lotus leaf surface is covered with micrometer-sized papillae decorated with nanometer branch-like protrusions. Apart from this unique hierarchical morphology, the surface chemistry originates from epidermal cells of waxy hydrophobic crystals. The roughness of the hydrophobic papillae reduces the contact area between the surface and a liquid drop, with droplets residing only on the tips of the epicuticular wax crystals on the tops of papillose epidermal cells. Water repellency stems from the synergy of dual length-scale roughness and hydrophobic surface chemistry. Thus, researchers are seeking simple micro- and nanomanufacturing methods that enable the reproducible construction of such surface topologies.

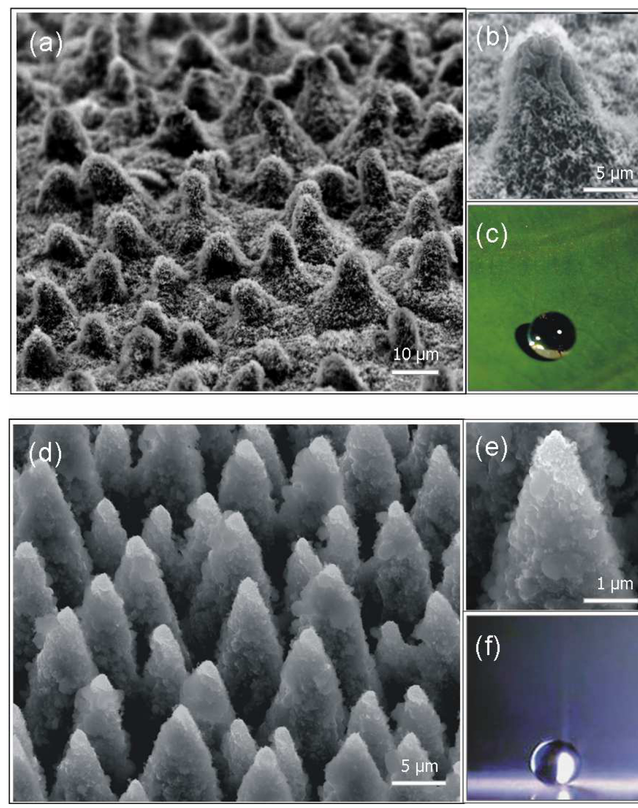

Figure 1. *(a) SEM image of the surface of a lotus leaf and (b) a higher magnification with hierarchical structures clearly resolved. (c) A water drop on the surface of the lotus leaf attains a nearly spherical shape. (d) SEM image of the artificial laser-structured silanized silicon surface and (e) a higher magnification showing the dual length-scale roughness. (f) A water drop on the structured surface.*

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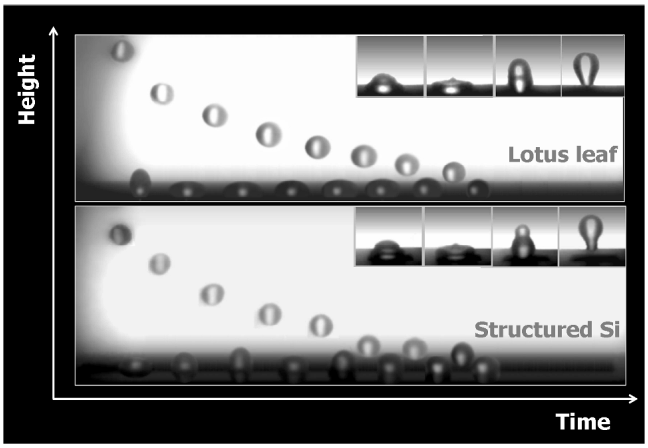

Figure 2. Snapshots of a water drop impinging on the surface of (a) the lotus leaf and (b) the artificial laser-structured silanized silicon surface. In both cases, the drop bounces many times before coming to rest after ∼400ms. The insets show the dynamics of drop deformation. For both systems, the drop stays in contact with the surface a total of ∼8ms.

We have developed a methodology to prepare artificial surfaces that possess hierarchical micro- and nanostructures. They are prepared with a simple one-step production process using ultrafast (femtosecond) laser irradiation of a silicon surface under a reactive gas atmosphere, followed by a chloroalkylsilane monolayer deposition.[2,3] The resulting silicon-based artificial surface structures, shown in Figure 1(d) and (e), mimic the morphology of the lotus leaf. This consists of microscale conical pyramidal asperities decorated with nanoprotrusions of up to a few hundred nanometers. The deposition of a hydrophobic silane coating on this surface leads to a contact angle value of $154 \pm 1°$ and a very small sliding angle (the minimum inclination under which droplet sliding is initiated) of $5 \pm 2°$. Both are very similar to the values of the lotus leaf ($153 \pm 1°$ and $4 \pm 2°$, respectively).

Contact and sliding angle measurements can probe the hydrophobicity of a surface, but they do not fully represent its water-repelling characteristics. Those can only be quantified by studying the dynamic behavior of droplets impinging on the surface. Figure 2 shows a sequence of snapshots of a water drop hitting both a lotus leaf and the artificial laser-structured and silanized surface. The minima and maxima of the drop trajectory are shown as a function of time. The shape changes significantly during impact as its kinetic energy transforms into stored energy. Despite the strong deformation of the liquid, however, both surfaces are so water repellent that the drop bounces back numerous times. By contrast, no rebound is observed when it hits the flat (unstructured) region of a silanized silicon surface.

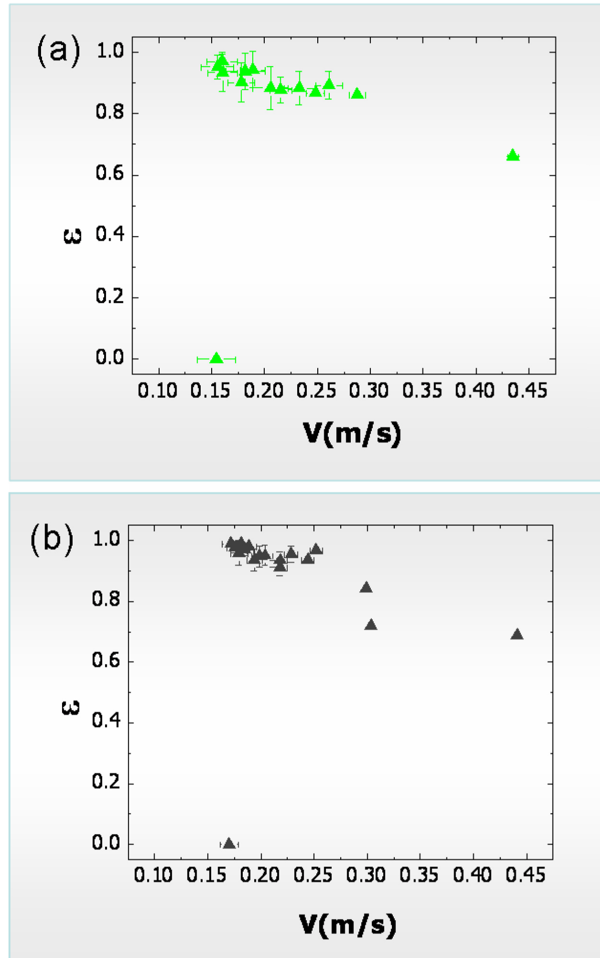

Figure 3. Restitution coefficient as a function of impact velocity for water drops hitting (a) a lotus leaf surface and (b) the artificial surface.

The elasticity of the collisions observed on both the artificial surface and that of the natural leaf indicate a high degree of water repellency. A direct measure of this elasticity is the restitution coefficient, $\varepsilon = V'/V$, defined as the ratio of the center of mass velocity just after impact, V', to that just before impact, V. This coefficient was deduced from recorded video images of the bouncing and is shown in Figure 3. The highest elasticity is observed at intermediate velocities where the restitution coefficient exceeds 0.90, indicating that 90% of the initial kinetic energy of the drop is restored upon impact. This value matches that of the lotus leaf and, as far as we know, is among the highest ever reported.

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We have shown that femtosecond laser structuring under reactive gas atmosphere can produce a surface that mimics the structural features of the lotus leaves as well as their water repellency. To our knowledge this is the first direct comparison of performance. It opens up the possibility for fabricating similar surfaces in metals, polymers, and optically transparent materials. These include self cleaning, water-resistant surfaces, low-frictional underwater coatings, controlled deposition, and guiding of water droplets and biofluids in biomicrofluidics.

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