Self-Cleaning Materials Through Nanotechnology

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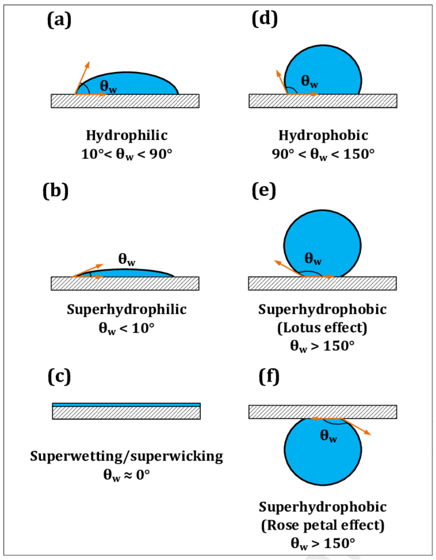
The objective of this paper is to introduce the concept of self-cleaning technologies and their botanical origins, how superhydrophobic and superhydrophilic materials are able to harness their properties for this purpose and to examine how scientists have tried to recreate this technology to create commercially viable and useful products and consider their far-reaching implications.

A self-cleaning surface, like the name suggests, is a surface that is able to readily remove any dirt or bacterial contamination on its own. This phenomenon was first observed on the lotus leaf, which perpetually stayed clean despite growing on muddy ponds and lakes. The leaves of the lotus plant (*scientific name: Nelumbo Nucifera*) have a waxy texture that repels water, and as the water rolls off the leaves, it washes residual dirt along with it. However, there is another factor that contributes to their hydrophobicity (water-hating behaviour). In 1977, Wilhelm Barthlott discovered that the surface of the lotus leaf was covered with microscopic bumps in the nanometer scale that reduces the contaminating particle's adhesion. These papillae were around 10 µm to 20 µm in height and 10 µm to 15 µm in width. Water droplets would sit on top of these waxy bumps in an almost spherical shape, in an effort to minimize their area of contact with the leaf's epidermis. A smooth surface covered with just the waxy material would have been hydrophobic, but the added presence of the bumps made the material superhydrophobic. Just like water, dirt too hovered at the peaks of the waxy bumps and thus, easily got washed away with natural or artificial rain. This effect was called the 'Lotus Effect'.



The wetting (hydrophilic) or non-wetting (hydrophobic) phenomena of a surface can be measured by the contact angle of the water drop on its surface. The contact angle is the angle, conventionally measured through the liquid, where a liquid-vapour interface meets a solid surface. The contact angle is determined by the attraction of the molecules of the liquid towards the surface (adsorption force, adhesion) and the attraction of the liquid molecules towards one another (cohesive force, cohesion). A liquid will not wet the surface if the cohesive force is much stronger than the adhesive force.

On a hydrophilic surface, a water drop has a contact angle less than 90° while on a hydrophobic surface, the water drop will bead up with a contact angle greater than 90°. If the contact angle is greater than 150°, then the surface is called superhydrophobic. The contact angle of smooth, flat surfaces can be calculated using Young's equation, which describes a direct relation between the apparent contact angle and the interfacial surface tensions and is the result of the thermodynamic equilibrium of the free energies at the solid-liquid-gas phase. However, real surfaces are neither always smooth nor homogenous and are modelled differently.

In the case of surfaces with a double structured surface like the lotus leaf, air that gets trapped between the waxy leaf surface and the water droplets in the space between and around the bumps increases the contact angle to around 170°. This phenomenon was modelled by Cassie and Baxter in their regime that described the event where there is a trapped air layer within the roughened or textured surface which causes a substantial increase in contact angle and a significant reduction in roll-off angle and contact angle hysteresis (the difference between advancing and receding contact angles, that are measured during the growth and shrinkage of the liquid droplet). According to the Cassie-Baxter equation, as a surface becomes rougher, packets of air start getting trapped between the nanostructures causing the roughness (in this case, papillae) and this makes it harder for water to permeate through the grooves. This leads to the water droplet resting on a composite surface consisting of the trapped air and the tip of the surface.

$$\cos \boldsymbol{\theta}^{CB} = f\,(1 + \cos\boldsymbol{\theta}) - 1$$

where $\boldsymbol{\theta}^{CB}$ is the apparent (Cassie-Baxter) contact angle, f is the fraction of the solid surface that is in contact with the liquid, and θ refers to Young's contact angle. According to this, to construct a superhydrophobic surface, we can either increase the roughness of the surface (to make f as small as possible) and follow it up with hydrophobization (to make θ as high as possible) or roughen the low-surface energy materials.

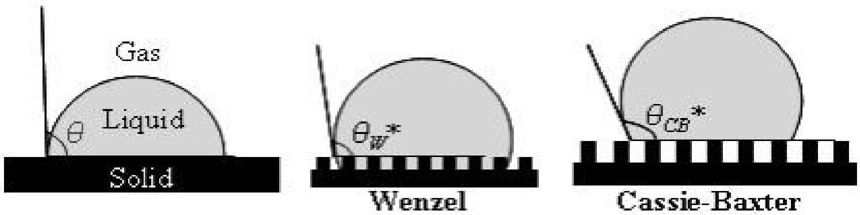


Figure 1: Shown are a droplet on a flat hydrophobic surface; a drop on a rough hydrophobic surface (full contact of water with substrate); and a superhydrophobic droplet (both air-liquid and substrate-liquid contacts).

Superhydrophobic surfaces play an important role in many applications, such as contamination prevention, enhanced lubricity, biocompatibility and durability of materials. Nanotechnologists have tried to harness the Lotus Effect by developing superhydrophobic materials like paints, treatments, fabrics etc. that are self-cleaning, anti-bacterial, corrosion-resistant etc. This is usually done through compositions containing micro-scale particulates or with special silicone or fluorochemical treatments on structured surfaces. Nano-Care and Nano-Sphere are two finishes applied to fabrics that result in self-cleaning properties - Nano-Sphere in particular was found to be water-repellent and stains from coffee, oily sauces and red wine were easily washed off. Nano-Care attached a 'fuzz' made of microscopic whiskers, less than a thousandth of the height of lotus bumps, to the cotton threads of the fabric while Nano-Sphere had nanoscopic particles of silica or of a polymer on the clothing fibres that replicated the bumpy roughness seen on the lotus leaf. Scientists developed superhydrophobic corrosion-resistant surfaces by depositing fluorinated silane (PTES) on titanium or coating zinc with carbon fiber, which led to air being trapped between the nanopores and limiting the water (and corrosive ions) accessibility. Another application is the production of self-cleaning metals using femtosecond pulse lasers, which reproduces the lotus effect, which can be used for self-cleaning latrines to reduce disease transmission.

On the opposite side of the spectrum, superhydrophilic materials were discovered showing self-cleaning properties too. Thin films of titanium dioxide, or titania, were able to split water into hydrogen and oxygen upon exposure to ultraviolet light. These nanoscale thin films of titania have a photocatalytic effect and are able to break down organic compounds into carbon dioxide and water. Titania has photocatalytic properties because it is a semiconductor, wherein a photon of ultraviolet light with a wavelength of about 388 nm is able to lift an electron from its valence band, across the band gap and into the empty conduction band, where electrons can flow and carry a current. Two mobile charges are produced - the electron in the conduction band as well as the electron-hole in the valence band, and these interact with water and oxygen at the surface of the titania film to produce highly reactive superoxide radical anions (O2–) and hydroxyl radicals (OH) that can break down organic compounds to carbon dioxide and water.

In the 1990s, it was discovered that when a thin film formed from an aqueous suspension of titania particles is annealed at 500℃ and exposed to ultraviolet light, the UV light removes some of the oxygen atoms from the surface of the titania. This results in a patchwork of nanoscale domains where hydroxyl groups are adsorbed, leading to the coating taking on the property of complete wettability i.e.: it exhibits a contact angle of 0°, for oil and water. This superhydrophilicity can be harnessed for self-cleaning, as water tends to spread across the whole surface, forming a sheet that carries away dirt as it flows. The coated surface is also fog-resistant as the water that condenses spreads out instead of becoming the thousands of tiny droplets that constitute a fog. Titania's photocatalytic ability enables it to deodorize and disinfect itself when coated by breaking down organic compounds and killing bacteria.

Titania nanocoatings are transparent and are used to manufacture treated glass by passing titanium tetrachloride vapour over cooled glass, depositing a layer of titania 20 nm thick. However, since UV wavelengths are blocked by regular glass, titania nanolayers are not as effective indoors. To solve this, titania can be doped with nitrogen or silver to decrease its band gap, so that indoor light with longer wavelengths can activate its photocatalysis.

Nanotechnologists tried to converge the two technologies - they tried to use titania to extend the life of hydrophobic lotus effect surfaces. In 2003, Rubner and Cohen had developed a layer-by-layer technique for making thin films out of polyelectrolytes. Polyelectrolytes are organic polymers or plastic materials that, unlike most polymers, carry a positive or negative charge. They stacked up alternating layers of positively charged poly(allylamine hydrochloride) and negatively charged silica particles (which had been used earlier to mimic the rough hydrophobic surface of the lotus leaf). They coated the multilayers with silicone at the end (a hydrophobic material) but noticed that because of the vast amount of nanopores created by the silica layers, a sort of sponge was formed that soaked up any surface water immediately. This is called nanowicking and resulted in the layer cake being hydrophilic before its final silicone coating. These silica-polymer multilayers were fog-resistant, even when held above steam. If its pores got saturated, water would start running off its edges and when it became dry again, the water in the nanowicks would slowly evaporate. These superhydrophilic coatings were transparent, antifogging and anti-reflective and were well-suited for being used in glass manufacture. Moreover, unlike titania, it didn't depend on the availability of light of the right wavelength to activate its properties.

in 2006, Rubner and Cohen drew inspiration from the *Stenocara* beetle's fog-harvesting back and created superhydrophilic spots of silica on superhydrophobic multilayers. This 'superwettability' arrangement helped with atmospheric water collection and made it possible to control the flow of liquid at the microscale and nanoscale. This further led to scientists experimenting with switchability - surfaces that are able to reverse their wettability at precise locations through tuners like (UV) light, solvents, temperature, electricity, acidity etc. In 2006, Kilwan Cho added an azobenzene-based compound to the siliconized (superhydrophobic) surface of a silica-polyelectrolyte multilayer to create a completely switchable surface. The new surface was superhydrophobic, but under ultraviolet light, the azobenzene compound changed configuration and converted it to a superhydrophilic surface. The change could be reversed with visible light.

The commercial viability of artificially manufactured self-cleaning surfaces has a lot more scope than discussed here - it can result in the windows and walls of a skyscraper cleaning themselves with a little rain, large fabrics like sails and marquees staying perpetually clean, deodorizing and antibacterial kitchens and bathrooms, waterproof electronics, fog harvesting in arid regions, unwettable swimsuits, reduced drag on ship hulls etc. Even in the emerging field of microfluidics, the control offered by tuning the wettability of surfaces with light can be used in the microarrays used for drug screening and other biochemical tests, by opening or closing hydrophilic pathways by switching parts of them to be hydrophobic or hydrophilic.

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