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Self-Cleaning Surfaces

Science & Working

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Introduction

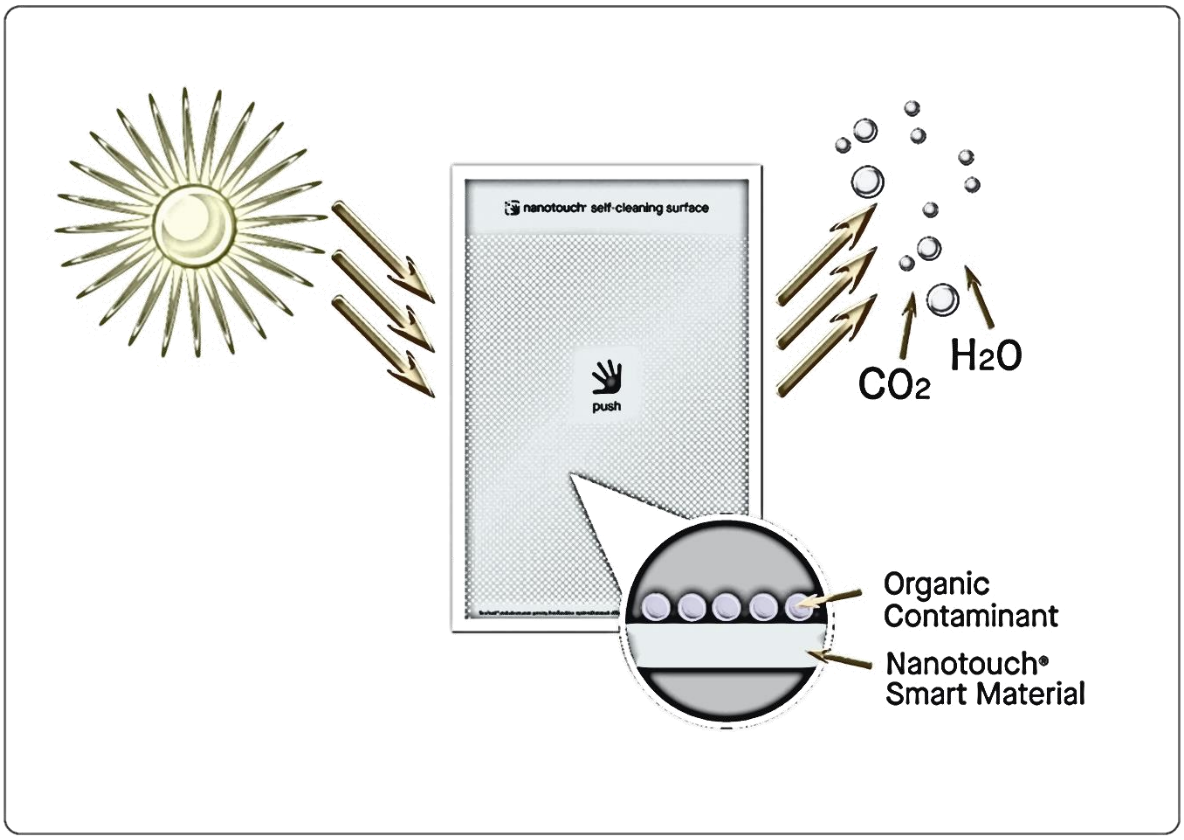
During COVID-19 Pandemic, the need to avoid touching various essential things became a necessity and a precaution against preventing the virus from spreading. People started using napkins, keys, toothpicks, and elbow arms as a medium to use buttons of the elevators, doorknobs and much more. These mediums, while being make shifters, were neither easy to use, nor the permanent solution. Then and there, Self-Cleaning Surfaces come into play.

The most asked question about self-cleaning surfaces is “How Do They Work?”.

The short answer is that NanoSeptic surfaces use nanocrystal technology to create a powerful oxidation reaction when exposed to any visible light.

A longer answer is that we bond microscopic mineral nanocrystals across our touchable surfaces, using the latest in material science. When natural or artificial light hits those mineral nanocrystals, the nanocrystals actively self-clean through a natural photocatalytic oxidation process.

The full answer is longer still and includes a lot of science.



Surface Characteristics

The ability of a surface to self-clean commonly depends on the hydrophobicity or hydrophilicity of the surface. Whether cleaning aqueous or organic matter from a surface, water plays an important role in the self-cleaning process. Specifically, the contact angle of water on the surface is an important characteristic that helps determine the ability of a surface to self-clean. This angle is affected by the roughness of the surface and the following models have been developed to describe the "stickiness" or wettability of a self-cleaning surface.

Young's Model

Young and colleagues proposed Young's model of wetting that relates the contact angle of a water droplet on a flat surface to the surface energies of the water, the surface, and the surrounding air. This model is typically an oversimplification of a water droplet on an ideally flat surface. This model has been expanded upon to consider surface roughness as a factor in predicting water contact angle on a surface. Young's model of wetting is used to describe the relationship between a water droplet and a perfectly flat surface. This model is typically used to explain the self-cleaning mechanism of lotus leaves. Young's model is described by the following equation:

$$\cos(\theta_0) = \frac{(\gamma SA - \gamma SL)}{\gamma LA}$$

$\theta_0 =$ Contact angle of water on the surface
$\gamma SA =$ Surface energy of the surface − air interface
$\gamma SL =$ Surface energy of surface − liquid interface
$\gamma LA =$ Surface energy of liquid − air interface

Wenzel's Model

When a water droplet is on a surface that is not flat and the surface topographical features lead to a surface area that is larger than that of a perfectly flat version of the same surface, the Wenzel model is a more accurate predictor of the wettability of this surface. Wenzel's model is described by the following equation:

$$\cos(\theta) = R_f \cos(\theta_0)$$

$\theta =$ Contact angle of water predicted by Wenzel's model
$R_f =$ Ratio of surface area of rough surface to the surface area of a flat projection of the same surface

Cassie-Baxter's Model

For more complex systems that are representative of water-surface interactions in nature, the Cassie-Baxter model is used. This model takes into consideration the fact that a water droplet may trap air between itself and the surface that it is on. The Cassie-Baxter model is described by the following equation:

$$\cos\theta_{\mathrm{CB}} = R_{\mathrm{f}} \cos\theta_0 - f_{LA}\left(R_f \cos(\theta_0) + 1\right)$$

$\theta_{\mathrm{CB}} =$ *Contact angle of water predicted by Cassie − Baxter's model*

$f_{LA} =$ *Liquid − air fraction, the fraction of the liquid droplet that is in contact with air*

Categories

Most self-cleaning surfaces can be placed into three categories:

Superhydrophobic

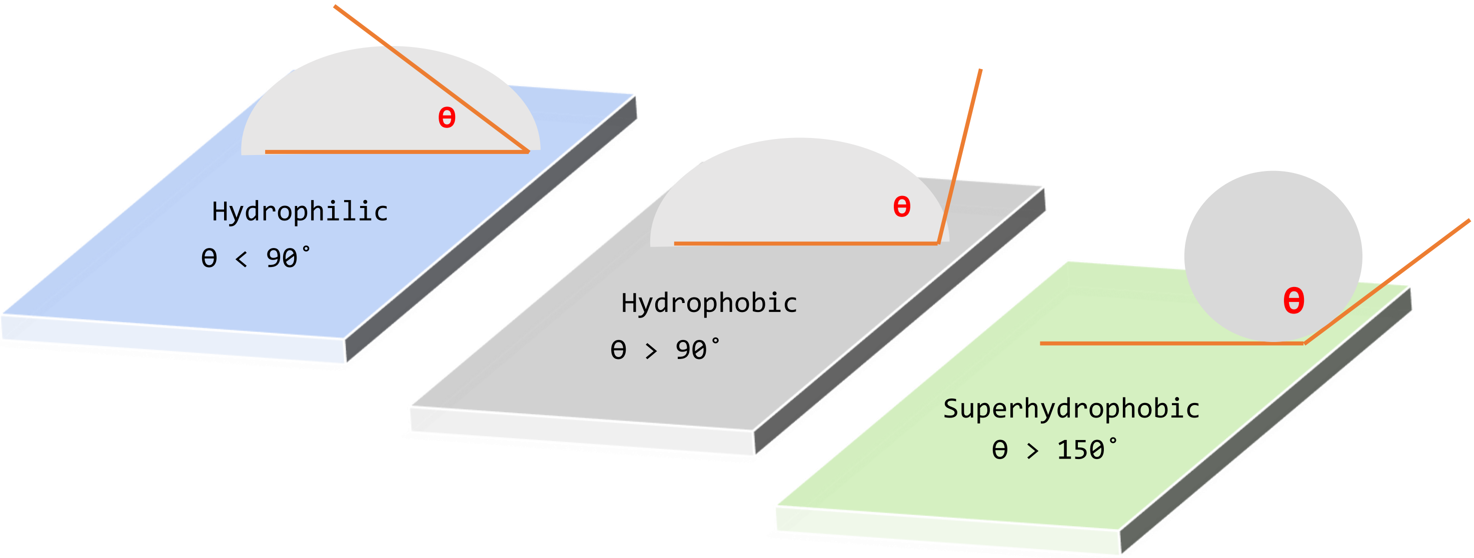
Ultra-hydrophobic (or superhydrophobic) surfaces are highly hydrophobic, i.e., extremely difficult to wet. The contact angles of a water droplet on an ultra-hydrophobic material exceed 150°. This is also referred to as the lotus effect, after the superhydrophobic leaves of the lotus plant.

Superhydrophilic

Superhydrophilicity refers to the phenomenon of excess hydrophilicity, or attraction to water; in superhydrophilic materials, the contact angle of water is equal to zero degrees. This effect was discovered in 1995 by the Research Institute of Toto Ltd. for titanium dioxide irradiated by sunlight.

Photocatalytic

The term “photocatalysis” is comprised of two parts – “photo” referring to the use of light and “catalysis,” referring to the use of a substance to speed up a reaction rate. Photocatalysis is defined as the acceleration of a reaction by the presence of light and a catalyst. There are various materials that show photocatalytic capabilities, but Titanium Dioxide (TiO2) has been the most widely studied photocatalyst over the past 40 years, not just because it works but also because it's safe (i.e., non-toxic).



Photocatalyst

Working

Upon absorbing energy from a light source, a photocatalyst material (like our self-cleaning surfaces) generates higher-energy electrons that fuel a process that results in the breakdown of toxic organic matter into carbon dioxide and water.

When light illuminates the surface, electrons are released and bind to oxygen (O_2) to form superoxide anions (O_2^-), which can degrade organic material. The photocatalyst then becomes positively charged and removes single electrons from moisture in the air, creating hydroxyl radicals (OH^*). Hydroxyl radicals are short-lived molecules that can also physically decompose organic contaminants into water and carbon dioxide. Superoxide anions and hydroxyl radicals are called reactive oxygen species (ROS). These ROS further react when exposed to oxygen and humidity leading to the formation of hydroperoxyl radicals (HO_2). ROS react with organic material, such as proteins and polyunsaturated fatty acids, leading to physical degradation of the contaminant. These processes are energized by any type of visible light, including incandescent, fluorescent, and LED.

Mechanical/Physical vs Chemical

A key distinction that needs to be made between smart materials like Nanotouch Self-Cleaning Surfaces and other surface treatments and technologies is whether the cleaning activity is due to physical/mechanical actions or due to a substance or mixture of substances. In other words, Nanotouch works by physical means (light and electricity) rather than a chemical substance that is generally toxic. The other main difference is with a catalytic process nothing is released from the surface. The technology is creating the cleaning action without sacrificing itself or releasing embedded toxins. A similar approach is used by ozone generators. They use electricity to split oxygen molecules. Nanotouch works in a similar way but gets the charge from light rather than from an electrical outlet; it’s a green solar approach.

Non-Toxic

And speaking of green: Not only does the Nanotouch surface create the self-cleaning action through a catalytic process rather than releasing toxins, but TiO_2 also has an exemption from toxicity tolerance because it is categorized as an inert ingredient. In fact, the U.S. Food and Drug Administration (FDA) also has deemed TiO_2 a Generally Recognized as Safe (GRAS) ingredient.

Fabrication

Transition Temperature (Tg)

To fabricate synthetic self-cleaning surfaces, there are a variety of methods used to obtain the desired nano topography and then characterize surface nanostructure and wettability.

Templating Strategies

Templating utilizes a mould to add nanostructure to a polymer. Moulds can come from a variety of sources including natural sources, such as the lotus leaf, due to their self-cleaning properties.

Nanocasting

Nanocasting is a method based on soft lithography which uses elastomeric moulds to make nano-structured surfaces. For example, polydimethylsiloxane (PDMS) was cast over the lotus leaf and used to make a negative PDMS template. PDMS was then coated with an anti-stick monolayer of trimethylchlorosilane and used to make a positive PDMS template from the first. As the natural lotus leaf structure enables pronounced self-cleaning ability, this templating technique was able to replicate the nanostructure, resulting in a surface wettability similar to the lotus leaf. Further, the ease of this methodology enables translation to mass replication of nano-structured surfaces.

Imprint Nanolithography

Imprint nanolithography also utilizes templates, pressing a hard mould into a polymer above the polymer glass transition temperature (*Tg*). Thus, the driving forces for this type of fabrication are heat and high pressure. Porous templates consisting of aluminium with anodized aluminium oxide (a hard mould) were used to imprint polystyrene. To achieve this, the polystyrene was heated well above its *Tg* to 130 degrees Celsius and pressed against the template. The template was then removed by dissolving the aluminium and producing either nano emboss or nanofiber surfaces. Increasing the aspect ratio of the nanofibers disrupted the uniform hexagonal pattern and caused the fibres to form bundles. Ultimately, the longest nanofibers resulted in the greatest surface roughness, which significantly decreased surface wettability.

Capillary Nanolithography

Like imprint nanolithography, capillary nanolithography employs a patterned elastomeric mould. However, instead of utilizing high pressure, when the temperature is raised above the Tg, capillary forces enable the polymer to fill the voids within the mould. Suh and Jon used moulds made from poly (*urethane acrylate*) (*PUA*). These were placed on spin coated, water-soluble polymer, polyethylene glycol (*PEG*), which was raised above PEG's Tg. This study found that the addition of nano topography increased the contact angle, and this increase was dependent on the height of the nano topography. Often, this technique produces a meniscus on the tip of the protruding nanostructures, characteristic of capillary action. The mould can later be dissolved away. Combinatorial lithography approaches are also used. One study used capillarity to fill PDMS moulds with PUA, first partially curing the polymer resin with UV light.

After microstructures were formed, pressure was applied to fabricate nanostructures, and UV curing was used again. This study is a good example of the use of hierarchical structures to increase surface hydrophobicity.

Photolithography

Photolithography and X-ray lithography have been used to etch substrates, often silicon. A resist, or photosensitive material, is coated onto a substrate. A mask is applied above the resist that often consists of gold or other compounds that absorb X-rays. The region exposed to light either becomes soluble in a photoresist developer (e.g., radical species) or insoluble in a photoresist developer (e.g., crosslinked species), ultimately resulting in a patterned surface. X-ray sources are beneficial over UV-visible light sources as the shorter wavelengths enable production of smaller features.

Plasma Treatment

Plasma treatment of surfaces is essentially a dry etching of the surface. This is achieved by filling a chamber with gas, such as oxygen, fluorine, or chlorine, and accelerating ions species from an ion source through plasma. The ion acceleration towards the surface forms deep grooves within the surface. In addition to the topography, plasma treatment can also provide surface functionalization by using different gases to deposit different elements on surfaces. Surface roughness is dependent on the duration of plasma etching.

Chemical Deposition

Generally, chemical deposition uses liquid or vapor phases to deposit inorganic materials or halides onto surfaces as thin films. Reagents are supplied in the appropriate stoichiometric amounts to react on the surface. Types of chemical deposition include chemical vapor deposition, chemical bath deposition, and electrochemical deposition. These methodologies produce thin crystalline nanostructures. For example, brucite-type cobalt hydroxide crystalline surfaces were produced by chemical bath deposition and coated with lauric acid. These surfaces had individual nanofiber tips with diameters of 6.5 nm, ultimately resulting in a contact angle as high as 178 degrees.

Surface Characterization

Scanning Electron Microscopy (SEM)

SEM is used to examine morphology of fabricated surfaces, enabling the comparison of natural surfaces with synthetic surfaces. The size of nano topography can be measured. To prepare samples for SEM, surfaces are often sputter coated using platinum, gold/palladium, or silver, which reduces sample damage and charging and improves edge resolution.

Contact Angle

As described above, contact angle is used to characterize surface wettability. A droplet of solvent, typically water for hydrophobic surfaces, is placed perpendicular to the surface. The droplet is imaged and the angle between the solid/liquid and liquid/vapor interfaces is measured. Samples are considered to be superhydrophobic when the contact angle is greater than 150 degrees. Refer to section on Wenzel and Cassie-Baxter models for information on the different behaviours of droplets on topographical surfaces. For drops to roll effectively on a superhydrophobic surface, contact angle hysteresis is an important consideration. Low levels of contact angle hysteresis will enhance the self-cleaning effect of a superhydrophobic surface.

Atomic Force Microscopy (AFM)

Atomic-force microscopy is used to study the local roughness and mechanical properties of a surface. AFM is also used to characterize adhesion and friction properties for micro and nanopatterned superhydrophobic surfaces. Results can be used to fit a curve to the surface topography and determine the radius of curvature of nanostructures.