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Students/
-1- BENADDA Abdelmadjid
-2- NOUARI Noureddine

Self-Cleaning Materials and Surfaces: A Nanotechnology Approach

DESCRIPTION

With increasing demand for hygienic, self-disinfecting and contamination free surfaces, interest in developing self-cleaning protective materials and surfaces has grown rapidly in recent times. This new title comprises of invited chapters from renowned researchers in the area of self-cleaning nano-coatings and the result is a comprehensive review of current research on both hydrophobic and hydrophilic (photocatalytic effect) self-cleaning materials.

Concepts of Self-Cleaning Surfaces

1.1 Superhydrophobicity

1.1.1 Introducing

Super hydrophobicity is where a surface repelsيصد water more effectively than any flat surface, including one of **PTFE (Teflon R).** This is possible if the surface of a hydrophobic solid is roughened; the liquid/solid interfacial area is increased and the surface energy cost increases. If the roughness is made very large, water drops bounce off the surface and it can become self-cleaning when it is periodically wetted. To understand more about this type of self-cleaning it is necessary to consider how normal surfaces become wetted and become dirty. The effect has been a focus of much recent research and has been reviewed recently. A good mathematical explanation can be found in a recent book chapter by Extrand

1.1.2 Contact Angles and Wetting

When a liquid rest on a surface the “contact angle” is measured through the droplet between the solid/liquid and liquid/air interfaces. The equilibrium angle that forms is known as Young’s angle after a theory proposed by Young, but not actually formulated in his work [9]. Young’s equation can be considered as a force balance of lateral forces on a contact line. In a perfect system the contact line cannot sustain any lateral force, so will always move to a position where the forces balance. This is achieved mathematically by taking the components of each force in the plane of the surface, at right angles to the contact line.

1.2 Self-Cleaning on Superhydrophobic Surfaces

1.2.1 Mechanisms of Self-Cleaning on Superhydrophobic

Surfaces Self-cleaning superhydrophobic surfacesالأسطح ذاتية التنظيف شديدة المقاومة للماء first received attention when a paper was published on the Lotus leaf. Lotus leaves remain clean in muddy water because of the way their surfaces are structured and water repellent. The leaves are strongly superhydrophobic and, although they collect particles of dust, they are fully cleaned by rain. One of the mechanisms for self-cleaning, and that initially suggested for the lotus leaf, depends on how the water drop moves. A drop on a surface with high contact angle and low contact angle hysteresis, usually a bridging super-hydrophobic surface, can roll instead of sliding. This type of motion allows the drop to collect more of the particles at the surface of the solid compared to the usual sliding mechanism. The question that then arises is why a rolling drop should collect hydrophobic particles from a superhydrophobic surface. Particles, even hydrophobic ones, are strongly attached to a liquid/gas interface. If the particle is modelled as a sphere its lowest energy configuration is when it is located in the interface; partially immersed so that the local contact angle can be the equilibrium contact angle. The energy of attachment of a particle on a liquid interface can be calculated by comparing the surface energies of three possibilities, the particle away from the liquid, the particle at its equilibrium position in the interface and the particle inside the liquid. For a hydrophobic particle and water, the third case will not be the lowest in energy so we can consider the energy change from the particle resting in air to being held at the interface. When a spherical particle of radius R and contact angle θe attaches to a liquid interface the angle between the surfaces is the contact angle. The area of the sphere that becomes wetted can be described by Eq., this is both the solid/gas interface that is lost and the solid/liquid interface gained. The liquid also loses some interface, the circular patch that is now covered by the particle, given by Eq. (Rs being the radius of the sphere.

As can be seen from the equation unless the equilibrium contact angle is 180◦ or 0◦ for a particle moving into the liquid it is always energetically favourable to attach a sphere to the interface. Very small particles may obtain enough energy from Brownian motion to escape. As the mass increases with radius cubed and the surface energy with radius squared, large particles can eventually become heavy enough to detach by gravity. This explains why most particles should adhere to a passing droplet, but not why a rolling drop should be more efficient at removing them. Examination of the rear edge of the drop as it pulls off the surface reveals some of the possible mechanisms for self-cleaning. On a flat or a rough Wenzel-type surface the liquid wets the whole surface and the contact line slides over it as it retreats. As the line reaches a particle at the surface it moves over the particle, exerting little or no upward force as it is pinned on the surface to both sides of the particle . On a bridging

Cassie–Baxter surface when the contact line reaches the particle it can detach from the features around the particle but remain attached to it as it is a little higher. This allows considerable upward force to be exerted on the particle by the liquid, which could dislodge it. If we consider that a thin film may be left on the surface after the drop has passed this alters the situation a little. On a flat or Wenzel surface the interfaces of the drop are being lost at its rear and regenerated at the front, like a slug leaving a trail. In this case any particles in the upper or lower interface will be dumped back onto the surface when the film evaporates, unless there is a very large flow carrying the particles away. Therefore, nearly all particles will return to their starting positions after the drop has passed. For the Cassie–Baxter bridging case leaving a water film, each interacting peak will spawn a tiny droplet as the main drop passes. This means that particles close to the peaks may not be carried away, but those further away will be plucked out of the surface as in the previous example. In most cases the hydrophobicity of the particle and the surface will prevent water from penetrating between the particle and surface. As the contact line recedes these particles can also be removed by attachment to the drop as liquid will in this case not be left on the surface. The adhesion between the particle and the solid surface can be a direct adhesion, in which case the surface energies of the two solids are high so bringing them together reduces the global surface energy. Alternatively, two hydrophobic surfaces can adhere by weaker van der Waals interactions, but if water is present, they will be held together by hydrophobic interactions because separation requires wetting of the two interfaces, which would cost surface energy. For a typical superhydrophobic surface the base material is hydrophobic, meaning that hydrophobic interactions will be important. In this case, the water would not be expected to wet the crack between the particle and the surface, making removal by the contact line most effective for rolling drops. A second factor in the removal of particulate material from a roughened surface is the reduction in solid/solid interfacial area. The particles sit on top of small-scale roughness and are not bound strongly because they do not contact a large surface area. The multilayer roughness of the Lotus leaf is important here, the smaller scale roughness prevents particles nesting into crevices and having larger contact areas than on a flat surface. The third factor is impacting drops – if a surface has different scales of roughness and the instantaneous pressure of the drop impact is only sufficient for it to enter the larger scale of roughness it can collect particles from the crevices of the larger scale roughness.

Superhydrophilic Self-Cleaning Surfaces

The opposite of super hydrophobicity is superhydrophilicity. In this case the surface energy of the base material is high, causing water to spread out over it, in other words to have a relatively low contact angle. In this case Wenzel's equation can be used to estimate the contact angle that will be observed on the rough surface. Unlike the superhydrophobic case there is no alternative state that takes over at high roughness, so the predicted contact angle soon reaches 0◦. Roughness can easily be increased past this point and the question then is what will happen. The surface wets fully but the rate of wetting inside the roughness of the surface can be more rapid than on a flat surface. Aqil et al. [52] showed that the rate of spread of a drop is greater on a rough surface and slows down less as it approaches 0◦. In fact the base of the drop can spread so fast that it breaks away from the top, generating a fried-egg shape. Such surfaces can clean themselves of hydrophobic particles when wet because water enters below the particles and lifts them off as they become attached to the air/water interface. This is also extremely effective against biological contamination but relies on the presence of lots of water [53]. Hydrophilic surfaces are usually strongly adhesive because they have a high surface energy and become coated with material that can bind chemically to them. This can make them very difficult to clean. Materials with a surface energy the same as that of water can remain very clean when wet because it is energetically favourable for water molecules to sit at the surface. An example of this is polyethylene oxide (PEO) which is used to prevent biofouling in many applications for exactly this reason. The surfaces do not self-clean, but do not become fouled in the first place. If surfaces of this type dry out they can become contaminated and often become damaged because they shrink when dry. Some self-cleaning products use a combination of superhydrophilic surface properties along with a photocatalyst. The high roughness and hydrophilicity generate a water film when wet and the photocatalyst oxidises organic species to charged species, making surfactants or ultimately completely oxidising them. This combined system allows the surface energy to be higher than that of water with the photocatalysis removing the film of organic matter that spreads over the surface in dry conditions. When wet the high roughness and surface energy causes a water film to lift off the contaminants.

The Role of Vanadium Dioxide Nanoparticles in the Production of Glass with Three Key Features

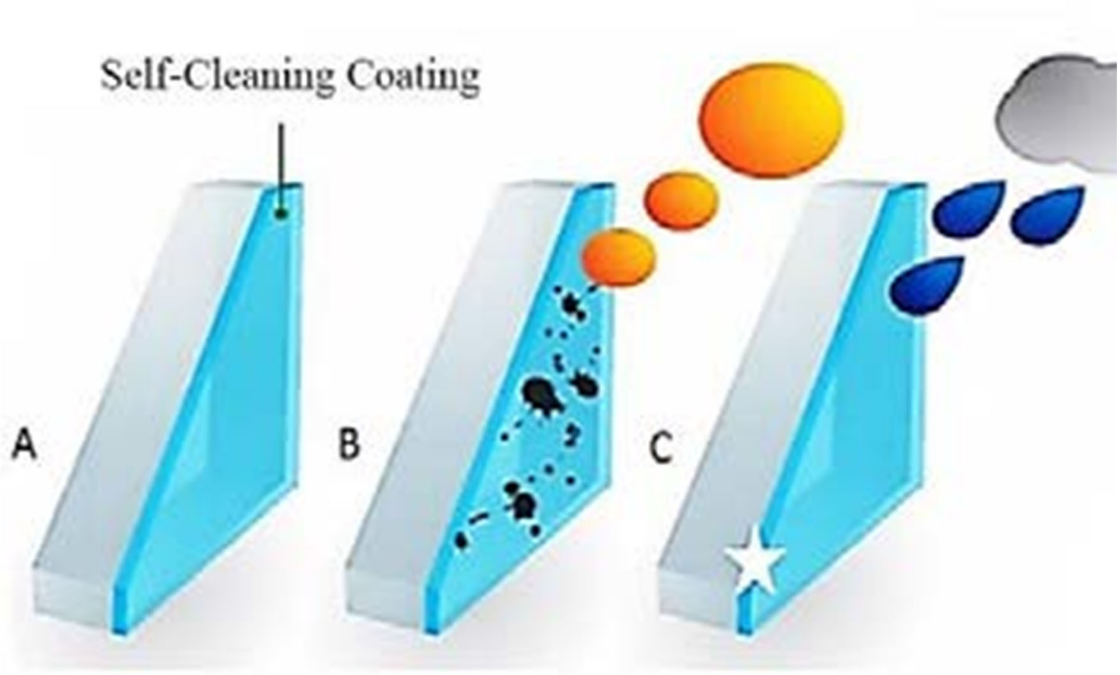
A particular type of glass with three unique features has been developed by the University College London (UCL) in collaboration with the Engineering and Physical Sciences Research Council (EPSRC). The features are discussed below.

- **Self-cleaning**: Glass coated with vanadium dioxide nanoparticles is ultra-resistant to water. The presence of the conical-shaped nanoparticles on the glass surface traps air and allows a minimal amount of water molecules to come into contact with the glass surface. Therefore, when rainwater hits the glass surface, a spherical droplet of rain removes dirt, grime, and dust as it slides down. In conventional glass, raindrops adhere to the surface of the glass and leave behind marks of dirt as they slide down slowly.

- **Energy-saving**: The ultra-thin film of vanadium dioxide coating on the glass surface of the window shows the dual effect, i.e., it restores the heat of the room by preventing the escape of thermal radiation during cold weather, and it also prevents infrared radiation from the sun entering the room during hot periods.
- **Anti-glare**: The nanostructures have anti-reflective properties similar to those found in the eyes of moths.

How Can “Self-Cleaning Glass” Stay Clean all by Itself?

Titanium dioxide coatings clean the dirt and grime present on the surface of the glass by following the two-step process:



Photocatalytic: This is a light-activated process where titanium dioxide acts as a photocatalyst. When ultraviolet light present in the sun rays hits the glass coated with titanium dioxide nanoparticles, electrons are generated. These convert water molecules from the air into hydroxyl radicals via a chemical reaction. These hydroxyl radicals degrade the carbon-based dirt into smaller bits that can be easily washed away by rain.

Hydrophilic: The presence of titanium dioxide nanoparticles (photocatalysis of titanium dioxide produces hydroxyl radical) on glass makes it hydrophilic. Therefore, when rainwater hits the dirty self-cleaning glass window, the water molecule evenly spreads out across the glass window and wipes it clean without leaving any dirt marks or smears.

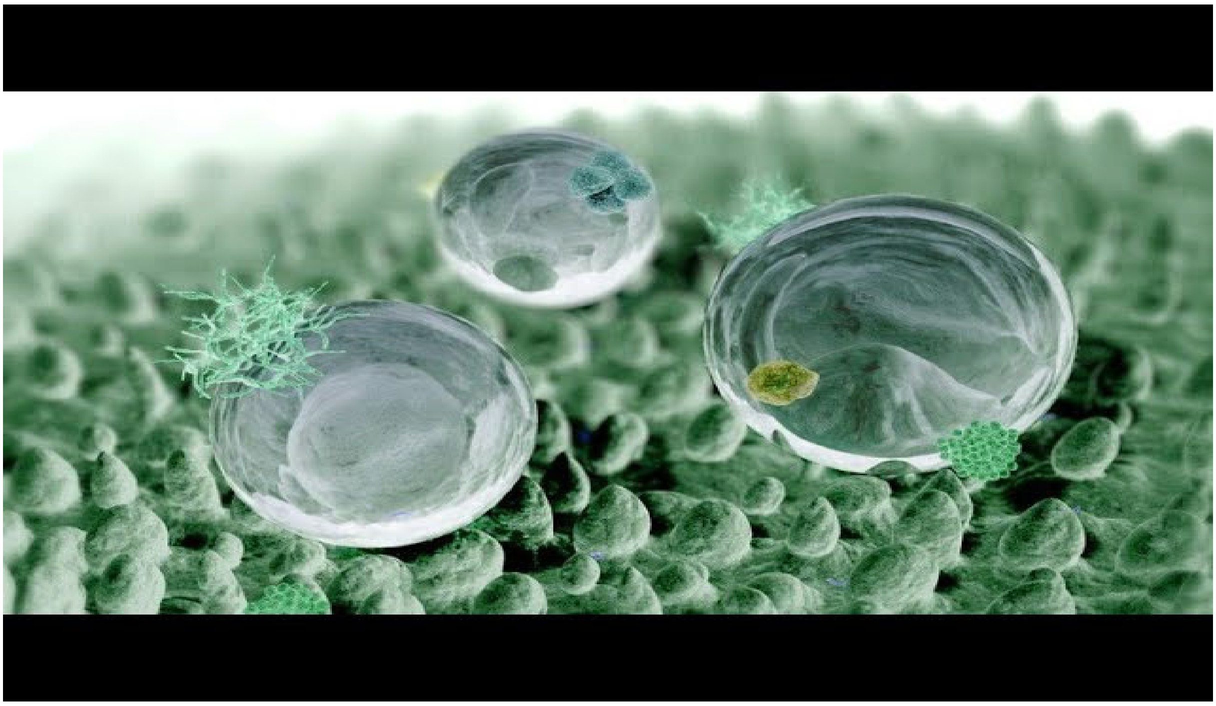
Other Applications of Self-Cleaning Glass

This technology is not only used for manufacturing “self-cleaning glass” windows but is also used for the production of self-cleaning solar panels and building facades.

Naureen Akhtar, a Physicist at the University of Bergen, explained the significance of this glass to retain its spotless form even underwater. While conducting research underwater, light-detecting sensors are used to analyze water quality and are positioned behind conventional glass (underwater).

The glass accumulates grime and dirt quickly so that that the sensors lose their efficiency. This problem was effectively rectified with the use of “self-cleaning glass”.

Gareth McKinley at the Massachusetts Institute of Technology in Cambridge also agreed with Akhtar about the important use of “self-cleaning glass” underwater, where frequent cleaning could be challenging. This technology could also be useful for ocean-exploration vessels.



Commercialization of Self-Cleaning Glass

The world’s first self-cleaning glass was commercially produced by Pilkington.

Pilkington introduced the Pilkington Activ, which contains both self-cleaning and solar control properties. The company claims that its products are eco-friendly and suitable for all exterior glazing situations.

Scientists Find Benefits in Using Some Types of Iron Nanoparticles for Environmental Clean-Up

Researchers at Oregon Health & Science University's OGI School of Science & Engineering, in collaboration with Pacific Northwest National Laboratory (PNNL) and the University of Minnesota, have discovered that at least one type of nano-sized iron may be useful in cleaning up carbon tetrachloride contamination in groundwater. The new discovery was published online in December, 2004, in Environmental Science & Technology, the leading environmental journal of the American Chemical Society. The study will be published in the print version of Environmental Science & Technology, March 1, 2005, in a special section on nanotechnology.

"The use of nano-sized particles of iron for cleaning up contaminants in groundwater, soil and sediments is one of the hottest new technologies to emerge in recent years," said Paul Tratnyek, Ph.D., an environmental chemist and professor of environmental and biomolecular systems at OHSU's OGI School of Science & Engineering, and a lead author of the study. "However, there are a lot of unanswered questions about the appropriate and optimal implementation of the nano-iron technology, and even some questions about its safety. We set out to answer some of the remaining questions that researchers have about the basic chemical processes that determine the fate and effects of metal nanoparticles in the environment."

The particles studies by Tratnyek and colleagues range in size from 10 to 100 nanometers. One nanometer is one-billionth of a meter. By comparison, many biomolecules are of similar size.

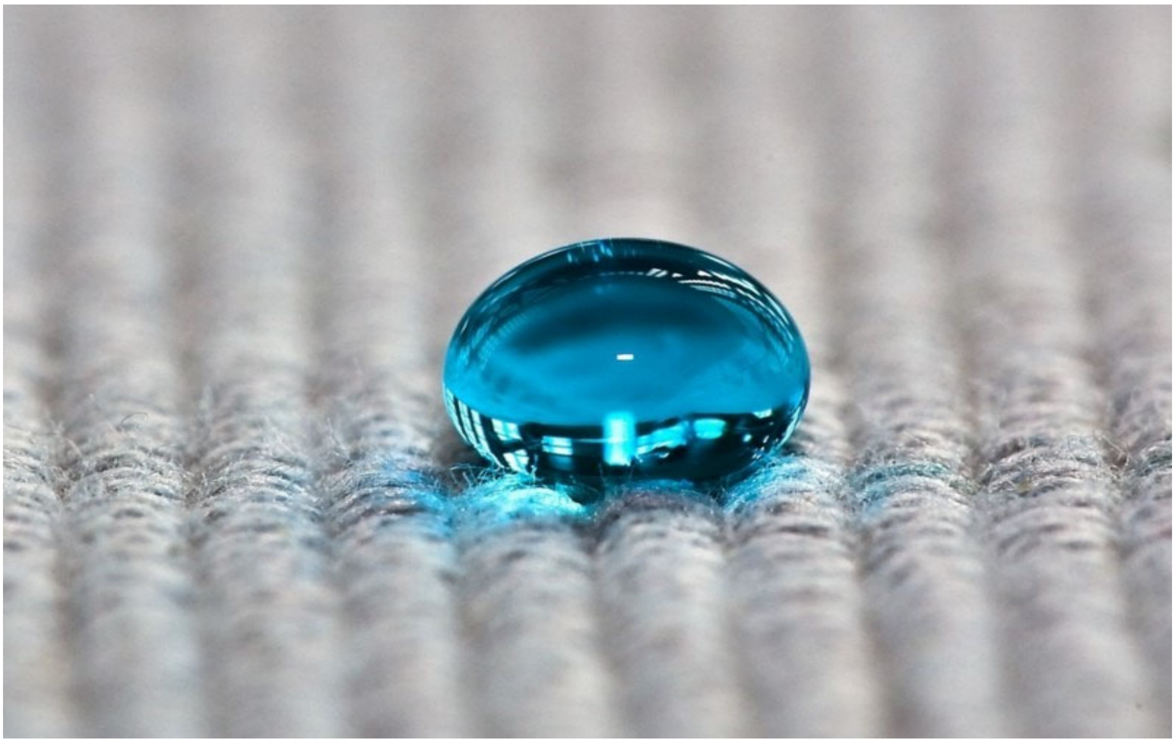
For the study, Tratnyek and his doctoral students James T. Nurmi and Vaishnavi Sarathy compared two leading types of nanoparticle-sized iron that are being promoted by others for groundwater remediation. They measured how fast these particles degrade carbon tetrachloride and they determined the major projects of the reaction.

Carbon tetrachloride is a manufactured chemical used mainly in cleaning fluids and degreasing agents. In a few locations, spills of these liquids infiltrated the soil and created very large areas of contaminated groundwater and soil. Carbon tetrachloride is a toxic chemical that has been shown to cause cancer in animals.

The research at OHSU was funded in part by a grant from the Department of Energy to the Pacific Northwest National Laboratory (PNNL) in Richland, Washington. The interdisciplinary team includes 10 researchers from PNNL, three from OHSU and two from the University of Minnesota.

The PNNL researchers, led by Donald R. Baer, Ph.D., technical group leader at PNNL's William R. Wiley Environmental Molecular Sciences Laboratory, first synthesized and characterized the nanoparticles using a variety of advanced microscopy and spectroscopy techniques. Once the nanoparticles were syntheisized and characterized, Tratnyek and his students studied their reactivity using electrochemical techniques they developed to help them systematically measure the microscopic particles. University of Minnesota scientists also helped with microscopy and some reactivity studies.

"Our team's study results show how the breakdown of carbon tetrachloride is influenced by some very subtle and transient differences between the two types of nano-iron," said Tratnyek.



One of the nano-irons studied, a commercially available product of iron oxide with a magnetite shell high in sulfur, quickly and effectively degraded carbon tetrachloride to a mixture of relatively harmless products. "This was an exciting find because it may provide the basis for effective remediation of real field sites with groundwater that is contaminated with carbon tetrachloride," said Tratnyek.

"Furthermore, since it may be possible to emplace nano-sized iron deep into the subsurface by injecting it through deep wells, this approach may be suitable for remediation of very deep plumes of carbon tetrachloride contaminated groundwater, such as the one at the Hanford site in Richland, Washington."

The other nano-iron studied by the OHSU-PNNL-University Of Minnesota team had a shell, or coating, high in oxidized boron. While the oxide-coated iron also rapidly degraded the carbon tetrachloride, the primary product was chloroform, a toxic and persistent environmental contaminant.

"The idea of using nanosized particles of iron for clean-up of groundwater contaminants has been around since 1997 and has gained a lot of momentum in the past four years," noted Tratnyek. "Nanotech iron has shown promise for environmental remediation, but previous work has not been particularly rigorous or thorough.

"Our report is the most comprehensive and rigorous characterization of the reaction to date between carbon tetrachloride and two leading types of nano-sized iron. We have taken a careful, second look at the chemistry of nano-iron for environmental cleanup in hopes of providing better science on which to found this promising technology."

Tratnyek's nano iron research may also someday have medical applications, for instance, in the diagnosis of brain tumors.

Nanoscale Cracks Reduce Glass Clarity - New Technology

Ever washed a glass repeatedly but never been able to get it quite as clean as when it was new. Researchers from Lehigh University have found that the problem may not be your fault. The answer could be nanoscopic cracks on the surface of the glass spoiling its transparency.

The findings, to be published by the American Ceramics Society, found that when molten glass is blown rapidly its outer surface sustains microscopic fractures when it comes into contact with air. The fractures are only nanometers in width and cannot be seen with the naked eye. When exposed to dishwashing soap the cracks etch, spread and dissolve faster than the rest of the glass. This results in the dirty look even though the glassware is clean.

The cracks are caused because as the glass is blown, the top couple of nanometers of the surface are solid but the rest is still liquid. As the material is blown and expands, the surface and interior expand at different rates resulting in cracks.

Conclusion

Nano-TiO2 and nano-SiO2 have become important nanoparticles to confer reduced need for cleaning. The overall environmental impact of a reduced need for nanoparticle-based cleaning is uncertain, as only limited information on direct and indirect environmental impacts is available. It would appear that, at present, there is no clear evidence that 'self-cleaning' surfaces have a net direct environmental benefit, when eco-efficient cleaning methods are used. The main barriers to realizing a direct environmental benefit stem from the inputs in creating “self-cleaning” surfaces, limitations in the durability of “self-cleaning” properties, and life-cycle releases of nanoparticles. Options to limit the environmental impact of a reduced need for cleaning based on nanoparticles are presented.