Self-cleaning coatings

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This review summarises the key topics in the field of self-cleaning coatings, concentrating on the materials that have been used in commercial applications and recent research that aims to improve these materials. Hydrophobic and hydrophilic coatings are discussed, and the various mechanisms of self-cleaning are described and related to the material properties of the coatings. Although several multinational companies have released products incorporating self-cleaning coatings, there remains much potential in this field.

1. Introduction

The technology of self-cleaning coatings has developed rapidly in recent years. As a commercial product, their potential is huge and their market truly global. Because of the wide range of possible applications, from window glass and cement to textiles, self-cleaning coatings may become an important labour-saving device. Already some of this potential is being realised: self-cleaning paint is currently available in Europe, and within the past few years self-cleaning windows have made an impact, with several multinational glazing companies releasing products.

The field of self-cleaning coatings is divided into two categories: hydrophobic and hydrophilic. These two types of coating both clean themselves through the action of water, the former by rolling droplets and the latter by sheeting water that carries away dirt. Hydrophilic coatings, however, have an additional property: they can chemically break down adsorbed dirt in sunlight. This review will discuss the materials and mechanisms involved in self-cleaning coatings, and will highlight challenges still to be met, together with recent innovations that may overcome them.

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2. Hydrophobic coatings – the Lotus-Effect

The self-cleaning action of hydrophobic coatings stems from their high water contact angles; water on these surfaces forms almost spherical droplets that readily roll away carrying dust and dirt with them. Dirty water falling onto the hydrophobic coating is removed before it can evaporate. The rolling motion of droplets is a vital process in self-cleaning and a complex physical phenomenon. When a droplet rolls, an hysteresis develops in the contact angles at the advancing and receding three-phase interface between solid, liquid and gas. Theory as to how this hysteresis varies with the chemical and topological properties of the surface is still being developed, but ideally the condition often quoted is $\theta_s < 160^\circ$, and a very low roll-off angle, i.e. the minimum inclination angle necessary for a droplet to roll off the surface. A surface with these two properties is known as superhydrophobic, or alternatively ‘ultraphobic’. Interestingly,

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ultraphobic surfaces are the self-cleaning coatings of choice for the natural world: over 200 species of plant are known to utilise rolling droplets of water to keep clean, perhaps most famously the Lotus plant native to south east Asia. Efforts to mimic this biological cleaning mechanism resulted in a 1998 patent issued to biologists Neinhaus and Barthlott describing the ‘Lotus-Effect’.

Understanding the behaviour of water droplets on a surface is critical to designing ultraphobic self-cleaning coatings. In the nineteenth century, Thomas Young modelled the static contact angle of a droplet on a smooth surface. He stated that interplay between the surface free energies of the solid–liquid, solid–gas and liquid–gas boundaries determined the water contact angle. If the wetted surface is more energetically favourable than the dry surface, the static contact angle will be less than 90° and the surface is termed hydrophilic. If the dry surface is more favourable, then the surface is hydrophobic, and its static contact angle will be greater than 90°.

By making films of chemically hydrophobic materials, such as fluorinated polymers, static contact angles as high as 130° can be achieved. While such polymers are widely used as ‘easy clean’ surfaces in a number of products, their contact angles are not high enough to cause the rolling motion necessary for true self-cleaning. The key to obtaining higher θw values can be seen in microscope studies of ultraphobic plant leaves. Fig. 1 shows electron micrographs of two different ultraphobic plant leaves: regular surface structures can clearly be seen, giving the leaves a rough texture on the micron scale. The influence of a textured surface on water droplet contact angles was described mathematically by Cassie and Baxter in the middle of last century. They found that a macro sized droplet placed on a micron-textured hydrophilic surface finds it favourable to follow the contours of the surface, sinking down and spreading out compared to the same drop on a smooth surface. Therefore increasing the roughness of a hydrophilic surface reduces the contact angle of a water droplet. On a rough hydrophobic surface the opposite occurs: the energy cost is typically too high for the water to follow the patterned surface, and as a result the droplet recedes, forming an even larger contact angle compared to the smooth surface. Both the chemical and structural properties of a surface therefore determine the contact angle – both must be tuned in order to design a synthetic ultraphobic surface.

Following nature’s lead

Several techniques are known for the micron-scale patterning of hydrophobic surfaces through the use of moulded polymers and waxes, by physical processing methods such as ion etching and compression of polymer beads, and by chemical methods such as plasma-chemical roughening, which can all result in ultraphobic coatings. While these surfaces are effective self-cleaners, they suffer from a number of drawbacks which have so far prevented widespread application. Batch processing a hydrophobic material is a costly and time consuming technique, and the coatings produced are usually hazy – precluding applications on lenses and windows, and fragile materials. The next generation of ultraphobic coatings must aim to combine the self-cleaning properties already achieved with additional functionality, such as optical transparency, in a coating that is easily deposited from cheap materials and that is durable enough for everyday use, if a viable commercial product is to result. Chemical vapour deposition (CVD) is a technique widely used in industry and research for the deposition of uniform coatings over a large area, and has also been exploited to deposit ultraphobic coatings. Lau et al. recently reported the deposition of a 2 μm thick film of vertically aligned carbon nanotubes (CNTs) via plasma enhanced CVD. This technique grows CNTs by discharging a high voltage through an atmosphere of acetylene and ammonia. Nanotubes grow from Ni catalyst islands on a silica substrate; the density and thickness of the nanotubes is controlled by the thickness of the Ni layer, and their length by the deposition time. The result is a ‘forest’ of vertically aligned, untangled nanotubes – a surface highly textured on the micron scale (Fig. 2). To induce ultraphobic behaviour, the CNTs must be rendered chemically hydrophobic, otherwise water will simply absorb into the forest. This was achieved by coating with a very thin conformal layer of polytetrafluoroethylene (PTFE) via a second CVD process. This layer coats the length of the CNTs down to the substrate, rather than forming a blanket over them – the result is a highly-textured surface with a hydrophobic coating. Advancing contact angles as high as 170° were achieved, with a hysteresis of 10°. Fig. 2 shows the suspension of a near-spherical macroscopic water droplet above an ultraphobic CNT forest. Owing to the very small scale of the surface texture, spherical droplets as small as 20 μm were observed using Environmental Scanning Electron Microscopy (ESEM). Polymer-coated CNT forests are ultraphobic and can be applied by CVD processes that might be

Fig. 1 Taking a leaf out of nature’s book: electron micrographs of ultraphobic leaves: Nelumbo nucifera, left, scale bar = 50 μm and Hygoryza aristata, right, scale bar = 20 μm, showing texture at different scales. Reproduced with permission from Oxford Journals, ref. 6.

Fig. 2 Left, a drop of water resting on a PTFE-coated carbon nanotube forest. Right, an electron micrograph of the same ultraphobic surface. Reproduced with permission from The American Chemical Society, ref. 14.
adapted by industry, although the durability of such coatings is the main barrier to application.\textsuperscript{15}

3. Hydrophilic photocatalytic coatings

The second class of self-cleaning surfaces to be discussed differ from Lotus-Effect\textsuperscript{1} coatings in that they are hydrophilic rather than hydrophobic, and do not rely solely on the flow of water to wash away dirt. These coatings chemically break down dirt when exposed to light, a process known as ‘photocatalysis’, although of course it is the coating not the incident light that acts as a catalyst. While the Lotus-Effect\textsuperscript{1} was inspired by the self-cleaning properties of plant leaves, hydrophilic coatings have parallels with photosynthesis, using sunlight to drive chemistry. Despite the commercialisation of a hydrophilic self-cleaning coating in a number of products, the field is far from mature; investigations into the fundamental mechanisms of self-cleaning and characterisations of new coatings are regularly published in the primary literature.

Titanium dioxide: the Activ\textsuperscript{2} photocatalyst

In 2001 Pilkington Glass announced the development of the first self-cleaning windows, Pilkington Activ\textsuperscript{2}, and in the following months several other major glass companies released similar products, including PPG’s Sunclean\textsuperscript{2}. As a result, glazing is perhaps the largest commercialisation of self-cleaning coatings to date. All of these windows are coated with a thin transparent layer of titanium dioxide (titania or TiO\textsubscript{2}), a coating which acts to clean the window in sunlight through two distinct properties: photocatalysis causes the coating to chemically break down organic dirt adsorbed onto the window, while hydrophilicity causes water to form ‘sheets’ rather than droplets – contact angles are reduced to very low values in sunlight (the coating becomes ‘super-hydrophilic’), and dirt is washed away. Titania has become the material of choice for self-cleaning windows, and hydrophilic self-cleaning surfaces in general, because of its favourable physical and chemical properties. Not only is titania highly efficient at photocatalysing dirt in sunlight and reaching the super-hydrophilic state, it is also non-toxic, chemically inert in the absence of light, inexpensive, relatively easy to handle and deposit into thin films and is an established household chemical – it is used as a pigment in cosmetics and paint and as a food additive. The latter point may explain the rapid transition of self-cleaning titania surfaces from the research laboratory to the marketplace. The mechanisms of the self-cleaning processes that occur on titania surfaces have been thoroughly investigated over the past decade,\textsuperscript{16} and although research continues to describe the exact mechanism for the destruction of specific pollutants,\textsuperscript{17–19} a basic model has gained wide acceptance. A thorough discussion of the theory of photocatalysis and super-hydrophilicity is beyond the scope of this article, hence only a brief summary follows. Greater detail can be found in one of several review articles on the subject.\textsuperscript{16,20–22} A semiconductor under normal conditions, titanium dioxide absorbs light with energy equal to or greater than its band gap energy, resulting in excited charge carriers: an electron, e\textsuperscript{-}, and a hole, h\textsuperscript{+} (Fig. 3). Although the fate of most of these charge carriers is rapid recombination, some migrate to the surface. There, holes cause the oxidisation of

\textbf{Fig. 3} Upon irradiation of TiO\textsubscript{2} by ultra band gap light, the semiconductor undergoes photo-excitation. The electron and the hole that result can follow one of several pathways: (a) electron–hole recombination on the surface; (b) electron–hole recombination in the bulk reaction of the semiconductor; (c) electron acceptor A is reduced by photogenerated electrons; and (d) electron donor D is oxidised by photogenerated holes.
adsorbed organic molecules while electrons eventually combine with atmospheric oxygen to give the superoxide radical, which quickly attacks nearby organic molecules. The result is a cleaning of the surface by ‘cold combustion’, the conversion of organic molecules to carbon dioxide and water (and other products if heteroatoms are present) at ambient temperatures. This process is remarkably effective and clean; e.g. the total decomposition of stearic acid \([\text{CH}_3(\text{CH}_2)_16\text{CO}_2\text{H}]\) in the presence of atmospheric oxygen to \(\text{CO}_2\) and \(\text{H}_2\text{O}\), a \(10^4\) electron oxidation, occurs with no detectable by-products on a \(\text{TiO}_2\) surface (Fig. 4). 23 A wide range of solid-, liquid- and gas-phase organic pollutants can be broken down in this way, including aromatics, polymers, dyes and surfactants, 16 although a much smaller range of inorganic materials have been successfully decomposed on titania. Photocatalysis is usually tested by monitoring the destruction of a model pollutant. Stearic acid, methylene blue and chlorophenol are popular choices as they are easy to quantitatively measure by spectroscopy.

Super-hydrophilicity in \(\text{TiO}_2\) is also a light-induced property. 24 Holes produced by photo-excitation of the semiconductor oxide lattice oxygen at the surface of the material, resulting in oxygen vacancies. These can be filled by adsorbed water, resulting in surface hydroxide groups that make the wetted surface more favourable compared to the dry surface, lowering the static contact angle to almost 0° after irradiation. 23 Both self-cleaning properties of \(\text{TiO}_2\) are therefore governed by the absorption of ultra band gap light and the generation of electron/hole pairs. The band gap of bulk anatase \(\text{TiO}_2\) is 3.2 eV, corresponding to light of wavelength 390 nm – near-ultraviolet (UV) light. The physical and chemical properties of \(\text{TiO}_2\) depend greatly on its form and the method of preparing the sample. Several polymorphs of \(\text{TiO}_2\) are known, the most significant of which are rutile and anatase. The positions of the conduction and valence bands relative to key redox potentials cause pure anatase to be very photoactive (photocatalytic and super-hydrophilic) while pure rutile is less so. 16,25 As highlighted by a recent Royal Society report, nanoscale (dimensions in the range 1–10 nm) and micro- or macro-scale titania show distinctly different properties. Semiconductors with physical dimensions of the order of the wavelengths of the electrons they contain display properties not observed in the bulk solid. Such materials are often referred to as nanoparticles, nanocrystals or quantum dots. Bulk or macroscale powder titania is a brilliant white solid, non-toxic and widely used as a pigment in paint, cosmetics and food, while nanoscale titania particles are used in sunscreens and their absorption properties, surface properties and band gap vary with their size and shape. 21

It is to be expected, therefore, that rates of photocatalysis will also vary strongly with sample preparation, and this is indeed the case. As a general rule, suspensions of macroscale \(\text{TiO}_2\) powder in water show higher rates of photocatalysis than immobilised macro \(\text{TiO}_2\) particles, which in turn display greater activity than smooth nanocrystalline \(\text{TiO}_2\) films; however, within these broad categories there is much variation. 16,23,25,26 The photoactivity of a sample is highly dependent on exact experimental parameters, which causes difficulties in comparing photocatalysis results from several sources. While surface area, surface defects, particle size and impurities are certainly important factors, their precise influence on the photocatalytic behaviour of \(\text{TiO}_2\) is still not completely clear. Theoretically, nanoparticulate titania should be more photoactive, due to its higher surface area and a wider band gap, leading to greater oxidation power of excited holes and greater reducing power of excited electrons. 21 Some studies have found the exact opposite, however. 25 Nanocrystalline films, essentially films made up of closely packed nanoparticles, that might be deposited by CVD or sol–gel techniques tend to display lower photoactivity than larger immobilised \(\text{TiO}_2\) particles. 23 Perhaps the most important factor here is surface area, since organic molecules are photocatalytically decomposed at or near the \(\text{TiO}_2\) surface, so samples with a high surface area and porosity will self-clean more quickly. The effect of surface area can be inferred from the kinetics of photocatalytic decomposition. Fig. 5 shows the decomposition of the same quantity of stearic acid by a nanocrystalline coating (Activ®) with a relatively low surface area and an immobilised film of \(\text{TiO}_2\) particles (Degussa P25) with a higher surface area. The zero order decomposition on the nanocrystalline film indicates that the reaction sites on the surface are saturated, while the onset of higher order decomposition that occurred on the immobilised particles indicates non-saturated surface reaction sites. 23 In addition, the band gap widening commonly associated with nanoscale semiconductors, and higher rates of electron–hole recombination thought to be due to the larger number of grain boundaries in the film, will increase the energy and intensity of light needed to activate nanoscale compared to macroscale titania. 27,28

Despite their lower photoactivity compared with other forms of titania, nanocrystalline \(\text{TiO}_2\) films are used in all self-cleaning windows released to date. This is because nanocrystalline films of titania can be made optically clear enough
for commercial window use. Pilkington Activ® consists of a 20–30 nm layer of nanocrystalline anatase titanium dioxide deposited by an atmospheric pressure CVD technique onto soda-lime silicate float glass. The result is a product with extremely favourable visible transmission and reflectance properties; Activ® has a visible reflectance of around 7% and a visible haze of less than 1%, but absorbs 20% of incident solar UV light which is used in the self-cleaning process. The coating is also robust and cannot be damaged by application of Scotch tape or moderate mechanical abrasion; Pilkington claim that the coating will last the lifetime of the window frame. Aside from window glass, many other titania-coated products have become available in the past five years. In Japan, where the photocatalytic properties of titania were first discovered, hundreds of companies produce self-cleaning products. Amongst the largest is TOTO Ltd., which manufactures several self-cleaning products with titania coatings, branded Hydrotect®. Hydrotect® outdoor tiles and paint have been used in the Marunouchi Building in Tokyo. Textiles impregnated with titania have been developed in Hong Kong. A sol–gel process was used to coat cotton substrates with anatase titania, which withstood boiling water treatment for 3 hours. It is hoped that these coatings will lead to self-cleaning clothes, although the results of functional tests have yet to be published – how the titania is to be prevented from breaking down the fabric itself is unclear.

Improving on titania

Titanium dioxide has become the ‘gold standard’ in photocatalytic hydrophilic coatings. Its high photoactivity and the ease of deposition coupled with its established use in many existing products have accelerated the release of commercial self-cleaning titania coatings. However, titania is not beyond improvement. In rendering titania optically clear and robust by depositing it in a smooth, nanocrystalline film, its photocatalytic activity is reduced compared to many other forms of the material. While the rigid optical requirements of the glazing industry clearly do not apply to all applications of self-cleaning surfaces, most of such applications will require a robust, easily deposited coating, and a nanocrystalline film matches these requirements; therefore, methods of improving the self-cleaning properties of nanocrystalline films are required. The present challenges in advancing photocatalytic coatings are challenges of understanding and innovation: understanding the physical, chemical and material aspects of these coatings; and innovation in applying this knowledge to improve them.

Some strategies for improved coatings might involve increasing the surface area of the film, increasing the number of electron–hole pairs generated, increasing the lifetime of the pairs in the material by reducing the recombination rate or creating coatings that are activated by lower energy light, thus using a higher proportion of the solar spectrum. As a widely available and uniform commercial product, Activ® is a useful reference against which to test designs for improved self-cleaning coatings. An immediately apparent method for increasing the UV absorbance of a coating and therefore the number of excited charge carriers is to make a thicker coating. Titanium dioxide coatings 3 µm thick, produced by spin coating and annealing a TiO₂ paste, have been tested for photocatalysis against Activ®, a 25 nm coating. The thicker coatings absorbed near-UV light more strongly and were more photocatalytically active, exhibiting quantum yields of around 0.15%, compared with 0.04% for Activ®. This indicates that not only does the thicker film absorb more light and thus generates more excited charge carriers, but crucially that these charge carriers have a lifetime long enough to reach the surface and participate in the chemistry that occurs there. Presumably there is a limit to the increase in activity that a thicker film can
afford; when all the available UV light is absorbed, or the distance to the surface is so great that charge carriers have little chance of reaching it before they recombine, a still thicker film will not increase the activity. That limit, however, is considerably larger than the 25 nm Activ®, Sunclean® and similar products. There are, of course, disadvantages to thicker films. A film two hundred times as thick as Activ® will be correspondingly more expensive per unit area, due to longer deposition time and the greater amount of material needed. Optical clarity and durability, crucial properties for a window coating, will also be poorer in the thicker film, although for other applications such problems may be less important.

**Improvements to TiO₂ by doping**

Doping of TiO₂ to improve its self-cleaning is an attractive approach and one that can easily be incorporated into a CVD or sol–gel process, and has been investigated for some years. Impurities can strongly affect titania photocatalysis even in low concentrations. Studies on particulate photocatalysis have shown that the presence of 10% rutile phase titania within anatase decreases photocatalysis in microscale particles but has little effect on nanoscale particles. Depending on the technique used to deposit the coating, dopants can exist as a single phase mixed oxide or as a separate phase, and a particular dopant may behave differently depending upon which form it is in. Transition metal dopants have been widely investigated, and when present as a mixed oxide can be divided into low oxidation state and high oxidation state, based on their effects. Metals with lower oxidation states lower than +4, such as Fe³⁺, Co²⁺ and Ni²⁺, inhibit photocatalytic activity, while metals with higher oxidations states, such as Mo⁶⁺, Nb⁵⁺ and W⁶⁺, increase photocatalytic activity. In a study by Park et al., differential scanning calorimetry (DSC) indicated that the low oxidation state dopants caused crystallisation to occur around 20 °C higher than high oxidation state dopants when present as a mixed oxide. An X-ray photoelectron spectroscopy (XPS) study showed that the high oxidation metal doped films had a higher proportion of hydroxyl groups adsorbed onto the surface than undoped and low oxidation doped TiO₂. Since hydroxyl groups are important in photocatalysis, this could explain the increase in activity in the presence of high oxidation dopants, and also suggests that these films would show super-hydrophilicity. Separate studies have verified the enhancement of photocatalysis that occurs in the presence of high valence dopants such as W, Ta and Nb.

Phase separated dopants may also be present, i.e. a phase of pure TiO₂ containing a pure phase of a second material. Recent studies have focussed on the use of nanoparticles as a method of incorporating a phase separated dopant.

**Incorporation of nanoparticles**

Nanoparticles can be incorporated into a coating via sol–gel or by spin coating a layer onto the surface of a pre-deposited film. Metallic gold or platinum nanoparticles can assist photocatalysis in TiO₂ by acting as charge separators: excited electrons are transferred from the conduction band of the semiconductor to the metal, thus preventing recombination. The accumulated electrons on the metal particle then go on to reduce surface adsorbed species, increasing the rate of self-cleaning as reduction on the surface of a metallic particle is more rapid than on the surface of the semiconductor. Phase separated semiconductors can be coupled to titania as either incorporated nanoparticles or as a separate layer, resulting in a semiconductor heterojunction. At such an interface, electrons and holes migrate between phases depending on the relative energies of their conduction and valence bands. This process can either activate or deactivate the TiO₂ phase, depending on the identity of the coupled semiconductor. By coupling a visible light absorbing semiconductor, such as CdS or WS₂, with TiO₂, visible light generated charge carriers are transferred to the titanium dioxide phase where they can induce photocatalysis and super-hydrophilicity.

**Other materials**

Although most semiconductor self-cleaning studies concentrate on irradiating TiO₂ with UV light, other materials and methods can be used. Several metal oxides and sulfides, including WO₃, ZrO₂, ZnO and CdS, and polyoxometallates have been investigated over the years, although none have managed to surpass TiO₂ using light alone to activate the catalyst. However, as essentially an electrochemical process, semiconductor photocatalysis is influenced by an electric field. The effect is to more efficiently separate photogenerated holes and electrons, and can be achieved by depositing the semiconductor onto an electrode. Since photogenerated holes are more efficient at decomposing pollutants, a positive bias applied to the electrode enhances photocatalysis as holes are pushed to the surface and electrons escape to the electrode. Titanium dioxide can be successfully used in this way as a photoelectrocatalyst as a sol–gel film deposited onto a platinum or tin oxide electrode, although it is not the most efficient. Tungsten oxide (WO₃) deposited in the same way, while less efficient as a photocatalyst, is a more efficient photoelectrocatalyst.

**4. Conclusions**

Self-cleaning coatings have been used in nature for millennia. It is only in the past decade that commercial self-cleaning products have become available to the consumer. The use of a self-cleaning coating is attractive as they are labour saving and effectively improve the appearance of the environment. Two main forms of self-cleaning films have been developed – hydrophobic films that repel water droplets, and hydrophilic films that cause water droplets to form sheets. A number of hydrophilic films also show attractive photocatalytic properties for the destruction of organic dirt. Such products have now been commercialised as self-cleaning window glass with a lifetime that is rated as long as that of a typical double-glazed unit. One interesting new development of the titania-based coatings is their ability to destroy harmful bacteria and viruses by photocatalytic action using sunlight. Such coatings are effective in the destruction of even the MRSA-‘superbug’ that plagues hospital environments.

The key factor that requires further development is the ability to extend the range of light that can be used for the photodestruction of dirt and bacteria. As the gold
standard – ‘titania’ can only use sub-390 nm light. Extending the absorption range by pushing this edge more into the visible region would significantly improve the efficacy of the coating. Some esoteric suggestions such as having self-cleaning clothes by incorporating titania particles into the fabric mixture sound impressive; however, the manufacturers will have to bind the titania in such a way that it does not photocatalytically decompose the fabric. Otherwise the “Emperor’s new clothes” phenomena could become a reality.

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References

1 http://www.lotusan.de/ (in German).

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