

Characterisation of the photocatalyst Pilkington Activ™: a reference film photocatalyst?

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Abstract

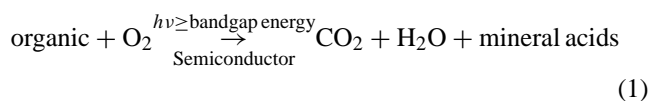
Pilkington Glass Activ™ represents a possible suitable successor to P25 TiO₂, especially as a benchmark photocatalyst film for comparing other photocatalyst or PSH self-cleaning films. Activ™ is a glass product with a clear, colourless, effectively invisible, photocatalytic coating of titania that also exhibits PSH. Although not as active as a film of P25 TiO₂, Activ™ vastly superior mechanical stability, very reproducible activity and widespread commercial availability makes it highly attractive as a reference photocatalytic film. The photocatalytic and photo-induced superhydrophilic (PSH) properties of Activ™ are studied in some detail and the results reported. Thus, the kinetics of stearic acid destruction (a 10⁴ electron process) are zero order over the stearic acid range 4–129 monolayers and exhibit formal quantum efficiencies (FQE) of 0.7×10^{-5} and 10.2×10^{-5} molecules per photon when irradiated with light of 365 ± 20 and 254 nm, respectively; the latter appears also to be the quantum yield for Activ™ at 254 nm. The kinetics of stearic acid destruction exhibit Langmuir–Hinshelwood-like saturation type kinetics as a function of oxygen partial pressure, with no destruction occurring in the absence of oxygen and the rate of destruction appearing the same in air and oxygen atmospheres. Further kinetic work revealed a Langmuir adsorption type constant for oxygen of $0.45 \pm 0.16 \text{ kPa}^{-1}$ and an activation energy of $19 \pm 1 \text{ kJ mol}^{-1}$. A study of the PSH properties of Activ™ reveals a high water contact angle (67°) before ultra-bandgap irradiation reduced to 0° after prolonged irradiation. The kinetics of PSH are similar to those reported by others for sol–gel films using a low level of UV light. The kinetics of contact angle recovery in the dark appear monophasic and different to the biphasic kinetics reported recently by others for sol–gel films [J. Phys. Chem. B 107 (2003) 1028]. Overall, Activ™ appears a very suitable reference material for semiconductor film photocatalysis.

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1. Introduction

The popular subject area of semiconductor photochemistry is dominated by research into photocatalysis, especially the use of the semiconductor titanium dioxide as a photocatalyst for the mineralisation of organic pollutants by oxygen [1–3]. The overall process can be summarized by the following reaction equation:



The number and type of organic pollutants that can be mineralized via reaction (1) is substantial and includes haloalkanes, aromatics, pesticides, insecticides, dyes and surfactants.

These pollutants may be dissolved in water or gaseous. Examples of semiconductor photocatalysts exist in the literature at least as early as 1929 when it was reported that the pigment “Titanium White”, i.e. titanium dioxide, was responsible for photochalking in paints [4]. The first suggestion that reaction (1) could be used as a method for destroying organic pollutants appeared much later, in 1983 by Ollis and co-workers investigating photomineralisation of halogenated hydrocarbons, including trichloroethylene, dichloromethane, chloroform and carbon tetrachloride, sensitized by titanium dioxide [5,6]. Reaction (1) offers the attractive possibility of creating a method of water and air purification that is capable of destroying completely most organic pollutants simply with a flick of a switch. Such systems can also be driven by the UV component of sunlight. It is not surprising therefore that reaction (1) has attracted a great deal of attention, from research groups in academia and industry alike, over the last three decades [2,3,7].

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It might be considered surprising at first to note that the semiconductor photocatalyst for reaction (1) used in 1983 by Ollis and co-workers [5,6] is still the preferred choice, namely titanium dioxide [7]. Titanium dioxide owes much of its continuing popularity as a semiconductor photocatalyst to the fact that it is chemically and biologically inert, very photoactive, cheap and easy to prepare. Its one major drawback is a high bandgap, i.e. $E_{BG} = 3.0$ eV, which means that it only functions when exposed to ultraviolet, rather than visible, light. However, the advantages of titanium dioxide as a photocatalyst far outweigh its one main disadvantage and so it continues to be the most popular photocatalyst for the purification of air and water via reaction (1).

Titanium dioxide can be made by a number of different methods including the sol–gel process [8], sputtering [9], chemical vapour deposition (CVD) [10] and thermal oxidation [11]. Early on in the area of research into titania photocatalysis it proved necessary to identify at least one source of titanium dioxide that all research groups can access and which is cheap and very photoactive, in order to facilitate comparisons between different titanium dioxide photocatalysts. From the ranks of all the commercial forms of titanium dioxide available Degussa P25 titanium dioxide has emerged as the reference semiconductor photocatalyst material. Degussa P25 titanium dioxide is a mixture of the crystalline phases, anatase and rutile, typically in a ratio of 70:30, respectively. It is also non-porous and possesses a moderately high specific surface area ($55 \text{ m}^2 \text{ g}^{-1}$). Even today Degussa P25 remains effectively the gold standard titania photocatalyst for reaction (1) (see references there in [2]).

In recent years, an increasing amount of research into semiconductor photocatalysis has moved away from the use of the semiconductors in the form of powder dispersions to their use, especially titanium dioxide, in the form of films. Thus, nowadays, most research into titanium dioxide films as photocatalyst for reaction (1) are based on hard glazes of the semiconductor titanium dioxide prepared by a number of different methods, including CVD, the sol–gel process, thermal methods and sputtering [2,7]. One of the problems beginning to emerge from such research is the difficulty in comparing titania photocatalyst films prepared by these different methods and studied by different groups; a problem that is reminiscent of that faced by researchers in this field in the early days of semiconductor photocatalysis using powder dispersions. In order to rectify this situation what is required is a standard titanium dioxide film which is physically well-defined, photocatalytically active, mechanically robust, readily available and cheap. Regrettably, although Degussa P25 titanium dioxide can be used to prepare films of titanium dioxide for reaction (1), these films are not mechanically stable, nor highly reproducible and typically can be readily wiped off using a cloth or thumb [12,13]. Thus, a standard titanium dioxide reference film needs to be made from something other than Degussa P25 TiO_2 .

In early 2001 the major glass manufacturing company, Pilkington Glass, began producing a titanium dioxide

coated glass called Pilkington Activ™ as a commercial self-cleaning glass product for use in the home improvement sector. This product was then successfully trialed in Ireland, Austria and North America and such was its success that production facilities now exist in Germany as well as the USA. Activ™ self-cleaning glass is now readily available in North America, Australasia and Europe and set to be a world-wide product [14].

Pilkington Activ™ glass is the worlds first commercially-available, self-cleaning glass, comprising a film of nanocrystalline titanium dioxide (about 15 nm thick) as the photocatalyst active layer. This layer is applied to clear float glass, via a on-line chemical vapour deposition process, to produce a hard, thin, transparent, mechanically-robust, photoactive coating of titanium dioxide on glass. This material appears the ideal, readily available titanium dioxide photocatalyst film with which to use as a benchmark for all other photocatalyst films that are being produced by research groups in academia and industry alike for light-driven air and water purification and self-cleaning purposes. As a consequence, in this paper we report the findings of a detailed study of the photocatalytic properties of Pilkington Activ™ glass as a possible successor to the gold standard Degussa P25 titanium dioxide and reference material for all other photocatalyst films.

2. Experimental

2.1. Materials

Unless stated otherwise all materials used were purchased from Aldrich Chemicals, UK and used as supplied. The samples of nanocrystalline films of titanium dioxide on 4 mm float glass were provided by Pilkington glass as examples of their commercially available product Activ™ self-cleaning glass. Activ™ glass is prepared by depositing a nanocrystalline film of titanium dioxide onto float glass using an atmospheric pressure chemical vapour deposition technique, APCVD, described in detail elsewhere [15]. Briefly, in the preparation of the Activ™ samples used in this work the glass substrate used was 4 mm soda-line silicate glass with a surface covering of a silicon oxide blocking layer (approximately 30 nm thick, as determined by XPS coupled to argon-ion bombardment) to prevent alkaline metal ion migration from the glass substrate to the deposited titanium dioxide layer. In Activ™ the titanium dioxide layer is deposited by an APCVD method onto the hot glass substrate (typically 615 °C) from a mixed vapour comprising mainly nitrogen as the carrier gas and the following reactive ingredients: titanium tetrachloride (bubbler temperature 50 °C) and as the source of oxygen, ethyl acetate (bubbler temperature 35 °C). An APCVD method of depositing the titanium dioxide film is preferred because it is especially suitable for producing large volumes of coated glass. Since the final titanium dioxide film has typically a thickness of ca. 15 nm, the

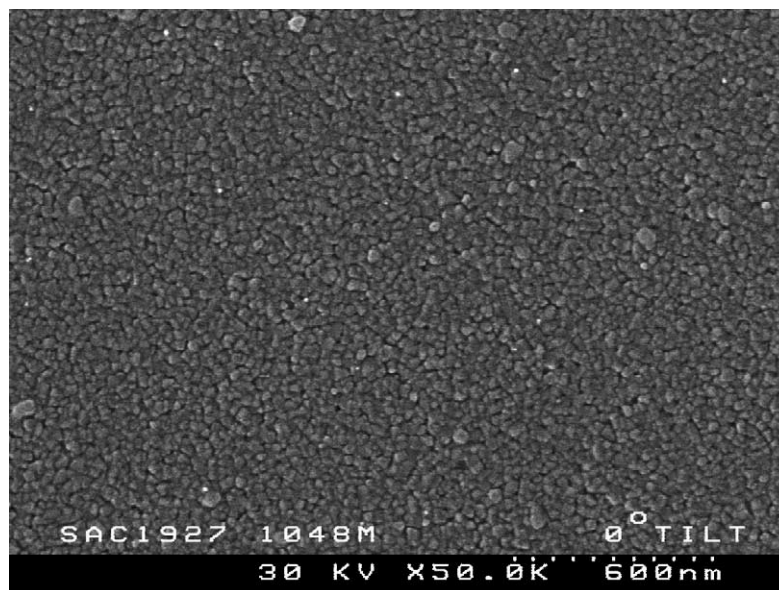


Fig. 1. Scanning electron micrograph of the surface of Activ™.

total thickness of the silicon oxide/titanium dioxide coat on the 4 mm float glass is approximately 45 nm. A typical SEM of the final film is illustrated in Fig. 1 and shows the surface titanium dioxide coating to comprise particles of ca. 30 nm diameter. Thus, given that the titania film is 15 nm thick, the coating appears to comprise a layer of broad domes of titania, 30 nm in diameter. The final product has a haze of less than 1%, a reflectivity of 5–7% and reduces the level of solar UV light transmitted through the glass by 20%. Activ™ is extremely robust mechanically. Thus, it is not damaged by the 3 M Scotch Tape™ test, nor easily damaged by vigorous rubbing or pencils of any hardness [14].

Films of Degussa P25 titanium dioxide were also prepared and used in order to effect a useful comparison in photocatalytic activity and mechanical robustness. Thus, the Degussa P25 TiO₂ films on glass substrates were cast by spin-coating 25 mm × 25 mm × 3 mm squares of barrier glass (Pilkington Glass, UK) with a 5% (w/v) aqueous slurry of Degussa P25 TiO₂. The P25 slurry was deposited by dropping pipette until the whole surface of the glass surface was covered and then spun at 2900 rpm for 30 s using a model 4000-1 spin coater (Electro-Micro Systems). The films were then washed with distilled water and dried, first in an air stream and then in an oven at 80 °C for 1 h. The films were always stored overnight in the dark before use and, unless stated otherwise, used without further treatment. Films produced by this method were stable to repeated washing with water but not to mechanical abrasion. Profilometry revealed that the films had a typical thickness of 90 ± 10 nm. Although Degussa P25 TiO₂ comprises fundamental particles that are nanocrystalline, i.e. typically 30 nm in diameter, the latter form an irreducible complex of primary aggregates, typically 0.1 μm in diameter. Thus, it appears more appropriate to refer to P25 TiO₂ films as microcrystalline, rather than nanocrystalline.

3. Methods

UV-Vis absorption spectra were recorded using a Lambda 20 UV-Vis spectrophotometer (Perkin-Elmer, UK). In the study of the photocatalytic activity of the various titanium dioxide films stearic acid was used as the organic material to be mineralized via reaction (1). Deposition of the stearic acid on the 25 mm² plates of the photocatalyst samples under the test was effected by dip coating the samples in a methanolic solution of stearic acid (0.02 mol dm⁻³) and drying at 80 °C. These samples were irradiated using six 8 W blacklight bulbs, contained in a semi-cylindrical lamp holder with an aluminium reflector and held 10 cm above the samples under test. Chemical actinometry was used to measure the intensity of the lamps [16]. Rates were calculated by measuring the integrated absorbance of stearic acid between 2700 and 3000 cm⁻¹ in the infrared and using the reported concentration value of 3.17 × 10¹⁵ stearic acid molecules per cm² per integrated absorbance unit over this range [12]. The necessary infra-red measurements were made using a 1600 FT-IR (Perkin-Elmer, UK).

Contact angles were measured using an FTA 200 contact angle instrument (Camtel, UK, agents for FTA, USA). This instrument allows the shape of a water droplet deposited on the surface of the photocatalyst film under test to be recorded by CCTV and then analysed using a computer loaded with the appropriate propriety FTA software. This analyses provides an accurate value for the contact angle made by the water drop with the test substrate. In this work, the reported contact angle for an test substrate refers to the contact angle made by a drop of water on its surface 30 s after the drop first falls on the test substrate. In all contact angle measurement work ultra-violet light radiation of the films under test

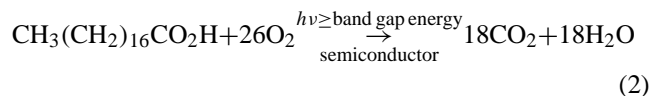
were carried out using two 8 W, 254 nm germicidal lamps (BDH, UK) for 30 min.

4. Results and discussion

The UV-Vis spectra of barrier glass, Activ™ and the P25 TiO₂ films were recorded and are illustrated in Fig. 2. The UV-Vis spectrum of plain barrier glass shows it to be non-scattering, i.e. the glass is clear and colourless, but is highly absorbing at wavelengths <310 nm, the normal cut-off for soda-lime-silicate glass. Similarly, the UV-Vis spectrum of a typical sample of Activ™ illustrated in Fig. 2 shows the coating to be only slightly scattering/reflecting at sub-bandgap wavelengths and increasingly absorbing at wavelengths below 360 nm, the approximate bandgap of nanocrystalline titania. The coated film is virtually invisible to the eye and it is often very difficult to determine which side of the glass has the coating. One method involves gently running the back of a fingernail along the surface of the glass as this will reveal the slight roughness of the coating if present. A better, less subjective, method involves placing the glass in a beam of 254 nm light from a spectrophotometer or fluorimeter, as the non-coated side fluoresces ($\lambda_{\text{max}} \approx 420$ nm). This fluorescence feature is a characteristic of glass prepared by the float method using molten tin since it is the latter that gives the glass its luminescence on its molten tin side. Fig. 2 also illustrates the UV-Vis spectrum of a spin-coat film of Degussa P25 TiO₂ on glass and shows the

film to be highly scattering at sub-bandgap wavelengths, i.e. $\lambda_{\text{max}} \approx 380$ nm, but also strongly absorbing at wavelengths <380 nm, the approximate bandgap of the microcrystalline TiO₂ particles.

A measure of photocatalytic activity that is commonly employed in semiconductor photocatalysis to assess the activities of films is the rate of photodestruction of stearic acid (CH₃(CH₂)₁₆CO₂H) [12,13,17,18–20], i.e.



a process that involves the transfer of a 104 electrons. Since the melting point of stearic acid is markedly above room temperature, i.e. 69.3 °C, it forms solid films when deposited under ambient conditions, usually by a spin- or dip-coating technique, on the photocatalyst substrate under test. The photocatalytic destruction of such solid compounds are of practical interest since they provide a reasonable model compound for the type of solid organic films that deposit on exterior glass surfaces such house or office windows [18]. The destruction of stearic acid is readily monitored by FT-IR absorbance spectroscopy, through the disappearance of the peak at 2957.5 cm⁻¹, due to the asymmetric in-plane C–H stretching mode of the CH₃ group, and the peaks at 2922.8 and 2853.4 cm⁻¹, due to the asymmetric and symmetric C–H stretching modes of the CH₂ group, respectively. In this work the integrated area under all these peaks (2700–3000 cm⁻¹) was measured and used to calculate the surface concentration

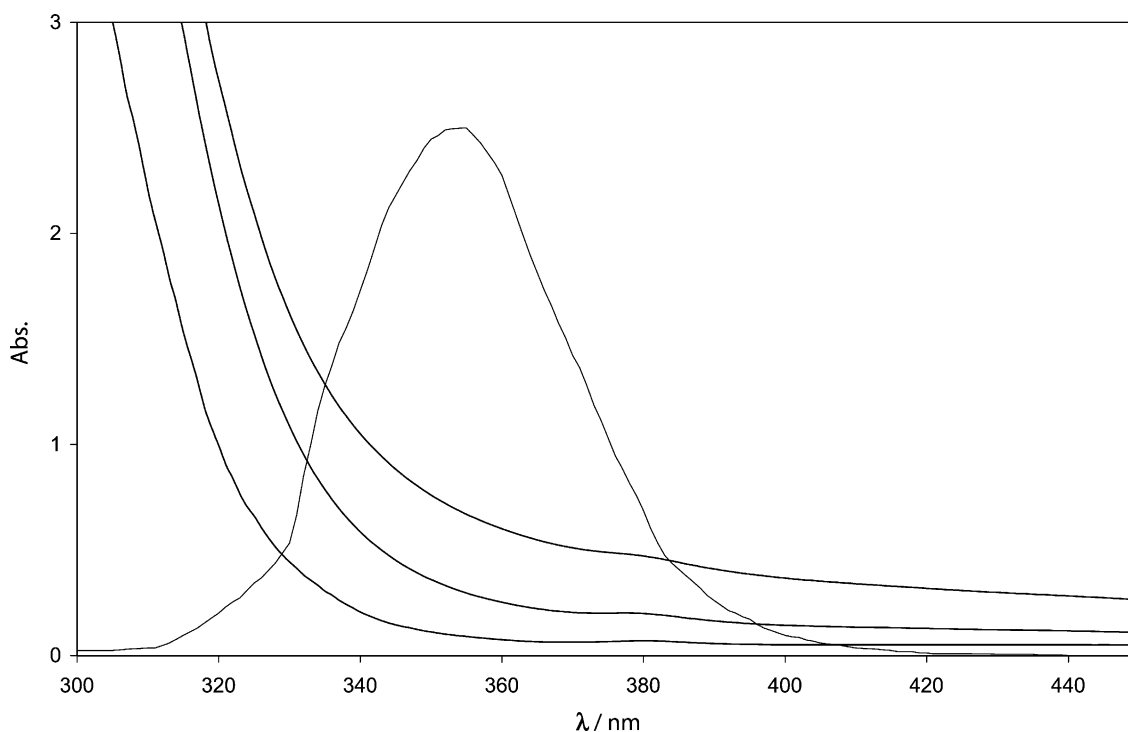


Fig. 2. UV-Vis absorption spectra of (from left to right): barrier glass, Activ™ and barrier glass coated with a 90 nm layer of Degussa P25. The lighter peak spectrum illustrates the emission spectrum of a typical blacklight bulb.

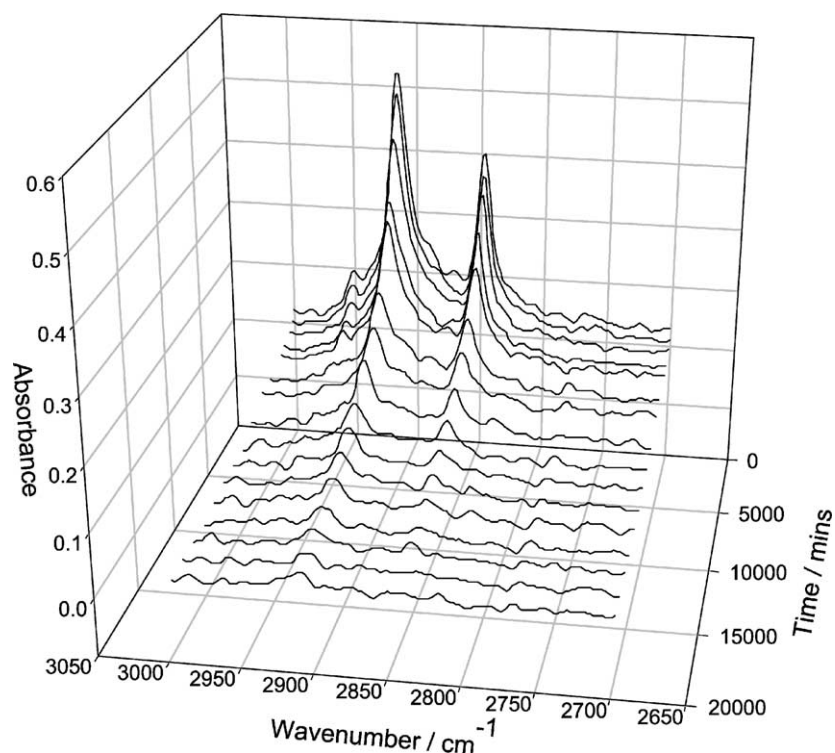


Fig. 3. FT-IR absorbance versus wavenumber, *s*, spectra, recorded for a sample of Activ™ coated with stearic acid, as a function of irradiation time. The irradiation source comprised six 8 W blacklight bulbs, i.e. 365 ± 20 nm light.

of stearic acid as a function of irradiation time, as outlined earlier [12,13]. The FT-IR method employed in this work actually measures the kinetics of disappearance of stearic acid and it is assumed that this is also a direct measure of the kinetics of reaction (2), the photocatalytic destruction of stearic acid, as would be the case if no major long-lived intermediates were generated. Support for this assumption is provided by the work of others that shows: (a) the removal of stearic acid by semiconductor photocatalysis produces no film component other than stearic acid that is detectable by FT-IR [18,20], (b) no gas phase products other than CO₂ and H₂O are generated during the course of the photocatalytic reaction [18] and (c) the ratio of the number of moles lost due to the disappearance of stearic acid and the concomitant appearance of carbon dioxide is as expected for the photocatalytic destruction reaction summarized by Eq. (2) [18].

Fig. 3 illustrates the observed variation in the FT-IR absorbance spectrum of a typical stearic acid film, deposited on an Activ™ CVD TiO₂ coated sample of barrier glass, as a function of irradiation time using 365 nm light as the irradiation source. From the data in Fig. 3 it is clear that the stearic acid peaks disappear, albeit slowly, with ultraband gap irradiation, as expected from Eq. (2). It is no surprise that the kinetics of reaction (2) are very slow for reaction (2) when Activ™ is used as the photocatalyst film and 365 nm light is used to drive the reaction forward, since, from the UV-Vis spectrum of this film illustrated in Fig. 2 it is clear that such thin films of titania hardly absorb in the near UV. Previous work carried out by this group on the spectral characteristics

of CVD coated titania on quartz indicate that the reciprocal absorption length of titania at 365 nm, i.e. $\alpha(\text{TiO}_2)_{365}$, is ca. $0.5 \times 10^5 \text{ cm}^{-1}$ [19]. Thus, a 15 nm film of titania would be expected to have an absorbance at 365 nm of only 0.0326, given $\text{Abs}_\lambda = 0.434\alpha_\lambda d$, where *d* is the film thickness (cm). From the UV-Vis absorption spectrum of the Activ™ film, illustrated in Fig. 2, the absorbance of the film at 365 nm appears to be ca. 0.157, but from the absorbance of the film at 400 nm (0.092) most of this appears to be due to light scattering and reflection and, encouragingly, the difference is 0.065, which is close to the predicted absorbance of a 15 nm film of titania at 365 nm.

Results of the kind illustrated in Fig. 3 allowed the integrated area under the infrared absorption peaks due to stearic acid to be calculated as a function of irradiation time for Activ™, P25 TiO₂ and barrier glass using either 365 or 254 nm light as the irradiation source. Using either of these light sources barrier glass showed little or no activity towards the photocatalytic destruction of stearic acid. In contrast, the integrated area versus time profiles for the Activ™ and P25 TiO₂ films illustrated in Fig. 4 show that both these films are able to photocatalyse the destruction of stearic acid, with P25 TiO₂ appearing much more active than Activ™. Note in Fig. 4 that although both films employed the same method of deposition of stearic acid there was about 20% more stearic acid on the P25 TiO₂ films, compared with the Activ™ films, at the beginning of the experiment, presumably because the former was more porous and rough than the latter and so more stearic acid was able to stick onto

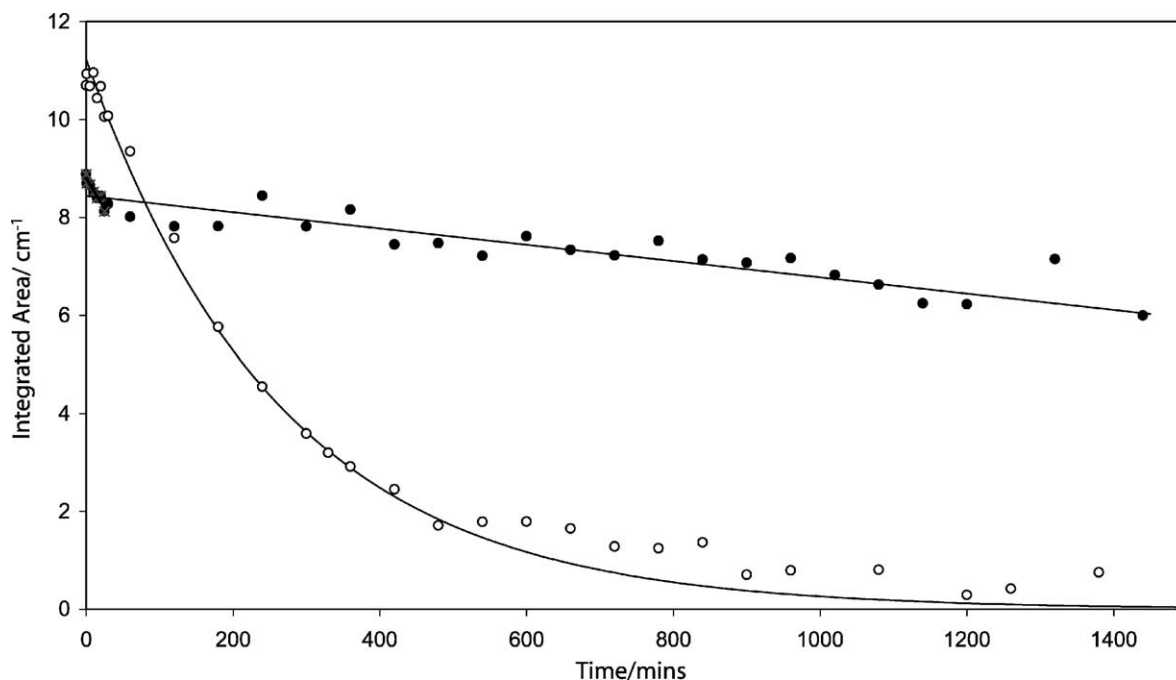


Fig. 4. Integrated area versus irradiation time profiles for Activ™ (closed circles) and Degussa P25 TiO₂ coated barrier glass (open circles), respectively. The irradiation source comprised six 8 W blacklight bulbs, i.e. 365 ± 20 nm light.

the surface of the titania during the spin-coating process of deposition. The greater photocatalytic activity of the Degussa P25 films compared to Activ™ upon irradiation with 365 nm light is very apparent from the results illustrated in Fig. 4. This observation is not too surprising, however, given that the P25 TiO₂ films are not only much thicker (ca. 90 nm compared to 15 nm) but also comprise large, almost microcrystalline, aggregates which are likely to have a lower density of electron-hole recombination centres, i.e. P25 titania particles may be intrinsically more active than nanocrystalline titania. The P25 TiO₂ film is almost certainly more macroporous than the nanocrystalline Activ™ film and so the stearic acid is likely to be much more evenly and thinly spread out over the surface of the titania particles.

For both Activ™ and P25 TiO₂ films the kinetics of stearic acid destruction appear initially to be zero-order with respect to stearic acid concentration. This observation is in agreement with those made by others also investigating reaction (2) using thick films of stearic acid and nanocrystalline films of titania made by a sol-gel method [12,13,18,20]. From the data in Fig. 4 it can be seen that the typical initial integrated absorbance for stearic acid lies in the range 9–11 cm⁻¹. However, an integrated absorbance unit of 1 cm⁻¹ corresponds to a stearic acid surface concentration of 3.17×10^{15} molecules of stearic acid cm⁻², i.e. 1.5 μg cm⁻², or a layer of stearic acid ca. 17 nm thick, assuming a density for stearic acid of 0.87 g cm⁻³. It has been reported that a monolayer of stearic acid is 2.5 nm thick, thus a 17 nm thick layer of stearic acid corresponds to ca. 6.8 monolayers of stearic acid [17]. As noted earlier in the work reported in this paper the initial integrated ab-

sorbance for stearic acid lies in the range 9–11 cm⁻¹, thus for both Activ™ and P25 TiO₂ films the stearic acid is initially 153–187 nm, 61–75 stearic acid monolayers, thick, i.e. much thicker than the particle size of the fundamental TiO₂ particles, which are typically 30 and 15 nm, respectively, for Degussa P25 and Activ™ photocatalyst films. For the 90 nm thick P25 TiO₂ film, even if it is assumed to have zero porosity and somehow still present a specific surface area of 55 m² g⁻¹, it can be shown that this would only increase the surface roughness by a factor of 21, i.e. initially the stearic acid would be at least 3–4 monolayers thick. In reality for both films the initial thickness of the stearic acid layer on the titania particles will be many monolayers thick and for the Activ™ film, may well approach the limiting value of 61–75 monolayers, given its highly compact (i.e. non-macroporous) state (see Fig. 1). From these calculations it is no wonder that the initial kinetics of stearic acid destruction appear zero order, as all the photocatalytically active sites are likely to be occupied by stearic acid molecules, above which will be many more to take their place once mineralized. Other work shows that, under the experimental conditions used in this work, using 365 nm light the kinetics of reaction (2), photocatalysed by Activ™, remains zero-order with a rate (1.9 nm h⁻¹ or 0.8 monolayer h⁻¹) that is independent of stearic acid concentration over the integrated absorbance range 0.6–19 cm⁻¹ (4–129 monolayers, respectively) of stearic acid. Further work shows that Activ™ films possess a photocatalytic activity that is highly reproducible, exhibiting little or no deterioration in stearic acid destruction rate with repeated (six cycles) deposition and destruction.

The results of the elegant work of Minabe et al. show that carbon dioxide is produced stoichiometrically in the photocatalytic destruction of stearic acid via reaction (2) mediated by titania [18]. However, these workers also note that for their titania films (400 nm thick, produced from titanium(IV) isopropoxide by a sol–gel method) the destruction of stearic acid ceases after ca. 69% of its destruction, possibly due to the formation of an inert, site-blocking reaction product. In contrast, in this work with both ActivTM and P25 TiO₂ films, stearic acid destruction was observed to go to completion, although the kinetics clearly deviated from zero order in the last 10–20% of the reaction. The latter feature was particularly clear in the study of thick (>10 monolayers) deposits of stearic acid, as might be expected if its cause lay with the accumulation of refractory, non-infrared absorbing, stearic acid degradation products. Interestingly, Minabe et al. report a stearic acid destruction rate of ca. 8.5 nm h⁻¹ using 365 nm light (1.1 mW cm⁻²) for their thick (400 nm) sol–gel titania films, which is not too dissimilar to the rate reported here (1.9 nm h⁻¹; light intensity 6.9 mW cm⁻²) for ActivTM with its thin (15 nm) titania photocatalyst coating [18]. Although a substantial cause for the differences in rate is the difference in absorbance of the two films at 365 nm, other factors, such as porosity (i.e. compactness) and density of trapping states will also be important. Impressively, P25 TiO₂ films are able to destroy stearic acid at very appreciable rates (371 and 35.5 nm h⁻¹) using, respectively, germicidal and blacklights of similar intensity, thus underlining its high activity as a photocatalytic film compared to nanocrystalline films prepared by CVD or sol–gel methods. The results of the kinetic study of reaction (2), photosensitized by Degussa P25 and ActivTM titanium dioxide films are summarised in Table 1.

As we have seen kinetic analysis of the plots of integrated absorbance due to the stearic acid infrared peaks as a function of time for both the ActivTM and P25 TiO₂ films, when irradiated with either 365 or 254 nm light allowed the calculation of initial rates which are reported in Table 1. However, in order to make some useful comparisons between the two sets of the initial rates of reaction (2), recorded for the various films using 365 and 254 nm ultra-bandgap light, the initial rates need to be corrected for the level of incident light impinging on the samples. Indeed, ideally, quantum yields

should be calculated. However, for the P25 TiO₂ films at least, it is difficult to estimate how much light is absorbed and how much lost through reflection and scattering. Thus, it is usual in semiconductor photocatalysis to calculate instead the formal quantum efficiency (FQE) of the system, δ , where formal quantum efficiency is defined as [2,21]

$$\delta = \frac{\text{rate of photoreaction (molecules/s)}}{\text{incident light intensity (photons/s)}} \quad (3)$$

Obviously, for any photochemical process, the formal quantum efficiency is, by definition, \leq quantum yield. Using the initial rate data in Table 1, and values for the incident light intensities measured by chemical actinometry, the values of δ for the removal of a stearic acid film, using 365 and 254 nm irradiation light, were calculated for each of the glass substrates tested and the results are given in Table 1. The values in Table 1 show apparently that the photocatalytic process, i.e. reaction (2), is very inefficient for all the films tested, since the values of δ lie in the range $(256\text{--}0.7) \times 10^{-5}$ molecules per photon. However, the situation is not so bad as it first may seem since it should be remembered that the complete mineralisation of stearic acid is a 104 electron process, thus the likely maximum value for δ for reaction (2) would be 1/104, i.e. 9.6×10^{-3} molecules per photon. The marked increase in initial rate and formal quantum efficiency for both the CVD and Degussa P25 TiO₂ films on changing from a 365 to a 254 nm irradiation light source can be attributed largely to the greater absorption coefficient for TiO₂ at 254 nm compared to 365 nm, since the reciprocal length, α , for TiO₂ is estimated to be ca. $0.5 \times 10^5 \text{ cm}^{-1}$ at 365 nm but $5.1 \times 10^5 \text{ cm}^{-1}$ at 254 nm [19,22].

If it is assumed, not unreasonably, that at 254 nm both the ActivTM and P25 TiO₂ films absorb all the incident light then the values of δ , i.e. 256 and 10×10^{-5} , respectively, represent quantum yields for reaction (2) using these photocatalyst films. Interestingly, the formal quantum efficiency for reaction (2), reported by Heller and his co-workers for a 1.3 mm thick film of Degussa P25 TiO₂ using 254 nm light as the irradiation source is similar to that reported in Table 1 for a 90 nm thick film of the same material, i.e. 270 and 250×10^{-5} , respectively. The similarity in results, despite the very different thickness of P25 TiO₂ film is not too surprising given that both films would absorb most, if not all,

Table 1
Photocatalytic properties of ActivTM and P25 TiO₂ films

Sample	Contact angle ^a pre-irradiation (°)	Contact angle ^a post-irradiation ^a (°)	Rate of photodegradation ^b (10 ¹³ molecules cm ⁻² min ⁻¹)		Rate of photodegradation ^{b,c} (nm of stearic acid h ⁻¹)		FQE ^d (10 ⁻⁵ molecules per photon)	
			365 nm	254 nm	365 nm	254 nm	365 nm	254 nm
P25 TiO ₂	8	0	11.2	117	35.5	371	15.3	256
Activ TM	67	0	0.6	4.7	1.9	14.9	0.7	10.0

^a Irradiation was achieved by exposing the samples to 2 × 8 W 254 nm germicidal lamps for 60 min.

^b Photoirradiations at 365 and 254 nm were conducted using 6 × 8 W blacklight (365 ± 20 nm) bulbs and 6 × 8 W germicidal (254 nm) lamps, respectively.

^c Rate (nm of stearic acid h⁻¹) = 3.17 × rate (10¹³ molecules cm⁻² min⁻¹).

^d FQE: formal quantum efficiency, as defined by Eq. (3). Photonic light intensities for 365 and 254 nm irradiations were calculated using values of 7.59×10^{17} photons cm⁻² min⁻¹ (6.9 mW cm⁻²) and 4.57×10^{17} photons cm⁻² min⁻¹ (6.0 mW cm⁻²).

the incident 254 nm light, since $a(\text{TiO}_2)_{254}$ is $5.1 \times 10^5 \text{ cm}^{-1}$ and $\text{Abs}_\lambda = 0.434\alpha_\lambda d$, i.e. both films should absorb at least 99% of the 254 nm light, assuming no losses due to reflection.

The kinetics of reaction (2), photosensitized by ActivTM were also studied as a function of oxygen partial pressure, P_{O_2} . Thus, in the absence of oxygen (i.e. in a nitrogen purged system) no appreciable photocatalytic destruction of the stearic acid was observed, whereas, in contrast, at 0.21 and 1 atm partial pressures of oxygen the rate of reaction (2) was appreciable and identical in value. Similar findings have been reported by Sitkiewitz and Heller in their study of the photocatalytic destruction of stearic acid by sol–gel titania films [20]. These findings are consistent with the often observed saturation kinetics, of the Langmuir–Hinshelwood type, associated with semiconductor photocatalysis, i.e.

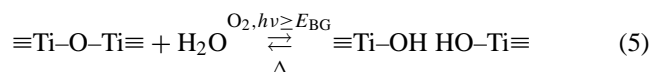
$$\text{Rate of photocatalysis} = \frac{kK_{\text{O}_2}P_{\text{O}_2}}{1 + K_{\text{O}_2}P_{\text{O}_2}} \quad (4)$$

where k is the maximum rate (typically 1.9 nm stearic acid h^{-1} for ActivTM) and K_{O_2} is a constant. Usually, K_{O_2} is assumed to be the Langmuir dark adsorption constant for oxygen adsorbed non-competitively onto the surface of titanium dioxide. A typical value for K_{O_2} has been reported as 0.044 kPa^{-1} for an aqueous powder dispersion of Degussa P25 TiO_2 used to photocatalyse the mineralisation, by dissolved oxygen, of 4-chlorophenol [23]. In contrast, in this work, the kinetics of reaction (2) were studied over the oxygen partial pressure range 5–100 kPa and from an analysis of the results using Eq. (4) a value for K_{O_2} of $0.45 \pm 0.16 \text{ kPa}$ was calculated for ActivTM. The difference between the two values for K_{O_2} is not too surprising given the very different circumstances of the two mineralisation processes, i.e. one involving near microcrystalline titania particles dispersed in solution destroying a soluble pollutant and the other a solid, largely non-porous photocatalyst film destroying an overlying solid film of pollutant. Interestingly, from the above two values of K_{O_2} it appears that oxygen adsorbs more strongly onto the surface of titania when it is covered with stearic acid than when it is dispersed in aqueous solution. Although this difference could be simply due to superior competitive adsorption by water compared to stearic acid, little should be read into these results as the it is not clear how much K_{O_2} varies between titania samples prepared by different methods.

The kinetics of reaction (2) were also studied as a function of temperature over the range 14–54 °C and an Arrhenius plot of the results revealed a value for the activation energy of $19 \pm 1 \text{ kJ mol}^{-1}$. The latter value is similar to the value of 16 kJ mol^{-1} reported by this group for the destruction of 4-chlorophenol sensitized by an aqueous dispersion of Degussa P25 TiO_2 [24]. The kinetics of reaction (2) were also studied as a function of relative humidity (0–100% at 25 °C; saturated vapour pressure of water = 24 torr) and found to be largely invariant over the range 10–100%. At 0% humidity the rate was ca. three times lower than that found at

all other humidities. The results of this work are similar to those reported by Sitkiewitz and Heller in their study of the photocatalytic destruction of stearic acid by sol–gel titania films [20] and highlight the importance of water in reaction (2) and the fact that, even under apparent extremely dry conditions, such titania films have enough surface bound water to enable reaction (2) to proceed at a rate that is sufficiently slow that it is replenished by the water generated as part of reaction (2). However, as noted by Sitkiewitz and Heller, it is likely that if the rate is increased significantly, e.g. by increasing the level of absorbed UV light, then water depletion would eventually stop the photomineralisation process [20].

Water droplets typically make a contact angle with ActivTM of 67°, provided the glass has not been exposed to UV light. Upon prolonged (i.e. >60 min using two 8 W germicidal lamps) exposure to UV light the contact angle drops down to 0°. Thus, if stored in the dark ActivTM appears to provide a relatively hydrophobic surface but upon prolonged exposure to UV light it becomes hydrophilic. This feature of titania is called photo-induced superhydrophilicity (PSH) and has been known for many years. Thus, as early as 1986 the Nihon Itagarasu K.K. company described in a patent a titanium coated glass plate (Reflight S) which exhibited PSH [25]. The authors attributed the phenomenon of PSH to the photocatalytic mineralisation action of titania on any organic substances deposited on the surface. However, the more thorough studies carried out by Fujishima, Hashimoto and co-workers in the last 5 years have established that an alternative mechanism exists other than the removal of organic species adsorbed on the surface of titania [1,26–30]. This alternative mechanism appears to involve the trapping of photogenerated holes at lattice, usually bridging, oxygen sites at, or close to, the surface. Such trapped holes appear to weaken the bond between the associated titanium and the lattice oxygen. As a result, at such a weakened site oxygen is liberated to create an oxygen vacancy, followed by the dissociative adsorption of water at the site to render it more hydroxylated. Since this process is repeated to lesser and greater extents depending upon the density of surface bridging oxygen groups the result is the photogeneration of a patchwork quilt of hydrophilic domains (typically 10 nm in size) on the surface of a polycrystalline titania film. Such a surface is not stable however, and over time, in the dark, these newly-formed, weakly-bound hydroxyl groups desorb to form hydrogen peroxide, or water and oxygen, leaving behind a lattice oxygen (usually a bridging oxygen). The result of this dark reaction is that a photo-induced superhydrophilic titania surface is restored to its original hydrophilic form when stored for long periods in the dark. The photogenerated electrons are assumed to be trapped by Ti(IV) sites, as Ti(III) which is subsequently oxidised by oxygen [1]. The overall process can be summarised as follows:



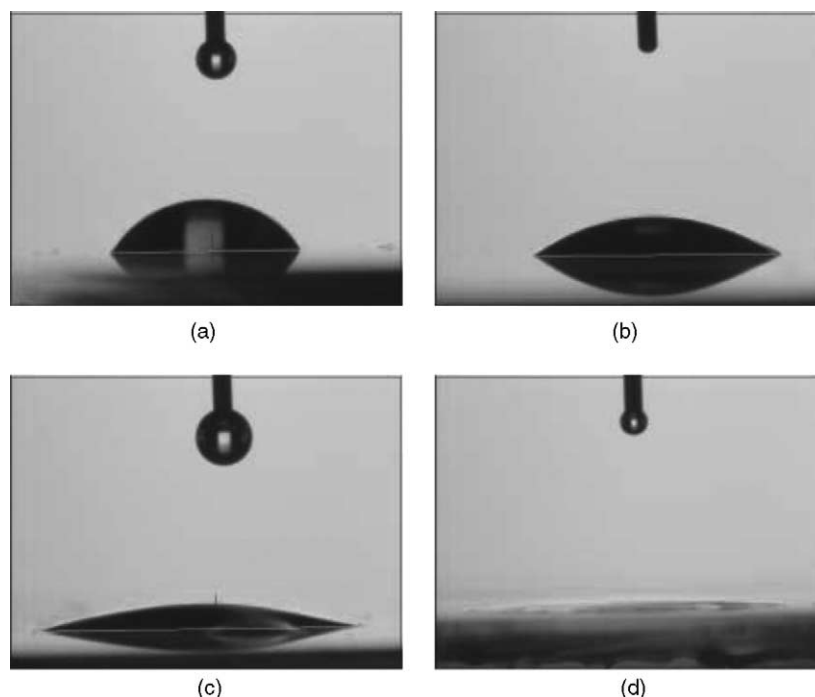


Fig. 5. Recorded change in water droplet profile as a function of irradiation time for an ActivTM film. The irradiation times were (a) 0 min, (b) 15 min, (c) 30 min and (d) 45 min, respectively. Images, such as these were used to generate the data illustrated in Fig. 6. The irradiation source comprised two 8 W germicidal lamps, i.e. 254 nm light.

The ubiquitous form of titania, Degussa P25, when cast as a film, also exhibits PSH and has contact angle of ca. 8° when stored in the dark and 0° when irradiated for 1 h. The results of the contact angle measurements made on ActivTM and P25 TiO₂ are given in Table 1. The forward process in PSH, i.e. Eq. (5), can be inhibited by placing on its surface a sacrificial electron donor, i.e. a mild reducing agent, such as sodium sulphite which competes with the bridging oxygens for the photogenerated hole [1,26]. The reverse process in Eq. (5), is usually slow under ambient conditions, usually taking days to complete. However, this reverse process can be made to occur faster (seconds rather than days) by (a) subjecting the film to ultrasound when dipped in water [31] or, (b) mechanical wet-rubbing [32]. Both are scouring processes and presumably provide sufficient energy to the surface to promote the reverse reaction. Ultrasound also generates reducing, as well as oxidizing species, and these may also play a part in promoting the reverse of reaction (5).

A more detailed study of the forward and reverse reactions that form the equilibrium process reaction (5) for ActivTM was undertaken. The study of the variation of the contact angle of ActivTM as a function of irradiation time required that after each different period of irradiation the sample be returned to its original hydrophobic state, with a water contact angle of ca. 67° . This rapid reversal of PSH was achieved by dipping the film in a beaker of water and subjecting it to 6 min of ultrasound from an ultrasound bath. This process of rapid return to the original hydrophobic state was carried out

on the film after each different period of irradiation followed by drying in air and subsequent contact angle measurement. Previous work carried out by others, and confirmed by this group, showed that air, or nitrogen drying of the films did not alter their water contact angles [1,26]. Fig. 5 illustrates some of the results of this work, i.e. the observed change in water droplet profile as a function of irradiation time for a sample of ActivTM. From these images it is clear that the contact angle made by a water droplet decreases with increasing irradiation time, as expected from Eq. (5). Fig. 6 illustrates the variation in the measured water contact angle as a function of irradiation time for ActivTM. The profile is quite different to those reported by others [1] for sol-gel films in that, initially, the contact angle does not appear decrease much with irradiation time but, instead, the rate of drop in contact angle appears to gradually to increase with increasing irradiation time and hydrophilicity. In contrast, sol-gel films usually exhibit a hyperbolic type variation in contact angle with irradiation time [17,26]. Indeed, typically for a sol-gel titania film, a plot of the reciprocal of the contact angle versus time yields a good straight line, the gradient of which provides some measure of the kinetics of the process [1,26]. Fig. 7 illustrates the observed variation in contact angle as a function of irradiation time for a $8\ \mu\text{m}$ thick titania film prepared by a sol-gel process [33]. The hyperbolic nature of the contact angle versus time profile is confirmed by the very reasonable linearity of a plot of the data in the form of $1/(\text{contact angle})$ versus time, illustrated in the insert

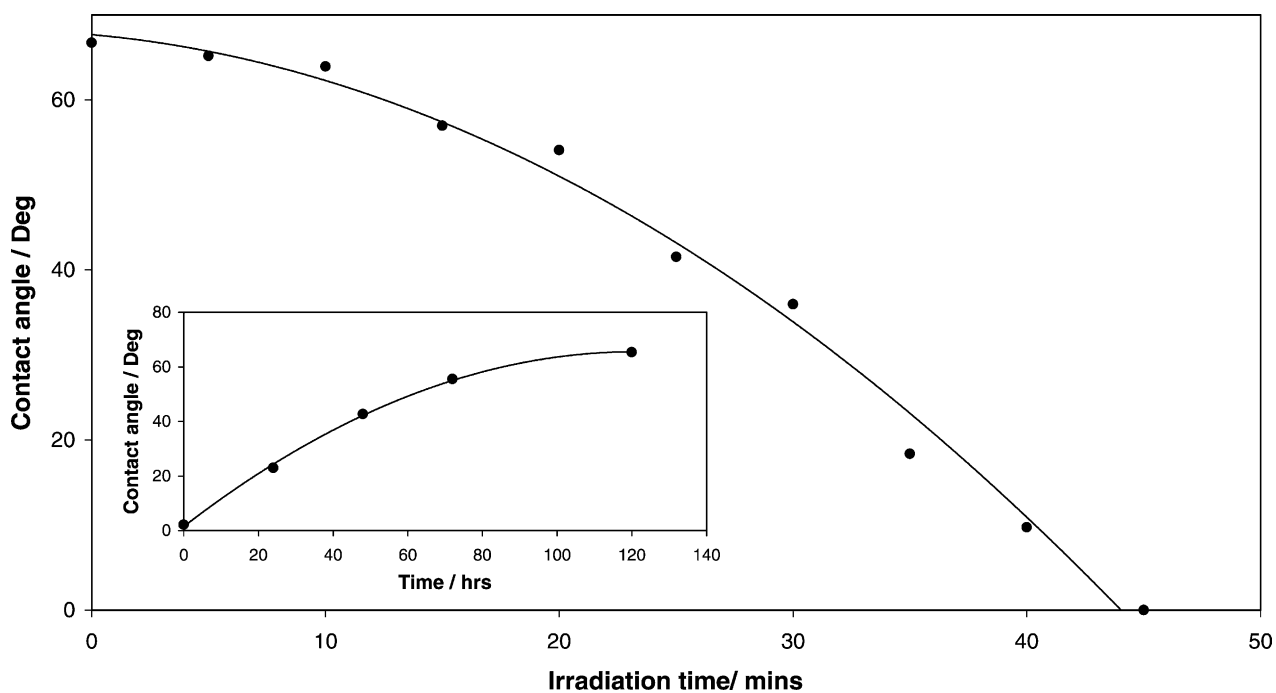


Fig. 6. Variation of water contact angle for Activ™ recorded as a function of irradiation time. The irradiation source comprised two 8 W germicidal lamps, i.e. 254 nm light. The insert diagram illustrates the observed dark recovery in the contact angle of a UV activated Activ™ film as a function of time.

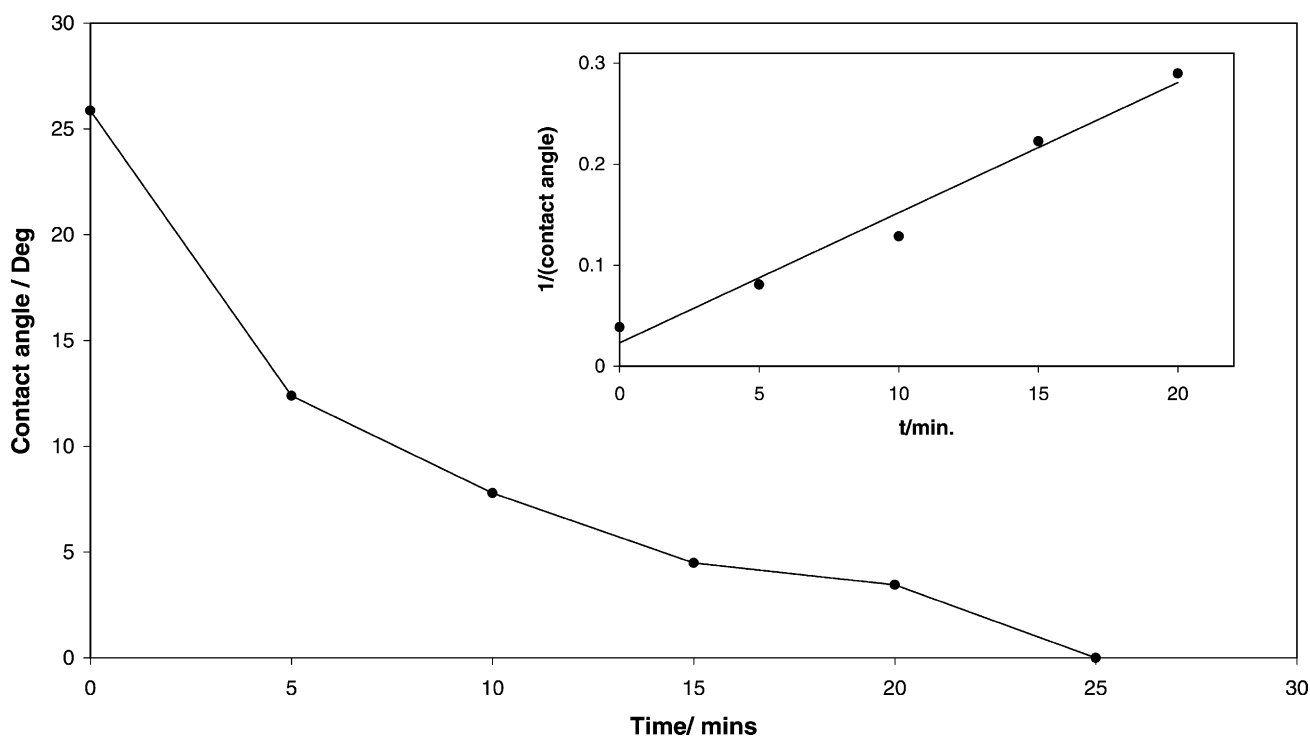


Fig. 7. Variation of water contact angle for an 8 μm thick film of titania prepared by a sol-gel method as a function of irradiation time. The irradiation source comprised two 8 W germicidal lamps, i.e. 254 nm light. The insert diagram illustrates a plot of the data illustrated in the main diagram in the form of a reciprocal of the contact angle as a function of time.

diagram in Fig. 7. Interestingly, the non-hyperbolic variation in contact angle versus irradiation time profile illustrated in Fig. 6 has been noted before by others looking at the effect of irradiation of fairly thick (0.4 microns) sol-gel films with low (0.1 mW cm^{-2}) intensity UV light [27]. Thus, this feature of a gradually increasing rate of change in contact angle with irradiation time appears to be associated with reaction (5) carried out under conditions of low absorbed light intensity. The latter can be achieved either by using very thin films of titania (15 nm in the case of ActivTM) and moderate UV light intensities (6.9 mW cm^{-2} in this work) or much thicker films (400 nm) and low (0.1 mW cm^{-2}) UV light intensities. It is not clear at present what is the underlying cause of the feature, although it does not appear to be a rapid reverse process since this is very slow at all contact angles compared with the light-activated forward process. Instead, it appears to be due to a preliminary surface conditioning process, possibly associated with the removal of a small amount of adventitious organic impurities in the surface of the titania.

In contrast to the forward process, the kinetics of the reverse process are relatively easy to measure. Thus, in this work a typical ActivTM sample was irradiated with two 8 W germicidal lamps for 60 min and then its water contact angle monitored as a function of time stored in air. After each measurement, made under low, ambient light levels, the film under test was dried in air and returned to the dark until its dark recovery was next probed. The results of this work for ActivTM are illustrated in the insert diagram in Fig. 6. The recovery of the contact angle of ActivTM is slow and its rate slowly decreases with increasing dark storage time. Although similar shaped, monophasic contact angle recovery profiles have been reported by others for sol-gel films [27], more recent work on the same type of film appears to show that the recovery process for such films is biphasic with a rapid first step (ca. 10° in ca. 12 h) followed by a more gradual process (ca. 20° over 35 days) [1]. Certainly in this work the latter biphasic kinetics appeared to be associated with the recovery of the contact angle of an $8 \mu\text{m}$ thick titania film, after its illumination with UV light for 1 h, with the rapid first step occurring within 11 h and with the film fully returned to its original contact angle of ca. 25° within 150 h. Thus, the kinetics of the reverse process in PSH and reaction (5) appear very different for ActivTM and thick sol-gel titania films. Interestingly, both the sol-gel films and the ActivTM films recover their original contact angles within 120–150 h, after UV irradiation. Of commercial significance is the fact that an ActivTM film, once rendered superhydrophilic, remains so when stored for up-to 12 h in the dark. Thus, once activated by UV light via PSH and reaction (5), ActivTM will remain hydrophilic over-night and with moderate UV irradiation during the day will stay this way ad infinitum. However, this conclusion is based on results obtained under ambient temperature conditions (typically 20°C) and it seems very likely that both the forward and, especially, the reverse processes that comprise reaction (5) will be temperature sensitive. Although the forward pro-

cess may not be too temperature sensitive, based as it is on a photocatalytic process, most of which have low activation energies, the same cannot be said for the reverse process which is likely to have a significant activation energy. Determination of the activation energies for these two processes is the subject of on-going research.

5. Conclusion

The commercial product manufactured by Pilkington Glass, ActivTM, is a glass product with a clear, colourless, effectively invisible, photocatalytic coating of titania that also exhibits PSH. Although not as active as a film of P25 TiO₂, ActivTM vastly superior mechanical stability, very reproducible activity and widespread commercial availability make it a suitable and necessary successor to P25 TiO₂ as a benchmark photocatalyst film against which all future photocatalyst or PSH self-cleaning films should be compared.

Acknowledgements

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