

Novel low-temperature photocatalytic titania films produced by plasma-assisted reactive dc magnetron sputtering

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Abstract

Robust, active, anatase titania films, 250 nm thick, are deposited onto glass at low temperatures, i.e., <100 °C, using plasma-assisted, reactive dc magnetron sputtering (PAR-DC-MS). The films are transparent and colourless and truly photocatalytic, exhibiting turnover numbers >2.0 for the photocatalytic mineralization of stearic acid. These films are typically 6.9 times more active than a sample of commercial self-cleaning glass, comprising a 15 nm layer of titania deposited by CVD, mainly because they are much thicker and, therefore, absorb more of the incident UV light. The most active of the films tested comprised particles of P25, but lacked any significant physical robustness. Similar results, but much more quickly obtained, were generated using a photocatalyst-sensitive ink, based on the redox dye, resazurin, RZ. All titania films tested, including those produced by magnetron sputtering exhibited photo-induced superhydrophilicity. The possible future application of PAR-DC-MS for producing very active photocatalytic films on substrates not renowned for their high temperature stabilities, such as plastics, is noted.

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1. Introduction

Semiconductor photocatalysis (SPC) continues to be the focus of many research groups, especially with regard to the ability of many semiconductors, most notably titania, to mediate the photomineralisation of many organics by oxygen [1–4], i.e.,



where E_{bg} is the bandgap of the semiconductor, 3.0–3.2 eV for TiO_2 . Such is the ability of titania to mediate reaction (1) that several major commercial products, based on titania photocatalyst films, have been launched successfully in recent years [5]. These include self-cleaning glass and tiles, such as ActivTM [6] and HydrotechTM [7], sold by Pilkington Glass and TOTO, respectively.

In most commercial manifestations of SPC, the active layer is a film of titania, usually produced via some high temperature treatment process, involving CVD or a sol–gel process. The high

temperatures (typically ≥ 450 °C) are needed to convert a largely inactive amorphous titania into a much more active crystalline form, usually anatase and to help produce a physically robust film. It follows that, so far, the titania-film supporting substrate must be resistant to such high-temperature treatment; clearly not a problem when it comes to self-cleaning glass and tiles [6–8]. However, there is an obvious future market for transparent photocatalytic films on plastics for use in street-light covers, car and plane windows and corrugated sheet roofing, for example. Exploitation of this potentially large market has been largely hindered by the inherent high-temperature step in titania film production.

Reactive magnetron sputtering is an example of a physical vapour deposition (PVD) method by which titania films can be generated [9–17]. However, this along with most other PVD methods, produces titania films which are usually non-stoichiometric, amorphous, not very active photocatalytically and poorly attached to the substrate (usually glass) without a post heat-treatment step to anneal and crystallise the film [10,13,17]. Note: a rather elegant method to produce low temperature active films of titania involves the combination of a sol–gel process, followed by a low-temperature oxygen plasma

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treatment [18]; however, use of the latter might pose problems if the substrate was easily oxidised, as might be in the case of a plastic.

Typically, in reactive dc sputtering, argon gas is used as the sputtering gas and a titanium metal target is bombarded with argon ions, producing a vapour of titanium atoms, which then reacts with the oxygen reactive gas, to produce TiO_2 that deposits onto the substrate. A ring magnet placed below the target enhances the sputtering process. The mechanical characteristics of the titania film that forms, in particular adhesion and compactness, depend upon the energy of the condensing particles and in most cases, this energy is insufficient to create mechanically robust, active, stoichiometric titania films [13]. However, by applying a radio-frequency ac-voltage to the non-conducting substrate, a plasma is created over the substrate area that allows the condensing particles to gain sufficient energy, via chemical activation and acceleration, to create mechanically robust, active, stoichiometric films of titania. Interestingly, these films are also quite crystalline, thus, no post high-temperature treatment step is required to activate these plasma-assisted, reactive dc magnetron sputtered (PAR-DC-MS) titania films and the maximum temperature endured by the substrate can be $\leq 100^\circ\text{C}$. Previous work has reported on the use of dc magnetron sputtering as a route to produce thin titania films. However, most require temperatures $>100^\circ\text{C}$ to produce the most active films [9–17] and few report on the mechanical stability of these films [13]. In this initial paper, the use of this low-temperature deposition technique to create robust titania films on glass is described. The photocatalytic activity of the titania films is assessed by two different methods and compared to that of a typical, commercial self-cleaning glass film, ActivTM. This system allows 3D objects, up to 30 cm across in any direction, as well as planar substrates, as used in this work, to be coated with titania.

2. Experimental

The plasma assisted reactive dc sputtering deposition, PAR-DC-MS, system used in this work was built on site. The system comprised a deposition chamber which utilised a batch vacuum system with a configuration commonly used for the production of optical components, i.e. a turbo-molecular pump and gas flow and process pressure control systems. The sputtering component comprised a standard dc magnetron sputtering source (Galileo Avionica) fed by a dc pulsed generator (Advanced Energy) that typically operated under the following conditions: power 3 kW, voltage 430 V, current 6.8 A, pulse frequency 10 kHz and pulse width 1 μs . A conductive target, 4 mm thick TiO_x , where x lies in the range 1–2, with planar dimensions 305 mm \times 127 mm, supplied by Bekaert VDS (Deinze), was used in this work. In most other work in which titania films are produced by reactive sputtering a titanium metal target is used, and a TiO_x target is used here because the sputtered sub-oxide of titania is easy to oxidise fully to titania and yet, being a sub-oxide is still sufficiently conducting to be sputtered using a dc magnetron. A fully oxidised titanium target would require an RF magnetron with significantly lower sputtering rates. The plasma assistance

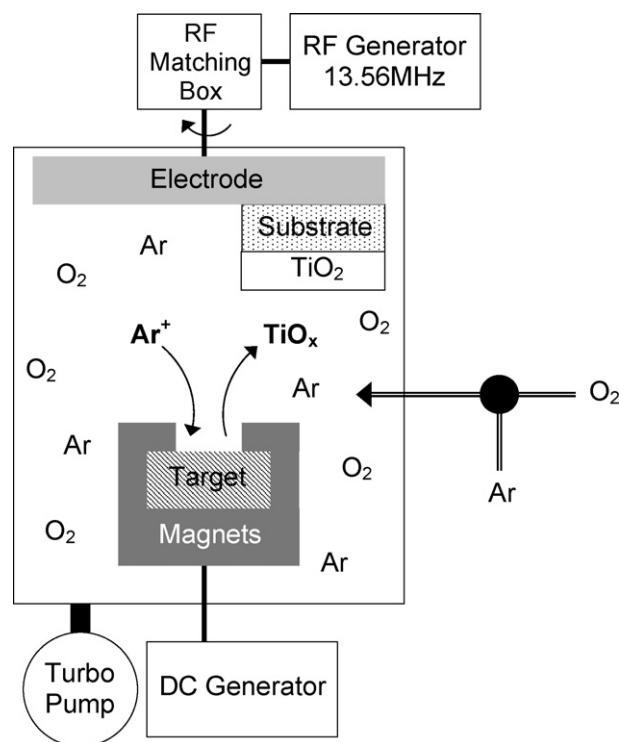


Fig. 1. Schematic illustration of the PAR-DC-MS system for producing low-temperature, active titania films.

was provided by a rotary metallic substrate holder connected to an RF system, operating at 13.56 MHz with a power density of 0.013 W cm^{-2} . Fig. 1 provides a schematic illustration of the PAR-DC-MS system, with its various major components.

In a typical run using this system, 3 mm thick glass samples (diameter: 25 mm) were placed in the chamber which was then pumped down to 10^{-4} mbar after which a 4:1 mixture of argon and oxygen was pumped in, to achieve a process pressure of 2×10^{-2} mbar. A typical run time was 270 min and the final thickness of the deposited titania film was ca. 250 nm. A long deposition time is required to ensure no excessive local heating of the substrate and the creation of a robust, crack-free, uniform film. The films produced using this procedure were optically clear and exhibited an XRD spectrum typical of anatase titania. In particular, the XRD spectrum, illustrated in Fig. 2(a), showed peaks corresponding to the 101, 200 and 211 crystal planes, with d -spacings of 3.52, 1.89 and 1.67 Å, i.e., $2\theta_{\text{B}} = 25.3^\circ$, 48.1° and 54.9° for $\text{CuK}\alpha_1$ radiation, respectively.

The films were mechanically very robust and were not removed or damaged by numerous abrasion and adhesion tests including: a pull test using 3M Scotch TapeTM and a moderate abrasion test, using a cheesecloth pad, with a 0.5 kg weight attached to the rubbing head for pressure, which was rubbed 25 times over the sample [13]. A typical AFM of the titania film is illustrated in Fig. 2(b) and shows the film to be comprised of closely packed particles, typically 60 nm in diameter. The R_{q} and R_{max} values for the PAR-DC-MS film were 4.6 and 41.7 nm, respectively; approximately twice those for ActivTM, indicating that the former are approximately twice as rough.

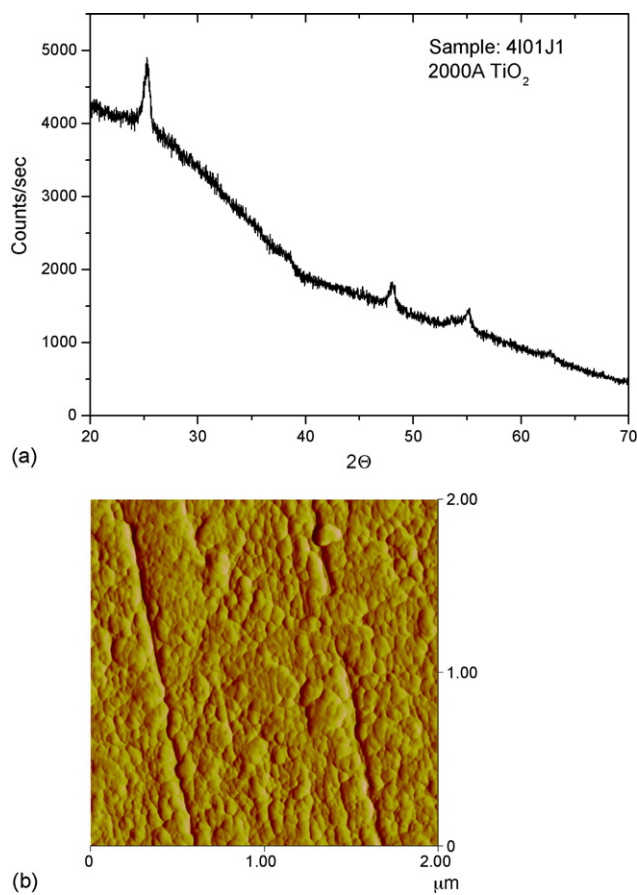


Fig. 2. (a) $\text{CuK}\alpha_1$ XRD spectra of PAR-DC-MS titania film on glass, with peaks at 25.3° , 48.1° and 54.9° , indicating an anatase only crystal phase present and (b) AFM image of the titania film produced by PAR-DC-MS, with most titania particles ca. 60 nm in diameter.

Other titania films used in this work were a commercial self-cleaning glass, ActivTM (Pilkington Glass), comprising a 15 nm thick titania film as the active coating, prepared by a CVD technique [19] and thick, 4 μm , titania films prepared by a sol-gel method [20]. In both cases, the titania was anatase. P25 titania films 90 nm thick were prepared using a dip-coat method described elsewhere [19]. As part of the assessment of the photocatalytic activities of the various TiO_2 films, stearic acid was used as the organic material to be mineralized via reaction (1) [20–26]. For each film tested, 1.0 ml of a 0.02 M stearic acid in chloroform solution was spread over the film, and then spun at 500 rpm for 15 s, in order to coat the film with a thin layer of stearic acid. The final coated film was dried in an oven at 80°C for 10 min, allowed to cool and then used directly. The infra-red spectrum of the film before and after the addition of the stearic acid layer was recorded using a Spectrum 1 FT-IR spectrometer (Perkin Elmer, UK). The same instrument was used to record the FT-IR spectrum of the film as a function of time of irradiation with ultra-band gap light. The FT-IR's software allowed the integrated area under the stearic acid peaks to be determined over the range $2800\text{--}3000\text{ cm}^{-1}$ for each FT-IR spectrum recorded and a plot of A_{int} versus irradiation time to be generated. A typical stearic acid film had an initial integrated absorbance over this range of 1.0 cm^{-1} , corresponding to ca. 9.7×10^{15}

molecules of stearic acid cm^{-2} [27]. In the stearic acid tests, all irradiation were performed using six 8 W blacklight bulbs (i.e. $365 \pm 20\text{ nm}$) set in a half cylinder unit, with back aluminium reflector, held 13 cm above the sample. In this work, the incident light intensity was 4.32 mW cm^{-2} . All incident light intensities were measured using a UV meter with a calibrated UVA detector (UVP model MS-100 with MS125 UVA sensor).

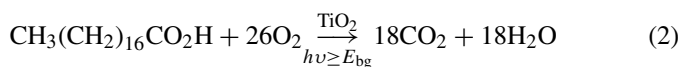
The photocatalytic activities of the titania films were also assessed using a photocatalyst ink [28] comprising: 3 g of a 1.5 wt% aqueous solution of hydroxyethyl cellulose (HEC), 0.3 g of glycerol and 4 mg of the redox dye, resazurin, Rz. Typically, a 25 mm^2 section of the sample under test was coated with a few drops of this ink, spun at 500 rpm for 10 s, and dried in an oven at 70°C for 10 min. Drying in air, rather than in an oven, did not alter the performance of the ink. A typical dried ink film was ca. 590 nm thick, as measured by weighing the film and using a weight-averaged density based on the relative amounts of HEC and glycerol present. In the ink tests, all UV irradiations were performed using a small UVA irradiation system (VWR), comprising two, 4 W black light blue lamps (typical output: $365 \pm 20\text{ nm}$); with an irradiance of 7.4 mW cm^{-2} when placed directly above the sample under test. All UV/Vis spectra were recorded using a Thermo Electron Helios Beta UV/Vis single beam spectrophotometer.

Contact angles were measured using an FTA200 contact angle instrument (Camtel). This instrument allows the deposition of a $10\text{ }\mu\text{L}$ water droplet onto the substrate under test via a $500\text{ }\mu\text{L}$ syringe coupled to a 27 gauge needle with a 90° bevel tip held above the test substrate. The shape of the droplet on the sample under test was stable for many minutes and so 30 s after its delivery its profile was recorded using a combination of a white light source, prism and CCTV, all in a horizontal plane, i.e., perpendicular, to that of its delivery. The resulting recorded profile image of the water droplet was then analysed and the contact angle determined using a computer and proprietary instrument software. In this part of the work, ultra-band gap irradiation of the films under test were carried out using two 8 W 254 nm germicidal lamps (BDH, UK) for 30 min.

3. Results and discussion

A popular method for assessing the activity of a self-cleaning titania photocatalyst film is the stearic acid (SA) test, in which a thin layer of SA is deposited onto the film and its photocatalytic destruction monitored as a function of time. This reaction has gained preference over the years [20–27] for a number of reasons, including (a) SA provides a reasonable model compound for the solid, wax-like, thin organic films that deposit on exterior and interior surfaces, (b) SA is very stable under UV illumination in the absence of a photocatalyst film, (c) SA films, typically >monolayer thick (i.e. $>2.5\text{ nm}$) [24], are very easily cast onto the photocatalytic film under test from a methanol or chloroform solution and (d) the kinetics of removal of $>2.5\text{ nm}$ thick SA films are usually simple and zero-order, and the thickness of the deposited SA film on a titania film under test is not usually a critical factor when assessing the photocatalytic activity of the titania film, making the test much easier.

The overall photocatalytic mineralization of SA can be summarized as follows:



Although there are likely to be many intermediates involved in reaction (2), none of significance are detectable in the gas phase above the SA film [26]. The lack of volatile intermediates helps ensure that reaction (2) goes to completion and that all the SA present on the titania film is mineralized [27]. The most commonly employed method to monitor the kinetics of this reaction is via the disappearance of the SA film using infrared absorption spectroscopy, since SA absorbs strongly in the region 2800–3000 cm^{-1} , with peaks at 2958 cm^{-1} , 2923 cm^{-1} , and 2853 cm^{-1} , due to asymmetric in-plane C–H stretching in the CH_3 group and asymmetric and symmetric C–H stretching in the CH_2 groups, respectively.

A number of different photocatalytic films, including that produced by PAR-DC-MS, were tested using this technique. The variation in the FT-IR absorbance spectrum of a typical PAR-DC-MS film, with an initial coating of stearic acid, as a function of UV irradiation time is illustrated in Fig. 3(a). These results show that after 200 min exposure to UVA light the stearic acid film is completely removed, in contrast to a similar experiment, carried out under otherwise identical reaction conditions, but using plain glass, for which the SA film remained largely unchanged, as indicated by the results illustrated in Fig. 3(b). The amount of stearic acid present on any of the photocatalytic films tested is proportional to the integrated area, A_{int} , under the corresponding FT-IR absorbance spectrum [23]. Thus, data of the form illustrated in Fig. 3 can be converted into associated A_{int} versus UV irradiation time plots for the different photocatalytic films tested and the results of this work are illustrated in Fig. 4. From this plot it appears that the PAR-DC-MS titania film is markedly more active (ca. 6.9 times) as a photocatalyst for the removal of stearic acid than the commercial self-cleaning glass, ActivTM. This marked difference is largely due to film thickness, since the PVD titania film is typically ca. 17 times thicker than the CVD titania film on ActivTM glass. The most active of the films tested was a 90 nm film of P25, which was ca. 25 times more active than a film of ActivTM glass and 3.8 times more active than the PVD titania film, as indicated by the initial rates for SA destruction given in Table 1.

One of the most active clear and robust photocatalyst titania films reported is produced using a sol–gel technique [20] and was used here to compare with the activity of the PAR-DC-MS film. Like the other two samples it utilizes an anatase film of titania, but is generated as a much thicker (ca. 4 μm) layer, so as to be able to absorb much more of the incident UVA light. As a consequence, in practice the best of the titania films tested in this work were the P25 and sol–gel films, as indicated by the results in Fig. 4 and summarized in Table 1, although the latter films are less robust physically than the PAR-DC-MS or CVD films. The initial rate of disappearance of stearic acid data in Table 1 can be recalculated in terms of activity per nanometer of titania and the results are also given in this table and show that the titania film on ActivTM is the most active of the four titania coated samples

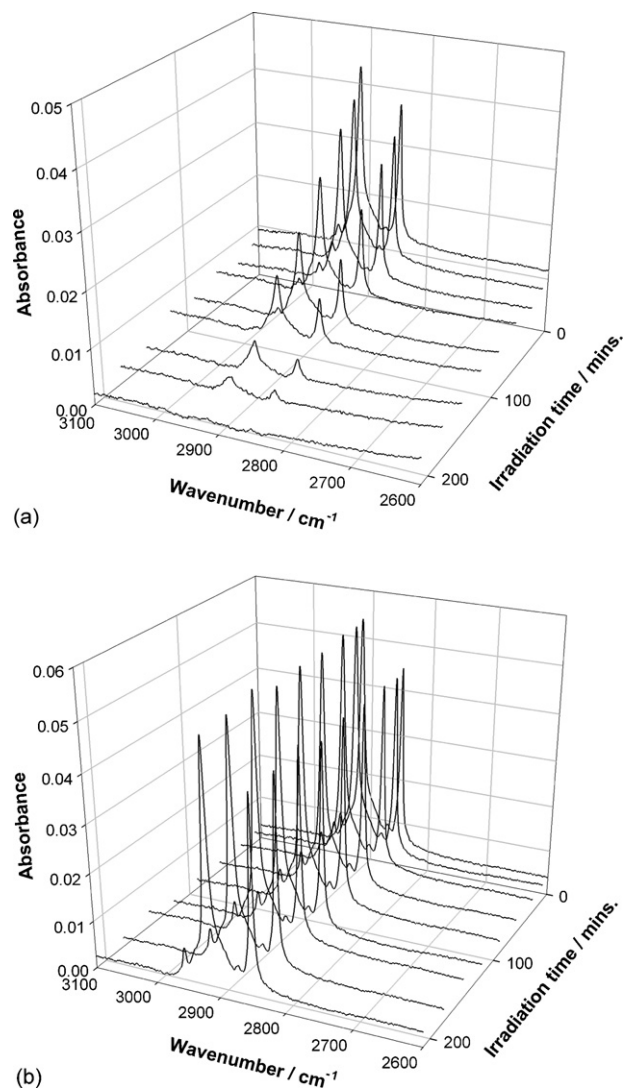


Fig. 3. Absorbance vs. wave number plot as a function of UV irradiation time of a stearic acid film on a sample of (a) PAR-DC-MS titania on glass and (b) plain glass.

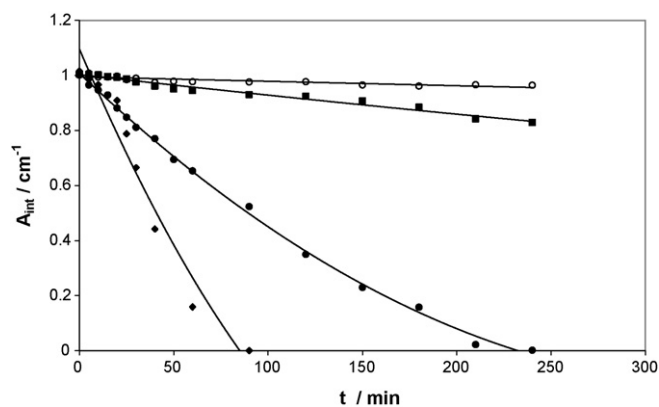


Fig. 4. Integrated IR absorbance (over the range 2800–3000 cm^{-1}) due to stearic acid, A_{int} , vs. UV irradiation time plots for the following underlying titania films on glass: (○) plain glass, (■) ActivTM, (●) PAR-DC-MS and (◆) sol–gel.

Table 1
Results of the stearic acid (SA) and resazurin (Rz) ink tests on the photocatalytic activities of various titania-on-glass films

Film	SA test		Rz ink test $R_{\text{ink}} = \text{dAbs}_{610}/\text{dt}$ (10^{-3} min^{-1})	Turnover number ^a
	$R_{\text{SA}} = \text{d}A_{\text{int}}/t$ ($10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$)	$R_{\text{SA}}/\text{thickness}$ ($10^{-6} \text{ cm}^{-1} \text{ min}^{-1} \text{ nm}$ of titania ⁻¹)		
PAR-DC-MS	4.8	19	97.2	2.1 ^b
Activ TM	0.7	47	13.6	6.9
Sol-gel	12.8	3.2	^c	0.03
P25 ^d	17.8	20	^c	12.6 ^e

^a Turnover number = No. of molecules of SA destroyed/No. of sites of TiO₂ present.

^b Based on the data in Fig. 5.

^c Too fast to measure accurately.

^d Ninety nanometer film as prepared and used previously [19].

^e Based on an initial SA absorbance of 11 data in Ref. [19].

tested for reasons which remain unclear, but could include differences in surface morphology, porosity, degree of crystallinity, to name but a few. The important difference between the PAR-DC-MS films and those produced by a sol-gel or CVD technique is that the latter two require a high temperature ($\geq 450^\circ\text{C}$) to create films with appreciable photocatalytic activity and a reasonable degree of mechanical stability, whereas the PAR-DC-MS titania films are prepared under ambient conditions, during which the substrate temperature does not exceed 100°C .

An essential feature of any photocatalyst film is its ability to work many times without losing its activity. Titania is a very photoactive material that, upon UV activation, generates conduction band electrons and valence band holes that are extremely reactive, with the former able to reduce ambient oxygen present and the latter able to oxidise most organics and many inorganics either directly or, more usually, indirectly via the intermediate generation of adsorbed hydroxyl radicals [1–3]. The striking oxidizing power of photoactivated titania is one of its key features since it ensures that few materials adsorbed on its surface are able to resist complete oxidative mineralization. Titania is also a photocatalyst that is recognized as showing little evidence of photochemical wear with prolonged use. The photocatalytic durability of the PAR-DC-MS films was tested by studying the repeated photomineralization of a stearic acid film using the same sample and the results are illustrated in Fig. 5. These show that even after the destruction of five, relatively thick, films of stearic acid, each compris-

ing ca. 9.7×10^{15} molecules of stearic acid cm^{-2} , the kinetics of reaction (2) remained largely unaltered. Since the density of anatase titania is 3.9 g cm^{-3} , the number of moles of sites per g of TiO₂ is 0.0004 [29] and the thickness of the film is ca. 250 nm, it follows that a typical PAR-DC-MS film has 2.35×10^{16} sites per cm^2 , (assuming 0% porosity). Thus, the turnover number (TN) [30] for the PAR-DC-MS photocatalyst film is $\geq (5 \times 9.7 \times 10^{15}/2.35 \times 10^{16})$, i.e., ≥ 2.06 . On this basis, turnover numbers can also be calculated for the P25, sol-gel and ActivTM films and the results are reported in Table 1. Turnover numbers for photocatalysts are rarely calculated, despite the fact that it has been argued that the epithet of ‘photocatalyst’ should be only applied when it has been established that the photocatalyst has a turnover number >1 [30]. From the results in Table 1, it appears that the PAR-DC-MS, P25 and CVD films of titania deserve to be called ‘photocatalysts’, whereas the thick, sol-gel film would need to destroy $>\text{ca. } 38$ consecutive layers of stearic acid to qualify.

A brief inspection of the results illustrated in Figs. 4 and 5 reveals the SA test is quite slow, even when a very active film, like that produced by PAR-DC-MS, is used. This is hardly surprising, given the film is thin (250 nm), only absorbing about 32% of the incident UVA light, and the photocatalytic reaction (2) is a 104 electron (each most probably generated by one photon) per SA molecule destroyed process, i.e. a process with a maximum possible quantum yield for reaction (2) of 0.96%.

In a recent paper [28], we reported on a much more photon efficient, rapid method for assessing photocatalytic activity, utilising a photocatalyst ink. This ink typically comprised a redox indicator dye, resazurin, Rz, a sacrificial electron donor, glycerol, a polymer binder, hydroxyl ethyl cellulose, and a solvent, water. Once deposited on a photocatalytic film for testing, upon its UV illumination, the Rz photocatalytic film interacts with different components of the ink, with the photogenerated electrons reducing the blue resazurin dye to its pink reduced form, resorufin (Rf), and the photogenerated holes oxidizing glycerol to glyceraldehyde and/or glyceric acid (Gly_{ox}). These basic processes are illustrated in the schematic in Fig. 6. The main advantage of this ink over the SA test, is that it is very rapid, and easily observed and monitored. These features are well illustrated by the recorded changes in the absorbance spectrum of an Rz ink film on a typical sample of the PAR-DC-MS film as a function of UV irradiation time, as shown in Fig. 7. These

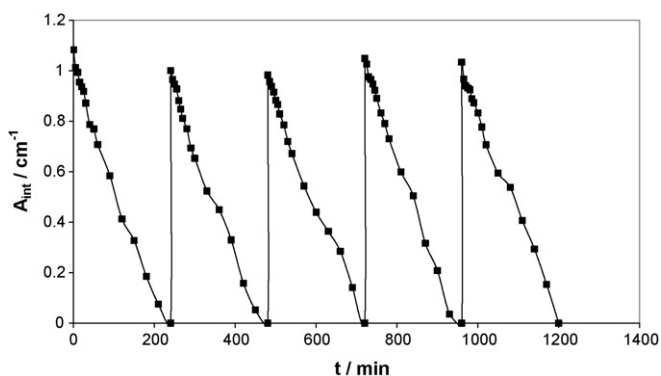


Fig. 5. A_{int} vs. UV irradiation time plot for a PAR-DC-MS sample of titania onto which a new layer of stearic acid is repeatedly deposited and then destroyed by photocatalysis.

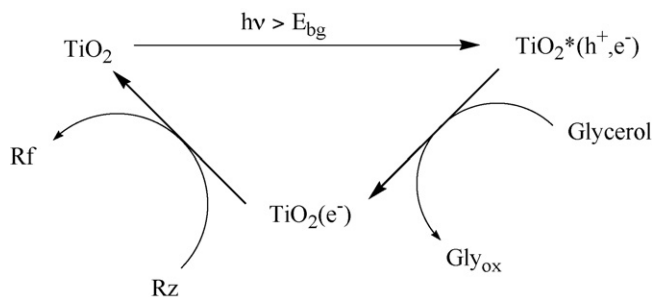


Fig. 6. Schematic highlighting the major photo-induced electron transfer processes associated with the Rz photocatalyst indicator ink.

results show that within 2 min irradiation, the initially blue films containing Rz ($\lambda_{\max} = 610$ nm) turns pink as all the Rz is converted to Rf ($\lambda_{\max} = 580$ nm). In contrast, the disappearance of a SA film takes hours and is not readily observed, with monitoring requiring FT-IR spectroscopy. Using the data illustrated in Fig. 7, the change in absorbance of the film at 610 nm, at any time, t , i.e. ΔAbs_{610} , can be calculated where

$$\Delta\text{Abs}_{610} = \text{Abs}_t - \text{Abs}_{\infty} \quad (3)$$

and Abs_t and Abs_{∞} are the absorbances of the film at 610 nm at time, t , and when all the Rz has been converted to Rf, respectively. This approach was used to construct the plots of ΔAbs_{610} versus t for plain glass, ActivTM and PVD films illustrated in Fig. 8 from the associated plots of absorption spectrum at different irradiation times, as illustrated in Fig. 7 for the PAR-DC-MS film. From the results in Fig. 8, it is clear that the PAR-DC-MS titania film is much more active than the CVD film (i.e. Activ), ca. 6.9 times, and that this assessment required only a few minutes UV irradiation to be made. In contrast, the SA test, which revealed a similar difference in activities between the PVD and CVD films (a factor $\cong 7.1$, see Table 1), requires typically 60 min UV irradiation time in order to make this assessment. Thus, the Rz ink test is excellent for assessing thin, photocatalytic films, of limited activity, however, it is too sensitive (responds in <1 s),

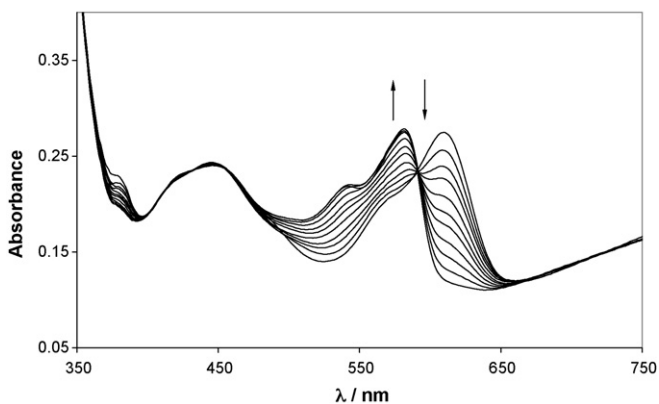


Fig. 7. UV/Vis absorption spectra of a PAR-DC-MS film with a coating of the Rz photocatalyst indicator ink recorded every 10 s upon exposure to UV light. With increasing irradiation time the absorbance of the peak due to Rz (610 nm) decreases and that due to the reduced form of the dye, Rf, at 580 nm, increases.

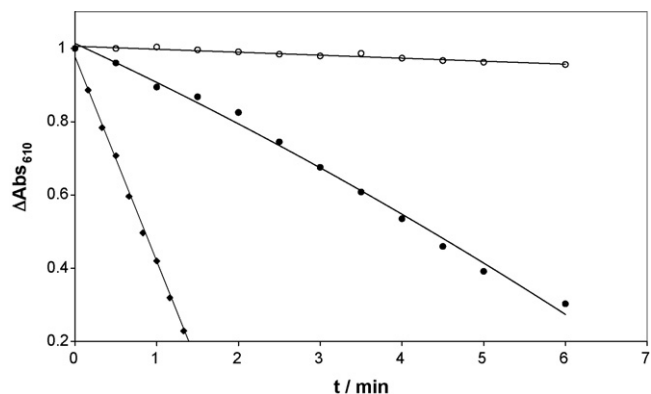


Fig. 8. Plots of the changes in absorbance at 610 nm of a Rz ink film, ΔAbs_{610} , as a function of UV irradiation time when the ink film was cast on: (○) plain glass, (●) ActivTM or (◆) PAR-DC-MS glass.

at the UVA levels employed, to be used on thick, highly active, photocatalytic films, such as the sol-gel film samples also used in this work. Other work shows more appropriate, i.e. less sensitive, photocatalyst inks can be created by using less easy to reduce dyes in its formulation.

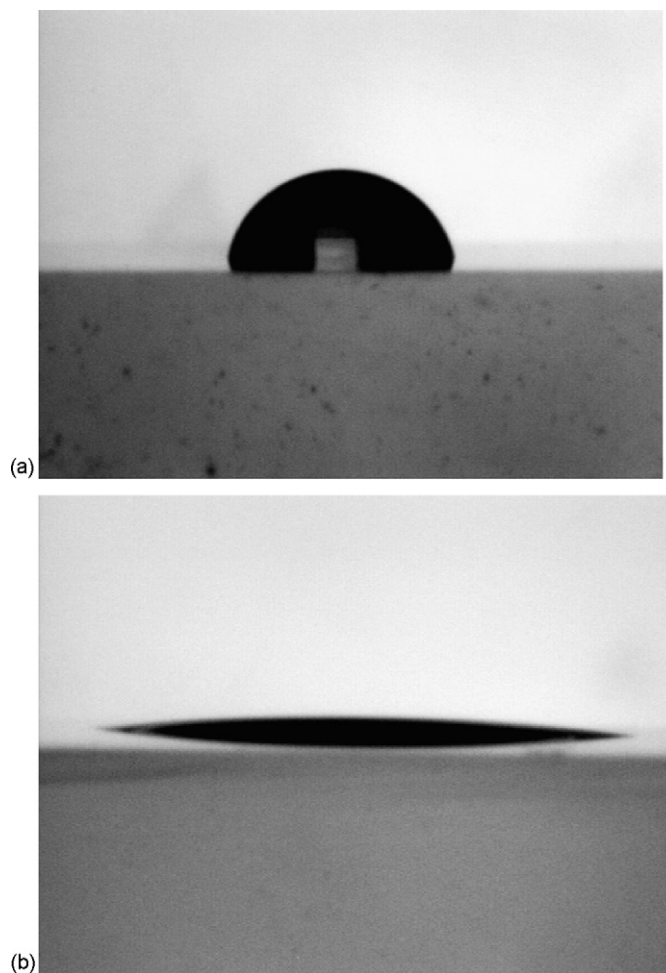
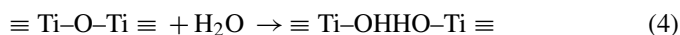


Fig. 9. CCTV profiles of a water droplet on the surface of PAR-DC-MS titania film (a) before and (b) after its illumination with UV light for 30 min. With a plain piece of glass the water droplet does not change shape with UV illumination.

Finally, all films were tested for photoinduced superhydrophilicity, i.e. PSH, which involves the conversion of the surface of the titania film from a hydrophobic to a hydrophilic nature, upon irradiation with UV light [31–33]. There is much debate as to the underlying cause of PSH, which may be simply due to the photocatalytic destruction of hydrophobic organics adsorbed on the surface of titania [32], i.e. reaction (1), or to a photo-induced hydration process [31,33], i.e.



Included in the PSH process is the feature that, once rendered hydrophilic, the titania film slowly regains its initial hydrophilic character in the dark, e.g. via contamination by airborne organics or via the dehydration of the surface (i.e. the reverse of reaction (4)). It appears to be generally true that any titania photocatalytic film also exhibits the PSH effect. The change in shape of a water droplet on the surface of a PAR-DC-MS titania film before and after UV irradiation is illustrated in Fig. 9. These results were typical for all the titania films tested, i.e. P25, sol-gel, ActivTM and PAR-DC-MS, and are indicative of the PSH effect. This effect enhances the self-cleaning nature of the titania film, which is able to remove organics not only by a photocatalytic mineralization process, i.e. reaction (1), but also by PSH, since organics which would otherwise spoil the surface of the glass, adhere poorly to a hydrophilic surface and are readily washed away by (rain) water.

4. Conclusions

Robust, active, anatase titania films can be deposited onto glass at low temperatures, i.e. <100 °C, using a PVD technique: plasma-assisted, reactive dc magnetron sputtering. The films are transparent and colourless and truly photocatalytic, exhibiting turnover numbers >2.0 for the photocatalytic mineralization of stearic acid. These films are typically 6.9 times more active than a sample of commercial self-cleaning glass, mainly because they are much thicker and, therefore, absorb more of the incident UV light. All titania films tested, including those produced by magnetron sputtering exhibited photo-induced superhydrophilicity. The low temperatures used in the production of the PAR-DC-MS films makes this technique promising with respect to producing robust, very active photocatalyst titania films on low temperature substrates, such as plastics, metals and artificial fibres. Further work in this area is in progress.

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