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Current and possible future methods of assessing the activities of photocatalyst films

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Abstract

The continuing interest in semiconductor photochemistry, SPC, and the emergence of commercial products that utilise films of photocatalyst materials, has created an urgent need to agree a set of methods for assessing photocatalytic activity and international committees are now meeting to address this issue. This article provides a brief overview of two of the most popular current methods employed by researchers for assessing SPC activity, and one which has been published just recently and might gain popularity in the future, given its ease of use. These tests are: the stearic acid (SA) test, the methylene blue (MB) test and the resazurin (Rz) ink test, respectively. The basic photochemical and chemical processes that underpin each of these tests are described, along with typical results for laboratory made sol–gel titania films and a commercial form of self-cleaning glass, Activ^{TM}. The pros and cons of their future use as possible standard assessment techniques are considered.

Keywords: Stearic acid; Methylene blue; Photocatalysis; Titania; Resazurin; Ink

1. Introduction

The basic process that underlies most examples of semiconductor photocatalysis, SPC, can be summarized as follows [1–5].

$$\text{Organic pollutant} + O_2 \xrightarrow[\text{Semiconductor}]{h\nu \geq E_{bg}} \text{minerals} \qquad (1)$$

where E_{bg} is the bandgap energy of the semiconductor and, usually, the semiconductor is anatase titanium dioxide. The latter form of titania is commonly chosen because of its chemical and biological inertness, mechanical toughness, high photocatalytic activity and low cost [1–5].

Extensive research into SPC using TiO_2 has shown that it is able to photocatalyse the complete oxidative mineralization of a wide range of organic materials, including many pesticides, surfactants and carcinogens, by oxygen [1–5]. Not surprisingly, many commercial products have emerged in recent years based on titania photocatalysis, including: water and air purification systems and self-cleaning tiles and glasses [6]. The latter in particular have met with significant commercial success and are now sold world-wide by most of the major glass manufacturers including the following (with the trade name of their commercial product in parentheses): Pilkington Glass (Activ^{TM}) [7], St-Gobain (Bioclean^{TM}) [8] and PPG (Sun-Clean^{TM}) [9].

In the case of the above, the thin, typically 15 nm, films of anatase titania on glass employed are self-cleaning in that most of the organic pollutants that go to make up the dirt and grime that deposit on window glass are readily mineralized by oxygen via the photocatalytic process (1) [10]. These films are also more easily wetted by water, i.e. hydrophilic, after UV irradiation, making it difficult for hydrophobic organic pollutants to adhere to the surface. Although it remains, as yet, unclear how UV-induced, hydrophilicity and SPC activity are related, it is clear that any titania film which is SPC active also exhibits UV-induced hydrophilicity. It follows that for a fully functioning, self-cleaning glass it is essential that the titania coating exhibits SPC activity.

In order to compare the effectiveness of one self-cleaning glass with that of another, and to be able to effect and demonstrate a commercially acceptable high degree of quality control on any SPC product, such as self-cleaning glass, it is essential to have a set of agreed standard methods of assessing SPC activity. The creation, validation and promotion of such a set of standard methods is currently in progress by an

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internationally-recognised body (ISO; TC206). Although the methods under consideration are not yet in the public domain, it appears timely to consider briefly some of those which have proved most popular in the past and one that has just recently been reported and appears most easily effected and to have a real future.

2. The stearic acid (SA) test

A popular method for assessing the activities of self-cleaning titania photocatalyst films, the stearic acid (SA) test involves the initial deposition of a thin layer of SA onto the photocatalytic film under test and the subsequent monitoring of its photocatalytic destruction, under defined conditions, as a function of time, from which a rate for the disappearance of SA is usually gleaned and can be compared with values determined for other samples under the same conditions [10–17]. This reaction has gained considerable preference over the years, especially with the self-cleaning glass companies, for a number of reasons, including (a) SA provides a reasonable model compound for the solid 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 i.e. $>$2.5 nm thick, are very easily laid down from a methanol or chloroform solution, (d) the kinetics of removal of SA are usually simple and zero-order, and so SA film thickness is not usually a critical factor when assessing photocatalytic activity, and (e) there are many possible ways in which the mineralisation process can be monitored (vide infra).

The overall reaction can be summarized as follows:

$$CH_3(CH_2)_{16}CO_2H + 26O_2 \xrightarrow[h\upsilon \geq E_{bg}]{TiO_2} 18CO_2 + 18H_2O \qquad (2)$$

Following on from point (e), it is no surprise that this process has been studied a number of different ways including by monitoring: (i) the amount of CO_2 generated, using gas chromatography [15] and (ii) the change in thickness of the stearic acid film, using ellipsometry [18]. However, the most commonly employed method of studying reaction (2) is via the disappearance of the SA film using infra-red absorption spectroscopy, since SA absorbs strongly in the region 2700–3000 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 [11,14,19–21]. The integrated area due to these peaks, over the range 2700–3000 cm^{-1}, A_{int}, is proportional to the amount of stearic acid present, i.e. [SA], in units: molecules cm^{-2}. A conversion factor of 9.7×10^{15} molecules of SA cm^{-2} $\equiv$ an integrated area of 1 cm^{-1}, for peaks in the FT-IR spectrum of SA over the range of 2700–3000 cm^{-1}, is now recommended [17], after recent work revealed that the previously estimated value for this conversion factor was ca. 3 x's too low. Fig. 1(a) illustrates the FT-IR absorbance versus wavenumber, spectra, recorded for a sample of Activ^{TM} coated with stearic acid, as a function of irradiation time, where the irradiation source comprised six 8 W blacklight bulbs, i.e. 365 ± 20 nm light [20]. An experiment carried out under the same conditions, but using plain glass instead, i.e. in the absence of a coating of titania, reveals no significant change in the stearic acid IR absorption spectrum over the irradiation period. Fig. 1(b) illustrates plots of A_{int} versus irradiation time profiles for plain glass, Activ^{TM} and a 90 nm thick film of Degussa P25, respectively. The greater activity exhibited by the latter, compared to Activ^{TM} is mainly due to its greater absorbance at 365 nm due to its greater film thickness [20].

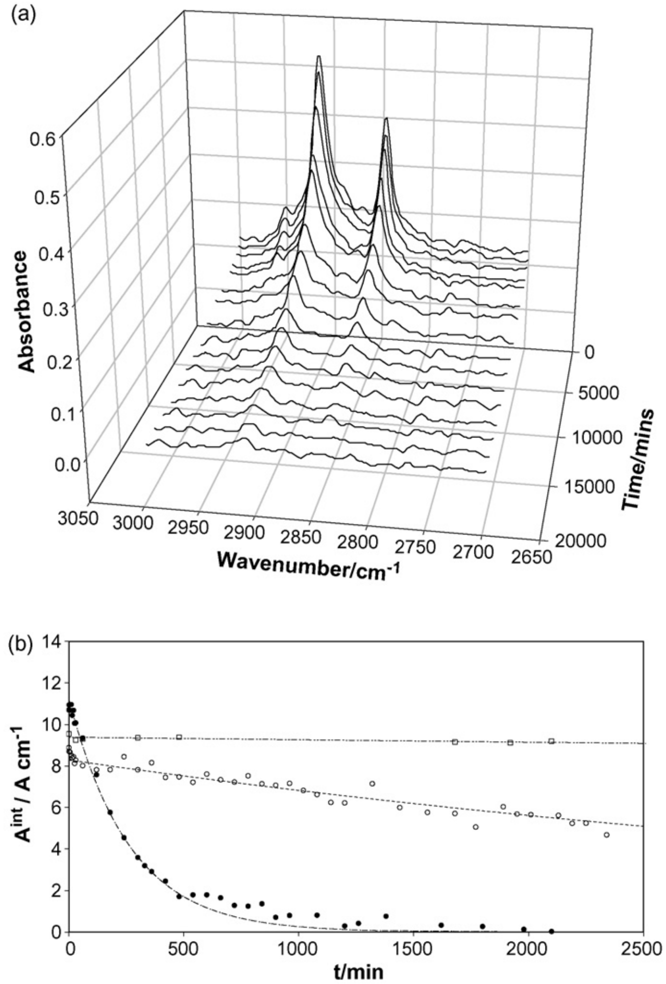

Fig. 1. (a) FT-IR absorbance spectra of a film of stearic acid on Activ^{TM} recorded as a function of irradiation time with UVA (6.9 mW cm^{-2}); (b) plots of the integrated area under (a), from 2700 to 3000 cm^{-1}, for stearic acid films on (□) plain glass, (○) Activ^{TM} and (●) a 90 nm thick P25 titania film [20].

A brief inspection of reaction (2) reveals that the overall mineralization process involves the transfer of 104 electrons and raises the concern that the observed temporal variation in [SA] upon UV irradiation of a SA layer on a titania film may not follow the stoichiometry indicated by reaction (2), due to the formation of recalcitrant or volatile intermediates. Certainly Minabe et al [15] have reported that the photocatalytic decomposition of SA sensitized by a TiO_2 sol–gel film does not go to completion, but instead halts after ca. 69% of the compound has been decomposed. This finding implies that long-lived, recalcitrant oxidation intermediate products are formed, preventing the SA:CO_2 stoichiometric ratio achieving the ultimate value of 1:18 as expected from reaction (2). In

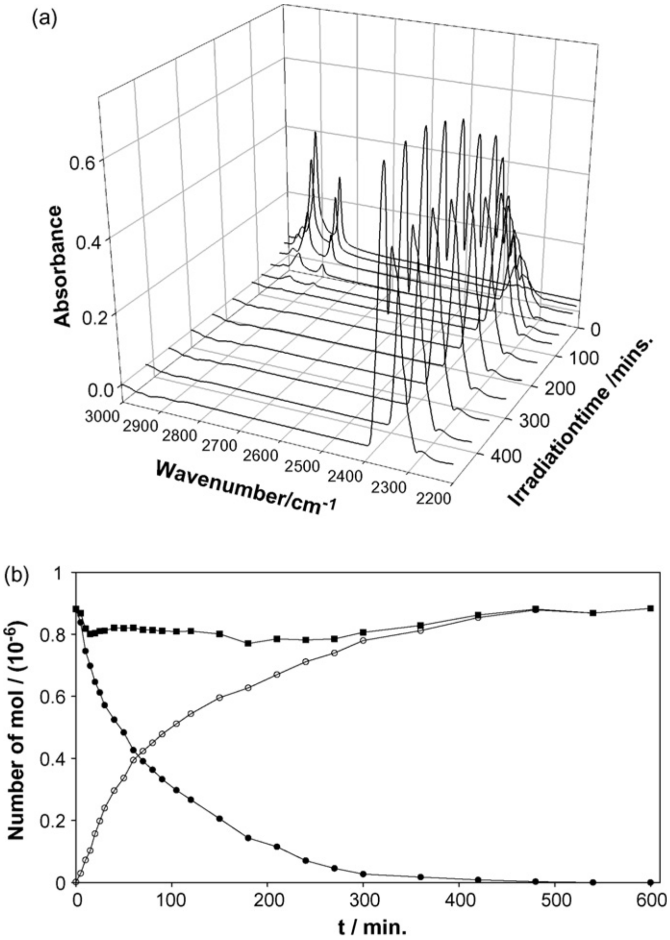

Fig. 2. (a) FT-IR absorption spectra of an IR gas cell with a quartz window, coated with a 900 nm thick P25 TiO_2 layer, which, in turn, was initially coated with a layer of stearic acid as a function of UVC irradiation time (8.2 mW cm^{-2}) [17]. Plots of the variations in: (i) the number of moles of stearic acid (●), (ii) (1/18) × the number of moles of CO_2 (○) and (iii) the sum of (i) and (ii) (■) as a function of irradiation time for a P25 TiO_2 film. The data for the plots was derived from the integrated areas under the IR peaks, such as shown in (a), and appropriate calibration plots.

contrast, and more reassuringly, others, including this group, have reported that sol–gel and CVD produced titania films are able to remove completely a SA covering layer via semiconductor photocatalysis [11,14,19–21]. In addition, very recently, both the destruction of SA and concomitant stoichiometric generation of CO_2 via semiconductor photocatalysis using a 900 nm thick P25 titania film, were monitored simultaneously using FT-IR spectroscopy [17].

A typical set of IR spectra recorded as part of this work are illustrated in Fig. 2(a) and show very well the disappearance of the SA film and simultaneous appearance of the CO_2 as a function of irradiation time [17]. This data, and other work, shows that no major intermediates, volatile or otherwise, are generated via the photocatalytic mineralisation of the SA film, i.e. the only major and readily observable IR active species present during the course of the photomineralisation process are SA and CO_2. The FT-IR data generated in this study were used to produce the plots illustrated in Fig. 2(b) of the variation in: (i) the number of moles of stearic acid, (ii) (1/18) × the number of moles of CO_2 and (iii) the sum of (i) and (ii) as a function of irradiation time for the P25 TiO_2 film. These plots show that, apart from the initial stages of the photomineralisation process, the degradation of SA and the concomitant generation of CO_2 are very well described by the reaction stoichiometry of reaction (2) [17].

3. The methylene blue (MB) test

The methylene blue (MB) test is fast-becoming the most popular method for assessing photocatalytic activity of titania films and powders and is based on the photobleaching of the cationic, thiazine dye, methylene blue, MB [22–33]. The overall mineralization process can be summarized as follows:

$$2C_{16}H_{18}N_3S^+ + 51O_2 \rightarrow 32CO_2 + 6HNO_3 + 2H_2SO_4 + 2H^+ + 12H_2O \tag{3}$$

The initial step in the mineralization of this dye appears to be the cleavage of the bonds of the $R–S^+=R'$ functional group in MB by a photogenerated $OH^•$ radical, both adsorbed on the surface of the titania photocatalyst, to form the sulfoxide [33], i.e.,

$$R-S^+=R' + OH^\bullet \rightarrow R-S(=O)-R' + H^+ \tag{4}$$

A second oxidative attack of the sulfoxide will produce an unstable sulfone, which is thought to dissociate to form the two benzenic rings and lead to a complete loss in colour of the original dye molecule. The elegant work of Herrmann and coworkers have established that prolonged, titania-based photocatalysis of MB in aqueous solution leads to its complete mineralization, as described by the reaction stiochiometry in Eq. (3) [33]. In most work where MB is used to assess the photocatalytic activity of a semiconductor, only the bleaching of the dye is monitored via UV–vis absorption spectroscopy, which is almost always assumed to be due to dye oxidation via reaction (4) [12,22–33].

In aqueous solution MB absorbs most strongly at ca. 660 nm and, given its molar absorbtivity is ca. 10^5 dm^3 mol^{-1} cm^{-1} at this wavelength [30], it is easy to translate any absorbance at 660 nm versus UVC irradiation time data generated in a study of the photocatalytic destruction of MB, into a plot of [MB] versus *t*, from which either an initial rate or a first order rate constant, k_1, can be obtained. Using this procedure as a guide, a series of UV–vis spectra of a stirred, 10^{-5} M MB, air-saturated, aqueous solution in a 1 cm spectrophotometer cell, one face of which was replaced with a piece of glass covered with a 4 μm sol–gel titania film, were recorded as a function of UVA (1 mW cm^{-2}) irradiation time and the results are illustrated in Fig. 3(a). The insert diagram is a plot of the change in absorbance of the MB solution at 660 nm, ΔAbs, as a function of irradiation time and fits first order kinetics, with $k_1 = 0.0097$ min^{-1}, using data from the main diagram. These results show that a thick titania film generated by the sol–gel process [19] is effective at bleaching MB under the reaction conditions used, i.e. an initially neutral solution with a UVA intensity = 1 mW cm^{-2}. Note that in the absence of a titania

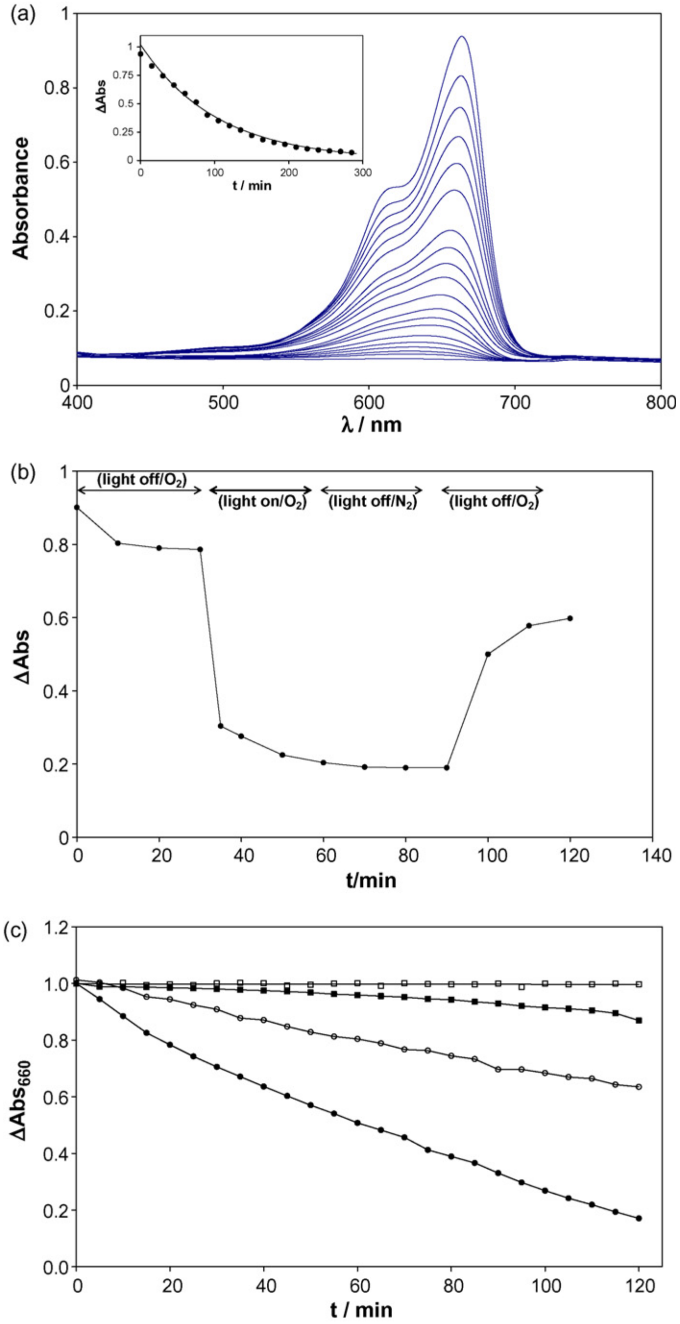

Fig. 3. (a) UV–vis spectra of a stirred, 10^{-5} M MB, air-saturated, aqueous solution in a 1 cm spectrophotometer cell, 1 face of which has been replaced with a piece of glass covered with a 4 μ sol–gel titania film. The spectra were recorded at the following UVA (1 mW cm^{-2}) irradiation times (from top to bottom): 0, 10, 50 min etc. The insert diagram is a plot of the change in absorbance of the MB solution at 660 nm, ΔAbs, as a function of irradiation time—data from main diagram. (b) Plot of the change in absorbance at 660 nm of 100 cm^3 of 10^{-5} M MB acidic (0.01 M $HClO_4$) aqueous solution in contact with a film of P25 titania (120 cm^2, 0.1 mg cm^2), ΔAbs, as a function of time, under different conditions of gas saturation and UVA light exposure (6.9 mW cm^{-2}), as indicated in the figure [30]. (c) Plots of the change in absorbance of the MB solution at 660 nm, ΔAbs_{660}, as a function of irradiation time, under the conditions in (a) except the photocatalytic film was: (☐) plain glass (stirred and unstirred), (■)Activ^{TM} (stirred and unstirred) and 4 μ sol–gel titania film unstirred (○) and stirred(●).

film, over the same irradiation period the [MB] remains largely unchanged. The ease of this method of assessment, and its ability to provide a very visible and dramatic demonstration of the efficacy of semiconductor photocatalysis for water purification, have helped contribute to the ever-increasing popularity of this test method.

The MB test method is not without its detractors, however, especially with regard to its possible ambiguous nature [30]. This ambiguity stems from the ease of reduction of MB to its doubly reduced form, *leuco*-methylene blue, LMB, which, *like the initially oxidized form of MB*, is colourless, i.e.,

$$\mathrm{MB} + 2e^- + H^+ \rightarrow \mathrm{LMB} \tag{5}$$

This reduction reaction is possible because the redox potential of the MB/LMB couple, i.e. E°(MB/LMB), is ca. 0.53 V versus NHE at pH 0, and the reduction potential of the photogenerated electrons on a titania photocatalyst is −0.32 V versus NHE at pH 0. Indeed, it is well-known that it is very easy to effect reaction (5) with UV light, using a titania photocatalyst, when a sacrificial electron donor, SED, such as methanol, is present, provided that great scavenger of photogenerated electrons, oxygen is absent from the reaction solution, e.g. by sparging with nitrogen [30,34–37].

The probability appears low that reaction (5) can be effected by a titania photocatalyst if a SED is not deliberately added to the system. However, in practice it is very readily effected by UV irradiation of a titania photocatalyst film or powder in contact with just an *anaerobic* MB solution, with no obvious SED present. In this case it appears that MB itself, or other adventitious impurities, are able to act as the SED [30]. That LMB has been generated in such an experiment is easily demonstrated, by exposing the final *anaerobic*, photo-bleached solution to air, which rapidly restores most of the original colour of the reaction solution [30], via the oxidation of to LMB to MB, i.e.,

$$2\mathrm{LMB} + O_2 \rightarrow 2\mathrm{MB} + H_2O \tag{6}$$

The above results pose the question: is the photobleaching of MB in *aerobic* solution – i.e. the process that is a fundamental feature of the MB test – due solely to the photo-oxidation of the dye, via reaction (4), and not some or all of the photoreduction, of MB, via reaction (5)? The good news is that in neutral or slightly alkaline solution, the kinetics of reaction (6) are so facile that any photo-bleaching of MB appears to be due solely to its photo-oxidation [30], i.e. reaction (4), as demonstrated by the results in Fig. 3(a). These results show that the neutral MB aqueous solution is photo-bleached upon irradiation with UV light and other work shows that it does not recover its colour even with continued purging with air in the dark. Thus, no LMB is photo-generated under the latter conditions, since any LMB present would have been expected to react with the oxygen in the dark and recover some of the original colour of the MB solution.

Interestingly, reaction (6) is much slower under acidic conditions and, as a result, the photo-bleaching of MB by titania is more likely to show some evidence of LMB production, via reaction (5), as well as photo-oxidation, via reaction (4) if carried out at a low pH. This is nicely demonstrated by performing an experiment in which a 10^{-5} M MB solution containing 0.01 M $HClO_4$ is placed in contact with a film of P25 titania and UV irradiated in an oxygenated solution for 30 min, and then left in the dark for a further 60 min during which the solution is purged with nitrogen (first 30 min) and then oxygen (last 30 min). The results of this work are illustrated in Fig. 3(b), plotted in the form of the change in absorbance at 660 nm of the MB solution, ΔAbs, as a function of time [30]. These show that, as with the MB in neutral water experiment, the MB is photo-bleached by the titania particles in an oxygen-saturated solution and does not recover any of its colour when the light is switched off and the solution purged with nitrogen for 30 min. However, in marked contrast to the work carried out in neutral solution, under acidic conditions, purging of the photo-bleached reaction solution with oxygen allows the MB solution to regain two thirds of its original colour, as illustrated by the results in Fig. 3(b) [30]. The most likely explanation for these observations is that *in oxygenated solution*, MB in aqueous solution is photo-oxidatively and irreversibly bleached under neutral or alkaline conditions, whereas under acidic conditions it is largely photo-reductively and reversibly bleached to LMB-reduced, which is quite stable, even in oxygen-saturated solution, since reaction (6) is very slow under acidic conditions [30]. Previous work also established that this latter reaction is favoured in neutral and acidic conditions upon UV irradiation of the MB/TiO_2 under *anaerobic* conditions [30].

Any ambiguity in the method of assessment, as exists for the MB test system, is clearly highly undesirable. Although reaction (5) is a possible cause for ambiguity in the MB test, it appears to be only a concern when the MB solution is quite acidic, or not fully saturated with oxygen, or air. However, less than fully air or oxygen saturated conditions may arise not only if the solution is poorly stirred or purged – both of which can be eliminated by good practice – but also if the photocatalyst under assessment is highly active. A rather nice demonstration of this is illustrated by the ΔAbs versus UV irradiation time profiles in Fig. 3(c) that were generated using samples of plain glass, Activ^{TM}, and a thick sol–gel film (4 μm) in contact with an unstirred, or stirred, air-saturated aqueous solution of 10^{-5} M MB. From these plots it is clear that MB in contact with plain glass is not photo-degraded by the UV light to any great extent, with or without stirring, over the timescale of the experiment. In addition, the ΔAbs versus t profile for Activ^{TM}, with its very low SPC activity, is largely the same with and without stirring (initial rate (r_i) = ca. 9.0×10^{-4} Abs U min^{-1}) for Activ^{TM}. However, for the much more active, thick sol–gel film, the measured initial rate of MB bleaching is 9.2×10^{-3} Abs U min^{-1} when stirred, but ca. 2.7 times less, when left unstirred, presumably due to oxygen depletion and/or LMB production.

The results of the above work show that a set of test conditions in which an air-saturated, neutral, quiescent MB solution is used may be appropriate if a slow-acting photocatalyst film, such as Activ^{TM} is under test, but clearly inappropriate if a more active photocatalyst film is being assessed. Clearly if the MB test does become a standard test procedure, – and there is a strong suggestion that it will – the protocol should be defined as such that the test is able to assess the activities of photocatalyst films with high and low activities.

4. The resazurin (Rz) ink test

Both the stearic acid and the methylene blue tests do not appear apt for making measurements in the field, since they require at least one piece of sophisticated and expensive electrical analytical equipment and, usually, a trained technician to run and maintain it. In addition, because most commercial self-cleaning glasses utilize only a very thin layer of titania, the kinetics of the photomineralisation of SA or MB are very slow and so it can take hours, if not days, to destroy completely a stearic acid layer or a MB solution under solar UVA conditions (typically ca. 4.5 mW cm^{-2} for a clear, sunny day).

It is apparent that the photocatalytic activity of a semiconductor film would be more easily assessed, and appropriate for use in the field, if the test involved a simple color change, especially if the latter were rapid, i.e. within a few minutes of UV exposure. Researchers have tried staining SPC films and powders directly with dyes [38–40], although little dye sticks to the surface, or, with more success, incorporating a dye in a deposited polymer film layer [41]. However, the major problem with these approaches is that they rely on the color change being effected by the photo-oxidation of the dye or dye/polymer combination and this is usually a slow process, as evidenced by the SA test. Such a dye or dye/polymer test might be adequate for assessing the SPC activities of very active, usually thick, titania films, where the kinetics of photomineralisation are rapid, but, clearly inappropriate for most commercial, self-cleaning photocatalytic products, including glasses and tiles, that exhibit much slower rates of photocatalysis. Instead, what is required is an indicator ink that can be printed, coated or written onto any SPC film, be it transparent or opaque, and which rapidly, i.e. within a few minutes at most, will change color upon UV irradiation of an underlying thin photocatalyst film.

Such an ink has been reported recently by this group [42,43] and comprises: 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. The film is usually spun-coated onto the substrate under test and dried in an oven at 70 °C for 10 min, although drying in air, rather than in an oven, does not alter its performance. A typical dried ink film is ca. 590 nm thick when coated in the above manner onto a test substrate, such as plain glass or Activ^{TM}, and blue in appearance. This initial color, and associated UV–vis. absorption spectrum, illustrated in Fig. 4(a), does not change upon prolonged UVA irradiation in the absence of an underlying photocatalyst film, i.e. when coated on plain glass. In contrast, as illustrated by the results in Fig. 4(a), the ink does change rapidly in color, i.e. within minutes, from blue to pink upon UVA irradiation when deposited on a commercial sample of self-cleaning glass, such

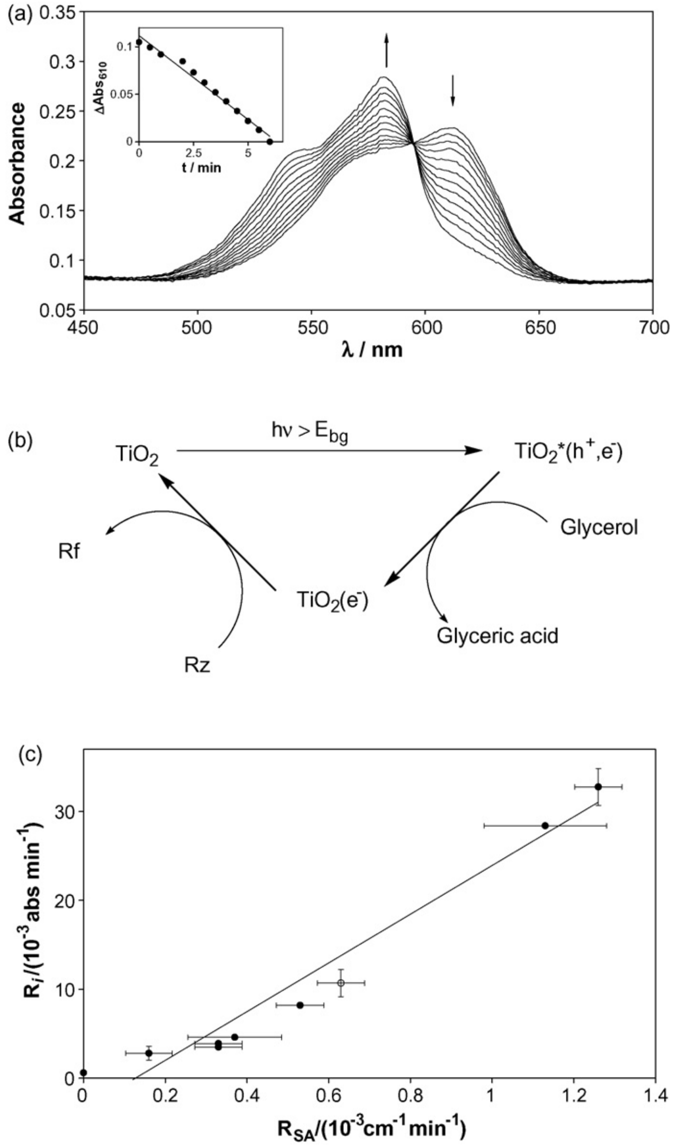

Fig. 4. (a) UV–vis absorption spectra, of a typical Rz photocatalyst indicator film deposited onto a sample of Activ™ glass, recorded as a function of time of illumination with a UVA lamp, 7.4 mW cm^{-2}, (1 spectrum every 30 s). The insert diagram is a plot of the change of absorbance at 610 nm, $\Delta\mathrm{Abs}_{610}$, determined using the data in the main diagram, as a function of illumination time and indicates zero-order kinetics. (b) Reaction scheme of the major processes associated with Rz photocatalyst activity indicator ink. (c) Plot of the R_i for a typical Rz indicator ink film and the initial rate of stearic acid removal, R_SA, when deposited onto a series of CVD titania films exhibiting a range of photocatalytic activities. The open circle data point is that for Activ™. In all cases the irradiance used was 0.32 mW cm^{-2} [42]. Note that the units for R_SA are cm^{-1} min^{-1} are those for a rate, since the cm^{-1} refers to the integrated area under the IR absorption spectrum from 2700 to 3000 cm^{-1}, so that for SA 1 cm^{-1} refers to 9.7×10^{15} molecules cm^{-2} [17]. Values for R_SA are derived from the initial gradients from Fig. 1(b) type plots of the SA vs. time decay data.

as Activ™. Other work shows that this color change always occurs if a titania photocatalyst is present, regardless of its form (film or powder) or supporting substrate (glass, tile, paper, plastic or metal). Further irradiation (hours) of this system bleaches the ink, although the polymer remains apparently intact [42,43] However, the unreacted polymer component of the ink is readily removed with a damp cloth, since the ink is water-soluble, or when subjected to prolonged UV irradiation (days), since this effects its complete mineralization by the underlying photocatalytic film.

In contrast to the stearic acid and methylene blue tests, the Rz photocatalyst indicator ink test described above does not work via a photo-oxidative mechanism, but rather by a novel, photo-reductive mechanism in which the photogenerated holes react irreversibly with the sacrificial electron donor present, glycerol, and the photogenerated electrons (E° ($\mathrm{TiO_2}$ ($\mathrm{e^-}$)) = −0.52 V, pH 7) [44] reduce the indicator ink dye molecules, Rz, contained therein, to a differently coloured form, namely, resorufin, Rf. The various steps of the process are summarised in Fig. 4(b).

The Rz/glycerol/HEC photocatalyst indicator ink described above works very rapidly for photocatalyst films with low SPC activities, such as commercial samples of self-cleaning glass, as illustrated by the results in Fig. 4(a) for Activ™ [43]. However, clearly its value as a photocatalyst indicator would be greatly enhanced if the initial rate of dye bleaching, R_i, correlated with the initial rate of stearic acid removal, R_SA, which is so often used to assess the SPC activities of such films. In order to address this issue a series of CVD coated samples of anatase titania on glass with different SPC activities were prepared by varying the deposition conditions. These films, and a commercial sample of self-cleaning glass, Activ™, were first assessed for SPC activity using the stearic acid test and then cleaned and coated with the photocatalyst ink and assessed for SPC activity via the measured values of R_i. A plot of the rate data arising from this work, i.e. R_i, versus R_SA is illustrated in Fig. 4(c) and reveals a good correlation between the two sets of rate data, the important difference being that for each sample the R_i data were obtained in a few minutes, whereas the R_SA data required hours of illumination [42].

Finally, the efficacy of the photocatalyst indicator ink for work in the field was illustrated by placing some of the Rz ink in an empty felt-tipped pen and using it to write on a piece of plain and Activ™ glass. Upon exposure to 3 min of UVA light (7.4 mW cm^{2}) the writing on the Activ™ coated glass had changed from blue to pink, whereas the writing on the plain glass remained blue even after prolonged (6 h) irradiation with the same UV source. Given that most methods of assessing photocatalyst activity are slow and require expensive analytical equipment to service them, the Rz photocatalyst indicator ink reported here appears an attractive test for SPC activity, either in the laboratory for quantitative work, or in the field, for a semi-qualitative assessment. It is of particular merit since it can be delivered using a simple felt-tipped pen or rubber stamp and it allows the semi-quantitative assessment of a photocatalytic film to be made in the field, using sunlight as the light source and the human eye as the detector of a colour change.

5. Conclusions

Two major established, and one new, methods of assessing the photocatalytic activities of films, such as found on self-cleaning glass, are reviewed. The SA test is currently most popular and very reliable. The MB test has a more checkered history, and there remain some genuine concerns regarding its reliability; despite this it is used increasingly in SPC. The new Rz ink test is much faster than the other tests and easier to use, especially in the field. Time will tell which one(s) of these tests, if any, the standardization committees, looking into identifying one or more methods for assessing SPC activity, will recommend. Hopefully, before any final recommendations are made, the standardization committees will seek feedback from, and the general approval of, the large photocatalyst community.

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