

A study of new photocatalyst indicator inks

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Abstract

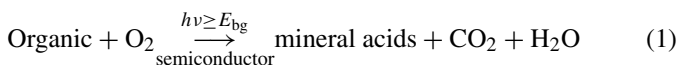
This article reports the behaviour of three photocatalyst indicator inks, based on the redox dyes: methylene blue (MB), resorufin (Rf) and 2,6-dichloroindophenol (DCIP), and assess their performance in comparison to the pioneering resazurin (Rz)-based ink for the rapid assessment of the activity of very thin, photocatalyst films, such as Activ™ self-cleaning glass. From a commercial ‘demonstrator of photocatalysis’ perspective, all three redox dyes appear more attractive compared to Rz since all generate colourless products in the ink formulation when photoreduced on Activ™ under anaerobic conditions, whereas, the reduced product from Rz, the redox dye resorufin, Rf, is pink in colour. However, the ink based on Rf is far too slow to effect the rapid measurement of photocatalytic activity even in the absence of oxygen, and in the presence of oxygen the latter inhibits the overall kinetics of photoreduction by re-oxidising the reduced product, dihydroresorufin, HRf, back to Rf. Similarly, despite the attractive rapid rate of photobleaching for MB under anaerobic conditions, compared to the other redox dyes, the reduced product of the MB-based ink, leuco-MB, is so oxygen-sensitive that the ink cannot be photoreduced under aerobic conditions, thus rendering the ink unsuitable for use in the field. The DCIP-based ink is slightly less easy to photoreduce under both anaerobic and ambient atmospheric conditions compared to the Rz-based ink. However, in addition to its more attractive colour change, the DCIP-based ink is unaffected by the ambient level of oxygen present (%O₂) and the relative humidity (%RH), whereas, for the Rz-based ink, both parameters effect the photoreduction kinetics. By incorporating the DCIP ink into a felt-tipped pen, the ink is suitable for use in the laboratory and field to perform not only a qualitative test, but also to allow a semi-quantitative analysis of photocatalytic activity by eye.

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1. Introduction

The oxidative mineralisation of organic pollutants by semiconductor photocatalysis (SPC), according to reaction (1), has been researched extensively over the last 20–30 years [1–3] and has received more recently significant commercial attention for both air and water purification and treatments [4].



where E_{bg} represents the bandgap of the semiconductor. Anatase TiO₂ (titania) has become the foremost semiconductor material for SPC applications since it is biologically and chemically inert, mechanically robust, relatively inexpensive and, usually, very active.

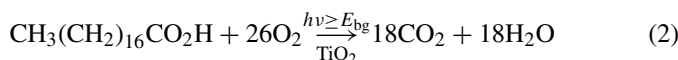
When titania is irradiated with ultra-bandgap light (typically $\lambda \leq 388$ nm), an electron is promoted from the semiconductor’s valence band to its conduction band, thereby simultaneously creating a hole in the valence band. Although this electron–hole pair is often produced within the bulk of the semiconductor and can recombine there, both species are also capable of migrating to the surface. Once at the surface, although they can still recombine, the photogenerated electrons can reduce atmospheric O₂ to superoxide, O₂^{•−}, which can be subsequently reduced further to H₂O. The photogenerated holes, on the other hand, are capable of oxidising any surface adsorbed OH[−] groups to form adsorbed hydroxyl radicals, OH[•] which are, in turn, capable of oxidising a range of organic pollutants into minerals, such as CO₂ and H₂O. The above processes underpin the photomineralisation of the organic by oxygen sensitised by titania, i.e. reaction (1).

In the last decade, Pilkington Glass have successfully launched Activ™, the world’s first commercially available self-cleaning glass [5], which is produced by an atmospheric pressure chemical vapour deposition (APCVD) technique, controlled to give a 15 nm thick layer of TiO₂ on the surface of float glass

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[6]. This product is available commercially for installation in offices and homes throughout the world, including in the UK. Most other major glass manufacturers have followed the lead of Pilkington Glass and now market a self-cleaning glass product based on the SPC activity of a titania film [7,8].

One of the most common, current methods used to assess the activities of photocatalytic films (mainly TiO_2) in research is the degradation of stearic acid, shown by reaction (2).



Stearic acid is easily deposited from solution and forms a waxy, solid film at room temperature which resembles that of a typical organic film that adheres to a window due to atmospheric pollution. Upon UV irradiation of a stearic acid film on self-cleaning glass, the stearic acid layer disappears according to reaction (2), as it is mineralised to CO_2 and H_2O . The most popular analytical method used to monitor this mineralisation is infra-red spectroscopy [9–13], which allows the change in the absorbance due to the stearic acid peaks in the region of $2700\text{--}3000\text{ cm}^{-1}$ to be monitored as a function of the UV irradiation time.

Despite these very positive features, the stearic acid test suffers from two major drawbacks. Firstly, the test is very slow and, for rapid (1–5 min) assessment, is usually only suitable for determining the activities of thick (i.e. $\geq 0.1\ \mu\text{m}$), highly active, TiO_2 films. Secondly, it requires a skilled operator in both the analytical method and the sample preparation to conduct the test, and so is relatively labour intensive and expensive to run. For thin titania films, such as those found in ActivTM and most self-cleaning products (e.g. glasses, tiles and paints), a more rapid method of assessing and demonstrating photocatalytic activity is needed, especially for use in the field. Recently, this group [14] developed an intelligent photocatalyst indicator ink to identify and measure the photocatalytic activities of thin semiconductor films such as ActivTM. In this ink, an oxidised redox dye, D_{ox} , e.g. resazurin (Rz), is mixed with a polymer, such as hydroxyethylcellulose (HEC), a sacrificial electron donor (SED), e.g. glycerol, and a solvent, usually water. The ink is cast on the surface of the photocatalyst and when the photocatalyst is illuminated, the photogenerated hole oxidises the SED, i.e. the SED essentially acts as a hole-trap to prevent electron–hole recombination, whilst the photogenerated electrons reduce the dye to its differently coloured, reduced form, D_{red} . A schematic illustration of the major steps involved in such a typical photocatalyst indicator ink is given in Fig. 1. In the case of the Rz photocatalyst indicator ink, Rz is D_{ox} , D_{red} is resorufin (Rf), and the reduction process, i.e. step 1 in Fig. 1, is accompanied by a colour change from blue to pink. Since the reduction of Rz to Rf is an irreversible reaction, Rf cannot be re-oxidised to Rz, i.e. step 2 in Fig. 1 is not possible, although, as we shall see, this does not rule out oxygen inhibiting the initial photoreduction process, e.g. via direct competition with Rz for the photogenerated electrons, $\text{TiO}_2(e^-)$.

Previous work [14] has established that the Rz ink, as found for all the inks tested here, can be cast on the photocatalyst surface by a number of different processes, including spin-coating,

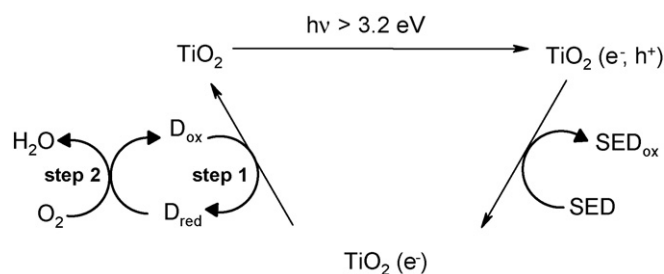


Fig. 1. Schematic illustration of the mechanism by which a typical photocatalyst indicator ink works. Thus, following illumination of the TiO_2 photocatalyst by ultra-bandgap light, an electron–hole pair (e^- , h^+) is produced. The hole oxidises the SED, e.g. glycerol, to SED_{ox} , e.g. glyceraldehyde and/or glyceric acid. The electron reduces the dye from its oxidised form, D_{ox} , to its reduced counterpart, D_{red} (step 1). If D_{red} is oxygen sensitive, its undesirable oxidation (from D_{red} to D_{ox}) can occur (step 2).

or via a felt-tipped pen. For a Rz ink the typically blue to pink colour change, signifying the completion of the photoreduction reaction, is achieved in under 7 min even for very thin (ca. 15 nm) commercial films of titania, such as that found on ActivTM, under a UVA illumination intensity of $\sim 7.2\text{ mW cm}^{-2}$. Since the reduction involves a change in colour, there is no need for a skilled operator or expensive analytical equipment to monitor reaction progress as the naked eye is sufficient for a qualitative indicator, or a semi-quantitative assessment, of photocatalytic activity [15]. Further work showed that the initial rate of the Rz to Rf colour change was directly related to the photocatalytic activity of the titania-coated glass, as measured by the stearic acid test.

Although the resazurin-based ink exhibits rapid reduction kinetics for thin, self-cleaning SPC films such as ActivTM, from an aesthetics and commercial demonstrator viewpoint an ink which changes from a highly coloured initial form to a colourless final form upon UV irradiation is more desirable, since market research shows that the process of bleaching is preferred by potential customers, as it is often associated with a cleaning action. As part of the search for a photocatalyst indicator ink that is bleached, this article reports the behaviour of three redox dyes, in an otherwise identical ink formulation to that of the original Rz-based ink, which are known to reduce to colourless products; namely, 2,6-dichloroindophenol (DCIP), resorufin (Rf) and methylene blue (MB). The different performances of these inks, compared to the Rz-based ink, are assessed and a possible, improved alternative to the Rz ink is suggested for the measurement of the photocatalytic activity of commercial, self-cleaning SPC films.

2. Experimental

Unless stated otherwise, all reagents were Analar grade, supplied by Sigma–Aldrich and used as received. All gases used were supplied by BOC.

Each different ink formulation utilised a basic solution comprising: 3 g of a 1.5 wt.% aqueous hydroxyethyl-cellulose solution (i.e. HEC, medium viscosity, supplied by Fluka) and 0.3 g of glycerol. To this solution was then added the dye under

test; for resazurin, 4 mg of the dye were added, whereas for 2,6-dichloroindophenol (supplied by Alfa Aesar), resorufin and methylene blue, 5 mg of dye were used to produce films of similar absorbance at their associated λ_{\max} values. The final ink solution of each of these dyes was sonicated for 5 min to help dissolve the dye, before being stirred for 30 min to ensure thorough mixing, after which time it was ready for casting on the surface of a photocatalyst substrate.

In this work, the photocatalyst substrate used was ActivTM, kindly supplied by Pilkington Glass, the preparation and characterisation of which have been described in detail elsewhere [6,16]. ActivTM was chosen as the model test photocatalyst substrate since it is commercially available in many countries and is of reproducible activity. Note that similar results to those reported here for ActivTM were also observed using other commercial SPC-based self-cleaning glasses and those made by a sol–gel method. Prior to use, the glass samples (~25 mm × 25 mm × 4 mm thick) were sonicated in a beaker of water for 5 min, and then wiped with a paper towel soaked in ethanol in order to remove any residual organics and/or grease from the photocatalyst surface. Typically, a few drops of the photocatalyst indicator ink under test were smeared over the surface of a sample of ActivTM before the ink-ActivTM sample was spun using an Electronic Micro Systems Model 4000-1 spin coater, set at 500 rpm for 15 s. The sample was then dried in an oven at 70 °C for 10 min resulting in a film thickness of ca. 0.7 μm, as measured by profilometry. Note also that drying the spun-coated samples in air, over a 1 h period, produced films which exhibited the same kinetic features for dye photoreduction as those that were oven-dried. Most experiments were conducted under ambient, aerobic atmospheric conditions (typically temperature ca. 20 °C and percentage relative humidity, %RH, ca. 60%). However, in experiments involving other than atmospheric conditions, e.g. anaerobic and oxygen-saturated atmospheres, it was necessary to place the sample in a gas cell that allowed gas of the desired composition and %RH to be flowed through it and spectrophotometric measurements to be made.

UV–vis spectra of the ink films were recorded using a Cary 50 Bio Varian spectrophotometer at different time intervals depending upon the observed rate of reduction. The samples were held in a specially designed sample cell holder and irradiated using 2 × 4 W black light blue bulbs (λ_{\max} 365 nm) with an incident light intensity of 4.8 mW cm⁻², when the sample was irradiated under ambient, open bench conditions. For experiments involving the gas cell, the effective incident light intensity was ca. 1.3 mW cm⁻², i.e. ca. three times lower than that used for the work carried out under ambient conditions, due to reflection losses from the optical faces of the cell and a greater distance between the UV source and the sample.

3. Results and discussion

3.1. Properties of the redox dyes and photocatalyst inks

Table 1 shows the structures of the oxidised forms of the dyes assessed in the ink formulation, namely methylene blue (MB), resorufin (Rf), resazurin (Rz) and 2,6-dichloroindophenol

(DCIP), along with some key spectral and redox properties of the dyes in solution. In the typical ink formulation, as also indicated by the spectral data in Table 1, all dyes, except Rf, gave a blue ink and a subsequent blue film when spun onto the surface of the photocatalyst substrate (ActivTM); for Rf, both the ink and the film were pink in colour. The electrochemical reduction of the oxidised forms of the redox dyes MB, DCIP and Rf, is reversible and the values of the redox potentials in Table 1 indicate that DCIP, with its positive redox potential of +0.228 V, should be the easiest of the dyes to reduce by the photogenerated electrons, e⁻, on thermodynamic grounds, since the respective redox potential at pH 7, E° (e⁻), is -0.52 V [2]. It follows that, on the same grounds, the reduced form of DCIP will be the most difficult for oxygen to re-oxidise, given E° (O₂/H₂O) = 0.82 V, followed by MB, then Rf, although, all are spontaneous reactions. In contrast, Rz reduction is, as noted earlier, electrochemically irreversible, thus no formal redox potential can be quoted for the dye. However, the results of work carried out elsewhere [17] suggest that the dye reduces at a potential somewhere between that of Rf and MB, i.e. between +0.011 and -0.051 V versus NHE.

In Table 1, the values of the wavelength of maximum absorbance in the visible region (λ_{\max}) for the oxidised form of each dye are also given, both in a typical solvent [18], such as water, and in the dried inks. In the latter case, most of the inks showed evidence of aggregate (dimer, trimer, etc.) formation, broader peaks being observed in their spectra with the wavelength of maximum absorbance, λ_{\max} , shifted significantly with respect to the monomeric form of the dye in solution (see Table 1).

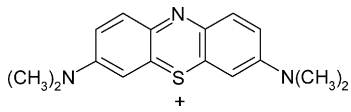
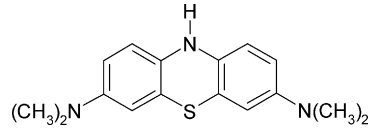
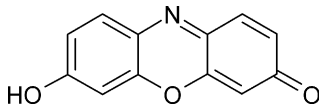
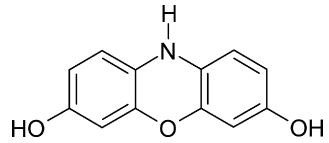
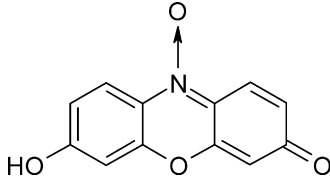
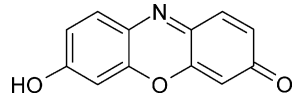
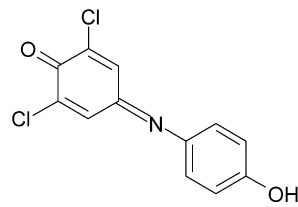
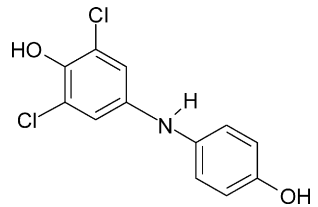
Table 1 also gives the structures of the final reduced forms of the dyes produced by the action of the titania photocatalyst and it can be seen that, in all cases, the overall photoreduction process involves a two electron transfer step accompanied by the addition of one or two protons. The final column in Table 1 identifies the observed colour change upon UV-photobleaching the oxidised dye, D_{ox} , to D_{red} in N₂, i.e. step 1 in Fig. 1. The resulting product arising from the reduction of Rz (blue), i.e. Rf, is pink in colour, whereas the reduced forms of all the other dyes screened are colourless, i.e. these dyes are photobleached.

3.2. Photocatalyst inks under anaerobic conditions

The UV photo-reduction of the inks was assessed initially under an atmosphere of N₂, since the presence of any oxygen added the possibility of its reaction with the photoreduced forms of the redox dye under test, D_{red} , as indicated in Fig. 1 (step 2), causing the latter's undesirable re-oxidation back to its original, oxidised form, D_{ox} . As noted earlier, since Rz is reduced irreversibly, its photoreduction appears most unlikely to be affected by the presence of oxygen, although direct reaction of O₂ with the photogenerated electrons, e⁻, cannot be ruled out. Fig. 2a–d show the spectral changes for the dyes: MB, Rf, Rz and DCIP, respectively, which occur when they are UV-irradiated as the dried ink on the surface of ActivTM, under anaerobic conditions, as a function of irradiation time.

The kinetic results of this work, in the form of a plot of the relative change in absorbance at λ_{\max} , i.e. $\Delta\text{Abs}_{\text{rel}}$, as a func-

Table 1
Structural, redox and absorption characteristics of the photocatalyst indicator ink dyes

Dye	Oxidised indicator dye (D_{ox})	Reduced indicator dye (D_{red})	$E^\circ (D_{ox}/D_{red})/V$ at pH 7	$\lambda_{max} (D_{ox})$ (nm)		Colour of ink (and after SPC-UV bleaching under N_2)
				In solvent	In dried ink	
MB			+0.011	661 (H ₂ O)	665 and 608	Blue (colourless)
Rf			-0.051	573 (CH ₃ OH)	580	Pink (colourless)
Rz			N/A	598 (H ₂ O)	610	Blue (pink)
DCIP			+0.228	605 (H ₂ O + 2 ml 1 N NaOH)	629	Blue (colourless)

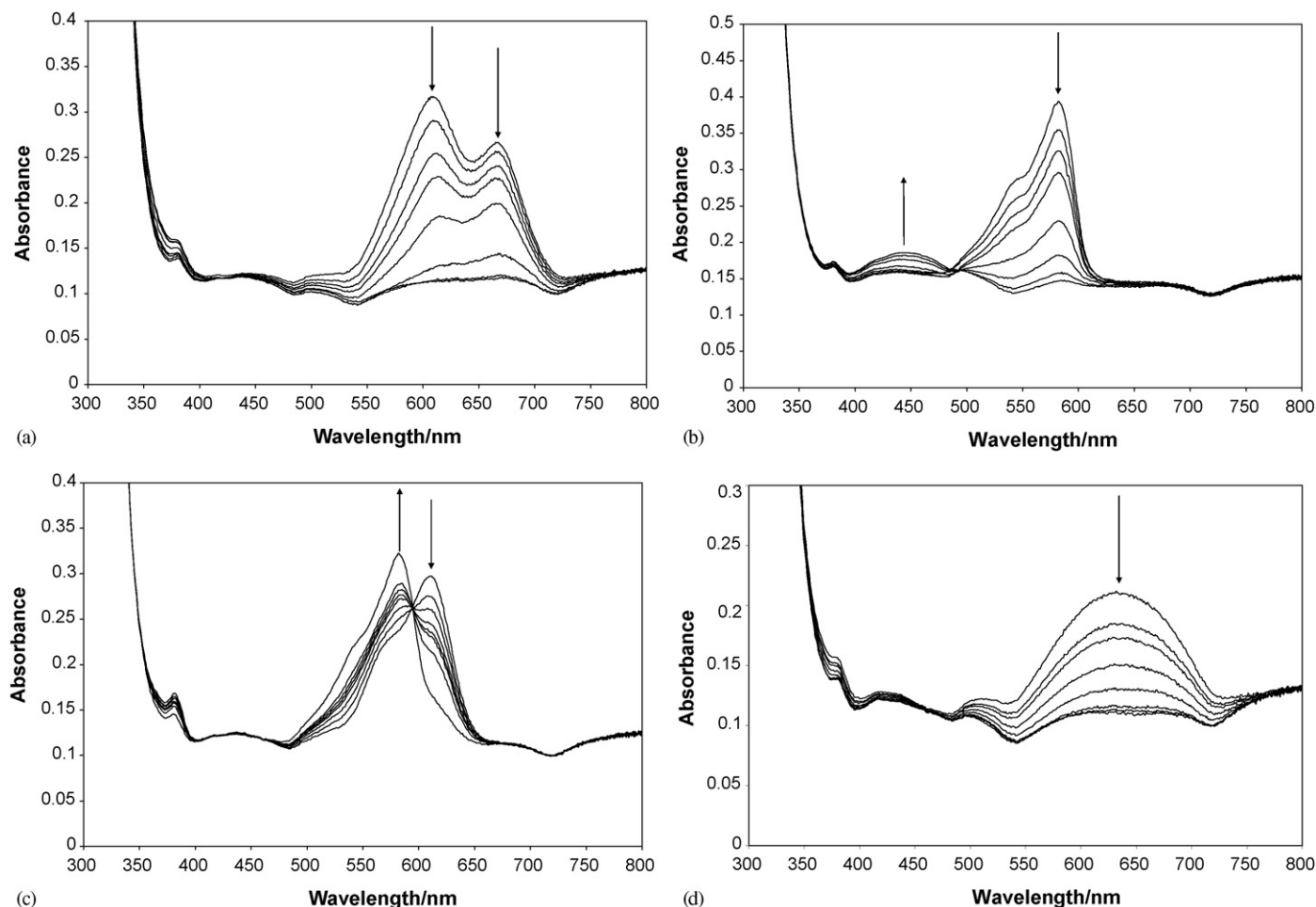


Fig. 2. Spectral profiles obtained for (a) MB, (b) Rf, (c) Rz and (d) DCIP dyes incorporated into an otherwise typical photocatalyst indicator ink formulation on ActivTM glass as a function of time of irradiation with UVA light under anaerobic conditions. The irradiation times were (top to bottom): (a) 0, 1, 3, 5, 10, 20, 40 and 70 min; (b) 0, 3, 5, 10, 30, 60, 90 and 120 min; (c) 0, 1, 2, 3, 4, 5 and 10 min; (d) 0, 3, 5, 11, 20, 40, 60 and 80 min, respectively.

tion of irradiation time, are summarised in Fig. 3, from which it can be seen that MB is the fastest of all the dyes to be photoreduced, followed by Rz, DCIP then Rf. From the first order plots of the data illustrated in Fig. 3 (inset diagram), the decay

kinetics of $\Delta\text{Abs}_{\text{rel}}$ as a function of UV irradiation time appear, for Rf, and possibly the other tested dyes, to be 1st order with respect to the dye concentration—yielding a series of different first order rate constant, k_1 , values. Such kinetics are expected if the rate-determining step is the diffusion of the oxidised dye from the deposited, thin ink film to the photoactivated titania film surface. It should be noted that the first order rate constants associated with the kinetics of the photobleaching of the various dyes reported in Fig. 3 are not fundamental constants and will vary with light intensity and sample orientation. Thus, as reported, they (and any $t_{50\%}$ values derived therefrom, *vide infra*) should be treated only as a measure of relative efficiency.

In this work, in most instances the total reduction of the ink occurs within 40 min, which is obviously not a rapid assessment of photocatalytic activity, despite being much faster than what would be observed with the stearic acid test for ActivTM [16]. However, the conditions under which this work was conducted (in a gas cell, under a N₂ atmosphere and a relatively low, incident UV light intensity of ca. 1.3 mW cm⁻²) are not representative of those which would be encountered in the field, for which the ambient UV intensity would usually be greater, from either solar UV (typically ca. 4 mW cm⁻²) or,

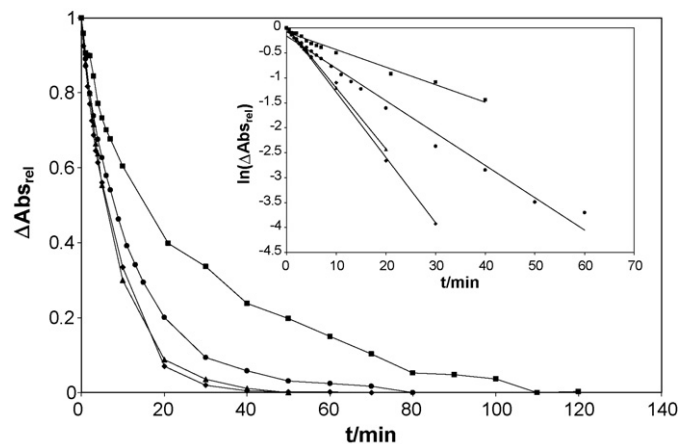


Fig. 3. The normalised changes in absorbance (at λ_{max}), $\Delta\text{Abs}_{\text{rel}}$, based on the data in Fig. 2, for the dyes: Rz (▲), MB (◆), Rf (■) and DCIP (●), and, inset, a first-order plot of this data over two half lives, generating the following respective rate constants (s⁻¹): 2.04×10^{-3} , 2.18×10^{-3} , 5.85×10^{-4} and 1.08×10^{-3} .

Table 2
 $t_{50\%}$ values for different dye-containing inks under anaerobic and aerobic conditions

Dye	$t_{50\%}$ (min) under N_2 ($I \approx 1.3 \text{ mW cm}^{-2}$)	$t_{50\%}$ (min) under ambient conditions (open bench, ca. 60% humidity, $I \approx 4.8 \text{ mW cm}^{-2}$)	Estimated ^a $t_{50\%}$ (h) under ambient conditions (open bench, ca. 60% humidity, $I \approx 4.8 \text{ mW cm}^{-2}$) on plain glass
MB	5.3	nc	nc
Rf	19.7	–	nc
Rz	5.7	1.0	15.0
DCIP	10.7	2.0	5.0

nc: no change after 1 h irradiation.

^a Estimated from the change in ΔAbs vs. time plots over the first 10% of photobleaching.

more likely, an artificial, UVA, hand-held light source (typically $7\text{--}8 \text{ mW cm}^{-2}$).

The apparent initial rate of reduction of each dye in the ink formulation can be quoted in terms of a $t_{50\%}$ value, i.e. the time taken for 50% of the overall colour change to occur upon UV irradiation under gas cell conditions, and the values for each of the dyes used are given in Table 2 based on the first order rate plots, since $t_{50\%} = \ln 2/k_1$. From Table 2, Rz and MB can be seen to have the fastest initial reduction rates (i.e. the shortest $t_{50\%}$ values under N_2), with DCIP close behind. In contrast, the $t_{50\%}$ observed for the Rf-based ink is ca. three times that observed for Rz, which makes it too slow to use as a possible alternative to Rz as a photocatalyst indicator ink of thin titania films, despite its attractive coloured (pink) to colourless, UV-induced colour change. Such a slow reduction compared to the other dyes is not entirely unexpected, since Rf has the most negative redox potential of the tested dyes [17], indicating that the thermodynamic driving force for its reduction by photogenerated, conduction band electrons, e^- , on titania would be less than that for the other dyes under test. However, for photocatalyst films which are much more active than ActivTM (i.e. film thicknesses $\gg 15 \text{ nm}$), the use of an ink based on Rf might be appropriate for the rapid assessment of their photocatalytic activities.

3.3. Photocatalyst inks under aerobic conditions: the elimination of MB

The above work allowed the efficacy of the dye photoreduction step by the photogenerated electrons, i.e. step 1 (see Fig. 1), to be studied without the complicating feature of interference by oxygen, e.g. step 2 in Fig. 1. However, in any practical system for use in the field as well as the laboratory, a photocatalyst indicator ink must work effectively under aerobic conditions, i.e. its photobleaching kinetics (step 1) should be independent of ambient levels of oxygen, thus implying step 2, and/or direct reaction of the photogenerated electrons with O_2 , should be negligible. It is this vital requirement which effectively rules out MB as a possible alternative to Rz as a photocatalyst indicator ink, since its reduced form, leuco-methylene blue (LMB), is known to be very oxygen sensitive [19]. This sensitivity is very nicely illustrated by the results of an experiment in which the initial photobleaching of a MB ink was effected under an anaerobic atmosphere and the photoreduced, clear and colourless film, containing LMB, was then exposed to air. The variation in the absorbance at λ_{max} for MB (608 nm) recorded during this experiment is illustrated in Fig. 4 and shows that whereas MB is rapidly photobleached to

LMB with UV-irradiation under anaerobic conditions, LMB is rapidly re-oxidised to MB upon the introduction of oxygen into the system. As a consequence, and not surprisingly, in a separate experiment it was observed that UV irradiation of MB ink on ActivTM in air produces no noticeable colour change upon UV irradiation over 40 min, whereas under anaerobic conditions, as demonstrated in Figs. 2a and 3, it is readily photobleached. Interestingly, this feature has been exploited recently to produce a UV photo-activated, oxygen sensitive ink, in which the key ingredients are similar to those observed here, namely MB, glycerol and nano-crystalline particles of titania, with the proposal that such oxygen-sensitive inks could realise a commercial, tamper-evident, leakage indicator for modified atmosphere packaging [20]. However, the high O_2 -sensitivity of LMB, i.e. the facile nature of step 2 for the MB ink, renders it unsuitable for use as an indicator of photocatalytic activity.

3.4. Photocatalyst inks under aerobic conditions: Rz and DCIP

Fig. 5 illustrates a set of normalised ΔAbs versus time profiles for a typical Rz and DCIP ink irradiated under ambient, aerobic conditions and it is not surprising to note from this plot, and the $t_{50\%}$ values given in Table 2, that the Rz-based ink appears superior to the DCIP ink for assessing rapidly the photocatalytic activity, since its $t_{50\%}$ time is shorter under aerobic and anaerobic conditions. However, the DCIP ink has the desirable feature of

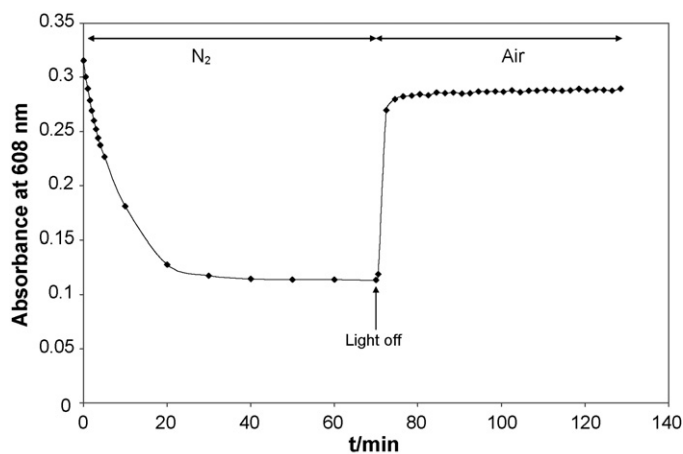


Fig. 4. The photoreduction (in N_2 for 70 min) and subsequent dark re-oxidation (in air) of a MB ink on ActivTM monitored via the change in absorbance at λ_{max} for MB in the ink formulation (608 nm).

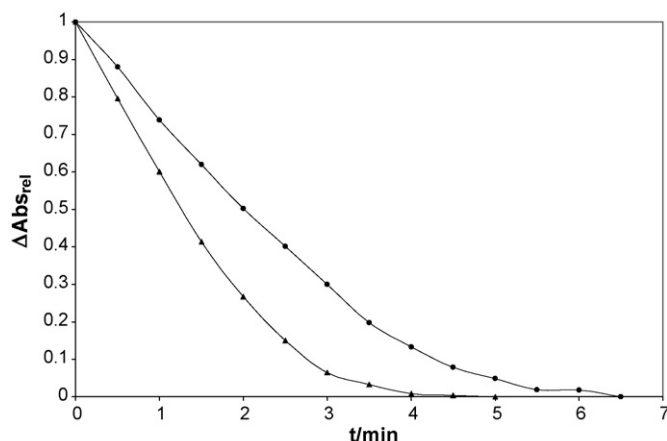


Fig. 5. The change in the normalised relative absorbance at λ_{\max} , $\Delta\text{Abs}_{\text{rel}}$, for DCIP (●) and Rz (▲) inks on Activ™ upon UVA irradiation ($I = 4.8 \text{ mW cm}^{-2}$) under ambient aerobic conditions, i.e. 21% O_2 and 60% RH at 22 °C.

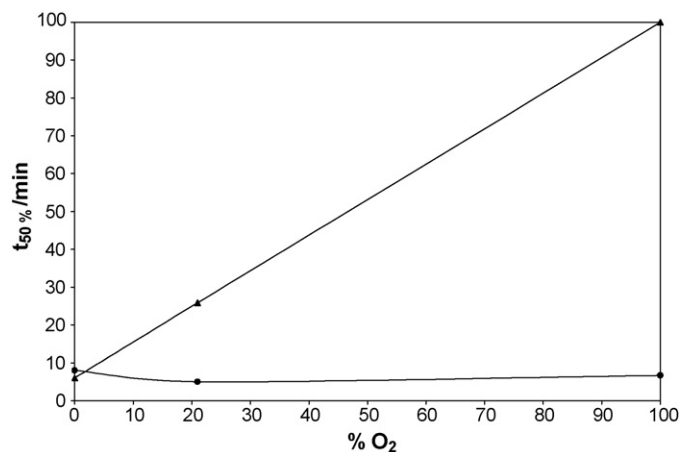


Fig. 6. Variation in the measured photobleaching $t_{50\%}$ values for Rz (▲) and DCIP (●) inks on Activ™ as a function of the % O_2 (0% RH) in the ambient gas phase.

being photobleached in step 1 in Fig. 1, i.e. its photoreduced product is colourless, unlike Rz with its pink reduced product, Rf. It could be argued that after Rz has been reduced, the product, Rf, can be reduced subsequently to its colourless counterpart (dihydroresorufin, HRf). However, as indicated by the results in Table 2, such a reduction is inherently slow under anaerobic conditions and slower still under aerobic conditions, since HRf is readily re-oxidised to Rf by ambient oxygen. Table 2 also contains the $t_{50\%}$ values, where they could be estimated, when the inks were UV irradiated on plain glass. Even the ink that was most susceptible to UV photodegradation, DCIP, appears to photobleach at a rate that was at least 150 times slower than that that observed when deposited on Activ™, i.e. all the inks tested appeared very stable towards photobleaching when deposited on plain glass.

3.5. DCIP and Rz inks under different partial pressures of oxygen

A more detailed study of the UV photoreduction of DCIP and Rz inks by Activ™ (i.e. step 1, Fig. 1) under an atmosphere of gas containing different percentages of oxygen revealed a surprising dependence of the observed $t_{50\%}$ value upon % O_2 for the Rz ink, as illustrated by the results in Fig. 6. Since the reduction of Rz to Rf is electrochemically irreversible, it might be expected that the kinetics of Rz photoreduction would be largely independent of oxygen concentration. Instead, much to our surprise, the results in Fig. 6 show that this photoreduction is very oxygen sensitive and that the presence of oxygen slows down considerably the photoreduction of Rz to Rf by the underlying titania film on Activ™. This sensitivity may, for example, be due to the formation of a semi-stable, semi-reduced form of Rz, i.e. $\text{Rz}^{\bullet-}$, which readily reacts with oxygen. In striking contrast to Rz, with DCIP ink, the rate of its photobleaching, i.e. $t_{50\%}$, is independent of % O_2 , as also illustrated by the results in Fig. 6, possibly because its semi-reduced form is much shorter-lived and therefore less able to react with oxygen.

The results in Fig. 6 raises the important question: why does the Rz ink work so well, and better, than the DCIP ink on the open bench (see Table 2), when the results in Fig. 6 indicate that the photoreduction of Rz should be significantly reduced by the presence of 21% oxygen? The underlying cause appears to be a humidity effect, demonstrated by separate experiments showing that the photoreduction of the Rz-based ink under anaerobic conditions is increased markedly if the relative humidity, %RH, is changed from 0 to ca. 60%, whereas the kinetics of DCIP photoreduction are largely independent of %RH, as they are of % O_2 . At present, it is not clear why the kinetics of photobleaching of the Rz ink are enhanced by increasing %RH, but unchanged for the DCIP ink. However, this humidity enhancement effect does help answer the initial question, since it indicates that the photoreduction step (step 1 in Fig. 1) in the Rz ink is sufficiently enhanced by the high humidity associated with ambient conditions (ca. 60% RH) as to counter the reaction-slowing, oxygen interfering step 2, thought to be responsible for the higher $t_{50\%}$ value observed for the Rz ink, compared to the DCIP ink, under 0% RH conditions (see Figs. 1 and 6). As a result of this humidity counter effect the overall photobleaching of the Rz-based ink remains more rapid than the DCIP ink under ambient, aerobic, open bench conditions. These results, however, indicate that the Rz ink may not be the best dye to test photocatalytic activity given its apparent sensitivity to both % O_2 and %RH. In contrast, the kinetics of photoreduction of DCIP are unaffected by changes in %RH and % O_2 , and it is photobleached; it follows that the DCIP ink is an attractive alternative to the Rz ink.

As with the Rz-based ink [15], the DCIP ink can be easily contained within a felt-tipped pen, as shown in Fig. 7(a), making it possible to apply the ink directly on to a photocatalytic material under test in the field or the laboratory. This material could be an example of any of the myriad commercial photocatalyst products that are already installed in homes and offices, such as photoactive glass, tiles or paints. To use the DCIP ink in a pen, it is necessary to increase the dye loading level from the standard 5 mg of dye used in the ink formulation in this work to 15 mg, in order to give a more striking initial blue film.

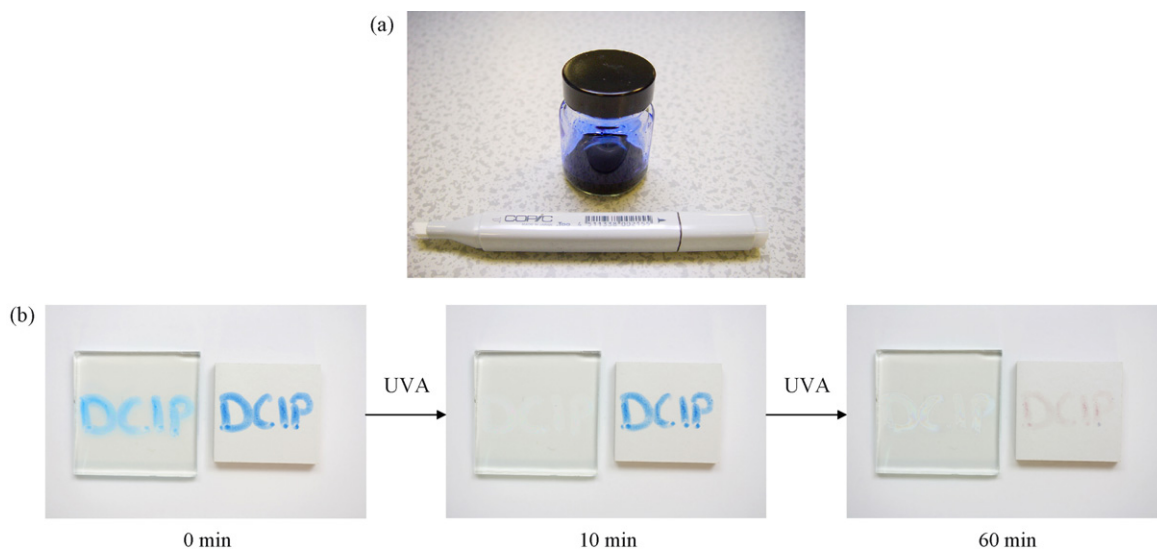


Fig. 7. (a) A typical, refillable felt-tipped pen and DCIP photocatalyst indicator ink sample and samples of Activ™ glass (left hand side) and Hydrotect tile with DCIP ink (b) prior to, after 10 min and finally after 60 min illumination with UVA light ($I = 7.42 \text{ mW cm}^{-2}$).

Using this high dye formulation, 6 mL of the ink was loaded into a refillable felt-tipped pen (Copic Marker) and used to mark a piece of Activ™ and a Hydrotect, photocatalytic tile (supplied by Deutsche Steinzeug [21]). Irradiation of these samples with UVA light (7.4 mW cm^{-2}), as expected, caused the DCIP ink on both the Activ™ glass and the Hydrotect tile to turn colourless. In contrast, over the same irradiation time periods used in Fig. 7(b), the DCIP ink was still clearly visible on both plain glass and a standard tile. The pen eliminates the need for a skilled operator or any expensive analytical equipment to carry out and/or monitor the reduction process, and hence presents industry with a cost effective and rapid, semi-quantitative way of demonstrating rapidly and effectively the efficacy of commercial or laboratory-made, UV-activated, photocatalytic materials.

The Hydrotect tiles used were not obviously porous, but rather had a smooth titania surface glaze. It is likely that only for macroporous materials would the inks be adsorbed to a significant extent, as they are reasonably viscous (ca. that of glycerol = 934 cP) and dry within minutes. Instead, for most materials, the inks are likely to form a predominately surface film and so assess the surface photoactivity of the material under test.

4. Conclusions

A photocatalyst indicator ink, based on the redox dye 2,6-dichloroindophenol (DCIP), can be used to assess the photocatalytic activity of self-cleaning glass and other photocatalytic materials via a UV-driven, coloured to colourless colour change. The DCIP-based ink out performs those based on the alternative redox dyes resorufin (Rf) and methylene blue (MB), since Rf reduces too slowly, and MB does not work in air since its reduced form, leuco-methylene blue, is highly oxygen sensitive. Although the reduction kinetics under ambient conditions for the DCIP ink are slower than those of an Rz ink, the latter is shown to be both oxygen and humidity sensitive, whereas

the DCIP ink is not. The DCIP ink, from a commercial demonstrator point of view, also features the more desirable feature of undergoing a coloured to colourless change upon UV irradiation in the presence of a photocatalyst underlayer and, as a consequence, has significant potential for use as part of a simple, rapid method for assessing qualitatively, or semi-quantitatively at least, the activities of photocatalyst films.

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