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A Simple, Inexpensive Method for the Rapid Testing of the Photocatalytic Activity of Self-cleaning Surfaces

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Abstract

A rapid, semi-quantitative, inexpensive method, using a simple digital scanner and an indicator ink, suitable for use in the laboratory, or in the field, for assessing the photocatalytic activity of commercial photocatalytic self-cleaning materials such as glass, is described. The repeatability of the current method is found to be high and better than many of the previously reported ISO photocatalyst tests.

Introduction

There exist many different methods to assess the photocatalytic activity of a film, but in almost all cases: expensive analytical equipment, technical support and a long analysis time are required[1-4]. In a recent paper[5] this group has reported the use of a photocatalyst activity indicating ink, containing a dye, Resazurin (Rz), and a sacrificial electron donor (i.e. SED, e.g. glycerol). The ink functions via a photo-reductive mechanism which can be summarized as follows: upon photoexcitation of an underlying photocatalyst film photogenerated holes react irreversibly with the SED in the overlying ink film, whereas photogenerated electrons reduce the Rz dye (blue) to Resorufin (Rf, pink) in the same ink film; the overall rate of the colour change, or time taken to change colour, provides a measure of the photocatalytic activity of the underlying self-cleaning film. In almost all cases of commercial self-cleaning films, the active coating is the semiconductor TiO_2, and so interaction between an underlying titania self-cleaning film and an overlying Rz ink coating can be summarised as follows:

$$TiO_2 \xrightarrow{h\upsilon \geq E_{bg}} TiO_2\,(h^+, e^-) \quad (1)$$

$$SED + TiO_2^*(h^+, e^-) \longrightarrow SED_{ox} + TiO_2\,(e^-) \quad (2)$$

$$Rz + 2e^- + 2H^+ \longrightarrow Rf + H_2O \quad (3)$$

Where E_{bg} is the band gap energy of the titania (3.2 eV for anatase), SED_{ox} is glyceric acid or glyceraldehyde. It should be noted that this test may not necessarily correlate with other tests of photocatalytic activity and that such correlations need to be established. Encouragingly, previous work reveals that the rate of the above, ink-based, photocatalyst driven process is linearly correlated with the much slower destruction of a film of stearic acid (SA)[2,5].

Experimental

Chemicals and Materials

All chemicals were purchased from Sigma-Aldrich and, unless otherwise stated, were used as received. The water used to produce all inks was double distilled and deionised. The commercial self-cleaning glass used to test the ink was BioClean® supplied by Saint-Gobain.

Ink Preparation and Coating

The Rz photocatalyst indicator ink comprised: 10 g of a 1.5 wt % aqueous hydroxyethyl-cellulose (HEC) solution, 1 g of glycerol, 10 mg of the Resazurin (Rz) dye (75 %, sodium salt) and 10 mg of Polysorbate 20 surfactant. Each photocatalytic, self-cleaning glass sample was cleaned by wiping lightly with an ethanol-soaked, lens cleaning tissue (silicone free Whatman 105 tissue) and allowed to dry before being coated with the indicator ink. The glass samples were then coated with the Rz ink by hand using a wire wound rod, manufactured by RK Print (K-bar #3). The wire gauge on the rod is 0.31 mm in diameter and gives a wet ink film of ~24 µm, which typically dries to give a film of ca. 800 nm thick, as measured by SEM.

Instrumentation

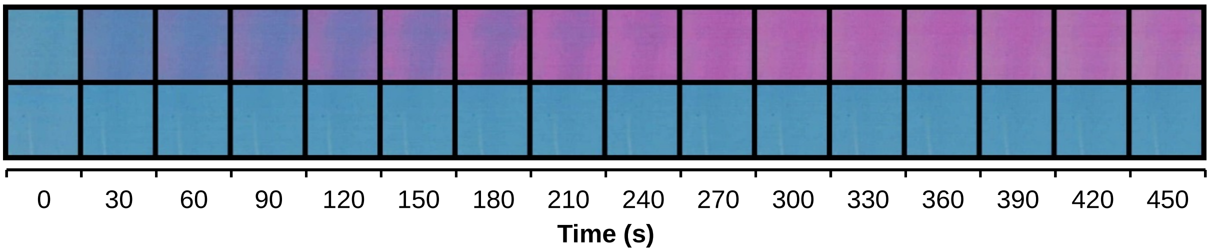
All irradiations were conducted using a Blak-Ray® XX-15 lamp and exposure stand purchased from Cole-Parmer. The bulbs used in the lamp were 15 W Blacklight tubes (Eiko) with λ_{max} emission of 352 nm. The sample tray was set so as to irradiate the samples under test with a UV-A irradiance of ~2 $mWcm^{-2}$, as measured using UVX Digital Ultraviolet Intensity Meter, with a UVX-36 sensor head for UV-A light (both from Cole-Parmer). UV-Visible spectra of the ink films were recorded using a Cary 50 Bio Varian spectrophotometer at different irradiation time intervals and, simultaneously, digital images of the ink-coated glass samples were recorded using an Ion CopyCat handheld document scanner. The scanner has rollers which ensure the small gap between sample and scanner is maintained and so a consistent image is obtained and for most laboratory-based studies a table scanner can be used instead. If used in the field, for in situ studies, the level of UV light falling on the sample would usually be ill-defined and/or variable as it would comprises sunlight and/or room light. Under such conditions, the ink would be appropriate mainly for qualitative analysis, i.e. just signalling the presence of a photocatalyst surface. Red, green and blue, i.e. RGB, values were extracted from the digital images of the ink films. A free download of the software used in the extraction is available[6] and a set of guide notes are given elsewhere[7], although most commonly available photo-editing software, like Adobe photoshop for example, allow RGB values to be similarly extracted from digital images. **Fig. 1.** Illustrates the main components used here to carry out the Rz ink test of the photocatalytic activity of a sample piece of self-cleaning glass, namely: the Rz ink, a K-bar (#3) and a hand-held scanner.

Fig. 1. - The equipment and materials used to conduct the test; a handheld document scanner, the Rz ink, a wire wound rod (K-bar #3) and a sample piece of self-cleaning glass.

Results

In a typical experiment a sample of the self-cleaning and plain glass were coated with the Rz ink, dried in an oven at 70 °C for 10 minutes and then irradiated with UV-A light (2 mW cm^{-2}). The UV/Vis. spectra and digital images of the ink on glass samples were then recorded as a function of irradiation time spanning the range 0 – 450 seconds. The latter are shown in **Fig. 2a** for the Rz ink on self-cleaning (top images) and plain (bottom images) glass. Other work shows that of the three different colour parameters making up the digital image of the ink, only the red component, RGB $(red)_t$, varies significantly, as the ink changes from blue (Rz) to pink (Rf) with increasing UV irradiation time, *t*, and so it is only this parameter that was extracted in all subsequent digital image work described here.

(a)



(b)

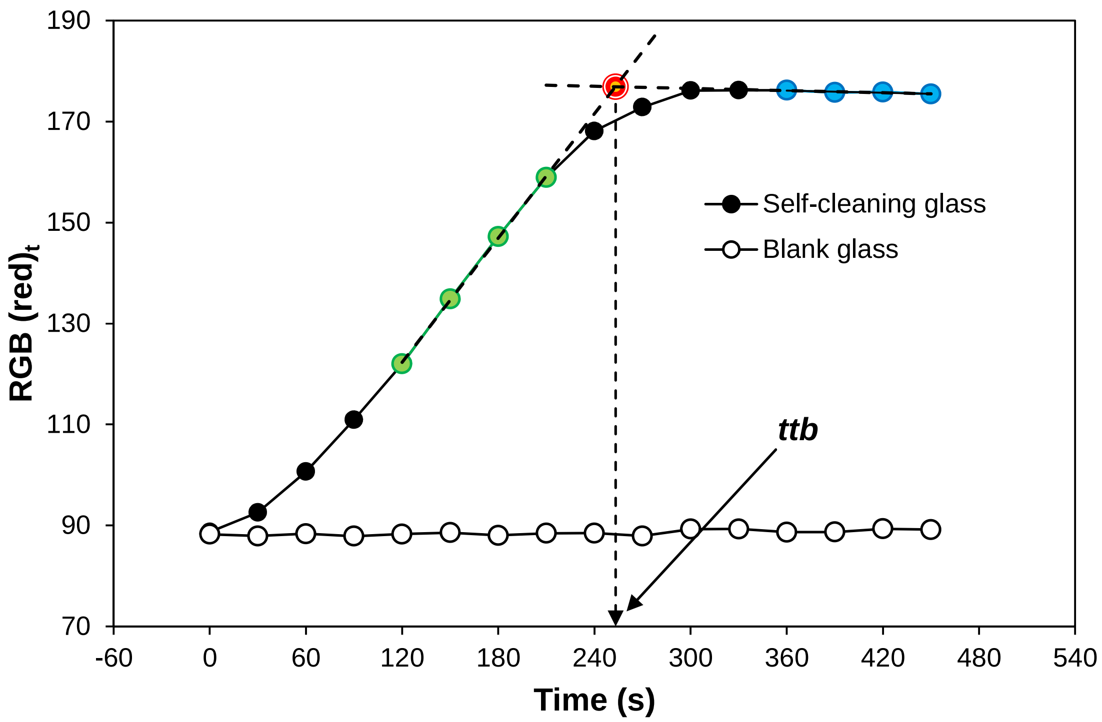


Fig. 2. – (a) A series of images recorded at 30 second irradiation intervals for two glass samples, namely; self-cleaning glass (top) and, plain glass (bottom). (b) A plot of variation of the RGB (red) with irradiation time, extracted from the images shown in (a). RGB $(red)_t$ is the value of the RGB

(red) component at irradiation time, *t*. The time taken to bleach the RGB (red) component, *ttb*, is determined graphically as illustrated.

A plot of variation of the RGB $(red)_t$ values extracted from the images in **Fig. 2a**, are illustrated in **Fig. 2b** for self-cleaning and plain glass samples. In the case of the self-cleaning glass sample, the point in time at which the red component in the digital image has been bleached is taken as a measure of the activity of the photocatalyst film under test and is referred to as the time to bleach (*ttb*). Note that no colour change occurs in the Rz ink if there is no photocatalyst coating present, c.f. plain glass data in **Fig. 2a**.

By definition, repeatability which is the degree of agreement of tests or measurements on replicate specimens by the same observer in the same laboratory, i.e. repeatability is a measure of how well the same experimenter can generate the same results. Reproducibility on the other hand is usually taken as the ability of an entire experiment to be reproduced by someone other than the experimenter working independently. Both repeatability and reproducibility are usually reported as a standard deviation. In order to highlight the reproducibility and repeatability of the above method for assessing the photocatalytic activity of self-cleaning films using an Rz ink, a series of round-robin tests were conducted on the self-cleaning glass between groups spread across Europe. The results of this work, in the form of the measured *ttb* values for 5 samples of self-cleaning glass, are reported in **Table 1**. From the data in the columns of table 1 the repeatability appears low and variable (10 to 0.8%), with a mean and average standard deviation of 246 ± 11 s, i.e. an average repeatability of 4.3%. The reproducibility was, as might be expected, a little less good, yielding from the data in the columns an average value of 246 ± 20 s, i.e. an average reproducibility of 8.1%. However, in terms of repeatability and reproducibility, these errors are very good when compared to most of the current ISO photocatalyst activity tests, such as the methylene blue test, ISO 10178:2010, where the results of the inter-laboratory tests revealed a repeatability varying from 4.9 to 16.6% and a reproducibility of 28%!

Other work shows that, for self-cleaning glass at least, the change in RGB (red) at any time, *t*, during an irradiation, i.e. $\Delta RGB\ (red)_t$ is related directly to the change in absorbance at 610 nm, $\Delta Abs_{610}(t)$, which, itself, is a measure of the $[Rz]_t$, the concentration of Rz in the ink film at irradiation time, *t*. This is relevant in that the rate of change of ΔAbs_{610} has been shown to correlate with the rate of destruction of stearic acid (d[SA]/dt) as noted earlier, implying d(RGB (red)$_t$)/dt will also correlate with d[SA]/dt.

Table 1. – The average time to bleach the red component of the digital images of the ink on the same photocatalytic surface of self-cleaning glass (*ttb*) in seconds.

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
Sample 1	253	260	214	259	251	282
Sample 2	239	252	227	262	252	245
Sample 3	239	257	208	265	248	207
Sample 4	238	259	215	269	247	260
Sample 5	271	250	206	250	247	248
Average /s	248	256	214	261	249	248
Std. Dev. /s	14	4	8	7	2	27

Conclusion

The use of an inexpensive digital scanner provides all the advantages of using a UV/Vis. spectrophotometry in recording the change in colour of the ink, without needing to use expensive, bulky equipment or significant technical support. The inter-laboratory repeatability of the Rz ink test is high (ca. 8.1%) and better than many of the current ISO photocatalyst tests. As a consequence, the above method appears particularly suitable for measuring the photocatalytic activity of self-cleaning glass (and, from other, recent work, also paints and tiles) both in the lab and in the field, at little cost and with little training, but with a reasonable degree of precision.

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