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Photocatalyst activity indicating adhesive labels for use in the field

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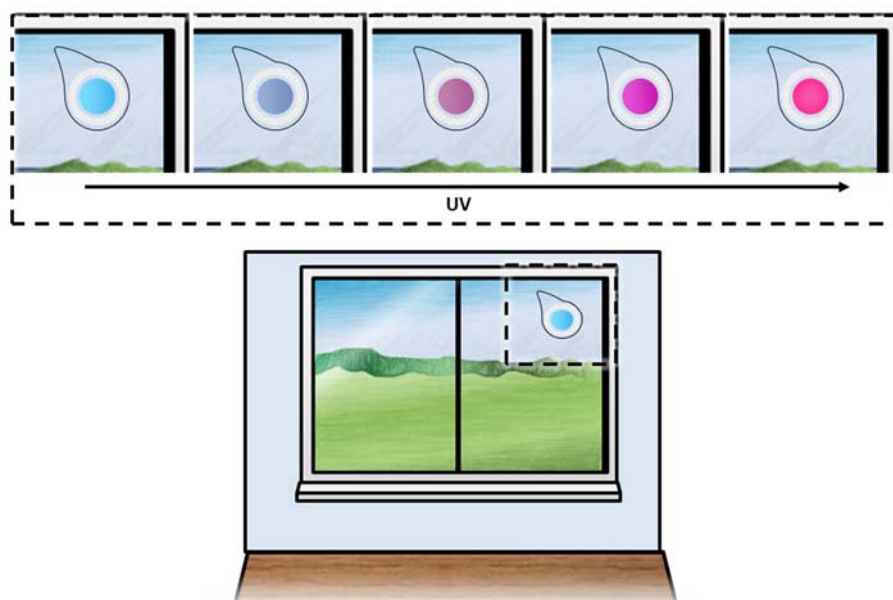
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Abstract

The preparation and characterisation of a resazurin-based photocatalyst activity indicator *label* is described. The label is applied to a number of different TiO₂-based, photocatalytic materials, including self-cleaning: glass, tile, paint and awning materials, as well as a thin, sol-gel film, produced in-house. In all cases, the label exhibited a blue to pink colour transition upon irradiation with UV light. In most cases, the time taken to bleach 90% of the red component of the digital image of the ink, *ttb(90)*, was twice that for a traditional Rz ink, produced by the drawdown method, since the former was twice as thick. Although not as fast as a drawdown Rz ink, by a factor of ca two, it still only takes minutes to change and the Rz label is much more easily used, stored and does not need the sample to be: very smooth, horizontal or flat. As such it appears ideal for testing samples, both quantitatively and qualitatively *in situ*, i.e. in the field.

Graphical Abstract



Key words: photo catalyst indicator, resazurin, label, indicator

1.0 Introduction

Commercial photocatalytic self-cleaning materials are finding increasing usage throughout the world, with the market's total worth being projected at over \$3 billion for 2020 [1]; the bulk of this use is in the form of architectural materials, such as self-cleaning: glass, paint, awning and concrete materials [2,3]. It follows that there is a real need for novel, accessible and economical testing methods for assessing the efficacies of such materials. Both the manufacturers and end-users of such materials are beginning to eschew the more traditional, costly photocatalytic testing techniques (the methylene blue ISO test, for example [4,5]), which are often slow and require dedicated technical support, in favour of more rapid assessment techniques, such as photocatalyst activity indicator inks, i.e. *paiis* [6,7].

A *paii* is an ink comprising a redox-indicating dye (usually the dye, resazurin, Rz), a sacrificial electron donor (SED), often glycerol, and a polymer binder, such as hydroxyethyl cellulose (HEC) [8]. The ink is used to coat a photocatalytic surface under test and, as such, may be applied using a felt-tipped pen [9,10], aerosol spray [11] or ink draw-down [8,12]. In the case of an Rz *paii*, the generation of surface electron/hole pairs by the photocatalytic material under test, when irradiated by light of sufficiently high energy ($h\nu \geq E_{bg}$), results in the subsequent rapid oxidation of the SED and the concomitant reduction of the Rz (blue) to resorufin, Rf (pink) in the *paii* [8,10]. *Paiis* of this, and other, closely related, formulations have been adopted widely in recent years as the primary testing technique in many research articles detailing the development of new photocatalysts, as well as in industry. Examples of the growing use of *paiis* are given in **Error! Not a valid bookmark self-reference..**

Table 1: Examples of *paiis* used as an assessment technique for a variety of photocatalytic surfaces [10–27]

Ref	<i>Paii(s)</i> used	Materials tested / comments
[10]	Rz/HEC	Activ™; CVD ^b TiO ₂ films; first use of pen as an application method
[11]	Rz/HEC	CVD TiO ₂ films; first use of aerosol spray as application method
[12]	Rz/HEC; BB66/HEC, AV7/HEC ^a	BioClean®; Deutshce-Steinzeug tiles; StoColor Climasan paint; <i>paiis</i> formulated with different dyes to suit the assessment of markedly different surfaces and activities
[13]	Rz/HEC	TiO ₂ films with varying porosity and loading; Rz ink dip-coated onto films cast onto glass.
[14]	Rz/HEC	C-doped sputter-formed TiO ₂ films
[15]	Rz/HEC	Coloured Zn/borophosphate glasses
[16]	Rz/HEC	N-doped CVD TiO ₂ films
[17]	Rz/HEC	Aerosol-assisted CVD TiO ₂ films influenced by electric fields
[18]	Rz/HEC	PbO-modified TiO ₂ films
[19]	Rz/HEC	CVD TiO ₂ films
[20]	Rz/HEC	Films of γ -Bi ₂ MoO ₆
[21]	Rz/HEC	N-doped CVD TiO ₂ films; Activ™; Rate data generated from RGB rather than Abs
[22]	Rz/HEC	TiO ₂ sol-gel modified with surfactant
[23]	Rz/HEC	Rutile and anatase TiO ₂ surfaces
[24]	Rz/HEC	Photocatalytic cements
[25]	Rz/HEC	Fe(III)-substituted hydroxyapatite photocatalyst
[26]	Rz/HEC	TiO ₂ films doped with various dopants and coated on various substrates
[27]	Rz/HEC	Photocatalytic cements; Rz <i>paii</i> used in industry

^a BB66 = basic blue 66 and AV7 = acid violet 7

^b CVD = chemical vapour deposition

Of all the techniques used to apply the ink, the drawdown method, using a K-bar, is the most popular, since it delivers a highly reproducible film on a smooth surface, yielding a wet ink film, thickness ca. 24 μm , which then dries within 10-15 min to form a film ca. 2.1 μm thick [28].

Figure 1(a) illustrates the results of a typical experiment in which an Rz *paii* has been coated using a K-Bar (No. 3) onto a photocatalyst glass surface and irradiated with UVA light, whilst its UV-vis spectrum is monitored as a function of irradiation time.

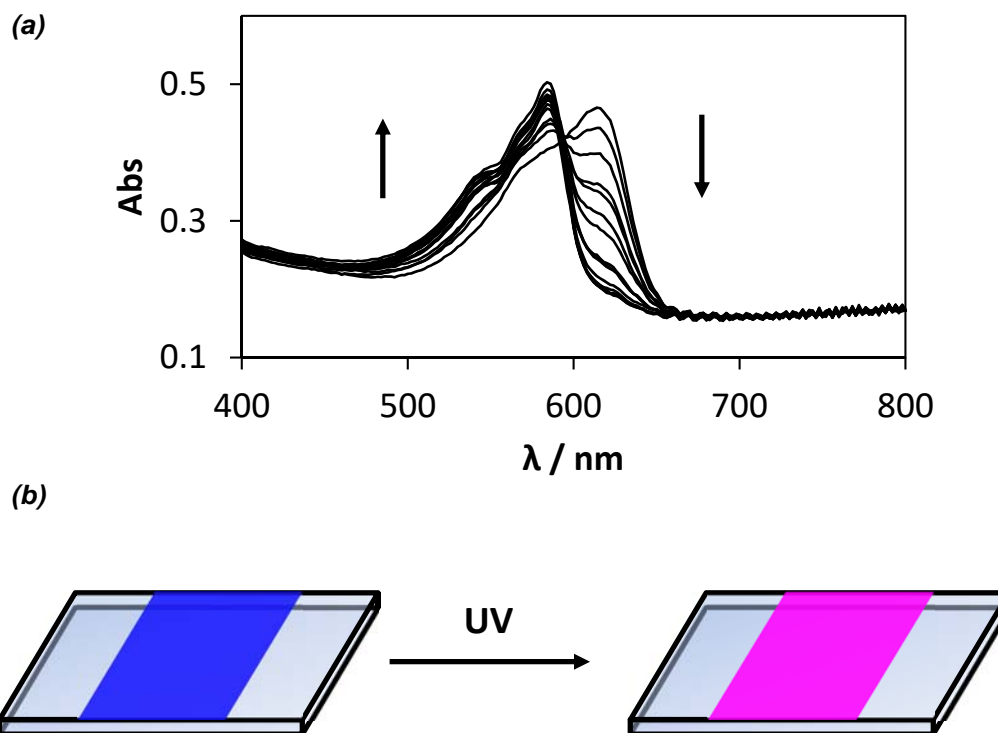
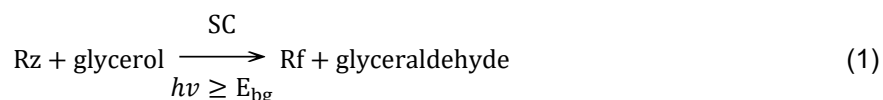


Figure 1: (a) UV-vis absorption spectra for a typical, K-bar coated *paii* film on a sheet of photocatalytic, self-cleaning glass, recorded as a function of UV irradiation time (i.e. every 30 s for 7 min using a blacklight, BL, lamp, $\lambda_{\text{max}} = 352 \text{ nm}$ (FWHM = 40 nm); 2.0 mW cm^{-2}); (b) schematic of the observed change in colour of the *paii* coated onto a photocatalytic ally active film, upon UV irradiation.

These results show that the photocatalytic film under test is able to mediate the rapid reduction of Rz to Rf by UV light, i.e.



Where SC = semiconductor photocatalyst, usually TiO_2 . However, this popular K-bar ink drawdown technique is not without its limitations. For example, it requires the photocatalyst surface to be largely horizontal, i.e. it is not really suitable for testing vertical or steeply inclined samples, as might be found when testing surfaces *in-situ*. Similarly, the photocatalytic film should also, ideally, be flat, since the more curved the surface, the greater the difficulty in producing a uniform ink film. In addition, some

practice is required in order to be able to generate routinely a uniform ink film using the draw-down technique. The photocatalytic film must be smooth, since any surface roughness of the material under test that is greater than ca. 24 μm [28], *vide supra*, this will tend to produce a non-uniform, i.e. patchy, ink film. Finally, carrying the ink and a K-bar around for testing samples in the field is not particularly convenient.

As a consequence, there exists a need for a more easily applied, non-invasive and cost-effective delivery method for the *paii* technology for use on a wide range of photocatalytic materials that are not necessarily horizontal, flat or very smooth and such a test would find particular use in the field. Thus, in this paper, we describe the production of an Rz-based *paii* label, produced by a screen printing process. The response of this label is tested using a range of commercially-available, photocatalytic surfaces of different types including photocatalytic glass, paint, and tile.

2.0 Experimental

2.1 Chemicals and materials

All materials were purchased at the maximum available purity grade from Sigma-Aldrich, unless stated otherwise. The pressure-sensitive adhesive polymer used to make the label was Tackwhite AT 4M1, from IChemCo. A list of the TiO₂-based photocatalytic test materials used in this work, and their features, are listed in Table 2.

Table 2: Photocatalytic test materials

Name	Manufacturer	Material features	Photocatalyst	Average surface roughness / nm ^b
Activ™	Pilkington [29]	Glass, 4 mm thickness	TiO ₂ , 15 nm thick [30]	34
BioClean®	Saint-Gobain Glass [31]	Glass, 4 mm thickness	TiO ₂ , 15 nm thickness + 2 nm Al-doped SiO ₂ (8%) [30]	13
Sheerfill® V with Everclean®	Saint-Gobain [32]	Poly(tetrafluoroethylene), 0.5 mm thickness	TiO ₂ , 1.5 μm thickness, ca. 25% surface coverage [33]	-
StoColor Climasan	Sto [34]	Silicate-based paint	TiO ₂ , 10% wt. loading in paint [35]	338
Hydrotect	Deutsche-Steinzeug [36]	Ceramic tile	TiO ₂ , 0.1 μm thickness [37]	59
Sol-gel	Produced in laboratory ^a	Coated glass slide of 1 mm thickness	TiO ₂ , ca. 250 nm thick	111

a: Sol gel films prepared as described elsewhere [38], then diluted to 1 wt.% concentration in 0.1 M HNO₃, so that they can be coated (using a doctor blade technique) to yield an appropriately thin (250 nm) film, but with ca. 5-15 nm particles [39] as measured by SEM (

Figure 2c).

b: Average roughness determined using AFM. The roughness of the Sheerfill V awning's photocatalyst coating could not be determined, as the bulk material is itself rough on a macroscopic scale.

The surfaces of the materials were probed using a scanning electron microscope (FEI Quanta FEG – Environmental SEM Oxford Ex-ACT) and the results of this work are illustrated in

Figure 2. In all cases, the EDX facility on the SEM revealed a surface covered with TiO₂. Studies investigating the morphology of each surface, conducted using AFM (a Nanosurf Flex-Axiom in dynamic force mode), showed that the surfaces exhibited a range of roughness, of which the two glass samples were the smoothest, and the Sto paint sample the roughest, see table 2.

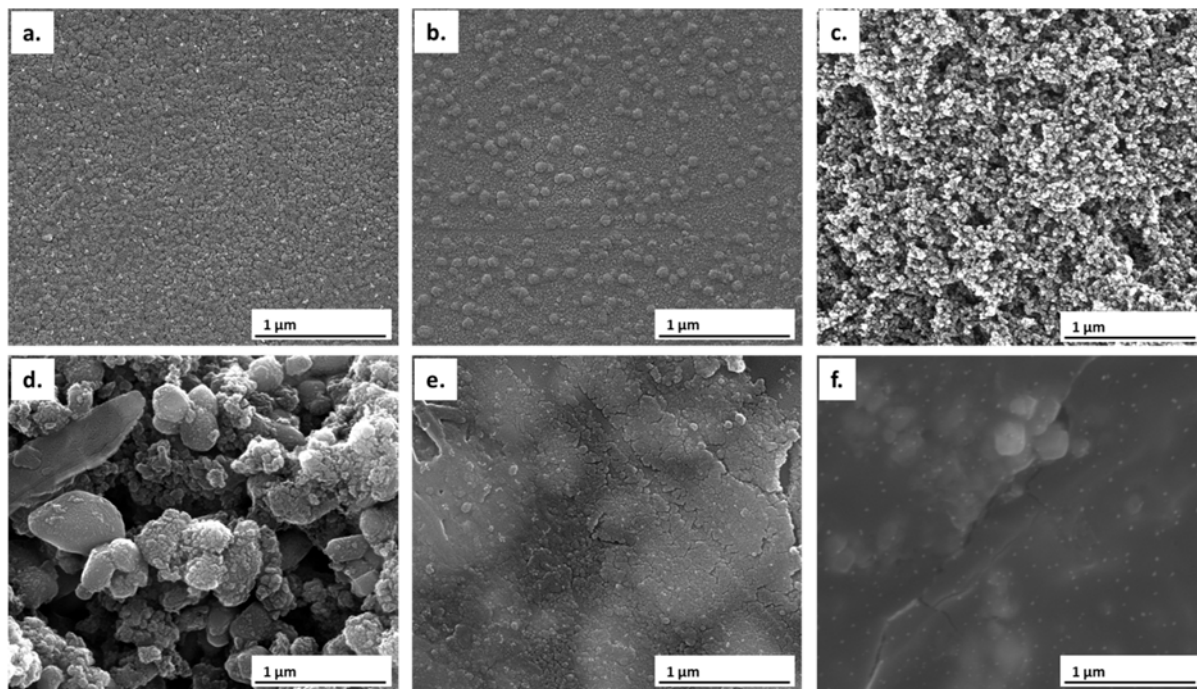


Figure 2: SEM Images of (a) Activ™ glass, (b.) BioClean® glass, (c) a TiO₂ sol-gel film, (d) StoColor Climasan silicate-based paint (e) Hydrotect ceramic tile and (f) photocatalytic awning material all at 100,000 magnification (the space bar in all the images is for 1 μm).

The SEM's of the two samples of self- cleaning glass (Activ™ and BioClean®), i.e. figures 2(a) and (b), respectively, showed the particles were ca. 20 nm in diameter, although the BioClean also had larger floret-like, growths distributed across its surface, measuring ca. 95 ± 10 nm. Lab-based, cast sol-gel paste films, figure 2(c), comprised ca. 10 nm particles, consistent with previously reported work of thicker films of the same sol-gel material [38]. StoColor Climasan silicate-based paint film, figure 2(d), had TiO₂ particles with apparent particle size of ca. 50 ± 6 nm. The ceramic tiles, figure 2(e), had TiO₂ particles of ca. 68 ± 8 nm distributed across the surface, which, in turn, appeared to be fused aggregates of smaller sized particles, ca. 30 ± 5 nm. The awning material, figure 2(f), was too fragile to be analysed using high-vacuum electron microscopy without being destroyed, however analysis using low vacuum SEM at the same magnification revealed an apparent TiO₂ aggregate particle size of 230 ± 20 nm. The above photocatalytic materials provide a reasonably diverse range of surfaces and activities with which to test the Rz labels.

2.2 Formulation of a typical Rz draw-down ink

A typical Rz ink was made by first adding 0.15 g of the water-soluble cellulose ether, hydroxyethyl cellulose (HEC; average MW = 320k g mol⁻¹) to 9.85 g of water, to give a polymer concentration of 1.5 wt%. To this were added 1 g glycerol and 10 mg Rz (Na salt) and the resulting ink was then stirred overnight on a magnetic stirrer plate to ensure all the components were fully dissolved.

2.3 Formulation of the screen-printable Rz ink

A typical screen-printable *paii* was produced by dissolving 3.5 g of the alcohol-soluble, cellulose ether, hydroxypropyl cellulose (HPC; average MW = 80k g mol⁻¹) in a binary solvent solution, comprising: 62 g *n*-butanol and 6.2 g ethanol, to give a polymer concentration of 5 wt%. To this were added 4 g of the sacrificial electron donor, glycerol, and 200 mg of the redox-active dye, Rz (Na salt). The ink was then allowed to stir overnight to ensure the complete dissolution and mixing of the ink components. Unlike the water-based ink reported in section 2.2 (viscosity = ca. 980 mPa s), this solvent-based Rz ink had a suitably low viscosity (ca. 105 mPa s) for screen printing.

2.4 Screen printing an adhesive *paii* label

In screen printing, ink deposition is achieved by forcing the ink through a negative template (formed from permeable portions of an otherwise impermeable screen), onto a substrate which is placed beneath the screen, using a squeegeeing action. In this work a model SD-05 screen printer (RokuPrint) was used to print both the solvent-based Rz ink and the adhesive, using appropriate different bespoke designed silk screen templates, made and supplied by GK Marketing Supplies Ltd. Thus, the solvent-based *paii* was printed through a 43 thread cm⁻¹ mesh screen, with an ink-permeable small disc-shape design (diameter = 1.7 cm) onto a sheet of polyethylene terephthalate (PET; 50 µm thickness), using a squeegee velocity of ca. 23 cm s⁻¹. The final dry disc ink film produced was approximately 4 µm thick. This was then followed by the printing of a ring layer of the pressure sensitive adhesive, i.e. PSA, (with: inner diameter = 2.25 cm and outer diameter = 3.0 cm, so that the thickness of the adhesive band was 3.75 mm, around the *paii* disc on the PET film. This second screen printing step used a differently designed, bespoke mesh screen, under otherwise identical printing parameters. A gap of 0.275 cm was maintained at all points between the central *paii* 'disc' layer and the surrounding PSA ring. In order to achieve this reproducibly, a screen with a slightly higher thread density (77 thread cm⁻¹) was chosen for the screen printing of the PSA (viscosity = 600 mPa s), since higher thread counts improve print definition [40]. The dry film thickness of the printed adhesive was ca. 10 µm.

The screen-printed adhesive and *paii* were allowed to dry in air in the dark for 48 h before being applied to a protective layer comprising: a cellulose acetate (CA) projection sheet (100 micron thickness, Hartwii), which was then laminated with PET (2 x 80 micron sheet laminator pouches, provided by Swordfish); this protective layer prevented any further drying out of the indicator film during storage. The CA sheet in the protective layer usually had black ink printed on its surface so as to protect the underlying Rz *paii* from photobleaching due to ambient light. Whilst the Rz ink/adhesive on PET film was cut into 3 cm circles, the CA/PET protected sheet was cut into a slightly larger, tear-shaped pattern so as to allow for its easy removal from the indicator layer when it came to peeling

them apart. In later work, using bigger screens, it was possible to print 18 identical labels simultaneously, using the above technique, which could then be cut into individual units using a custom-designed die cutting template. **Figure 3** shows a digital image and a schematic illustration of a typical label, although, in this case, the CA sheet was not printed with black ink, so as to render the underlying Rz *paii* visible.

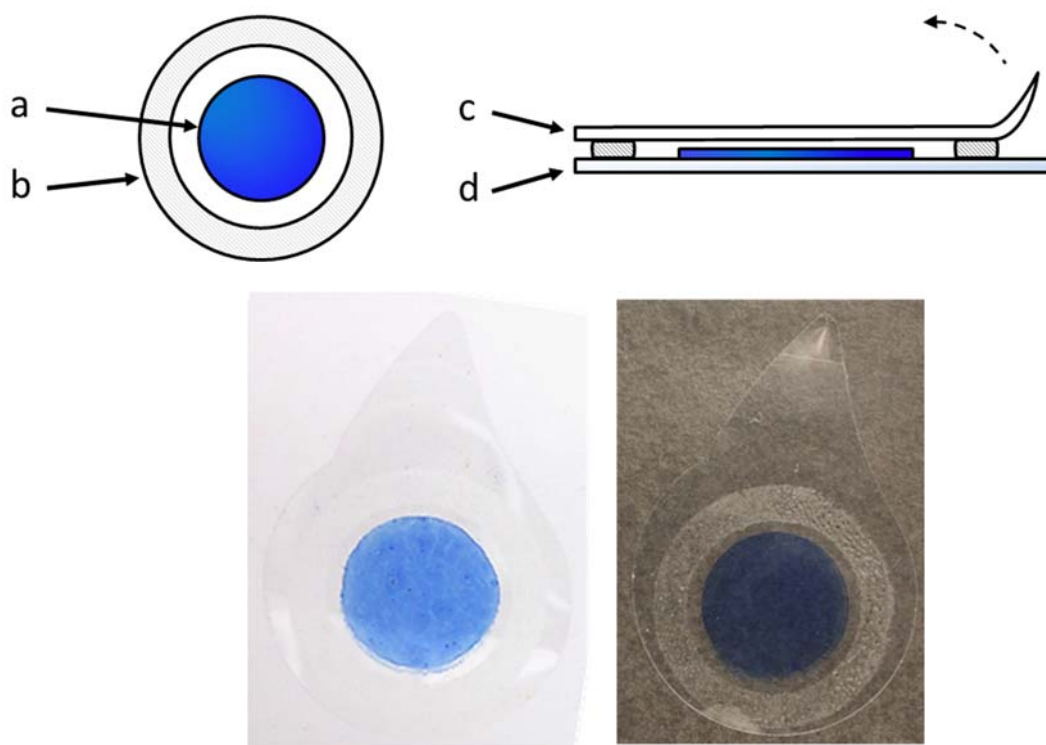


Figure 3: Top and side-views of the label, showing (a) the Rz *paii* circle (17 mm diameter, 4 μm dry film thickness), (b) the PSA ring band (3.75 mm band thickness, 10 μm dry film thickness), (c) the protective, removable PET-laminated CA transparency cover (ca. 260 μm dry thickness; 2 x 80 μm laminate sheets that make up the laminating pouch, plus 1 x 100 μm CA transparency sheet in between), (d) the underlying PET ink-printed substrate layer (ca. 50 μm dry thickness). Lower: Digital images of the label on a white background to emphasise the blue *paii*, and on a grey background to emphasise the translucent PSA layer.

Note: since the irradiation of the semiconductor photocatalyst is usually carried out through the label (an obvious necessity for opaque samples) it follows that the dye (Rz), and its pink reduced form (Rf), and the ink's supporting substrate (50 μm PET here) must not absorb strongly this radiation. Fortunately, both Rz and Rf absorb little UVA (315 - 400 nm) [28] and the same is true for the PET film, which, for example, had an absorbance of ca. 0.05 at 352 nm, i.e. the maxima of the UVA BL used in this work.

2.5 Assessment of photocatalytic surface activity using the label and ink

For the purposes of this work, unless otherwise stated, all irradiations were carried out using a 15 W black light lamp (Eiko), with an emission peak maximum, λ_{em} , at 352 nm (FWHM = 40 nm), and an

irradiance of 2.0 mW cm^{-2} . All photocatalytic test samples were pre-treated under the same UV irradiation conditions for 1 h prior to testing, so as to clean the surface photocatalytically by mineralising any organic pollutants that may be on the surface of the sample under test, and also to render the surface superhydrophilic, so as to improve the adhesion of the screen-printed label when applied subsequently.

Once the sample under test was cleaned using UV light, a screen-printed label was peeled from its PET/CA protecting top-cover film and stuck to the surface carefully, so as to avoid trapping any air bubbles. The label was then smoothed, by thumb or cylindrical roller, to remove any remaining trapped air and enhance its contact with the underlying sample. The label-covered sample was then irradiated with UV light, as described above, and its colour monitored regularly using digital photography. The images of the label were analysed using RGB colour analysis, *via* the software package *ImageJ* [41], which then allowed the average values of the red, RGB(red), blue, RGB(blue), and green, RGB(green) components of the image, to be extracted for each image, *i.e.* each image sampled at time, t . This in turn allowed the normalised value of the RGB(red), *i.e.* R_t to be calculated, *via* the expression:

$$R_t = \frac{\text{RGB}(\text{red})_t}{\text{RGB}(\text{red})_t + \text{RGB}(\text{green})_t + \text{RGB}(\text{blue})_t} \quad (2)$$

The normalised red component was chosen since it gave the biggest change in value, as the R_z was photoreduced to R_f . Thus, from the photographic images of the change in colour of the R_z label recorded for each sample tested, a plot of R_t vs irradiation time, t , was generated; a typical example of which, for the label on Activ™ self-cleaning glass, is given in **Figure 4**, *vide infra*. Further details regarding this method of colour analysis are given elsewhere, [42,43]. The camera used in all this work was a Canon EOS 7D.

3.0 Results & Discussion

3.1 R_z label vs. a traditional R_z *paii* ink

All initial tests on the label's response were carried out on Pilkington Activ™ photocatalytic glass, as it is a well-studied material that has served as a commercial benchmark photocatalytic surface in many other studies, including ones using *paiis* [12,44,45]. In a typical experiment, the R_z label on Activ™ was irradiated with UV light and photographed as a function of irradiation time. These images and the results of the RGB analysis, *i.e.* a plot of R_t vs. t , are illustrated in **Figure 4** and reveal a value for $ttb(90)$ (*i.e.* the time taken to reach 90% of the maximum value of R_t) of 8.8 min (highlighted in by a red dot in Figure 4). The same sample of self-cleaning glass was also tested, under the same conditions, using the traditional drawdown R_z ink, which was monitored and analysed in the same manner as the R_z label so as to yield an R_t vs. t plot that that was noticeably sharper in response to that shown by the R_z label, with a $ttb(90)$ of 3.8 min [12]. The drawdown R_z ink ($2.1 \mu\text{m}$ thick)

obviously responds much faster (by about a factor of two) than the screen-printed label (4 μ m thick), which is not surprising, given the kinetics of R_z reduction have been found to be inversely dependent upon film thickness [28].

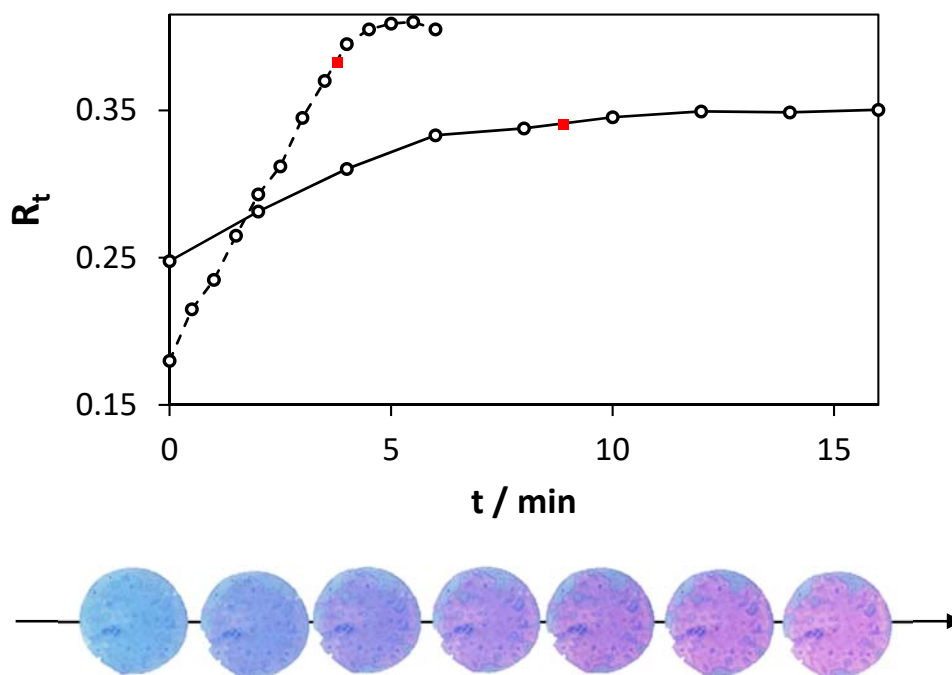


Figure 4: Photographs and accompanying normalised R_t data recorded of a R_z *paii* label affixed to a sheet of Activ™ glass and irradiated using two 15 W BL lamps with $\lambda_{ex} = 352$ nm (FWHM = 40 nm), 2.0 mW cm⁻² for 15 min (solid line) and of a R_z *paii* ink under the same conditions for 6 min (broken line). The red dots signify *ttb*(90) values of 3.8 min for the ink, and 8.8 min for the label.

A repeatability test carried out using five R_z labels produced on the same day, yielded an average *ttb*(90) value of 8.8 ± 0.16 min, i.e. ca. 1.8 %, which compares well with that reported previously for the R_z ink test ($\pm 4.3\%$ [46]). Other work showed that the R_z label remained unchanged in colour and responsivity when stored in the dark, under otherwise ambient conditions for over 6 months.

3.2 Assessment of photocatalytic surface activities

The screen-printed R_z label was tested on a number of different commercial photocatalytic samples, the details of which are given in Commercial photocatalytic self-cleaning materials are finding increasing usage throughout the world, with the market's total worth being projected at over \$3 billion for 2020 [1]; the bulk of this use is in the form of architectural materials, such as self-cleaning: glass, paint, awning and concrete materials [2,3]. It follows that there is a real need for novel, accessible and economical testing methods for assessing the efficacies of such materials. Both the manufacturers and end-users of such materials are beginning to eschew the more traditional, costly photocatalytic testing techniques (the methylene blue ISO test, for example [4,5]), which are often slow and require dedicated technical support, in favour of more rapid assessment techniques, such as photocatalyst activity indicator inks, i.e. *paiis* [6,7].

A *paii* is an ink comprising a redox-indicating dye (usually the dye, resazurin, Rz), a sacrificial electron donor (SED), often glycerol, and a polymer binder, such as hydroxyethyl cellulose (HEC) [8]. The ink is used to coat a photocatalytic surface under test and, as such, may be applied using a felt-tipped pen [9,10], aerosol spray [11] or ink draw-down [8,12]. In the case of an Rz *paii*, the generation of surface electron/hole pairs by the photocatalytic material under test, when irradiated by light of sufficiently high energy ($h\nu \geq E_{bg}$), results in the subsequent rapid oxidation of the SED and the concomitant reduction of the Rz (blue) to resorufin, Rf (pink) in the *paii* [8,10]. *Paiis* of this, and other, closely related, formulations have been adopted widely in recent years as the primary testing technique in many research articles detailing the development of new photocatalysts, as well as in industry. Examples of the growing use of *paiis* are given in **Error! Not a valid bookmark self-reference..**

Table 1. Unless stated otherwise, all irradiations were carried out using the BL lamps and irradiance reported in Figure 4. Some of these digital photographic images generated as a result of this work are shown in **Figure 5**.

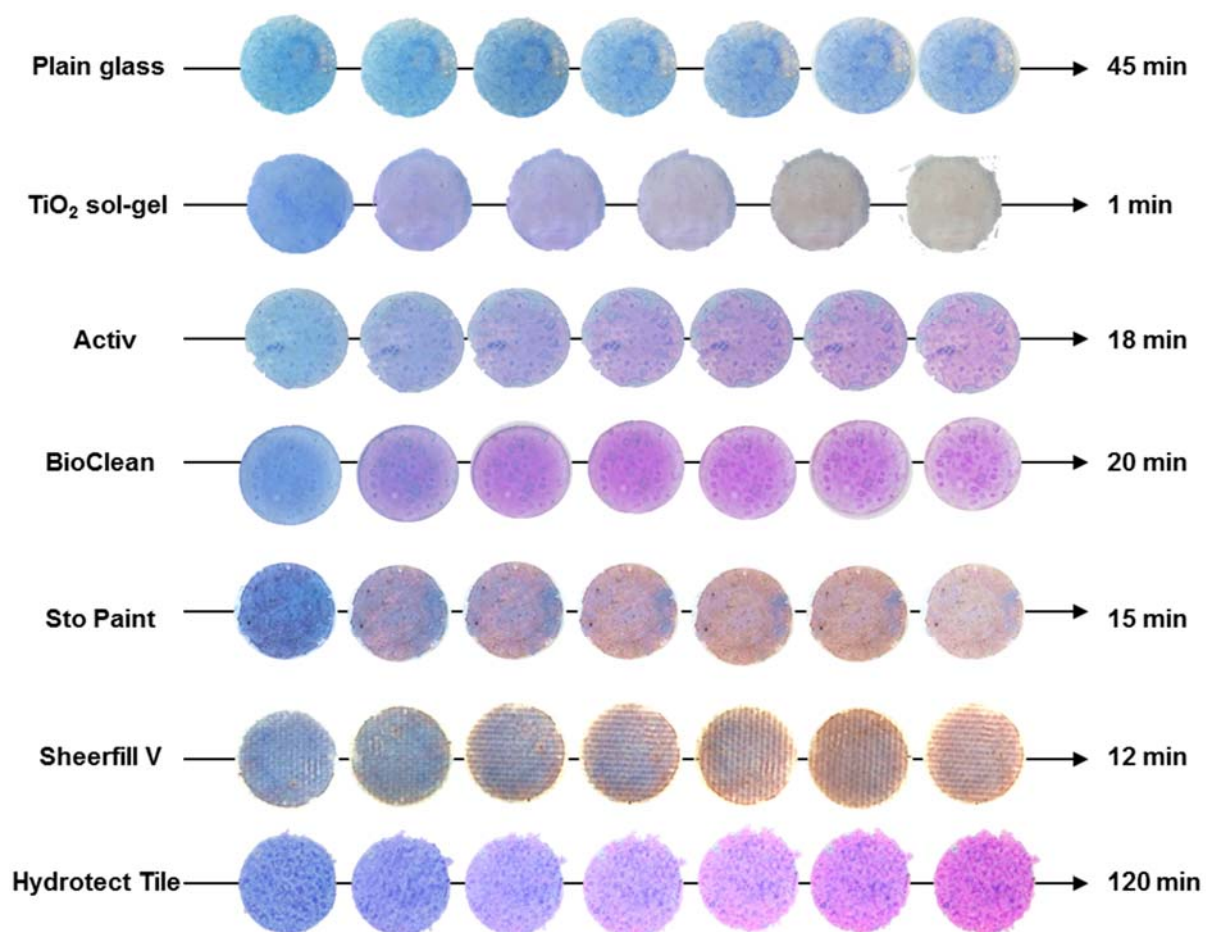


Figure 5: Digital photographic images, recorded of the RZ labels on a variety of different photocatalytic materials as a function of irradiation time. Note: in all cases the UV irradiance was 2.0 mW cm^{-2} , except for the sol-gel film, for which it was 0.5 mW cm^{-2} .

The photographic images generated in this study allowed the construction of a R_t vs. t plot, and determination of the $ttb(90)$ value, for each of the different photocatalytic materials tested; an example of which, generated using a typical RZ label applied to a sample of the photocatalytic awning material and irradiated under the usual conditions for 24 min, is shown in **Figure 6**.

The $ttb(90)$ data (generated from the R_t vs. t plots for each material shown in **Figure 5**) are collected in **Table 3**, along with $ttb(90)$ values reported previously for these same materials, or determined here, using the RZ ink test. The apparent order of photocatalytic activity (which is inversely proportional to the $ttb(90)$ value [46]), is, for both the RZ label and ink, $\text{TiO}_2 \text{ sol-gel} > \text{awning/tent material} > \text{paint} > \text{glass} > \text{tile}$. It is worthwhile noticing that, for many of the samples, the formation of the reduced pink form of RZ, i.e. R_f , is transitory, and that further irradiation causes this colour to fade. The latter feature is due to the further photocatalytic reduction of R_f to dihydroresorufin, which is

colourless. The various observed colour transitions are slightly complicated by the fact that the samples of photocatalytic paint, awning and tile used here were all beige coloured to different extents, i.e. not perfectly white or colourless. However, for each of these samples, this background colour did not inhibit at all the creation of the necessary R_t vs. t , plot, and determination of the associated $ttb(90)$ value, as illustrated by the R_t vs. t , profiles in Figures 3 and 6 for Activ™ and the commercial photocatalytic awning material, respectively.

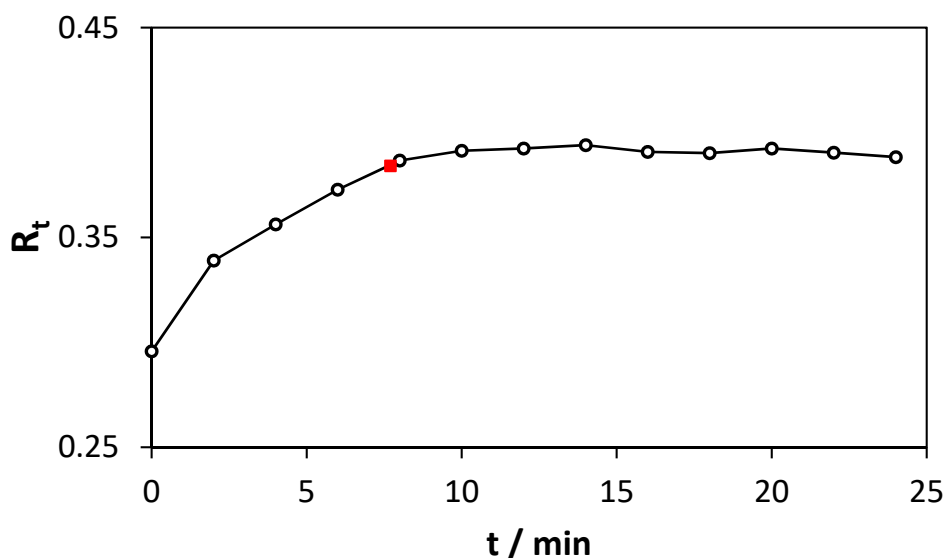


Figure 6: A typical R_t vs. t plot used to generate $ttb(90)$ data in **Table 3** (red square), in this case for a typical R_z label tested on a sample of Sheervill V awning with EverClean photocatalyst coating, and irradiated under standard irradiation conditions of 352 nm (FWHM = 40 nm) and 2.0 mW cm⁻².

The awning photocatalytic material, Sheerfill V, is an example of where the R_z new label is particularly advantageous over the more traditional *paii* application methods. Sheerfill V has a smooth, *hydrophobic* surface, so that when the traditional R_z ink is applied, *via* the draw-down method, the ink has a tendency to reticulate and so doesn't form a film, rendering the traditional R_z ink test method unusable on this material. In contrast, the screen-printed R_z label has sufficient tack that it adheres to the awning material, thereby allowing the label to provide a measure of its photocatalytic activity. A brief inspection of the results in **Table 3** show that, for the different materials tested, usually the $ttb(90)$ of the ink is *ca.* half that of the label, for reasons outlined earlier.

Table 3: *t_{tb(90)}* values of the Rz screen-printed label, and reported Rz ink, on different photocatalytic materials surfaces

Surface Type	Product Name	Label <i>t_{tb(90)}</i> / min	Ink <i>t_{tb(90)}</i> / min
Glass	Plain glass	> 60	
	Sol gel [38] ^a	<< 0.1	<< 0.1
	Pilkington Activ™ [29]	8.8	3.8 [12]
	St. Gobain BioClean® [31]	13.6	6.3 [47]
Architectural Membrane	St. Gobain Sheerfill V with Everclean™ [32]	7.7	<i>Not determined – vide supra</i>
Paint	Sto Color Climasan [34]	11.8	6.1 [12]
Tile	TOTO Hydrotect™ coating system [48]	105	63 ^b

a: Sol gel films prepared as described in Table 1, with dry thickness *ca.* 8x lower than a typical sol-gel film as described in cited literature [39], and yet it still requires < 6 s UV irradiation to change the colour of the Rz label or ink.

b: Value measured in this work

Finally, one of the key features of the Rz label is that it can be used readily *in situ* and, in particular, it can be used to assess the activity of vertical or tilted samples, such as glass panes, *in situ*. An illustration of this is given in Figure 7, which shows the colour changes undergone by an Rz label stuck to a vertical sheet of self-cleaning glass upon its UV irradiation.

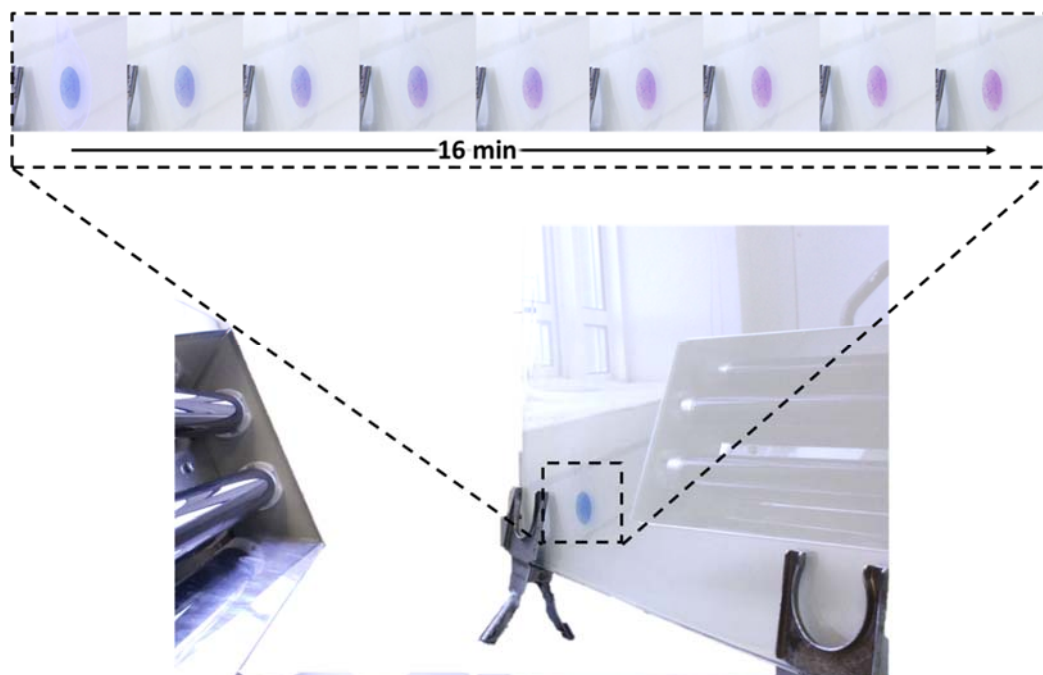


Figure 7: The *in-situ* application of the RZ label on a vertically-oriented sample of self-cleaning glass. Also in the picture is the UV irradiation source (two 15 W BLB lamps with λ_{em} at 365 nm, and with a UV irradiance of 2.0 mW cm⁻²). The insert plot shows the colour changes undergone by the label as a function of irradiation time. RGB data analysis of these yields a *t_{tb(90)}* value of 8.5 min.

4.0 Conclusions

A novel delivery system for the established resazurin photocatalyst activity indicator ink (*pai*) system is reported, comprising a central RZ ink film, which uses HPC as the encapsulating polymer, and a PSA ring which helps secure the label in place. The label is about 2 times slower than the more commonly used RZ photocatalytic activity indicator ink. However, it is very stable, easily stored, readily utilised and applicable to vertical as well as horizontal surfaces, making it well suited for use in the field, i.e. for the *in situ* assessment of the activity of photocatalytic active films, i.e. quantitative analysis, or the identification of a photocatalytic surface, qualitative analysis.

5.0 References

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