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Smart, reusable labels for assessing self-cleaning films

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Novel, reversible (reusable) photocatalyst activity indicator labels, which undergo a rapid colour change when in contact with a photocatalytic film via the photoreduction of methylene blue contained within the label's adhesive, are explored as a method for assessing the activity of self-cleaning glass *in-situ* and the laboratory, using digital photography.

Semiconductor photocatalysis (SPC) is the technology that underpins a wide range of emerging commercial 'self-cleaning' materials. In this role, SPC is used to promote a number of different processes, such as removing air- and water-borne pollutants [1], sterilising surfaces [2] and mineralising surface-adsorbed organic compounds [3, 4]. It is mainly this latter feature, coupled with photoinduced superhydrophilicity, which is utilised and highlighted by manufacturers of self-cleaning photocatalytic materials. For clarity, in this paper, all mention of 'self-cleaning' materials is with reference to those based on photocatalysis.

As a result of the rapidly growing market for such materials, the biggest of which is self-cleaning glass, there exists a need for a rapid, facile test to detect the presence, and assess the activity, of the underlying photocatalyst film. Prior to the development of photocatalyst activity indicator inks (*paii*'s) – the first and most popular of which is a resazurin based *paii* [5] - testing methods for assessing the photocatalyst activities of self-cleaning materials were slow, expensive and labour intensive, and unsuitable for use on the production line, or by the end-user, especially in situations that require an *in-situ* assessment. These more laborious testing methods have since been developed into ISO standards [6, 7, 8] that typically take 3-5 hours, utilise expensive analytic equipment, and, usually, require a dedicated technician to run them.

A *paii* comprises an aqueous solution of a water soluble polymer – hydroxyethyl cellulose (HEC) or (poly)vinyl alcohol (PVA) – with an added dye, resazurin (Rz) or methylene blue (MB) usually, which is reduced photocatalytically by the photogenerated conductance band electrons, to produce a striking colour change (blue to pink for Rz and blue to colourless for MB). At the same time, in order to preserve system electroneutrality, a sacrificial electron donor (usually glycerol) reacts irreversibly with the photogenerated holes. A *paii* can be used to assess the activity of self-cleaning materials in typically less than 10 minutes by monitoring the colour change by eye or, more quantitatively, using a UV-vis spectrophotometer [5] or digital photography [9] (discussed in greater detail below).

Figure 1 illustrates the key processes involved in the photocatalytic reduction of a *paii*. Thus, the semiconductor (SC) generates electron-hole pairs when irradiated with ultra-bandgap light, step I. The photogenerated valence band holes then rapidly oxidise the SED, step II_a [10]. This allows the photogenerated conductance band electrons to reduce the brightly-coloured redox dye, D_{ox}, also present in the *paii*, to its very differently coloured reduced form, D_{red}, step II_b. When D_{ox} = MB, as in this work, D_{red} = colourless leuco-methylene blue, LMB, which is O2-sensitive, and so can be slowly re-oxidised back to D_{ox}/MB by ambient O_2, via step III. In contrast, when, more usually, D_{ox} = Rz, D_{red} = pink resorufin, Rf, which is not O_2-sensitive and no re-oxidation/step III is possible.

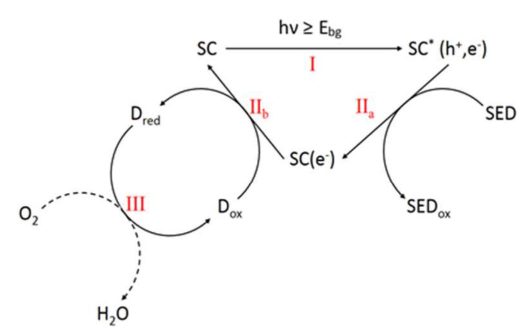

Figure 1. Schematic of the key processes in a *paii*.

A number of different studies have shown that the photocatalysed oxidation of model pollutants, such as stearic acid [11] and NO_x, both by O_2 [12] are correlated to that of the photocatalysed reduction of the dye in a *paii*; i.e. a *paii* provides a useful, quick guide to the photocatalytic activity of the underlying material under test.

In a typical, traditional experiment using a *paii*, briefly, the *paii* is drawn down directly onto the photocatalytic test material using a k-bar 3, so as to give a highly reproducible wet film thickness of 24 µm, which, when dry, typically yields an ink film ca. 2 ± 0.2 µm thick. Once dried, the *paii*-covered semiconductor photocatalyst film, is irradiated with UVA light, and the photocatalyst-driven colour change of the dye in the *paii* is monitored using one of the various methods noted above. Although use of *paii*s is convenient, inexpensive and simple, the current application method is restricted to use with flat, horizontal surfaces and requires a k-bar to ensure deposition of a known, reproducible and constant thickness of ink onto the semiconductor photocatalyst film under test, in order to ensure the generation of comparable kinetic information. In this work we explore the use of *paii*-based **labels**, rather than inks, so as to make the use of *paii* technology even easier and more versatile, since these labels can be applied to both vertical and horizontal surfaces of any size and in any location. This creation of a *paii*-based label is achieved by substituting the HEC used in most previous *paii* formulations, with (poly)vinyl alcohol (PVA), a polymer known for its ability to act as a pressure sensitive adhesive. The redox dye chosen for the *paii* label was methylene blue (MB), a strongly-absorbing blue cationic dye (λ_{max}: 665 nm) that can be reduced photocatalytically to its colourless form, leuco-methylene blue (LMB), and renders the label reusable.

A TiO_2 photocatalyst is able to reduce MB to LMB, and when this process is effected using a MB *paii* **label** on a photocatalyst film, the LMB, although normally O_2 sensitive, is stable for many hours in air due to the very low gas permeability of the *paii* labels' polymer support substrate, polyethylene terephthalate, PET. However, when the label is peeled back, exposing the LMB in the adhesive to air, the original colour of the MB is restored and the label is ready to be used again.

To make a MB *paii* label, the MB *paii* was drawn down onto a PET sheet (thickness: 45 µm) using k-bar 3, giving a wet film thickness of 24 µm, and a subsequent dry film thickness of ca. 2 ± 0.2 µm after 30 minutes of air drying. The *paii* film was then cut into labels, which were placed and stored on silicone release paper. The images in figure 2 show the colour change (blue to colourless) observed typically in the photocatalysed reduction of a MB-based *paii* label on a sample of commercial photocatalytic self-cleaning glass following UVA irradiation.

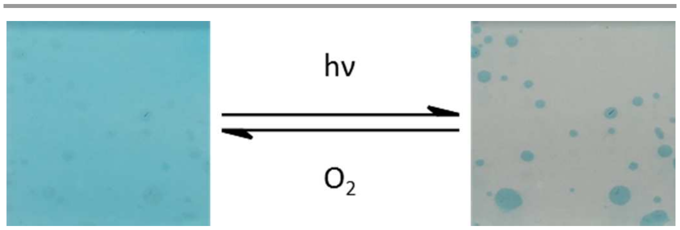

Figure 2. Digital image of a MB *paii* label affixed to a sample of commercial self-cleaning glass, before (i) and after (i) exposure to UVA irradiation (2 mW cm^{-2}, 352 nm, 2 x 8 W BLB lamps).

Longevity studies show that MB *paii* labels prepared in this way retain their adhesive nature, and their photocatalyst detection capacity, for at least > 6 months, although the shelf-life of these labels may actually be much longer than this. The labels can be readily removed and reapplied to most smooth material surfaces without loss of efficacy, i.e. the reversible nature of MB reduction to LMB renders the MB *paii* label reusable.

In a typical experiment, a MB *paii* label was affixed to the glass sample under investigation by applying firm pressure to the PET label back. The *paii* label covered sample was then irradiated with UVA light, and the subsequent SC-photocatalyst driven colour change in the *paii* label adhesive was monitored using both digital photography, with subsequent RGB analysis, and UV-vis spectrophotometry and the results of this are illustrated in figure 3.

RGB analysis of the digital images of a paii as it changed colour, and the acquisition of *ttb(90)* data (the point at which 90% of the zero-order reduction of the *paii* dye is complete) is described in greater detail elsewhere [13], but, briefly, at any irradiation time, t, the value associated with the red (RGB_{Rt}) component of the digital images of the *paii* label is normalised (R_t) with respect to the green (RGB_{Gt}) and blue (RGB_{Bt}) component values, in order to eliminate any light variation between images, i.e.:

$$R_t = \frac{RGB_{Rt}}{(RGB_{Rt} + RGB_{Gt} + RGB_{Bt})} \tag{1}$$

This normalised red value, R_t, was then plotted against irradiation time, t, to yield a growth profile that inversely correlated with the decay profile in absorbance at 665 nm, *△abs(665)*, associated with the photocatalysed bleaching of MB as it is reduced to LMB obtained using UV-vis spectrophotometry, as illustrated in figure 3.

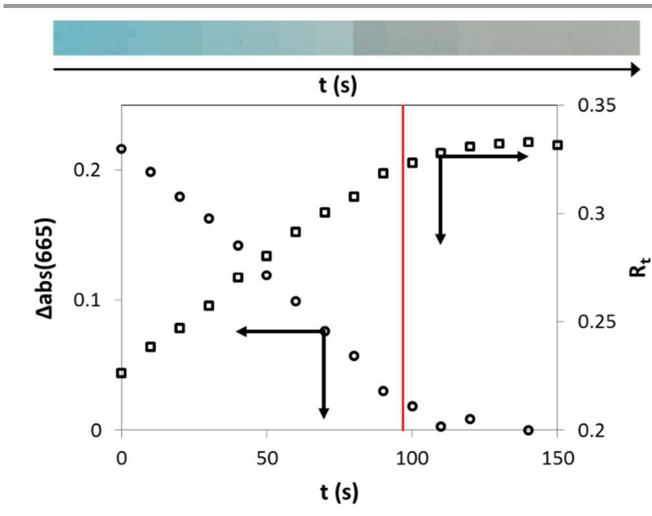

Figure 3. UV-vis spectral decay profile (*△abs(665)*) and digital image RGB growth (R_t) profiles for the reduction of MB *paii* label as a function of UVA irradiation time, t, in contact with a sample of commercial self-cleaning glass, with, at the top, corresponding digital images of the *paii* label (from which the R_t was derived). The *ttb(90)* value, identified by the red line, = 95 s.

The results in figure 3 show that a *paii* label is able to indicate the presence of a photocatalyst film, by changing colour and, in the laboratory, provide a quantitative assessment of the activity of the underlying photocatalytic film.

The dark recovery of the original colour of the label was recorded after the initial reduction of MB to LMB, and subsequent peeling back and exposure to air of the photocatalytically bleached label from the surface under test. After recovery of its initial colour (ca. 15 minutes) upon exposure to air, the label with its coloured adhesive was reapplied to the commercial self-cleaning glass surface, and the UVA light-driven photocatalytic reduction of the MB was carried out again. The reusability of the label was thus demonstrated, in a series of fast photocatalysed reductions, followed by slow dark oxidative recovery, cycles, the results of which are shown in figure 4 below.

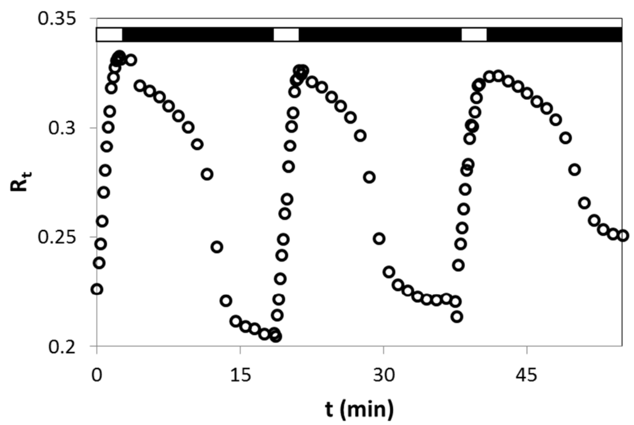

Figure 4. Repeated reduction and recovery of MB *paii*. For recovery, the label is removed from the SC photocatalyst material. The bars across the top correspond to the *paii* label applied to the sample with UVA irradiation (white bar) and dark recovery with the peeled-back adhesive exposed to air (black bar).

The colour-recovery process is much slower (ca. > 5 hours) when the label is left affixed to the test surface, as the PET film acts as an effective oxygen barrier, thereby inhibiting the recovery of LMB. Further work is in progress to determine exactly how many cycles these labels can undergo before they show significant deterioration in performance, most likely not due to the loss of glycerol in the system, which is in vast excess, but to the accumulation of interfering oxidation products such as glyceraldehyde and glyceric acid.

In order to test the ability of the *paii* label to detect and assess the photocatalytic activities of self-cleaning materials *in-situ*, the label was applied to a vertical test sample of commercially-available, self-cleaning glass, stored outside. The reduction of the *paii* label was monitored using digital photography, as in the controlled, lab experiments, but in this exterior work the UVA light source used was sunlight.

Figure 5, below, shows the measured change in R_t activity obtained using digital image analysis of a complete set of digital images derived from the irradiation of a MB *paii* label on self-cleaning glass when used to assess the activity of a sample of self-cleaning glass, both indoors and outside.

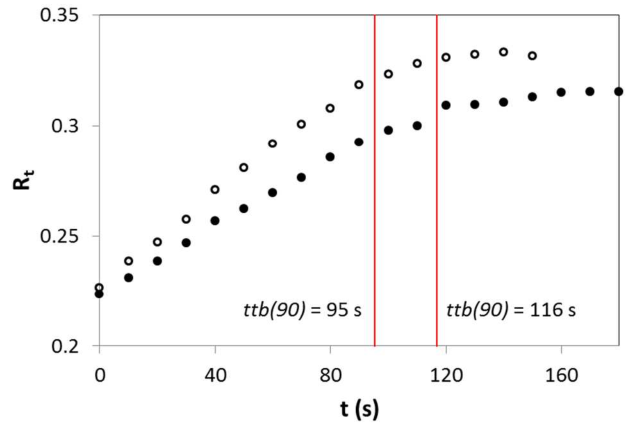

Figure 5. Change in the normalised red value, R_t, as a function of UVA irradiation time, *t*, for an MB *paii* label in contact with commercial self-cleaning glass, for indoor (o) and outdoor (•) irradiations, the *ttb(90)* values are 95 and 116 s, respectively.

Clearly, when sunlight is used as the source of UV, the *paii* labels are more suited for the qualitative, rather than quantitative, assessment of photocatalytic activity. This label technology should be appropriate for testing visible light active photocatalytic films which absorb up to $\lambda \approx 600$ nm, since above this limit MB is increasingly absorbing, with a maximum at 665 nm. This assumes the photogenerated electrons on the visible light absorbing photocatalyst are as, or more, reducing than those produced by TiO_2; $E^o(e^-(\text{anatase } TiO_2)) = -0.2$ V [14].

In summary, the assessment commercial self-cleaning glass *in-situ*, using a smart *paii*-based label, has been demonstrated for the first time. The technique can be used at least qualitatively using solar light irradiation and colour detection by eye or digital camera, for end-user applications, or quantitatively in a lab or industrial environment where the incident UV irradiance can be controlled, using digital photography. The method provides a rapid, effective way to detect the presence, and assess the activity of flat, robust photocatalyst coatings, such as those found on commercial self-cleaning glass. The label's long shelf life makes it suitable for research, and a number of other commercial and industrial applications, such as quality assurance, marketing and *in-situ* assessment of activity. A summary of other high-throughput methods is given elsewhere.[15].

Notes and references

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1 Aguia, C., Angelo, J., Madeira, L. M., Mendes, A., *J. Environ. Managemt*., 2011, **92,** 1724-1732.
2 Noimark, S., Dunnill, C. W., Parkin, I. P., *Adv.Drug Deliv.Rev.,* 2013, **65**, 570-580.
3 Chin, P., Ollis, D. F., *Catal. Today*, 2007, **123**, 177-188.
4 Petrovic, V., Ducman, V., Skapin, S. D., *Ceram. Int.,* 2012, **38**, 1611-1616.

5 Mills, A., Wang, J., Lee, S-K, Simonsen, M., *Chem. Commun.*, 2005, 2721-2723.

6 ISO 10676: 2010, International Organization for Standardization: Geneva, Switzerland, 2010.

7 ISO 22197-1: 2007, International Organization for Standardization: Geneva, Switzerland, 2007.

8 ISO 10678: 2010, International Organization for Standardization: Geneva, Switzerland, 2010.

9 Mills, A., Wells, N., O'Rourke, C., *Catal. Today*, 2014, **230**, 245-249.

10. Tamaki, Y., Furube, A., Murai, M., Hara, K., Katoh, R., Tachiya, M., *J. Am. Chem. Soc.,* 2006, **128**, 416-417.

11 Mills, A., Lepre, A., Elliott, N., Bhopal, S., Parkin, I. P., O'Neill, S. A., *J. Photochem. Photobiol., A*, 2003, **160**, 213-224.

12 Mills, A., O'Rourke, C., Lawrie, K., Elouali, S., *Appl. Mater. Interfaces*, 2014, **6**, 545-552.

13 Mills, A., Hepburn, J., Hazafy, D., O'Rourke, C., Wells, N., Krysa, J., Baudys, M., Zlamal, M., Bartkova, H., Hill, C. E., Winn, K. R., Simonsen, M. E., Soegaard, E. G., Banerjee, S., Fagan, R., Pillai, S. C., *J. Photochem. Photobiol., Chem: A*, 2014, **290**, 63-71.

14 Fujishima, A., Zhang, X., Tryk, D.A. *Surf. Sci. Reports*, 2008, **63**, 515-582.

15 Sun, S., Ding, J. Bao, J., Luo, Z. Gao, C., Comb. Chem. High Thoughput Screen., 2011, **14**, 160-172.