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Novel pH-Based Photocatalyst Activity Indicator Hydrogel

Film (*Hpaii*)

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Abstract

A novel, hydrogel-supported photocatalyst activity indicator, *Hpaii*, is presented, based on an agar gel containing the pH indicator dye propyl red (PR), and the photoacid generator, diphenyliodonium nitrate (DPIN). The latter is broken down when the film is on an active photocatalytic film, and the acid released protonates the PR, turning the gel from a yellow colour to a red. Initially tested on a TiO₂ sol-gel film, the *Hpaii* is shown to be effective in indicating the activity of several different commercially available photocatalytic surfaces, including: glass, tiles and paint. This is the first example of a water-based photocatalyst activity indicator ink based on monitoring a photocatalytic process *via* the change in pH induced in the indicator films, as revealed by the pH-indicator, propyl red.

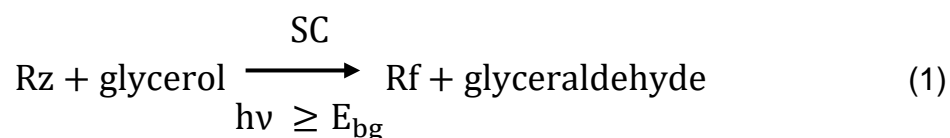
Key words: photocatalyst; indicator; pH; photoacid generator; hydrogel

1.1 Introduction

Photocatalytic self-cleaning surfaces are a growing and significant subject area, associated with an ever-growing number of novel photocatalytic materials for use in a wide number of applications, the most important of which, commercially at least, are: self-cleaning glass, concrete, paving, paint, and tiles [1,2]. According to a 2015 report published by n-tech research, the self-cleaning surface industry is projected to be worth over \$3 billion worldwide by the year 2020, of which \$1.6 billion will be from construction (i.e. self-cleaning glass, concrete etc.) [3]. In turn, the need for effective, rapid and economical techniques for assessing the efficacy of such surfaces is gaining importance, as both manufacturers and consumers seek testing methods which allow an easy comparison between products, not least for quality assurance

purposes. Traditional, solution-based tests (such as the methylene blue (MB) ISO test [4]) are often employed, but are slow. Thus, in recent years, photocatalytic activity indicator inks (i.e. *paii*'s [5-20]), have attracted increasing attention, since they are faster, cheaper and more easily performed than many of the more traditional assessment methods, including the MB ISO test [21-22].

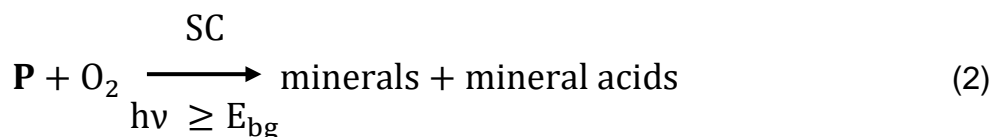
Current *paii* technology is based on the photocatalysed reductive bleaching of an ink which can be delivered *via* a pen [6], aerosol spray [12], or even adhesive label [18], directly onto the photocatalytic surface under test. Monitoring the colour change quantitatively can be effected using UV/Vis absorption or diffuse reflection spectroscopy, or, more easily and often these days, using a mobile phone camera or hand-held scanner – coupled with RGB colour analysis [17,23]. A typical *paii* comprises a readily and irreversibly reduced redox indicator dye, such as resazurin (Rz; blue coloured), dissolved in an aqueous solution with a small amount of polymer binder and a vast excess of a sacrificial electron donor (SED), such as glycerol. When cast onto the surface of the semiconductor photocatalyst under test, SC, and exposed to ultra-bandgap radiation, i.e. $h\nu \geq E_{bg}$, the Rz in the dry, ink-coated surface is reduced, by the photogenerated electrons on the semiconductor, so as to produce a striking colour change (blue to pink for Rz); this reduction reaction is accompanied by the oxidation of the glycerol, by the photogenerated holes. The overall photocatalytic process can be summarised as follows:



where Rf is resorufin (pink coloured). Note that although reaction (1) is a photocatalysed redox reaction, the dye itself is *reduced* which is in contrast to the more traditional methods of assessing photocatalytic activity, such as the MB ISO test mentioned earlier, in which the monitored test reagent, such as MB, is *oxidised* (and usually O₂ reduced). Fortunately, other work on Rz-*paii*s has shown that the initial rate of reaction (1) is directly related to the rate of oxidation of common test 'pollutants' such as MB, NO_x, and stearic acid.

Although the use of *paii*s is proving to be increasingly popular [24-47], it is also understandable that some researchers appear to prefer to stick to the more

traditional, slower, **oxidative**, test methods, such as the MB ISO, since the latter are related to the usual function of self-cleaning photocatalytic materials, namely to facilitate the photocatalysed *oxidation*, by oxygen, of pollutants (**P**) such as: dissolved dyes (e.g. MB), organic pollutant coatings (such as stearic acid) or airborne pollutants (such as VOCs or NOx gases), i.e.:



where the minerals are usually CO₂ and water (for carbon and hydrogen-containing pollutants), although mineral acids are formed if Cl, N, and/or S are present in **P**. Note that the rate of reaction (2) can be affected by environmental parameters such as temperature and humidity [48].

Interestingly, research into semiconductor photocatalysis has made use of the fact that if **P** contains a heteroatom, the rate of reaction (2) can be monitored not only via the disappearance of **P**, but also *via* the concomitant appearance of the acid [49-51]. The monitoring of the latter using a pH electrode is usually much simpler and less expensive than monitoring the disappearance of **P**, which usually requires HPLC if **P** is colourless. Building on from this established method of measuring the rate of reaction (2), this paper describes the first example of a water-based photocatalyst activity indicator ink based on monitoring a photocatalytic process *via* the change in pH induced in the indicator film, as revealed by an embedded pH-indicator. The latter comprises a photoacid generator (PAG) diphenyliodonium nitrate (DPIN), as **P** in reaction (2), a pH-indicator dye, propyl red, PR (pK_a = 5.48), and sufficient agar dissolved in the ink's solvent, water, to form a stable hydrogel film when cast onto a photocatalyst film. A quaternary ammonium ion-base (namely: tetrabutyl ammonium hydroxide) is used to adjust the initial pH of the hydrogel ink so that initially the pH dye is in its deprotonated form.

2 Experimental

2.1 Materials

DPIN was purchased from Alfa Aesar, and all other chemicals were purchased from Sigma-Aldrich. All chemicals were purchased at the highest purity grade available, and were used as delivered. The photocatalyst films used for most of this work were TiO₂ sol-gel films, the preparation details for which are described in detail elsewhere [52]; these films were cast from a sol-gel paste onto borosilicate microscope slides using a doctor blade technique and calcined at 450°C for 1 h. In addition, the hydrogel *paii*, i.e. *Hpaii* was also tested on commercial samples of a: (i) self-cleaning glass, namely, Activ™ from Pilkington Glass-NSG, (ii) a self-cleaning tile, supplied by Deutsche -Steinzeug, and (iii) a photocatalytic paint, supplied by STO Ltd.

2.2 Preparation and application of the *Hpaii*

The *Hpaii* was prepared by adding 30 µL of tetrabutylammonium hydroxide (TBAH; 40% in water) and 4 mg of the pH-indicating dye, PR, to 20 mL of distilled water. The solution was sonicated to ensure the complete dissolution of the various components, then heated to 85°C in a water bath, with constant stirring, at which point 0.2 g of dry agar were added along with 15.6 mg of the PAG, DPIN, and the mixture then left stirring for 1 h to ensure complete mixing. A typical film of the *Hpaii* hydrogel was prepared subsequently by transferring 3 mL of the hot solution, by pipette, into a 25 x 75 mm plastic 'picture frame' placed on top of a PET sheet (45 µm in thickness). This combination was allowed to cool in the dark for 20 min until a semi-rigid hydrogel, ca. 1 mm in thick, was formed, at which point the mould frame was lifted, and the remaining hydrogel on PET film usually covered with a second PET sheet, to stop the hydrogel drying out, and stored in a fridge for use when needed. This process is illustrated in figure 1.

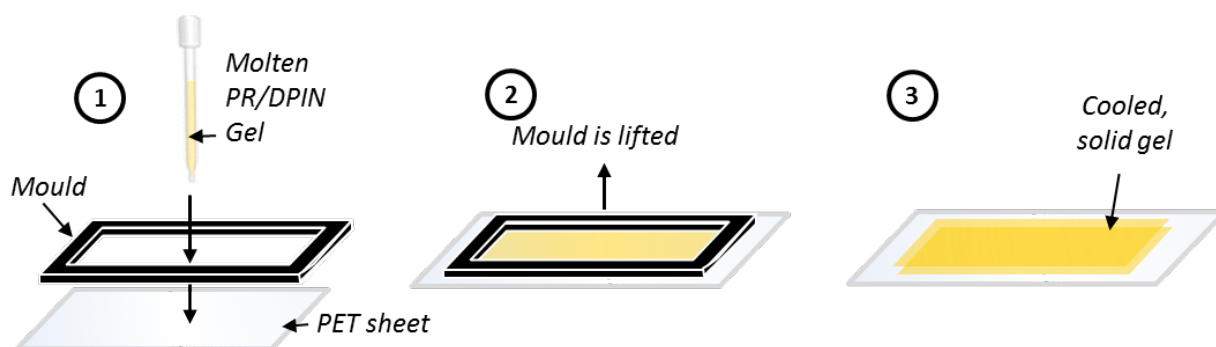


Figure 1: Schematic showing the methodology behind the formation of the moulded PR/DPIN/agar hydrogel indicator on PET film.

When used to assess the activity of a photocatalytic film, a sample of the hydrogel/PET film first had its top PET layer removed and then was placed hydrogel-facing onto of the photocatalyst film. A gentle pressure was applied to ensure a good contact between the two films, before carefully peeling off, from the top of the hydrogel film, the second supporting PET layer, rendering the hydrogel film exposed to air on one side and in contact with the photocatalytic film, on the other. In this form it was ready to respond the photoactivity of the underlying film under test, upon UV irradiation of the system. The steps in this process are illustrated in figure 2.

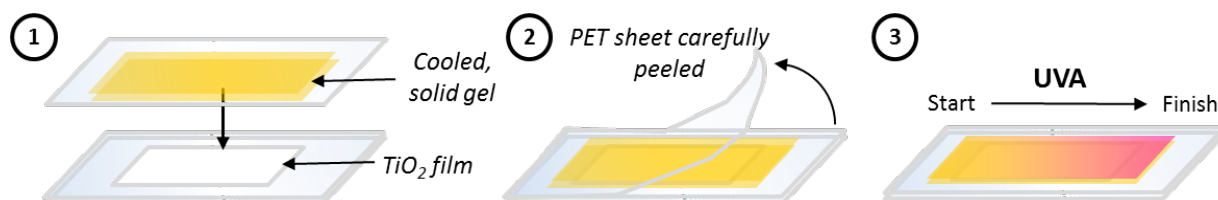


Figure 2: Schematic showing the application of the prepared *Hpaii* hydrogel to a photocatalytic surface in order to assess its photocatalytic activity.

2.3 Methods

All irradiations were carried out using a black light blue lamp (Blak-Ray® model XX-15), with 368 nm blacklight tube bulbs (Eiko) providing an irradiance of 0.5 mW cm⁻² at the active surface. UV-vis measurements were taken using a Cary 60 model UV-vis spectrometer (Agilent), and photographs taken using an EOS 550D model digital camera (Canon).

3 Results and Discussion

3.1 Studies in aqueous solution

In order to demonstrate the principle of the *Hpaii*, *i.e.* the acidification of the solution due to the destruction of a hetero-atom containing organic species, as in reaction (2), 15 mL of a 1.5 mM aqueous solution of the DPIN were placed into a 15 mL borosilicate glass vial, in which was suspended either: (i) a 1 x 5 cm blank glass slide, or (ii) a glass slide with a coating of a TiO₂ sol gel film. In both cases, the slide was then irradiated using a UVA BLB for 180 min (with constant stirring) and the pH of the aqueous solution measured, as a function of UV irradiation time, using an electrochemical pH probe (Cole-Parmer).

The data arising from the measured pH as a function of irradiation time profiles generated as a result of this work were used to generate the [H⁺] vs. time profiles illustrated in figure 3. These results show that, in the absence of the TiO₂ film, no significant change in pH occurs, whereas in its presence, the photocatalyst-induced acidification of the aqueous solution was striking (overall change in pH = -2.6 over the course of a 3 h irradiation).

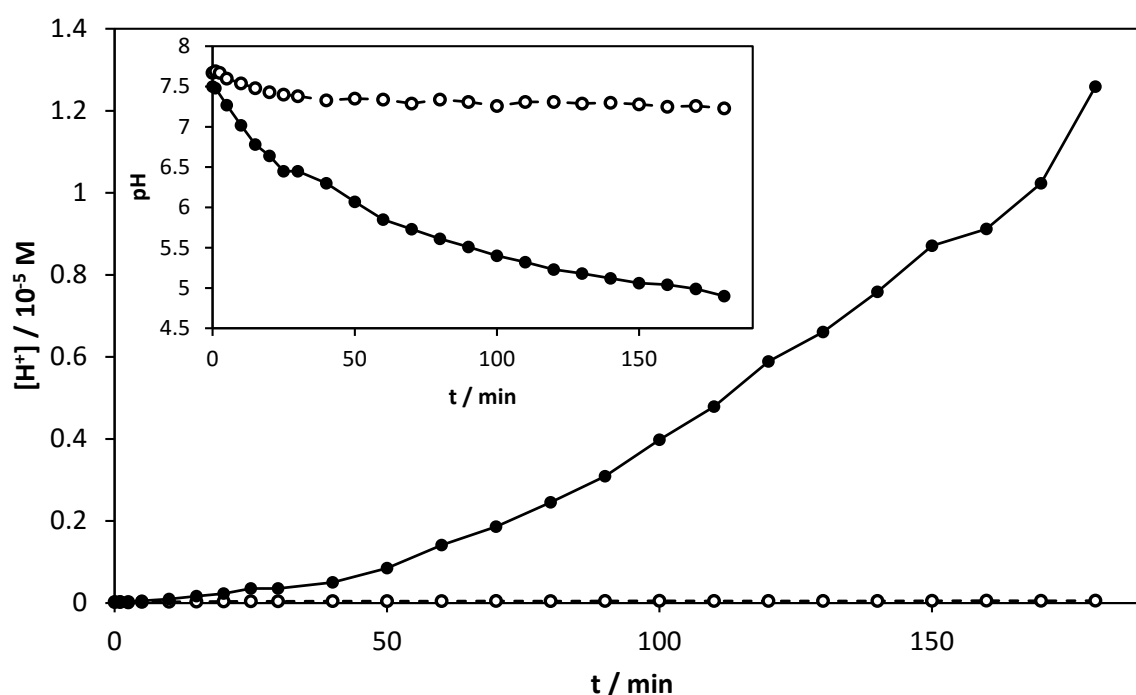
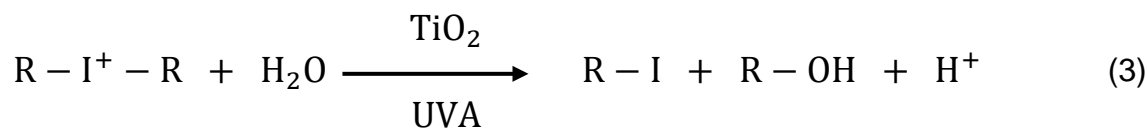


Figure 3: The change in [H⁺] of a 1.5 x 10⁻³ M solution of DPIN in water over time, as measured by an electrochemical pH probe, when irradiated in the presence (solid line, filled circles) and absence (broken line, open circles) of a TiO₂ sol-gel film and irradiated by a 368 nm black light bulb. The insert diagram shows the change in measured pH of the same solution under the same conditions.

The photocatalytic process responsible for the acidification of the solution is most likely the photo-sensitised hydrolysis of the DPIN, i.e.:



where, R = phenyl group, since this process is similar to that reported for DPIN when the latter is used as a PAG; although, obviously, in the latter case the electronically excited state of the DPIN reacts with water. A possible mechanism for reaction (3) involves the initial generation of an adsorbed OH radical on the surface of the TiO₂, by a photogenerated hole, which then attacks the DPIN to generate R-OH and the R-I+• radical, which is then subsequently reduced by the photogenerated electron.

Following on from the work illustrated in figure 3, the pH electrode was then replaced with the pH indicator dye, Propyl Red (PR; pK_a = 5.48), which is yellow in its deprotonated form (PR⁻; absorbance λ_{max} = 454 nm), and pink/red upon protonation (PRH; λ_{max} = 528 / 554 nm; see figure 4).

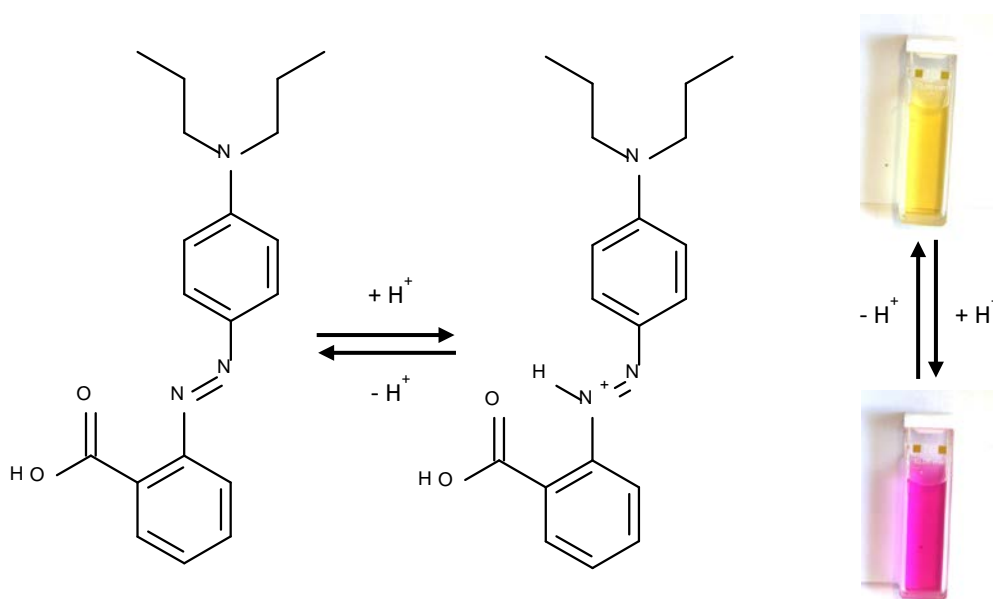


Figure 4: The molecular structure of PR in its deprotonated (left) and protonated (right) forms, i.e. PR⁻ and PRH, respectively. Photographs of the dye in alkaline (yellow) and in acidic solution (red/pink) are also displayed.

Not surprisingly, given the results illustrated in figure 3, when PR (ca. 0.75 mM) was added to the same DPIN solution as used before, the solution instantly coloured yellow, due to the PR adopting its deprotonated, PR⁻ form, thereby reflecting the initial pH of the non-irradiated aqueous solution (i.e. ca. pH 7.5, see figure 3). The

yellow colour of the solution and the initial pH of the solution remained unchanged upon UV irradiation when just a blank slide was present in the solution. However, under otherwise identical conditions, but in the presence of a TiO₂ sol-gel film, upon UV irradiation the solution turned increasingly pink with UVA irradiation time, due to the photocatalysed destruction of the PAG and concomitant acidification of the solution *via* reaction (3), and concomitant generation of PRH. The colour of the solution was monitored using digital photography (as well as UV/Vis absorption spectroscopy) and the photographic images of the reaction solution as a function of irradiation time – in the absence and presence of the TiO₂ film – are illustrated in figure 5.

As noted above, also in this work, the absorbance of the solution was measured at 554 nm (i.e. λ_{\max} for PRH) as a function of irradiation time, and the results are illustrated in figure 5(b), revealing, as expected, that the acid generated as a result of reaction (3) is able to protonate the pH indicating dye, PR to PRH, over the same timescale as the most significant recorded change in pH, as noted above by the pH data in figure 3. These findings confirm the feasibility of monitoring the photocatalytic destruction of a heteroatom containing pollutant, DPIN *via* the associated change in pH, measured using a pH electrode or a pH indicating dye.

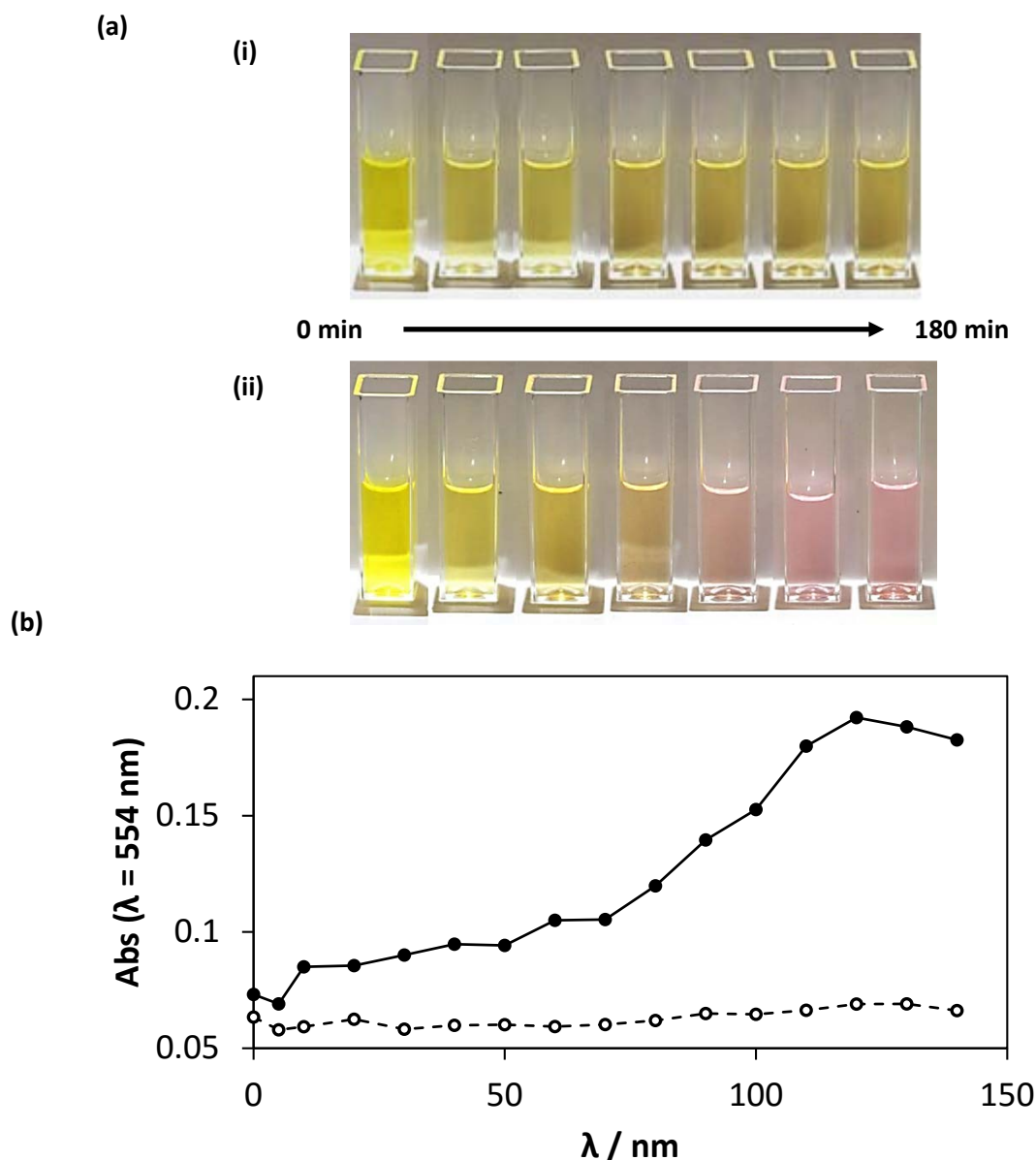


Figure 5: (a) Photographs taken of samples of the reaction solution used to probe reaction (3) for a solution containing: (i) a plain, non-coated glass slide or (ii) a TiO₂ sol-gel film. In both cases, the samples were taken at the following irradiation times (left to right: 0, 30, 60, 90, 120, 150 and 180 min). (b) The measured absorbance (at 554 nm) of the 1.5×10^{-3} M solution of DPIN containing the dye, PR, in the presence (solid line, filled circles) and absence (broken line, open circles) of a TiO₂ sol-gel film, as a function of UVA irradiation (368 nm) time; all other conditions as per figure 3.

3.2 Studies using the PR-*Hpail*

Given the central role of pH in the proposed *Hpail* technology, it is essential to use a polymer encapsulating medium which retains a significant level of water when stored under ambient conditions, and this can best be achieved using a hydrogel encapsulation medium, like agar. When the agar/PR-based *Hpail* hydrogel film was

applied to a blank microscope slide and irradiated with UV light, the initially yellow colour film did not change in colour, as illustrated by the photos in figure 6(a_i). In contrast, when it was placed on top of a TiO₂ –sol-gel film and irradiated with UVA light, the PR *Hpaii* changed colour rapidly from yellow to orange-red, as illustrated by the photos in figure 6(a_{ii}).

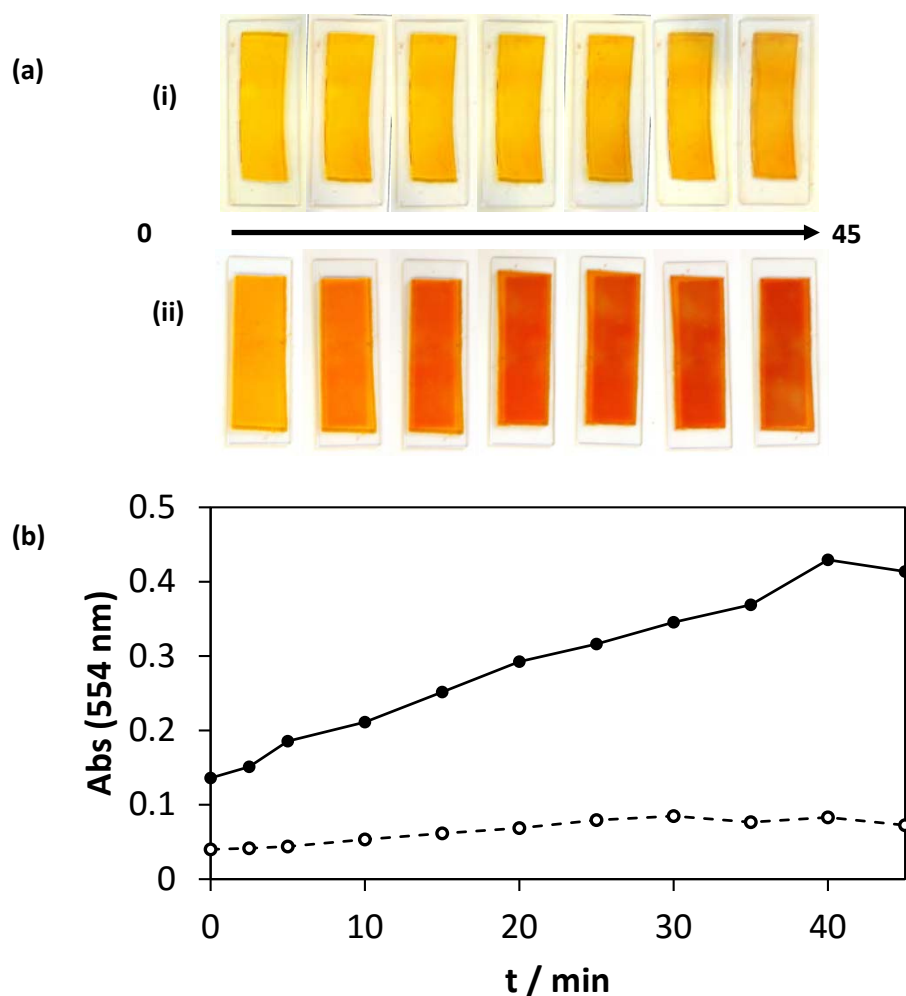


Figure 6: (a) Photographs recorded as a function of UV irradiation time of the PR-*Hpaii* film covered on: (i) a plain glass substrate or (ii) a TiO₂ coated glass substrate; (b) measured absorbance (at 554 nm) of the same systems in (a), revealing a change in absorbance with irradiation time only for the PR-*Hpaii* film on a TiO₂-coated glass slide (solid line, filled circles) and on plain glass (broken line, open circles).

In both cases, the changes in absorbances of the two films were also monitored as a function of irradiation time, and the results are illustrated in figure 6(b); the data show that the PR pH indicator dye, encapsulated in the agar/PR-based *Hpaii* film, is able to respond to the acid generated *via* the photocatalysed hydrolysis of the DPIN by the underlying sol-gel TiO₂ film, i.e. reaction (3). Thus, UV/Vis spectroscopy

confirmed that the orange colouration illustrated in figure 6(a) is due to the protonated form of the pH-indicating dye in the *Hpaii*, PR.

Further work showed that the agar/PR-based *Hpaii* film produced the same colour change, but at different rates, when deposited on samples of different commercial photocatalytic materials, such as self-cleaning glass, paint and tiles, as illustrated by the photographic images in figure 7. From this data, the apparent order of photocatalytic activities of the various different materials tested is: sol-gel > paint > tile >> glass, with plain glass exhibiting no photocatalytic activity, as expected. The same order of activities has been observed using a conventional Rz *paii* [38]. The apparent low activity of self-cleaning glass is due to the very thin (ca. 15 nm thick) coating of TiO₂, which is necessary since anything much thicker would render it too reflective for use for most windows. The sol-gel film is the most active of all the films tested as it is: thick, i.e. ca. 2 μm, nanocrystalline, mesoporous and comprised of pure anatase titania, all of which favour high activity. In contrast, the commercial samples have a thinner, and usually less pure layer of anatase titania. For example the paint contains an organic binder and the commercial tile, contains a high level of rutile and a high level of silica [53].

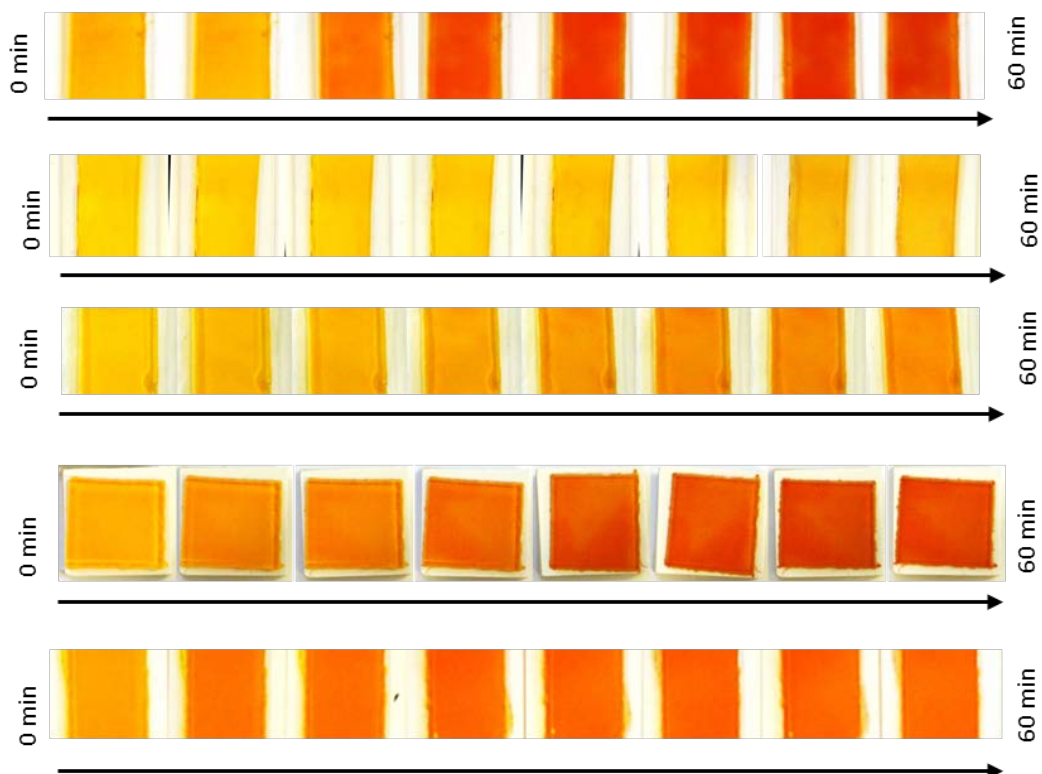


Figure 7: Photographs taken of the PR/DPIN/agar *Hpaii* indicator mounted on various surfaces (from top to bottom: TiO₂ sol-gel; plain glass; commercial self-cleaning glass; commercial self-cleaning tile; commercial self-cleaning paint, The photographs were recorded at regular intervals over the course of 60 min under UV irradiation; UV irradiance = 0.5 mW cm⁻²).

1.4 Conclusions

A novel approach to the assessment of photocatalytically active surfaces has been developed based on a self-indicating acid-generating hydrogel ink film. The latter comprises: a pH indicator, propyl red, PR, a photoacid generator, diphenyliodonium nitrate, DPIN, and a hydrogel encapsulating medium (agar). When cast onto a photocatalytic material, such as a TiO₂-based: sol gel film, UV activation of the photocatalyst induces the destruction of the PAG, with the concomitant acidification of the indicator film, and associated change in colour of the pH indicator dye (yellow to red). This PR photocatalyst indicator ink, which works by responding to one of the products of a photocatalysed hydrolysis, in this case acid, is a *Hpaii*, and differs from previous *paiis* which relied upon a colour change due to the photocatalysed *reduction* of a dye in the indicator film. It is the first of its kind and has advantages over the more traditional methods of assessing photocatalytic activity, such as the MB test, in that it is easily made, handled, employed and relatively fast (30-50 min on

most commercial samples). The *Hpaii* appears very stable (>5 weeks) when stored in a refrigerator in an airtight container, to prevent the hydrogel film from drying out. The inherent tackiness of the *Hpaii* allows it to be applied to different sized and shaped surfaces.

References

- [1] C. Han, J. Andersen, S.C. Pillai, R. Fagan, P. Falaras, J.A. Byrne, P.S.M. Dunlop, H. Choi, W. Jiang, K. O'Shea, D. D. Dionysiou, *Green Nanotechnology: Development of Nanomaterials for Environmental and Energy Applications*, in N. Shamim, V.K. Sharma (Eds.), *Sustainable Nanotechnology and the Environment: Advances and Achievements*, ACS, Washington D.C., 2013, 201-229.
- [2] D. Synnott, N. Nolan, D. Ryan, J. Colreavy, S.C. Pillai, *Self-cleaning tiles and glasses for eco-efficient buildings*, in F. Pacheco-Torgal, M.V. Diamanti, A. Nazari, C. Goran-Granqvist (Eds.), *Nanotechnology in Eco-Efficient Construction*, Woodhead Publishing Ltd., Derbyshire, 2013, 327-342.
- [3] R. Tiwari, Self-Cleaning Surfaces Market and Coatings Segments of Self-Cleaning Materials Forecast to 2022 in new Research Report, RnR Market Research, PR Newswire website, 2015. Accessed Online June 2017: http://ntechresearch.com/market_reports/markets-for-self-cleaning-coating-and-surfaces-2015-to-2022
- [4] ISO 10678: 2010, 'Fine ceramics, advanced technical ceramics – determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue', ISO, Geneva, 2010.
- [5] A. Mills, J. Wang, S-K. Lee and M. Simonsen, An intelligence ink for photocatalytic films, *Chem. Commun.*, 2005, 2721-2723.
- [6] A. Mills, J. Wang and M. McGrady, Method of rapid assessment of photocatalytic activities of self-cleaning films, *J. Phys. Chem. B.*, 2006, 110, 18324-18331.
- [7] A. Mills and M. McFarlane, Current and possible future methods of assessing the activities of photocatalyst films, *Catalysis Today*, 2007, 129, 22-28.
- [8] A. Mills and M. McGrady, A study of new photocatalyst indicator inks, *J. Photochem. Photobiol. A*, 2008, 193, 228-236.
- [9] A. Mills, M. McGrady, J. Wang, J. Hepburn, A Rapid Method of Assessing the Photocatalytic Activity of Thin TiO₂ Films Using an Ink Based on the Redox Dye 2,6-Dichloroindophenol, *Int. J. Photoenergy*, 2008, 2008-2013.
- [10] J. Zita, J. Krysa, A. Mills, Correlation of oxidative and reductive dye

- bleaching on TiO₂ photocatalyst films, *J. Photochem. Photobiol. A*, 2009, 203, 119–124.
- [11] A. Mills, J. Hepburn and M. McFarlane, A Novel, Fast-Responding, Indicator Ink for Thin Film Photocatalytic Surfaces, *ACS Applied Mater. Interf.*, 2009, 1, 1163–1165.
- [12] A. Kafizas, A. Mills and I.P. Parkin, A comprehensive aerosol spray method for the rapid photocatalytic grid area analysis of semiconductor photocatalyst thin films, *Anal. Chim. Acta*, 2010, 663, 69-76.
- [13] A. Mills, A. Cusick and J. Hepburn, The kinetics of semiconductor photocatalysis in activity-indicator films, *J. Adv. Ox. Tech.*, 2009, 12, 152-157.
- [14] A. Mills, C. O'Rourke, K. Lawrie, and S. Elouali, Assessment of the Activity of Photocatalytic Paint Using a Simple Smart Ink Designed for High Activity Surfaces, *ACS Appl. Mater. Interfaces*, 2014, 6, 545–552.
- [15] A. Mills, N. Wells, C. O'Rourke, Correlation between Δ Abs, Δ RGB (red) and stearic acid destruction rates using commercial self-cleaning glass as the photocatalyst, *Catalysis Today*, 2014, 230, 245-249.
- [16] A. Mills, C. O'Rourke, N. Wells, A smart ink for the assessment of low activity photocatalytic surfaces, *Analyst*, 2014, 139, 5409-5414.
- [17] A. Mills, N. Wells, Indoor and outdoor monitoring of photocatalytic activity using a mobile phone app. and a photocatalytic activity indicator ink (paii), *J. Photochem. Photobiol. A*, 2015, 298, 64-67.
- [18] A. Mills, N. Wells, Smart, Reusable labels for assessing self-cleaning films, *Chem. Commun.*, 2015, 51, 4161-4163
- [19] A. Mills, N. Wells, C. O'Rourke, Correlation between the photocatalysed oxidation of methylene blue in solution and the reduction of resazurin in a photocatalyst activity indicator ink (Rz Paii), *J. Photochem. Photobiol. A.*, 2016, 330, 86-89
- [20] A. Mills, D. Yusufu, N. Wells, C. O'Rourke, Assessment of activity of 'transparent and clear' and 'opaque and highly coloured' photocatalytic samples using a fluorescent photocatalytic activity indicator ink, *FPaii, J. Photochem. Photobiol. A.*, 2016, 330, 90-94.
- [21] A. Mills, C. Hill, P.K.J. Robertson, Overview of the current ISO tests for photocatalytic materials, *J. Photochem. Photobiol. A.*, 2012, 237, 7-23.
- [22] A. Mills, J. Hepburn, D. Hazafy, C. O'Rourke, N. Wells, J. Krysa, M. Baudys,

- M. Zlamal, H. Bartkova, C. E. Hill, K. R. Winn, M. E. Simonsen, E. G. Søgaard, S. Banerjee, R. Fagane, S. C. Pillai, Photocatalytic activity indicator inks for probing a wide range of surfaces, *J. Photochem. Photobiol. A*, 2014, 290, 63-71.
- [23] ISO NP21066 (under development as of April 2017): 'Fine ceramics (advanced ceramics, advanced technical ceramics) – Qualitative and semi-quantitative assessment of the photocatalytic activities of surfaces by the reduction of resazurin in a deposited ink film.', ISO, 2017.
- [24] S. In, A.H. Kean, A. Orlov, M. S. Tikhov, R.M. Lambers, A versatile new method for synthesis and deposition of doped, visible light-activated TiO₂ thin films, *Energy Environ. Sci.*, 2009, 2, 1277-1279.
- [25] A. Kafizas, D. Adriaens, A. Mills and I.P. Parkin, Simple method for the rapid simultaneous screening of photocatalytic activity over multiple positions of self-cleaning films, *Phys Chem. Chem. Phys.*, 2009, 11, 8367-8375.
- [26] C.W. Dunnill, Z. Aikin, J. Pratten, M. Wilson, I. Parkin, N-doped titania thin films, prepared by atmospheric pressure chemical vapour deposition: Enhanced visible light photocatalytic activity and anti-microbial effects, *ECS Trans.*, 2009, 25, 65-72.
- [27] I. Parkin, A. Kafizas, C.W. Dunnill, G. Hyett, Combinatorial CVD: New Oxynitride Photocatalysts, *ECS Trans.*, 2009, 25, 1239-1250.
- [28] A. Kafizas, C. Crick, I. P. Parkin, The combinatorial atmospheric pressure chemical vapour deposition (cAPCVD) of a grading substitutional/interstitial N-doped anatase TiO₂ thin-film; UVA and visible light photocatalytic activities, *J. Photochem. Photobiol. A*, 2010, 216, 156-166.
- [29] J. Zita, J. Krýsa, U. Černigoj, U. Lavrenčič-Štangar, J. Jirkovský, R. Rathouský, Photocatalytic properties of different TiO₂ thin films of various porosity and titania loading, *Catalysis Today*, 2011, 161, 29-34.
- [30] E. L. Cuellar, A. Martinez-de la Cruz, K. H. L. Rodrigues, U. O. Mendez, Preparation of γ -Bi₂MoO₆ thin films by thermal evaporation deposition and characterization for photocatalytic applications, *Catalysis Today*, 2011, 166, 140-145.
- [31] S. Kundu A. Kafizas, G. Hyett, A. Mills, J.A. Darr, I.P. Parkin, An investigation into the effect of thickness of titanium dioxide and gold–silver nanoparticle titanium dioxide composite thin-films on photocatalytic activity

- and photo-induced oxygen production in a sacrificial system, *J. Mater. Chem.*, 21, 6854-6863.
- [32] C. Edusi, G. Hyett, G. Sankar, I.P. Parkin, Aerosol-Assisted CVD of Titanium Dioxide Thin Films from Methanolic Solutions of Titanium Tetraisopropoxide; Substrate and Aerosol-Selective Deposition of Rutile or Anatase, *Chem. Vap. Depos.*, 2011, 17, 30-36.
- [33] S. Ponja, S. Sathasivam, N. Chadwick, A. Kafizas, S.M. Bawaked, A.Y. Obaid, S.A.Thabaiti, S.N. Basahel, I.P. Parkin, C.J. Carmalt, *J. Mater. Chem. A*, 2013, 1, 6271-6278.
- [34] V. Diesen, M. Jonsson, I.P. Parkin, *Chem. Vap. Depos.*, 2013, 19, 355-362.
- [35] N. Farahani, P.J. Kelly, G. West, C. Hill, V. Vishnyakov, *Coatings*, 2013, 3, 177-193
- [36] L. Romero, A.B. Jorge-Sobrido, P.F. McMillian, R. Binions, *Thin Sol. Films*, 2015, 584, 320-325.
- [37] A. Anderson, R. Binions, The effect of Brij® surfactants in sol–gel processing for the production of TiO₂ thin films, *Polyhedron*, 2015, 85, 83-92.
- [38] A. Mills, J. Hepburn, D. Hazafy, C. O'Rourke, J. Krysa, M. Baudys, M. Zlamal, H. Bartkova, C. E. Hill, K. R. Winn, M. E. Simonsen, E. G. Søgaaard, S. C. Pillai, N. S. Leyland, R. Fagan, F. Neumann, C. Lampe, T. Graumann, *J. Photochem. Photobiol. A*, 2013, 272, 18–20.
- [39] A. Kafizas, N. Noor, P. Carmichael, D.O. Scanlon, C.J. Carmalt, I.P. Parkin, Combinatorial Atmospheric Pressure Chemical Vapor Deposition of F:TiO₂; the Relationship between Photocatalysis and Transparent Conducting Oxide Properties, *Adv. Funct. Mater.*, 2014, 24, 1758-1771,
- [40] D.S. Bhachu, S. Sathasivam, C.J. Carmalt, I.P. Parkin, PbO-modified TiO₂ thin films: a route to visible light photocatalysts, *Langmuir*, 2014, 30, 624.
- [41] S. Sathasivam, D.S. Bhachu, Y. Lu, S. Bawaked, A.Y. Obaid, S. Al-Thabaiti, S.N. Basahel, C.J. Carmalt, I.P. Parkin, Highly Photocatalytically Active Iron (III) Titanium Oxide Thin films via Aerosol-Assisted CVD., *Chem. Vap. Deposit.*, 2015, 21, 21-25.
- [42] X. Wang, A. Kafizas, X. Li, S.J.A. Moniz, P.J.T. Reardon, J. Tang, I.P. Parkin, J.R. Durrant, Transient absorption spectroscopy of anatase and rutile: the impact of morphology and phase on photocatalytic activity, *J. Phys.*

- Chem. C*, 2015, 119, 10439–10447.
- [43] E. Jimenez-Relinque, M. Castellote, Quantification of hydroxyl radicals on cementitious materials by fluorescence spectrophotometry as a method to assess the photocatalytic activity, *Cem. Concr. Res.*, 2015, 74, 108-115.
- [44] A.L. Anderson, R. Binions, A preferential precursor for photocatalytically active titanium dioxide thin films: Titanium bis-ammonium lactato dihydroxide as an alternative to titanium tetra iso-propoxide, *Polyhedron*, 2016, 118, 81-90.
- [45] C. Tupberg, N. Chandet, K. Wattanavichan, C. Randorn, Catalytic and antibacterial activities of novel colored zinc borophosphate glasses, *RSC Adv.*, 2016, 6, 79602-79611.
- [46] N. W. Portal, P. Rogers, N. Silva, K. Malaga, 'Photocatalytic activation of textile-reinforced concrete façade panels', H-House Project website, 2016. http://www.h-house-project.eu/images/04_Documents/02_Publications/WSED_2016_Photocatalytic_activation.pdf; accessed online June 2017.
- [47] M. Baudys, J. Krysa, A. Mills, Smart inks as photocatalytic activity indicators of self-cleaning paints, *Catalysis Today*, 2017, 280, 8-13.
- [48] E. M. Simonsen, Z. Li, E. G. Søgaard, Influence of the OH groups on the photocatalytic activity and photoinduced hydrophilicity of microwave assisted sol-gel TiO₂ film, *Appld.. Surf. Sci.*, 2009, 255, 8054-8062.
- [49] H. Al-Ekabi, N. Serpone, Kinetic Studies In Heterogeneous Photocatalysis. 1. Photocatalytic Degradation of Chlorinated Phenols in Aerated Aqueous Solutions over TiO₂, Supported on a Glass Matrix, , *J. Phys. Chem.*, 1988, 92, 5726-5731.
- [50] J. Theurich, M. Lindner, D.W. Bahnemann, Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: a kinetic and mechanistic study, *Langmuir*, 1996, 12, 6368-6376.
- [51] J. Giménez, D. Curcó, M.A. Queral, Photocatalytic treatment of phenol and 2, 4-dichlorophenol in a solar plant in the way to scaling-up. *Catalysis Today*, 1999, 54, 229-243.
- [52] A. Mills, N. Elliot, G. Hill, D. Fallis, J.R. Durrant, R.L. Willis, Preparation and characterisation of novel thick sol-gel titania film photocatalysts, *Photochem. Photobiol. Sci*, 2003, 2, 591-596.

[53] *Introduction to Photocatalysis*, by Y. Nosaka and A. Nosaka, RSC, London, 2016.