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Correlation between the photocatalysed oxidation of methylene blue in solution and the reduction of resazurin in a photocatalyst activity indicator ink (Rz *Paii*)

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Abstract

The initial rate of the photocatalysed oxidation of methylene blue, MB, by dissolved oxygen in solution, $r_i(MB)$, is measured for a series of titania on glass samples exhibiting a wide range of activities. The samples used include two different types of commercial self-cleaning glass and a lab-made sol-gel titania film. The activities of these samples are also assessed using a resazurin-based photocatalyst activity indicator ink, i.e. Rz *paii*, for which the initial rates of the photocatalysed reduction of Rz were measured, $r_i(Rz)$. A plot of $r_i(MB)$ vs. $r_i(Rz)$ reveals a good straight line, thereby demonstrating a linear correlation (for TiO₂ films on glass at least) between the slow (usually hours) photocatalysed oxidation of organic materials, such as MB, and the fast (typically minutes) photocatalysed irreversible reduction of a dye, like Rz, in a *paii*. The possible use of *paii* technology for assessing, in a simple, quick and inexpensive manner, photocatalytic films both in the laboratory and *in situ* is discussed briefly.

Key words: methylene blue; oxidation; resazurin; reduction; inks; correlation

1. Introduction

Semiconductor photocatalysis is a well-established and growing area of research, innovation and commercialisation [1]; major examples of the latter include most 'self-cleaning' architectural materials, such as: glass, tiles, concrete, paint and fabrics [1,2]. In almost all such commercial products the active ingredient is TiO₂, which absorbs UV light, from a solar and/or artificial light source, to produce electron-hole pairs, which can recombine, in the bulk of the semiconductor or, at its surface, recombine or *react* with surface-adsorbed species [3]. Most commercial photocatalytic materials use the TiO₂ to mediate the photo-oxidation of adsorbed, usually organic, species to their mineral form, with the concomitant reduction of adsorbed O₂ to water, i.e.

where mineral acids are generated if the organic species has one or more heteroatoms, such as S, Cl or N, in its structure [1]. The ability of TiO₂ to photocatalyse reaction (1) is the primary photocatalytic property responsible for the promoted ability of commercial photocatalytic products to maintain a clean, sterile, hydrophilic surface [1,2]. Other work shows that TiO₂ is also able to mediate the photo-oxidation of NO_x, i.e. NO and NO₂, to nitrate [4].

In the ever-expanding field of photocatalysis it is essential to be able to assess and compare the activities of new and existing commercial and research photocatalytic materials. As a consequence, over the years a number of different tests for this purpose have been developed into ISO standards [5]. These tests include: the photo-oxidative bleaching of methylene blue (MB) in aqueous solution, i.e. reaction (1), with organic = MB, [6] and the photo-oxidation of NO_x gases [7]. However, it is worthwhile noting that these tests take a long time to run (3-5 hours) and require the use of expensive analytical equipment [5].

Recent work within the group has focused on the development of a rapid, simple method for assessing the activities of photocatalytic films, involving the use of a photocatalyst activity indicator ink (*paii*) [8-10]. The *paii*, when coated onto the photocatalyst film under test and irradiated with UV light, produces a striking colour change within a few minutes, at a rate which provides a measure of the activity of the underlying photocatalytic film [8-10]. The most used and effective of the *paiis* developed to date, contains the redox dye, Resazurin (Rz) which is blue, and readily and irreversibly reduced by the photogenerated electrons on the TiO₂, to resorufin (Rf), which is pink [9,10]. This reduction reaction is balanced by the concomitant rapid, irreversible reaction of the photogenerated holes with a sacrificial electron donor, glycerol, which is also present in the ink film. As a consequence, the overall photocatalytic process can be summarised as follows:

Since both reactions (1) and (2) are semiconductor photocatalysed redox reactions, it might be expected that an effective photocatalyst for reaction (1) will also be effective for reaction (2), i.e. that the measured rates for the two very different processes will be related directly to one another. However, such a direct correlation cannot be assumed and needs to be demonstrated. Previous work established the existence of such a correlation in the rate of reduction of Rz in an Rz *paii*, via reaction (2) with that of oxidation of a thin solid organic film (stearic acid) via reaction (1), as mediated by a TiO₂ photocatalytic film [9,11]. Clearly, more and different demonstrations of such direct correlations in rates are needed before it can be reasonably assumed that the Rz *paii* technology usually provides a quick route to assessing the activity of a photocatalyst towards the photo-oxidative mineralisation of organics. This short paper seeks to provide more of this evidence via a study of the correlation in rate of reaction (2) with that of reaction (1), where the organic is MB. Two schematic diagrams of the main electron transfer reactions associated with these two very different processes are illustrated in figure 1.

Figure 1 – Reaction scheme for the semiconductor photocatalyst driven processes: (a) reduction of resazurin to resorufin, and concomitant oxidation of a sacrificial electron donor (SED, usually glycerol) present and (b) the oxidative destruction of methylene blue to yield, eventually, CO₂, H₂O and mineral acids, by ambient oxygen. The many lines in the latter indicate that many electrons, the complete mineralisation of MB is a 102 electron process [12], need to be transferred to effect the mineralisation process, whereas the reduction of Rz is a 2e⁻, 2H⁺ process.

2. Experimental

Unless otherwise stated, all materials were purchased from Sigma Aldrich and used as received. All UV-vis spectra were recorded using an Agilent Technologies Cary 60 UV/vis Spectrophotometer. All irradiations were carried out using UVA light, from 2 x 15 W broadband BLB tubes, with a principal wavelength of 352 nm, and an irradiance of 2 mW cm⁻².

2.1 Preparation of commercial self-cleaning glass samples with different activities

The different activities of commercial self-cleaning glass samples, BioClean™ (manufacturer: Saint-Gobain) and Activ™ (manufacturer: Pilkington), were both altered by heat treating the samples at 500°C in a furnace for different times. Previous work had established that at this temperature, the longer the heating time employed, the lower the activity of the thin TiO₂ photocatalytic film, since the heat-treatment process promotes the diffusion of Na⁺ ions from the underlying float glass, through the protective (usually SiC) barrier layer, to the surface titania layer [13]. In this work, it was found that Activ™ samples required a markedly longer period of heat treatment (days vs. only hours for BioClean™) in order to achieve a significant loss in activity. Thus, typical heat treatment times used here were: 0, 6 and 24 hours for BioClean™ and 0, 5 and 20 days for Activ™ samples, so as to produce a number of different glass samples exhibiting a wide range of activities, in which the TiO₂ remains in its anatase form. As with most photocatalytic tests, it is very likely that the kinetics of photocatalysis will be a function of surface morphology, and as a consequence, it was important that in this work the samples tested were all similar in this respect, appearing under SEM analysis to have a cobblestone-like surface, with particles typically 30 nm in diameter [14]. Under SEM analysis, there was no change in the appearance of the film (ink or TiO₂) after UV irradiation, details of the latter have been reported previously [14]. Another obvious route – not used here - to create TiO₂ on glass samples of different activity but of similar morphology, is to alter the thickness of the TiO₂ film, as this has been shown, for CVD films at least, to have a direct effect on the photocatalytic activity via the fraction of incident UV light absorbed by the film [15].

2.2 Sol-Gel film preparation

In order to ensure that the correlation was appropriate for both commercial (usually CVD produced) samples and lab-based, in this case sol-gel, titania films, a TiO₂ sol-gel film was also tested in this study. The latter was prepared using a previously published method [16] in which briefly, 20 mL of titanium (IV) isopropoxide (Ti(OPri)₄) were added to a 100 mL round bottomed flask containing 4.65 g of glacial acetic acid using a syringe. The resulting Ti(OPri)₄ solution was then transferred by syringe to a 250 mL conical flask containing 120 mL of distilled water and 1.08 g of concentrated nitric acid, and stirred at 80°C for 8 h, before being filtered through a 0.45 µm syringe filter to remove any aggregated oxide. The filtrate was then transferred to an acid digestion bomb and heated at 220°C for 12 h. After cooling, the resulting paste was subjected to ultrasound to disperse the particles, and then concentrated, via rotary evaporation, to form a thick white paste with a 10% wt. loading of TiO₂. Polyethylene glycol (PEG), 5 wt%, was mixed into the paste to provide greater stability and the product was then stored at ~5°C. The final sol-gel film was prepared by diluting the paste by 100 fold using ethanol as the diluent, to produce a much less viscous solution that was then applied to a microscope slide using a doctor blade technique to create the TiO₂ sol-gel film. In the latter case, two parallel lines of adhesive tape, 2 cm apart were laid down onto the slide and the

diluted sol-gel paste drawn down between them, so as to generate a 48 μm wet film of the sol-gel. This film was then annealed at 450°C for 30 minutes to yield a robust, clear film of titania, measured to be ca. 200 ± 20 nm thick using SEM. The annealed TiO_2 films are in their anatase crystal form [16].

2.3 Reduction of resazurin *paii*

The preparation of the resazurin *paii* is described in detail elsewhere [17]. Briefly, 10 mg of resazurin sodium salt and 1 g of glycerol were added to 10 mL of a 1.5 wt.% solution of hydroxyethyl cellulose. The solution was stirred overnight to ensure complete dissolution of the dye. When not in use, the ink was stored in the fridge, and was stirred for 10 minutes prior to use. The Rz *paii* was applied using the draw-down method, with a K-bar #3 (delivering a 24 μm wet film thickness), which was dried in air for at least 20 min before use. The dried Rz ink film was ca. 2.1 μm thick, as measured using the Swanepoel method [18].

3. Results

3.1 The MB test

A modified version of the MB ISO, i.e. ISO10678:2010 [6], was used to quantify the activities of the different titania-based photocatalyst films on glass, in which one wall of a 1 cm plastic cuvette was replaced with the sample under test, as illustrated in figure 2(a). The photocatalytic sample under test was affixed to the cell using a silicone sealant (Wacker Silicones Elastosil A07 translucent silicone sealant) deposited around the outside of the cuvette. In a typical run, 3 mL of a 5 μ M methylene blue aqueous solution were added to the reaction vessel, followed by a crown stirrer, which was spun continuously at 800 RPM to ensure that the MB solution remained aerated throughout the irradiation.

Figure 2 – (a.) Schematic illustration of the reaction setup for the modified BS ISO 10678:2010 MB photocatalysed oxidation test. The sample under test was affixed to a three-walled cuvette, and irradiated through the MB solution and the UV/Vis spectra of the solution monitored as a function of irradiation time and (b) a typical set of UV-vis spectra recorded using the system illustrated in (a) for a non-heat-treated sample of Activ™, with the inset diagram showing the absorbance decay profile at 665 nm (taken from the main diagram) vs irradiation time, t .

The system was then irradiated with UV light (2 mW cm^{-2}) and the UV/Vis absorption spectrum of the MB solution recorded as a function of irradiation time. The results of this work for a typical (non-heat-treated) sample of commercial self-cleaning Glass (Activ™) are illustrated in figure 2(b), along with an insert plot of the decay in the absorbance, at 665 nm, due to MB, which yielded a value for the initial rate, $r_i(\text{MB})$, for reaction (1), where the organic = MB.

3.2 The Rz test

Each photocatalytic film tested using the MB test, was then coated with the Rz ink and irradiated (irradiance = 2 mW cm^{-2}) with UV light and the change in the UV/Vis absorbance

spectrum of the Rz film monitored as a function of irradiation time. A schematic of the reaction setup is illustrated in figure 3(a). The UV/Vis spectrophotometry results generated using this system, for a typical (non-heat-treated) piece of commercial self-cleaning Glass (Activ™) are illustrated in figure 3(b), along with an insert plot of the decay in the absorbance, at 608 nm, due to the photocatalysed reduction of Rz, which yielded a value for the initial rate, $r_i(Rz)$, for reaction (2).

Figure 3 – (a.) Schematic illustration of the Rz *Pail* ink irradiation system, in which an Rz ink covered sample turns from blue to pink upon UV irradiation and (b.) a typical set of UV/Vis spectral changes for a non-heat-treated sample of Activ™, arising from the Rz ink test, with the inset diagram showing the decay profile at 608 nm vs irradiation time, t , from which a value for the initial rate, $r_i(Rz)$ for reaction (2) could be gleaned.

An analysis of the decays in the insert diagrams in figures 2(b) and 3(b), reveals that the photocatalysed oxidation of the MB is first order, whereas that of Rz reduction in the Rz *pail* is zero order, as has been noted previously [6,10,12,18].

3.3 MB oxidation vs Rz reduction

The MB and Rz tests described above were used to determine the initial rates of MB oxidation, $r_i(MB)$ (units: absorbance units h^{-1}), and Rz reduction, $r_i(Rz)$, (units: absorbance units min^{-1}), for 3 differently-heated samples of BioClean™ and 3 differently-heated samples of Activ™, and the lab-made TiO₂ sol-gel film, all of which exhibited different photocatalytic activities. Each pair of $r_i(MB)$ and $r_i(Rz)$ values for each sample tested were then plotted against each other, i.e. $r_i(MB)$ vs. $r_i(Rz)$ and the results of this work are illustrated in figure 4. The latter is a good straight line, which suggests that for thin film of titania, on glass at least, the rate of MB photo-oxidation in solution, via reaction (1), is linearly correlated with that of Rz dye reduction in a *pail*, via

reaction (2). The significant difference between the two processes is that the former is slow whereas the latter is fast. For example, for a typical piece of Activ™ self-cleaning glass, reaction (1) (with organic = MB) takes about 5 h whereas reaction (2) takes 12 min, see figures 2(b) and 3(b).

Figure 4 – Plot of the measured initial rate of MB oxidation, $r_i(\text{MB})$, vs the initial rate of Rz reduction, $r_i(\text{Rz})$, for samples of BioClean™ (red empty circles), Activ™ (black empty circles) of different activity and a lab-made TiO₂ sol-gel film (full black circle).

4. Conclusions

The initial rate of the photocatalysed oxidation of methylene blue by dissolved oxygen in solution, $r_i(\text{MB})$, correlates linearly with the rate of reduction of resazurin in a *Paii*, $r_i(\text{Rz})$. This correlation provides further support for the contention that, when comparing photocatalytic materials of similar physical form, such as self-cleaning glass samples as used here, the Rz *paii* provides a simple and quick method for assessing photocatalytic activity for the much slower oxidative mineralisation of organics, such as MB. The fact that other work shows that the Rz *paii* technology can be used to assess the activities of photocatalytic films *in situ*, using only a simple mobile phone and a RGB colour analysis app, both of which are very inexpensive and simple to use, adds to the attraction of the *paii* technology as a quick method for testing such materials [19].

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