



Correlation between ΔAbs , ΔRGB (red) and stearic acid destruction rates using commercial self-cleaning glass as the photocatalyst



Andrew Mills*, Nathan Wells, Christopher O'Rourke

Department of Chemistry and Chemical Engineering, Queen's University of Belfast, University Road, Belfast, United Kingdom

ARTICLE INFO

Article history:

Received 16 July 2013

Received in revised form

13 September 2013

Accepted 1 November 2013

Available online 8 December 2013

Keywords:

Photocatalysis

Resazurin

Stearic acid

Titania

Self-cleaning surfaces

ABSTRACT

A resazurin (Rz) based photocatalyst indicator ink is used to test the activity of a commercial self-cleaning glass, using UV–vis spectroscopy and digital photography to monitor the photocatalyst-driven change in colour of the ink. UV–vis spectroscopy allows the change in film absorbance, ΔAbs , to be monitored as a function of irradiation time, whereas digital photography is used to monitor the concomitant change in the red component of the RGB values, i.e. ΔRGB (red). Initial work reveals the variation in ΔAbs_t and ΔRGB (red)_t as a function of irradiation time, t , are linearly correlated. The rates of change of these parameters are also linearly correlated to the rates of oxidative destruction of stearic acid on self-cleaning glass under different irradiances. This work demonstrates that a measure of photocatalyst activity of self-cleaning glass, i.e. the time taken to change the colour of an Rz photocatalyst indicator ink, can be obtained using inexpensive digital photography, as alternative to more expensive lab-based techniques, such as UV–vis spectrophotometry.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Semiconductor photocatalysis has been shown to be effective in the photosensitised destruction of: (i) dissolved and air borne inorganic and, more usually, organic pollutants [1,2], (ii) surface contaminants [3] and (iii) biological species [4]. In most of this work the photocatalyst concerned is titania, which is inexpensive, active and readily utilised in powder or film form, although its large bandgap, i.e. 3.0 and 3.2 eV for rutile and anatase TiO_2 , respectively, renders it effective using only UV, rather than visible light [5].

The use of TiO_2 as a photocatalyst goes back to at least 1929, when it was reported to be responsible for the photochalking of paint, via the photocatalytic degradation of the binder [6]. However, its more recent growing popularity as a semiconductor photocatalyst may be traced to work in the late 70s and early 80s by, amongst others, the groups of Bard and Ollis [7,8], working on the photocatalysed oxidation of acetic acid and chlorinated hydrocarbons, respectively. Since that time many thousands of papers have been written on the efficacy of titania as a photocatalyst, and an increasing number of commercial products have arisen.

The commercial photocatalyst product areas include, but are not limited to: photodeodorisation [9], NO_x capture in roadside paving [10], anti-microbial textile surfaces [11], indoor air purification [2] and general indoor and outdoor self-cleaning surfaces, such

as glass, paints and tiles [12–14]. With these established and emerging commercial products there exists a need for agreed methods to assess their photocatalyst activities to ensure high quality control and delivery on product specification. A popular method for assessing the activities of photocatalyst films is through the oxidative destruction of stearic acid [15], as it is considered a model compound for typical surface organic pollutants. Further details of this test are provided later. Another such method of assessing the activity of a photocatalyst film is through the oxidation of a dye in solution, and a number of different dyes have been used for the purpose, including the thiazine dye, methylene blue, MB [16]; indeed, the photocatalysed bleaching of MB is now an ISO standard [17]. However, this and other ISO standards for assessing photocatalytic activity are lab-based and usually require expensive analytical equipment and technical support to run them.

This group has recently devised a simple method for the semi-quantitative/quantitative assessment of the activity of thin-film semiconductor photocatalyst films, such as those found on self-cleaning glass, using a redox dye, usually resazurin, Rz, incorporated into an ink with a sacrificial electron donor, usually glycerol [18]. Briefly, this ink is applied to the photocatalytic film under test and upon UV irradiation of the latter, the ink rapidly changes in colour due to the photocatalysed irreversible reduction of the resazurin (Rz) dye (blue), to resorufin (Rf; pink). A schematic illustration of the key processes are given in Fig. 1.

With most commercial examples of self-cleaning glass, under moderate UV illumination (3 mW cm^{-2} , UVA light from $2 \times 8 \text{ W BLB}$ lamps), this colour change is usually effected within 10 min, and

* Corresponding author. Tel.: +44 028 9097 4339; fax: +44 028 9097 6524.

E-mail address: andrew.mills@qub.ac.uk (A. Mills).

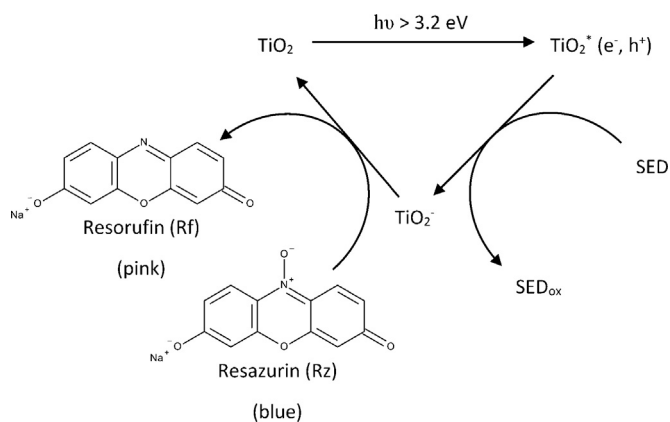


Fig. 1. Reaction scheme of the RZ ink on an underlying semiconductor photocatalyst (TiO₂) where SED/SED_{ox} represents the reduced/oxidised forms of the sacrificial electron donor, glycerol.

is much faster than most other photocatalytic activity test methods, such as the photomineralisation of stearic acid, SA [19] or the destruction of MB [20], most of which usually take 2–3 h. Note: in the former case other work has shown that the rate of oxidative SA removal, R_{SA} , is linearly correlated with the reduction of resazurin, as measured in the rate of overall change in absorbance, due to RZ at 608 nm, of the RZ ink test, i.e. $d\Delta\text{Abs}_{608}/dt$ [18]. This correlation can be attributed in part to the common zero order nature of the kinetics of the two different photocatalytic processes [21].

The RZ ink can be readily used without resorting to expensive analytical instrumentation, as the time taken to change colour (which is a measure of the activity of the underlying photocatalytic film), can be assessed by eye. However, this is only able to provide, at best, a semi-quantitative method for assessing the activity of the underlying semiconductor photocatalyst (SPC). For more careful, quantitative work, access to a UV–vis spectrophotometer appears essential and so usually relegates the assessment method, along with all the other methods of assessing photocatalyst activity, to the laboratory, and not for use in the field. In order to open up the RZ ink test method for use in the laboratory and in situ (field) work, a study was carried out in which a much less expensive method was used to monitor the change in colour of the RZ ink, namely: digital photography, rather than UV–vis spectrophotometry, when assessing the photocatalytic activity of self-cleaning glass. The results of the work are reported below.

2. Experimental

2.1. Materials

Unless otherwise stated, all materials were supplied by Sigma–Aldrich and obtained in the highest purity possible. We thank Pilkington Glass for supplying samples of their commercial self-cleaning glass, Activ™.

2.2. Methods

All UV–vis spectra and absorbance data were recorded using a Varian Cary 60 Bio UV-Visible spectrophotometer. FT-IR absorption spectra were recorded using a Perkin Elmer Spectrum 1. All photographs were taken using a Canon EOS 550D digital SLR under controlled light condition (two tungsten lamps and a portable white photo studio, purchased from Xenta [22]). Unless otherwise stated, all ink-coated films were irradiated and monitored under ambient conditions (20 °C, 57% RH) using a UVA light source comprising:

2 × 8 W BLB's with a maximum output at 365 nm, and a typical irradiance of 3 mW cm⁻².

2.3. Preparation of a typical RZ ink and film

The ink was prepared by adding 4 mg of resazurin sodium salt and 0.4 g of glycerol to 3 g of a 1.5 wt.% aqueous hydroxyethylcellulose (HEC) solution. The ink was stirred vigorously for 8 h to ensure uniform mixing of the dye throughout the solution. The resulting blue ink product is very stable when stored in a dark, cool place, and can be used for at least 6 months without showing any signs of deterioration.

In a typical experiment, prior to UVA irradiation, the RZ ink was drawn down onto a 25 mm × 25 mm square glass sample of the self-cleaning glass, using a K-hand coater, K-bar 3 (RK Printcoat Instruments), generating a wet ink film thickness of 24 μm. The ink coated sample was then dried at 70 °C for 10 min, whereupon the film had a thickness of ca. 800 nm, as measured using SEM and UV–vis absorption spectroscopy.

2.4. Irradiation of ink-coated film

In a typical experiment, the UV–vis absorbance spectra and digital photos of an ink coated film were recorded at regular intervals, as a function of UVA irradiance time, t . RGB colour values can be extracted from most digital images using many of the current image editing software packages, of which Adobe Photoshop and Microsoft Paint are typical examples. However, such programmes do not lend themselves to: (i) easy recording of multiple red, green, blue (i.e. RGB) values from a collection of images, as required in this work, and, (ii) their subsequent copying and pasting into a plotting programme, such as Excel®, so that plots of the variations in R, G and B values versus irradiation time can be generated, as required here. As a consequence, one of us, CO'R, created a macro in Excel® that allows the RGB values of any digital image to be determined, and automatically placed in the spreadsheet, ready for plotting, using a custom colour extractor tool. A downloadable copy of this macro, embedded in an Excel® file, along with guide notes as to its use, are available from [23].

A typical set of digital images recorded for an RZ ink on a sample of the self-cleaning glass as a function of UVA irradiance time, t , are illustrated in Fig. 2. The plots of the results of the RGB analysis of these digital images, as a function of t , are also illustrated in Fig. 2. From the latter, it appears that, not surprisingly, the variation in the red component, i.e. RGB (red), of the digital images of the ink provides the smoothest indication of the change in colour of the RZ ink film as it changes from blue to pink due to the UV-driven action of an underlying photocatalytic film.

2.5. Preparation of stearic acid films

In this work a coating solution of 0.1 M stearic acid dissolved in chloroform was employed and 25 mm × 25 mm samples of self-cleaning glass were dip coated into the stearic acid solution using a KSV NIMA dip coater, with a 1 s immersion time and an extraction rate of 1 cm s⁻¹. After the chloroform evaporated from the surface of a glass sample (i.e. ca. 10 min), the non-active side was cleaned with chloroform to remove the stearic acid film on that side before subsequent irradiation with UV light and monitoring of the destruction of the SA film on the titania (active) side, as a function of irradiation time via FT-IR.

Download English Version:

<https://daneshyari.com/en/article/6505348>

Download Persian Version:

<https://daneshyari.com/article/6505348>

[Daneshyari.com](https://daneshyari.com)