Research Article

A Rapid Method of Assessing the Photocatalytic Activity of Thin TiO$_2$ Films Using an Ink Based on the Redox Dye 2,6-Dichloroindophenol

Andrew Mills, Mark McGrady, Jishun Wang, and James Hepburn

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

Correspondence should be addressed to Andrew Mills, a.mills@strath.ac.uk

An indicator ink based on the redox dye 2,6-dichloroindophenol (DCIP) is described, which allows the rapid assessment of the activity of thin, commercial photocatalytic films, such as Activ. The ink works via a photoreductive mechanism, DCIP being reduced to dihydro-DCIP within ca. 7.5 minutes exposure to UVA irradiation of moderate intensity (ca. 4.8 mW cm^{-2}). The kinetics of photoreduction are found to be independent of the level of dye present in the ink formulation, but are highly sensitive to the level of glycerol. This latter observation may be associated with a solvatochromic effect, whereby the microenvironment in which the dye finds itself and, as a consequence, its reactivity is altered significantly by small changes in the glycerol content. The kinetics of photoreduction also appear linearly dependent on the UVA light intensity with an observed quantum efficiency of ca. 1.8×10^{-3}.

1. INTRODUCTION

Semiconductor photocatalysis (SPC) has progressed significantly since the early research into the possible use of semiconductor photochemistry to split water 30 years ago [1], such that it is now one of the most actively researched areas in photochemistry and is associated with several, major commercial products [2]. Its potential use in environmental remediation, based on the following reaction:

$$\text{Organic material} + O_2 \xrightarrow[\text{UVA light}]{\text{TiO}_2} \text{Mineral acids} + H_2O + CO_2, \tag{1}$$
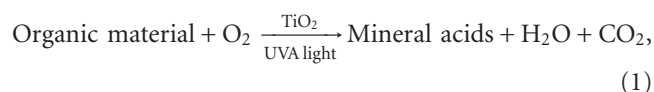
has been the main reason for much of the interest and the semiconductor which has been the most heavily exploited for this purpose is titania (TiO$_2$). Despite having a relatively large band gap (ca. 3.2 eV), thus necessitating the use of ultraviolet light (UV) to initiate the photocatalytic process, titania is chemically and biologically inert, mechanically robust, inexpensive, and highly active. Of the three known forms of titania (anatase, rutile, and brookite), it is generally accepted that anatase TiO$_2$ is the most active form for SPC applications.

Upon activation of the titania with UV light, an electron-hole pair is produced within the bulk of the material. These species usually recombine rapidly; however, for reaction (1) to occur, the electron-hole pair must migrate to the surface of the semiconductor, whereupon the photogenerated electron reduces atmospheric O$_2$ to superoxide, O$_2{}^-$, which can be reduced further to water through a number of highly active intermediates, one of which is believed to be the strongly oxidising hydroxyl radical, OH$^{\bullet}$. Conversely, the photogenerated hole is capable of oxidising surface TiOH groups to radicals, that is, TiOH$^{\bullet}$, that are capable of oxidising many organic materials/pollutants into mineral acids and CO$_2$.

One of the reasons why titania has proved successful in the removal of both aqueous and atmospheric contaminants is that it is easily adhered to a suitable supporting substrate, which can subsequently be exposed to either an aqueous or airborne pollutant. Suitable methods for preparing titania films on the surface of a substrate include using a sol-gel method [3, 4], physical vapour deposition (i.e., sputtering) [5, 6], and chemical vapour deposition (CVD) [7, 8]. All of these techniques have been exploited in the research laboratories, but the method which has met with the most
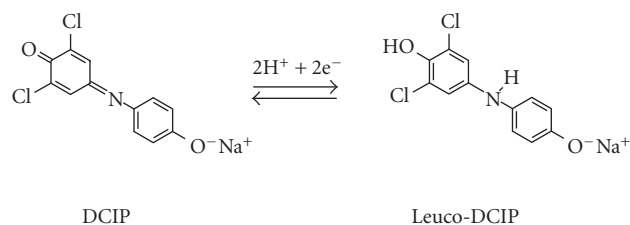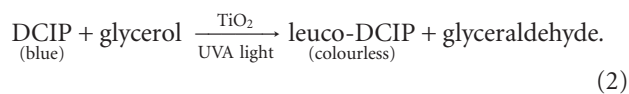
FIGURE 1: The structures of the sodium salt of DCIP (left) and its reduced product, dihydro-DCIP.

commercial success is CVD. Indeed, the world first self-cleaning glass, Activ [9], formulated by Pilkington Glass (Lathom, UK), is manufactured using an atmospheric pressure CVD (APCVD) technique [10]. Many of the World's other major glass manufacturers have followed the lead of Pilkington Glass and now manufacture their own self-cleaning product [11, 12]. More recently, there has also been the emergence of self-cleaning tiles [13], paints [14], and concrete [15] products, particularly from Japan.

With so many photocatalytic materials appearing on the market, there is an increasing interest in the development of one or more standard methods for assessing the activity of both laboratory and commercial samples. To date, there are many tests which have been used in the research laboratories to elucidate film activity, including the destruction of nitrogen oxides [16–18], the mineralization/degradation of dyes [19, 20] (particularly methylene blue [21, 22]), and the destruction of stearic acid [23, 24]. However, with all the methods outlined above, whilst suitable for use in the research laboratories, the prospect of using them in the field, for example, to demonstrate the efficacy of the photocatalytic film to potential customers, or test samples in situ, is limited, since each involves some degree of sample preparation, use of expensive, often bulky, analytical equipment, and technical skill to run the method and assess the results. From an industrial perspective at least, what is needed is a rapid, semiquantitative (if not quantitative) method of demonstrating and assessing rapidly the activity of any photocatalytic coating.

One possible route is to use a photocatalyst indicator ink which, when deposited onto a photocatalytic coating, changes colour upon UV activation of the coating. Such an ink has been proposed recently based on the blue redox dye, 2,6-dichloroindophenol (DCIP) [25], the structure of which is illustrated in Figure 1. The overall process involving the ink is as follows:

$$\text{DCIP} + \text{glycerol} \xrightarrow[\text{UVA light}]{\text{TiO}_2} \text{leuco-DCIP} + \text{glyceraldehyde.}$$
(blue) (colourless)

(2)

The DCIP ink has the striking feature that it is blue before UV irradiation, but colourless, due to the formation of leuco-DCIP (the structure of which is also shown in Figure 1), afterwards. The photocatalytic process is very rapid, that is, within 7 minutes using typical solar UVA levels (ca. 4.5 mW

cm^{-2}) on a commercial self-cleaning glass, such as Activ. In addition, the photoreduction of the dye has also been shown to be unaffected by both the level of O$_2$ and the humidity of the environment under which the ink is being used. This article reports the characterisation of a DCIP photocatalyst indicator ink when used on a typical, commercial self-cleaning glass (Activ).

2. EXPERIMENTAL

Unless stated otherwise, all reagents were Analar grade and used, as received, from Sigma-Aldrich. The conditions referred to as "ambient atmospheric conditions" are on the open bench at room temperature (ca. 20°C) and a relative humidity of ca. 60%.

A typical DCIP ink was prepared as follows: 3 g of a 1.5 wt% hydroxyethylcellulose (Fluka, medium viscosity) solution in water were placed in a sample bottle and to it were added 0.3 g of glycerol. The resulting solution was gently stirred whilst 5 mg of 2,6-dichloroindophenol (supplied by Alfa-Aesar, sodium salt hydrate, 98%) were added slowly. The solution was placed in an ultrasound bath and sonicated for 5 minutes in order to ensure complete dissolution of the dye, before being subjected to further gentle stirring for 30 minutes. Ink produced in this manner appeared stable and unchanged for at least 1 month, and was used as required. In terms of parts per hundred resin (pphr), the level of polymer/SED/dye in the ink formulation is equivalent to a ratio of 100/667/11. Such a DCIP ink is referred to henceforth as the standard formulation.

The photocatalyst substrate used in this work was Activ™, kindly supplied by Pilkington Glass. Full details on its preparation can be found elsewhere [10]. The bulk Activ™ samples received were cut into 25 mm × 25 mm × 4 mm thick samples so that it was possible to place them in a home-made cell holder for making spectral measurements using a UV-vis spectrophotometer. Coating of a typical glass sample was achieved by smearing approximately 1 mL of the ink under test over the sample surface and spinning the sample, using an Electronic Micro Systems Model 4000-1 spin coater, at 500 rpm for 15 s, which generates a film ca. 900 nm thick on the photocatalyst surface. The ink was then further dried by placing the spun-coated Activ™ substrate in an oven at 70°C for 10 minutes, although similar kinetic results were also observed when the ink-coated substrate was simply allowed to dry in air in the absence of light for 1 hour.

The UV-driven reduction of the dye on the photocatalyst surface was monitored via UV-visible spectroscopy, using a Cary 50 Bio UV-visible spectrophotometer. The instrument was configured to scan in the wavelength range 300–800 nm, with scans taken at time intervals between UV irradiations typically ranging from 10 s to 10 minutes depending upon the observed rate of photoreduction (i.e., photobleaching). UV irradiations were conducted using a hand-held, 2 × 4 W Black Light Blue (BLB) UVA source (peak wavelength 365 ± 20 nm). Unless stated otherwise, the UVA irradiance used for all irradiations was ca. 4.8 mW cm^{-2}, which is comparable to the standard UVA irradiance on a sunny day (ca. 4.5 mW cm^{-2}) [26].

3. RESULTS AND DISCUSSION

Both the DCIP ink and the resulting dried ink film on the desired substrate are blue in colour, and this blue colour persists when the ink is cast on plain glass, or indeed any substrate with nil photocatalyst, and irradiated with UVA light for an extended (ca. 1 hour) time period. With such films, no significant change in the absorbance was noted over this time period at the wavelength of maximum absorbance, λ_{max} (ca. 629 nm and HPBW ca. 100 nm). In aqueous solution, a dilute (i.e., 10^{-4} M) solution of DCIP has a λ_{max} at 600 nm and a half peak band width (HPBW) of ca. 130 nm (measured in house). Therefore, in the ink it is observed that the λ_{max} is slightly red shifted compared to what is observed in solution. However, a similar HPBW is observed with the dried ink film, which is indicative of multimer (dimer, trimer, etc.) formation. The formation of said multimers in the dried film is not surprising given the effective dye concentration of 0.064 M.

In contrast, when cast on Activ, the blue ink film is observed to be rapidly photobleached upon irradiation with UVA light. Figure 2(a) shows the observed absorption spectra obtained for a DCIP ink cast as a film on the surface of Activ and subsequently irradiated with UVA light. Thus, upon UV irradiation of a typical DCIP film on Activ, the absorbance of the film decreases with time (as indicated by the arrow) and the ink is completely bleached, that is, the dye is fully reduced to dihydro-DCIP, after ca. 7.5 minutes. The change in the absorbance ($\Delta Abs = Abs_t - Abs_\infty$, where Abs_t and Abs_∞ are the absorbance of the film at UV irradiance times t and after complete photobleaching, resp.) at λ_{max} is shown more explicitly in Figure 2(b). The initial rate of reduction of the ink, r_i, is derived from the absorbance data recorded over the time necessary for the initial absorbance of the ink to decrease by ca. 20% of its initial value. Based upon the data presented in Figures 2(a) and 2(b), the initial rate of reduction of a typical DCIP ink under ambient atmospheric conditions using 4.8 mW cm^{-2} UVA light is ca. 4.5×10^{-4} AbsU s^{-1}, where AbsU is used to denote absorbance units, thus avoiding confusion that the value quoted is a rate constant.

Since DCIP is a redox dye (E°(DCIP/dihydroDCIP) = + 0.228 V at pH 7 versus SHE [27]), it is possible that, once DCIP has been reduced on the surface of Activ to dihydro-DCIP, the latter may be reoxidised by atmospheric O_2, regenerating the initial level of DCIP, and thus restoring the original blue colour of the ink film. However, monitoring the absorbance at λ_{max} of a typical DCIP film on Activ before and after UV bleaching revealed that the photobleached DCIP only partially (ca. 38%) recovers its original colour over a period of many hours (see Figure 2(c)).

The initial rate of recovery in absorbance at 629 nm of the ink, from Figure 2(c), is typically 1.8×10^{-6} AbsU s^{-1}, a rate which is more than 100 times slower than its initial rate of reduction, thus allaying any concerns that the "dark" reoxidation of dihydro-DCIP by ambient O_2 would compete with the reduction of the dye during irradiation, that is, effectively, the photobleaching of the DCIP ink on Activ appears an irreversible process. This observation supports
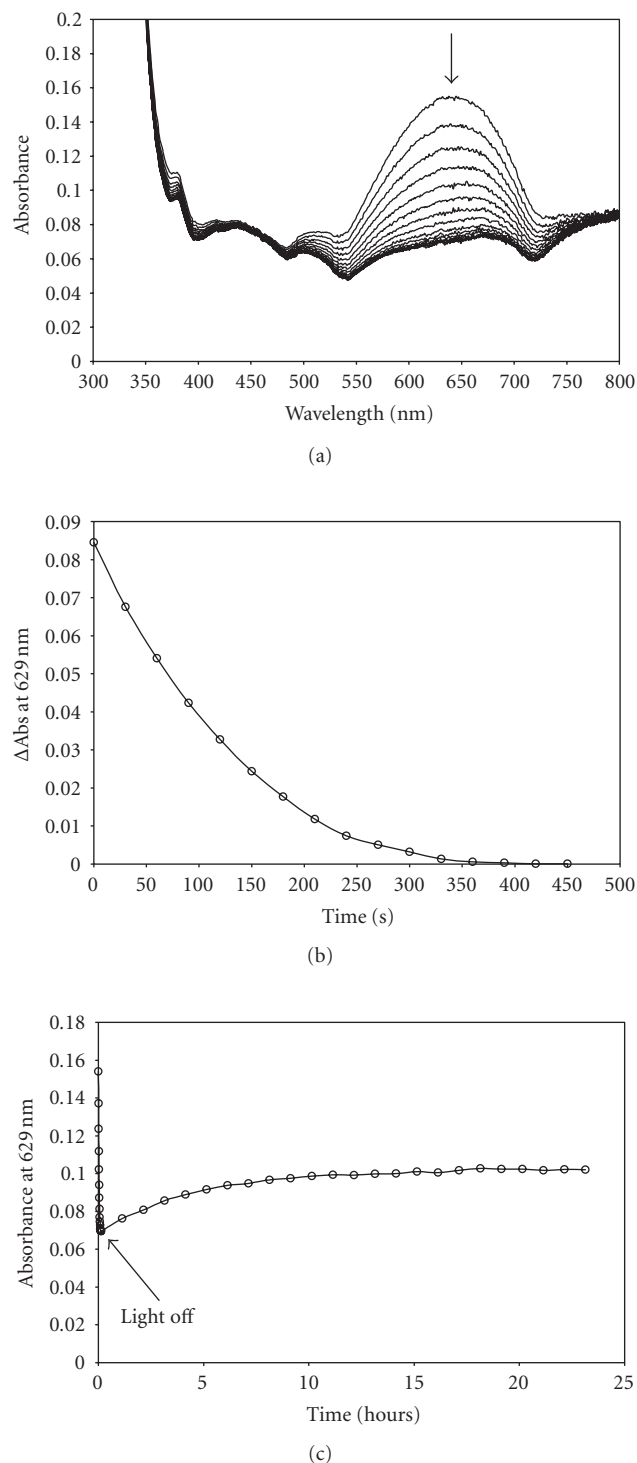

(a)

(b)

(c)

Figure 2: (a) The spectral shape obtained for a standard DCIP ink cast on the surface of Activ, and the subsequent changes (from top to bottom) in this spectral shape as the sample is irradiated with UVA light at an intensity of ca. 4.8 mW cm^{-2}. Spectra were recorded at 30-second intervals. (b) The change in the absorbance (ΔAbs) at λ_{max} (629 nm) with UVA irradiation of a DCIP ink, based on the data presented in Figure 2(a). (c) The reduction, and subsequent recovery, of a DCIP ink on the surface of Activ at 629 nm. The reduction conditions were similar to those detailed previously in Figure 2(a), whereas the ink recovery was monitored in the dark with spectra recorded at 1 hour intervals.
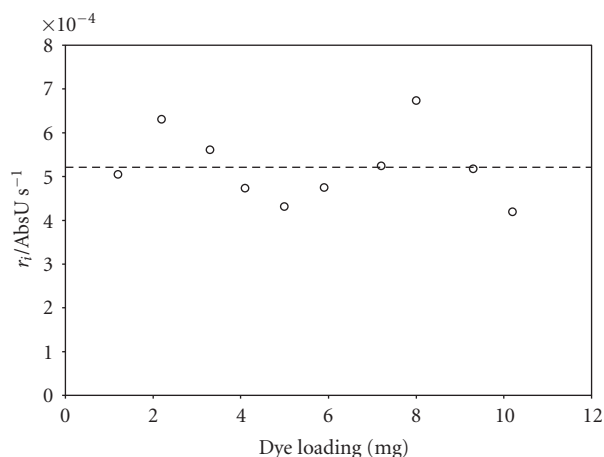
FIGURE 3: The variation in the initial rate of reduction (r_i) of a DCIP ink on Activ as the level of dye in the ink formulation is altered between 1 and 10 mg. The dotted line indicates the calculated average r_i of 5.21×10^{-4} AbsU s^{-1}.
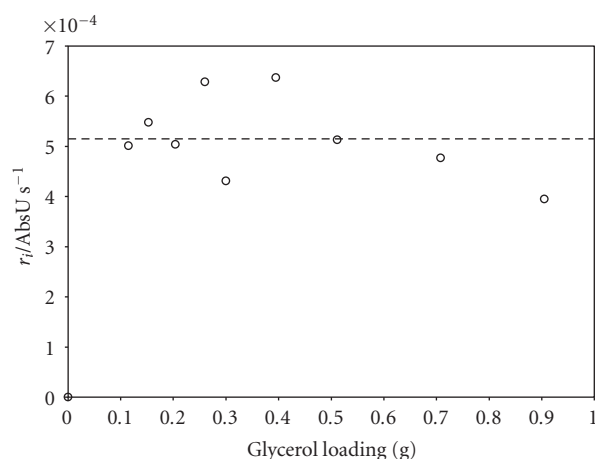

FIGURE 4: The variation in r_i as the level of glycerol in the ink formulation is altered between 0.1 and 0.9 g. As in Figure 3, the dotted line in the plot indicates the average r_i of 5.15×10^{-4} AbsU s^{-1}.

the results of previous work on the ink, where the kinetics of photoreduction by Activ were assessed under varying levels of oxygen and noted to be the same under both anaerobic and O$_2$-saturated conditions [25].

3.1. The effect of dye loading on the initial rate of photoreduction of a typical DCIP film on Activ

The variation of r_i as a function of dye loading (5 mg dye per 45 mg polymer in a typical ink formulation) was studied over the range 1–10 mg (equivalent to 2.2–22 pphr) and the results of this work are illustrated in Figure 3. From these results, it appears that r_i is approximately independent of dye loading, with an observed average r_i of 5.2×10^{-4} AbsU s^{-1}. This result is in stark contrast to the behaviour of the Rz photocatalyst indicator ink reported previously [28] over a similar dye loading range, where the initial rate of reduction was observed to decrease by a factor of 4 as the dye level was increased from 1 to 8 mg. This latter effect was attributed to an increasing level of less reactive Rz dimers with increasing dye loading, supported by spectral changes showing a shoulder peak emerging at 570 nm as the dye loading was increased up to 40 mg. In contrast, the shape of the absorption spectrum of the DCIP ink did not change as a function of dye loading. The invariance of r_i as a function of [substrate] is not unusual in semiconductor photochemistry and implies that either all the reactive sites associated with dye reduction are occupied by molecules of DCIP; or that the rate-determining step in reaction (2) does not involve the reduction of DCIP.

3.2. Effect of glycerol level on the initial rate of photoreduction

In the standard ink formulation, glycerol is present to act as a sacrificial electron donor (SED); essentially, the glycerol molecules act as "hole traps," preventing recombination of the photogenerated electron-hole pair by undergoing oxidation, thus allowing any photogenerated electrons to reduce the dye molecules in the ink at the photocatalyst surface. If an ink formulation is prepared with no glycerol present, cast on the surface of Activ, and irradiated with UVA light over a prolonged irradiation period (ca. 1 hour), there is no observed photobleaching/reduction of the dye on the photocatalyst surface, indicating that the removal of the SED from the DCIP ink results simply in electron-hole recombination becoming the predominant process.

Experiments show that r_i is independent of glycerol loading over the range 0.1–0.9 g (typically, 0.3 g glycerol is present in the formulation), as demonstrated in Figure 4. However, r_i does vary markedly from 0–0.1 g (0–222 pphr) glycerol loading, as illustrated by the results in Figure 5. The initial rate of reduction, r_i, is observed to increase steadily as the glycerol level is increased from 0 to ca. 0.03 g (0–66 pphr), after which point a plateau value is achieved. In addition to the above kinetic data, Figure 5 also charts the observed variation in the λ_{max} of the resulting DCIP ink as the glycerol level is varied over the same range. It would appear from this plot that the variations in λ_{max} and r_i are linked in some way, with λ_{max} being blue-shifted as the glycerol level is increased. The likely cause of this shift in the peak wavelength is a solvatochromic effect, brought about by a change in the solvation shell of the dye molecules in the ink formulation and subsequent ink film as the glycerol level is increased. Such a change in the solvation shell is likely to alter the reactivity of the DCIP and may be responsible for the variation in r_i with glycerol loading illustrated in Figure 5.

However, there may be other effects working here since the work by Van Keuren and Schrof [29] showed that in a PVA/glycerol solution, where the glycerol content was varied between 10 and 40 wt%, the diffusion coefficient for
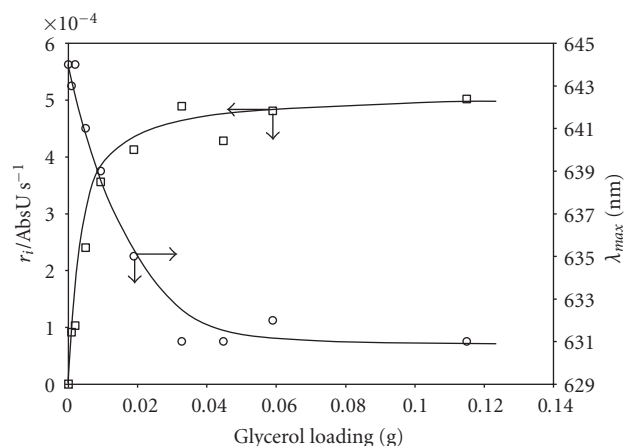
FIGURE 5: The variation in r_i(□) and the $\lambda_{\max}$(○) as the level of glycerol in the ink formulation is altered between 0 and 0.1 g.

FIGURE 6: The variation in r_i with UVA irradiance.

a dye, rhodamine B, increased by a factor of 10^4. Beyond 40 wt% glycerol, the dye exhibited a diffusion coefficient similar to that observed for the dye in neat glycerol. In the DCIP ink formulations presented here, with a 0.1 g glycerol loading, the glycerol wt% is 66 wt%, and thus the variation in r_i as a function of glycerol loading illustrated in Figure 5 could be simply due to the variation in the diffusion coefficient of the dye from the bulk film to the surface of Activ, assuming that this is the rate determining step for the photoreduction/bleaching process. In this instance, the maximum rate observed at glycerol loading ≥0.1 g is due to the diffusion coefficient for DCIP in the film (HEC/glycerol) reaching a limiting value, as was observed by Van Keuren for rhodamine B in PVA/glycerol.

3.3. *The effect of UVA light irradiance on the initial rate of photoreduction*

In a final set of experiments, the initial rate of reduction of a typical DCIP film was determined as a function of UVA light irradiance, varied from 0.44 to 7.41 mW cm^{-2}, and the results are illustrated in Figure 6. Not surprisingly, r_i increases with increasing light irradiance, since the number of photons reaching the photocatalyst surface, and hence the number of photogenerated electrons produced, will increase. The strong linear dependence of r_i on the UV light irradiance is attributed to the relatively low light intensities used here to reduce the dye, the low absorbance of the underlying Activ photocatalyst layer, and the fact that, at such low UV irradiance levels, the reduction reaction will be controlled by the reactions at the ink/photocatalyst interface of the photogenerated electron-hole pairs, as opposed to their recombination (which is expected at high irradiance levels). A similar linear dependence of r_i on the UV irradiance was observed for the Rz-based photocatalyst indicator ink [28].

Since ΔAbs_t for the reduction of DCIP is ca. 0.085 AbsU, as illustrated earlier in Figure 2(b), for the standard ink formulation, and since it is known that 1 mW cm^{-2} of

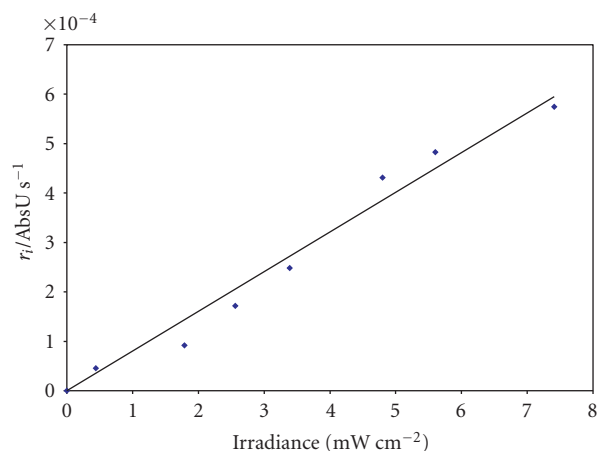365 nm light is equivalent to 1.1×10^{17} photons per cm^2 per minute, the quantum efficiency for the process can be estimated to be 0.0018 molecules per photon. It is also known from spectral studies conducted elsewhere that Activ only absorbs ca. 7.2% of the incident UVA irradiation from black light blue lamps [30], thus the quantum yield for the reduction of DCIP on the substrate can be estimated to be 2.5%. Both of these estimated values are greater than those observed for the Rz ink (2.5×10^{-4} molecules per photon and 0.35%, resp.) [28], although in practice the initial rate of photoreduction of DCIP is slower than that of Rz in the ink formulation under ambient atmospheric conditions [25].

4. CONCLUSIONS

A characterisation study of an indicator ink based on the redox dye 2,6-dichloroindophenol for assessing the photocatalytic activity of thin photocatalytic films of titania has been conducted. The initial rate of photoreduction of the dye in the ink formulation is independent of the dye loading level but highly sensitive to the level of glycerol present, reaching a plateau above a loading of 0.1 g glycerol. Accompanying this trend in the reduction rate is an inverse shift in the $\lambda_{\max}$ of the dye, believed to be due to changes to the solvent shell surrounding the dye with changing glycerol content. As anticipated, the rate of photoreduction increased with increasing UV irradiation intensity, similar to what has been reported for an Rz ink. The quantum yield for the photoreduction of DCIP by an Activ film was estimated to be 2.5%, which is greater than that observed for the Rz-based ink communicated previously.

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