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Correlation of oxidative and reductive dye bleaching on TiO_2 photocatalyst films

Jiří Zita[a,*], Josef Krýsa[a], Andrew Mills[b]

[a] Department of Inorganic Technology, Institute of Chemical Technology Prague, Technická 5, Prague 166 28, Czech Republic
[b] Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

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ABSTRACT

A series of titania films of different thicknesses (60–420 nm), and therefore activities, are produced using a sol–gel method and assessed for photocatalytic activity using three test methods. The first two involve the photo-oxidative bleaching of common dyes, namely methylene blue (MB), a cationic thiazine dye, and Acid Orange 7 (AO7), an anionic, azo dye, in aerated aqueous solution. The third test uses an ink comprising, amongst other things, a redox dye, Resazurin (Rz), and an easily oxidized species, glycerol. When deposited on a titania film and irradiated with UV light the colour of this Rz ink (initially blue) changes to pink due to the titania-sensitized reduction of Rz. The initial rates of destruction of MB and AO7 and the initial rate of reduction of Rz depend directly upon the thickness of the titania films, indicating a strong correlation between the different tests. The significance of these results is discussed in the context that the MB test is currently being considered by International Organization for Standardization (ISO) as a standard method for assessing the photocatalytic activities of the surfaces. Compared with MB, Rz ink test is much faster and easier to implement, which suggests that there would be significant advantages to employing the Rz test, instead of another dye test, for assessing the photocatalytic thin films activities.

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1. Introduction

Semiconductor photocatalysis, SPC, on anatase TiO_2 can be used as a method for the decomposition of organic pollutants by light, resulting in the production of non-toxic CO_2, H_2O and, in the case of hetero atom-containing species, mineral acids [1–3]. The overall process can be summarized as follows:

$$\text{Organic polutant} + O_2 \xrightarrow[\text{semiconductor}]{h\upsilon \geq E_{bg}} \text{Mineral acids} \qquad (1)$$

As a consequence a number of commercial manifestations of this technology now exist and the market appears to be growing [4,5]. Most popular are UV-driven, self-cleaning films, tiles, paints, concrete and fabric. In most cases the active ingredient is a thin layer of anatase titania, chosen because of its high photocatalytic activity, biological and chemical inertness, inexpensive nature, mechanical robustness, optical transparency (when cast as nanoparticulate films) and superhydrophilic nature (in its pristine form) [3,6–8].

The increasing commercial and academic activity in photocatalytic film production and application has given rise to significant interest in the development of standard methods for assessing their activities. One popular approach involves the destruction of stearic acid (SA), a waxy material which is readily deposited as a thin film from solution and simulates the hydrophobic organic substrates that tend to deposit on exterior surfaces, such as windows and walls. However, the SA test is slow and requires expensive, lab-based equipment, such as FT-IR or GC, for monitoring the disappearance of SA with irradiation time [9]. This has prompted many researchers to investigate other, potentially quicker and easier, methods of assessing the photocatalytic activity of semiconductor photocatalyst films, most popular of which is the destruction of a dyestuff, since it is easy to measure its disappearance either semi-quantitatively (by eye), or quantitatively (by visible absorption spectroscopy). Of all the dyes tested for this work, the most popular is methylene blue, MB [10–12].

The semiconductor-sensitized photo-oxidative degradation of dye test reagents is considered to proceed via the following general mechanism.

$$\text{Semiconductor} + h\upsilon \geq E_{bg} \rightarrow h^+ + e^- \qquad (2)$$

$$h^+ + \text{Dye} \rightarrow \text{products} \qquad (3)$$

$$h^+ + H_2O \rightarrow HO^\bullet + H^+ \qquad (4)$$

$$HO^\bullet + \text{Dye} \rightarrow \text{products} \qquad (5)$$

$$e^- + O_2 \rightarrow O_2^{\,-} \qquad (6)$$

$$O_2^{\,-} + \text{Dye} \rightarrow \text{products} \qquad (7)$$

where h^+ and e^- refer to the holes and electrons, respectively, that are generated upon UV excitation of semiconductor with light of energy $\geq E_{bg}$, the bandgap of the semiconductor (3.2 eV for anatase

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[*] Corresponding author. Tel.: +420 2 2044 4112; fax: +420 2 2044 4410.
E-mail address: Jiri.Zita@vscht.cz (J. Zita).

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titania). The photogenerated holes are able to oxidize the dye either directly (3), or indirectly, via the production of adsorbed $HO^\bullet$ radicals, i.e. via reactions (4) and (5). The photogenerated electrons are able to reduce adsorbed oxygen to superoxide (6), which may then also react with the dye, reaction (7), or undergo subsequent reduction to H_2O_2 and, subsequently, water. Note: H_2O_2 may also act as source of $HO^\bullet$ radicals, which can oxidize the dye.

MB, a cationic thiazine dye, is a popular choice of dye for assessing photocatalytic activity because it is inexpensive, has a strong adsorption in the visible ($\lambda_{max} = 664$ nm; $\varepsilon_{664} = 7.4 \times 10^4\ M^{-1}\ cm^{-1}$) and does not absorb strongly in the UVA. The semiconductor-sensitized photobleaching of MB is complicated to some extent, especially when, as is usually the case, titania is used, because it is able to bleach the dyestuff via both an oxidation process (8) (leading to completely mineralization of the dye) and a reductive process (9) (which produces the leuco form of the dye, LMB).

$$MB + h^+ \rightarrow \text{ mineralized products} \quad (8)$$

$$MB\ +\ 2e^- + H^+ \rightarrow\ LMB \quad (9)$$

The former process (8) is favored by aerobic, neutral/alkaline conditions and the latter (9) by anaerobic, acidic conditions, since at pH ≥ 7, the leuco form of the dye (LMB) is rapidly re-oxidized by dissolved oxygen: [13,14]

$$2LMB\ +\ O_2 \rightarrow\ MB \quad (10)$$

Thus, in most work in which the MB (in aqueous solution) test is used to assess the photocatalytic activity of semiconductor photocatalyst films, aerobic, neutral/alkaline conditions are used. Under such conditions, the bleaching of the MB dye is accompanied by the generation of carbon dioxide, nitrate ions and ammonium ions as products, indicating the dye is photomineralized [15]. Such is the perceived effectiveness of the MB test, it is currently being considered by the International Organization of Standardization (ISO) as a standard test for photocatalytic surfaces [16]. It might be argued that MB is a well-known, effective singlet oxygen generator and so, initially, not an obvious choice test dye for semiconductor photocatalysis. However, MB does not absorb significantly in the UVA region and so is reasonably stable photochemically under UVA irradiation. This feature, combined with its highly coloured and inexpensive nature and otherwise good chemical stability has rendered it a popular test dye in semiconductor photocatalysis.

An emerging alternative to MB, as a dye-based test reagent for assessing photocatalytic activity, is Acid Orange 7 (AO7), an anionic azo dye. This mono azo dye is used in the textile industry, but as it is barely degradable by biological treatment and so often represents a significant pollutant in textile industry waste water. Like MB, AO7 absorbs strongly in the visible ($\lambda_{max} = 485$ nm; $\varepsilon_{485} = 2.1 \times 10^4\ M^{-1}\ cm^{-1}$) and does not absorb strongly in the UVA; indeed, it has an absorption minimum at around 350 nm. Moreover, none of degradation intermediates of AO7 absorb at wavelengths longer than 300 nm and so do not produce a transient, rate-lowering, UV screen to the titania photocatalyst film under test [17,18].

When dyes are used as test organics for assessing the photocatalytic activity of coatings via their *oxidation*, the latter is usually placed in contact with an aerated, neutral solution containing the test dye and its absorbance is monitored as a function of irradiation time. The photobleaching process is often slow (>30 min), as the dye is usually present at a low concentration (typically 1×10^{-5} M) and the semiconductor films are thin; however, the absorbance measurements are easy to make and the irradiation system simple to set up. A much faster test, based on an ink utilising a redox indicator, Resazurin (Rz), has been reported recently by one of this group [19,20]. The ink is deposited (by pen, stamp or spin coating) onto the photocatalyst layer under test and changes colour (blue to pink) at a rate that reflects its photocatalytic activity, due to its *reduction* to Resorufin (Rf) by the photogenerated electrons; the photogenerated holes are trapped by a sacrificial electron donor in the ink, glycerol [19]. In the Rz ink test method, the dye colour change is not only striking but also exceedingly sensitive, and much faster than *any* photocatalytic *oxidative* test method. For example: when used on commercial samples of self-cleaning glass, which employ a very thin, 15 nm, layer of titania as the active coating, the Rz ink changes colour within a few minutes, whereas the SA, MB and AO7 tests take many hours to effect a similar marked change in absorbance, under the same irradiation conditions [9].

Other work shows that the kinetics of Rz reduction correlate well with those for SA oxidation for a series of titania films with different photocatalytic activities, prepared by CVD [20,21]. Such a correlation is not too surprising given that under steady state irradiation a good photocatalyst must be able to effect efficiently both the coupled oxidation and reduction reactions, so that under steady state radiation a high rate of oxidation is matched by one for reduction. In support of this on recent works, others have noted that there is a correlation between the ability of titania to: (i) photomineralize organic substances, such as propan-2-ol in the presence of oxygen, and (ii) photo-reduce compounds, such as the stable radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) [22].

Following on from this work, in this paper we report on a study of the correlations between the rates of photo-oxidation of the commonly used test dyestuffs MB and AO7, one of which is a proposed ISO test [16], and those of a simpler, easier, photo-reduction Rz test ink by a series of titania films of different thickness, and therefore activities, prepared by the sol–gel method.

2. Experimental details

2.1. Chemicals

Titanium(IV) isopropoxide (97%; Sigma–Aldrich) and tetraethyl orthosilicate TEOS (purum 98%; Fluka) were used to prepare the titania and silica in the TiO_2/SiO_2/glass films. Ethanol absolute (p.a. Penta) and ethyl acetoacetate (puriss p.a. 99%; Fluka) served as solvents and hydrochloric acid (p.a. 36%; Penta) and nitric acid (p.a. 65%; Penta) were used as a sol–gel catalysts. Glycerol (99.5% Sigma–Aldrich) and hydroxyethyl-cellulose (Fluka) were used for preparing the Rz ink. The dyes AO7 (dye content ∼ 85%), MB (dye content ≥82%) and Rz (dye content ∼92%) were used as supplied by Sigma–Aldrich. The major impurities associated with these dyes are inorganic salts, typically NaCl. The structures of MB, AO7 and Rz are illustrated in Fig. 1.

2.2. Thin film SiO_2/TiO_2 preparation

For all titania films an underlayer, ca. 50 nm thick, of SiO_2 was first deposited on the microscopic glass substrate using the following sol–gel method. 10 g of the TEOS solution were diluted with 15 cm^3 of ethanol and the product stirred for 90 min. Small amounts of pure H_2O (2.5 cm^3) together with concentrated hydrochloric acid (0.5 ml) were then added to produce the sol–gel, which was stirred for 1 h and then stored, for up to 1 month, under cool, dark conditions and used as required.

The subsequent TiO_2 thin film overlayer(s) was prepared using Ti-isopropoxide as the Ti precursor in a sol–gel method, based on that reported by Haga *et al.* [23], but with slightly modified reaction conditions in order to produce titania films with an optimum activity. Thus, under vigorous stirring, 7 g of Ti-isopropoxide solution were added drop wise to 10 cm^3 of ethanol to create an initial titania sol. 10 cm^3 of ethanol together with 2 g of ethyl acetoacetate and nitric acid were then added to this solution, stirred for 24 h, and

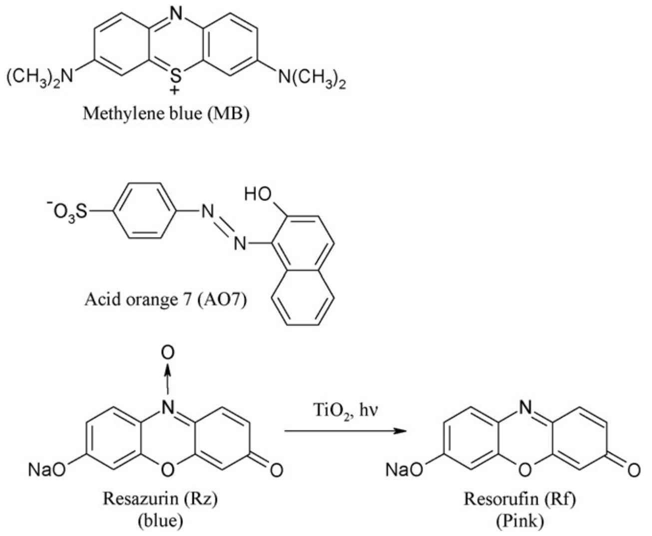

Fig. 1. Structures of the dyes: MB, AO7 and redox dye, Resazurin (Rz) and in its reduced form, Resorufin (Rf).

the produced titania sol stored for up to 3 months under cool, dark conditions and used when required.

The microscope (75 mm × 25 mm × 1 mm) soda-lime glass substrates, were first dip-coated (withdrawal speed: 60 mm min^{-1}) into the SiO_2 sol to form the necessary SiO_2 barrier against metal ion (mainly Na^+) diffusion from the glass substrate into the titania film. Sodium ion diffusion needs to be avoided since it: (a) raises the temperature of anatase formation and increases titania particle size [24], (b) promotes the recrystallization of anatase to rutile [25], (c) perturbs the crystallinity of TiO_2, preventing the formation of the anatase phase, producing recombination centers for photogenerated electron-hole pairs [26] and (d) produces an activity-lowering sodium titanate ($Na_2O{\bullet}xTiO_2$) and/or a brookite phase [27]. The SiO_2 interlayer was calcined at 550 °C for 3 h and the titania layer was then produced by subsequent dip-coating in the titania sol. After this dip-coating the titania film was calcined at 550 °C for 3 h. By repeating the above procedure, films comprising 2, 3, 4, 5 and 7 layers of titania on the SiO_2/glass substrate were created.

2.3. Dye oxidative degradation studies

The oxidation of the MB by dissolved oxygen, photosensitized by the titania films, was studied using a stirred, air saturated aqueous solution (3.5 ml) of the dye (10^{-5} M, pH = 6.7), placed in a 1 cm spectrophotometric cell, which had one of its faces replaced with the TiO_2/SiO_2 glass sample under test [7], with the photocatalyst film facing inwards. In this part of the work, all irradiations were carried out using the UVA light (1.0 mW cm^{-2}) from two 8 W BLB lamps (Vilber Lourmat, France).

The oxidation of the AO7 by dissolved oxygen, photosensitized by the titania films was performed as follows. The TiO_2 film under test was suspended in a glass cuvette (2.0 cm path length × 3.0 cm × 5.0 cm depth) into which was added an aqueous solution of AO7 test dye pollutant (10^{-5} M, pH = 6.6, 25 cm^3). All irradiations were carried out using the UVA light (1.5 mW cm^{-2}) from an 11 W BLB Sylvania Lynx light source.

In both of the above dye photobleaching studies, the dye solution was left in contact with the titania film under test for 45 min in the dark to ensure any dye adsorption was complete, before irradiating the system with UVA. A simple spectroscopic analysis of the dye solution before and after this equilibration step revealed that in all cases <2% of the dyes tested were adsorbed by the titania films.

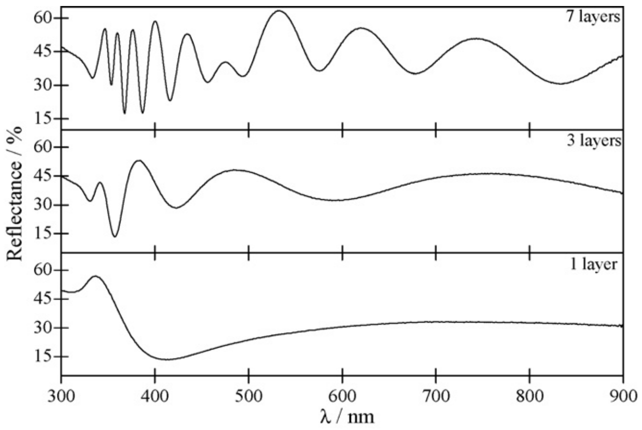

Fig. 2. Reflectance spectra for 1, 3 and 7 layers of TiO_2 on a SiO_2/glass substrate.

2.4. Rz ink preparation

The Rz ink used in this work comprised: 3 g of 1.5% aqueous solution of hydroxycelulose (HEC), 0.3 g of glycerol and 4 mg of the redox dye, Resazurin, Rz. A film of the ink is spun-coated onto the substrate under test and dried in an oven at 70 °C for 10 min. A typical dried ink film was ca. 590 nm thick when coated in the above manner and blue in colour. In this work, each Rz ink coated TiO_2/SiO_2/glass film was irradiated using the same light source as that used in the MB test.

3. Results and discussion

3.1. Characterization of TiO_2/SiO_2/glass films

Fig. 2 illustrates typical reflectance spectra of some of the TiO_2/SiO_2/glass films produced in this work. The films exhibited the typical interference spectra associated with thin films; a feature which allowed the thicknesses of the titania layer films to be calculated from the reflectance spectra using the NanoCalc software (Ocean Optics). The results show a linear dependence of layer thickness on number of deposited TiO_2 layers, i.e. the thickness of a single layer of titania was 60 ± 2 nm and increased approximately 60 nm for every added layer. The same dependence of titania layer thickness on the subsequent dip-coating with intervening calcinations was observed by J. Tschirch *et al.* [28].

The crystalline nature of the titania films were studied by XRD, using a Seifert XRD 3000 P diffractometer with Co radiation. Fig. 3

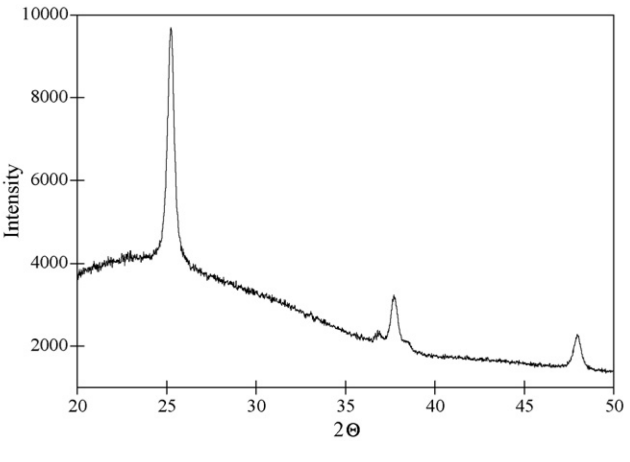

Fig. 3. Typical XRD spectra of photocatalytic film consisting of 7 titania layers, thickness 420 nm.

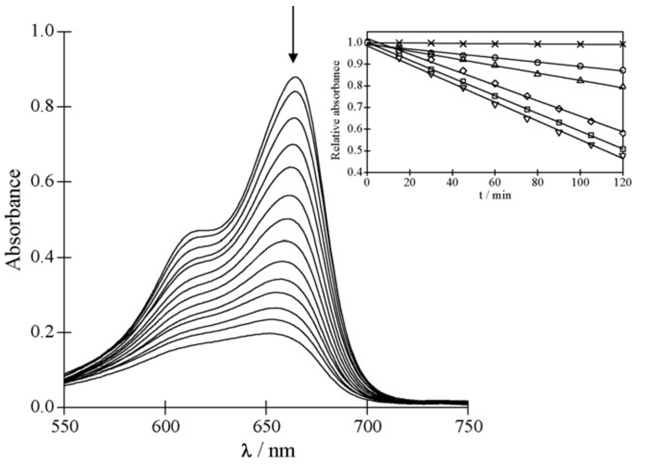

Fig. 4. Variation of absorbance spectra of MB solution (10^{-5} M) in contact with TiO_2/SiO_2/glass films with 7 titania layers as function of UVA (1.0 mW cm^{-2}) irradiation time (1 spectrum every 20 min). The insert diagram is a plot of the relative absorbance at 680 nm for: 0 (×), 1 (○), 2 (△), 4 (◊), 5 (□) and 7 (▽) layered TiO_2/SiO_2/glass films as a function of illumination time and indicates zero-order kinetics.

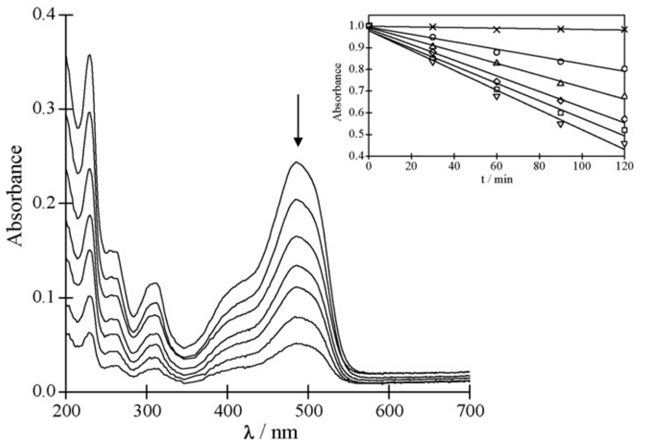

Fig. 5. Variation of absorbance spectra of AO7 solution (10^{-5} M) in contact with TiO_2/SiO_2/glass films with 7 titania layers as function of UVA (1.5 mW cm^{-2}) irradiation time (1 spectrum every 30 min). The insert diagram is a plot of the relative absorbance at 485 nm for: 0 (×), 1 (○), 2 (△), 4 (◊), 5 (□) and 7 (▽) layered TiO_2/SiO_2/glass films as a function of illumination time and indicates zero-order kinetics.

illustrates the X-ray diffractogram recorded for the 7 titania layers (420 nm thick) on SiO_2/glass substrate, which is characteristic of anatase titania. Similar results, i.e. same peak positions, were obtained for all the other layered titania films.

3.2. MB photodegradation

In this work, for each titania film under test a series of UV–vis spectra of the MB solution in the spectrophotometric cell were recorded as a function of UVA irradiation time; the results for a typical, 7 layer titania film are illustrated in Fig. 4. The variation in the absorbance at λ_{max} (660 nm) of the MB solution as a function of irradiation time was determined from such data for each of the layered films and the result plotted in the form of relative absorbance vs. irradiation time, illustrated in the insert diagram in Fig. 4. From the slope of the dependences the initial rate of the dye absorbance change, R_i [abs min^{-1}] was calculated.

3.3. AO7 photodegradation and correlation results

Similarly, each titania film was tested for activity using AO7 as the test dye. The results for a typical, 7 layer titania film are illustrated in Fig. 5 and reveal a rate of destruction not too dissimilar to that of MB. The variation in the absorbance at λ_{max} (485 nm) of the AO7 solution as a function of irradiation time was determined from such data for each of the layered titania films and the results, plotted in the form of relative absorbance vs. irradiation time, are illustrated in the insert diagram in Fig. 5.

Fig. 6 shows that the thicker the titania film the greater the rate of MB and AO7 degradation, R [mol min^{-1} cm^{-2}]. The analysis shows that there is a direct linear relationship between R and film thickness in the range of 1–5 titania layers (0–300 nm). For higher values of titania layer thickness the degradation rate of the dyestuff shows some deviation from the linearity, which is as expected given that with increasing layer thickness some plateau of R will be reached, when presumably all the UVA light is absorbed, and the rate of degradation will not increase any further. The plateau was observed also in the case, where particular titania layers were prepared by sedimentation from aqueous suspension of TiO_2 (Degussa P25) particles on glass [29].

As with the MB study, an analysis of the latter results reveals a direct relationship between R_i and film thickness and so it follows that there is a direct correlation between the initial rates of photooxidation of MB, R_i(MB), and AO7, R_i(AO7), as illustrated by the plot of the relevant initial rate data in Fig. 7.

The pH of the dyestuffs solutions was neutral, 6.7 and 6.6 for MB and AO7, respectively and in consequence such a correlation is not too surprising, given that the organics tested were both dyestuffs (albeit from quite different structural families, i.e. thiazine (MB) and azo (AO7) and, although of opposite overall charge, the titania films tested, prepared using the same, sol–gel, method (and so having the same surface morphology), will be near neutral an so likely to absorb either dye weakly and to an equal extent.

Previously, Lakhshmi *et al.* [15] reported that the rate of MB photocatalysed degradation increased with an increase in pH, exhibiting a maximum around pH 6.9–8.0. Ling *et al.* [30] observed the same dependence, but a degradation rate for MB which increased to maximum at around 12. In contrast, the degradation rate of AO7 increased with decreasing pH, reaching a minimum at pH 5.5–6.0 [31] but Li *et al.* [32] did not observe any minimum till the pH 7.5.

The direct comparison of MB and AO7 degradation at pH 4.2 was done by Yamazaki and Nakamura [33]. At these experimental conditions the degradation rate of AO7 was higher by factor 6.8 than that of MB. The present results show that the degradation rate of AO7 is higher that that for MB by factor 1.8, but that this fac-

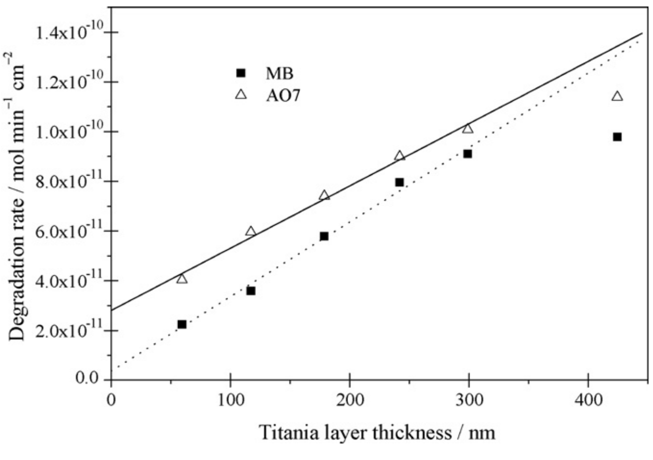

Fig. 6. Degradation rates of MB and AO7 as a function of layer thickness.

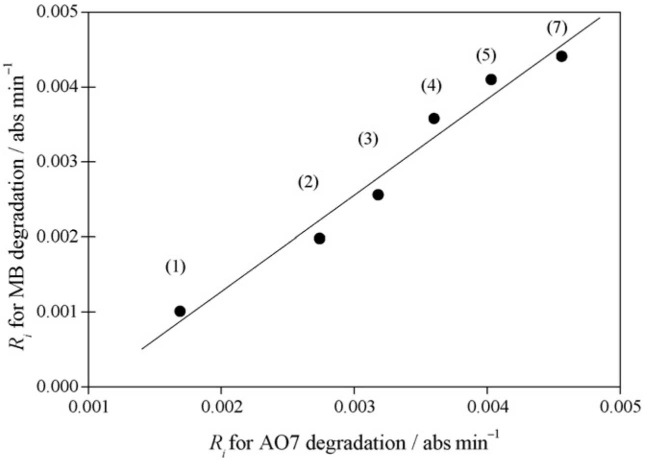

Fig. 7. Correlation of initial rates of MB degradation (data from Fig. 4) MB and AO7 degradation (data from Fig. 5) using sol–gel titania films of different thicknesses. The numbers in parentheses refer to the number of layers of titania.

tor decreases with increasing titania film thickness. Under the near neutral conditions of the work reported here the charge on the TiO_2 is negligible, and thus the overall charge of the dyestuff should not have any effect on the degradation rate. This is probably why the MB and AO7 photocatalytic degradation rates at the pH values used in this work are rather similar.

3.4. *Rz ink test*

In the Rz test, as noted earlier, the glycerol acts as a hole trap, allowing the photogenerated electrons to reduce the blue Rz, dye to its pink, reduced form, Resorufin, Rf, i.e.

$$\text{Glycerol} + h^+ \rightarrow \text{Glyceric acid} \quad (11)$$

$$\text{Rz} + e^- \rightarrow \text{Rf} \quad (12)$$

All the layered titania films were assessed for photocatalytic activity using the Rz ink test and the spectral variations observed as a function of irradiation time for a typical 7 layer titania film are illustrated in Fig. 8. Note the very short times (every 5 s) between recording each spectrum compared with those for MB (every 20 min) or AO7 (every 30 min); i.e. the Rz test is >240 faster than the other tests, as well as being simpler to use, under otherwise identical irradiation conditions.

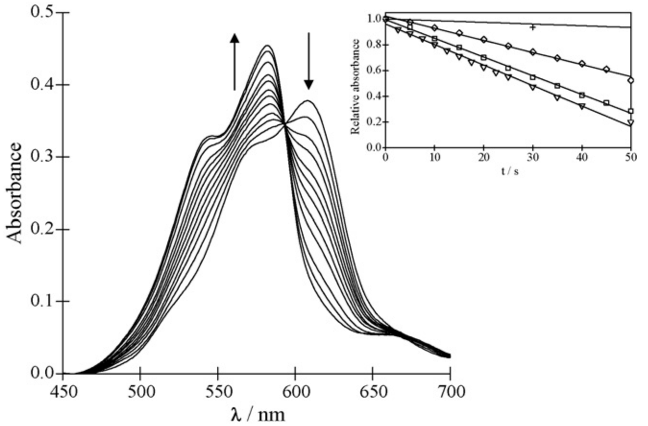

Fig. 8. UV–vis absorption of a typical Rz ink film in contact with TiO_2/SiO_2/glass films with 7 titania layers as function of UVA (1.0 mW cm^{-2}) irradiation time (1 spectrum every 5 s). The insert diagram is a plot of the relative absorbance at 610 nm for: 3 (+), 4 (◊), 5 (□) and 7 (▽) layered TiO_2/SiO_2/glass films as a function of illumination time and indicates zero-order kinetics.

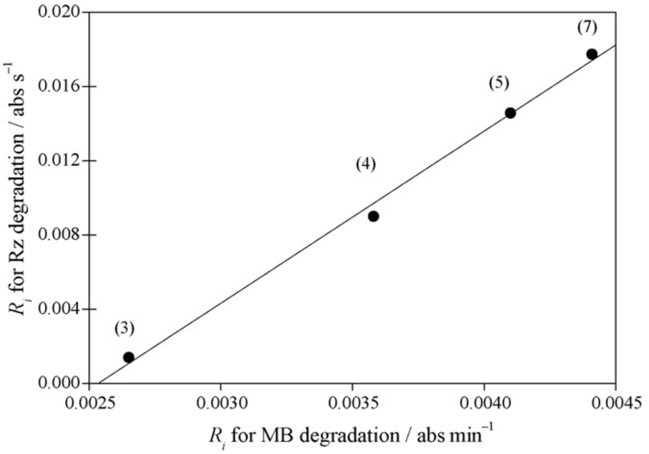

Fig. 9. Correlation of initial rates of Rz reduction (data from Fig. 8) and MB degradation (data from Fig. 5) using sol–gel titania films of different thicknesses. The numbers in parentheses refer to the number of layers of titania.

As with the MB and AO7 work, the initial rate of the dye absorbance change, R_i(Rz) for the Rz ink was found to be directly proportional to the number of titania film layers and so the initial rate of Rz to Rf conversion, R_i(Rz), was found to be directly proportional to that for MB photo-oxidation, R_i(MB), as is clear from the plot of the results illustrated in Fig. 9. It follows from Fig. 6 that R_i(Rz) and R_i(AO7) are also directly related.

It has to be mentioned that it is not obvious that the rate of photo-reduction of a *dried Rz ink* on these same titania films will correlate with the *solution based* photo-oxidative bleaching of MB or AO7. Thus these findings are particularly novel.

4. Conclusions

Titania films, produced using a sol–gel method, when immersed in aqueous solution are able to photosensitize the oxidation of MB, and AO7, by dissolved oxygen. The initial rates of destruction of these dyes, R_i(MB) and R_i(AO7), both depend directly upon the thickness of the titania films over the range 50 to 350 nm. R_i(MB) and R_i(AO7) values, derived using titania films of different thickness, not only correlate well with each other, but also with the rate of reduction of an Rz ink film. The Rz ink film test is much faster and simpler to use than either of the dye solution tests and shows promise as a possible semi-quantitative and quantitative method for assessing the photocatalytic activities of titania films, especially when they have been prepared using a similar method and so have a similar surface morphology. Given that: (i) the likelihood that the MB test will be adopted by ISO as a standard test for photocatalytic films, (ii) there is a good correlation between R_i(MB) and R_i(Rz) and (iii) the latter is much faster and easier to implement, there appears to be some justification for employing the Rz test, instead of another dye test, for assessing the activities of photocatalytic films, especially as an aid in: rapid quality assurance, correct fitting, marketing, *in situ* assessment and the identification of fake (i.e. non-photocatalytic) products. Further work is in progress to assess the ability of the Rz ink test to correlate with the MB test when using titania films of very different surface morphologies and degrees of crystallinity.

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