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Probing the activities of UV and visible-light absorbing photocatalyst *powders* using a resazurin-based photocatalyst activity indicator ink (*Rz P_{aii}*)

Andrew Mills*, Nathan Wells, Christopher O'Rourke

Queen's University of Belfast, School of Chemistry and Chemical Engineering, Stranmillis Road,
Belfast, BT95AG

e-mail: andrew.mills@qub.ac.uk

Abstract

A variety of semiconductor photocatalyst powdered materials, i.e. TiO_2 , CdS , WO_3 and C_3N_4 , are able to mediate the UV (365 nm) photocatalysed reduction of *Rz* (blue) to *Rf* (pink) by glycerol, when used as a dispersion in **deaerated**, aqueous solution. Under the same conditions, but using visible (455 nm) light, the same reaction is promoted by the visible-light absorbing semiconductors, CdS , WO_3 and C_3N_4 . These powders are mixed with SiO_2 and PTFE powder and pressed as discs, for assessment using a **Rz Photocatalyst Activity Indicator Ink**, i.e. *Rz p_{aii}*, coated onto the surface of each disc. Results show that only the TiO_2 pressed film, with UV irradiation, is able to photocatalyse the reduction of *Rz* to *Rf*, under ambient conditions, due to competition from ambient air. However, when covered with SellotapeTM to exclude O_2 , all but the C_3N_4 photocatalyst demonstrated photocatalytic activity, and in the same order as observed in solution for this reduction reaction, using UV or visible light. Irradiations carried out using 617 nm light on the same systems reveal that the dye is slowly bleached, at a rate that is largely independent of the semiconductor/insulator present, and no *Rf* is generated, suggesting dye degradation *via* photolysis rather than dye sensitisation. This is the first example of the use of an *Rz p_{aii}* responding to visible light absorbing photocatalysts and the first example of an *Rz p_{aii}* being used to assess the photocatalytic activity of powdered SC photocatalysts.

Key words: resazurin; reduction; inks; powder; UV; visible

1. Introduction

Semiconductor photocatalysis is a well-established research subject which has led to a number of significant commercial products, such as: 'self-cleaning' glass, tiles, concrete, paint and fabrics [1,2]. In almost all such commercial products the active ingredient is a semiconductor, SC, where SC = TiO₂, which absorbs ambient light (UV light if TiO₂ is used), from a solar or artificial light source, to produce electron-hole pairs, which can recombine, in the bulk or at the surface of the semiconductor or, most importantly for semiconductor photocatalysis, react with surface-adsorbed species [3]. Most commercial photocatalytic commercial materials use the SC, usually TiO₂, to mediate the photo-oxidation of adsorbed organic species, either dissolved in solution, or in the form of volatile organic carbons, to their mineral form, with the concomitant reduction of adsorbed O₂ to water, i.e.

where, $h\nu$ is the energy of the incident light which must be greater than or equal to the bandgap energy of the SC, E_{bg} , and where too, mineral acids are generated if the organic species has one or more heteroatoms, such as S, Cl or N, in its structure [1]. Another important application is the use of some SC's, TiO₂ in particular, to mediate the photooxidation of NO_x, i.e. NO and NO₂, to nitrate [4].

In research and industry it is obviously essential to assess and compare the activities of new and existing photocatalytic materials. It is not surprising, therefore, to note that in recent 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].

At present there is no ISO for testing photocatalytic *powders*, despite the fact that many of the new photocatalytic materials that are reported in the literature are in powder form. In research, however, the most popular approach to assessing the photocatalytic activity of powdered SCs is to disperse the semiconductor photocatalyst powder under test in an aqueous solution of a dye, such as MB or Acid Orange 7, AO7, and monitor the rate of photobleaching of

the dye, which is presumed to be *via* the oxidation reaction (1) [8]. This method of testing is appropriate when the excitation light, i.e. $h\nu$, is NOT absorbed, or absorbed very weakly, by the dye itself. Thus, the MB ISO [6], for photocatalytic films specifies that it is for UVA (NOT visible) excitation only, since MB absorbs very little UVA light emitted by the black light (BL) or blacklight blue (BLB) lamps required by this ISO.

If the excitation light does comprise a significant level of photons of wavelengths which will be strongly absorbed by the dye, then a non-photocatalytic, dye-bleaching processes, such as dye photolysis [9,10], or dye-photosensitisation [8,11,12], can be very effective in bleaching the dye.

The dye photosensitisation process usually involves the electronic excitation of the dye, D, to D^* , by light of sufficient energy, $h\nu'$, which allows it to inject an electron into the conduction band of the semiconductor, SC, which in turn then reacts with an oxidizing agent, Ox, present in the system [8,11]. The process can be summarized as follows:

where $D^{+\bullet}$ is an oxidized radical of the dye that is unstable and able to react further to produce colourless degradation products. Usually, Ox is O_2 , although other oxidizing agents, such as H_2O_2 , Fe^{3+} and Cu^{2+} , have been used for the same purpose. A classic example is provided the work of Wu *et al.*, in their study of the photosensitized bleaching of Rhodamine B under visible light in aqueous dispersion of TiO_2 [12], and the reviews of Rochin *et al.* [11] and Rajeshwar *et al.* [8] provide many more such examples. Note, however, that in most, if not all reported cases, an oxidizing agent, usually O_2 , is present and, in contrast, most of the work described here is carried out under **anaerobic** conditions, in the presence of a notable sacrificial electron donor, glycerol, rendering a dye-photosensitisation reaction unlikely.

If dye photolysis or dye photosensitisation occurs, then a photocatalyst can appear to exhibit visible light photocatalytic activity, whereas in fact the observed photobleaching of the dye is NOT associated with semiconductor photocatalysis, i.e. reaction (1), but instead is due to a dye photolysis and/or dye photosensitisation processes (reaction (2)).

An excellent example of the above has been reported by Ohtani and his co-workers [13], in a study of the MB/TiO₂/O₂ system which showed that the action spectrum (wavelength dependence of photoinduced reaction rate) resembled that of the diffuse-reflectance spectrum of surface-adsorbed MB, as would be expected for a dye-sensitised reaction. Interestingly, using the same system and technique, these workers also reported that a sulfur-doped TiO₂ catalyst 'has activity under visible light and that the decomposition mechanism depends upon excitation wavelength', implying that using a dye to assess photocatalytic activity is possible, provided a suitable wavelength of excitation is used, as in the case of the S-TiO₂. Clearly it is vital to identify and utilize a wavelength region(s), **WR(SC)**, where the semiconductor absorbs and the dye does not, before any claim of photocatalysis (especially visible light photocatalysis) can be made. These workers also suggest rightly here [13] and later [14] that the usual control experiments, i.e., negligible photoinduced MB degradation in the absence of TiO₂, cannot exclude the participation of dye-sensitization and so is flawed.

Although Ohtani *et al.* suggest that in such a system an action spectrum is needed in order to identify the 'origin of the photoresponse' [13], this is often unnecessary, especially if the object is to identify a **WR(SC)**. Instead, it is more usual, quicker and convenient to run the UV/Vis absorption or diffuse reflectance (DRS) spectroscopy of the system, and the individual components, so as to reveal where the SC and dye absorb, and, more crucially, if there is a suitable **WR(SC)** from which to select an excitation wavelength. In addition, such work will reveal if a charge transfer, CT, complex is formed between the SC and the substrate, which are well-known for TiO₂, for example, when using simple molecules, such as: catecholate-type ligands [15], phenols [16,17] and aromatic carboxylic acids [17], as the 'test pollutant'. These CT complexes are usually identified *via* the appearance of additional absorption bands, often in the visible, in the DRS.

In a SC/dye system where a **WR(SC)** can be identified, by UV/Vis absorption or DR spectroscopy, it is reasonable to use it to select an excitation wavelength to assess the activity of the SC, i.e. without recourse to recording an action spectrum. A classic example of this is MB, which, from its absorption spectrum, absorbs little in the UVA region, especially around 365 nm, and as a consequence has been used routinely over the years in the assessment of the activity of many UV-absorbing semiconductors [8] and is the basis of one of the most established ISO tests [6,18]. In contrast, as noted above, Ohtani *et al* found MB unsuitable for assessing the photocatalytic activity of visible light photocatalysts, at high

concentrations at least ($5 \times 10^{-5} \text{M}$), because its absorption spectrum is appreciable throughout the visible region, 400-680 nm; *i.e.* $\lambda_{\text{max}} = 665 \text{ nm}$, Half (Peak) BandWidth (HBW) = ca. 150 nm [13].

The above concern has not stopped many from using MB, and other dyes, to test the photocatalytic activity of **visible-absorbing** semiconductors *via* reaction (1), however, nowadays, the more wary researcher tends to shy away from using it, and other dyes, such as AO7, due to the often potentially ambiguous nature of the results. In summary, although dyes can be used as a method for testing photocatalyst activity, great care needs to be taken to ensure that the incident excitation light is NOT absorbed, or absorbed very weakly, by the dye itself [19].

In recent years, this group has developed a rapid, simple method for assessing the activities of photocatalytic films, involving the use of photocatalyst activity indicator inks (*paiis*) [20-22]. The most used and effective of the *paiis* developed so far employs the redox dye, Resazurin (Rz), which is blue and readily, and irreversibly, reduced by the photogenerated electrons on TiO_2 for example, to resorufin (Rf), which is pink [20,21]. This reduction reaction is accompanied by the concomitant rapid and irreversible reaction of the photogenerated holes with glycerol, which is also present in the ink film. The overall photocatalytic process is as follows:

where, in the case above, SC = TiO_2 and $\text{hv} = \text{UV}$. Other work has established the existence of a direct correlation in the rate of photocatalysed reduction of Rz in an Rz *paii*, via reaction (3) with that of the photocatalysed oxidation of a thin solid organic film (stearic acid) or MB in solution, via reaction (1), when mediated by a TiO_2 film, and electronically excited using UVA radiation [21,23]. Typically, the Rz *paii* test is completed within a few minutes, and so much faster than any of the more traditional tests based on reaction (1). For example, the Rz *paii* test is typically 45 times faster than the MB in solution ISO test, when using commercial self-cleaning glass.

To date, the Rz *paii* test has been developed and used for testing **films** of UV-absorbing photocatalysts, such as TiO₂; it has never before been used to test the activities of SC **powders**, especially not **visible light** absorbing powders. However, as described above, under certain conditions this is possible and enables us to study the use of an Rz *paii* as a probe of the activities of pressed **powder** discs of a number of established **UV** and **Visible** light-absorbing SC's, using either UVA radiation (365 nm), or visible light (455 nm) as the excitation radiation. Specifically, in this work high energy LEDs, with peaks at 365 and 455 nm, are used to provide, the necessary narrow bands (average HBW = 13 nm) of excitation light, the peak wavelengths of which were chosen, based on UV/Visible absorption and diffuse reflectance, spectroscopy, so that the incident excitation light is NOT absorbed, or very weakly so, by the Rz dye itself.

2. Experimental

2.1 Materials:

P25 titania was supplied by Degussa (Evonik). Unless otherwise stated, all other materials were purchased from Sigma Aldrich and used as received. All UV-vis spectra were recorded using an Agilent Technologies Cary 50 UV/vis spectrophotometer. The C₃N₄ photocatalyst powder was prepared using a literature method [24], in which, briefly, 10 g of urea were placed in a crucible and heated to 550°C at a ramp rate of 15°C min⁻¹ and held there for 2 h, before being allowed to cool in air. Once cooled to room temperature, the pale yellow powder was used without further treatment. The XRD pattern recorded for the powder corresponded to that reported for C₃N₄ [25].

2.2 Characterisation of the semiconductor photocatalysts

The specific surface area of each of the different semiconductor powders used in this work was determined using the BET N₂ adsorption method (Micromeritics Tristar 3020 instrument). The X-ray diffraction patterns, used to identify the crystal phase of each of the semiconductor

photocatalyst powders, were determined using a Panalytical X'pert powder X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ nm) at 40 kV and 40 mA with a step size of 0.06°. Bandgap (E_{bg}) [26], band position (*i.e.* of the conduction and valence band, E_{CB} and E_{VB}) [26] and point of zero charge values [26-31] were gleaned from the literature. Table 1 lists these key characteristics of the tested semiconductor powders.

Table 1: Semiconductor photocatalysts characteristics

Powder	Colour	E_{cb}/V^a	E_{vb}/V^a	E_{bg}/eV	Surface Area	Crystalline	p.z.c
					$/m^2 g^{-1}$	Form	
SiO ₂ (Aldrich, S5631)	White	--	--	ca. 9.3	6.9	quartz	3.7
P25 (TiO ₂)	White	-0.29	2.91	3.2	53	anatase, rutile	6.2
C ₃ N ₄	Yellow	-0.83	1.87	2.7	111	graphite like	7.2
WO ₃ (nano) (Aldrich, 550086)	Green	0.17	2.87	2.7	23	monoclinic	1.5
CdS (Aldrich, 217921)	Orange	-0.52	1.88	2.4	54	hexagonal	2

a: Band positions quoted with respect to the NHE at pH 0.

2.3 Irradiation sources

All irradiations were carried out using one of three different high power light emitting diodes, LEDs, purchased from RS Components. The three LEDs had emission peaks (see figure 1) at the following wavelengths; **365 nm** (HBW = 10 nm; LED Engin, LZ1 UV LED 365 nm Gen 2 (Maximum wattage = 2.8 W), **455 nm** (HBW = 16 nm; OSOLON+ PowerStar Deep Blue 455nm (Maximum wattage > 2.2 W), and ThorLabs; **617 nm** (HBW = 14 nm; Thorlabs High-Power LED M617D2 (Maximum wattage = 2.2 W).

Figure 1: Emission spectra of the 365, 455 and 617 nm LEDs (HBW's = 10, 16 and 14 nm, respectively) and bandgap energies (broken red lines) of the different semiconductors used in this work. The broken blue line is the energy associated with the $\lambda(\text{max})$ value for Rz in aqueous solution. The intensity of each LED has been normalised to the peak LED emission output, measured with respect to power (i.e. $\mu\text{W cm}^{-1} \text{ eV}^{-1}$)

The emission spectra (irradiance: in units: $\mu\text{W cm}^{-1} \text{ eV}^{-1}$ (or nm^{-1}) versus wavelength) of the LEDs used in this work were recorded using a spectroradiometer (model: OL756, Gooch & Housego) and are illustrated in figure 1, along with the bandgap energies of the different

semiconductors used and the $\lambda(\text{max})$ value for Rz in aqueous solution. The same spectroradiometer was used to determine the typical irradiance value exhibited by each LED, when used to irradiate the different samples (solutions and films). Thus, the irradiance values used for the films were: 1.5, 14 and 10 mW cm⁻² for the 365, 455 and 617 nm LEDs, respectively, at a distance of 3 cm from the film sample (beam size = ca. 6.5 cm). For the solution work, the LED was held 2 cm from the side of the cuvette giving a beam size of ca. 5 cm and irradiances of 5, 20, and 15 mW cm⁻² for the 365, 455, and 617 nm LEDs respectively.

2.4 Solution irradiations

Solutions were prepared by adding the photocatalyst powder under test (usually 5 mg, but for WO₃ and C₃N₄, 10 and 50 mg, respectively) to an aqueous solution of glycerol, in order to generate dispersions that absorbed sufficient incident light so as to effect measurable rates of dye photo-bleaching. The latter translated to a typical background absorbance for each dispersion at 800 nm of ca. 0.18; and the higher concentrations of WO₃ and C₃N₄ were required because they didn't form very good, stable dispersions, in comparison to the other semiconductors. Note also that for WO₃ only, the pH of the dispersions, before dye addition was ca. 4.1, and given the pK_a of Rz is 5.7, the dispersions had to be pH-adjusted to 7.5.

The solution to which each semiconductor powder was added comprised 100 g of 10 wt.% aqueous solution of glycerol. The resulting dispersion was then agitated to ensure a uniform suspension of the catalyst. For each irradiation, the suspension under test was purged with argon under constant stirring for 10 minutes, after which 3 mL of the suspension were transferred to an argon purged, 1 cm cuvette equipped with a crown-shaped stirrer (VWR, product no: 442-0502). To this dispersion, a 30 μL plug of 2×10^{-2} M Rz was injected to give an initial dye concentration of 2×10^{-5} M. The cuvette was then sealed to prevent air leaking into the reaction cell, and placed inside a UV-vis spectrophotometer, where it was irradiated *in-situ*, using one of the specified LEDs, see section 2.3, under constant stirring and the change in absorbance spectrum of the dye solution monitored spectrophotometrically as a function of irradiation time, t .

2.5 Preparing pressed film photocatalyst

A range of semiconductor powders were pressed into 13 mm diameter (1 mm thick) discs using an IR pellet press die (Specac). When the neat semiconductor powders, with 15 wt% PTFE powder binder (Aldrich Chemicals) were used to make the discs, see figure 2, they proved – for the most part – to be much too photoactive to enable their ready assessment using the Rz ink. Thus, instead, the discs were made using usually SiO_2 – a non-photocatalytic, insulator oxide - mixed with the PTFE powder binder in a 50:50 ratio, and 1 wt% of the semiconductor under test. In such cases, 20 mg of the semiconductor (P25 , WO_3 , CdS) were added to 1.98 g of the 50:50 SiO_2 /PTFE mixture and ground together in a mortar and pestle to produce a well dispersed 1% SC loaded powder, 200 mg of which were then transferred into a 13 mm KBr die and subjected to 2 T of pressure for ca. 5 s. Photographs and diffuse reflectance spectra, of the original powders, the neat discs (15 wt% PTFE) and the more SiO_2 diluted discs are illustrated in figure 2.

(a)

(b)

Figure 2: (a) Photographs of the semiconductor powders and their pressed discs used in this work and (b) diffuse reflectance spectra of the different neat semiconductor discs, *i.e.* from right to left): CdS, WO₃, C₃N₄ and TiO₂. The broken lines illustrate the emission spectra of the 455 and 365 nm LEDs. The intensity of each LED has been normalised to the peak LED emission output, measured with respect to power (*i.e.* $\mu\text{W cm}^{-1} \text{ nm}^{-1}$).

2.6 Film disc irradiations

The preparation of the Rz ink used in this work has been described elsewhere [32] and comprised: 20 g of 1.5% HEC, 2 g glycerol and 20 mg Rz. For all Rz-ink-on-SC-disc irradiations, a few drops of the Rz ink were pipetted onto the pressed semiconductor disc and spun at 2000 rpm for 30 s. The semiconductor disc, with Rz ink film coating, was then placed 3 cm away from the LED and irradiated. The progress of reaction (3) was then monitored periodically by removing and photographing the ink-coated disc using a digital SLR (Canon 7D, 24–70mm f2.8 L USM lens) as a function of irradiation time. This was repeated until no further colour change was observed in the Rz ink, or after a period of 10 min, whichever was the shorter period of time. All photographs were analysed using the free ImageJ (v 1.51d) software [33], which allowed the extraction of the RGB data from each photographed image of the disc as a function of irradiation time. This data was used to calculate the normalized red component (RGB_R') at each sampled irradiation time, t , for each disc. From a plot of this data for each disc, i.e. RGB_R' vs. t , a value for an associated time taken to bleach 90% of the red component of the Rz ink, i.e. $t_{tb}(90)$, was determined. The latter parameter corresponds to the time taken to lose 90% of the blue colouration, due to Rz ink, as the dye is reduced to Rf and the reciprocal of this parameter is taken as a measure of the rate of the photocatalysed reaction (3) by the SC under test. Further details concerning this type of analysis are reported elsewhere [34].

3. Results

The recorded band positions of the semiconductor photocatalysts used in this study are illustrated in figure 3.

Figure 3: Band positions (at pH = 0) and band gaps of the semiconductors used in this work, along with the pseudo redox potential for the Rz/Rf couple.

The reduction of Rz to Rf is an irreversible process and so the reporting of a redox potential for this couple is inappropriate, however, others [35] have estimated that Rz 'is reduced at potentials below MB [$E^\circ(\text{MB/LMB}) = 0.011$ at pH7]) and above Rf [$E^\circ(\text{Rf/DHRf}) = -0.051$ V at pH 7]'. Thus, for the purposes of the schematic illustrated in figure 3, an approximate empirical value of $E^\circ(\text{Rz/Rf})$ of ca. -0.020 V at pH 7 is indicated, which is equivalent to 0.220 V at pH 0. A brief inspection of figure 3, reveals that $E^\circ(\text{Rz/Rf})$ should be more positive than the redox potentials of the conduction bands for all the different semiconductors used in this work, indicating that the reduction of Rz, to Rf, by the photogenerated conduction band electrons, should be thermodynamically feasible for all the SC's used here, even for WO_3 , which has an $E^\circ(\text{e}_{\text{CB}}^-)$ value of 0.17 V. However, in order to check the feasibility of reaction (3), for all the

semiconductors used here, the photocatalysed reaction (3) was first probed using: (i) an argon-purged, aqueous solution containing Rz (2×10^{-5} M) and glycerol (10 wt%), and a dispersion of the photocatalysts under test, and (ii) either the UV (365 nm) or visible (455 nm) LED as the irradiation source. The results of this work are described in the next section.

3.1 The photocatalysed reduction of Rz in solution

As noted above, dispersions of each SC were irradiated with visible (455 nm LED) and UV (365 nm LED) radiation and, in each case, the absorption spectrum of the anaerobic Rz-containing dispersion was recorded as a function of irradiation time. A typical set of absorption spectra arising from this work is illustrated in figure 4; in this case for the visible light irradiation of a dispersion of CdS. The observed rapid changes in spectra, i.e. the disappearance of the peak at 608 nm (due to Rz) and concomitant appearance of the peak at 585 nm (due to Rf) suggest that the photocatalytic reaction (3) in aqueous solution, mediated by a powdered dispersion of CdS, is rapid under visible light irradiation.

Figure 4 Recorded spectral changes for the photocatalysed reduction of 3 ml, of an argon purged, aqueous solution, containing Rz (2×10^{-5} M), glycerol (10 wt%) and 0.5 wt% dispersion of CdS, in a 1 cm cuvette. Spectra were recorded for every 20 seconds of visible (455 nm) light irradiation.

Subsequent work demonstrated that all the SC photocatalysts tested, under visible and UV illumination, produced the same changes in absorption spectrum, showing they were all able to convert Rz to Rf via reaction (3), but at different rates.

A brief comparison of (i) the spectrum illustrated in figure 4 for Rz, which is typical of all such irradiations in solution, and (ii) the emission spectra of the UV (355 nm) and (especially) visible (455 nm) LED excitation sources illustrated in figure 2, reveals that there is little or no spectral overlap between the two, i.e. both emission spectra fall in wavelength regions where the active semiconductors absorb the excitation energy, **but the dye (Rz) does not**. Thus, the LEDs used are operating in **WR(SC)'s**, and so fulfil one of the key conditions for studying photocatalytic reactions involving a dye as the test substrate. The observation of no additional spectral peaks, nor significant shifts in λ_{max} for Rz and Rf, when in the presence of any of the semiconductors, suggests no semiconductor-dye CT formation.

Note that although Rz is initially reduced to Rf, via the photocatalytic reaction (3), as the irradiation progresses the Rf is subsequently reduced to dihydro resorufin (dH-Rf) which is colourless, *via* the following photocatalytic reaction:

Thus, in order to gain a measure of the overall photocatalysed reduction of Rz, just the change in absorbance, at 608 nm, ΔAbs_{608} , is reported here as a function of irradiation time, although, in all cases, the initial large decrease in ΔAbs_{608} was found to correlate directly with the much smaller (and less easy to measure) increase in ΔAbs_{585} , due to Rf production.

The light-induced spectral changes of the type illustrated in figure 4, were recorded for each of the SCs tested, and an associated ΔAbs_{608} versus irradiation time, t , profile extracted; the results of this work, arising from the **visible light irradiation** study, are illustrated in figure 5(a). From these decay profiles, it is apparent that both TiO_2 and SiO_2 do not show any appreciable visible light photocatalytic activity, as would be expected given their large (UV only absorbing) band gaps. These two 'blank' runs also demonstrate that the non-photocatalytic processes associated with dye photobleaching, such dye photolysis and dye photosensitization, are also negligible when using a 455 nm LED as the visible light source. These observations are not too

surprising given the absorption spectra of both R_z and R_f, as illustrated in figure 4, reveal that neither species absorb strongly at 455 nm.

In contrast to the ΔAbs_{608} vs. t profiles for TiO₂ and SiO₂, the remaining SCs do appear to show activity with respect to the photocatalysed bleaching of R_z to R_f, i.e. reaction (3), with activities in the order: CdS (0.5) >> WO₃ (1) > C₃N₄ (5) >> TiO₂(0.5), SiO₂ (0.5), where the numbers in parenthesis refer to the different loadings used (in wt%) so as to create dispersions with approximately the same background absorbance at 800 nm, i.e. 0.18. If the same loading was used, the order is likely to stay the same but the differences would be more striking. In listing the order of activities here, and elsewhere, this is not to say that this would be the order found for all samples of the same semiconductors, given photocatalytic activity depends markedly on so many different parameters including: surface area, crystalline plane, defect sites and density, impurities etc.

The much lower activity of the C₃N₄, when compared to WO₃, see figure 5(a), despite the fact that the reported band gaps are the same (see figure 1), is not too surprising given the colours and diffuse reflectance spectra illustrated by these two powders are quite different (see figure 2). Thus, the relevant spectra illustrated in figure 2 show clearly that the yellow C₃N₄ overlaps much less well with the emission spectrum of the 455 nm LED, than does that of the green WO₃. It follows that the above difference in rate is most probably due to the difference in spectral overlap with the 455 nm LED. In contrast with the C₃N₄ and WO₃ powders, the diffuse reflectance spectrum of the orange/red CdS powder overlaps significantly with the emission spectrum of the 455 nm LED (see figure 2) and so this SC exhibits the greatest rate for the photocatalysed reaction (3), under visible light irradiation of all the SC's tested.

Figure 5 Plots of (a) visible (455 nm; 20 mW cm⁻²) and (b) UV (365 nm; 5 mW cm⁻²), ΔAbs_{608} vs illumination time, t , profiles determined for the different SCs for the photocatalysed reduction of Rz in aqueous solution containing 10 wt% glycerol. The SC dispersion concentrations used for TiO₂, C₃N₄, CdS, WO₃ and SiO₂, were: 0.05, 0.5, 0.05, 0.1 and 0.05wt %, respectively.

Figure 5(b) illustrates the recorded ΔAbs_{608} , vs t , profiles, when the same set of SCs, dispersed in an anaerobic aqueous solution of Rz, were irradiated with UV (365 nm) light, under otherwise the same experimental conditions. In contrast to the previous (visible light) study, there is no issue of poor spectral overlap with the emission spectrum of the LED, as illustrated by the data in figure 2(b) and the order of photocatalytic activities for reaction (3) appears to

be: TiO_2 (0.5) > CdS (0.5) > C_3N_4 (5) >> WO_3 (1) > SiO_2 (0.5); figures in parenthesis refer to semiconductor loading (in wt%). Note that the UV decay profiles were recorded over a much shorter period of time than the visible light irradiations (i.e. 60 instead of 240 min), because the activity of TiO_2 was so high, even though the UV irradiance was 4 times lower, i.e. 5, instead of 20 mW cm^{-2} . It appears reasonable, given the noted high photocatalytic activity of P25 TiO_2 , that this SC is the most active of all those tested, and that SiO_2 , with its bandgap of 9.3 eV, appears, once again, to be inactive.

From a brief inspection of the decay profiles illustrated in figure 4, it might be thought odd that WO_3 appears so much lower in activity (rate = 1.6×10^{-3} absorbance per min), given the comparatively striking activity (rate = 4.3×10^{-3} absorbance per min) it exhibited when illuminated with visible (455 nm) light. However, the latter low rate is consistent with the UV irradiance used, which was four times lower than the visible irradiance, i.e. 5 instead of 20 mW cm^{-2} . From the results in figure 5(b), C_3N_4 appears to have a greater photocatalytic activity than WO_3 , presumably because it – like WO_3 – absorbs all incident UV light photons, due to its significant spectral overlap with the emission spectrum of the UV LED, and its much greater surface area (see Table 1). Note, however, if the same loading for each semiconductor was used here, the order of activities would most likely be different. But, overall, the relative rates of reaction (3) for the different SC's tested, when dispersed in aqueous solution, under visible and UV irradiation appear consistent with what we know about these SCs.

3.2 The photocatalysed reduction of Rz by pressed semiconductor films

In almost all previous work carried out on semiconductor films, such as self-cleaning glass and paint, using photocatalyst indicator inks, the Rz ink coating on the semiconductor film under test was irradiated in air [32]. This is in sharp contrast with all the work carried out in aqueous solution described above which was carried out under O_2 -free conditions.

Typically, using a commercial sample of self-cleaning glass, under aerobic conditions, the transformation in colour of an Rz ink (blue to pink) is usually effected within 10 minutes or less,

using a UV irradiance of ca. 1 mW cm⁻². However, it is known [32] that the O₂ present in air is able to compete with the Rz for reduction by the photogenerated electrons, i.e.

and so effect a decrease in the rate of reaction (3), typically by ca. 40% for TiO₂ self-cleaning films; although, to be able to conduct the test in air makes it much more useful and easier to effect. Fortunately, since reaction (5) is a constant, competitive background kinetic feature, it has been shown that it is still possible to correlate the activity of a SC film as measured using an Rz *paii* in air with that measured using a more traditional method, such as the oxidation of a film of stearic acid [23] or MB in solution [36]. Thus, in this work, the initial study of the pressed films of the SCs, illustrated in figure 2, was carried out in air. Disappointingly, under these conditions, of all the SCs tested, only TiO₂, under UV irradiation, exhibited a striking, rapid colour change, (blue to pink), as illustrated in figure 6(a) below, a photographic record of the Rz ink-coated discs as a function of irradiation time, for the TiO₂ and SiO₂ discs only; the latter serving as a blank. These results show that in air, only TiO₂ demonstrates a sufficiently high enough activity for Rz reduction, i.e. reaction (3), so as to be able to compete with reaction (5) and effect the blue to pink colour change associated with the reduction of Rz to Rf.

It follows from the above findings that to be able to effect reaction (3) using films of SC's other than TiO₂, the reaction needs to be conducted under anaerobic conditions. Obviously, this can be achieved by sparging the system with argon, however, this is not particularly easy, nor practical. Instead, a simpler and quicker method that achieves the same result is to cover the surface of the ink-coated disc with a clear adhesive tape, such as Sellotape™, since the latter acts as a significant diffusion barrier to ambient air [37]. This approach was used here to probe the activities of the different SC discs, using visible and UVA light and the results of this work are illustrated in figures 6(b) and 6(c), respectively. However, for reasons that remain unclear, even with this O₂-barrier coating, an Rz ink film on C₃N₄, under either UV or visible light

irradiation, exhibited no significant change in colour and so the unchanging photographs recorded for this film as a function of t have been omitted from figures 6(b) and 6(c).

(a)

(b)

(c)

* CdS irradiations performed at 5.5 mW cm⁻²

Figure 6 Photographs of the colour change of the Rz ink on pressed disks upon irradiation under (a) 1.5 mW cm⁻² UVA (365 nm) (in air), (b) 14 mW cm⁻² visible (455 nm) (under Sellotape[™]), and (c) 1.5 mW cm⁻² UVA (365 nm) (under Sellotape[™]).

Using the images in figures 6(b) and 6(c), plots of the variation in the normalized red component of the digital image of the films, RGB_R' [23], which provides an effective measure of any change in the blue colouration, as a function of irradiation time t , were generated for all the films and the results are illustrated for the visible (455 nm) and UV (365 nm) irradiations, in figures 7(a) and 7(b), respectively.

Figure 7 Plot of the variation of the normalised red component (RGB_R') vs. time from digital photographs (see figures 6(b) and 6(c)) for the irradiation of the Rz ink on each of the pressed disks; (●) 50% SiO_2 , (○) 1% P25 , (■) 1% WO_3 , (□) 1% CdS , under (a) 14 mW cm^{-2} visible (455 nm) light, and (b) 1.5 mW cm^{-2} UVA (365 nm). All irradiations were performed under Sellotape™. The red dots highlight the calculated values for the time to bleach 90% of the red component of the ink, i.e. the $t_{tb}(90)$ for the different SCs; these were: 1, 2.6 and 5.8 min for TiO_2 , CdS and WO_3 , respectively, under UV illumination and 2.2 and 5.8 min for CdS and WO_3 , respectively, under visible illumination.

From the images of the ink films as a function of **visible** irradiation time illustrated in figure 6(b), it appears that tape-covered pressed films of the TiO_2 and SiO_2 powders under visible (455 nm; 14 mW cm^{-2}) light irradiation showed little change in colour over a 10 minute irradiation period, which is not too surprising given neither absorb visible light. The associated RGB_R' vs. t for the same films, illustrated in figure 7(a), confirm this impression gleaned from the photographs, although, since the profiles have small positive gradients, a slight bleaching of the Rz dye is indicated for both SiO_2 and TiO_2 , suggesting that a very slow photobleaching of the Rz dye does occur, due to some dye photolysis most likely, even though Rz absorbs only very weakly at 455 nm, see figure 4.

In contrast to SiO_2 and TiO_2 , **visible** light irradiation of CdS and WO_3 pressed discs produced, within 10 min, the colour change expected for the photocatalysed reduction of Rz (blue) to Rf (pink) and the subsequent further reduction of the latter to dihydro-resorufin, dH-Rf, which is colourless. The observed (i.e. photographed) colour changes appear different for these two SC due to the original underlying colour of the semiconductor pressed disc, illustrated in figure 2, although, in both cases, diffuse reflection spectroscopy confirms the intermediate generation of Rf, before this is, in turn, reduced to dH-Rf, *vide infra*.

A brief examination of both the photographs illustrated in figure 6(b) and the associated RGB_R' vs. t profiles, illustrated in figure 7(a), reveals that CdS is much more active than WO_3 as a visible light catalyst for the reduction of Rz to Rf. This finding is not too surprising, and similar to that found from the work carried out in solution, given its much bigger spectral overlap with the emission spectrum of the 455 nm LED (see figure 2). The overall order in activity, after omitting C_3N_4 , is: $\text{CdS} \gg \text{WO}_3 \gg \text{TiO}_2, \text{SiO}_2$, which is the same as was found in the Rz solution study, see section 3.1.

The images of the ink films as a function of **UV** (365 nm; 1.5 mW cm^{-2}) irradiation time are illustrated in figure 6(c) and show, for a tape-covered, Rz ink film coated sample of SiO_2 , that there is little, if any, change in the colour of the original ink as might be expected, given its insulator nature. In contrast, for the TiO_2 film, within 1 min of irradiation not only has all the Rz been converted to Rf, but also much of the Rf has been subsequently reduced to dH-Rf [20]. It is also clear from the photographs in figure 6(c) and the associated RGB_R' vs. t profiles,

illustrated in figure 7(b), that the order of activity: $\text{TiO}_2 > \text{CdS} > \text{WO}_3$ is the same as found in the Rz solution study, see section 3.1.

Finally, figure 8 provides two typical illustrations of the recorded changes in the diffuse reflectance spectrum of the SellotapeTM-coated, Rz ink film on (a) CdS (visible irradiation) and (b) TiO_2 (UV irradiation) pressed discs. In both, the conversion of the blue Rz (610 nm) to pink Rf (580 nm) is clear as is the subsequent reduction of Rf to dH-Rf, a pink to colourless transition.

Figure 8 Change in the diffuse reflectance spectra of; **(a)** Rz on a 1% CdS disc under visible light (455 nm, 14 mW cm^{-2}) at 10 s intervals, and **(b)** Rz on a 1% P25 disc under UVA light (365 nm, 1.5 mW cm^{-2}) at 5 s intervals. All irradiations were performed under tape and monitored using a hand-held spectrophotometer (Konica Minolta, CM-2500d). λ_{max} (Rz) = 610 nm (608 nm in solution), and λ_{max} (Rf) = 580 nm (582 nm in solution).

3.3 Dye photostability studies using 617 nm light

This work seeks to utilise an Rz-*paii* to probe, amongst other things, the visible light activity of established visible light photocatalysts, and, in so doing, to use excitation light that only the semiconductor, and not the dye, can absorb, such as 365 and 455 nm light, i.e. **WR(SC)** light. However, it is instructive to probe what happens when the two different systems ('SC+ Rz/glycerol/water' and 'SC

+ Rz-*paii'*) are exposed to light which the semiconductors employed in this study cannot absorb, but the dye can, namely: 617 nm light. Since most of these irradiations are carried out under anaerobic conditions, it seems unlikely a traditional dye-photosensitised process, as summarised by reaction (2), can occur, and thus any bleaching is most likely due to dye photolysis.

In aqueous solution, under anaerobic conditions, using the usual dispersions of SiO₂, TiO₂, CdS, WO₃, under irradiation with 617 nm light (10 mW cm⁻²) all solutions were found to be bleached very slowly, **whilst exhibiting no evidence of R_z formation**, *i.e.* the initial blue colouration due to R_z gradually faded. A typical spectral decay profile is illustrated in Figure 9(a) for the R_z/CdS/glycerol/water (concentrations same as in figure 4), and **similar profiles, and kinetics, were recorded for all the other SCs/insulator**. From this work the half-life for dye photobleaching, $t_{1/2}$, was found to be 4.3 ± 1 h for all the oxides. Similar kinetics with a similar $t_{1/2}$ value for all the SCs/insulator is what would be expected if the degradation process was due to a dye dependent (but semiconductor independent) degradation process, like dye photolysis, and opposite to that expected if it were due to dye photosensitisation. In contrast, for the same system, but using: 'visible' light (455 nm, 20 mW cm⁻²), the rates were found to be much faster and to vary greatly (depending on how well if, at all, the SC absorbed the incident UV light), revealing $t_{1/2}$ values of: 0.02, 1.36, 9.3 and 16 h for CdS, WO₃, TiO₂ and SiO₂, respectively and, in which R_f generation was clearly observed, in the first two cases, as illustrated in figure 4 for CdS. The observation of $t_{1/2}$ values that vary depending upon the amount of (455 nm) light absorbed by these semiconductors, is what would be expected for a photocatalytic process. The very low rate recorded for TiO₂ (and SiO₂) in the 455 nm irradiation study is because neither the TiO₂ (or SiO₂), nor the R_z, absorb strongly at this wavelength, in contrast to CdS and – to a lesser extent - WO₃.

SellotapeTM-covered, *i.e.* anaerobic, R_z pressed semiconductor films of SiO₂, TiO₂, CdS, WO₃, were also irradiated with 617 nm light (10 mW cm⁻²) and, once again, the dye was seen to bleach slowly, at approximately the same rate, with a *t_{tb}(90)* ca. 40 min, **whilst exhibiting no evidence of R_z formation**. Figure 9(b) illustrates a typical diffuse reflectance spectrum decay profile for an R_z-*paii* on CdS pressed disc, recorded as a function of time, upon irradiation with 617 nm light, which is in marked contrast to that illustrated in figure 8(a), in which 455 nm light was used as the excitation source. From Figure 7 we see that the measured *t_{tb}(90)* values for CdS and WO₃ (irradiated with 455 nm light) were 2.2 and 5.8 min, respectively, and so much faster than the average value of 40 min found for all the SCs/insulator when irradiated with 617 nm light. As with the solution work, the bleaching of the R_z *paii* on TiO₂ (or

SiO₂) using 455 nm light was incredibly slow ($t_{tb(90)} > 8$ h) because neither the TiO₂ (or SiO₂) nor the RZ absorb strongly at 455 nm.

The results of the above work suggest that when either of the 'SC+ RZ/glycerol/water' and 'SC + RZ-*paii*' systems are irradiated with 617 nm light, which the dye absorbs strongly but the SCs do not, the dye is bleached slowly, most likely due to a photolytic, rather than dye-photosensitised, process. At no time is there any evidence that Rf is produced as part of this slow degradation process. These results suggest strongly that the previous irradiations, conducted using 365 and 455 nm light, in which Rf is rapidly generated, were photocatalytic in nature, which is not surprising since they utilised light that the SC photocatalysts involved absorbed strongly, but the dye did not.

Figure 9: Using 617 nm light (10 mW cm^{-2}): (a) change in absorption spectrum recorded under otherwise the same CdS/Rz/glycerol/water system as reported in figure 4, each spectrum recorded every 30 min and (b) change in DRS, absorption spectrum recorded under otherwise the same 'CdS + Rz-*paii*' system as reported in figure 8(a); the spectra were recorded after the following irradiation times (top to bottom): 0, 1, 2, 3, 4, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60 min.

These latter findings help highlight the need, when using dyes to assess the activities of photocatalysts, to use light sources that provide: (i) only a narrow range of wavelengths, such as LEDs, and (ii) radiation that is NOT absorbed significantly (preferably not at all) by the dye itself. Failure to observe (i) and (ii) may easily lead to mistaken claims of photocatalytic activity. In addition, even if the degree of spectral overlap between the absorption spectrum of the dye and the emission spectrum of the light source is small, as in the case of R_z and the 455 and 365 nm LED light sources, the longer the irradiation time and higher the irradiance, the more likely some, if not all the observed colour change will be due to dye photodegradation, rather than photocatalysis.

4. Conclusions

A variety of semiconductor photocatalyst materials, i.e. TiO₂, CdS, WO₃ and C₃N₄, when used as a dispersion in deaerated, aqueous solution, appear able to mediate the **UV** (365 nm) photocatalysed reduction of R_z to R_f by glycerol, i.e. reaction (3). Under the same conditions, but using **visible** (455 nm) light, the same reaction is promoted by the visible-light absorbing semiconductors, CdS, WO₃ and C₃N₄. When mixed with SiO₂ and PTFE powder and pressed as discs, and covered with Sellotape™ to exclude ambient O₂, the C₃N₄ photocatalyst exhibited little activity under UV or visible irradiation, for reasons that remain unclear, although the other semiconductors, i.e. TiO₂, CdS, WO₃, showed the same order activity as when they were used in aqueous solution. Thus, for the established SC photocatalysts, like TiO₂, CdS and WO₃, the tape-covered, R_z *paii* film on pressed discs method appears to work using either **UV** (365 nm) radiation or **visible** (455 nm) light. The latter results represent the first example of the successful use of an R_z *paii* for probing the activity of visible-light absorbing photocatalysts and of semiconductor **powders**, as opposed to **films**, in general.

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