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Multifunctional anthraquinone-based sensors: UV, O$_2$ and time

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Abstract

An anthraquinone dye, Remazol brilliant blue R, RBBR, is used to create an indicator which can function as: (i) a UV dosimeter, (ii) an O$_2$ indicator and (iii) a 'Consume within' indicator, *CWI*, for fresh, refrigerated foods. The dye is encapsulated in an ink containing a polymer, glycerol and a UV-activated semiconductor photocatalyst, titanium dioxide. When cast as a film, the dye is readily reduced by the TiO$_2$ photocatalyst nanoparticles, thereby changing the colour of the film from blue to yellow, via a transitional green colour. The RBBR indicator is appropriately formulated, and covered with a film of Sellotape, which acts as an O$_2$ barrier, so as to act as a sunburn warning indicator for people with skin type II. In the absence of the layer of Sellotape the RBBR indicator is used as an, albeit slow, sensor for measuring ambient levels of O$_2$. Finally, by keeping the Sellotape layer, a UV-activated, yellow-coloured, RBBR indicator film is found to take ca. 42 h at 5°C in ambient air to attain a green colour, and, on this basis, it is demonstrated as a possible *CWI* for refrigerated fresh foods.

1. Introduction

There is a great deal of interest in optical sensor technology because such sensors are generally inexpensive, easily miniaturised and do not suffer electrical interference [1]. These sensors usually use dyes that change fluorescence intensity, or colour, upon exposure to the analyte under test [2]. Many different such optical sensors have been created to respond to a variety of analytes including: pH, CO_2, ammonia/volatile amines, humidity and O_2 [3-9].

In a recent series of papers this group has reported on inexpensive, UV-activated, colour-based optical sensors for O_2 [10-11]. The advantage of a colour-based sensor is that it readily allows a qualitative assessment to be made by eye, as to whether O_2 is, or is not, present, and quantitative assessment, using either UV/Vis spectrophotometry, or, nowadays, the much less expensive and more commonly available combination of digital photography with colour analysis, based on average Red, Green and Blue colour values, especially as this can now be carried out using a mobile phone and colour analysis app [12]. In these O_2 indicators, semiconductor nanoparticles present in the sensor film absorb *ultra*-bandgap light thereby creating-electron hole pairs, the positive holes of which then react rapidly [13] with a sacrificial electron donor, SED, present also in the indicator film, so as to leave the photogenerated electrons to reduce a redox-indicator dye also present in the film, D_{ox} to its reduced form, D_{red}. Note, the redox dye is selected so that D_{ox} and D_{red} are very different in colour and that D_{red} is also O_2-sensitive. Thus, with this type of O_2 indicator, a UV activation step, step 1, produces a striking initial colour change which is then reversed if O_2 is present (via step 2), as the latter is able to re-oxidise (in the dark) D_{red} to D_{ox}. A schematic illustration of these key processes is given in figure 1.

For example, the UV-activated, colour-based optical sensor for O_2 reported recently [10] by this group combined used methylene blue (MB) as D_{ox} , nanoparticulate TiO_2 as SC, glycerol as the SED, and a polymer binder, hydroxyl ethyl cellulose, HEC, to create a printable, aqueous UV-activated, O_2-sensitive ink [14], which shall henceforth be referred to as an 'MB-O_2 indicator'.
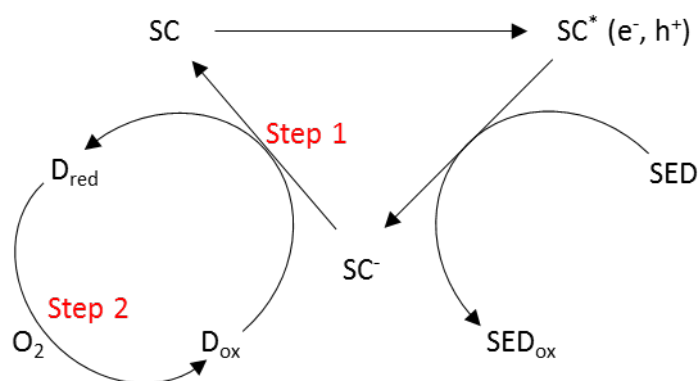
Figure 1 – Schematic diagram of the main processes underpinning a UV-activated photocatalyst-based oxygen indicator, comprising step 1: the UV driven reduction of D_{ox} to D_{red} and step 2: the dark O_2-response step, in which D_{red} is reoxidised to D_{ox}.

The MB-O_2 indicator was commercialised by UPM as a label to indicate when the seal on an O_2-free food package had been compromised so as to let air leak in [15]. The label was use to improve quality control in modified atmosphere food packaging, MAP; a technology which is prevalent in the packaging of most foods (such as: meat, bread, and many dry goods) and usually involves flushing the food package with an inert gas, such as N_2 or CO_2, to remove the O_2 and extend the shelf life of the food.

If it is possible to turn off the dark, O_2-sensing step, i.e. step 2 in figure 1, the indicator could be used, instead, to measure the UV dose the indicator received during steps, which would then add to the potential functionality of the indicator ink. Unfortunately, the MB-O_2 indicator is too O_2 sensitive to do this easily through a simple manipulation of the ink formulation, but it can be achieved by placing a O_2-barrier film, such as Sellotape™, on top of the indicator, so as to effectively stop reaction (2) and so allow the indicator to function as a UV dosimeter instead.

One other potential area of application of the O_2 indicator technology, apart from MAP leak indicator, relates to food waste. UK households throw away 7 million tonnes of food and drink annually, more than half of which is still safe to eat [16]. As noted above, most perishable foods are MAPed and, obviously, once opened, the food inside starts to deteriorate in quality at a temperature-dependant rate. As there are usually no obvious visual clues as to the length of time a package has been opened, it is often left to a combination of memory and guesswork on the behalf of the user, to judge as to whether the food inside an opened package is safe to eat. Understandably, most consumers tend to err on the side of caution and so throw away quite a lot of food that actually could have been consumed safely. It follows that an indicator which was able to act as a timer over a period of ca. 24 or 48h at 5°C (usual fridge temperature) after a MAPed food package is opened, would in effect be able to act as a 'consume-within' indicator, *CWI,* for fresh foods.

A *CWI* would be able to help inform the consumer whether the fresh food in an opened package is still safe to eat, and so lead to an overall reduction in the amount of household food waste and the concomitant burden it places on the environment. Although the development of a *CWI*, based on the UV-activated, O_2 sensor technology illustrated in figure 1, is possible, in practice, the MB O_2 indicator is too sensitive in its response towards O_2 for the time taken to restore its colour (after UV activation) to be easily extended from the usual value of 10 min, to 24 or 48 h , even at 5°C. In

addition, even if this hurdle could be overcome, the change in colour associated with the recovering MB O_2 indicator– from colourless to a gradually deepening blue - would make it hard to assess exactly what stage it was in with regard to the recovery process and so what time had elapsed.
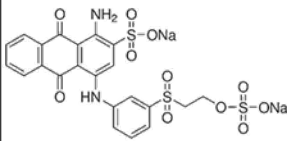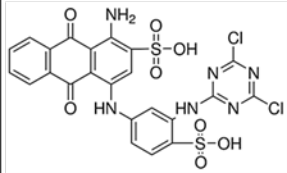
In this work, a number of different dyes, other than MB, were quickly screened as possible suitable alternatives to MB as $D_{ox.}$ in a UV-activated O_2 indicator, functioning as illustrated in figure 1. From the results of this initial screening process, three anthraquinone dyes appeared particularly promising, not only as UV-activated O_2-senstive inks, but also as potential 'consume-within' indicators and UV-dosimeters. Thus, in this paper we describe the results of a study of the best of these AQ dyes, Remazol Brilliant Blue R, RBBR, when used as to create a multifunctional sensor, based on the UV-activated processes illustrated in figure 1.

2. Experimental

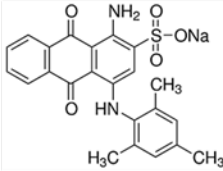Unless otherwise stated, all chemicals were obtained from Sigma Aldrich in the highest available purity and used as received. Ink samples were prepared using an Electronic Microsystems Model 4000-1 Spin-Coater. UV-vis spectra were recorded using a Cary 60 (Agilent Technologies), and all digital images were recorded using a Canon 600D digital camera.

The three anthraquinone dyes used here are listed in table 1, along with their structures and photographed appearances, with measured λ_{max} absorbance values, in their oxidised and reduced forms, when used as UV-activated O_2 sensitive AQ dye indicator films, based on the reaction scheme illustrated in figure 1.

Table 1 – Anthraquinone dyes studied: names, structures and appearances with λ_{max} absorbance values when in indicator form.

Name	Structure	Indicator Appearance	
		Oxidised	Reduced
Remazol Brilliant Blue R (RBBR)		(λ_{max} 595 nm)	(λ_{max} 475 nm)
Reactive Blue 4		(λ_{max} 595, 606 nm)	(λ_{max} 473 nm)
Acid Blue 129		(λ_{max} 640 nm)	(λ_{max} 468 nm)

* oxidised (form): i.e. form in the indicator before UVA activation; reduced (form): after UVA activation

Unless stated otherwise, all photocatalyst-based, anthraquinone (AQ) dye-containing, O_2 sensitive inks were formulated as follows: 375 mg of the AQ dye under test, 450 mg P25 TiO_2 (3:1 anatase rutile mix, 55 m^2 g^{-1} surface area) and 2.25 g of glycerol were added to 5 mL of a 1.5 wt.%, acidified (0.1 M HCl) solution of hydroxyethyl cellulose (MW ≈ 250k) dissolved in double distilled deionised water. The mixture was stirred for at least 12 hours to ensure thorough mixing and dissolution of all the soluble components, and stirred continuously in a cool, dark place when not being used to create indicator films.

Indicator films of each of the AQ inks listed in table 1 were prepared by spin-coating 0.2 mL of the ink onto borosilicate cover slips (24 mm diameter) at 800 RPM for 20 s and then allowing each film to dry fully under ambient conditions for 10 minutes. The typical thickness of a final, dry, spin-coated AQ ink film was ca. 3.1 ± 0.3 µm, as measured using SEM. The initial UVA light activation step (step 1 in fig 1) was performed using a lamp equipped with 2 x 8 W 368 nm narrow band black-light blue tubes, with a UVA irradiance of ca. 1.5 mW cm^{-2}. In the study of the effect of different irradiances on the rate of colour change exhibited by the indicator, the incident irradiance level falling on the indicator was adjusted by moving the UVA light source closer to, or further away from, the sample under test. Although it is possible to UV-activate the AQ indicator films in air, in this work, unless stated otherwise, the photoactivation of the indicator film under test (i.e. step 1) was performed in an oxygen-free environment, by placing the AQ indicator in a gas cell, with glass optical

faces front and back, and flushing it with argon. In much of the UV dosimeter work, an oxygen barrier, in the form of a layer of (ca. 58 μm) Scotch™ tape, was placed over the AQ indicator under test.

3. Results and Discussion

3.1 UV light activation: step 1: initial study

As indicated earlier, in the dried AQ ink films the reduction of the AQ redox dye (see table 1) was effected by the UV-activation of the TiO_2 nanoparticles, via step 1 in figure 1. In all cases, this reaction was a 2 electron, 2 proton transfer, as illustrated for the example AQ dye: RBBR (table 1), in figure 2.
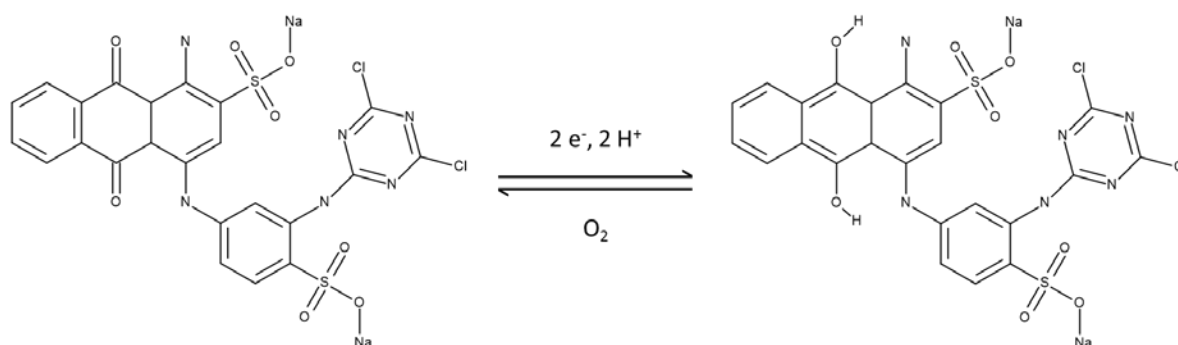

Figure 2 – Chemical structure of Remazol Brilliant blue R, and its reduced, yellow form.

In the cases of all the anthraquinone dye indicator films tested, see table 1, upon UVA irradiation, the dye underwent a rapid (within 4 minutes in air or Ar – *vide infra*) reduction, with the concomitant oxidation of glycerol in the film, and produced a striking colour change in the indicator film, as shown by the images in table 1 above. The most striking of the three different anthraquinone indicator films tested was that containing RBBR as the redox dye, and as a consequence all of the subsequent results reported below relate to the O_2-sensitive ink based on this anthraquinone dye, although the other two AQ dyes reported in table 1 showed similar response characteristics when used in the same indicator film form.

Figure 3 illustrates the UV-vis spectrophotometric data and accompanying digital photographic images for a typical RBBR O_2 sensitive indicator film upon UVA activation in an argon atmosphere, i.e. under O_2 free conditions. Other work shows the same UV-driven colour change, blue to yellow, could be effected in almost the same time (ca. 4 min) if the UVA activation step was carried out in air, because step 2 in figure 1, i.e. the dark recovery step in air, is very slow for the RBBR film at ambient temperature (*vide-infra*).
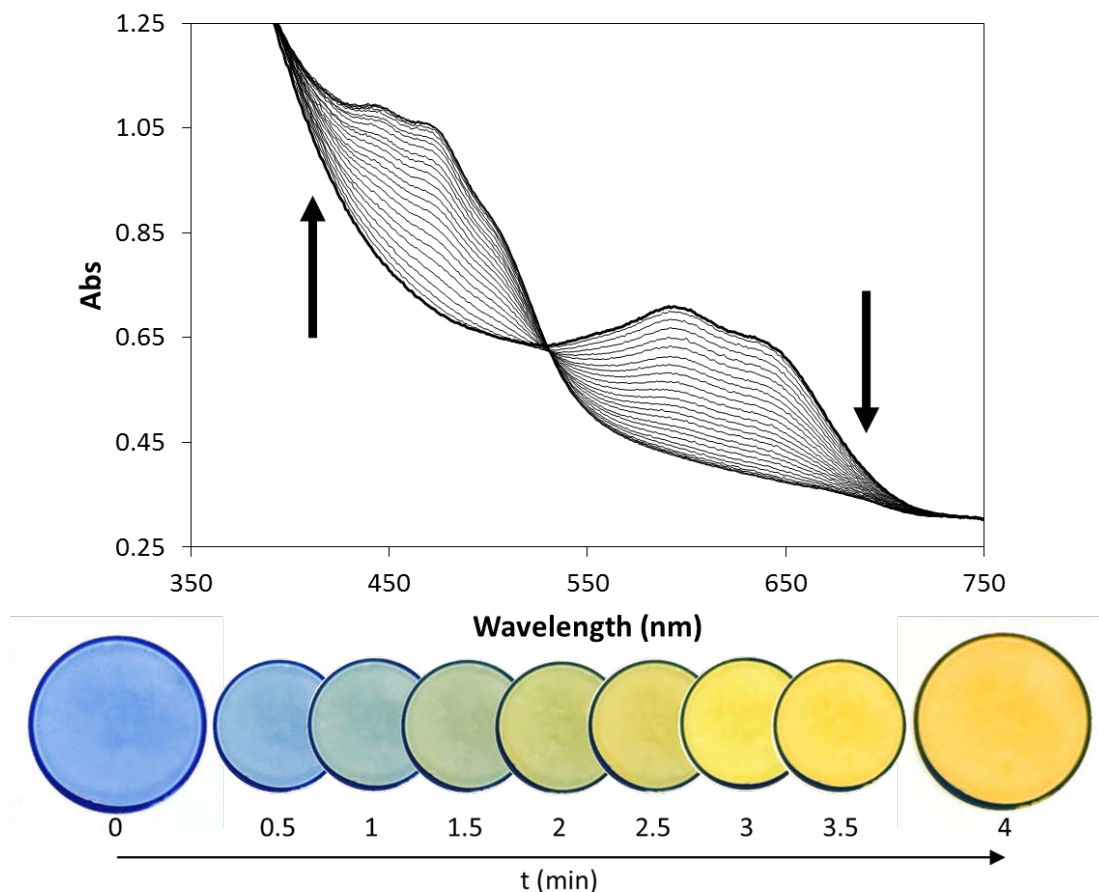
Figure 3 – UV-vis spectra of the reduction of a typical RBBR ink film from blue (λ_{max} = 595 nm) to yellow (λ_{max} = 472 nm) as a function of UVA irradiation time, t. Spectra were recorded every 10 seconds of UVA light irradiation. Also shown is the colour change as a series of digital images. I = 1.5 mW cm^{-2} 368 nm.

These results show that, in the absence of O_2, the initially blue-coloured, quinone form of RBBR dye in the indicator film is photoreduced, by the TiO_2 photocatalyst nanoparticles present in the indicator film, to the dye's yellow hydroquinone form (see figs 1 and 2). The excellent isosbestic point in the recorded spectra (Figure 3, λ_{iso} = 542 nm) indicates the UV-driven reduction process, step 1 in Figure 1) involves only two species, namely: the quinone (blue) and hydroquinone (yellow) forms of RBBR.

3.2 UV light activation: step 1: dependence of rate on I and $n(TiO_2)$

Unless stated otherwise, in the study of the UV activation step as a function of the incident irradiance, I, and the amount of TiO_2 used to formulate the film, $n(TiO_2)$, which are described below, all irradiations were performed using the AQ indicator film in a gas cell flushed with Ar.

The rate of change in colour of a typical RBBR indicator film upon UVA activation in the absence of O_2, was studied as a function of UVA irradiance, and the results of this work are illustrated in Figure 4, which is a plot of the relative change in absorbance of the RBBR film at 595 nm, ΔAbs_{595}, as a function of irradiation time for a range of different irradiance values, I.
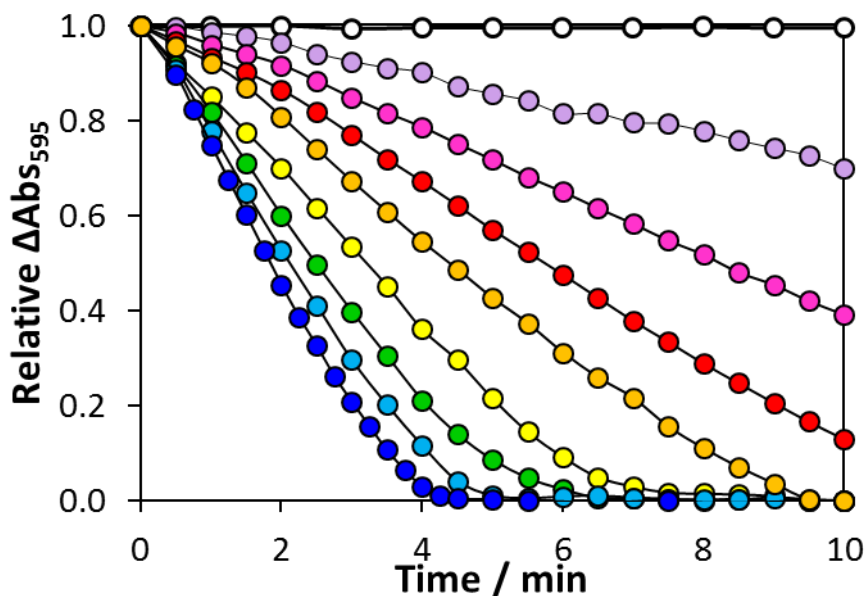

Figure 4 – Relative change in film absorbance at 595 nm vs time for the photoreduction of RBBR in Ar as a function of UVA incident irradiance, I, (derived from two 368 nm narrow band BLB's). From top to bottom the I values used were as follows: 0.0, 0.1, 0.2, 0.4, 0.5, 1.0, 1.5, 2.0, and 2.5 mW cm^{-2}.

From the results of this work it is clear that, in the absence of UVA, the indicator film is stable, and, indeed, RBBR indicator films appear stable for > 6 months when stored were stored in the dark, but otherwise ambient conditions. It is also apparent from the data in figure 4, that the kinetics of the photocatalysed reduction of the AQ dye are zero order with respect to the concentration of RBBR, [RBBR]. The latter feature is not uncommon in semiconductor photocatalysis [17], in which the rate is usually related to the key reactant concentration, which is RBBR in this case, i.e. [RBBR], via an expression of the form:

$$r = kI^{\Theta}K[RBBR] / (1 + K[RBBR]) \qquad (1)$$

where k is the maximum rate and K is an apparent Langmuir adsorption constant [18]. A brief inspection of equation (1) reveals the prediction of zero order kinetics if K[RBBR] is >> 1, i.e. if the dye is strongly bound to the surface of the photocatalyst particles. Similar zero-order kinetics have been observed for other photocatalyst-based indicator films, including those using resazurin [12]. The rate expression (1), also predicts that the initial rate is directly proportional to I^{Θ}, where I = incident UV irradiance and Θ lies in the range of 0.5-1, the former value is found when recombination is the dominant decay process for the photogenerated electrons and holes, whereas

a value of Θ = 1 value is usually taken to indicate that photogenerated electron and/or hole scavenging is very efficient in competing with electron-hole recombination. Further analysis of the results in figure 4, in the form of a plot of initial rate of dye reduction vs. *I*, yields a straight line and thus indicates that *Θ* ≈ 1, i.e. the rate of dye reduction, is directly proportional to UV irradiance for the RBBR indicator in Ar, which is as might be expected if the glycerol present in the indicator film functions as a very efficient hole scavenger.

Obviously the rate of UVA activation must also depend upon the amount of semiconductor photocatalyst, i.e. $n(TiO_2)$, used to make up the indicator ink, thus in this work the initial rate of the UV photoreduction of the dye in the RBBR indicator, was studied as a function of $n(TiO_2)$, over the range of 0 to 400 mg, in Ar, and the results of this work, shown in Figure 5, reveal that r_i is directly dependent upon $n(TiO_2)$.
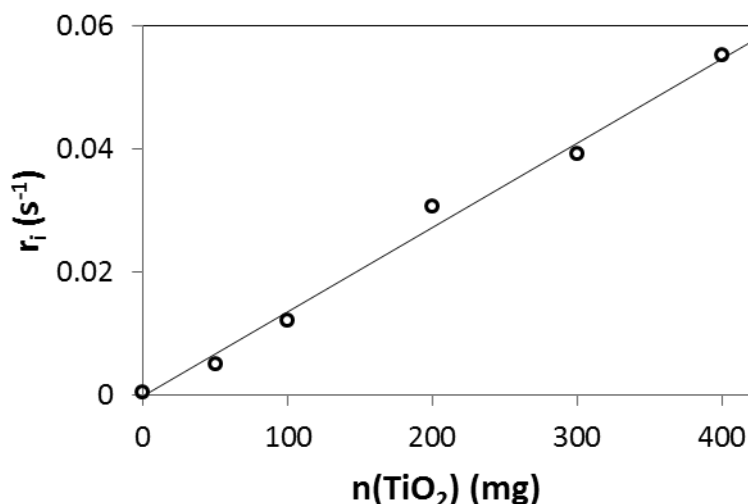

Figure 5 – initial rate of reduction versus $n(TiO_2)$, a typical ink uses 300 mg of TiO_2. 1.5 mW cm^{-2} 368 nm.

The results illustrated in figures 4 and 5 suggest that the UV-sensitivity of the RBBR indicator is dependant linearly on irradiance and $[TiO_2]$ and thus, the UV-sensitivity of the RBBR indicator can be controlled by altering the amount of TiO_2 present in the sensor. These results also reveal that the AQ dye in the film (i.e. when no TiO_2 is present) is itself very photostable under UV illumination and thus, the colour change observed in the presence of TiO_2, is due to the photocatalysed reduction of the AQ, as illustrated in Figure 1, step 1.

3.3 UV dosimeter/Sunburn warning indicator

In an exploration of the three different potential functional aspects of the RBBR indicator, initial work focussed on the creation of a UV dosimeter based on the RBBR/glycerol/TiO_2 indicator. Obviously, for such an indicator to be of any practical use it must be able to function in air. In the

case of the RBBR film, therefore, it is necessary that only step 1 in figure 1 is able to operate, i.e. the UV activation step, and not step 2, the O_2 sensing step. Thus, the AQ indicator must be indifferent to the presence of ambient O_2, and this necessary condition was achieved by covering the film with a layer of Scotch[TM] tape, which comprises a 60 micron layer of regenerated cellulose which is able to act as a very effective barrier to O_2 barrier.

It is relevant to note at this point that, in contrast to the blue to colourless colour change exhibited a $MB-O_2$ indicator, upon UV activation, a RBBR indicator, on changing from blue to yellow, exhibits an intermediate green colour, ass illustrated in Figure 3, which will be used here as an easily identified point in the overall colour transition. Thus, the work on a Sellotape covered RBBR indicator films, as a UV dosimeter and potential sunburn warning indicator, which is described below, focussed on controlling the value of the UV dose necessary to turn the UV dosimeter film green.

The control and monitoring of UV dose is an important part of skin care, especially in any effort to tan but avoid sunburn. For such work what is ideally required is a UV dosimeter that changes colour so as to indicate when the skin has received a sufficient UV dose, a minimal erythemal dose (MED), for the day that further exposure needs to be stopped if sunburn (erythema) is to be avoided.

The RBBR ink was reformulated so that, in its Sellotape-covered form, it changed green upon exposure to sufficient UV light to start to cause sunburn, a MED value = 1, in a person with skin type II, which is the most common skin type associated with sunburn and skin cancer [19] and that associated with Caucasians. The revised RBBR ink comprised: 10 g of 1.5 wt.% HEC, containing 1 g of glycerol, 200 mg of RBBR and 10 mg P25, with the resulting solution adjusted to pH 1 using hydrochloric acid. The RBBR-based sunburn indicator film was then made by drawing down the reformulated ink a K-bar 7 (which deposited an 80 μm wet film). The ink film was then left to dry in air for one hour, before being covered with a layer of Sellotape. This RBBR-based sunburn indicator film was exposed to sufficient UV light to exceed a MED value of 1, during which time it was photographed at regular intervals. Figure 6 shows the recorded photographic images of the RBBR film: (i) before, (ii) after exposure to an MED = 1, and (iii) after exposure to MED > 1.5. These results indicate that Sellotape-covered, reformulated RBBR film has potential as a sunburn warning indicator. Given that the UV sensitivity of the film can be varied, by altering the level of $n(TiO_2)$, it should be able to make similar sunburn waring indicators that are appropriate for all 6 different skin types.
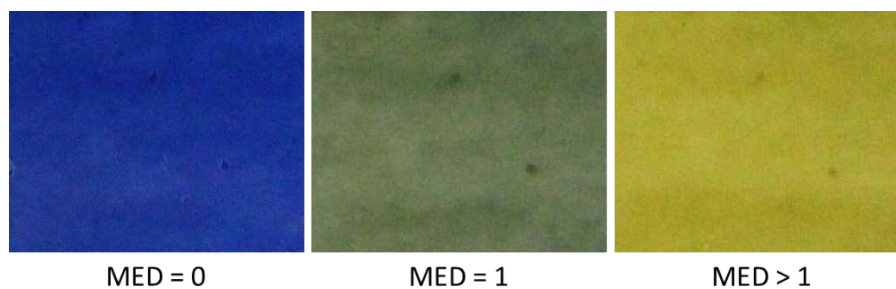
| MED = 0 | MED = 1 | MED > 1 |

Figure 6 – Photographs of a typical Sellotape-covered RBBR film before (left) and after (centre) irradiation with UVA light equivalent to an MED = 1, which was achieved after 80 minutes of UVA exposure. Subsequent irradiation leads to the film changing to a yellow colour when MED = 1.5 (right hand image).

3.4 O_2 indicator

The second possible, and most obvious, functional feature of the RBBR film is as an O_2 indicator. As noted earlier (see figure 4), after the UV photoactivation step (step 1, figure 1), the ink is stable in its reduced form when stored in an oxygen free environment but when exposed to ambient air, the photoreduced AQ indicator ink film recovers its original colour (albeit very slowly, i.e. ca. 1 day), as illustrated by the data in figure 7 for a standard RBBR film, after its initial UV activation in air, and subsequent 'dark' recovery its initial blue colour. Interestingly, this recovery is much slower ($\approx$ 70 times less) than the equivalent MB-O_2 indicator, presumably due to the more positive redox potential of the RBBR dye (+0.177 compared to +0.1 V (MB/LMB)) [20].
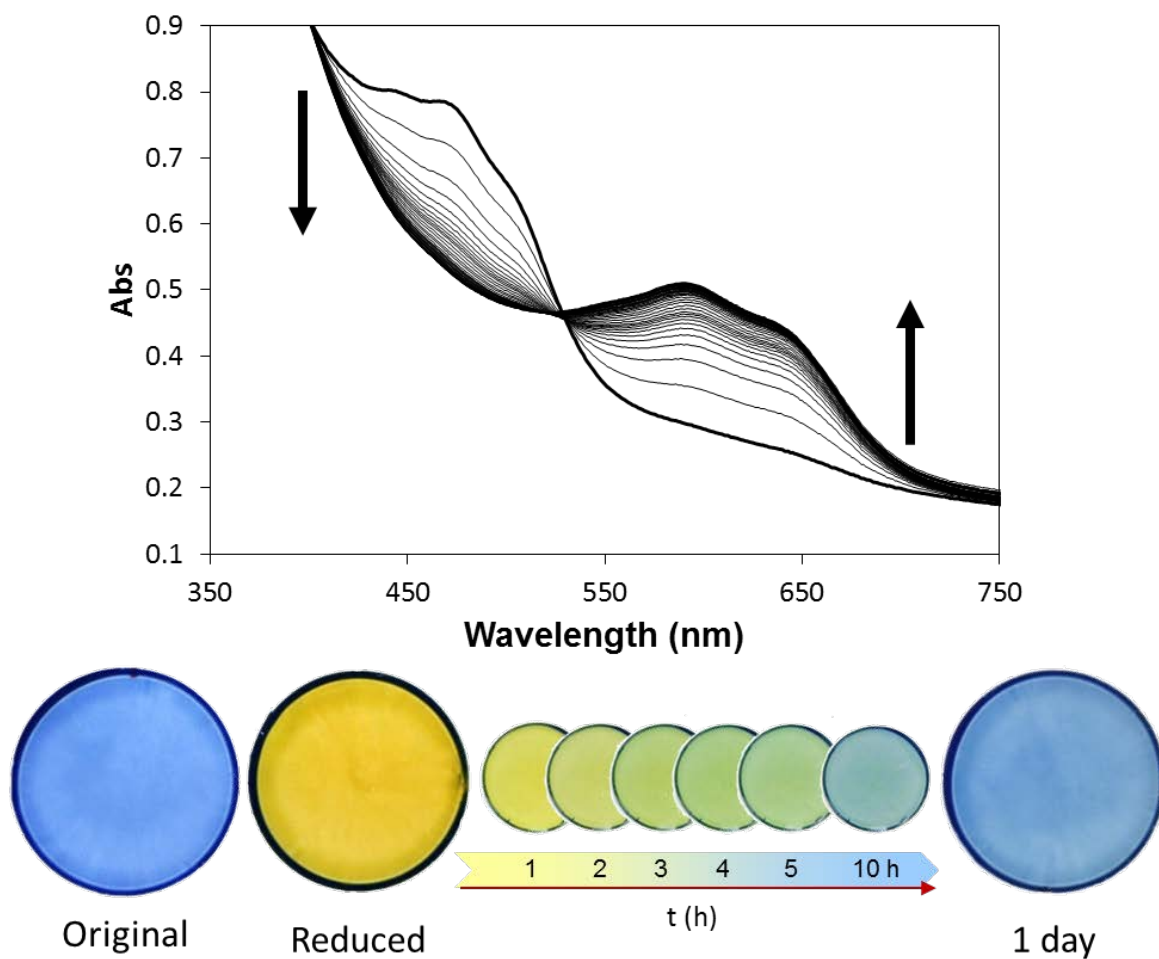
Figure 7 – UV-vis spectra and accompanying digital images of the dark recovery of RBBR ink film at 23°C spun onto a cover slip. The recovery step is evidenced by 2 distinct colour changes, firstly a rapid (~ 5 hour) change from yellow to green, followed by a much slower recovery to its original blue colour. The UV activation step was achieved using I = 1.5 mW cm^{-2} 368 nm for 4 min.

From the data illustrated in figure 7, which is more clearly illustrated in figure 8, which is a plot of the absorbance of the UV-activated RBBR ink film at 595 nm as a function of time (in air), it can be seen that, at 23°C, the ink film recovers from its photo-reduced, yellow, form, to its original blue form within a 24 hour period, and once again, shows a distinct transitional green colour at around 5 hours.
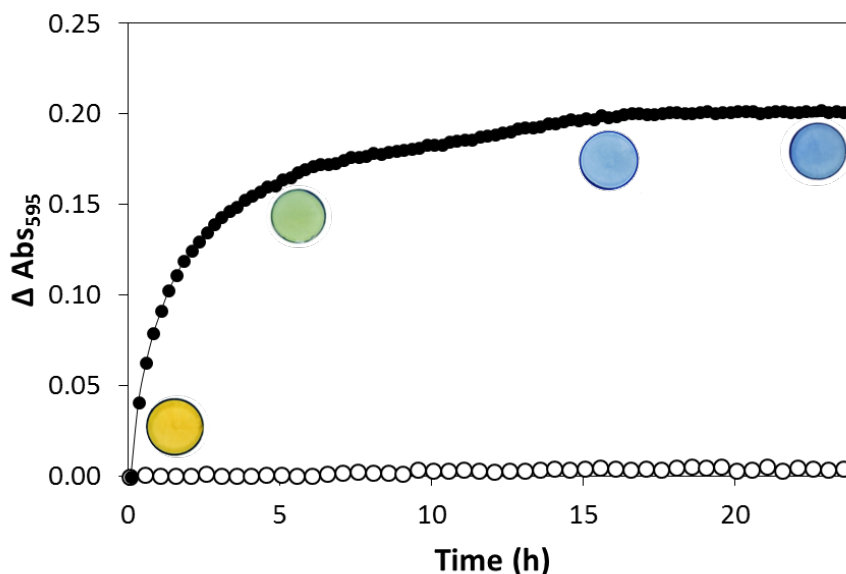
Figure 8 – Change in the absorbance at 595 nm of a typical RBBR film, under 'dark' recovery conditions, following its UV activation (step 1), i.e. ∆Abs vs time when the film is in an air (filled circles) or Ar (empty circles) atmosphere. The former data set taken from Figure 7.

Further work shows that the initial rate of recovery of the original blue colour, i.e. $dAbs_{595}/dt$ at t=0, is proportional to the ambient level of O_2, which suggests that it is possible, although perhaps impractical, to use the RBBR indicator to assess the level of ambient O_2, via the measure value of its initial rate of colour recovery, after UV activation. Further work involved the investigation of the dependence of the time taken for a UV-activated, yellow, RBBR film to recover to its green – transitional form, *t(green)*, as a function of ambient O_2, the results from which are illustrated in figure 9.

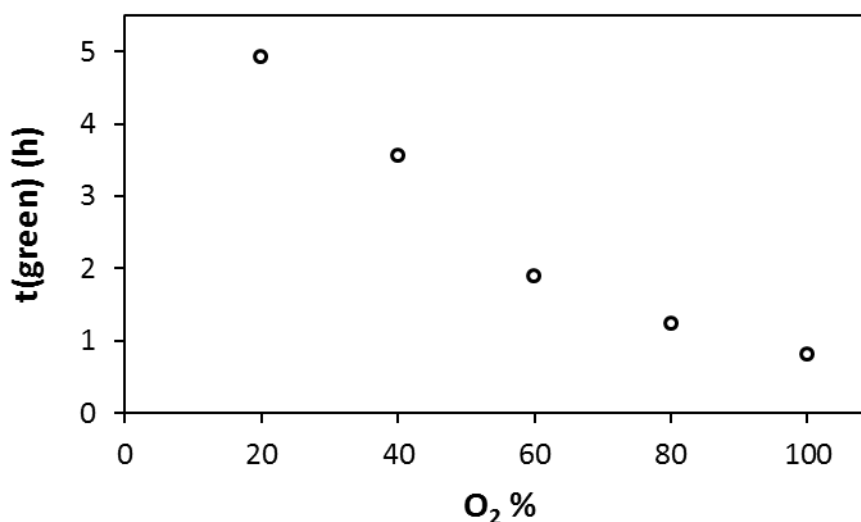**Figure 9 – Plot of t (green) vs. % O_2 after the initial UV-activation of a RBBR indicator film (4 min, 2.5 mW cm^{-2}) in air at 23°C. The absorbance value taken as t(green) was 0.15 for ∆Abs$_{595}$, as denoted in figure 8.**

The above results suggest that, once activated with UV light the value of t(green) exhibited by the film can be used to determine the ambient level of O_2, via a calibration graph of the form illustrated in figure 9.

3.5 Consume-within indicator (*CWI*)

Of all the different potential functions of the RBBR indicator, possibly the most novel is that of a 'consume-within' indicator, *CWI*, for fresh food, since the long recovery time, which is over 70 times slower than that exhibited by a MB-O_2 indicator, suggests that it might find a role as such. Thus, in a final study, the values of *t(green)* were determined for the standard RBBR indicator at both 23° and 5°C, in both covered (with Scotch^{TM} tape) and uncovered forms, and the results of this work are reported in table 2. The latter indicates that the uncovered (i.e. no O_2 barrier) and covered RBBR indicator may find a role as consume-within indicators for fresh food at 5°C (where consume-within lifetimes of 24/48 h are of relevance for fresh foods like meat and seafood). Note that the recovery time can be controlled by simply using O_2 barrier films, such as Sellotape, of different thicknesses.

Table 2 – Yellow to green recovery times (i.e. *t(green)* values) for an RBBR 'consume-within' indicator under different conditions of temperature and O_2-barrier coverage.

T (°C)	O_2 barrier	t(green) (h)
5	✘	20
5	✔	42
23	✘	5
23	✔	12

4. Conclusions

A new O_2-sensitive ink system, utilising the anthraquinone dye RBBR, can be used as: (i) a UV-dosimeter/sunburn warning indicator, (ii) a 'consume-within' indicator and, possibly less likely, (iii) an [O_2] sensor. In the case of this indicator, the initially blue-coloured (quinone) dye in the film is rapidly photoreduced to its yellow (hydroquinone) form when exposed to UVA irradiation and when an oxygen barrier is put in place, the time taken to achieve a green colour can be used to assess the level of UV dose received by the indicator and whether it is more or less that require to cause sunburn. In the absence of an O_2 barrier, the photoreduced, yellow from of the indicator recovers to its original blue colour in ca. 24 h in air. Other work shows that the time taken to recover to an intermediate green colour can be used to assess the level of ambient O_2. Finally the time taken for

an initially photoreduced (yellow) film to turn green colour at 5°C, once exposed to air, makes it a possible candidate as a 'consume-within' indicator for refrigerated fresh food.

Acknowledgements

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