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Research Article

UV-Activated Luminescence/Colourimetric O_2 Indicator

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An oxygen indicator is described, comprising nanoparticles of titania dispersed in hydroxyethyl cellulose (HEC) polymer film containing a sacrificial electron donor, glycerol, and the redox indicator, indigo-tetrasulfonate (ITS). The indicator is blue-coloured in the absence of UV light, however upon exposure to UV light it not only loses its colour but also luminesces, unless and until it is exposed to oxygen, whereupon its original colour is restored. The initial photobleaching spectral (absorbance and luminescence) response characteristics in air and in vacuum are described and discussed in terms of a simple reaction scheme involving UV activation of the titania photocatalyst particles, which are used to reduce the redox dye, ITS, to its *leuco* form, whilst simultaneously oxidising the glycerol to glyceraldehye. The response characteristics of the activated, that is, UV photobleached, form of the indicator to oxygen are also reported and the possible uses of such an indicator to measure ambient O_2 levels are discussed.

1. INTRODUCTION

The presence of oxygen in food packaging usually has a detrimental effect on the food products contained therein. Oxygen does not only react chemically with food to cause oxidative rancidity, but moulds, growths, and aerobic microorganisms—which discolour and decompose food and make it offensive to smell and dangerous to eat—thrive in the presence of oxygen [1]. Therefore, it is no surprise that the removal of oxygen in the food packaging industry is of immense importance. This is usually achieved via modified atmosphere packaging (MAP), a process in which the atmosphere within the food package is flushed and replaced with an inert gas, such as nitrogen or carbon dioxide, often combined with an efficient oxygen scavenger, resulting in an oxygen level of 0.1% or less within the food package [1, 2]. MAP increases the shelf life of many food products by a factor of 3-4 compared to that in air, making it a popular method of packaging food in the wholesale and retail food packaging industry.

There are many established methods for the detection of oxygen, which include the Clark electrode [3] and gas chromatography [4], however, such methods are too expensive and time consuming to allow 100% quality assurance. Consequently, there is an increasing interest in the development of cheap, easy-to-use oxygen indicators [5]. This area of research has been dominated by the quenching of a polymer-encapsulated lumophore, such as ruthenium(II)-tris(4,7-diphenyl-1,10-phenanthroline), $Ru(dpp)_3^{2+}$, by oxygen. One of the few commercially-available products based on this approach is the OxySense system [6], whereby, $Ru(dpp)_3^{2+}$ is encapsulated in silicone rubber dots, called O_2xyDots^{TM}, which can be attached to the inside of a package or bottle. The O_2xyDot is illuminated and the readily measured luminescence lifetime of the lumophore is equated to the oxygen level within the package. Unfortunately, the detection of oxygen using the OxySense system, or any optical sensor based on luminescence, requires the use of relatively expensive instrumentation for making the required lifetime or intensity measurements.

Unlike changes in luminescence intensity or lifetime, a sensor that changes colour in the presence of oxygen would be most desirable for MAP, given that the human eye can then act as the detector. Such indicators can take several forms, such as a tablet [7, 8] or a printed layer [9, 10]. This technology is typified by the Ageless Eye oxygen indicator, manufactured by the Mitsubishi Gas Company in Japan [7, 8, 11], that comprises a redox-indicator, usually methylene

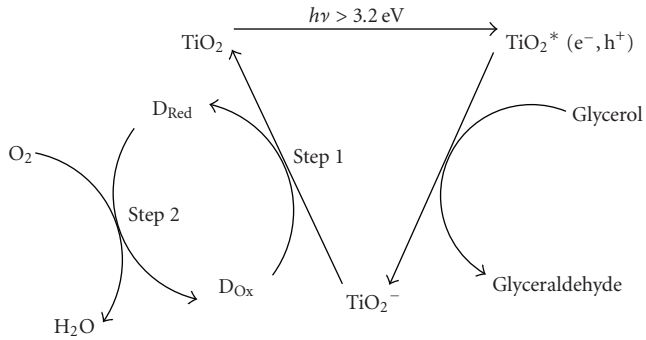

Figure 1: Schematic illustration of the key processes involved in the UV activation and subsequent response towards oxygen of a TO_2/redox dye, D_{OX}/glycerol/HEC oxygen indicator, such as that used in this work, where D_{OX} = ITS.

blue, which, in the absence of oxygen, is maintained in its colourless, chemically reduced, *leuco* form, by a reducing agent, such as glucose in an alkali medium. In the presence of oxygen *leuco,* methylene blue is oxidised to a highly coloured form. All components are mixed together, along with a nonredox dye, such as Acid Red 52, which provides a pink background colour, and pressed together to form a pellet, which is subsequently encapsulated in an oxygen-permeable, ion-impermeable plastic sachet to avoid any contact with the food. In the presence of oxygen, the Ageless Eye indicator changes from pink to purple in 2-3 hours, in a quasireversible process. However, this indicator needs to be stored and handled under anaerobic conditions. Such oxygen indicators are used in the food packaging industry, but mostly used as a research tool or fault diagnostic, since they have limited use elsewhere, because of cost and storage issues.

Lee et al. [12, 13] recently developed a new range of colourimetric oxygen indicators that are irreversible, reusable, and UV-light activated. Such "intelligent ink" oxygen sensors comprise a UV-absorbing semiconductor, such as TiO_2, a redox-indicator, such as methylene blue, a sacrificial electron donor, such as triethanolamine, and an encapsulating polymer such as hydroxyethyl cellulose; the ingredients are mixed together, with water as the solvent, to form an ink. The ink can be coated or printed subsequently onto a variety of substrates to produce a blue oxygen indicator film, which, when activated by UV light, becomes colourless. The activated, that is, UV-photobleached, film remains colourless unless, or until, exposed to oxygen, at which point the reduced methylene blue is reoxidised back to its original blue form.

The basic working principles, by which such an irreversible oxygen indicator works, are illustrated in Figure 1. Thus, upon UVA irradiation, ultraband gap illumination ($h\nu$) of the TiO_2 semiconductor particles create electron-hole pairs, $TiO_2{}^*(e^-,h^+)$. The photogenerated holes, h^+, oxidise the mild sacrificial electron donor (SED) present, glycerol in this case, in the ink film and the remaining photogenerated electrons, that is, e^- or $TiO_2{}^-$, as in Figure 1, reduce the redox-sensitive dye, D_{OX} to a reduced form, D_{Red}, which has a different colour to D_{OX}. In an ink film, the above key components are encapsulated in a polymer, such as hydroxyethyl cellulose (HEC) that is soluble in a common solvent (usually water). Thus, UV irradiation causes an O_2-sensitive ink film to change colour (step 1, Figure 1). In the absence of oxygen, the photobleached dye will stay in this reduced—usually colourless—state indefinitely. However, upon exposure to oxygen, it is reoxidised to its original, highly coloured form (step 2, Figure 1).

In this paper, we describe a very oxygen sensitive version of this type of UV-activated indicator, in which the sacrificial electron donor is glycerol and the redox dye is indigo-tetrasulfonate (ITS). The latter is highly coloured and nonluminescent in its oxidised state but virtually colourless, highly luminescent, and very oxygen-sensitive in its reduced state, *leuco* indigo-tetrasulfonate (*leuco*-ITS).

2. EXPERIMENTAL

2.1. Materials

Unless stated otherwise, all chemicals were purchased from Aldrich Chemical Company (Gillingham, Dorset, UK). The semiconductor, titanium dioxide (TiO_2), was P25 provided by Degussa (Frankfurt, Germany) and comprised particles *ca*. 30 nm in diameter, with an 80 : 20 anatase : rutile crystal phase composition.

2.2. Preparation of indigo-tetrasulfonate (ITS) based films

A typical example of an UV-activated luminescence/colourimetric oxygen-sensitive, ITS-based indicator ink, used to make the indicator films reported in this work, was prepared by adding 200 mg of glycerol to 2 g of a 5% wt hydroxyethyl cellulose (HEC) aqueous solution, to which 20 mg of P25 TiO_2 and 5 mg of the redox indicator indigotetrasulfonate (ITS) had been added. The resulting mixture was stirred magnetically for 15 minutes, followed by 15 minutes sonication to disperse the usually aggregated titania particles, followed by a further 15 minutes stirring. Typically, an oxygen indicator film was prepared by placing 3-4 drops (*ca*. 0.4 ml) of this ink onto a cut-glass microscope slide (0.8×3.8 cm), which was subsequently spun at 2500 rpm for 15 seconds. The resulting blue, transparent film was allowed to dry in the dark for 30 minutes before use.

2.3. Methods

All UV/V is spectra and absorbance versus time profiles were recorded using a Cary 50 BioVarian spectrophotometer. Luminescence spectra and luminescence intensity versus time profiles were recorded using a PerkinElmer LS50 fluorimeter and lifetime measurements were made with an IBH Fluorocube time-correlated single-photon counting system, using a NanoLed-03 source, which has its excitation peak wavelength at 370 nm. All UV irradiations were conducted using a 2×4 W BLB handheld UVA light source (typical irradiance = 4 mW cm^{-2}).

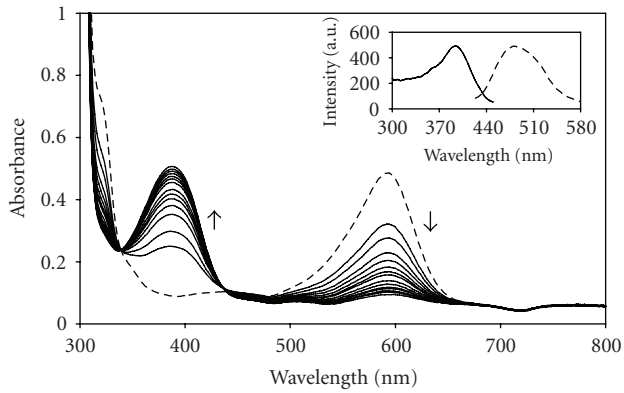

Figure 2: UV/Vis spectra recorded for an indigotetrasulfonate (ITS) deoxygenated aqueous solution 2.8×10^{-5} mol dm^{-3}, pH4): broken line. Upon reaction with a zinc amalgam pellet, the blue ITS solution is reduced to *leuco*-indigotetrasulfonate (*leuco*-ITS), signalled by the decrease in absorbance at 590 nm and the increase at 390 nm (spectra were recorded every 30 minutes). The insert diagram illustrates the excitation spectrum (solid line; λ_{em} = 485 nm) and emission spectrum broken line; λ_{ex} = 390 nm) of a 2.8×10^{-5} mol dm^{-3} *leuco*-ITS deoxygenated aqueous solution, at pH4.

3. RESULTS AND DISCUSSION

3.1. Chemical reduction of an ITS solution

An aqueous solution of *leuco*-ITS can be readily prepared from an ITS solution *via* the addition of a reductant, such as zinc amalgam. However, *leuco*-ITS is very oxygen-sensitive and readily oxidized back to ITS by ambient oxygen and so, in order to prevent this re-oxidation step occurring whilst recording the spectral properties of the reduced redox dye in solution, any oxygen needs to be removed. Thus, in a typical experiment, a dilute solution of ITS (2.8×10^{-5}), at pH4, was prepared and the absorbance spectra recorded, as illustrated in Figure 2 (broken line). ITS absorbs in the blue region of the visible spectrum, with a wavelength of maximum absorbance, λ_{max}, at 590 nm, which is typical for this dye [14]. This solution was then deoxygenated *via* 5 cycles of a freeze-thaw process. Addition of a zinc-amalgam pellet to the deoxygenated ITS solution reduced the highly coloured ITS solution to its very pale yellow *leuco*-ITS form, as shown by the decrease in absorbance at 590 nm and the increase in absorbance at 385 nm in Figure 2 (spectra were recorded every 30 minutes). Excitation of *leuco*-ITS at this wavelength (385 nm) revealed a blue luminescence with an emission maximum at 485 nm. The uncorrected excitation (λ_{em} = 485 nm) and emission spectrum (λ_{excit} = 390 nm) of the *leuco*-ITS aqueous solution are illustrated in the insert diagram of Figure 2. Single-photon counting revealed the lifetime of luminescence of *leuco*-ITS in aqueous solution, at pH4, to be 0.24 ± 0.02 microseconds.

3.2. Photobleaching of an ITS oxygen indicator film

A parallel study, to that above, was carried out on a typical ITS oxygen indicator film, with one set of experiments carried out under vacuum (10^{-3} mbar), that is, O_2 free, and the other under ambient conditions, that is, 21% O_2. A typical absorbance spectrum of a blue-coloured indicator film under vacuum before (broken line) and after activation with UVA light is illustrated in Figure 3(a). From these results it can be seen that the initially blue-coloured ITS film is activated, that is, converted from ITS to *leuco*-ITS via the photoreduction of ITS by the UV-excited titania particles (see Figure 1) in under 3 minutes of UVA irradiation. This photoreduction process (step 1, Figure 1) produces a fall in absorbance of the film at 600 nm as a function of UVA irradiation time as indicated by the data in Figure 3(a) insert diagram. In contrast, under otherwise the same conditions, a typical oxygen indicator in an ambient environment takes twice as long to activate using the same UVA light source (I = 4 mW cm^{-2}). The lower rate of photobleaching in the latter system is due to the presence of oxygen in the ambient environment which is able to reoxidise the reduced form of the dye *via* a dark reaction, that is step 2 in Figure 1.

Figure 3(b) contains photographs of a typical TiO_2/ITS/glycerol/HEC ink spun coated onto a coverslip (i) before and (ii) after photobleaching by UV irradiation (30 seconds, I = 7 mW cm^{-2}) in air. Photograph (iii), in Figure 3(b), is after *ca*. 15 minutes in the dark under ambient conditions, during which time the ITS film regains its original colour (and loses its luminescence), due to the reoxidation of *leuco*-ITS to ITS by oxygen. Photographs (i)–(v) confirm that the ITS indicator films can be photoactivated under ambient conditions to produce a luminescent yellow, *leuco*-ITS film that is oxygen-sensitive.

The UV activation of a typical ITS oxygen indicator film can also be monitored by luminescence, given that *leuco*-ITS luminesces at 470 nm in the film (see Figure 3(b), photographs (iv) and (v)). The observed change in the emission spectrum of an ITS oxygen indicator film, under vacuum, upon exposure to UVA light as a function of time is illustrated in Figure 4. The insert diagram illustrates a plot of the variation in a film's luminescence intensity as a function of UVA irradiation time, and, as in the absorption spectral changes in Figure 2, shows that in the absence of oxygen the film is activated in less than 3 minutes, in comparison to an oxygen indicator film in an ambient environment, which takes *ca*. 6 minutes due to the dark back reaction, that is, step 2 in Figure 1.

3.3. Dark oxidation of an activated ITS film

Once activated, that is, photobleached, via step 1 in the reaction scheme in Figure 1, the stability of the photobleached oxygen indicator film depends on the level of oxygen present in the environment in which it finds itself. Thus, in the dark and in the absence of oxygen, the UV-activated oxygen indicator remains bleached indefinitely, whereas in the presence of oxygen, its colour is restored within seconds and the luminescence associated with the reduced form of ITS is quenched. This is nicely illustrated by the data in Figures 5 and 6 (broken lines), which depict the recorded change in absorbance at 600 nm and luminescence intensity at 470 nm, respectively, as a function of time, of an

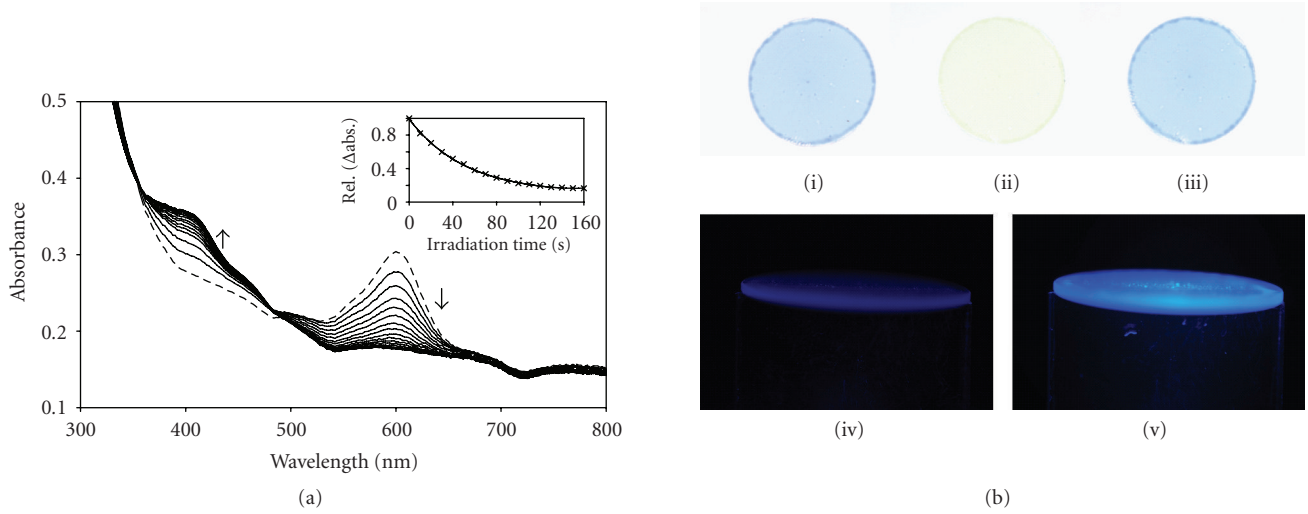

Figure 3: (a) Recorded change in the UV/Vis spectrum of an ITS oxygen indicator film (broken line), in the absence of oxygen, upon exposure to UVA light (intensity: 4 mW cm^{-2}) as a function of time. The spectra illustrated were irradiated (from top to bottom at 600 nm) for 0 second up to 160 seconds, in 10-second intervals. The insert diagram illustrates the change in absorbance of the indicator film at 600 nm as a function of irradiation time, derived from the data in the main diagram. (b) Photographs of an oxygen indicator film on a coverslip. (i) TO_2/ITS/glycerol/HEC film before and (ii) after 30 seconds UVA irradiation (I = 7 mW cm^{-2}), and (iii) film in photograph (ii) allowed to recover after 15 minutes in air. (iv) Photograph of film (i) under very low UV-light illumination in the presence of oxygen. (v) Photograph of film (ii) also under very low UV-light illumination.

ITS-based oxygen indicator film that has been UV irradiated in a vacuum and subsequently exposed to an ambient atmosphere by opening up the system to air. In contrast to this data, the solid lines in Figures 5 and 6 correspond to the recovery of an UV-activated oxygen indicator film, irradiated under ambient conditions (i.e., 21% O_2) and maintained in this environment once the photobleaching process was stopped. Not surprisingly, the oxygen indicator film in an evacuated environment recovered its original blue colour when exposed subsequently to oxygen in the dark. However, the ITS indicator film which was initially photobleached in air recovered only *ca*. 50% of its original colour, possibly due to some photodegradation of the redox dye, presumably caused by the longer exposure to UVA light in air needed to photobleach the film, which probably promotes dye degradation via singlet oxygen production.

The insert diagrams in Figures 5 and 6 show that the dark process (step 2, Figure 1) gives a good fit to first-order kinetics for a UV-activated oxygen indicator film when photobleached and left to recover in an ambient atmosphere, or when photobleached in a vacuum and subsequently exposed to air. Such first-order kinetics are typical for UV-activated oxygen film indicators and provide support for the proposed scheme, that the kinetics of step 2 in the reaction scheme in Figure 1 depend directly upon the rate of diffusion of O_2 through the film. Other work indicates that the rate of this dark recovery process is first order with respect to the partial pressure of oxygen in the ambient atmosphere as with similar UV-activated, oxygen-sensitive film indicators. The first-order rate constants for the recovery of a typical UV-activated oxygen indicator film in an ambient environment and in a vacuum are given in Table 1. It remains

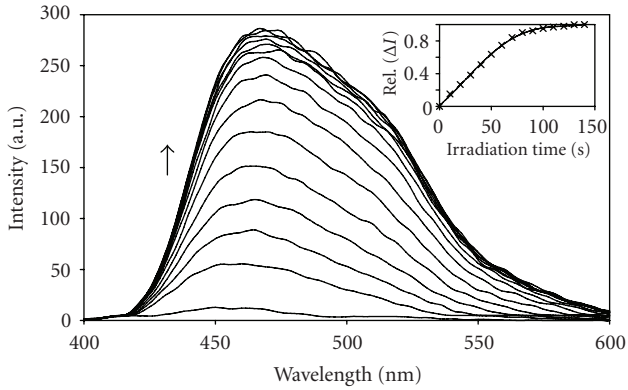

Figure 4: Recorded change in the emission spectrum of an ITS oxygen indicator film (broken line), under vacuum, upon exposure to UVA light as a function of time. The spectra illustrated were irradiated (from bottom to top) for 0 second up to 140 seconds, in 10-second intervals. The insert diagram illustrates the change in luminescence intensity of the indicator film at 470 nm as a function of irradiation time, derived from the data in the main diagram.

unclear why the kinetics of step 2, the dye recovery step, are slower for an ITS film irradiated in air, compared to that for films irradiated in a vacuum, although an appreciable degree of dye degradation is observed for the latter process (*vide supra*). The above results stress the need for oxygen-free conditions when UV-activating these ITS-based indicators.

4. CONCLUSION

A novel, fast acting luminescent and colourimetric oxygen indicator ink is described, containing a sacrificial electron

Table 1: Photobleaching and recovery kinetics of a typical UV-activated oxygen indicator.

	Photobleaching kinetics				Recovery kinetics			
Environment	Abs·k_1(s^{-1})	r^2	Int·k_1(s^{-1})	r^2	Abs·k_1(s^{-1})	r^2	Int·k_1(s^{-1})	r^2
Ambient	0.0063	0.99	0.0075	0.96	0.0062	0.99	0.0091	0.99
Vacuum	0.013	0.99	0.015	0.97	0.033	0.99	0.027	0.98

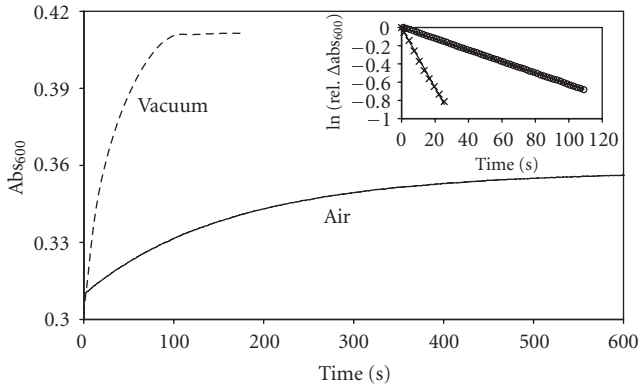

Figure 5: Change in the absorbance, at 600 nm, of a typical UV-activated ITS oxygen indicator film as a function of time, under an ambient atmosphere (solid line) and an ITS film UV-activated under vacuum and subsequently exposed to air (broken line). Each film was fully photobleached, using UVA light, before being allowed to recover. The insert diagram is a first-order plot (natural log of the change in the absorbance, that is, ln (ΔAbs), at 600 nm versus time), over one half life, derived from the data in the main diagram. The rate constants for this recovery step are given in Table 1.

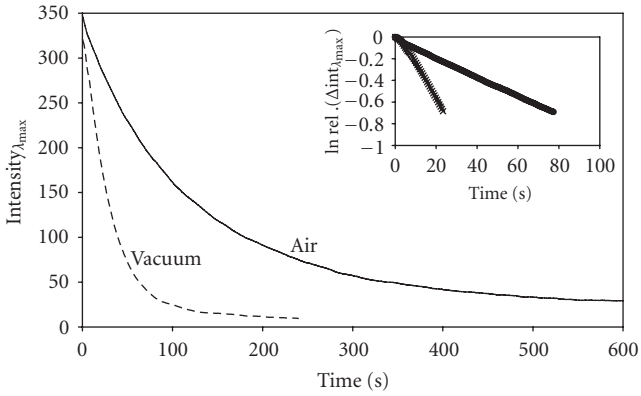

Figure 6: Change in the luminescence intensity, at 470 nm, of a typical, UV-activated ITS oxygen indicator film as a function of time, under an ambient atmosphere (solid line) and when exposed to air (broken line), having been first UV-activated under vacuum. Each film was fully photobleached, using UVA irradiation, before being allowed to recover in air. The insert diagram is a first-order plot, over one half life, derived from the data in the main diagram.

donor (glycerol) and the redox indicator (indigotetrasulfonate). The indicator is blue coloured in the absence of UV light, however, upon exposure to UV light it not only loses its colour but also luminesces, unless and until it is exposed to oxygen, whereupon, under dark conditions, its colour is restored. The initial photobleaching spectral (absorbance and luminescence) response characteristics in air and in vacuum are described and discussed in terms of a simple reaction scheme involving UV activation of the titania photocatalyst particles, which are used to reduce the redox dye, ITS, to its *leuco* form. The response characteristics of the activated, that is, UV-photobleached form of the indicator, to oxygen are also reported. This indicator appears more sensitive towards oxygen than previous UV-activated indicators, based on methylene blue, probably due to the lower redox potential [14] of ITS (−0.046 V versus SHE) compared to that of methylene blue (+0.028 V versus SHE) at pH7. This indicator appears susceptible to appreciable photodegradation when UV-activated under ambient (21% O_2) conditions. In the absence of oxygen, however, UV activation is not only more rapid, but also does not produce any significant photodegradation. Thus, the ink appears particularly suited for use in systems that are usually oxygen free, before UV activation, as a means of indicating any subsequent leak or tampering.

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