Novel UV-Activated Colorimetric Oxygen Indicator

Soo-Keun Lee, Martin Sheridan, and Andrew Mills*

Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, United Kingdom

Received December 20, 2004. Revised Manuscript Received March 9, 2005

The results of a detailed characterization study of a novel UV-activated colorimetric oxygen indicator are described. The indicator uses nanoparticles of titania to photosensitize the reduction of methylene blue by triethanolamine in a polymer encapsulation medium, using UVA light. Upon UV irradiation, the indicator bleaches and remains in this colorless state in the dark, unless and until it is exposed to oxygen, whereupon its original color is restored. The indicator is reusable and irreversible. The rate of color recovery is proportional to the level of oxygen present. A layer of PET (poly(ethylene terephthalate)), of thickness *b*, placed on top of the indicator film slows down its response, and the 90% recovery time is proportional to *b*.

Introduction

The detection and measurement of oxygen, whether it be in the gaseous phase or dissolved in solution, is an important part of analytical chemistry, since oxygen plays a significant, if not vital, role in such a myriad of different areas. For example, the measurement of oxygen is an essential feature in the monitoring of the well-being of many biological systems, e.g., in environmental analysis, patient monitoring, and biotechnology. It is also important in a wide range of industries, including food packaging, steel production, sewage treatment, petroleum processing, glass, pulp and paper manufacture, and beer production.[1,2]

There are many established methods for the detection and measurement of oxygen, including the Clark electrode,[1] and gas chromatography.[3] However, such systems are usually expensive, both in terms of initial capital outlay and running costs, and so there is increasing interest in inexpensive and disposable sensor technologies, such as that offered by optical sensors.[4] Not surprisingly, the most studied of all the optical sensors are those for oxygen. This area of research has been dominated by the quenching of polymer-encapsulated lumophores, such as the dication, ruthenium (II), tris (4,7 diphenyl, 1,10 phenathroline), i.e., $Ru(dpp)_3^{2+}$, and platinum (II) octaethyl porphyrin, by oxygen. Commercial products based on this work include the elegant OxySense system, in which $Ru(dpp)_3^{2+}$ is encapsulated in silicone rubber dots, and the oxygen level surrounding dot is determined using an excited-state lifetime measuring device based on a phase modulation technique.[5] Such a system is proving extremely popular and useful in food and beverage packaging research, since an OxySense dot can be placed inside any package/bottle and the oxygen concentration within can be measured, using the lifetime measuring device on the outside. Other commercial manifestations of this technology include: diagnostic systems, such as the BD 960 system for microbacteria testing[6] and a number of systems from PreSens for monitoring oxygen in cell cultures and inside plastic packaging.[7]

The use of such oxygen sensors in packaging is very important, as it helps establish easily and quickly what materials, closures and seals are effective in minimizing oxygen ingress. Oxygen is responsible, directly or indirectly, for most food spoilage, since without oxygen most of the responsible bacteria and moulds would not thrive. Indeed, typically, the lifetimes of most foods can be extended by 3−4 times those in air, if the oxygen present is removed when it is packaged.[2] Thus, Modified Atmosphere Packaging (MAP), in which the food package is flushed with carbon dioxide, nitrogen, or simply vacuum packed in order to remove oxygen, is a major method of packaging in the food and beverage industry, with over 41 billion packages MAPed in 2004 alone, and this number predicted to rise to 52 billion by 2007.[8] Unfortunately, the detection of oxygen using the OxySense system, or any optical sensor based on luminescence,[4,9] involves the use of relatively expensive instrumentation, and so has not yet found application in the routine analysis of all MAPed packages. The latter is a highly desirable goal, as it would make possible 100% quality assurance in MAP and lead to greater consumer confidence in the integrity of food packaging.

Unlike changes in luminescence intensity or lifetime, which really require measurement or assessment based on the response of dedicated, purpose-built optical instrumentation, a change in color can be observed and assessed by eye. Unfortunately, there have been comparatively few reports

* Corresponding author. E-mail: a.mills@strath.ac.uk.

(1) Hitchman, M. L. *Measurement of Dissolved Oxygen*; John Wiley: York, ME, 1978.
(2) Brody, A. L.; Strupinsky, B. R.; Kline, L. R. *Active Packaging for Food Applications*; Technomic Publishing Co.: Lancaster, PA, 2001.
(3) Valenty, S. J. *Anal. Chem.* **1978**, *50*, 669−671.
(4) Wolfbeis, O. S. *Fiber Optic Chemical Sensors*; CRC Press: Boca Raton, FL, 1991.
(5) OxySense Inc. http://www.oxysense.com/about.html (accessed Dec. 2004).
(6) BD Inc. http://www.bd.com/Clinical/products/mycob/mgit960.asp (accessed Dec. 2004).
(7) PreSens GmbH. http://www.presens.de/html/start.html (accessed Dec. 2004).
(8) Anon. *Active & Intelligent Pack News* **2004**, *2* (13), 4−5.
(9) Papkovsky, D. B.; Papkovskaia, N.; Smyth, A.; Kerry, J.; Ogurtsov, V. I. *Anal. Letts.* **2000**, *33*, 1755−1777.

10.1021/cm0403863 CCC: $30.25
Published on Web 04/15/2005

of colorimetric oxygen sensors and most of those that have been reported have not been without problems. Thus, the work of Zhujun and Seitz[10] on an early example of such a sensor reported that although oxyhemoglobin, immobilized on a cation resin, gave a measurable color change over an oxygen partial pressure range, P_{O2}, 20−100 Torr, the sensor was stable for only 2 days when stored at room temperature. A flurry of papers in the early nineties[11−14] reported on the colorimetric detection of oxygen using the complex, bis-(histodinato) cobalt (II), $Co(His)_2$, either in solution or immobilized on a TLC plate, subsequently coated with silicone rubber. Unfortunately, this sensor did not work in dry air, was very pH-sensitive, and the color changes were not striking. Following on from this work on oxygen-binding metal complexes, Valentine and co-workers[13] reported that myoglobin (Mb) could be encapsulated in a glass matrix by a sol−gel method. The resulting sensor was used to measure dissolved oxygen levels spanning the range 2−8 ppm and the rate of change of the visible absorption spectrum was found to be proportional to the dissolved oxygen concentration. To reuse the sensor again the oxy-Mb gel needed to be reconverted to deoxy-Mb gel using a dithionite solution. Unfortunately, as a consequence of the irreversible nature of the sensor, it needed to be stored in an anaerobic, reducing environment before use, which rather limited its possible areas of application.[13]

Problems of expense and stability are also associated with the most well-known of the commercial colorimetric oxygen indicators, the Ageless Eye, manufactured by the Mitsubishi Gas Company in Japan.[15−17] The basic chemical reactions underpinning this excellent, but relatively expensive, indicator are those of the equally well-known Blue Bottle Experiment, in which a redox indicator, invariably methylene blue, MB, is dissolved in an aqueous solution containing a reducing sugar (usually glucose in an alkaline solution), which is then sealed in a bottle.[18−20] The quiescent solution is colorless, since under such conditions the dominant reaction is the reduction of the blue-colored MB to its colorless, leuco form, LMB, by the sugar, i.e.:

$$\text{MB} + \text{glucose} \rightarrow \text{LMB} + \text{gluconic acid} \qquad (1)$$

However, upon shaking the bottle, oxygen in the headspace dissolves in the solution, and the dominant reaction becomes the oxidation of LMB to MB, i.e.:

$$\text{LMB} + \text{O}_2 \rightarrow \text{MB} + \text{H}_2\text{O} \qquad (2)$$

Thus, on shaking the solution turns blue. Upon leaving it to stand, reaction 1 quickly dominates reaction 2 again, and the solution returns to its colorless initial form, as all the MB is converted to LMB, ready to be shaken again.[18,19] The process can be repeated many times until eventually the reducing sugar is used up; at which point the dye remains in its blue, oxidized, form, even when the solution is not shaken.

In the Ageless Eye, the MB, glucose, and alkali, usually $Ca(OH)_2$ or $Mg(OH)_2$, along with a red, redox-insensitive dye, such as Acid Red 52, are mixed together and pressed to form a pellet.[15,16] In the absence of oxygen, reaction 1 dominates, and the pellet appears pink. In the presence of air, reaction 2 dominates, and the pellet is purple.[15] This indicator, like the blue-bottle reaction, is reversible, but requires storage under anaerobic conditions otherwise the reducing sugar is rapidly consumed and the indicator stops working. The pellet obviously must not make contact with any food or beverage; thus, it is usually sealed in a small, clear, oxygen-permeable, ion-impermeable plastic bag. In addition, its response is affected by humidity (it works best under humid conditions), and the presence of carbon dioxide (a major MAP gas, it interferes with the response of the Ageless EyeTM by reacting with the alkali present).[21] As a result, although the Ageless Eye, and other optical sensors based on the same, or similar reaction chemistry can, and are, used as indicators of oxygen ingress in the food packaging industry[21,22] — their use is limited because of cost and storage issues. Another type of oxygen indicator is required for the routine use in MAP.

In addition, it is generally acknowledged[21] that any oxygen indicator for the food packaging industry must exhibit an irreversible response; a feature obviously absent from the Ageless Eye and most other colorimetric and lumophoric-based sensors developed to date. The reason for wanting this feature of irreversibility is that if a package develops only a very small leak, oxygen will get in and the subsequent microbe growth is likely to be rapid. Any reversible optical oxygen indicator present would respond at this point, e.g., by changing color or luminescence intensity. However, a position is likely to be reached where the rate of oxygen ingress is equalled by the rate of microbe metabolism and a reversible indicator would, correctly, then revert to its initial color or luminescence intensity. Thus, any consumer, looking at the indicator in the package several days on from the initial leak would assume incorrectly from its color/luminescence intensity that the package's integrity had not been compromised and that food inside was safe to eat.[21] This problem would not arise if the oxygen indicator employed exhibited an irreversible optical response.

In this paper the results of a detailed study of an irreversible, reusable, UV-activated colorimetric oxygen indicator are reported, brief details of which have been the subject of a recent preliminary communication.[23] This indicator is

(10) Zhujun, Z.; Seitz, W. R. *Anal. Chem.* **1986**, *58*, 220−222.
(11) Bianco, A. D.; Baldini, F.; Bacci, M.; Klimant, I.; Wolfbeis, O. S. *Sensors Actuators B* **1993**, *11*, 347−350.
(12) Baldini, F.; Bacci, M.; Kosi, F.; Bianco, A. D. *Sensors Actuators B* **1992**, *7*, 752−757.
(13) Chung, K. E.; Esther, H. L.; Davidson, M. S.; Dunn, B. S.; Valentine, J. S.; Zink, J. I. *Anal. Chem.* **1995**, *67*, 1505−1509.
(14) Kuncova, G.; Fialova, M. *Biotechnol. Technol.* **1995**, *9*, 175−178.
(15) Mitsubishi Gas Chemical Co. Inc. http://www.mgc.co.jp/eng/ company/ materials/products/ageless/related/index.html (accessed Dec. 2004).
(16) Yoshikawa, Y.; Nawata, T.; Otto, M.; Fujii, Y. US Patent 4169811, 1979.
(17) Goto, M. JP Patent 62259059, 1987.
(18) Snehalatha, T.; Rajanna, K. C.; Saoprakash, P. K. *J. Chem. Educ.* **1997**, *74*, 228−233.
(19) Mowry, S.; Ogren, P. J. *J. Chem. Educ.* **1999**, *76*, 970−973.
(20) Adamcikova, L.; Pavlikova, K.; Sevcik, P. *Int. J. Chem. Kinet.* **1999**, *131*, 463−468.
(21) Smolander, M.; Hurme, E.; Ahvenainen, R. *Trends Food Sci. Technol.* **1997**, *8*, 101−106.
(22) Eaton, K. *Sensors and Actuators B* **2002**, *85*, 42−51.
(23) Lee, S.-K.; Mills, A.; Lepre, A. *Chem. Commun.* **2004**, 1912−1913.

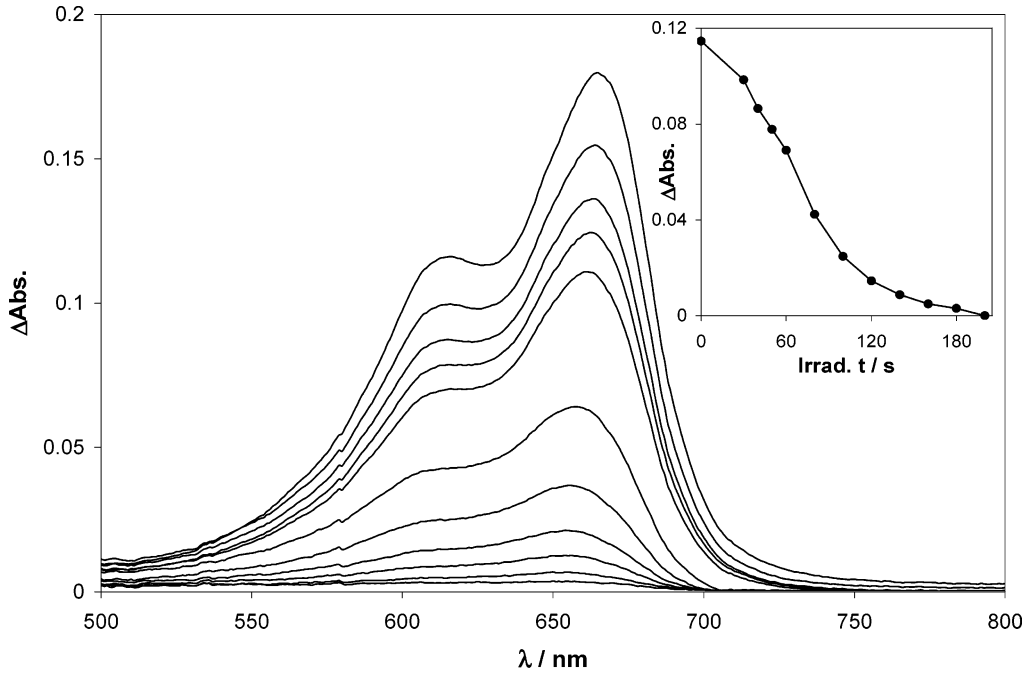

Figure 1. Recorded change (ΔAbs) in the visible absorbance spectrum of an indicator film upon exposure to UVA light (intensity: 4.1 mW cm^{-2}) as a function of irradiation time. The change in absorbance (ΔAbs) at any wavelength was taken as the actual absorbance of the film minus the absorption of a fully bleached film (i.e., one irradiated for ca. 200 s). The ΔAbs vs wavelength absorption spectra illustrated correspond to the following irradiation times (from top to bottom): 0, 30, 40, 50, 60, 80, 100, 120, 140, 160, and 180 s, respectively. The insert diagram illustrates the change in absorbance of the indicator film at 610 nm as a function of irradiation time, derived using data from the main diagram.

the first of a new generic range of gas indicators that are likely to feature strongly in the burgeoning area of intelligence, i.e., information, inks for the packaging of food, pharmaceuticals, beverages and other materials.

Experimental Section

Materials and Indicator Preparation. Unless stated otherwise, all chemicals were purchased from the Aldrich Chemical Co. (Gillingham, Dorset, UK). The semiconductor, titanium dioxide (TiO_2), was P25 provided by Degussa (Frankfurt, Germany). Degussa P25 TiO_2 is a semiconductor that is commonly used in photocatalyst research. It is a white powder comprising titania particles, typically ca. 30 nm in diameter, with an 80:20 anatase: rutile crystal phase composition and an overall specific area of ca. 50 m^2 g^{-1}. All solutions were made up using doubly distilled, deionized water. All gases were provided by BOC (London, U.K.).

A typical example of the irreversible, reusable, UV-activated colorimetric oxygen indicator ink, used to make the indicator films reported in this work, comprised: 5 g of a 5 wt % aqueous dispersion of P25 TiO_2, 1 g of a 5 wt % aqueous solution of the redox indicator dye, methylene blue (MB), 0.3 g of a mild sacrifical electron donor (SED), triethanolamine (TEOA), and 20 g of a 5 wt % aqueous solution of an encapsulating polymer, hydroxyethyl cellulose (HEC). The indicator ink components were mixed together, subjected to 3 min ultrasound from an ultrasound bath, to disperse the usually aggregated titania particles, and then stirred magnetically for 30 min to produce the final oxygen intelligence ink for casting. A typical colorimetric oxygen indicator was prepared from this ink by placing 2−3 drops (ca. 0.1 mL) on to a 22 mm diameter glass coverslip which was subsequently spun at 6000 rpm for 30 s. The final oxygen indicator film on the glass disk proved stable for over 1 year in the dark, under otherwise ambient conditions. The oxygen indicator films are blue and transparent, with absorbance maxima at 610 and 665 nm.

Methods. All UV/vis spectra and Absorbance versus time profiles were recorded using a Perkin-Elmer Lamda 20 UV/Vis spectrophotometer (Seers Green, UK). O_2/N_2 gas mixtures, of different known ratios, were prepared by blending nitrogen/air and nitrogen/oxygen using a Cole Parmer gas-blender, (London, UK). All UV radiations were conducted using UVA light, provided by a 100 W black-light-blue (BLB) lamp (Blak-Ray, Upland, CA). The intensity of which, at the film, was measured using a UV meter as 4.1 mW cm^{-2}.

Results and Discussion

Initial Experiments and Fundamental Reactions. In air, under ambient room light conditions, the blue indicator films do not change color in the absence or presence of oxygen. However, upon irradiation with UVA light, under aerobic or anaerobic conditions, they are bleached within 3 min, as illustrated by the recorded changes in the visible absorption spectrum of a typical oxygen indicator film as a function of irradiation time, shown in Figure 1. The insert diagram in Figure 1 shows the measured change in the absorbance of the film at 610 nm as a function of UVA irradiation time.

The fate of a photobleached oxygen indicator film, once the UVA light is switched off, depends on the environment in which it finds itself as illustrated by the data in Figure 2, which depicts the recorded changes in absorbance of a typical oxygen indicator film at 610 nm as a function of dark time after illumination for 2 min in nitrogen and then exposure to a variety of different gaseous atmospheres ranging from 0 to 100% oxygen. Thus, in the absence of oxygen, the UV-activated oxygen indicator remains bleached indefinitely, whereas in the presence of oxygen, its color is restored and at a rate that increases with increasing % oxygen. A typical indicator film used in this work has a mass per cm^2 of 3.6×10^{-4} g cm^{-2}, of which only 3.1 wt % is MB. It follows that once fully activated, i.e photobleached, such a film would

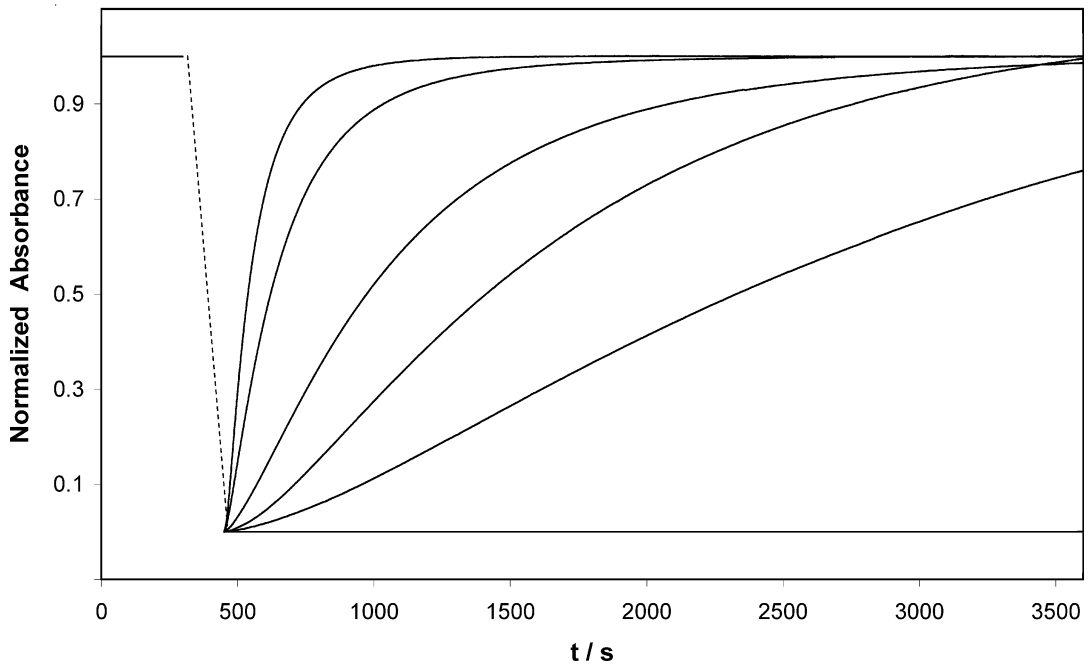

Figure 2. Change in the normalized absorbance (measured at 610 nm) of a typical, UV-activated, colorimetric oxygen indicator film as a function of time, under an ambient atmosphere with different levels of O_2 present. Each film was UV-irradiated for 2.5 min (100 W BLB) (broken line) under aerobic conditions before being exposed to a range of different oxygen levels. The $\%O_2$ levels used to generate the different profiles were as follows: 100 (fastest recovery), 60, 21, 10, 5, and 0 (slowest, i.e., no, recovery) % oxygen.

require only 3.6×10^{-4} cm^3 of oxygen per cm^2 of film to return it to its original color.

Additional work shows that visible light irradiation does not bleach the indicator film under either aerobic or anaerobic conditions. Thus, the oxygen indicator is only activated, i.e., photobleached, with UV light. Although most white fluorescent lights, such as found in a food display cabinet, do have a small amount of UVA light component, this is not sufficient to bleach a typical indicator film under aerobic conditions. However, under anaerobic conditions, the indicator films can be bleached upon prolonged exposure to such light. This possible limitation may be overcome by using larger band gap semiconductors, such as tin(IV) oxide. Other experiments show that such oxygen indicator films do not function as oxygen indicators if one or more of the key ingredients, such as semiconductor photocatalyst, redox indicator and sacrificial electron donor (SED), is omitted from the formulation. The activation and detection chemistry of the indicator film are unaffected by the presence of carbon dioxide. Thus, there appears to be no difference in the kinetics of the photobleaching step when carried out in an anaerobic nitrogen or carbon dioxide atmosphere. Nor is there any significant change in the response time of an activated indicator toward 21% oxygen, when the remaining gas is nitrogen or carbon dioxide. Although most of the experiments reported here were conducted using dry gases, additional work showed that, whereas the UV activation step was not affected by high levels (relative humidity = 100% at 25 °C) of humidity, the detection step was significantly (ca. 13x's) faster, probably due to the plasticizer action of water on the HEC polymer film, which increases the rate of oxygen diffusion within the film.

The choice of ink formulation key ingredients requires careful consideration, based upon an understanding of the general mechanism of operation of these colorimetric oxygen indicator films. In this work the semiconductor photosensitizer is responsible for the UV-driven activation step, and as a consequence, the semiconductor used should be photocatalytically active using UV light. Ultra-band-gap irradiation of the semiconductor generates electrons and holes that are able to reduce the redox indicator and oxidize the SED, respectively.[24] A number of visible light absorbing semiconductors, such as CdS and CdTe, can be used to fulfill this role in the indicator films. However, one of the attractive features of the oxygen indicator reported here is that it is activated by UV light only, since visible light activated oxygen indicators, which are already known,[25,26] can find little application in MAP as they would be continually reactivated by ambient visible light. Fortunately, there exists a number of only-UV light-absorbing semiconductors, such as ZnO, SnO_2, and TiO_2 that can be used as the semiconductor in the UV-only activated oxygen indicator film technology reported here. Of these, Degussa P25 TiO_2 appears to work best and so was used throughout. Work showed that only the kinetics of UV activation step were changed by the amount of semiconductor; increasing with increasing $[TiO_2]$. The amount of TiO_2 used in the film formulation reported here was chosen so as to provide a reasonably rapid response to the UV light, i.e., within a few minutes.

Titania is a very stable and inexpensive pigment that is widely used in the food industry and, with a band gap of 3.0−3.2 eV, and a recognized high photocatalytic activity, appears an ideal candidate for the role of UV-absorbing only

(24) Mills, A.; LeHunte, S. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 1−35.
(25) Barmore, C. R.; Bull, C. US Patent 5483819, 1996.
(26) Blinka, T. A.; Bull, C.; Barmore, C. R.; Speer, D. V. US Patent 5583047, 1996.

semiconductor in the oxygen indicator film.[24] The photogenerated holes on titania are sufficiently oxidizing, $E°(h^+) = 2.91$ V, to oxidize most organics, either directly or indirectly, through the generation of hydroxyl radicals. The photogenerated electrons on titania, $E°(e^-) = -0.32$ V, are sufficiently reducing to reduce many redox-indicators, as well as oxygen. It is preferred that this dye-reduction reaction dominates even if some oxygen (up to 21%) is present, so that the reduction of the redox indicator, rather than that of oxygen, by the photogenerated electrons takes place during the photoactivation step. This feature then allows the oxygen indicator to be UV-activated, i.e., switched on, even under aerobic conditions. Thus, the selected redox indicator should be readily and almost exclusively reduced by the photogenerated electrons on the semiconductor particles.

In addition, the redox indicator should also not absorb significantly in the UVA region (315−380 nm) at least, i.e., where the UV-only absorbing semiconductor absorbs, otherwise the UV activation step is likely to be slow since the indicator will screen the semiconductor particles from the incident, activating UV light. Also, the redox indicator should not have such an active photochemistry that it is readily photobleached by UV or visible light illumination when placed in contact with the other film ingredients. In particular, in the film formulation the electronically excited state of the dye should not react directly with the SED or oxygen. Finally, the reduced form of the redox indicator should be: of a different color to its original oxidized form, stable (under anaerobic conditions), and readily re-oxidized back to its original oxidized form by oxygen.

The above demanding list of desired properties for the redox indicator are well addressed by methylene blue, a common redox-indicator, that is readily reduced,[27] by photogenerated conductance band electrons on titania semiconductor particles, to its leuco form, i.e., leuco-methylene blue, via the following reaction:

$$MB + 2e^- + H^+ \rightarrow LMB \qquad (3)$$

since $E°(MB/LMB) = +0.53$ V and $E°(e^-) = -0.32$ V (as noted earlier). Although methylene blue is a recognized photosensitizer,[27] its electronically excited states do not appear to undergo reaction with any of the ingredients in the typical oxygen indicator film formulation reported here, to form any permanent products. It is also a poor absorber of UVA light, since it has no major absorption bands in the region 300−400 nm. As a consequence, it is no surprise to note that a typical indicator film, lacking only the UV-absorbing semiconductor, does not bleach or change color under aerobic or anaerobic conditions upon irradiation with either UVA or visible light.

The sacrificial electron donor must be chosen so that it is readily and irreversibly oxidized by the photogenerated holes or hydroxyl radicals, on the surface of the semiconductor particles and does not reactively quench the excited states of the redox indicator dye. Once oxidized, the SED products must not react with the photogenerated electrons, or reduced redox indicator, since this would lower the efficiency of the UV activation step. The SED must not be capable of reducing directly the redox indicator and so must be a mild reducing agent. Although a number of SED's were tested, including EDTA, glycerol, cysteine, glucose and triethanolamine (TEOA), the latter appeared one of the best and was used throughout this work in the preparation of the oxygen indicator films. Work showed that only the kinetics of UV activation step were changed by the amount of SED; initially increasing with increasing [TEOA] until reaching a limiting value. The amount of TEOA used in the film formulation reported here represented a level that lay in the plateau region and so provided a rapidly responding film to UV activation.

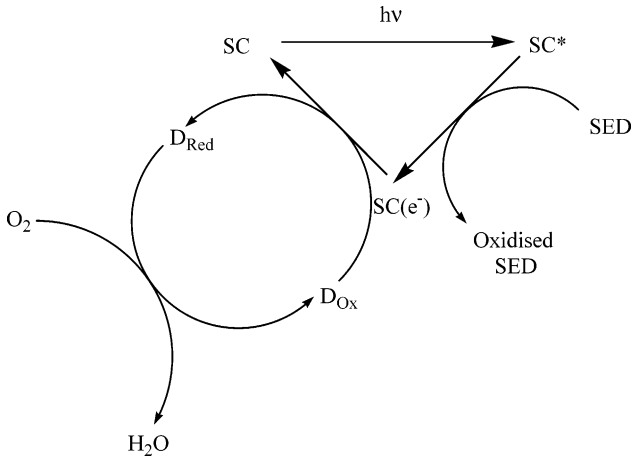

Figure 3. Schematic illustration of the key process associated with the operation of a generic oxygen indicator comprising: semiconductor (SC)/redox-indicator (D_{ox}/ D_{Red})/sacrificial electron donor and mild reducing agent (SED), encapsulated in a polymer environment.

As for the encapsulation medium, it must not be easily oxidized by the photogenerated holes, otherwise the indicator would very quickly lose its feature of reusability (vide infra) and must not be easily reduced by the photogenerated electrons, which otherwise might interfere with the photoactivation step. A wide number of polymers satisfied this set of criteria and hydroxyethylcellulose (HEC) was chosen from among them.

Finally, all the film components must be readily soluble, or easily and well dispersed in the case of the semiconductor, in a common solvent in order to generate an ink, from which the colorimetric oxygen indicator can be cast, printed or spun. In this work, water appeared to be a suitable solvent for all the selected components identified above. The typical oxygen indicator formulation reported here, comprising: TiO_2/MB/TEOA/HEC, is just one of many that can be created based on the generic formula outlined above and which may be summarized as follows: semiconductor/redox indicator/SED/polymer.

The key processes behind the operation of the above generic novel oxygen indicator are illustrated in Figure 3 and can be summarized as follows. Ultra-band-gap illumination of the semiconductor particles creates electron−hole pairs, the photogenerated holes of which rapidly oxidize irreversibly the SED present and the photogenerated electrons reduce the redox indicator dye, D_{ox}, to a differently colored stable reduced form, D_{red}, which is oxygen sensitive. As a result, in the absence of oxygen, ultra-band gap illumination of this type of oxygen indicator produces a color change

(27) Kamat, P. V. *J. Photochem.* **1985**, *28*, 513−524.

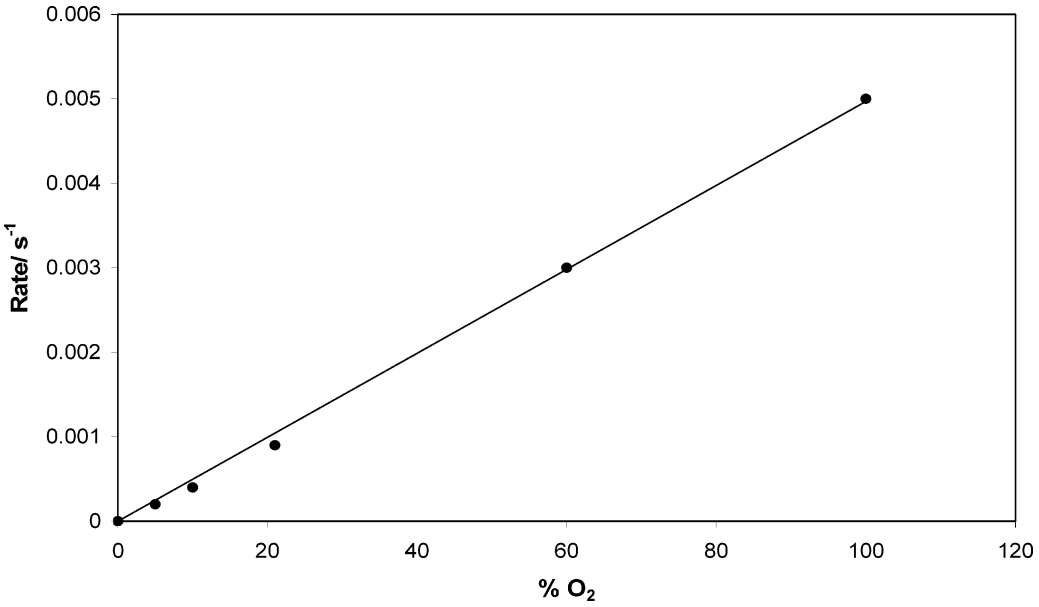

Figure 4. Plot of the initial rate of change in the absorbance of a photobleached, i.e., UV-activated, colorimetric oxygen indicator as a function of the $\%O_2$ in the ambient gas phase. Data taken from the normalized absorbance vs time profiles illustrated in Figure 2.

which, after the cessation of the illumination, i.e., the UV-light activation process, will persist until oxygen is allowed in, whereupon, the indicator will return to its original color, that being the color associated with the initial, oxidized form of the redox indicator, i.e., D_{ox}.

In the oxygen indicator example of this technology reported here, the semiconductor, redox indicator, and sacrificial electron donor are TiO_2, MB, and TEOA, respectively. When using MB (which is bright blue in color) as the redox indicator, D_{ox}, note that the reduced stable form of this dye, i.e., D_{red}, is LMB (which is colorless) and that the reduction step requires the overall transfer of two electrons and a proton,[19−21] i.e.

$$2\ TiO_2(e^-) + H^+ + MB \rightarrow 2TiO_2 + LMB \qquad (4)$$

At present it is not clear if, in a typical indicator film, this reduction process occurs via a concerted two electron-transfer step, or via the intermediate formation of a semi-reduced methylene blue radical, and its subsequent disproportionation, as is often found in homogeneous solution kinetic studies of the reduction of methylene blue by reducing agents, such as Fe^{2+}, ascorbic acid.[18,19,28]

Film Storage and Reuse. The typical example of the colorimetric oxygen indicator reported here exhibits an irreversible response once activated using UV light. Thus, following UV activation and subsequent reaction with oxygen, the indicator, now restored to its initial blue color, will not bleach subsequently, even if the ambient atmosphere is changed from aerobic to anaerobic. Thus, these oxygen indicators are not oxygen sensitive unless and until they are activated using UV light. Indeed, early prototypes have been stored for years under ambient conditions, with no loss in function upon UV activation, since it is only when they are switched on in this way that they become irreversible oxygen sensors. This feature of long shelf life under ambient conditions is in contrast to most other types of colorimetric oxygen indicators, including the Ageless Eye, which are usually reversible in response and so continually consume the reducing agent, usually glucose in alkali, when oxygen is present[15−17,22] and require storage under anaerobic conditions.

Another feature of the TiO_2/MB/TEOA/HEC indicators reported here is that the amount of SED consumed, when the indicator has been used once, is small, making it possible to reuse any such colorimetric oxygen indicator many times.

Quantitative Analysis. Although the TiO_2/MB/TEOA oxygen indicators are ideal for identifying the ingress of air, i.e., package leak indicators, they can also be used for quantitative analysis. Thus, using the data in Figure 2, it was possible to determine the initial rate of recovery of the indicator film as a function of % oxygen and the results of this work are illustrated in Figure 4. From the latter results, it appears that the rate of recovery of the color of a typical oxygen indicator film is directly proportional to the level of O_2 present in the gas phase. Thus, through an 'activate and monitor color recovery' procedure it would be possible to use this type of indicator to provide a quantitative measure of the level of ambient oxygen.

Delayed Indicator Response. The recovery of the initial color of the typical colorimetric oxygen indicator, after UV-activation, depends not only upon the level of ambient oxygen present, but also on the rate of diffusion of the gas into the indicator film. This latter parameter can be controlled by altering the oxygen permeability of the indicator film by using polymer encapsulating materials with different oxygen permeabilities, i.e., the recovery time of the activated films can be controlled by using different encapsulating polymers. Alternatively, and more simply, an additional barrier to oxygen diffusion from the surrounding atmosphere to the film can be used to delay the recovery of the initial color of the UV-activated indicator. Such a delayed-response oxygen

(28) Wildes, P. D.; Lichtin, N. N.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1975**, *97*, 2288−2293.

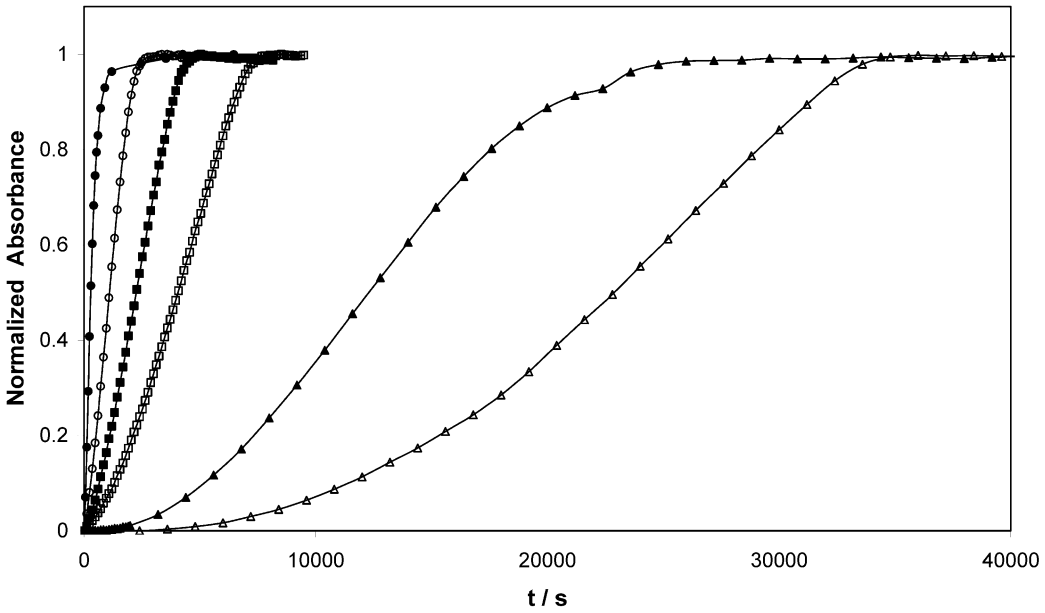

Figure 5. Normalized change in absorbance (at 610 nm) as a function of time, after initial activation (3 min UVA), for a series of identical typical colorimetric oxygen indicator films covered with PET of different thicknesses to slow the film recovery time. The PET thicknesses used were (from left to right): 0, 15, 35, 60, 130, and 230 μm, respectively. The profiles were recorded in air, i.e., at 21% oxygen.

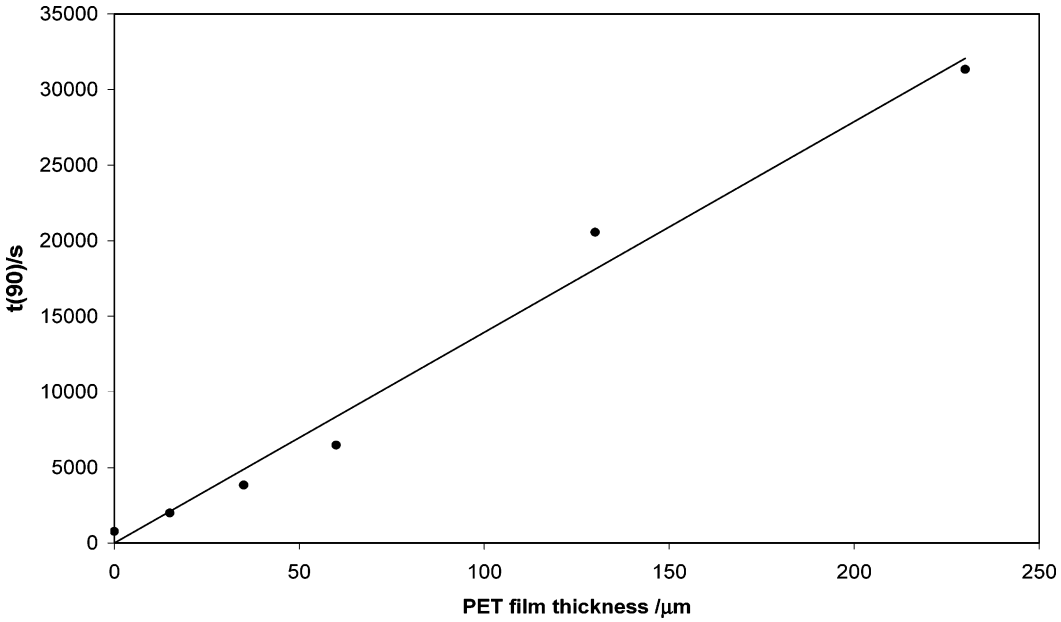

Figure 6. Plot of the measured time for a PET-covered indicator film to recover the 90% of its initial absorbance, i.e., *t*(90) as a function the thickness of the PET covering layer using the data in Figure 5. The data were generate under aerobic conditions, and so the amount of oxygen present was 21%.

indicator has potential in the food packaging industry, since a strip of oxygen indicators, with a series of different delayed responses, could be used to provide a measure of how long the indicator strip had been exposed to air and so used to indicate not only if a MAPed package was leaky, but also, if opened, how long for.

In order to demonstrate the principle behind such a delayed oxygen indicator, a series of identical, typical, colorimetric oxygen indicators were made and then covered with different thicknesses of a polymer, poly(ethylene terephthalate) (PET), noted for its low oxygen permeability (0.42−0.17 cm^3 (STP) cm m^{-2} day^{-1} atm^{-1}).[29] The different thicknesses of PET used in this work spanned the range 0−230 μm. Each film was UV-irradiated in air for 3 min with UVA light, i.e., photobleached and then its color recovery monitored by absorbance spectrophotometry. A plot of the results arising from this work, in the form of a series of normalized absorbance changes as a function of recovery time profiles, is illustrated in Figure 5. From these results it can be seen that, not surprisingly, the thicker the oxygen barrier PET film overlaying the colorimetric oxygen indicator, the slower the recovery of the color of the film in air, once activated with UVA light. A measure of the recovery time for such a film is the time it takes to recover most of, i.e., 90%, its initial color, i.e., *t*(90). Using the data in Figure 5, a plot of *t*(90) versus PET film thickness, *b*, yields a reasonable straight line, as illustrated by the plot of the data in Figure 6.

(29) Liu, R. Y. F.; Hu, Y. S.; Schiraldi, D. A.; Hiltner, A.; Baer, E. *J. Appld. Polymer Sci.* **2004**, *94*, 671−677.

Interestingly, if the process were purely diffusion controlled, the film response time would be expected to depend on b^2 and not the *b*, as observed.[30] Whatever the rate determining step, the results in Figures 5 and 6 indicate that by varying the barrier to diffusion, a series of delayed-response, oxygen indicators can be created that could be used to tell how long a MAPed package had been open. Obviously PET is just one of a number of oxygen barrier materials and to make an indicator that would respond over days, rather than the period of 8h indicated for the thickest PET layer in Figure 5, would require a material with a significantly lower oxygen permeability, such as a ceramic film.

Conclusions

A new type of oxygen indicator is created by mixing a finely divided, UV-only absorbing, semiconductor powder, such as TiO_2, with an appropriate redox-indicator, such as MB, a sacrificial electron donor, such as TEOA and a polymer, such as HEC, in a suitable common solvent/dispersion medium, such as water. This type of intelligence ink can be coated or printed onto a variety of substrates, to produce an oxygen indicator film that is activated, i.e., switched on, by UV light. Most clear polymer materials commonly used in packaging are transparent to UVA light. The colorimetric oxygen indicator is irreversible, reusable, and can be used for quantitative analysis. The response of the indicator film can be altered using a polymer covering layer with a low oxygen permeability, such as PET. The indicator formulation is novel and generic and many other examples, based on the same basic combination of semiconductor/redox indicator/SED/encapsulating polymer can be made. Thus, depending upon the ingredients chosen it is possible to create both colorimetric and fluorimetric indicators that are activated by either UV or visible and UV light. Such indicators, and their ink precursors, are likely to find ready application in a number of areas, including MAP in the food and drug industries.

Acknowledgment. This work was supported by Synergy Fund of the Universities of Strathclyde and Glasgow.

CM0403863

(30) Mills, A.; Chang, Q. *Analyst* **1992**, *64*, 1383−1389.