Journal of Photochemistry and Photobiology A: Chemistry 237 (2012) 7–23

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Invited feature article

# Overview of the current ISO tests for photocatalytic materials

Andrew Mills[a,*], Claire Hill[b], Peter K.J. Robertson[c]

[a] School of Chemistry and Chemical Engineering, Queen's University Belfast, Stranmillis Road, Belfast BT9 5AG, UK
[b] Cristal Global, P.O. Box 26, Grimsby, NE Lincs., DN41 8DP, UK
[c] IDeaS, Innovation, Design and Sustainability Research Institute, Robert Gordon University, School Hill, Aberdeen, AB10 1FR, UK

ARTICLE INFO

*Article history:*
Received 7 November 2011
Received in revised form 26 January 2012
Accepted 4 February 2012
Available online 7 April 2012

*Keywords:*
Photocatalysis
ISO
Standards
Titania
UV

ABSTRACT

The current eight published ISO standards associated with semiconductor photocatalysis are considered. These standards cover: (1) air purification (specifically, the removal of NO, acetaldehyde and toluene), (2) water purification (the photobleaching of methylene blue and oxidation of DMSO) (3) self-cleaning surfaces (the removal of oleic acid and subsequent change in water droplet contact angle), (4) photosterilisation (specifically probing the antibacterial action of semiconductor photocatalyst films) and (5) UV light sources for semiconductor photocatalytic ISO work. For each standard, the background is first considered, followed by a brief discussion of the standard particulars and concluding in a discussion of the pros and cons of the standard, with often recommendations for their improvement. Other possible standards for the future which would either compliment or enhance the current ones are discussed briefly.



## 1. Introduction

Semiconductor photocatalysis is a burgeoning field of photochemistry, with many uses, such as: the photomineralisation of volatile and non-volatile organics and (to a lesser extent) inorganics, photoinduced superhydrophilicity and photosterilisation [1–3]. In addition to its wide range of application, the process also benefits from having a few significant semiconductors, such as titanium oxide, that are extremely robust both chemically and photochemically and inexpensive. It is small wonder therefore, that a number of notable different commercial products have arisen from the wide-scale research conducted in this area. These include: (i) self-cleaning glass, concrete, tent/awning materials and tiles, (ii) odour-removing paint for indoor applications, (iii) $NO_x$ removing paint, concrete and tiles for exterior applications, (iv) photo-induced sterile surfaces (ceramics and metals), (v) water and air purification units and (vi) defogging mirrors [4]. Such new materials and diverse commercial products require standards by which their effectiveness can be gauged, compared and contrasted.

The ISO is the world's leading developer and publisher of international standards, comprising a network of the national standards institutes of 162 countries, with a central co-ordinating secretariat based in Geneva, Switzerland [5]. It is a non-governmental organisation that bridges the public and private sectors and so is able to generate, via a consensus among experts in the field, standards that meet the requirements of both business and society. ISO standards are developed by technical committees, comprising national experts from those sectors that have asked for the standards.

Standards help manufacturers develop and deliver products which have the defined characteristics desired by their customers, such as activity, robustness, appearance and low cost. Thus, for industry, standards ensure their products are widely accepted and competitive, whereas, for the consumer they ensure product quality and reliability. Although the ISO has no legal authority to enforce the implementation of its standards, it is worth noting that countries sometimes choose to refer to them in regulative legislation. All international standards are reviewed at least 3 years after publication and every 5 years after the first review. Given the emergence of a number of commercial products based on semiconductor photocatalysis it is appropriate that the international standards organisation (ISO) has begun to address the need for the quantification of performance ability of such materials through the publication of a series of standards [6–13].

There are a large and growing number of research groups and industries associated with semiconductor photocatalysis, many of which are relatively unaware of the recently published ISO standards in this area, since there is little in the literature about them. It appears appropriate, therefore, 5 years on from the first published ISO standard in this area [6], to review concisely the background, main features, typical outputs and pros and cons of each of the

* Corresponding author.
*E-mail addresses:* andrew.mills@qub.ac.uk (A. Mills), claire.hill@cristalglobal.com (C. Hill), peter.robertson@rgu.ac.uk (P.K.J. Robertson).

1010-6030/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochem.2012.02.024

**Table 1**
Sample pre-conditioning step conditions.

| Test | UVA irradiance/mW cm$^{-2}$ | Duration/h |
|---|---|---|
| $MB^{2+}$ | >1 | 24–72 |
| NO | ≥1 | ≥5 |
| Acetaldehyde | ≥1.5 | 16–24 |
| Toluene | ≥1.5 | 16–24 |
| DMSO | 2 | ≥5 |
| Contact angle | 2 | 24 |
| Antibacterial | None | None |

published tests and the tests as a whole. This is the aim of this feature article along with a brief discussion of other possible standards which might usefully compliment or reinforce those already in place.

## 2. ISO 10678; 2010, the 'determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue' [9]

Methylene blue ($MB^+$) is a highly popular test pollutant in semiconductor photocatalysis used in the assessment of such key features as: new photocatalytic materials, photoreactors and light sources. Its popularity lies in its simplicity, since all that is required for an assessment is the measurement of the rate of photocatalytic bleaching of $MB^+$ in aqueous solution via UV/vis spectrophotometery [14].

Matthews demonstrated that films of titania were able to mediate the complete photo-mineralisation of $MB^+$ ($C_{16}H_{18}N_3SCl$) [15] as early as 1989, i.e.

$$C_{16}H_{18}N_3SCl + 25.5O_2 \xrightarrow[h\upsilon \geq 3.2\,eV]{TiO_2} HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \quad (1)$$

and observed, not surprisingly, that this mineralisation process occurs on a longer timescale than the oxidative photobleaching of the dye. As an aside, it is worth noting, therefore, that the measurement of the rate of photobleaching of $MB^+$ is not equivalent to the rate of mineralisation of the dye, which is usually and necessarily a slower process.

One of $MB^+$'s attractive features is its large molar absorptivity, $\varepsilon_{MB}$, although a brief examination of the literature reveals a startling range of reported values for this parameter, i.e. with $\varepsilon_{MB}$ ranging from (4.0 to 9.5) × $10^4$ $M^{-1}$ $cm^{-1}$ at $\lambda_{max}$ = 665 nm [16–23]. Whatever value is taken or measured for $\varepsilon_{MB}$, the high molar absorptivity of $MB^+$ ensures a striking and easily measured colour change, from blue to colourless, when the dye is photo-bleached by the semiconductor photocatalyst under study.

$MB^+$ is still used, albeit no longer on a large scale, as a textile, leather and paper dye and so is a reasonable choice as a test pollutant dye for the photocatalytic remediation of water, although not quite as obvious as a test pollutant for assessing self-cleaning films, as proposed in this ISO standard.

### 2.1. The standard

The main photoreaction system referred to in the standard is illustrated in Fig. 1, and comprises: a sample (with an active coating) plate (typically, 10 cm square) onto which is fixed a glass cylinder (3–4.7 cm diameter). The sample has previously been preconditioned by exposing it to UVA light for a period of time, details of which are given in Table 1. Into this sealed, cylinder/plate combination is first placed 35 ml of a 'conditioning' solution of 2 × $10^{-5}$ M $MB^+$ for 12 h in the dark. If, after this period, the [$MB^+$] is <$10^{-5}$ M the conditioning step needs to be repeated using a fresh

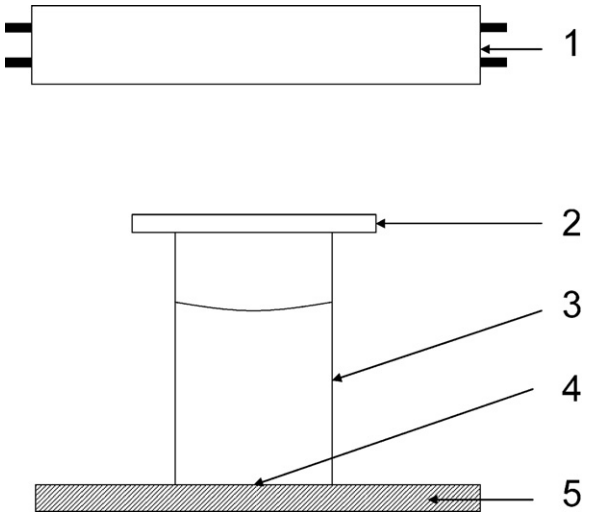



**Fig. 1.** Irradiation set up for the methylene blue standard, comprising: (1) UV light source, (2) glass cover, (3) testing cylinder, (4) testing area and (5) sample under test.

conditioning step. If this is not the case, then 35 ml of a $10^{-5}$ M reaction $MB^+$ solution are added and the cylinder covered with a UV transparent glass pane. The system is then irradiated with UVA light (1.0 mW $cm^{-2}$) and the reaction solution agitated every 20 min. The variation in the concentration of the methylene blue as a function of irradiation time is measured spectrophotometrically, either directly (through the test solution) or by sampling the solution and returning the sample after the measurement, via the solution's absorbance at 665 nm. The irradiation process is carried out for 3 h or anytime less if the solution is decolourised sooner. The reaction temperature should be 23 ± 2 °C, and the reaction solution should be stirred at least every 20 min. An otherwise identical blank (dark) experiment is then run. A typical set of data for a non-active and active sample are illustrated in Fig. 2, from which the %photonic efficiency of the active sample, $\xi_{MB}$, can be calculated, via the following expression:

$$\xi_{MB} = \frac{100 \times r(MB^+)}{I_{UV}} \quad (2)$$

where $r(MB^+)$, rate of methylene blue photocatalysed bleaching (units: molecules $cm^{-2}$ $s^{-1}$) and $I_{UV}$ is the UVA irradiance in units: number of photons $cm^{-2}$ $s^{-1}$. *Note*: any run in which the solution is fully discoloured within 120 min generates an unreliable value for $\xi_{MB}$ (i.e. >0.1%) due to mass transfer effects, vide infra.

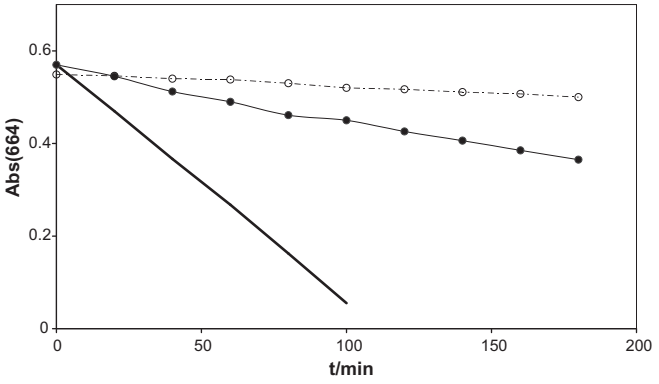



**Fig. 2.** Typical set of results for the MB ISO standard using test samples with (●) and without (○) a photocatalyst coating. The solid line is the calculated maximum allowable decay curve observable under standard conditions without a significant mass transfer contribution.

### 2.2. Pros and cons

The main advantages of this standard are its simplicity and ease of use. The disadvantages stem from its underlying assumptions, of which the major ones are given below. Obviously, it is highly desirable when using the standard, to ensure the conditions are such that these assumptions are likely to hold and, with this in mind, we have suggested slight improvements (mainly a tightening up of the specified conditions) that may be made to the standard to improve repeatability (within a lab) and reproducibility (between labs).

#### 2.2.1. Dye purity

The ISO standard assumes that the $MB^+$ used is of a high purity, with $\varepsilon_{MB} = 7.4 \times 10^4\ M^{-1}\ cm^{-1}$ at 664/5 nm [24]. However, as already noted above, $\varepsilon_{MB}$, values quoted in the literature span a wide range, including values much larger and smaller than $7.4 \times 10^4\ M^{-1}\ cm^{-1}$ at 664/5 nm. This variance is most likely a reflection of the different purities of commercial sources of methylene blue, as noted by others [17]. The high variance in the purity of commercial samples of $MB^+$ means that it is not possible to make up readily a $10^{-5}$ M $MB^+$ solution with confidence. This problem is exacerbated by the fact that the kinetics of $MB^+$ photobleaching are highly dependent, in a non-linear fashion, upon the $MB^+$ concentration [25]. This difficulty of $MB^+$ purity may be rectified if the $MB^+$ reaction solution is made up so as to have a defined absorbance at 665 nm in a 1 cm cell (as opposed to a defined concentration of $10^{-5}$ M as in the original standard) and we suggest an absorbance value of 0.74, which is what it should be if the $MB^+$ used does exhibit an $\varepsilon_{MB} = 7.4 \times 10^4\ M^{-1}\ cm^{-1}$, as cited by the standard.

#### 2.2.2. Adsorption and pH

At solution pH values below the point of zero charge (pzc) of the semiconductor (ca. pH 6.6 for $TiO_2$) the adsorption of $MB^+$, onto a titania semiconductor photocatalyst, via coloumbic attraction is likely to be negligible, but increasingly substantial at pH's above this pzc [26]. It is important, therefore, in the standard that the initial pH of the $MB^+$ solution is a defined value. Significant deviation from this set pH will alter the amount of $MB^+$ adsorbed which will alter the measured rate and so the calculated value of $\xi_{MB}$. The initial pH of the reaction solution is not stipulated in the current ISO test, but a value of pH 5.5 seems appropriate and is recommended here.

#### 2.2.3. Stirring and diffusion

The ISO standard assumes that the reaction kinetics for reaction (1) are activation, rather than diffusion controlled, as evidenced by the standard's recommended token degree of stirring (every 20 min). In the event that a highly efficient photocatalytic surface is tested the standard suggests that when $\xi_{MB} > 0.1\%$, the experiment should be repeated but with an irradiance of $0.25\ mW/cm^2$. However, this process is unlikely to generate values of any greater import, since the kinetics of $MB^+$ photobleaching are highly dependent in a non-linear fashion, upon $I_{UV}$ [25,27]. As a result, the ISO standard is limited in application to low activity photocatalytic films, for which $\xi_{MB} \leq 0.1\%$,. The $[MB^+]$ decay profile for a film with $\xi_{MB} = 0.1\%$ is illustrated by the thick black line in Fig. 2, which extrapolates to a complete bleaching time of 120 min. It follows that any film that generates a steeper $[MB^+]$ decay profile than this will yield a $\xi_{MB}$ value > 0.1%, which will be unreliable due to mass transfer effects.

#### 2.2.4. Mechanism

The overall photomineralisation of $MB^+$ by semiconductor photocatalysis (SPC) is summarised by the following reaction:

$$C_{16}H_{18}N_3SCl + 25.5O_2 \xrightarrow[h\upsilon \geq E_{bg}]{\text{Semiconductor}} HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \quad (3)$$

However, it is worth noting, when using such a dye test system for assessing SPC activity, that dye photobleaching can also occur via a dye photosensitised process in which the electronically excited state of the dye, $D^*$, injects an electron into the conduction band of the semiconductor, SC, to produce an oxidised dye radical, $D^{\bullet+}$, which is unstable and able to decompose subsequently to bleached products [26,28,29], i.e.:

$$D^* + SC \rightarrow D^{\bullet+} + SC(e^-) \quad (4)$$

$$D^{\bullet+} \rightarrow \text{bleached products} \quad (5)$$

The injected electron can also promote this process via its subsequent reaction with $O_2$ to produce a number of different oxidising species, such as hydrogen peroxide. Not surprisingly, it appears that for reactions (4) and (5) to occur efficiently the dye must be adsorbed onto the surface of the semiconductor [29]. Dye-sensitised photobleaching is minimised in the ISO standard by using (i) $MB^+$ as the dye under test, since $MB^+$ adsorbs little light at 365 nm, and (ii) an initial solution pH of 5.5, since this ensures the $MB^+$ is poorly adsorbed on any semiconductor with a pzc > ca. 6.0, such as titania [29].

It also follows from the above discussion that the test should not be adapted for assessing the activity of visible light absorbing photocatalysts, using a visible light source instead of the recommended UV light source, since dye-sensitised photobleaching, via reactions (4) and (5), could make a significant (non-photocatalytic) contribution to the observed photobleaching of the dye. The standard is appropriate, however, for assessing photocatalytic activity of a visible light absorbing semiconductor photocatalyst, using UVA light.

## 3. ISO 22197: test methods for air-purification performance of semiconductor photocatalytic materials [6,12,13]

To date there are three published photocatalyst air-purification ISO methods, each dedicated to the removal of a different airborne pollutant, namely: nitric oxide (NO), ISO 22197-1: 2007 [6]; acetaldehyde ($CH_3CHO$), ISO 222197-2: 2011 [12] and toluene ($CH_3C_6H_5$), ISO 22197-3: 2011 [13], although others are almost at the publication stage (e.g. for: formaldehyde and methyl mercaptan). All three photocatalytst, air-purification published standards use the same photoreactor system, the key features of which are illustrated in Fig. 3. Thus, a UVA light (1) is used to illuminate, through a quartz or borosilicate glass window (2), the sample (3) under test (a 5 cm × 10 cm rectangle), typically ca. 5 mm thick. The test pollutant (4) is mixed with air (5), humidified (RH = 50% at 25 °C) using a water-filled Drechsel bottle (6). The flow rate of the different gas streams are managed by mass-flow rate controllers (7) and the inlet and outlet gas streams are sampled by a gas sampling valve attached to a suitable analytical system (8). The reactor is built out of material that is inert with regard to the test pollutant and UV, such as stainless steel, Perspex, or PTFE. Fig. 4 provides a side view illustration of the photoreaction cell for a sample that is either a solid, Fig. 4(a), or highly porous (e.g. honeycomb), Fig. 4(b). In the former system, Fig. 4(a), the gas stream (2) flows through the narrow (5 mm) gap between the glass window (1) and the

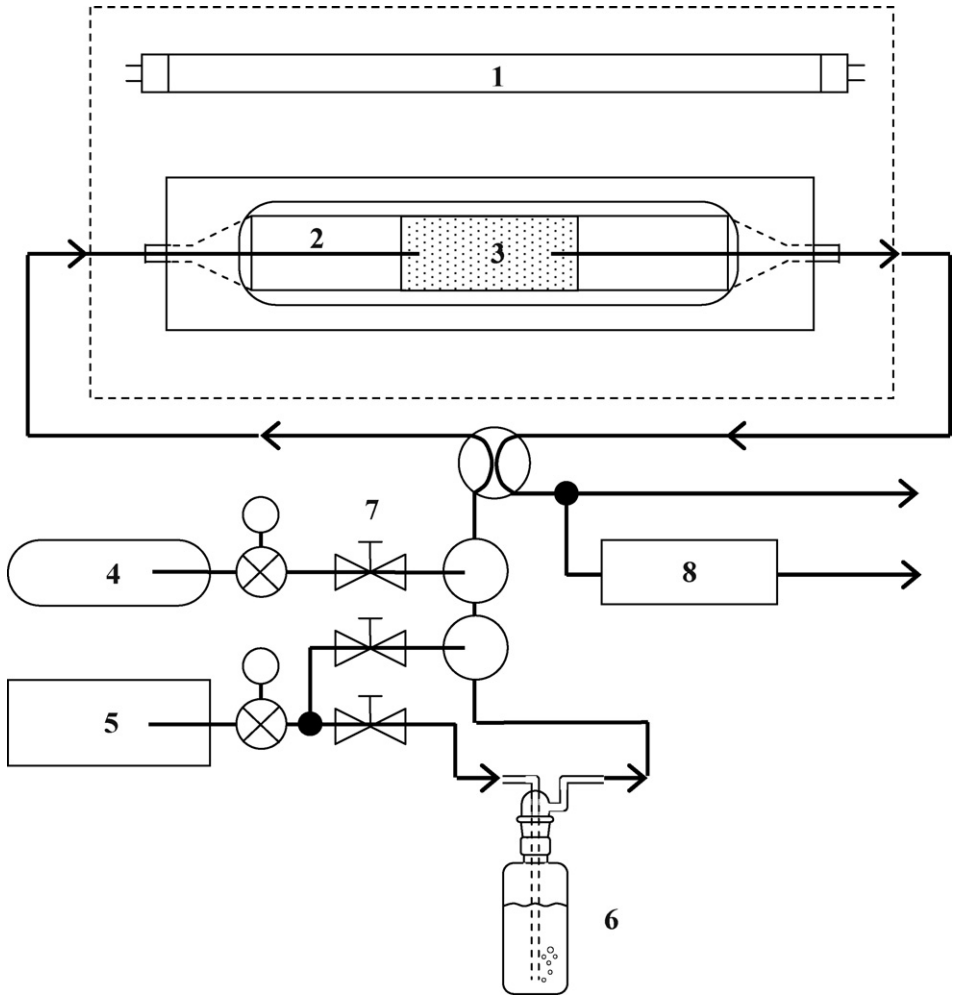



**Fig. 3.** Irradiation set up for the air purification ISO standards, comprising: (1) UV light source, (2) glass cover, (3) sample under test, (4) standard gas (i.e. test pollutant), (5) purified air source, (60 humidifier, (7) mass-flow controllers and (8) pollutant gas analyser.

sample (3), which is on a height-adjustable plate. In the latter system, Fig. 4(b), the gas flows through the sample (5).

Details of the test pollutant concentration, [*X*], overall gas stream flow rate, *f*, sample run test time, *t*, and analysis system(s) employed in each of the air-purification standards are given in Table 2. Before carrying out the test each sample is cleaned photocatalytically by exposing it to UV light for a set period of time, details of which are given in Table 1, then immersed in water for 5 h and, finally, air-dried at room temperature. If the test pieces are not used immediately they are stored in an air-tight container. Note: in all these air-pollution tests the flow rate is normalised for STP and dry gas conditions. It is also suggested to correct *f* for the water vapour present (by multiplying by 1.016), although for simplicity this correction has been omitted from the simplified calculations given below.

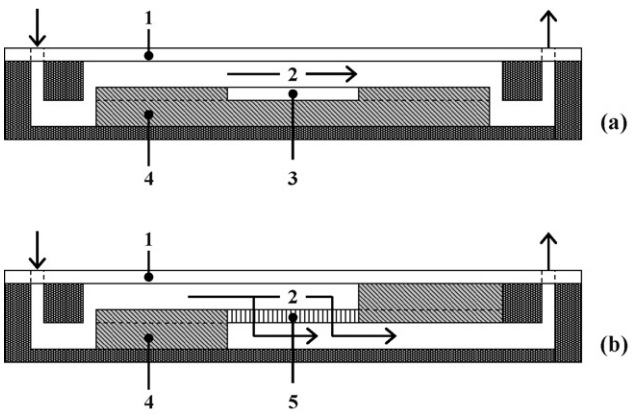



**Fig. 4.** Cross-sectional view of the photoreaction illustrated in Fig. 3 for test pieces which are (a) flat or (b) honeycomb in structure. The components are: (1) glass cover, (2) test gas flow, (3) flat test sample, (4) height-adjusting plate and (5) honeycomb test piece.

### 3.1. The standard

After placing the cleaned test piece in the photoreactor and adjusting the space between the detachable window and the sample so that it is ca. 5 mm, the test gas is allowed to flow into the photoreactor without illumination for ca. 30 min before the light is switched on. The concentration(s) of the analyte(s) of interest are monitored regularly during this 'dark' absorption time, and subsequently, i.e. when the system is illuminated and 30 min after the light has been switched off. The concentration vs. time data profile(s) are then processed so as to provide one or more measures of the efficiency of the test piece to remove photocatalytically the air-pollutant under test.

**Table 2**
Air purification standard test conditions.[a]

| Parameter | Nitric oxide | Acetaldehyde | Toluene |
|---|---|---|---|
| Concentration [X]/ppmv | 1.0 | 5.0 | 1.0 |
| Flow rate, $f$/dm$^3$ min$^{-1}$ | 3.0 | 1.0 | 0.5 |
| Test time, $t$/h | 5 | 3 | 3 |
| Total pollutant load/μmol | 40.2 | 40.2 | 4.02 |
| Analytical method | Chemiluminescence: NO, $NO_2$Ion chromatography: $NO_3^-$ | Acetaldehyde: GC-FID$CO_2$: IR | Toluene: GC-FID |

[a] Common standard conditions include: (1) photoreactor (see Fig. 4); (2) irradiance (1.0 mW cm$^{-2}$); (3) light source: BL or BLB; (4) temperature: 25 °C and (5) relative humidity: 50%.

### 3.2. The NO test system: ISO 22197-1 [6]

Nitric oxide is an important intermediate in the chemical industry and a major air pollutant produced by the combustion of substances in air, such as gasoline in automotives and fossil fuels in power stations. In the absence of a catalyst NO is oxidised relatively slowly to nitric oxide by oxygen ($t_{1/2} \sim 70$ h for 1 ppmv of NO in air). It is used on a large scale in the manufacture of nitric acid, the bleaching of rayon, and as a stabiliser in the production of propene and methyl ether. It is an important signalling molecule in most biological systems and, along with $NO_2$, is associated with sick building syndrome and acid rain production. Given its widespread commercial use and, maybe more importantly, its occurrence as a common air-borne, environmentally damaging pollutant, the removal of NO and its $NO_x$ counterpart, $NO_2$, by semiconductor photocatalysis has attracted a great deal of attention. Although the apparent efficacy of the NO removal process by semiconductor photocatalysis is not particularly high (quantum efficiency ca. 0.5%) [30], the attraction of removing such a ubiquitous indoor and outdoor pollutant using light has resulted in the promotion of many commercial photocatalyst products, such as paint, tiles, paving stones, for their $NO_x$ removing ability.

#### 3.2.1. Key reactions

The titania-sensitised, photocatalytic oxidation of NO proceeds to nitric acid, via nitrous acid and a radical based mechanism [30–34]. The two key photocatalytic reactions are:

$$4NO + O_2 + 2H_2O \xrightarrow[h\upsilon \geq E_{bg}]{TiO_2} 4HNO_2 \quad (6)$$

and

$$2HNO_2 + O_2 \xrightarrow[h\upsilon \geq E_{bg}]{TiO_2} 2HNO_3 \quad (7)$$

Recent work [30] reveals that the accumulation of nitric acid on the surface promotes its photocatalysed reaction with NO that generates the toxic product $NO_2$, i.e.

$$2HNO_3 + NO \xrightarrow[h\upsilon \geq E_{bg}]{TiO_2} 3NO_2 + H_2O \quad (8)$$

This can lead to an eventual steady state where the rate of NO removal is matched by the rate of $NO_2$ production; which is clearly highly undesirable. It follows that for any $NO_x$-removing photocatalyst product to work effectively it is necessary that the $HNO_3$ photogenerated, via reactions (6) and (7), must be removed at regular intervals, by rinsing with water, e.g. from rain or a damp cloth.

The standard sets out to measure the photocatalyst's overall ability to remove the oxides of nitrogen, i.e. $NO_x$, using a NO-containing (1 ppmv) air stream. A measure of this ability is taken as the difference between the total NO removed ($n_{NO}$) and $NO_2$ generated ($n_{NO_2}$) during the irradiation period.

#### 3.2.2. Procedure

The general procedure for the NO test is as described above in Section 3.1, along with the specific reaction details in Table 2; the standard gas contains 30–100 ppmv of NO in $N_2$ and this is mixed with air to produce the reaction test stream of 1 ppmv of NO and 21% $O_2$. As we shall see, the NO test as it stands deviates from the other two procedures in that, at the point the illumination process ceases, the composition of the gas stream is also switched from the test pollutant to just the air carrier gas, although it's not readily apparent why this is required. Indeed, in a recent, published application of the standard, the inlet gas composition was not changed at the end of the irradiation process [34].

Under the conditions specified in the standard, typical plots of the observed temporal variations in [NO] and [$NO_2$] generated by the test for a titania sample are illustrated in Fig. 5. The hatched area 'A' is proportional to the amount of NO adsorbed by the test piece in the dark, $n_{ads}$, whereas marked areas 'B' and 'C' are proportional to $n_{NO}$ and $n_{NO_2}$, respectively; the latter three parameters have units: μmol, whereas the units of the hatched areas are: (μl/l) h. The standard suggests that the integrated areas due to (i) NO 'dark' adsorption ('A') and (ii) NO 'dark' desorption (the area under the [NO] decay curve after the light is switched off), i.e. at point 3 in Fig. 6 and beyond, should be calculated. However, since these are approximately the same and these two values are then subtracted from each other, i.e. they will roughly cancel each other out, it is simpler (although technically less exact) to calculate the net amount $NO_x$ removed by the test piece, $n_{NO_x}$, as follows:

$$n_{NO_x} = \left(\frac{60f}{22.4}\right)(B–C) \quad (9)$$

given $f$ is in units: dm$^3$ min$^{-1}$, see table 2.

In the standard, in what is referred to as the elution test, it is proposed that the used sample is then immersed in a known quantity of water for 1 h and this soaking process repeated. Analysis, via ion chromatography, of the two water samples generated by this procedure then reveals the amount of $HNO_2$ and $HNO_3$ that resides on the surface of the semiconductor photocatalyst test piece after the

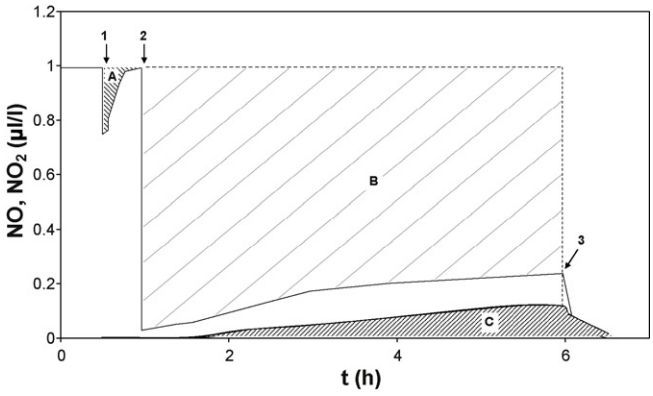



**Fig. 5.** Typical data set generated, i.e. NO removed and nitric acid generated, in the NO ISO standard, for which the feed stream [NO] is 1 ppmv. The hatched areas 'A' and 'B' are proportional to the amounts of NO adsorbed and photo-oxidised/removed, respectively. Hatched area 'C' is proportional to the amount of nitric acid generated. The key points are: (1) start of contact with NO-containing feed, (2) UV lights on and (3) UV lights off, feed gas changed to zero calibration gas (i.e. air).

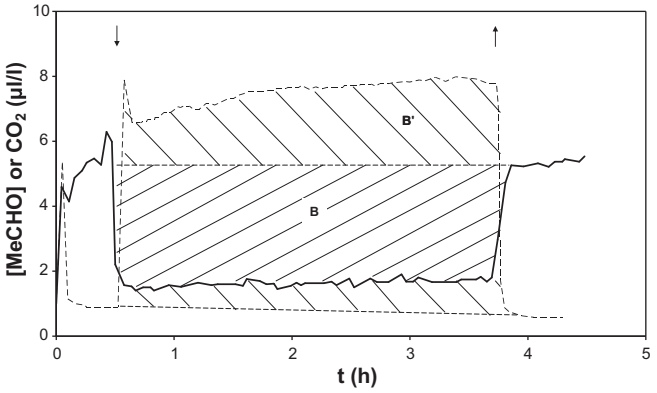



**Fig. 6.** Typical data set generated, i.e. acetaldehyde removed and carbon dioxide generated, in the acetaldehyde ISO standard, for which the feed stream [acetaldehyde] is 5 ppmv. The hatched areas 'B' and 'B′' are proportional to the amounts of acetaldehyde removed and carbon dioxide generated, respectively. The key points are: (1) start of contact with the acetaldehyde feed ($t = 0$), UV lights on (↓) and UV lights off (↑).

illumination process is complete, i.e. $n_{NO_2/NO_3}$, and so allows the fractional nitrogen mass balance to be calculated, i.e. $n_W$, where:

$$n_W = \frac{n_{NO_2/NO_3}}{n_{NO_x}} \tag{10}$$

For many titania photocatalysts, $n_W$, is usually > 0.9, and often this elution test is omitted, especially for a more rapid screening of samples [30,31].

Given in the standard, the total pollutant load is 40.2 μmol, and UVA irradiance is 1 mW cm$^{-2}$, a quick calculation indicates that the standard is only applicable to samples which exhibit a photon efficiency of ca. < 1.5%, since anything higher would remove all the NO from the inlet stream. This would seem appropriate if the quantum efficiency of the process is 0.5%, as has been reported for titania [30]. If such a high-performing sample (i.e. quantum efficiency > 1.5%) was tested, the simplest adaption of the standard to assess such a sample would be to lower the available surface area. However, the gas flow velocity is relatively slow (0.2 m s$^{-1}$) and there may be some concern that the system is not able to distinguish very well between samples of high photon efficiency (e.g. >1%) due to mass transfer effects. There is also a concern that the level of pollutant used (1 ppmv) in this standard is excessive given that such a level is not commonly encountered, except in heavily polluted urban areas. For example, the latest EU directive suggests [35] the hourly mean for a calendar year should be 40 μg m$^{-3}$ (i.e. 22 ppbv) and even NO levels in a busy street (Marylebone) in London in 2010 were on average 67 ppbv, with typical daytime values of 112 ppbv [36]. Operating at these levels however will increase the likelihood of the unwanted feature of some mass transfer control in the observed kinetics of NO removal.

### 3.3. The acetaldehyde test system: ISO 22197-2 [12]

Acetaldehyde occurs widely in nature, since it is produced by plants as part of their metabolism and also during the ripening process. It is also a product of combustion (wood, oil, petrol and diesel) and so is a constituent of car exhaust fumes and tobacco smoke. It is a significant industrial chemical which is used in the manufacture of acetic acid, perfumes, flavours, aniline dyes, plastics and synthetic rubber. It is a cancer suspect agent, an irritant and large doses can cause death by respiratory paralysis. It is an important indoor air pollutant as it is released by building materials such as polyurethane foams, adhesives, coatings and inks. Along with formaldehyde and other volatile organic carbons, i.e. VOC's, such as toluene, it is associated with sick building syndrome. It has been chosen for use in this ISO standard as it is a typical VOC with a low molecular mass and has apparently an offensive odour.

#### 3.3.1. Key reactions

The photocatalytic oxidation of acetaldehyde has been well studied [37–39] using titania photocatalysts, although the reaction pathway, and the major intermediates, are still the subject of debate [40]. Recent work indicates that it is first oxidised to acetic acid and then to formic acid, formaldehyde (the acids being adsorbed onto the surface of the titania) and then, finally to $CO_2$ [40], i.e.

$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH \tag{11}$$

$$2CH_3COOH + O_2 \rightarrow 2HCOOH + 2HCHO \tag{12}$$

$$2HCOOH + 2HCHO + 3O_2 \rightarrow 4CO_2 + 4H_2O \tag{13}$$

#### 3.3.2. Procedure

The general procedure for the acetaldehyde test is as described above in Section 3.1, along with the specific reaction details in Table 2. In this standard the disappearance of the acetaldehyde and, if possible, the appearance of the $CO_2$ are monitored as a function of irradiation time. The standard notes that 'the measurement of $CO_2$ may not always be feasible for some test pieces' possibly due to a high ability to adsorb and react with any $CO_2$ generated, as might be expected for alkaline, cement-based samples.

A typical dark adsorption then irradiation decay time profile for [acetaldehyde] and concomitant [$CO_2$] photogenerated time profile are illustrated in Fig. 6. As before the shaded area '**B**', with units of (μl/l) h, is proportional to the amount of acetaldehyde removed, $n_A$; units: μmol. It follows that the average fraction of the acetaldehyde removed in 3 h, $F_A$, can be calculated as follows:

$$F_A = \frac{B}{3\phi_{Ao}} \tag{14}$$

where $\phi_{Ao}$ is the supply level of acetaldehyde (ca. 5 ppmv). In addition

$$n_A = \left(\frac{60f}{22.4}\right) B. \tag{15}$$

Although this approach to the calculation of $F_A$ and $n_A$ is consistent with the previous (NO) air-pollution standard tests described earlier, curiously the ISO standard itself for acetaldehyde suggests the initial (i.e. supply; $\phi_{Ao}$) and exit (the average of 3 or more measurements in the last hour of the testing period; $\phi_A$) values of [acetaldehyde] should be used instead in the calculations, so that:

$$F_A = \frac{\phi_{Ao} - \phi_A}{\phi_{Ao}} \tag{16}$$

and

$$n_A(60) = 60 \cdot (\phi_{Ao} - \phi_A)\left(\frac{f}{22.4}\right) \tag{17}$$

where $n_A$ (60) is the amount of acetaldehyde removed (in μmol) in the last hour of the test.

If it is possible to measure the [$CO_2$] vs. irradiation time profile (as illustrated in Fig. 6) then the area, B′, underneath the [$CO_2$] vs. irradiation time profile can be used to calculate a value for the %conversion of acetaldehyde to two molecules of carbon dioxide by the photocatalyst, $R_{CO_2}$, via the photocatalysed reactions (11)–(13) since, $R_{CO_2} = 100B'/(6\phi_{Ao})$. In addition a value for the number of moles of $CO_2$ photogenerated, $n_{CO_2}$, can be calculated using Eq. (15), by substituting B′ for B.

Alternatively, and as suggested by the standard, it is possible to calculate a value for $n_{CO_2}$ (60), using a modified version of Eq. (17). In this case, values for $\phi_{Ao}$ and $\phi_A$, would be replaced, respectively, by values for the fractional amount of $CO_2$ in the gas phase: (i) before illumination ($\phi_{CO_2o}$) and (ii) in the last hour of the illumination

process (derived from 3 measurements made in that period), $\phi_{CO_2,L}$ (units: μl/l). In this case a value for $R_{CO_2}$ can be then calculated via:

$$R_{CO_2} = 100\frac{\phi_{CO_2,L} - \phi_{CO_2 o}}{2\phi_{Ao}} \quad (18)$$

The standard notes [12] that the amount of acetaldehyde removed should be reported, i.e. $n_A$ (60), if the ISO calculations are followed rigidly. Alternatively, as suggested here, the value of $n_A$ should be reported instead, as calculated using Eq. (15), since it is more consistent with the NO ISO standard. Reporting of the other values, such as $R_{CO_2}$ or $N_{CO_2}$(60), are optional.

Interestingly, whereas the criticism can be made that the NO level chosen in the ISO standard is too high (1 ppmv), that used in the acetaldehyde standard appears too low, since permissible exposure limit as an 8 h time weighted average is 100 ppmv, although it should also be noted that the odour threshold is 0.21 ppmv and exposure to a 50 ppmv vapour of acetaldehyde causes mild eye irritation within 15 min [41]!

### 3.4. The toluene test system: ISO 22197-3 [13]

Toluene is a widely used chemical feedstock and industrial solvent. As a solvent, it is used in paints, paint thinners, silicone sealants, printing inks, glues, resins and disinfectants. It is also used as an octane booster in gasoline fuels. In industry it is also used in the manufacture of: benzoic acid, benzaldehyde, explosives, dyes and many other organic compounds. Toluene is toxic, although less so than benzene, and is a component of the volatile organic compounds associated with sick building syndrome.

#### 3.4.1. Key reactions

Many papers have been published on the removal of toluene via its photocatalytic mineralisation [42–48]. In the absence of water vapour the photoreaction quickly stops due to the inhibition of the hydroxyl regeneration process and the accumulation of reaction products, such as benzoic acid. In the presence of water vapour this deactivation process can be much slower, depending on how readily the reaction intermediates, such as benzoates, are adsorbed. For example Schiavello et al. reported that Merck $TiO_2$ exhibited a stable photocatalytic activity, whereas Degussa P25 continuously deactivated upon illumination [46]. In the photocatalytic oxidation of toluene the major initial product appears to be benzaldehyde which is then subsequently oxidised to benzoic acid and eventually to carbon dioxide and water, provided the reaction intermediates do not adsorb so strongly to the surface of the titania as to render it photo-inactive [48], i.e.

$$C_6H_5\text{-}CH_3 + O_2 \rightarrow C_6H_5\text{-}CHO + H_2O \quad (19)$$

$$2C_6H_5\text{-}CHO + O_2 \rightarrow 2C_6H_5\text{-}COOH \xrightarrow{15O_2} 14CO_2 + 6H_2O \quad (20)$$

#### 3.4.2. Procedure

The general procedure for the toluene test system is as described above in Section 3.1, along with the specific reaction details in Table 2. In this standard only the disappearance of the toluene, i.e. reaction (19), is monitored as a function of irradiation time.

A typical set of [toluene] (units: (μl/l)) vs. time data generated from a run using a titania photocatalyst sample is illustrated in Fig. 7. As in the NO standard, the shaded areas 'A' and 'B', with units of (μl/l) h, are proportional to the amounts of toluene adsorbed, $n_{ads}$, and removed, $n_T$; units: μmol. It follows that fraction of the toluene removed, $F_T$, can be calculated using equations identical in form to those used in the acetaldehyde test, i.e. Eqs. (14) and (15), replacing $\phi_{Ao}$ with the supply concentration of toluene, $\phi_{To}$ (ca. 1 ppmv). Once again the standard suggests, that in stead of measuring the area 'B', as illustrated in fig. 7, their preference is to measure

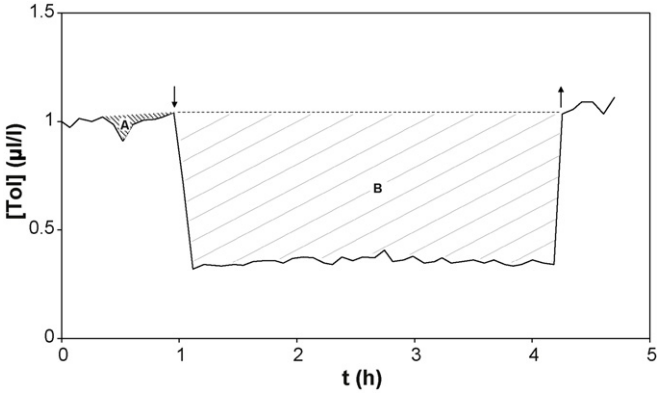



**Fig. 7.** Typical data set generated, i.e. toluene removed, in the toluene ISO standard, for which the feed stream [toluene] is 1 ppmv. The hatched area B′ is proportional to the amount of toluene removed. The key points are: (1) start of contact with the acetaldehyde feed ($t$ = 0), UV lights on (↓) and UV lights off (↑).

$\phi_{To}$ and the exit level (the average of 3 or more measurements in the last hour of the testing period; $\phi_T$). These values should then be used in equations of the same form as Eqs. (16) and (17), i.e.

$$F_T = \frac{\phi_{To} - \phi_T}{\phi_{To}} \quad (21)$$

$$n_T(60) = 60 \cdot (\phi_{To} - \phi_T)\left(\frac{f}{22.4}\right) \quad (22)$$

where $n_T$ (60) is the amount of toluene removed (in μmol) in the last hour of the test. As with the acetaldehyde test it is suggested that the value of $n_T$ (60) should be reported, but the reporting of the fraction of toluene removed, $F_T$, is optional. Once again, we suggest here that the value of $n_T$ should be reported instead, as calculated using Eq. (15), since it is more consistent with the NO ISO standard.

### 3.5. General Pros and cons

All three air-purification systems described above are reasonable standards since the test pollutants, i.e. NO, acetaldehyde and toluene, are well-recognised, common pollutants, found in indoor and outside air. NO is particularly popular as a test pollutant as many photocatalysts appear able to effect its removal; which is possibly not surprising given the standard electrode potential for NO oxidation to $NO_3^-$ is only 0.957 V vs. NHE, whereas the redox potential of valence band holes on anatase titania, for example, is +3.0 V vs. NHE at pH 0 [1].

One possibly unavoidable concern with respect to the air-pollution photocatalyst standards is that each individual sub-test requires often different and expensive analytical equipment. Details of the analytical equipment required are given in Table 2 and in most cases they also require a reasonable degree of technical support for operation and maintenance. Another concern is that the preconditioning treatment is inconsistent for the three different standards, and poorly defined. This situation can be markedly improved by simply adopting the same, well-defined preconditioning protocol, such as conducting it in the photoreactor itself, with an air flow rate of 3 l $min^{-1}$, with a UVA irradiance of 1 mW $cm^{-2}$ and a relative humidity of 50%, for say 24 h. This set of conditions would, of course comply with the pre-condition protocol set out in the existing acetaldehyde and toluene standards. However, by defining the preconditioning step more exactly and making it the same for all three air-pollutant published ISO standards, it is likely to improve the lab-to-lab repeatability of the standards. For the sake of streamlining and unifying the tests, it would also seem sensible and consistent that all three adopt the same approach towards data analysis. Thus, we suggest that all

three tests use the relevant simple area related Eqs.: e.g. (9) (for $n_{NO_x}$ in NO test)) and (14) and (15) for the acetaldehyde removal (and $CO_2$ generation) and toluene removal tests, when calculating pollutant removal efficiencies.

## 4. ISO 10676: 2010: test method for water purification performance of semiconductor photocatalytic materials by measurement of forming ability of active oxygen [10]

This standard has been designed 'to determine the water purification performance of photocatalytic materials by exposing a [photocatalyst] specimen [under test] to model water [model water]: in that it has a well defined level of a test pollutant, [dimethyl sulfoxide, i.e. DMSO] under illumination of ultraviolet light'; thus this standard is meant to relate to waste-water treatment. DMSO is a colourless, highly hygroscopic, thermally and chemically stable organic solvent widely used in the laboratory and industry. It is used in the production of microelectronic devices, polymers, dyes and membranes. It is used as a bio-preservative, especially in stem cell banking, and is an effective, safer paint stripper compared to the more conventional dichloromethane. It is not, however, a well recognised waste-water pollutant, nor a well-studied test pollutant for photocatalysis. As a consequence, its choice as a model test pollutant for photocatalytic materials seems initially incongruous, especially when there are many other pollutants, such as methylene blue [15], acid orange 7 [49], phenol [50], 4-chlorophenol [51], and dichloroacetic acid [52], which have been very well-studied as photocatalytic test pollutants for waste-water remediation.

### 4.1. Key reactions

As the rather long and slightly unclear title for the standard suggests, DMSO was selected as the test pollutant because of its established rapid reaction with hydroxyl radicals ($k = 5.4 \times 10^9\ M^{-1}\ s^{-1}$) [53]. This reaction leads to the formation of methane sulfinic acid, which is rapidly oxidised to methane sulfonic acid and, ultimately, sulphuric acid [54,55]. Presumably the overall photocatalytic process can therefore be summarised as follows:

$$(CH_3)_2SO + 2O_2 \rightarrow CH_3SO_2H + CO_2 + H_2O \quad (23)$$

$$2CH_3SO_2H + O_2 \xrightarrow{\text{fast}} 2CH_3SO_3H \quad (24)$$

$$CH_3SO_3H + 2O_2 \rightarrow H_2SO_4 + CO_2 + H_2O \quad (25)$$

Note: it is also possible some intermediate level of formaldehyde may be generated as is known to occur during the reaction of DMSO with hydroxyl radicals.

### 4.2. Procedure

Before carrying out the test, each sample is cleaned photocatalytically by exposing it to UV light for a set period of time, details of which are given in Table 1. The photoreactor test system is illustrated in Fig. 8 and comprises a UV light source (1), irradiance 2 mW cm$^{-2}$, irradiating the sample (3), 10 cm square, over which is passed a circulated 5 mm deep stream of water (2), containing the test pollutant, DMSO, (10 ppm), pumped using a peristaltic pump (4). The concentration of the DMSO is monitored by ion or gas chromatography, during a 5 h illumination of the system. The room in which the test is carried out should be maintained in the range: 20–25 °C.

A plot of a typical data set, i.e. the measured concentration of free (i.e. not adsorbed) DMSO, $[DMSO]_f$, vs. irradiation time, for a granular photocatalyst is illustrated in Fig. 9, along with the first-order plot of the data (insert diagram). The latter can be used to determine the first order rate constant, $k_1$, for the photocatalysed reaction (23), and the half-life for the photoreaction, $t_{1/2}$, given: $t_{1/2} = \ln 2/k_1$; in the case of the data in Fig. 9: $t_{1/2} = 2.23$ h. In this ISO standard, it is the value for $t_{1/2}$ that is reported.

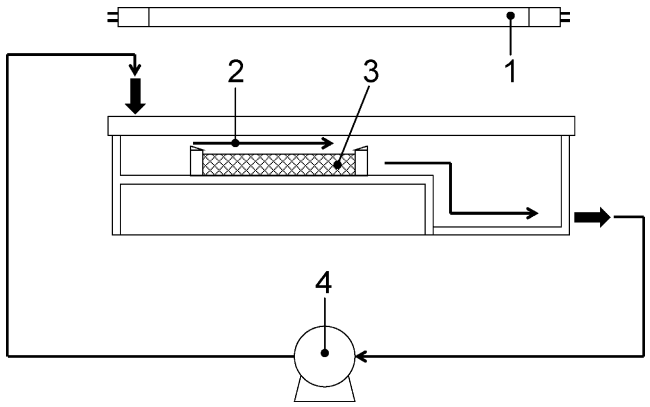



**Fig. 8.** Irradiation set up for the DMSO water purification ISO standard, comprising: (1) UV light source, (2) polluted test water stream containing 10 ppm of DMSO, (3) sample under test and (4) a peristaltic pump for circulating the pollutant.

### 4.3. Pros and cons

The test appears very straightforward and the number of intermediates generated is limited and easily monitored. Significant adsorption of the test pollutant appears unlikely, which cannot always be said for some dye tests, such as those using methylene blue [26] or acid orange 7 [29].

As for the disadvantages, it is not an obvious choice for a test pollutant and it is not clear why, say, phenol was not used instead, or as an alternative, since it can be readily monitored not only by HPLC but also UV/Vis spectrophotometry and it also is unlikely to adsorb strongly on most photocatalytic materials [56,57]. The DMSO ISO test requires access to ion-chomatography or gas chromatography; possibly both if the concentration of methyl sulfonic acid (MSA) photogenerated needs to be monitored as well as that of DMSO. In terms of procedure, the temperature of the test would be better defined as 25 °C, rather than the broad range of 20–25 °C and the initial pH of the reaction solution, in contact with the photocatalyst, should be set, say at pH 5.5.

Curiously, the test stipulates a test validation condition that, after the 5 h illumination period the measured DMSO concentration

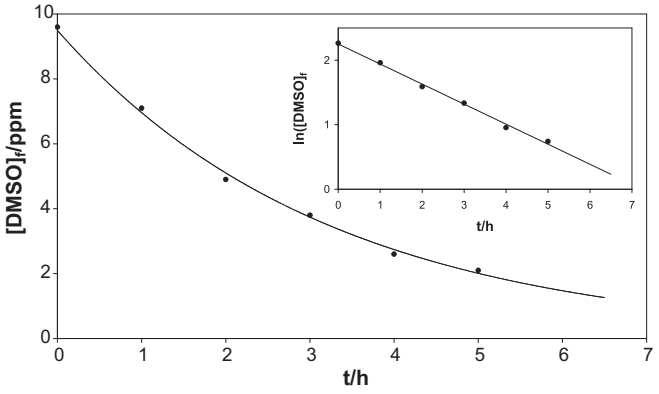



**Fig. 9.** Typical data set generated, i.e. DMSO removed vs. irradiation time, in the DMSO ISO standard, for which the feed stream [DMSO] is ca. 10 ppm. The insert diagram is a log plot of the data in main diagram, revealing the first order nature of the kinetics of DMSO removal by semiconductor photocatalysis and from which a first order rate constant, $k_1$, and so half-life can be calculated.

must be less than that of the original (dark) DMSO solution! This validation condition appears unnecessary, given that if it did not hold the material under test would simply be reported as being non-photocatalytic! The standard also suggests that it is necessary to confirm that 'MSA products accompany DMSO oxidative decomposition'. This second validation requirement appears to add little as it is not suggested to relate the MSA generated to the DMSO removed, but rather just to confirm the presence of MSA as an intermediate; it seems unlikely that DMSO is photoadsorbed to any significant extent. If the generation of MSA has to be confirmed, the latter may be achieved (albeit indirectly) via a pH measurement, rather than the more expensive application of ion-chromatography.

## 5. ISO 27448: 2009: test method for self-cleaning performance of semiconductor photocatalytic materials – measurement of water contact angle [7]

In this test, an organic material (oleic acid, $C_{18}H_{34}O_2$) is applied and the change in the wettability of the semiconductor substrate, as measured via its water droplet contact angle, is then monitored as a function of UVA irradiation time. When the contact angle is <5°, the measurement is finished and the value of the contact angle and the time taken to achieve it are reported. It is claimed that the test 'simultaneously evaluates the decomposition of the organic substance and change of water affiliation [sic, affinity].'

### 5.1. Key reactions

An important, if not essential, feature of a self-cleaning, photocatalyst-based coating is that they are able to improve their wettability upon illumination. This process is often termed the photoinduced superhydrophilic effect (PSH) and was first reported in 1988 by Kume and Nozu [58], working for the Nippon Itagarasu company on titania films on glass. At the time it was explained as being due to the simple photocatalytic destruction of adventitious hydrophobic organic material deposited on the titania coating on glass. This model of PSH has found strong support in recent years [59,60] and underpins this ISO test. It should be noted others [1,61] have suggested that PSH may be due to a photo-induced restructuring of the surface of the surface of titania, indicating that semiconductor metal oxide photocatalysts which show this effect are intrinsically hydrophobic in the dark and rendered hydrophilic by a photoinduced surface restructuring process that is able to revert back to the former less hydrophilic form in the dark.

Regardless of mechanism, in the ISO test, once all the oleic acid has destroyed via the photocatalytic mineralisation of the organic top layer, i.e.

$$C_{18}H_{34}O_2 + 25.5O_2 \xrightarrow[h\upsilon \geq 3.2\,eV]{\text{photocatalyst}} 18CO_2 + 17H_2O \quad (26)$$

it is then expected that the water droplet contact angle will be reduced to ≤5° for most photocatalytic materials used in self-cleaning systems [62].

### 5.2. Procedure

Before carrying out the test, each sample, which is suggested to be 10 cm square, is cleaned photocatalytically by exposing it to UV light for a set period of time and details of this pre-treatment step are given in Table 1. The measured contact angle at this point could be used to judge when the photocatalytic process has removed all the oleic acid, i.e. it may be a more appropriate guideline to a clean surface than the stipulated contact angle of <5°. The application of oleic acid can be made manually or by dipping. If carried out manually, the sample is first weighed and then 200 μl of oleic acid are poured onto the centre of the sample and spread evenly over the entire surface using a piece of non-woven cloth. Excess acid is then removed so that the total mass of the oleic acid deposited is $2 \pm 0.2$ mg, i.e. 20 μg cm$^{-2}$, as measured by the increase in mass of the sample. If dipping is chosen as the deposition method, the sample is placed in a 0.5% (by volume) solution of oleic acid in n-hexane. However, this instruction begs the question: how long for?, since it will make a difference for mesoporous films for example. Once placed in the oleic acid solution the sample is then withdrawn at a rate of 60 cm min$^{-1}$. Curiously, no attempt appears to be made to identify how much oleic acid is taken up via this dipping procedure, which appears an oversight. Finally, the sample is then dried at 70 °C for 15 min.

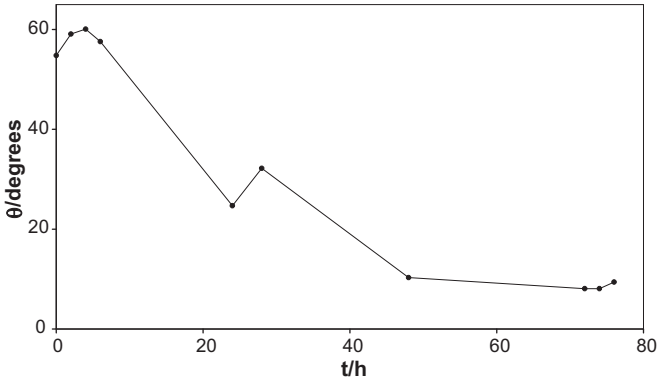



**Fig. 10.** Typical data set generated, i.e. water droplet contact angle, $\theta$, vs. irradiation time, in the contact angle/oleic acid ISO standard.

After this coating procedure, the contact angle, $\theta$, made by a water droplet (no volume is recommended, which appears an unnecessary omission) on each test piece is then measured at 5 different points on the sample under test before and during UV irradiation. For samples which have had a manual coating of oleic acid, a UV irradiance of 2 mW cm$^{-2}$ is recommended, whereas dipped samples should be exposed to 1 mW cm$^{-2}$ of UVA. The process should be repeated 5 times using 5 identically prepared samples. The average of a typical set of results for 5 identically dipped sample pieces is illustrated in Fig. 10. The standard suggests what should be reported are, amongst other things, the initial and final values for $\theta$, and the UV irradiation time required. For samples which cannot be coated with oleic acid and for which the initial value for $\theta$ is ≥20°, the final contact angle can be obtained as above, but obviously without the pre-treatment step.

### 5.3. Pros and cons

On the face of it the test is simple and effective in identifying self-cleaning substrates that function via UV photocatalysis. But, the test conditions are not as well defined as they could be (e.g. no stated operating temperature, %RH nor water droplet volume). It is not clear why two coating processes are suggested, since dipping is likely to be the more reproducible of the two. It is also not clear why different UVA irradiances should be used for the two differently coated samples. As a consequence, there is plenty of scope for tightening up the standard, making it simpler and easier to reproduce by laboratories across the world, which is a key requirement of such standards.

The data illustrated in Fig. 10 is interesting, not only for the very odd transitory increase in $\theta$ at 28 h, for which there is no obvious explanation, but also because the final contact angle is not <5°, as appears to be stipulated in the test as a marker of the end of the experiment. Thus, in the example data given in the standard [8], it would appear technically the irradiation is unfinished. In practice, it is increasing difficult to measure contact angles reliably for

decreasing contact angles below 10°, and most would assume that a contact angle $\leq 10^\circ$ (not $\leq 5^\circ$) recorded in 3 consecutive measurements, is a condition at which the UV illumination of the sample should then cease and allows the claim that the substrate is rendered superhydrophilic and so photocatalytically self-cleaning (assuming the initial contact angle was much higher).

Interestingly, the standard suggests [8] an apparent alternative to the $\leq 5^\circ$ rule for deciding if the irradiation and measurement process is finished. Thus, it will also be deemed complete if the coefficient of variation in the contact angle, a measure of how much the contact angle changes with illumination time, is $\leq 10\%$ for three consecutive measurements on each test piece; under this condition, the average of the three values of $\theta$ will be taken as the final contact angle, $\theta_f$. The problem with this definition of the end of the process is that it assumes the contact angle instantly and rapidly decreases upon illumination and yet clearly from the data illustrated in Fig. 10, which is not atypical of other work [59,60,62,63], it does not. Indeed, it is quite usual for the contact angle not to change (as the organic layer is consumed) for much of the irradiation and then drop rapidly to $\leq 10^\circ$. Thus, for example, the first 3 sets of data points in Fig. 10 have a coefficient of variation of 4.9% and so technically the irradiation should have finished at 4 h and not continued for another 72 h until the contact angle was $<10^\circ$ and the self-cleaning credentials of the sample had been established! It is suggested here that the irradiation should be deemed over, and the sample is photocatalytically self-cleaning, if it is reduced to $\leq 10^\circ$, by a stated period, such as 72 h.

In conclusion, in order to improve the repeatability of the standard, it is also suggested here that: (i) the water droplet volume should be stipulated (e.g. 5 μl), (ii) the samples should be dipped in the way stated, although initial placement in the solution would be for 15 min before withdrawal, (iii) a UVA irradiance of 2 mW cm$^2$ should be employed, (iv) the irradiation of the sample is effected under an ambient relative humidity of 50% at 25 °C, and (v) the process is deemed complete when a contact angle $\leq 10^\circ$ (not $\leq 5^\circ$) is recorded in 3 consecutive measurements, space 1 h apart. Without these conditions, it appears likely there would be a significant variance in results emanating from different laboratories, when testing the same sample, for example.

## 6. ISO 27447: 2009, 'test method for antibacterial activity of semiconducting photocatalytic materials [8]

The photo-catalytic destruction of pathogenic micro organisms has been detailed in a number of publications since the first report in 1985 on the destruction of *Lactobacillus acidophilus* and *Escherichia coli* [64]. In particular in the past 5 years there has been significant growth in papers reporting the disinfection of pathogenic bacteria in water or on surfaces [65–70].

Typically *E. coli* has been used as a test bacteria, however, a huge range of other micro organisms have now been investigated ranging from *Salmonella enteritis* to *Clostridium perfringens*. The basic photocatalytic disinfection process is believed to involve an attack on the cell membrane of the bacteria, resulting in the subsequent rapid death of the cell [71–73].

### 6.1. The standard

This International standard specifically applies to the assessment of antibacterial activity on photocatalytic ceramic materials or other materials that are generated through coating or mixing with photocatalysts. The standard does not, however, apply to test materials which are permeable or rough surfaces and under such circumstances it is suggested other test methods are required.

This ISO focuses on photocatalytic materials used in construction materials such as boards, flat sheets or textiles and does not include powder, granule or porous photocatalytic materials. Since this standard focuses on the photocatalytic disinfection of surfaces, it does not cover the disinfection of other forms, such as that of water or air. Consequently another standard will be needed for the photocatalytic assessment of materials designed for water and air disinfection.

A fairly comprehensive set of terms and definitions are detailed in the standard including: definitions of photocatalysis and photocatalytic materials and explanations of what is meant by antibacterial and what types of lamps that should be used for this assessment.

The two main approaches are used in this test are: (i) a film adhesion method and (ii) a glass adhesion method. The film adhesion method is used for the assessment of "flat surface materials" that have a photocatalytic coating. The glass adhesion method is recommended for the evaluation of the photocatalytic antibacterial properties of cloth materials.

- For the film adhesion method the following two bacteria are selected for testing: *Staphylococcus aureus* and *E. coli*, With the glass adhesion method, *S. aureus* and *Klebsiella pneumoniae* are the selected test bacteria types.
- Specific, commonly available strains of the bacteria are identified in this standard and detailed below.

*S. aureus* strains

- *S. aureus* the strain numbers include the ATCC6538p from the American type culture collection
- DSM346 from German collection of the micro organism and cell cultures (DSMZ)
- NBRC 12732 from the NITE Biological Resource Centre.

*E. coli* strains

- *E. coli* the strains include ATCC8739 from the American type culture collection
- DSM1576 from German collection of the micro organism and cell cultures (DSMZ)
- NBRC3972 from the NITE Biological Resource Centre.

*Klebsiella pneumoniae* strains

- *K. pneumoniae* strain numbers are ATCC4352, from the American type culture collection
- DSM789 from German collection of the micro organism and cell cultures (DSMZ)
- NDRC13277 from the NITE Biological Resource Centre.

Details are given for the preparation of the: nutrient broth, diluted nutrient broth (1/500 NB), nutrient agar, Soybean-caesin digest broth with lecithin and polysorbate (SCDLP), physiological saline and physiological saline for washout, respectively.

The standard provides a detailed description for the preparation of the micro-organism from each of these parent strains. Thus, for the film adhesion method the parent strain is inoculated into a nutrient agar culture medium (slant culture) and incubated at 37 °C for between 16 and 24 h. Unless stated in all this work, 37 °C is always the incubation temperature. The bacteria are then transferred to a new agar slant and incubated for 16–24 h. A small quantity of the bacteria is then transferred to a diluted form of the nutrient broth (1/500 NB) with a platinum loop and the bacteria count measured using an optical microscope or optical density absorbance method (common methods

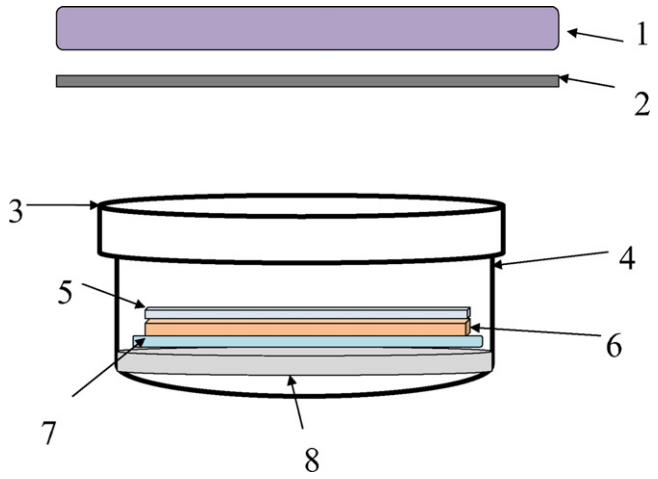



**Fig. 11.** Irradiation set up for the antibacterial ISO standard, comprising: (1) UV light source, (2) perforated metal plate (for adjusting irradiance level), (3) glass lid, (4) petri dish, (5) adhesive plastic or glass film, (6) sample under test with inoculated bacteria on its surface, (7) U-shaped glass rod or tube and (8) moist filter paper.

for determining bacteria concentrations in dispersions). This bacterial suspension is then diluted with 1/500 NB to obtain a count of $6.7 \times 10^5$–$2.6 \times 10^6$ cells ml$^{-1}$ which is then used to inoculate the sample under test. If the test bacteria are not used immediately the bacteria are stored at 0 °C and used within 4 h. The standard states that a maximum of 10 subcultures taken from the original strain and the slant culture must not be used after one month.

In the glass adhesion method the stock strain is used to inoculate the nutrient agar medium with a platinum loop for 24–48 h and used within 1 week (inoculation A). A colony from incubation A is then used to inoculate 20 ml of the nutrient broth in a 100 ml Erlenmeyer flask and incubated with agitation (110 min$^{-1}$ with about 3 cm amplitude) for 18–24 h (incubation B). Finally, 0.4 ml of the bacterial suspension in incubation B (cell concentration: $(1–2) \times 10^8$ cells ml$^{-1}$ are used to inoculate 20 ml of nutrient broth in a 100 ml Erlenmeyer flask and incubated with agitation to reach a cell level of $10^7$ cells ml$^{-1}$ (incubation C). The bacteria concentration in inoculation C is, as before, measured using an optical microscope or optical density absorbance method. A 1:20 diluted form of the nutrient broth is used to dilute a sample of inoculation C, so that it has a level of $1 \times 10^5$ cells ml$^{-1}$, which is then used to inoculate the sample under test.

Curiously, unlike any of the previous ISO photocatalyst tests, there is no sample pre-treatment step (see Table 1), which appears an oversight. Instead, the material being tested for its antibacterial activity is first autoclaved, inoculated with the bacteria under test, and then placed directly in a test chamber covered with a glass cover to maintain a high moisture level in the chamber. Adhesive film or glass with a transparency of greater than 85% for UV light between 340 and 380 nm covers the test sample which is suspended on a U-shaped glass rod or tube laid horizontal, i.e. resting on filter paper (Fig. 11). It is not clear why the film or glass has to be adhesive and what effect this has on the bacteria film on the sample under test. The sample is then irradiated using a black light blue (BLB) fluorescent lamp with a peak light source (emission wavelength maximum = 351 nm). This is the only ISO photocatalytic test where just one type of UV light source has been recommended and, as noted earlier, it is a recommendation of this report that all the ISO standards should, wherever possible, use just one specified type of BLB UV light source, vide infra. In this standard, if the light intensity cannot be varied sufficiently by altering the lamp height, it may be attenuated using a metal sheet perforated with holes.

For both the film and glass adhesion methods the test piece is prepared as follows. A 50 × 50 mm sample (±2 mm) of up to 10 mm thickness is used as the standard test specimen. Nine samples of untreated (i.e. no photocatalyst coating) and six photocatalytically treated specimens (i.e. with photocatalyst coating) are prepared.

Each of the samples is then placed in an individual glass Petri dish, autoclaved and dried on a clean lab bench for 60 min.

### 6.2. Film adhesion method

For the film adhesion method a sterilised filter paper is placed at the bottom of the Petri dish and between 4 and 6 ml of sterilised water added to the bottom. The U-shaped glass rod is then placed on top of this moistened paper and the test sample placed on top of this. A 0.15 ml specimen of the test bacterial suspension is pipetted onto the surface of the test specimen using a sterilised pipette. The adhesive film is then placed on top of the suspension and lightly depressed in order to spread the bacterial suspension over the surface. The Petri dish is then covered with a glass cover to maintain moisture levels in the test cell.

Three untreated bacterial suspension control samples (with adhesion film and non-illuminated sample piece) are each placed in a Stomacher bag. To this, 10 ml of Soybean-casein digest broth with lecithin and polysorbate 80 (SCDLP) are added and the specimens rubbed from outside of the bag to wash out the test bacteria. The number of viable cells (before illumination) in this test solution are then determined for each of the samples, from which the number of viable bacteria can be determined, A. This is typically performed by carrying out serial dilutions using physiological saline solution for washout measurements and then pipetting aliquots onto nutrient agar plates which are then incubated at 37 °C for 24 h. Colony counts are then performed directly on the plate and the viable colony counts (CFU), i.e. number of viable bacteria cells, determined.

In performing the illuminations, the ISO standard suggests the UV irradiance used, (adjusted by altering the height of the BLB lamps from the sample) will be governed by the circumstances where the materials are likely to be used. For example: 0.25 mW cm$^{-2}$ for beside a window, 0.10 mW cm$^{-2}$ in a room (1.5 m from a window), 0.01 mW cm$^{-2}$ (3 m from window) and 0.001 mW cm$^{-2}$ in a room without a window and with indoor lighting alone.

The same treatment as described above, i.e. inoculation, illumination and viable bacteria count of washout, is applied to the photocatalytic and non-photocatalytic samples under test illuminated for 8 h, so as to determine the average number of viable bacteria left after the illumination period for photocatalytic samples ($C_L$) and non-photocatalytic samples ($B_L$). The apparent photocatalyst antibacterial activity value after 8 h irradiation with UV light of irradiance, $L$, mW cm$^{-2}$, is $R_L$, where:

$$R_L = \log\left(\frac{B_L}{C_L}\right) \tag{27}$$

In addition, dark control specimens, with and without the photocatalyst coating are also prepared and kept in the dark for the same 8 h period. The average number of viable bacteria left after 8 h in the dark for these non-photocatalytic and photocatalytic samples, are then determined as: $B_D$ and $C_D$, respectively. From which a value for the overall photocatalyst antibacterial activity with irradiation, $\Delta R$, can be determined since:

$$\Delta R = \log\left(\frac{B_L}{C_L}\right) - \log\left(\frac{B_D}{C_D}\right) \tag{28}$$

### 6.3. Glass adhesion method

For the glass adhesion method the test chamber is set up in the same manner as described for the film adhesion method with

respect to the moistened filter paper and U-shaped glass rod or tube. A sterilised glass plate is then placed on the U-shaped rod/tube and the test sample (e.g. a cloth with or without a photocatalyst coating)) is placed on the surface of this material. 0.2 ml of the bacterial suspension is then dripped onto the surface of the test material using a sterilised pipette and spread over the surface of the test sample. The sample chamber is then covered with the glass lid prior to irradiation.

As with the film adhesive method the standard, non-treated (i.e. no photocatalyst) cloth samples are inoculated with the test bacteria and placed in a Stomacher bag together with the adherence sterilised glass and glass pane. 20 ml of physiological saline solution are added and the Stomacher bag rubbed by hand from the outside to extract out all the bacteria into the washout solution. The number of viable cells (before illumination) in this test solution are then determined from the washout solution as before. The same procedure as used in the film adhesive method is then employed to determine values for: $B_L$, $C_L$ and $B_D$, $C_D$, allowing values for $R_L$ and $\Delta R$, via Eqs. (27) and (28), respectively, to be calculated.

### 6.4. Pros and Cons

Given the significant number of antimicrobial commercial products based on semiconductor photocatalysts, this is a necessary standard and yet, in general the methods described in this standard for assessing both the "flat surface materials" and the cloth samples are rather complicated and could be simplified.

For example, as detailed above the bacteria preparation section of the ISO describes how the micro-organisms can be subcultured from an initial culture with a maximum of 10 subcultures from the original strain being recommended. However, this appears unnecessarily involved and a simpler method, which would avoid the need for subculture, would be to store the bacteria at −80° in Protect bacterial preservation beads [74] and use these for subsequent assessments. Protect beads are ceramic beads suspended in cryopreservative fluid encapsulated in vials which are specially designed to protect cells from damage under freezing or thawing [74]. Alternatively, Krysa et al. [75] propose the use of gelatinous pill cultures which contain a lyopilisated form of the bacteria containing approximately $10^8$ CFU $ml^{-1}$. These pills are then dissolved in saline prior to cultivation at 37 °C for 24 h.

The bacterial suspensions used to inoculate the samples are created by diluting the initial 'stock' solution (which also contains nutrient broth) to their correct concentrations (ca. $10^5$ cell $ml^{-1}$) using a diluted form (1:20) of the nutrient broth, but this appears an inappropriate suspension medium for a number of reasons. Firstly, even in the presence of diluted nutrient broth, the bacteria may continue to grow and hence this may lead to anomalous results in the control and treated samples. This point is underlined by the fact that in the example log(survived bacteria) vs. irradiation time data, provided in Appendix C of the original standard, the level of bacteria increases in the dark control samples, e.g. by ca. one log order in 24 h for *E. coli*. Furthermore as highlighted recently by Krysa et al. [75], this growth medium obviously contains organic compounds, the decomposition of which may compete for destruction with the bacteria on the photocatalytic surface. As a consequence, these workers recommend the use of saline as an alternative suspension/dilution medium.

Interestingly, even this improved 'saline dilution' approach can lead to anomalous results as the chloride may be oxidised to hypochlorite on the photocatalyst surface and this in turn may destroy the bacteria but not through the desired direct photocatalytic action of the semiconductor. Evidence for this is provided by the work of Cushnie et al. [76] who report enhanced disinfection when a chloride medium is used as the bacteria suspension medium (no nutrient broth) in the photocatalytic destruction of a range of bacteria on photocatalytic glass specimens. As an alternative, these workers recommend that the best suspension medium for the assessment of the photocatalytic materials is distilled water and that, following incubation in nutrient broth, the cells can be harvested by centrifugation, and then washed and re-suspended in sterile distilled water [76].

The standard recommends the use of *S. aureus* and *E. coli* for the film adhesion method while for the glass adhesion method *S. aureus* and *K. pneumoniae* are recommended as model pathogens. However, it would appear more sensible and simpler to use only *E. coli* (or *K. pneumoniae*) as the standard gram negative pathogen for both procedures.

Another concern is that a photocatalytic sample under test has the bacterial suspension dropped onto the surface and is then covered with either a film or glass slide, with care taken to avoid leakage from the sides. This, however is not easy and it is suggested here that an alternative approach could be adopted using a simple well system, into which a standard volume of the bacterial suspension is applied to the sample which lies at the bottom of the well. For example, Tim Cushnie et al. [77] reported the use of a glass cell ring which was aseptically applied to photocatalytic glass slides. The suspension (300 μl) was carefully pipetted into the ring cells and the material subsequently irradiated. The advantage of this type of approach is that it allows the bacterial suspension to be accurately deployed to a known area of the surface under investigation.

As noted earlier, in both the film and glass adhesion methods, the presence of the adhesive on the film and glass appears an unnecessary complicating factor, since the adhesives will contain organic compounds which can undergo photocatalytic degradation by the sample under investigation and hence compete with the bacteria for destruction and so affect the measured photocatalytic activity of the material under investigation. Assuming the role of the adhesive is simply to retain the film/glass in place, four small patches of adhesive in the corners would appear much more appropriate, than complete coverage of the film and glass with adhesive.

One of the challenges of antibacterial coatings in general is that even if the number of colony forming units is reduced to a non detectable level, there may still be some residual colonies, which under favourable conditions may multiply and hence recolonise the surface. The standard should note this limitation and indicate that continued monitoring, when it appears that complete bacterial destruction has been achieved, would help identify how much a problem regrowth is for any system under test.

Finally the method for calculating the results suggested by the ISO test appears rather complicated and it is not clear why a slightly different method is used for the film adhesion method compared to the glass adhesion method. It would seem more logical if a common approach for calculating the antibacterial activity was adopted for both methods, as we have suggested in the description of the calculations reported above.

## 7. ISO 10677: 2011: Ultraviolet light source for testing semiconducting photocatalytic materials [11]

All the ISO tests reported previously make reference to the use of a suitable a UV light source. A typically statement of what to use is (from ISO10676 [10] for example): 'the so-called black light (BL) and black light blue (BLB) fluorescent lamps, . . ., and xenon arc lamps with optical filters that block irradiation below 300 nm'. It is not surprising, therefore, to have the type of light source to be used in such ISO standards more clearly defined in an ISO standard of its own, which focuses on the two types of BLB and a xenon arc lamp.

### 7.1. Key features

Black light fluorescent lamps are made as normal white light fluorescent tubes except that only one phosphor is used, and the

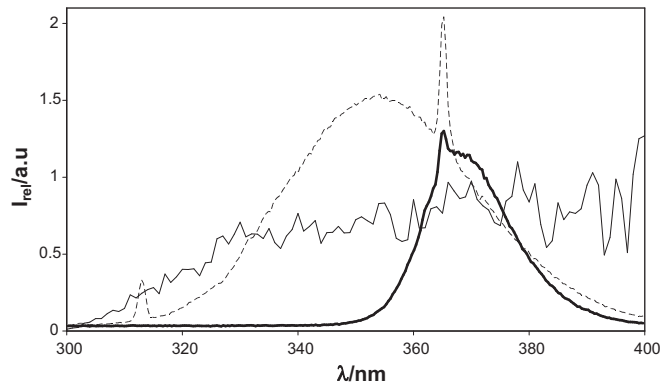



**Fig. 12.** Relative light intensity vs. wavelength profiles for (a) a xenon arc lamp (solid line), (b) a BLB light source with $\lambda_{max}$ (other than peak at 365 nm) at ca. 351 nm and (c) a BLB light source with $\lambda_{max}$ (other than peak at 365 nm) at ca. 368 nm.

glass envelope has a blue filter which ensures that most of the light emitted is UVA light. The two types of BLB arise because there are two types of phosphor, namely: (i) europium-doped fluoroborate, which produces a UV emission peak ranging from 368 to 371 nm and a band width of 20 nm and (ii) lead-doped barium silicate with a UV emission peak ranging from 350 to 353 nm and a band width of 20 nm [78]. The emission spectra of the two different types of BLB are illustrated in Fig. 12. It is recommended in the standard that xenon arc lamps should be used to evaluate photocatalytic materials for use in sunlight, as their emission spectra in the UV are not too dissimilar to that of the sun, over the region 300–400 nm; see Fig. 12 for the emission spectrum of an appropriately filtered xenon arc light source (vide infra). The standard also recommends use of a radiometer, for measuring the UV irradiance, that is calibrated against the light source used in the test, so usually at 365 nm for BLB lamps. Measurement of UV irradiance should be made at least 15 min after the lamp is switched on and at the start and end of the test period.

### 7.2. Pros and cons

The specification of a suitable UV light source is paramount to the repeatability (between labs) and reproducibility (within a lab) of the standard tests reported above and the light sources chosen in this standard are readily available, commonly used and eminently sensible. However, as noted in the standard itself 'the photocatalytic efficiency [of a system] depends upon the spectral distribution and radiant intensity [of the light source]. Thus, the problem with the three different light sources recommended is that they all have different emission spectra, as is clearly illustrated in Fig. 12. It is suggested here that only one type of BLB should be recommended, namely one with an europium-doped fluoroborate phosphor, since it is much nearer a monochromatic source of UV light (band-width ca. 20 nm) compared to the other type (band-width 40 nm). In addition, standards in which a xenon arc lamp is used as the source of UV should clearly state that a very different type of light source is being used so as to assess the activity of the material under test under solar UV simulation conditions. For any standard it would be quite incorrect to compare the activity value of a sample measured under BLB light conditions, with one measured under xenon arc lighting conditions.

When using a xenon arc lamp the standard suggests using a UV filter to remove any light below 300 nm. However, a much better approach to producing solar simulated UV light (and ensuring the significant visible component is removed) is to use a UG5 filter (cuts out most light between 400 and 650 nm [79]) in combination with a WG320 filter (cuts out light below 300 nm [80]). Such filters are commonly used with xenon arc lamps in the evaluation of new sun blocks or UV dosimeters since the overall emission has been shown to be a very good fit to the actual solar UV emission spectrum [81]. The removal of most of the visible light produced by the Xe arc lamp is also a very important feature, since the standards are designed for UV absorbing systems only. As we have seen [28,29], the presence of a significant level of visible light can lead to false positive effects, such the photo-sensitised bleaching of $MB^+$, in the $MB^+$ ISO standard.

## 8. Final comments

Overall, the ISO standards probe the properties of UV-absorbing semiconductor photocatalyst films/surfaces quite well. The methylene blue test [9] appears appropriate for assessing the ability of the photocatalyst to purify water (not self-cleaning as the ISO test suggests). This ability can also be probed using the DMSO removal test [10]. The measurement of total organic carbon levels in such water purification tests would help improve their usefulness, but place an additional cost burden. The removal of air-borne pollutants, such as NO [6], acetaldehyde [12] and toluene [13] appear reasonable first choices for pollutants and will be strengthened by additional tests for formaldehyde and (and possibly less obvious) methyl mercaptan, which are soon to be published. In such work with VOCs, the determination of degree of mineralisation, as assessed by $CO_2$ generation, would be a useful additional feature if the necessary reproducible, inexpensive, very sensitive analytic systems are available and if carbon dioxide adsorption is not a major feature. The contact angle test is an interesting approach to assessing the self cleaning ability of a photocatalyst [7]. The noted ability of semiconductor photocatalyst films to kill bacteria [8] will be supported soon by one on fungi destruction. The definition of the type of UV light source is essential and a useful standard [11]. A summary of these standards and their appropriate application area are given in Table 3 [82–91], along with forthcoming and suggested additional tests.

With regard to the suggested additional ISO tests in table 3 that would compliment or reinforce those already in place, the only one which has not been discussed so far is the use of inks to rapidly screen the photocatalytic activity of self-cleaning films. All the inks suggested work on the same principle, namely: as usual ultra-bandgap irradiation of the semiconductor photocatalyst generates conductance band electrons ($e^-$) and valence and holes ($h^+$). The ink contains a sacrificial electron donor, SED, such as glycerol, which reacts irreversibly and rapidly with the photogenerated holes, leaving the photogenerated electrons to reduce the indicator ink dye molecules, D, contained within the ink film. The various steps associated with this mechanism are summarised in the schematic illustrated in Fig. 13. All these steps take place in the encapsulation medium of the polymer, HEC, which features in the ink formulation.

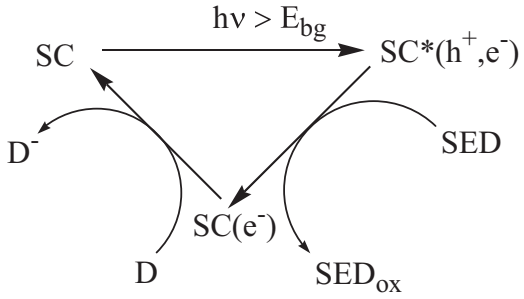



**Fig. 13.** Schematic of reaction steps involved in the photocatalysed reduction of a redox dye (D), such as resazurin, by a sacrificial electron donor (SED, such as glycerol).

**Table 3**
Summary of existing, forthcoming and suggested ISO tests.

| Property under test | Test pollutant | ISO? | Comments |
|---|---|---|---|
| Air purification | NO | ISO 22197-1: 2007 | |
| | Acetaldehyde | ISO 22197-2: 2011 | |
| | Toluene | ISO 22197-3: 2011 | |
| | formaldehyde | Pending | |
| | Methyl mercaptan | Pending | |
| | Acetone | Suggestion | A simple test, which can be monitored by FTIR, which allows both disappearance of the acetone and appearance of $CO_2$ to be observed simultaneously [82] |
| Water purification | Methylene blue | ISO 10678: 2010 | Despite the claim by the ISO test that it is for testing self-cleaning surfaces, it is most appropriate to classify it as a water-purification test. |
| | DMSO | ISO 10676: 2010 | |
| | Acid Orange 7 | Suggestion | Another very popular, but this time anionic dye, for assessing the photocatalytic activity of new materials [49] |
| | Phenol | Suggestion | A simple reagent, which is not destroyed by UVA light and can be monitored by UV/Vis spectroscopy, as well as the more traditional hplc; proposed previously as a quantum yield standard in photocatalysis [51] |
| | 4-Chlorophenol | Suggestion | An extremely well-studied pollutant in semiconductor photocatalysis [50,56,57,83], which can also be monitored by pH change as well as UV/Cis spectroscopy |
| | Dichloroacetic acid | Suggestion | A very simple pollutant easily monitored by the pH change due to HCl production [52] |
| Self-cleaning | Contact angle/oleic acid | ISO 27448: 2009 | |
| | Stearic acid | Suggestion | Possibly one of the most used photocatalytic reagents for probing the activity of self-cleaning films (such as glass) that allow monitoring the photocatalytic oxidation process via transmission FTIR [84,85] |
| | Inks | Suggestion | Photoreductive inks (MB [86], Rz [87] and DCIP [88]) offer the possibility of rapid visual qualitative and quantitative assessment of activity of photocatalytic surfaces |
| Disinfection | Bacteria | ISO 27447: 2009 | |
| | Fungi | Pending | |
| | Viruses | Suggestion | Others have already shown that photocatalytsts are able to inactivate viruses such as: human adenovirus GB, Influenza A and B [89], Hepatitus B [90] and SARS [91] |

Table 4 provides details of the structures of the oxidised and reduced forms of the dyes most often used, as well as typical UV irradiation times taken for the various inks containing these different dyes to change colour when applied to a typical, commercial self-cleaning glass sample. From Table 4 it is clear that, unlike all the ISO tests reported above, and those about to be published, the photocatalyst indicator inks are extremely rapid in response. Other work shows there is a reasonably good correlation between the rate at which the dyes are photocatalytically reduced and the ability of the same material to photooxidise stearic acid [87] or a dye in solution, such as acid orange 7 [92].

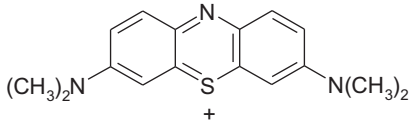
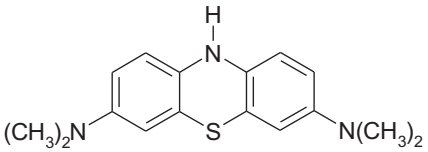
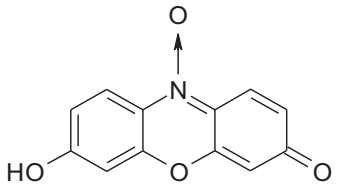
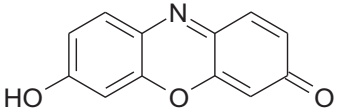
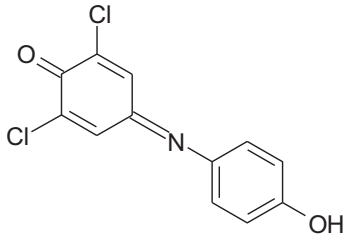
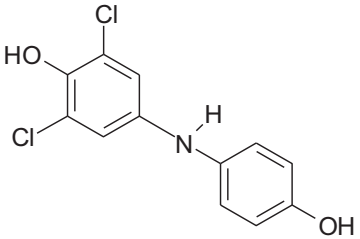
All standards that assesses the photocatalytic activity of a material, whether they be for air or water purification, self-cleaning or disinfection, provide – with varying degrees of success – just a snapshot of the activity of the sample. These measured activities should NOT be assumed to be everlasting, since there are many substances that deactivate semiconductor photocatalysts, mainly by forming inert (or at least highly recalcitrant) and/or UV-blocking coatings. These species maybe photocatalytically generated: metal oxides and hydroxides, such as $SiO_2$ (e.g. from any silicone-based cleaning solution or sealing compound), metal oxides, from metal ions (e.g. $Fe_2O_3$ from the Fe(III) ions in waste water), polymeric, coloured, UV-blocking aromatics (e.g. polyaromatics from toluene in air purification) and carbonaceous materials (such as, soot, carbonates and even dead cells).

For the future, therefore, it is essential that the existing standards are extended to probe the longevity of photocatalyst materials when exposed to realistic conditions, based on their likely area of application. For example, an exterior photocatalyst paint, glass, tile or awning material should be tested with regard to activity stability under accelerated weather conditions. A photocatalyst cloth (as used in clothing say) should be tested for durability when repeatedly washed. The air and water purification activity of materials should be tested over a significant amount of time under non-laboratory conditions, i.e. using locations in cities with high levels of pollution and on real waste water streams, respectively. Such work will expose the strengths and weaknesses of any new photocatalyst material and help identify those with longevity and therefore of true commercial promise. For example, a visible light photocatalyst is of little commercial use as such if it quickly loses its ability to absorb visible light through an oxidative photobleaching mechanism, as many of the current doped titania samples appear prone.

It might be thought that accelerated weathering, or long-term testing will inevitably lead to a decrease in photocatalytic activity and the key question with regards commercialisation potential and usefulness will always be one about the rate of this decrease. However, many have shown that quite often a much reduced photocatalytic activity, due to recalcitrant organic film or soot formation say, can be largely regenerated under sufficient UV illumination and humidity. In addition, with some materials it is positively essential some degree of weathering/use occurs for their true potential to be revealed, as in the case of some photocatalytic paints. This feature is rather nicely illustrated by the data in Fig. 14, for two different photocatalyst-based $NO_x$-removing paints. This work, a plot of NO removing ability vs. accelerated weathering time shows that such systems need to be used for a little while before realising their optimum performance, presumably because the pigment particles first destroy the organics that coat their surface and which form part of the paint formulation that bind them. In this case, it can be argued that the presence of $NO_x$ actually helps preserve the coating, as the air-borne pollutant is oxidised in preference to the binder. What is particularly interesting is that one of the paints illustrated in Fig. 14 exhibits no initial photocatalytic activity, implying that an initial assessment would indicate no activity and so possibly prompt its rejection, even though accelerated weathering or repeated use would reveal its true photocatalytic potential.

It is clear that existing standards need to be used to probe the activities of photocatalytic materials subjected to extensive use under real conditions to identify the truly useful materials/products. Encouragingly, for some materials at least, like photocatalyst paints, activity can go up as well as down.

**Table 4**
Structural, redox and absorption characteristics of the photocatalyst indicator inks.

| Dye | Oxidised indicator dye ($D_{ox}$) | Reduced indicator dye ($D_{red}$) | $E^{\circ}$ ($D_{ox}/D_{red}$)/V at pH 7 | □$_{max}$ ($D_{ox}$)/nm In dried ink | Colour of ink before (and after) UV irradiation if photocatalyst present | Time to change colour on commercial self cleaning glass[a]/s |
|---|---|---|---|---|---|---|
| MB |  |  | +0.011 | 665 and 608 | Blue (colourless) | 17 |
| Rz |  |  | – | 610 | Blue (pink) | 132 |
| DCIP |  |  | +0.228 | 629 | Blue (colourless) | 56 |

[a]UV irradiance: 3 mW cm$^{-2}$

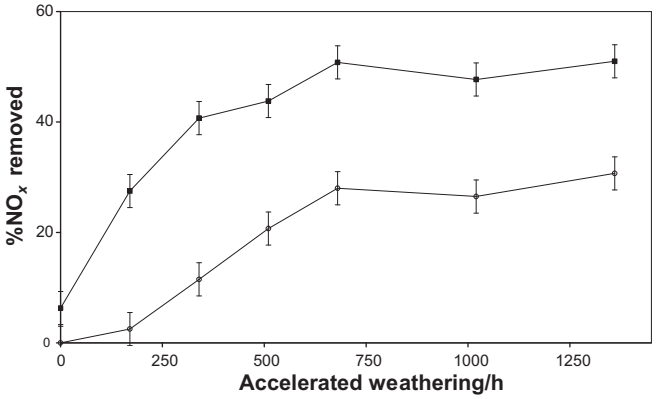



**Fig. 14.** %NO removed by two different photocatalyst paints as a function of their accelerated weather exposure time (1000 h is approximately equivalent to 2 years outdoor exposure in UK).

Finally, it is worth noting that there is a technical committee working on photocatalysis standards for the European Committee of Standardisation, CEN/TC 386 [93]. It has working groups on: terminology, air-purification, water purification, self-cleaning applications, light sources and new technologies. A number of different preliminary work items have been created in the areas of air purification, self cleaning applications and light sources, and so we can expect soon to see CEN standards in these areas to emerge.

## Acknowledgements

The authors wish to thank Christopher O'Rourke for help preparing the diagrams and Dr. Jeanette Robertson for help and advice on the antibacterial section.

## References

[1] A. Fujishima, X. Zhang, D.A. Tryk, Surf. Sci. Rep. 63 (2008) 515.
[2] A. Mills, S. LeHunte, J. Photochem. Photobiol. A 108 (1997) 1.
[3] O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem. 32 (2004) 33.
[4] A. Mills, S.K. Lee, J. Photochem. Photobiol. A 152 (2002) 233.
[5] http://www.iso.org/iso/home.html (accessed January 2012).
[6] ISO 22197-1: 2007, 'Fine ceramics, advanced technical ceramics – test method for air-purification performance of semiconducting photocatalytic materials – part 1: removal of nitric oxide', ISO, Geneva, 2007.
[7] ISO 27448: 2009, 'Fine ceramics, advanced technical ceramics – test method for self-cleaning performance of semiconducting photocatalytic materials – measurement of water contact angle', ISO, Geneva, 2009.
[8] ISO 27447: 2009, 'Fine ceramics, advanced technical ceramics – test method for antibacterial activity of semiconducting photocatalytic materials', ISO, Geneva, 2009.
[9] ISO 10678: 2010, 'Fine ceramics, advanced technical ceramics – determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue', ISO, Geneva, 2010.
[10] ISO 10676: 2010, 'Fine ceramics, advanced technical ceramics – test method for water purification of semiconducting photocatalytic materials by measurement of forming ability of active oxygen', ISO, Geneva, 2010.
[11] ISO 10677: 2011, 'Fine ceramics, advanced technical ceramics – ultraviolet light source for testing semiconducting photocatalytic materials', ISO, Geneva, 2011.
[12] ISO 22197-2: 2011, 'Fine ceramics, advanced technical ceramics – test method for air-purification performance of semiconducting photocatalytic materials – part 2: removal of acetaldehyde', ISO, Geneva, 2011.
[13] ISO 22197-3: 2011, 'Fine ceramics, advanced technical ceramics – test method for air-purification performance of semiconducting photocatalytic materials – part 3: removal of toluene', ISO, Geneva, 2011.
[14] A. Mills, M. McFarlane, Catal. Today 129 (2007) 22.
[15] R.W. Matthews, J. Chem. Soc. Faraday Trans. 85 (1) (1989) 1291.
[16] E. Rabinowitch, L.F. Epstein, J. Am. Chem. Soc. 63 (1941) 69.
[17] S. Mowry, P.J. Ogren, J. Chem. Educ. 76 (1999) 970.
[18] D.R. Lemin, T. Vickerstaff, Trans. Faraday Soc. 43 (1947) 491.
[19] Y. Zhang, R.J. Field, J. Phys. Chem. 95 (1991) 723.
[20] W. Spencer, J.R. Sutter, J. Phys. Chem. 83 (1979) 1573.
[21] S.J. Atherton, A. Harriman, J. Am. Chem. Soc. 115 (1993) 1816.
[22] G.N. Lewis, O. Goldschmid, T.T. Magel, J. Bigeleisen, J. Phys. Chem. 65 (1943) 1150.
[23] K. Bergmann, C.T. O'Konski, J. Phys. Chem. 67 (1963) 69, 2169.
[24] S. Prahl, Oregon Medical Centre, http://omlc.ogi.edu/spectra/mb/index.html (accessed January 2012).
[25] J. Tschirch, R. Dillert, D. Bahnemann, J. Adv. Oxid. Technol. 11 (2008) 193.
[26] A. Mills, C. O'Rourke, Green 1 (2011) 105.
[27] J. Tschirch, R. Dillert, D. Bahnemann, B. Proft, A. Biedermann, B. Goer, Res. Chem. Intermed. 34 (2008) 381.
[28] X. Yan, T. Ohno, K. Nishijima, R. Abe, B. Ohtani, Chem. Phys. Lett. 429 (2006) 606.
[29] C. O'Rourke, A. Mills, J. Photochem. Photobiol. A: Chem. 216 (2010) 261.
[30] Y. Ohko, Y. Nakamura, N. Negishi, S. Matsuzawa, K. Takeuchi, J. Photochem. Photobiol. A: Chem. 205 (2009) 28.
[31] T. Ibusuki, K. Takeuchi, J. Mol. Catal. 88 (1994) 93.
[32] S. Devahasdin, C. Fan, K. Li, D.H. Chen, J. Photochem. Photobiol. A: Chem. 156 (2003) 161.
[33] N. Bowering, G.S. Walker, P.G. Harrison, Appl. Catal. B: Environ. 62 (2006) 208.
[34] M.M. Ballari, M. Hunger, G. Husken, H.J.H. Brouwers, Appl. Catal. B: Environ. 95 (2010) 245.
[35] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF (accessed January 2012).
[36] http://www.londonair.org.uk/london/asp/datadownload.asp (accessed January 2012).
[37] M.L. Sauer, D.F. Ollis, J. Catal. 158 (1996) 570.
[38] Y. Ohko, D.A. Tryk, K. Hashimoto, A. Fujishima, J. Phys. Chem. B 102 (1998) 2699.
[39] E. Obuchi, T. Sakamoto, K. Nakano, Chem. Eng. Sci. 54 (1999) 1530.
[40] B. Hauchercorne, D. Terrens, S. Verbruggen, J.A. Martens, H. Van Langenhove, K. Demeestere, S. Lenaerts, Appl. Catal. B: Environ. 106 (2011) 630.
[41] http://www.cdc.gov/niosh/91112_55.html#Silverman%20et%20al.%201946 (accessed January 2012).
[42] V. Augugliaro, S. Coluccia, V. Lodo, L. Marchese, G. Martra, L. Parmisano, M. Schiavelllo, Appl. Catal. B. Environ. 20 (1999) 15.
[43] A.J. Maira, J.M. Coronado, V. Augugliaro, K.L. Yeung, J.C. Conesa, J. Soria, J. Catal. 202 (2001) 413.
[44] H. Einaga, S. Futamura, T. Ibusuki, Appl. Catal. B: Environ. 38 (2002) 215.
[45] M.C. Blount, J.L. Falconer, Appl. Catal. B: Environ. 39 (2002) 39.
[46] G. Marci, M. Addamo, V. Augugliaro, S. Coluccia, E. Garcia-Lopez, V. Loddo, G. Martra, L. Parmisano, M. Schiavello, J. Photochem. Photobiol. A: Chem. 160 (2003) 105.
[47] J.M. Coronado, J. Soria, Catal. Today 123 (2007) 37.
[48] O. Debono, F. Thevenet, P. Gravejat, V. Hequet, C. Raillard, L. Lecoq, N. Locoge, Appl. Catal. B: Environ. 106 (2011) 600.
[49] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B: Environ. 49 (2004) 1–14.
[50] J. Theurich, M. Lindner, D.W. Bahnemann, Langmuir 12 (1996) 6368.
[51] H. Tahiri, N. Serpone, R. LevanMao, Langmuir 93 (1996) 199.
[52] S. Sakthivel, M.C. Hidalgo, D.W. Bahnemann, S.U. Geissen, V. Murugesan, A. Vogelpohl, Appl. Catal. B. Environ. 63 (2006) 31.
[53] H. Bardouki, M. Barcellos de Rosa, N. Mihalopoulos, W.U. Palm, C. Zetzsch, Atmos. Environ. 36 (2002) 4627.
[54] M. Mori, K. Tanaka, H. Taoda, M. Ikedo, H. Itabashi, Talanta 70 (2006) 169.
[55] M.N. Abellan, R. Dillert, G. Gimenez, D. Bahnemann, J. Photochem. Photobiol. A: Chem. 202 (2009) 164.
[56] A. Mills, S. Morris, R. Davies, J. Photochem. Photobiol. A: Chem. 70 (1993) 183.
[57] A. Mills, S. Morris, J. Photochem. Photobiol. A: Chem. 71 (1993) 75.
[58] S. Kume, T. Nozu, Difficulty stainable glass product; Office, JP Patent Application. No.: Sho 63-100042, 1988.
[59] T. Zubkov, D. Stahl, T.L. Thompson, D. Panayatov, O. Diwald, J.T. Yates, J. Phys. Chem. B 109 (2005) 15454.
[60] A. Mills, M. Crow, J. Phys. Chem. C 111 (2007) 6009.
[61] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Nature (1997) 388.
[62] J.T. Yates, Surf. Sci. 603 (2009) 1605.
[63] K.R. Denison, C. Boxall, Langmuir 23 (2007) 4358.
[64] T. Matsunaga, R. Tomoda, T. Nakajima, H. Wake, FEMS Microbiol. Lett. 29 (1985) 211.
[65] D. Gumy, A.G. Rincon, R. Hajdu, C. Pulgarin, Sol. Energy 80 (2006) 1376.
[66] C. McCullagh, J.M.C. Robertson, D.W. Bahnemann, P.K.J. Robertson, Res. Chem. Intermed. 33 (2007) 359.
[67] Y. Kikuchi, K. Sunada, T. Iyoda, K. Hashimoto, A. Fujishima, J. Photochem. Photobiol. A: Chem. 106 (1997) 51.
[68] K. Sunada, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A: Chem. 156 (2003) 227.
[69] P.S.M. Dunlop, C.P. Sheeran, J.A. Byrne, M.A.S. McMahon, M.A. Boyle, K.G. McGuigan, J. Photochem. Photobiol. A: Chem. 216 (2010) 303.
[70] T.P.T. Cushnie, P.K.J. Robertson, S. Officer, P.M. Pollard, C.M. McCullagh, J.M.C. Robertson, J. Photochem. Photobiol. A: Chem. 216 (2010) 290.
[71] P.-C. Maness, S. Smolinski, D.M. Blake, Z. Huang, E.J. Wolfrum, W.A. Jacoby, Appl. Environ. Microbiol. 65 (1999) 4094.
[72] Z. Huang, P.-C. Maness, D.M. Blake, E.J. Wolfrum, S.L. Smolinski, W.A. Jacoby, J. Photochem. Photobiol. A 130 (2000) 163.
[73] P. Amézaga-Madrid, R. Silveyra-Morales, L. Córdoba-Fierro, G.V. Nevárez-Moorillón, M. Miki-Yoshida, E. Orrantia-Borunda, F.J. Solís, J. Photochem. Photobiol. B 70 (2003) 45.
[74] http://tscswabs.co.uk/downloads/Protect%20Flyer%20Web% (accessed January 2012).
[75] J. Krysa, E. Musilova, J. Zita, J. Hazard. Mater. 195 (2011) 100.

[76] T.P. Cushnie, P.K.J. Robertson, S. Officer, P.M. Pollard, C. McCullagh, J.M.C. Robertson, Chemosphere 74 (2009) 1374.
[77] T.P. Tim Cushnie, Peter K.J. Robertson, Simon Officer, Pat M. Pollard, Cathy McCullagh, Jeanette M.C. Robertson, J. Photochem. Photobiol. A: Chem. 216 (2010) 290.
[78] http://en.wikipedia.org/wiki/Black_light (accessed January 2012).
[79] http://www.optical-filters.com/ug5.html (accessed January 2012).
[80] http://www.heliosoptical.net/html/schott_wg_320_colorless_uv_fi.html (accessed January 2012).
[81] B.L. Diffey, Methods 28 (2002) 4.
[82] J.M. Coronado, M.E. Zorn, I. Tejedor-Tejedor, M.A. Anderson, Appl. Catal. B: Environ. 43 (2003) 329.
[83] C.M. Teh, A.R. Mohamed, J. Alloys Compd. 509 (2011) 1648.
[84] A. Mills, A. Lepre, N. Elliott, S. Bhopal, I.P. Parkin, S.A. O'Neill, J. Photochem. Photobiol. A: Chem. 160 (2003) 213.
[85] A. Mills, J. Wang, J. Photochem. Photobiol. A: Chem. 182 (2006) 181.
[86] A. Mills, J. Hepburn, M. McFarlane, Appl. Mater. Interfaces 1 (2009) 1163.
[87] A. Mills, J. Wang, S.-K. Lee, M. Simonsen, Chem. Commun. (2005) 2721.
[88] A. Mills, M. McGrady, J. Photochem. Photobiol. A: Chem. 193 (2008) 228.
[89] H. Takagi, K. Sugiyama, Kansenshogaku Zasshi 85 (2011) 244.
[90] L. Zan, W. fa, T. Peng, Z.K. Gong, J. Photochem. Photobiol. B: Biol. 86 (2006) 165.
[91] W. Han, P.H. Zhang, W.C. Cao, D.L. Yang, S. Taira, Y. Okamoto, J.I. Ara, X.Y. Yan, Prog. Biochem. Biophys. 31 (2004) 982.
[92] J. Zita, J. Krysa, A. Mills, J. Photochem. Photobiol. A: Chem. 203 (2009) 119.
[93] http://www.cen.eu/cen/sectors/technicalcommitteesworkshops/centechnicalcommittees/pages/TCStruc.aspx?param=653744&title=Photocatalysis (accessed January 2012).