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An intelligence ink for photocatalytic films

Andrew Mills,* Jishun Wang, Soo-Keun Lee and Morten Simonsen

An ink is described which, when printed or coated onto a photocatalyst film, changes colour irreversibly and rapidly upon UV activation of the photocatalyst film and at a rate commensurate with its activity.

Semiconductor photocatalysis, SPC, has been the subject of extensive research over the past two decades as a possible route to providing clean water, air and surfaces.[1–4] The basic process of SPC can be summarised as follows:

$$\text{Organic pollutant} + O_2 \xrightarrow[\text{Semiconductor}]{h\nu \geq E_{bg}} \text{Minerals} \qquad (1)$$
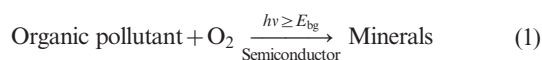
where E_{bg} is the bandgap energy of the semiconductor.

As a result of this research many commercial products have been generated including: water and air purification systems and self-cleaning tiles and glasses.[5] The latter are now major commercial products, sold by most of the glass manufacturers throughout the world; examples include: Activ™ (Pilkington Glass), Bioclean™ (St. Gobain), SunClean™ (PPG) and Radiance Ti™ (AFG).[5–7] In all cases, the photocatalyst employed is titania in its anatase form, often deposited onto the glass as a thin film (typically 15–20 nm) by a CVD technique. Anatase is preferred as the semiconductor photocatalyst in most examples of SPC because of its excellent photocatalytic activity, robustness, chemical inertness and ease of deposition.[1–5]

Photocatalyst films are self-cleaning in that most of the organic pollutants that go to make up the dirt and grime that deposit on window glass are readily mineralised by oxygen *via* the photocatalytic process [eqn. (1)]. In addition, titania, along with some other semiconductors, has the additional feature of photo-induced superhydrophilicity, PSH, in which the surface of the photocatalyst becomes much more wettable, *i.e.* more hydrophilic, upon irradiation with ultra-bandgap light.[5,8] PSH makes it difficult for hydrophobic organic pollutants to stick on a UV-activated, *i.e.* hydrophilic, photocatalyst film. In addition, even if such pollutants do stick, they are then readily washed off by water. Although at present it remains unclear how, if at all, the properties of PSH and SPC activity are related, it appears to be generally true that any titania film that is SPC active is also PSH active. Thus, for a fully functioning, self-cleaning glass it is important that the coating exhibits SPC activity. However, the assessment of this activity is not trivial.

For example, the generally preferred[9–13] method for assessing the SPC activity of a semiconductor photocatalyst is the stearic acid test, in which a thin layer of stearic acid is deposited onto the

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film and its photocatalytic destruction monitored under known illumination conditions.

$$CH_3(CH_2)_{16}CO_2H + 26\ O_2 \xrightarrow[\text{Semiconductor}]{h\nu \geq E_{bg}} 18\ CO_2 + 18\ H_2O \quad (2)$$
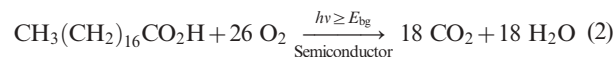
Over the years, the destruction of stearic acid has been monitored *via* the amount of CO_2 or H_2O generated using gas chromatography[10] and *via* the change in thickness of the stearic acid film (ellipsometry).[13] However the most popular[7,9,11,12] method is *via* the disappearance of the infra-red absorption of the stearic acid film, in the region 2500–3500 cm^{-1}, as a function of time.

The above methods of assessing SPC activity are not appropriate for making measurements in the field, since sophisticated and expensive analytical equipment and a trained technician are usually required. In addition, since most commercial self-cleaning glass utilises only a very thin layer of titania, the kinetics of photo-mineralisation reactions, such as eqn. (2), are very slow and it can take many days, if not weeks, to completely destroy a stearic acid layer, even under intense UVA irradiation.[12]

The photocatalytic activity of a semiconductor film would be more accessible to assessment if it could be associated with a colour change. The simplest approach to this end is to incorporate a dye in a polymer layer, that is deposited on the surface of the semiconductor film, and monitor the photo-oxidative mineralization of the dye/polymer system *via* the bleaching or discolouration of the dye. The major problem with such an indicator system is that the dye is likely to disappear at a rate that is similar to that of the usually slow photomineralisation of the encapsulating polymer, since both will be destroyed *via* a common reaction intermediate, namely photogenerated hydroxyl radicals. Such an indicator might be adequate for assessing the SPC activity of very active, usually thick, titania films, where the kinetics of photomineralisation are relatively rapid, but, clearly inappropriate for most commercial, self-cleaning photocatalytic glasses, since these exhibit much slower rates of photocatalysis. Instead, what is required and is described in this communication is an indicator ink that can be printed, or coated onto any self-cleaning glass sample and which rapidly, *i.e.* within a few minutes at most, changes colour upon UV activation of the underlying thin photocatalyst film. Unless stated otherwise, all formal redox potentials quoted are in water, *vs.* NHE, and at pH 7.

A typical photocatalyst intelligent ink comprised: 3 g of a 1.5 wt% aqueous solution of hydroxyethyl cellulose (HEC), 0.3 g of glycerol and 4 mg of the redox dye, resazurin (Rz). The structures of Rz and its reduced form, resorufin (Rf) are illustrated in Fig. 1. Typically, samples of glass with, and without a photocatalyst layer, were spin-coated with this ink (1000 rpm for 10 s), although this ink could also be readily printed onto glass
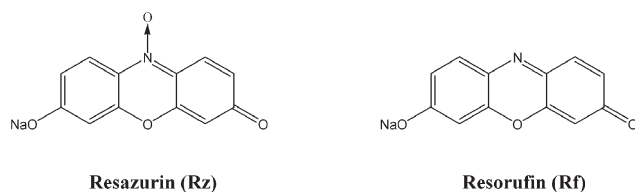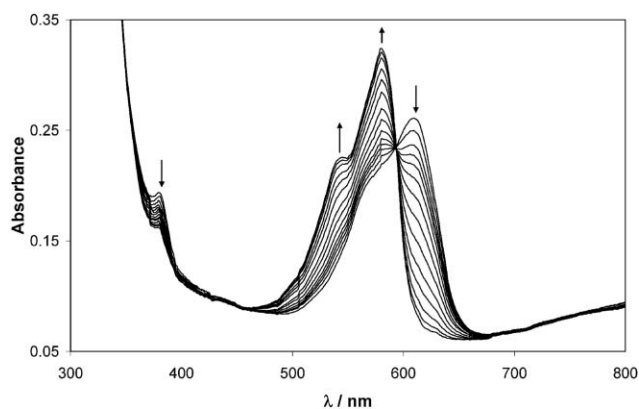
Fig. 1 Structures of resazurin and resorufin.

using the combination of a rubber stamp and ink pad and appeared to work just as effectively. This photocatalyst indicator ink formulation will be referred to throughout as a Rz/glycerol/HEC ink.

The appearance of the coated Rz/glycerol/HEC ink on glass was blue and its colour and UV/visible absorption spectrum, illustrated in Fig. 2, did not change upon prolonged UVA irradiation in the absence of an underlying photocatalyst film, *i.e.* when coated on plain glass. In contrast, as illustrated by the results in Fig. 2, the ink did rapidly (*i.e.* within minutes) change colour from blue to pink upon UVA irradiation when coated on a commercial sample of self-cleaning glass (Activ™). Subsequent work showed that all titania semiconductor photocatalyst films, regardless of preparation methods (*e.g.* CVD, sol–gel, sputtering) and substrate (*e.g.* glass, metal, paper) changed the colour of the ink at a rate commensurate with their individual SPC activities, as measured using the stearic acid test (*vide infra*). Further irradiation (hours) of this system bleaches the ink, although the polymer remains apparently intact. At this stage the unreacted polymer component of the ink may be readily removed with a damp cloth since the ink is water-soluble. Alternatively, after prolonged irradiation (days) the clear, transparent, colourless polymer film can be completely removed *via* its photocatalytic mineralisation.
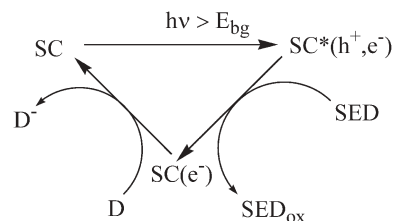
In contrast to the stearic acid test, and any other indicator dye/polymer system, the photocatalyst indicator ink described here does not work *via* a photo-oxidative mechanism. Instead, it functions *via* a novel photo-reductive mechanism in which the photogenerated holes react irreversibly with the sacrificial electron donor (SED) present, glycerol, and the photogenerated electrons (E° (TiO$_2$ (e$^-$)) = -0.52 V),[14] or, most likely, a subsequently generated reduced species, possibly O$_2^-$ or HO$_2$·, with redox potentials -0.28 V and 0.12 V (pH 0), respectively, are able to move through the polymer ink film and reduce the indicator ink dye molecules, D, contained therein. The dye selected for the photocatalyst ink, D, is resazurin, which is blue and is readily and irreversibly reduced to a pink reduced form, D$^-$, called resorufin (Rf), (E°(Rz/Rf) $\cong$ -0.020 V),[15] see Fig. 1. The various steps associated with the mechanism by which the photocatalyst indicator ink functions are summarised in the schematic illustrated in Fig. 3. All these steps take place in the encapsulation medium of the polymer, HEC, which features in the ink formulation.

The Rz/glycerol/HEC photocatalyst indicator ink reported above works rapidly for photocatalyst films of low SPC activity, such as commercial samples of self-cleaning glass like Activ™, as illustrated by the results in Fig. 3, and thus is an excellent qualitative indicator of SPC activity. However, its value as a photocatalyst indicator would be greatly enhanced if it can be shown also that the initial rate of dye bleaching, R_{ink}, correlates well with the initial rate of stearic acid removal, R_{SA}, which is so often used to assess the SPC activities of such films. In order to address this issue a series of CVD coated samples of anatase titania on glass with different SPC activities were prepared by varying the deposition conditions. These films, and a commercial sample of self-cleaning glass, Activ™, were first assessed for SPC activity using the stearic acid test and then, after cleaning, were coated with the photocatalyst ink and assessed for SPC activity *via* the measured values of R_{ink}. A plot of the rate data arising from this work, *i.e.* R_{ink}, *vs* R_{SA} is illustrated in Fig. 4 and reveals a good correlation between the two; the important difference being that, for each sample, the R$_{ink}$ data were obtained in a few minutes, whereas the R_{SA} data required hours of illumination. This feature is very nicely illustrated by the results in Fig. 5 which show the measured variations in relative concentrations of resazurin and stearic acid, as a function of irradiation time for Activ™. These results, along with those in Fig. 2, show that within a few minutes of irradiation the concentration of resazurin in the Rz/glycerol/HEC ink had changed considerably and was accompanied by a noticeable colour change. In contrast, even after 10 minutes UVA irradiation of a thin film of stearic acid on Activ™ the change in stearic acid concentration was slight. Thus, the Rz/glycerol/HEC


Fig. 2 UV/Visible absorption spectra of a sample of Activ™ (Pilkington Glass) coated with a film of the Rz/glycerol/HEC photocatalyst ink before and after UVA irradiation (using two 4 W BLB lamps; I = 12.4 mW cm^{-2}). The spectra were recorded every 30 seconds until no further significant changes occurred (after 6.5 mins). The dye initially present, resazurin, has an absorption peak at 610 nm and is reduced upon UV illumination, in the presence of a photocatalyst, to resorufin, which absorbs at 585 nm. Note: if coated on plain glass, the ink has the same spectrum as that shown for t = 0 (*i.e.* spectrum where absorbance at 610 nm is a maximum), and does not change even after prolonged UVA irradiation (*i.e.* >1 h).

Fig. 3 Proposed reaction scheme of the photocatalyst ink identifying the major underlying reactions. SC is the underlying semiconductor and D/D$^-$ and SED/SED$_{ox}$ are the oxidised/reduced forms of the indicator dye and sacrificial electron donor, respectively, encapsulated in the polymer film printed or coated onto the semiconductor.
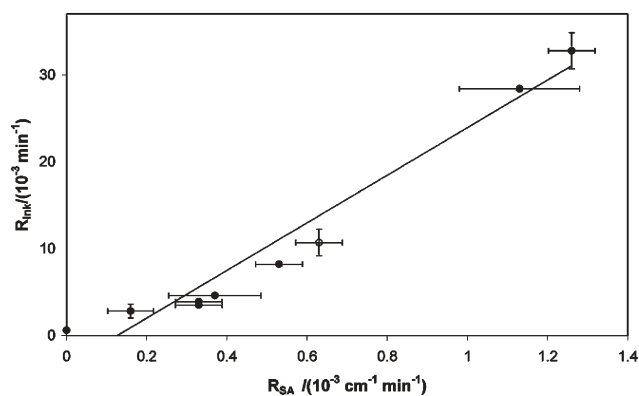
Fig. 4 Plot of the measured initial rate of Rz/glycerol/HEC ink colour change (resazurin to resorufin), R_{ink}, (units: Absorbance units s^{-1} measured at 585 nm), *versus* the measured initial rate of stearic acid removal, R_{SA}, for a series of CVD titania films of different SPC activities on glass. The open circle datum point is that for Activ™. In all cases the data were obtained using as a light source two 8 W BLB lamps and an incident UVA light intensity of 0.32 mW cm^{-2}.
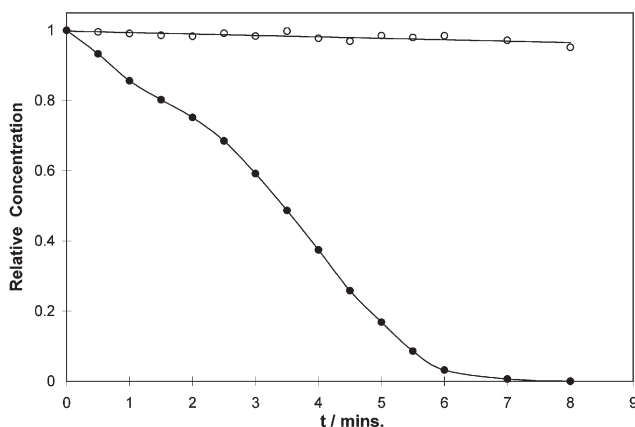
Fig. 5 Measured relative concentrations of resazurin (Rz), in a typical Rz/glycerol/HEC ink, and stearic acid, deposited on Activ™, as a function of irradiation time, using the same conditions as in Fig. 3. The initial stearic acid film had an integrated peak area[12] of 1.1 cm^{-1}.

photocatalyst ink is much faster acting than the stearic acid test and opens the way for rapid testing of most commercial photocatalytic products, including self-cleaning glass.

In conclusion, the photocatalyst ink described here provides a rapid and convenient method for assessing the SPC activity of a photocatalyst film. It is known, for powders at least, that the relative SPC activities of a range of titania samples can be different for different reactions. In spite of this and the fact that the ink functions *via* a reductive rather than oxidative process, the ink has

the attractive feature that its photo-induced rate of change of correlates very well with the rate of photomineralisation of stearic acid, which is *the* current method of assessing the SPC activity of such films, by researchers in academia and, more importantly, the self-cleaning film industries. Further work shows that the SPC activities of most photocatalyst films can be assessed readily using just a stamp and ink pad to create the ink film and a hand-held UVA lamp of known intensity, *i.e.* no expensive analytical equipment and technician are required. The ease with which such an assessment can be made using this intelligence, *i.e.* information, ink makes it an ideal, inexpensive method, usable even by a novice, to evaluate in the field, as well as the laboratory, the efficacy of many of the photocatalyst products that are entering the market, including self-cleaning glass, tiles and paving stones. Such an assessment method is important and valuable not only to the producer, as a quick and simple route to achieve 100% quality assurance, but also to the consumer who may wish to know if, after a few years, these seemingly 'magic' self-cleaning coatings still work their spell.

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