An intelligence ink for photocatalytic films

Mills, Andrew ; Wang, J; Lee, S K; Simonsen, Morten Enggrob

Published in:
Chemical Communications

Publication date:
2005

Document Version
Accepted author manuscript, peer reviewed version

Link to publication from Aalborg University

Citation for published version (APA):
An intelligence ink for photocatalytic films

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

Received (in Cambridge, UK) 26th January 2005, Accepted 23rd March 2005
First published as an Advance Article on the web 14th April 2005
DOI: 10.1039/b501131k

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:

\[
\text{Organic pollutant + O}_2 \xrightarrow{h\nu \geq E_{bg}} \text{Minerals} \quad (1)
\]

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 preferred6–13 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 film and its photocatalytic destruction monitored under known illumination conditions.

\[
\text{CH}_3\left(\text{CH}_2\right)_{16}\text{CO}_2\text{H} + 26 \text{O}_2 \xrightarrow{h\nu \geq E_{bg}} \text{Semiconductor} \quad 18 \text{CO}_2 + 18 \text{H}_2\text{O} \quad (2)
\]

Over the years, the destruction of stearic acid has been monitored \(via\) the amount of \(\text{CO}_2\) or \(\text{H}_2\text{O}\) generated using gas chromatography10 and \(via\) the change in thickness of the stearic acid film (ellipsometry).13 However the most popular7,9,11,12 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 hydroxethyl 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.

*a.mills@strath.ac.uk
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 \( (E^0 (\text{TiO}_2 (e^-)) = -0.52 \, \text{V}) \) or, most likely, a subsequently generated reduced species, possibly \( \text{O}_2^- \) or \( \text{HO}_2^- \), with redox potentials \(-0.28 \, \text{V and 0.12} \, \text{V (pH 0)} \), 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, \( \text{D}^- \), called resorufin (Rf), \( (E^0 (\text{Rf}/\text{Rz}) \approx -0.020 \, \text{V}) \), 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, \( R_{\text{ink}} \), correlates well with the initial rate of stearic acid removal, \( R_{\text{SA}} \), 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 \( R_{\text{ink}} \). A plot of the rate data arising from this work, i.e. \( R_{\text{ink}} \) vs \( R_{\text{SA}} \) is illustrated in Fig. 4 and reveals a good correlation between the two; the important difference being that, for each sample, the \( R_{\text{ink}} \) data were obtained in a few minutes, whereas the \( R_{\text{SA}} \) 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
The incident UVA light intensity of 0.32 mW cm\(^{-2}\) was used in the experiments. Data were obtained using two 8 W BLB lamps and an integrated area of 1.1 cm\(^2\) of irradiation time, using the same conditions as in Fig. 3. The open circle datum point is that for Activ\(^{[8]}\). In all cases, the data were obtained using a light source two 8 W BLB lamps and an incident UVA light intensity of 0.32 mW cm\(^{-2}\).

Photocatalyst ink is much faster acting than the stearic acid test, which is that for Activ\(^{[8]}\). In all cases, the data were obtained using a light source two 8 W BLB lamps and an incident UVA light intensity of 0.32 mW cm\(^{-2}\). The open circle datum point is that for Activ\(^{[8]}\). In all cases, the data were obtained using a light source two 8 W BLB lamps and an incident UVA light intensity of 0.32 mW cm\(^{-2}\).

In conclusion, the photocatalyst ink described here provides a rapid and convenient method for assessing the SPC activity of a photocatalyst ink, (units: Absorbance units s\(^{-1}\)) and opens the way for rapid testing of most commercial photocatalytic products, including self-cleaning glass.

Notes and references