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Visible illustration of the *direct*, *lateral* and *remote* photocatalytic destruction of soot by titania

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Abstract

Visual evidence of the *direct*, *lateral* and *remote* photocatalytic destruction of soot by a thick film titania is provided via a series of simple experiments. The results provide strong evidence for the photogeneration of an oxidising species which is both surface mobile and capable of air-borne diffusion.
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1. Introduction

Semiconductor photocatalysis for air and water purification is an active area of research. The basic process can be summarised as follows:

$$\text{Organic} + O_2 \xrightarrow[\text{Semiconductor}]{h\nu \geq E_{bg}} CO_2 + H_2O + \text{Mineral acids}$$

(1)
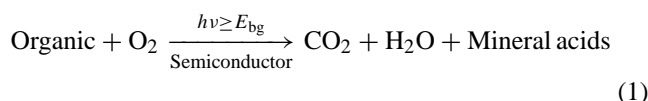
where E_{bg} is the bandgap energy of the semiconductor photocatalyst. The latter is usually titania, since it is chemically and biologically inactive, cheap, photostable and usually very photoactive; although it does have a large bandgap (ca. 3.2 eV) and so only absorbs in the UV (i.e. $\lambda < 388$ nm). Early work on reaction (1) centred on using the semiconductor as a powder dispersion, however, the added requirement of a filtration step in any practical system has resulted in an increased interest in fixed semiconductor films. This interest has been boosted recently with the news that a number of major glass manufacturing companies (such as: Pilkington Glass, PPG, AFG and St-Gobain) have launched self-cleaning glass window products for office and household buildings, in which the active ingredient is a thin (typically 15–30 nm thick) film of titania that is activated by the UV component of sunlight [1].

Despite this substantial commercialisation of semiconductor photocatalysis, the actual mechanism of reaction (1) remains the subject of some debate. Thus, in the case of titania, although ultra bandgap irradiation of the semiconductor generates an electron hole pair, it is still not clear if oxidation of the organic substrate in reaction (1) is effected directly by photogenerated holes and/or, indirectly, by hydroxyl radicals, $OH^\bullet$; the latter being generated by the reaction of photogenerated holes with absorbed surface OH^- groups [2–5]. The photogenerated electrons are assumed [2–6] to react with adsorbed oxygen to produce, eventually, water, although any peroxide produced as an intermediate may act as a secondary source of $OH^\bullet$.

So far, most of the evidence generated by research in this area points to hydroxyl radical attack as the major mode of organic oxidation via reaction (1), and, until recently, it was generally assumed [2–6] that, given the reactivity of this species (E° ($OH^\bullet/H_2O$) = 2.8 V versus NHE), it must react either at, i.e. be absorbed, or very close to the surface of the semiconductor. This understanding appears to be undermined by the recent work of Fujishima and his group [7,8] on reaction (1), using a sandwich system comprising: a film of titania on a glass slide and a film of a test pollutant on another glass slide; where the pollutants tested were methylene blue, rhodamine 6G, or one of a selection of different polymers. In this work, the two glass slides were held slightly apart from (typically 12–50 μm), but facing each other and the gap between the two films, i.e. the 'sandwich' filling, was invariably air. Using this 'sandwich' system Fujishima and his co-workers report that prolonged irradiation (i.e. tens of

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hours) with near UV light leads to the photomineralisation of all the test pollutants via reaction (1), despite their lack of contact with the semiconductor film, i.e. all the organics appeared to be oxidised *remotely* by some, as yet unidentified, photogenerated, air-borne oxidising agent [7,8]. In this work, although there is the obvious concern that, instead of the above rationale, the destruction of the organic test pollutants may simply be the result of their direct UV photolysis and not reaction (1), the results of blank experiments carried out by these workers appear to indicate that this is not the case.

More recent work carried out by Lee and Choi [9] found that soot, generated by burning *n*-hexane, deposited onto titania films could be destroyed by semiconductor photocatalysis, i.e.

$$C + O_2 \xrightarrow[\text{TiO}_2]{h\nu \geq E_{\text{bg}}} CO_2 \tag{2}$$

Most striking amongst the results arising from this work is the observation that soot deposited *alongside* the titania film is destroyed and that with prolonged UV irradiation a gap between the titania and the soot films appears, the size of which is approximately proportional to irradiation time (e.g. a 40 μm gap appeared after 58 h irradiation) [9]. Given the small size of the gap, this evidence for the *lateral* destruction of soot was only made possible using SEM, i.e. it was not a visible effect. This *lateral* oxidation of a test pollutant was attributed to the spill-over of a photogenerated, highly oxidising species [9]. In this paper [9], as elsewhere [8], it is assumed that this mobile photogenerated oxidising species is a desorbed OH•. It is also worth noting that in this work [9] evidence for the *direct* destruction of soot via reaction (2) is also reported, but *not* for its *remote* destruction.

Finally, the results of work carried out by Haick and Paz [10] on 2.5–40 μm strips of self-assembled monolayers of octodecyltrichlorosilane (OTS) anchored near to strips of the same size of titanium dioxide appears to support the suggestion that titania is able to photogenerate an oxidising species that can induce mineralisation *laterally*, but *not remotely*, i.e. *not* via a through air diffusion mechanism far from their place of photogeneration [10] (in this work an air gap of just 15 μm was used).

In a recent paper, we reported a method of producing very photoactive, thick (4 and 8 μm), transparent, robust films of titania on glass [11]. Because of their thickness, mesoporosity and optical clarity these films are much more photon efficient as photocatalysts than most (usually thin) titania films that have been used in the past to study the *direct*, *lateral* and *remote* destruction of organic pollutants via reactions (1) and (2). As a consequence, such thick titania films are expected to exhibit much clearer evidence of these effects. Thus, in this paper we explore whether the *direct*, *lateral* and *remote* destruction of a carbon-containing pollutant, such as soot, can be easily demonstrated and, for the first time, visualised using thick titania films.

2. Experimental

2.1. Materials

Unless stated otherwise, all chemicals and materials were purchased from Aldrich Chemicals and used as received. 'T-lite' paraffin-based candles, used to produce the soot films, were purchased from a local supermarket.

In this work, thick (4 μm) titania films were cast on standard (7.6 cm × 2.6 cm) microscope slides as 1.1 cm wide strips via a doctor-blade technique. The method of preparing such films is described in detail elsewhere [11]. In experiments designed to illustrate both the *direct* and *lateral* destruction of a test pollutant, a 'gapped' titania film was used. This film was prepared by laying down a thin (0.7 mm wide) strip of Sellotape™ across the path of the 1.1 cm channel, in turn made by two strips of Sellotape laid along the length of the slide, used to create the 4 μm titania film. The final form of the 'gapped' titania film comprised a 1.1 cm wide, 7.6 cm long strip of titania, centred along the length of the supporting microscope slide, split in the middle by a gap, free of titania, of 0.7 mm width.

2.2. Methods

All UV irradiations of the films were carried out using six 8 W germicidal light bulbs ($\lambda_{\text{emission}} = 254$ nm), placed 10 cm from the surface of the sample under test. Digital photography of the films was carried out using a Sony 'Cyber Shot' F707 digital camera.

3. Results and discussions

In a typical experiment, a 0.7 mm 'gapped' titania film strip (1.1 cm wide, 7.6 cm long), had soot deposited onto its surface using a burning 'T-lite' candle. The final thickness of the soot layer was typically 0.5 μm, as determined by SEM. The soot-covered 'gapped' titania film was then irradiated with far UV light and the appearance of the film photographed as a function of irradiation time. The results of this work are illustrated in Fig. 1a and show that upon UV irradiation a slow but gradual destruction of the soot deposited on the surface of titania takes place, leading eventually to the emergence of the outline of the 'gapped' film as all the soot on the surface of the titania film is removed. These results demonstrate that the *direct* photocatalytic destruction of soot can be easily effected on the surface of a thick film titania film, via reaction (2) (i.e. within 4.5 h). Further irradiation (4.5–155 h) of the same 'gapped' film resulted in the images illustrated in Fig. 1b. These images illustrate clearly that with prolonged irradiation even the removal of the soot in the 0.7 mm 'titania free' gap between the two halves of the titania strip is possible. The results in Fig. 1b provides excellent visual evidence of the *lateral* destruction of soot by the highly oxidising photogenerated species produced
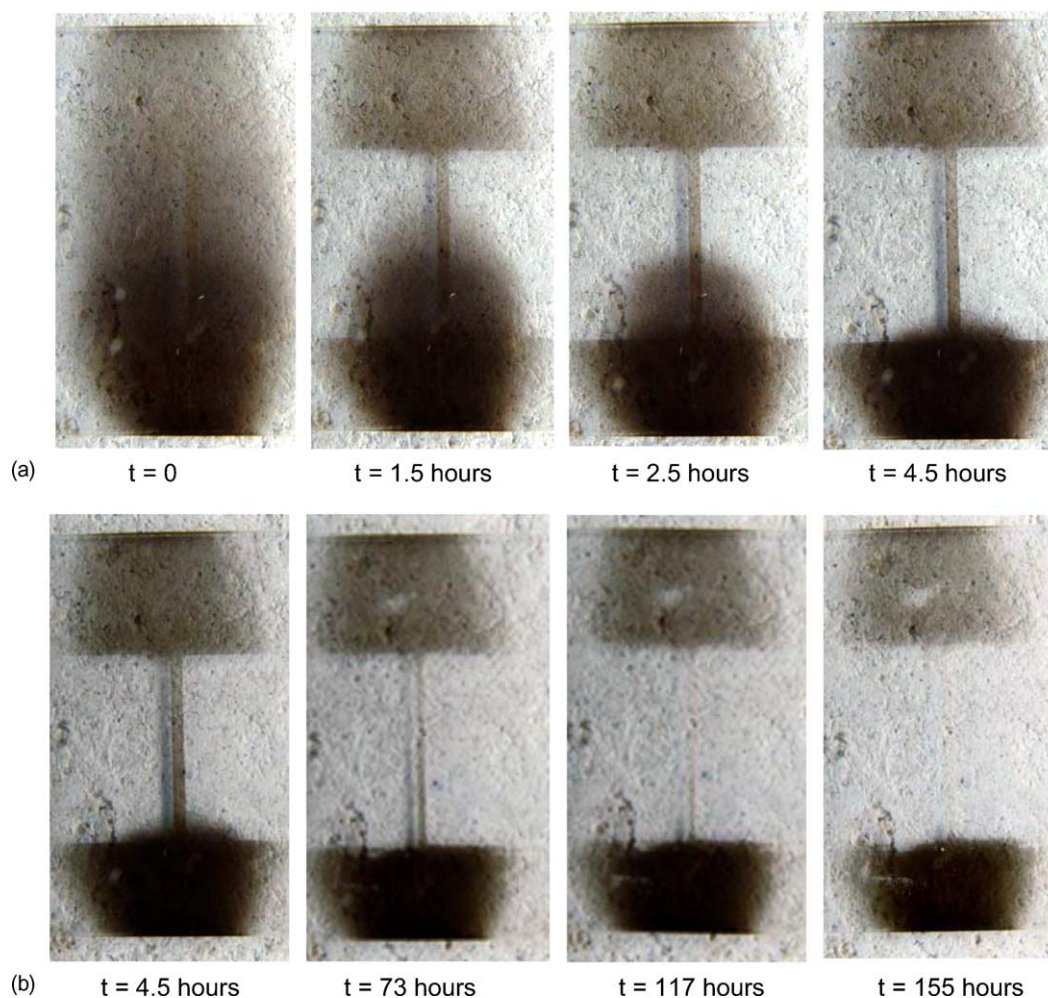
Fig. 1. Series of photographic images of part of a microscope slide with a 1.1 cm wide, 0.7 mm 'gapped', 4 μm thick titania film, covered initially with soot (0.5 μm thick) as a function of far UV irradiation time over a period of (a) 0–2.5 h to illustrate direct destruction and (b) over a period 4–155 h to illustrate lateral destruction of soot via reaction (2).

originally on the surfaces of the two halves of the titania film. Although, as stated above, the identity of these surface mobile species has still to be determined definitively, they are thought to be hydroxyl radicals. *Lateral* destruction of the soot film in the gapped region is thus made possible because these highly oxidising species are produced at, and spill-over, the surfaces of the UV-irradiated two halves of the titania film into the 0.7 mm titania free gap. It is important to note at this point that in similar experiments conducted in the absence of titania, no destruction of soot is observed upon UV illumination. The only exception to this observation is when the soot film is adjacent to, or in a narrow gap in, the titania film, i.e. when *lateral* oxidation is possible.

In order to demonstrate the *remote* oxidation of soot via reaction (2), a square (25 mm × 25 mm), quartz glass slide was coated with soot and placed on top of two separated 175 μm glass spacers, laid on top of a typical, bare titania strip on a microscope glass, as illustrated in Fig. 2. The system was irradiated with far UV light from above as before and photographic images of the initially soot-covered quartz slide were recorded periodically. The results of this work are illustrated in Fig. 3 and show that the soot on the *remote* quartz slide disappeared very slowly (over 305 h) in the area where it had been held directly above the titania film but not elsewhere. As a consequence, and as illustrated by the images in Fig. 3, upon prolonged irradiation
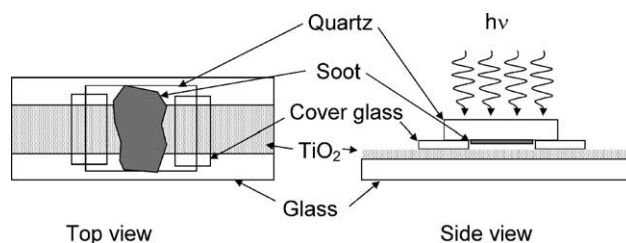

Fig. 2. Schematic top and side-view illustrations of the arrangement of the titania film-covered microscope slide, 175 μm glass spaces and soot-covered quartz slide used to demonstrate the remote destruction of soot by semiconductor photocatalysis.
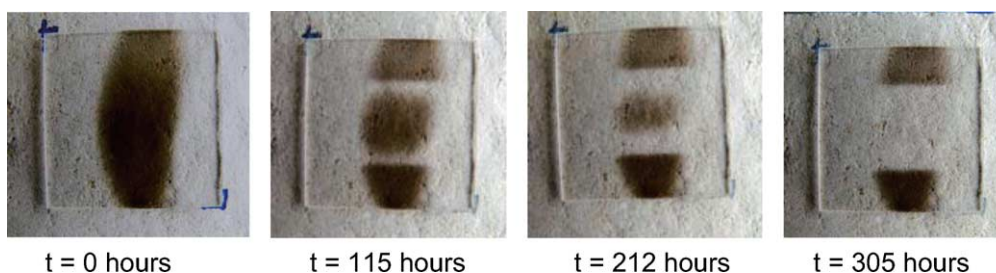
| t = 0 hours | t = 115 hours | t = 212 hours | t = 305 hours |

Fig. 3. Sequence of photographic images taken for the 25 mm × 25 mm square quartz slide initially covered with soot (see Fig. 2) and used in the demonstration of the remote destruction of soot via reaction (2) as a function of far UV irradiation time. Note. Only the soot directly held over the thick titania film, 175 μm away, is removed.

the 'negative' image of the titania film slowly appears on the soot-covered *remote* quartz slide. These results provide clear visible evidence of the *remote* destruction of soot via reaction (2) and for the air-borne diffusion of a photogenerated, desorbed highly oxidising species that may, or may not, be hydroxyl radicals. Further work shows that the same sequence of images can be obtained in approximately half the time when the air gap is reduced by a factor of 2, i.e. the smaller the air gap between the 'titania-on-glass' and the 'soot-on-quartz' films the shorter the time taken for the soot to be removed. The above results are a marked advance compared to those reported by others as they provide clear, unambiguous, *visual* evidence of all three processes associated with reactions (1) and (2), namely: the *direct*, *lateral* and *remote* destruction of a carbon-containing pollutant, in this case soot, via semiconductor photocatalysis. Although the overall timescale for all these processes (especially *remote* destruction) are quite substantial (i.e. up to 305 h), that it is possible to achieve this cleaning process within this timescale can be attributed to the marked photoactivity of the thick porous titania films employed in this work. Given the strikingly different timescales of the three processes (i.e. in terms of process kinetics *direct* ≫ *lateral* > *remote*), it is not surprising to note that with any photocatalyst coating,

the *direct* destruction of an organic pollutant is expected to dominate over that of its *lateral* and *remote* destruction. However, the results of this work show that the latter two processes should not be ignored and would contribute to the overall mineralisation action exhibited by semiconductor photocatalyst films.

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