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Ring Photocatalysis: Bands of Activation Surrounding Macro-sized (≥ 1 mm radius) Pt Islands Deposited on TiO₂ Films

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ABSTRACT

Clearly discernible rings of high photocatalytic activity, i.e. rings of activation, RoAs, are formed around Pt macro-sized (radius: $r_o \geq 1$ mm radius) Pt islands, i.e. Pt ‘dots’, deposited on TiO₂ films, which have been covered with a visible pollutant, such as soot, or a dye, such as acid orange 7, AO7. The features of the RoA region appear very similar for soot or dye-covered films. Thus, the radius of the RoA region, r_a , appears to depend weakly, if at all, on r_o , and is typically 0.60-0.68 mm $> r_o$. The rate of photocatalytic removal of the surface pollutant inside the RoA is uniform and significantly greater, i.e. ca. 3.2 - 5 x's, than that *outside* the RoA region. RoA region formation is observed for: (i) Pt dots which have been photodeposited or created through thermal reduction, (ii) Pt dots on sol-gel and commercial (paints and tiles) TiO₂ films and (iii) Pd dots, but less clearly for Au dots. A simple mechanistic rationale for RoA region formation is presented and the potential importance of this feature, with regard to improving the performance of commercial photocatalytic films, is discussed briefly.

1. INTRODUCTION

Much of the work on semiconductor photocatalysis has been on TiO_2 , because of its inert chemical and biological nature, low cost and high photocatalytic activity for a wide range of applications. Given the latter features, it is not too surprising that TiO_2 (usually in its anatase phase) is the semiconductor photocatalyst that is employed in all the well-established commercial photocatalytic products, such as self-cleaning glass¹, tiles² and paint³. A key feature of most commercial photocatalytic products is their ability to photocatalyse the mineralisation of organic pollutants by oxygen⁴, i.e.

where, mineral acids are generated if there are one or more heteroatoms in the organic pollutant, e.g. Cl in 4-chlorophenol. The photocatalysed mineralisation of organic pollutants by TiO_2 is a very well-studied reaction and many have tried – with varying degrees of success⁵⁻⁶ – to improve the performance of TiO_2 as a photocatalyst, often through the deposition of a co-catalyst. Not surprisingly, it is found that the value of the rate enhancement factor for reaction (1), i.e. ξ , where,

$$\xi = \text{rate of reaction (1) with co-catalyst deposit} / \text{rate without} \quad (2)$$

varies enormously, with reported values from $\xi = 0.1$ to 8.0, depending on the nature of the pollutant, TiO_2 (e.g. phase, morphology (if a film) and particle size (if film or powder dispersion)) and co-catalyst (e.g. nature, loading, particle size, method of deposition)⁶.

The most studied co-catalyst is Pt, usually photodeposited from chloroplatinic acid, i.e.

Any enhancement in photocatalytic activity observed using a Pt co-catalyst with a TiO₂ photocatalyst is usually ascribed to the Pt acting (i) as a sink for the conduction band electrons, photogenerated in the TiO₂, and (ii) as a catalyst of the reduction reaction between these conduction band electrons and O₂ to form water in reaction (1). However, the commonly assumed 'sink' process noted above appears at odds with the fact that the Pt work function (5.2 eV)⁷ and TiO₂ electron affinity (4.0 eV)⁸ are such that the theory of metal/semiconductor junctions predicts that a Schottky, i.e. rectifying, junction, should be formed between the TiO₂ and the Pt, so that the Pt would act as a sink for the photogenerated holes! Fortunately, the work of Bard *et al.*⁹ and others¹⁰ has shown that the type of junction formed at a TiO₂-metal junction depends markedly on how the metal is deposited and treated subsequently. For example, Bard *et al.*⁹ showed that Pt sputtered onto rutile TiO₂ yields an ohmic junction if the sample is annealed, due to inter-diffusion between the Pt and rutile layers. Similarly, the work of Gerischer *et al.*¹⁰, suggests that the work function of Pt can be lowered sufficiently so that an accumulation layer between Pt and TiO₂ is produced, if the metal is saturated with H₂. Thus, it now appears generally accepted that in most cases of photocatalysis involving a Pt/TiO₂ photocatalyst, in film or powder form, an accumulation layer is formed at the metal-semiconductor junction, *i.e.* not a Schottky junction, and, as consequence, the Pt acts as a sink for any conduction band electrons generated nearby. A recent review by Zhang and Yates¹¹ provides an excellent overview of band-bending in semiconductors in general, in which these features are discussed.

It follows from the above discussion that small islands of Pt (typically 1-5 nm in diameter) deposited onto TiO₂ powder particles (typically 20-30 nm diameter) are likely to impose an electric

field in the neighbouring TiO₂ that will help separate any electron-hole pairs photogenerated therein, resulting in a greater photocatalytic efficiency⁹⁻¹⁰. Some support for this concept is provided by model studies on the Schottky barrier formed between a small circular metal disc (30-1000 nm) and an underlying semiconductor film, which predict that the depletion layer formed, in the surrounding semiconductor film, is dependent upon the size of the metal disc and, for small discs, is significantly (ca. x 5) bigger than the size of the disc¹¹⁻¹². Thus, around each metal nano-disc or island, there will be a 'ring of activation', i.e. RoA, of significant size associated with the electric field, which helps effect the separation of photogenerated electron-hole pairs.

If it is assumed that this RoA feature is also exhibited by the accumulation layer formed between a nano-sized photodeposited Pt island and the TiO₂ that surrounds it, then it follows that the associated electric field would enhance the overall rate of photocatalysis by channelling the conduction band electrons generated in the surrounding TiO₂ to the Pt island. Thus, in the photocatalysed reaction between an electron acceptor, A, and an electron donor, D, by such a system, the Pt island would, (i) effectively 'hoover' up the conduction band electrons, photogenerated on the surrounding TiO₂ surface, and (ii) catalyse their reaction with the electron acceptor, A, such as O₂, leaving the photogenerated holes to oxidise the electron donor, D, such as an organic pollutant, adsorbed on the surrounding TiO₂. It seems reasonable to assume that the combination of factors (i) and (ii) are responsible for the values of $\delta > 1$, which have been reported for Pt/TiO₂ powders⁶.

A schematic illustration of this simple model of Pt-enhanced photocatalysis is illustrated in Figure 1 and is similar to that proposed by Gerischer *et al.*¹⁰ for Pt-island coated TiO₂ particles used for water reduction.

Figure 1: Schematic illustration of the features of a Pt 'island', or 'dot' (hatched hemisphere, radius, r_o) on a TiO_2 photocatalytic film, under UV irradiation creates electron-hole pairs in the surrounding TiO_2 , the photogenerated conduction band electrons of which are drawn to the Pt island due to the surrounding electric field associated with the accumulation layer that forms between it and the TiO_2 . The Pt island catalyses the reduction of the electron acceptor, A, such as O_2 , by the channelled conduction band electrons, whilst the photogenerated holes, that remain in the surrounding TiO_2 film, oxidise the electron donor, D, such as an organic pollutant.

This model is also consistent with the 'extended area' kinetic model¹³⁻¹⁵ used recently to provide a rationale for the observed variation in rate of H_2 production, due to the dehydrogenation of MeOH by Pt island coated TiO_2 powder particles, as a function of co-catalyst loading. In the latter work, the radius of the ring of activation, RoA, that encircles the Pt islands appears 12-15 times that of the Pt islands themselves (radius, r_o , = 0.5 nm)¹⁵.

The model studies noted above¹¹⁻¹² suggest that band bending can create large (up to 12-15 x's r_o) rings of high photocatalytic activity around Pt nanoparticles deposited on TiO₂, but for large Pt particles, with $r_o \gg 1 \mu\text{m}$, this electric field based effect will be negligible¹¹⁻¹². In a recent study carried out by this group¹⁶, using a thin layer of soot as the pollutant, and a 1 mm wide photodeposited Pt 'wire' on a TiO₂ film, it was noted that *whilst* the whole film was able to sensitise the slow photomineralisation of the soot film, *via* the following reaction:

the ca. 1 mm wide area of TiO₂, surrounding the Pt wire, was much more active than the TiO₂ photocatalyst film laying outside this area. This suggests that something similar to the 'extended area' model, which appears to apply to nano-particulate islands of Pt deposited onto TiO₂¹³⁻¹⁵, may also apply to very much larger ($r_o = 1 \text{ mm!}$) Pt dots, i.e. macro Pt islands. This paper describes the results of a series of experiments designed to explore the features of this phenomenon of a significant ring of (photocatalytic) activation, RoA, surrounding any Pt dot ($r_o \geq 1 \text{ mm}$) deposited on a TiO₂ film, including commercial photocatalytic films; for brevity we shall refer to this phenomenon as 'ring photocatalysis'.

2. MATERIALS AND METHODS

2.1. Materials declaration. Unless otherwise stated all chemicals were purchased from Aldrich Chemicals and used as received. All gases were purchased from BOC and certified to be of 99.999% purity. Commercial tiles (Hydrotech) and StoColor Photosan paint were purchased from Hydrotech, Deutsche Steinzeug AG and Sto Ltd. UK respectively.

2.2. TiO₂ (sol-gel) film preparation. The thick ($2.75 \pm 0.05 \mu\text{m}$) mesoporous anatase films most often used in this work were prepared *via* a sol-gel, hydrothermal process, described in detail elsewhere¹⁷. Briefly, 4.65 g of acetic acid were added to 20 ml of titanium isopropoxide under an inert nitrogen atmosphere, followed by 120 ml of 0.1 mol L⁻¹ nitric acid and, after mixing, the reaction solution was heated rapidly to 80 °C, whereupon it turned milky white and opaque. The reaction solution was maintained at 80 °C for 8 h and then allowed to cool to room temperature and any remaining aggregate particles removed using a 0.45 μm syringe filter. A measured amount, 80 ml, of the resulting colloidal solution were then placed in a Teflon pot, with lid, in an autoclave (Parr Instruments, UK) and heated to, and maintained at, 220 °C for 12 h. Upon removal of the solution from the autoclave, the separated out colloidal particles were redispersed using ultrasound. The reaction solution was then concentrated to about 12 wt.% using a rotary evaporator, and 50 wt.% Carbowax 20 M added to help prevent the formation of small surface cracks when the paste is cast and allowed to dry. The final product was a white, mayonnaise-like, TiO₂ paste which is stable for many months when kept in the fridge.

A typical TiO₂ (sol-gel) film was prepared from the TiO₂ paste as follows: a borosilicate microscope slide was fixed on a clean glass surface with a single layer of Scotch Magic Tape™ (thickness 60 μm) placed either side of the slide. Some, 0.5 mL, of TiO₂ sol-gel were then

deposited onto the top of the microscope slide and drawn down using a glass rod, thereby creating a 60 μm wet sol-gel film, which was allowed to dry in air for 20 min, before being calcined at 450 $^{\circ}\text{C}$ for 30 min. The product was a colourless, transparent film of anatase TiO_2 , ca. 2.8 μm thick, as determined using scanning electron microscopy, SEM. Further SEM analysis revealed the film to be mesoporous (ca. porosity ca. 59%) and comprising ca. 15 nm, radius, TiO_2 particles¹⁸. Figure 2(a) illustrates a typical SEM of the TiO_2 film which highlights its nanoparticulate, mesoporous nature.

Figure 2: SEM images of (a) A typical sol gel film showing an average particle size of 15 nm radius as well as the mesoporous structure. (b) A typical photodeposited (macro, i.e. $r = 1$ mm) Pt dot reveal it to have a cracked surface and comprising Pt particles ca. 4 nm radius. (c) A side-on image of soot layered onto a TiO_2 sol-gel film showing the film thickness, ca. 2.8 μm and soot thickness, ca. 1.2 μm .

2.3. Pt deposition. A Pt ink for photocatalysed deposition was prepared by adding 2 g of glycerol to 20 g of the 7.5 wt.% PVA solution, followed by 0.1 g of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$). The orange-coloured solution was then stirred in the dark for 1 h and stored in a fridge until required. The ink was deposited onto the surface of the sol-gel film using the tip of a fine paintbrush (i.e. 2/0 round Golden Taklon brush, 5 x 1 mm tip size, Daler Rowney), and was used to produce an ink dot ca. 1 mm radius, although the size of the deposited ink droplet could be

increased systematically by repeating the deposition procedure. Once deposited the dried ink dot was then irradiated for 20 minutes (UVA irradiance of 3.4 mW cm^{-2} , 352 nm) using two 8 W 352 nm black light blue lamps and then thoroughly rinsed with water to remove any unreacted H_2PtCl_6 . ICP analysis of a typical photodeposited Pt dot, radius, $r_o = 1 \text{ mm}$, and supporting TiO_2 layer, revealed the mass of the Pt dot was $6.22 \text{ }\mu\text{g}$ sitting on $63 \text{ }\mu\text{g}$ of TiO_2 , i.e. a loading of ca. 9.9 wt.%. SEM images of a typical photodeposited Pt dot, illustrated in Figure 2(b), reveal it to have a cracked surface and comprising Pt particles with an average radius of ca. 4 nm; the Pt dot itself was ca. 92 nm thick. Side-on photographic images taken of the drop deposition process, and a subsequent plot of the contact droplet radius as a function of time, are illustrated in section S1 in the Electronic Supplementary Information (ESI) section. These results show that, once the ink droplet comes into full contact with the sol-gel surface, the diameter of the ink deposit is constant (neither increasing nor decreasing), see Figure S1(a), and does not change even during irradiation, i.e. the photodeposition process, as illustrated by the images in Figure S1(b). Thus, the deposited Pt ink droplet's diameter never exceeds that of the original droplet, so that no Pt is deposited outside the original perimeter of the photodeposited Pt dot. This feature was also confirmed by Pt mapping of the surface of the TiO_2 film, carried out using the Energy Dispersive Spectroscopy feature of the SEM, the results of which are illustrated in Figure S1(c), along with a top-down photograph of the Pt dot, and reveal no evidence of any spill-over or nanoparticulate Pt island formation near the Pt dot.

2.4. Soot deposition. In much of this work, a thin layer of soot was deposited onto the surface of the Pt dot (typically $r_o = 1 \text{ mm}$)/ TiO_2 sol-gel film using the flame of a T-Light paraffin wax candle placed 5 cm from the sample. To create a soot film of sufficient thickness, i.e. ca. $1.2 \text{ }\mu\text{m}$, the sample was passed over the flame 10 times. An SEM image of the soot covered film is illustrated

in Figure 2(c) and reveals the soot layer to be highly porous and comprised of thin wispy filaments ca. 1.0-1.2 μm in length.

2.5. AO7/MB deposition. A thin film of dye, such as acid orange 7 (AO7) or methylene blue (MB), was deposited onto the Pt dot/TiO₂ sol-gel film, using the ion-pair adsorption method for deposition of anionic, or cationic, dyes onto TiO₂ sol-gel films described in detail elsewhere¹⁹. Thus, briefly, in the deposition the anionic dye, AO7, the Pt dot/TiO₂ sol-gel film was placed in a 100 mL of a 0.17 mM AO7 aqueous acidic solution (HCl, pH 3) and stirred for 10 minutes. The dye-containing solution was then removed to reveal an orange-stained film, which was then left to dry in air before use. Similarly, in the deposition the cationic dye, Methylene Blue (MB), the Pt dot/TiO₂ sol-gel film was placed in 100 mL of a 0.16 mM MB aqueous basic solution (NaOH, pH 11) and stirred for 10 minutes. The dye-containing solution was then removed to reveal a blue-stained film, which was then left to dry in air before use. In both cases dye staining is due to ion-pair formation between the anionic (or cationic) dye and the oppositely charged surface of the TiO₂ film; the latter feature is effected through the choice of pH of the staining solution, given the point of zero charge of TiO₂ is ca. 6.5²⁰.

2.6. Irradiations, digital photography and RGB. Unless stated otherwise, all irradiations of the Pt dot/TiO₂ sol-gel films were carried out using two 8 W 352 nm blacklight blue (BLB) lamps, which provided a UVA irradiance of *ca.* 2 mW cm⁻². In contrast, all irradiations of the commercial photocatalytic samples, i.e. self-cleaning paint and tiles, were carried out using a 254 nm germicidal lamp with an irradiance = 7 mW cm⁻², in order to speed up the process. All irradiances values reported here were determined using a calibrated spectroradiometer (Gooch & Housego, OL 756).

All digital photographs were taken using a digital camera (700D, Canon) fitted with a macro lens (24-70 mm macro0.38m/1.3ft, Canon) and illuminated by a HiraLite 14 W full spectrum Daylightlamp (colour temperature (CT): 5000 K). Before each photographic session the Custom White Balance (CWB) feature of the camera was activated on the camera using a white card, so that the camera locked onto the colour temperature of the white light lamp from the light reflected from the card. In the calculation of greyscale values (see S2 in ESI) , the red (R), green (G) and blue (B), values were extracted from the digital images ImageJ software (ImageJ, NIH)²¹.

2.7. Film characterisation. Electron microscopy was carried out using Field Emission Scanning Electron Microscopy, FESEM, (SU5000, Hitachi) and prior to this SEM analysis, all samples were sputter coated in a thin layer of Au nanoparticles ca. 10 nm using a sputter coater (Q150R S, Quora). Elemental analysis and mapping was carried out using Energy Dispersive Spectroscopy, EDS, (Ex-Act, Oxford) as an attachment to the SEM (Environmental SEM, FEI Quanta FEG). Metal loadings were determined using Inductively Coupled Plasma-Optical Emission Spectroscopy, ICP-OES, (5110, Agilent).

3. RESULTS AND DISCUSSION

3.1 Rings of activation (RoAs). In this work, the typical Pt 'dot' on any of the TiO₂ films tested, i.e. sol-gel and commercial tiles and paint, was produced by the photocatalytic deposition method, outlined in section 2.3 and summarised by reaction (3), and had a radius, r_o , of ca. 1 mm. Figure 3 illustrates photographs of a typical Pt 'dot' on a TiO₂ sol-gel film, covered in either a layer of soot, or stained with the dye, AO7, before and after UV irradiation.

Figure 3: Photographs of a typical Pt dot on a TiO₂ sol gel film, coated with either soot (top images) or AO7 (bottom images), before (left hand side images) and after (right hand side images) UV irradiation (352 nm BLB lamp radiation, 2 mW cm⁻², irradiation times: 48 and 4 h for soot and AO7, respectively). The solid white bar in the photos indicates a scale of 1 mm.

Note, similar images as those for AO7 were found for Pt dot on a TiO₂ sol gel film stained with the dye, MB. A brief inspection of the images in Figure 3 reveals that a white, i.e. apparently soot, or AO7, free, ring-shaped region of TiO₂ around the Pt dot is produced with UV irradiation, i.e. a RoA, with a radius, r_a . The lack of colour in this region indicates a much faster rate of photocatalytic oxidation of the soot, *via* reaction (3), or AO7, *via* reaction (1), than that effected in the area of TiO₂ outside the RoA. Colour analysis of these images, *vide infra*, indicates the enhancement in rate within the RoA region, compared with outside, is by a factor of ca. 3.2 for soot and 5 for AO7. Outside the RoA, the level of surface 'pollutant', be it soot or AO7, is also

reduced with increasing irradiation time, as revealed by a gradual bleaching in colour, but at a much lower rate than that inside the RoA. This latter observation is consistent with the results of previous work carried out by this group and others^{19, 22-27}, which has established that a TiO₂ sol gel film, such as used here, is able to effect the photocatalytic oxidative mineralisation of soot and AO7, without a Pt co-catalyst. Whether inside or outside the RoA, the rate of photocatalytic oxidation, and therefore bleaching, of soot is much slower than that of AO7, by a factor of ca. 10. This striking difference in bleaching rate is probably due to the more refractory nature of soot compared to that of AO7²²⁻²⁴.

EDS analysis combined with SEM of the soot covered Pt dot/TiO₂ film showed that after UV irradiation there was no carbon in the RoA, whereas, in contrast, the level of carbon *on* the Pt dot itself remained unchanged, see Figure S1(d) in the ESI. This observation is interesting as it not only shows that, with UV irradiation, the surface of the RoA is scoured of soot more rapidly than outside the RoA, as indicated by the photos in Figure 3 and EDS, but that the soot layer on top of the Pt dot itself is not oxidised, which is consistent with the schematic illustration in Figure 1, with A = O₂ and D = soot. It would appear that the wispy (non-compact) nature of the soot allows ambient O₂ to readily diffuse to the surface of the Pt dot to be reduced by the channelled photogenerated conduction band electrons from the irradiated band of TiO₂ that surrounds the Pt dot. In the absence of O₂ no soot is photo-oxidised. Other work, carried out using the same Pt macro dot on TiO₂ film, but this time immersed in a 1 M methanol (MeOH) aqueous solution showed that upon UV irradiation, bubbles of H₂ were generated at the Pt macro dot, which helps support the suggestion that the Pt is the reduction site (A = H₂O and D = MeOH). In the absence of Pt no H₂ was generated.

When considering the schematic, illustrated in Figure 1, which ostensibly is for nano-particulate Pt islands on TiO₂ powder particles, it is clear that the RoA regions so clearly formed by the macro ($r_0 \geq 1$ mm) Pt dot/TiO₂ film systems cannot be due the combination of an electric field and catalysis, as is usually proposed for nano-particulate Pt islands on TiO₂ powders and operates on the nanometer scale, typically 100 nm¹¹⁻¹². Instead, RoA formation on Pt dot/TiO₂ films is more likely to be due to the rapid reduction of O₂ at the Pt dot, by the conduction band electrons photogenerated in the RoA, thereby creating a concentration gradient in photogenerated conduction band electrons in the surrounding TiO₂, which effectively draws them to the Pt dot, leaving the remaining photogenerated holes to slowly oxidise the pollutant. As a consequence, the schematic for such a mechanism on Pt dot/TiO₂ film systems would be similar in appearance to that illustrated in Figure 1, except the scale would be mm, not nm.

At first, it may appear unlikely that that the efficient diffusion of photogenerated conduction band electrons over long (≥ 1 mm) distances through a film of TiO₂, as illustrated in Figures 1 and 3, can occur, especially as work on DSSC electrodes suggest that the electron diffusion length in TiO₂ sol gel films, similar to those used here, is only ca. 10 μm ²⁸. However, others have reported diffusion lengths in water of 400 μm ²⁹, due to effective hole scavenging and so increased electron lifetime. In addition, electron diffusion length may be much greater when the photocatalytic process is carried out in the gas phase, as in this work. In addition, recent work on pressed powder disc wafers of TiO₂ (ca. 350 μm thick), with a surface covering WO₃ (82 μm) in an anaerobic methanolic solution, showed that electron transport over such long distances (≥ 1 mm) can be readily achieved³⁰. In this latter work, the TiO₂/WO₃ pressed powder wafer was exposed to UVA radiation from the TiO₂ side only through a shaped template, the image of which then appeared within minutes on the WO₃ ‘dark’ side, due to its reduction by the photogenerated conduction band

electrons on the TiO₂ side³⁰. Other work by us shows that this same experiment works when the pressed disc TiO₂ film is ca. 1 mm thick, which suggests that the transfer of photogenerated conduction band electrons can occur over long (in this case, ca. 1 mm) distances, if there is an appropriate ‘sink’ to create the necessary concentration gradient. Finally, it should be noted that the surface radicals photogenerated on the surface of TiO₂, such as hydroxyl radicals, can only diffuse upto ca. 20 microns³¹.

3.2 Features of the RoA for soot-covered Pt dot/TiO₂ (sol-gel) films. Key features of the RoA region were probed further for both soot and AO7 covered TiO₂ films and in all cases found to be very similar. As a result, for brevity, only the results for the soot-covered films are described in detail below.

If the RoA was simply an edge effect associated with the Pt dot, which is a common feature of thermal catalysis³², it might be expected that the white (i.e. fully bleached) RoA region would grow from the edge of the Pt dot and increase in radius, r_a , with increasing irradiation time. However, this doesn't appear to be the case, as illustrated by the irradiation time sequenced photographs illustrated in Figure 4 and their subsequent analysis. Thus, from each of these photographs, it is possible to discern a RoA region during the UV irradiation of the soot-covered Pt dot/TiO₂ film and plot its value of r_a as a function of irradiation time, as illustrated in Figure 4. The shape of this plot suggests that the RoA has a fixed value of r_a which does not increase with increasing irradiation time, but rather the RoA simply becomes more discernible with irradiation time. This latter feature can be quantified through the use of an average grey scale, based on RGB analysis of the whole RoA region, which varies from 1 (a measure of the original greyness due to soot) to 0 (the grey scale value associated with the white of a soot-free TiO₂ film). Further details

concerning the calculation of the average grey scale values reported here are given in section S2 in the ESI.

An illustration of the typical variation of the average grey scale value as a function of irradiation time is illustrated in the plot in Figure 4 and reveals the photocatalytic removal of soot to be a very gradual process, with a time for the grey scale to reach 0.5, i.e. $t_{1/2} = 30$ h inside the RoA and 96 h outside. A more detailed analysis of the variation of $t_{1/2}$ at all points inside the RoA region revealed it to be constant, i.e. 30 h and the same at all values of r from: r_o to r_a . These observations suggest that the rate of oxidation of the soot (and AO7 for that matter) in the RoA region is uniform throughout that RoA region and is not faster at or near the edge of the Pt dot. The latter kinetic feature is consistent with a kinetic model in which the rate of hole oxidation of the soot is the rate-determining step, with the steady state concentration of photogenerated holes inside the RoA region being simply much greater than that outside, due to the rapid hoovering up of the photogenerated electrons by the Pt (macro) dot, thereby reducing significantly (by a factor of 3-5) the rate of electron-hole recombination in the RoA region, compared with outside the region.

Figure 4: Photographs of a typical Pt dot ($r_o = 1$ mm) recorded as a function of UV irradiation time (2 mW cm^{-2}) and the plots they generate of the values of ring of activation radius, r_a , and greyscale, as a function of irradiation time. The solid white bar in the photo indicates a scale of 2 mm.

Another key feature of the RoA region is the dependence of its radius, r_a , on that of the Pt dot, r_o . Thus, a series of Pt dots of different radius, r_o , were deposited on the same photocatalytic TiO_2 sol-gel film, which was then covered with a thin layer of soot and irradiated with UVA light for 72 h. The film was photographed before and after irradiation and the results are illustrated in Figure 5. Values of r_a and r_o were then extracted from these photographs and used to generate the plot r_a vs. r_o , illustrated in Figure 5(a), from which it appears that r_a is directly proportional to r_o . The data suggests the following general relationship between r_a and r_o for the (dot)/ TiO_2 sol-gel film initially covered with a thin film of soot:

$$r_a = (1 + \alpha) r_o + \beta \quad (5)$$

where, $\alpha = 0.48$ and $\beta = 0.22$ mm. Interestingly, the same experiment conducted on an AO7-covered Pt-dot/TiO₂ film, the results of which are illustrated in Figure 5(b), revealed values for α and β of 0 and 0.68 mm, respectively. These different values for α and β suggest that the relationship between r_a and r_o is pollutant dependent.

The intercept values, β , are particularly interesting in that it suggests that even for nanometer or micrometer sized Pt islands the associated RoA region will be very large, although, it seems unlikely it would be as big as 0.22-0.68 mm as suggested by the values of β for soot and AO7, respectively! Other simple relationships between r_a and r_o were also tested, such as r_a^2 vs. r_o^2 and $(r_a^2 - r_o^2)$ vs. r_o^2 , but all yielded a less good fit to the data than that provided by eqn (5).

The above results indicate that a finely dispersed layer of photodeposited Pt dots, or another similar co-catalyst, onto a photocatalytic film could enhance significantly the ability of the latter to destroy pollutants on its surface photocatalytically. Thus, if a macro dot of Pt was replaced by the same mass of micro, or nano, sized particles of Pt on the surface of the TiO₂, the rate of photocatalysis would be enhanced to the increase in RoA area and light absorption by the underlying TiO₂. To our knowledge no commercial photocatalytic film (such as tiles, paint concrete and glass) use a co-catalyst coating to enhance the activity of the underlying photocatalyst film, most likely for the very reasonable reason of cost and yet it would appear to merit further investigation.

Figure 5: Photographs of a TiO₂ sol-gel photocatalytic film with photodeposited Pt dots of different radius, r_o , before and after irradiation with UVA light and a plot of the radius of the ring of activation, r_a , as a function of r_o , where both values are taken from the photographs after UV irradiation. The illustrated results are for: (a) a soot covered film before and after 72 h irradiation and (b) a AO7 stained film before and after 4 h irradiation. The solid white bar in the photos indicates a scale of 5 mm.

Interestingly, RGB analysis of the RoA region associated with each of the Pt dots, derived from the photograph after UV irradiation illustrated in Figure 5(a), reveals the same average grey scale value after the same period of irradiation (72 h) regardless of Pt dot size, which suggests that the average rate of soot removal, *via* reaction (4), is independent of the size of the Pt dot, i.e. independent of r_o . This same feature was observed using AO7 as the test pollutant. The above observations lends support to the suggestion that ring photocatalysis is not an edge effect, where

the rate would be expected to depend directly upon r_o , but one in which the rate of soot (or AO7) oxidation on Pt dot/TiO₂ films is largely independent of r_o , as noted earlier.

3.3. A different Pt deposition method and depositing other platinum group metals. In order to ensure the RoA feature of Pt-dot/TiO₂ films is not specific to Pt-dots prepared by the photodeposition method, an alternative Pt-dot deposition method, the incipient wetness method was used, as the latter method is often employed in the preparation of thermal- as well as photo-catalysts³³⁻³⁴. Briefly this involved the deposition of an ink, which contains a Pt salt, and its subsequent thermal reduction under H₂ at ca. 200°C. A commercial Pt ink from Dyesol, comprising H₂PtCl₆ dissolved in terpineol, was used for this work and a more detailed description of the deposition procedure is given in Section S3 of the ESI. As with previous studies, the product, a Pt dot, $r_o = 1$ mm, on a TiO₂ sol-gel film, was covered with a thin layer of soot and subjected to UVA radiation (48 h, 352 nm, 2 mW cm⁻²). Photographs of the soot-covered Pt-dot/TiO₂ film, before and after irradiation, are illustrated in Figure 6(a) and clearly show the formation of a RoA region, although the latter doesn't appear as wide ($r_a - r_o = 0.25$ mm) as that formed using a photo-deposited Pt-dot ($r_a - r_o = 0.70$ mm), which suggests that this width depends upon the method of deposition.

Figure 6: Photographs taken before and after UVA irradiation (352 nm ; 2 mW cm^{-2}), illustrating: (a) a soot-covered Pt dot ($r_o = 1\text{ mm}$)/ TiO_2 sol-gel film, where the Pt has been deposited by the incipient wetness method before and after 48 h of UVA irradiation, and (b) Pt, Pd and Au photodeposited dots ($r_o = 1\text{ mm}$) on the same soot-covered TiO_2 sol-gel film before and after 5 h of UVC irradiation. The solid white bar in the photos indicates a scale of 1 mm.

In another study, dots ($r_o = 1\text{ mm}$) of the platinum group metals PGM's) : Pd and Au, in addition to Pt, were photodeposited onto the same TiO_2 sol-gel film, then covered with a thin layer of soot and irradiated with UVA radiation. The results of this work are illustrated by the photographs in Figure 6(b) and show that while both Pt and Pd dots appear able to generate well-defined rings of activation, the Au dot does not. The striking difference in RoA region formation between Pt or Pd and Au does not appear to be associated with any striking difference in work function, as the values for three PGM's are very similar (i.e. Pt: 5.12-5.93, Pd: 5.22-5.60 and Au: 5.10-5.47³⁵). Instead, it appears more likely that this difference between Pt or Pd and Au, in terms of RoA region formation, is due to the difference in catalytic activities for O_2 reduction by the photogenerated conduction band electrons. It is well known from studies of O_2 reduction, in fuel-cell cathodes for example, that Pt and Pd exhibit a much greater activity than Au, and this feature is ascribed to the similar, and apparently optimal, binding energies for O_2 exhibited by Pt and Pd (i.e. 1.57 and 1.53

eV, respectively) which are much lower than that (2.75 eV) exhibited by Au³⁶. As a consequence, the Pt and Pd dots would be expected to be much better ‘sinks’ for the photogenerated conduction band electrons than the Au dot, which appears to be borne out by the results illustrated in Figure 6(b).

3.4. RoAs and commercial photocatalytic films. Pt dots ($r_o = 1$ mm) were also photodeposited onto a commercial photocatalytic tile (Hydrotect, Deutsche Steinzeug) and paint (Climasan Colour, STO) film, using the same method as described in the experimental, but with UVC radiation (254 nm, germicidal lamp). UVC radiation was here needed when using these TiO₂-based commercial films for photocatalysis as they have much lower photocatalytic activities than the TiO₂ sol-gel film usually used in this work and UVC radiation overlaps much more strongly with the absorption spectrum of TiO₂³⁷ than UVA and so is able to drive the photocatalytic process at a much greater rate than if UVA was used as the irradiation source. The low activity of photocatalytic tiles is usually due to the high (> 1000 °C) annealing temperature used in their production which reduces the photocatalyst particle size significantly and converts the TiO₂ from its highly active anatase phase to its less active rutile form³⁸. The initial low activity of the photocatalytic paint is due to the fact that the TiO₂ particles are largely embedded in the resin of the paint and so rendered passive; thus such paints often show marked improvement in activity with prolonged irradiation, since the latter results in the destruction of the surface resin, thereby roughing the surface and exposing much more of TiO₂ to the ambient atmosphere³⁹.

Note that, unlike many other substances, soot is largely inert to UVC irradiation, and, therefore, the observed photo-induced bleaching is only due to its photocatalysed oxidation *via* reaction (4). As in previous work, using TiO₂ sol-gel films, both Pt-dot/commercial TiO₂ films were covered with a thin layer of soot and irradiated with UVC radiation (7 mW cm⁻²; 254 nm). The results of

this work are illustrated by the photographs in Figure 7 and reveal both commercial products form a ring of activation around the Pt dot.

Figure 7: Photographs of a soot-covered Pt dot ($r_o = 1$ mm)/commercial TiO_2 film taken before and after UVC irradiation (254 nm; 7 mW cm^{-2}), where the commercial TiO_2 films were a photocatalytic: (a) tile (Hydrotect, Deutsche Steinzeug) and (b) paint (StoColour Photosan, STO). The solid white bar in the photos indicates a scale of 1 mm.

The results illustrated in Figure 7 are important in that they show that RoA formation is a common feature of Pt-dot/ TiO_2 films in general, since it is exhibited *both* by TiO_2 films often used in research, such as sol-gel films, and those found in commercial photocatalytic products, such as tiles and paint. In addition, these results, when extrapolated, suggest that the activities exhibited by many commercial photocatalyst films, such as tiles, paint and glass, will be enhanced significantly, most likely by a factor of 3-5, when a homogeneously dispersed nanoparticulate Pt-island co-catalyst film is present. Although it seems unlikely that such an enhancement in activity would merit the use of a Pt co-catalyst in such products, there may be a commercial case if a suitable, much less expensive substitute, such as Ni, can be shown to be as effective in generating rings of activation.

3.5. Ring photocatalysis and previous photocatalytic studies.

As noted earlier, many studies have been reported on the enhancement in the rate of photocatalysis of the oxidation of organic pollutants by O_2 , i.e. reaction (1); and that this work shows the rate enhancement factor, ξ , is a function of the nature of the pollutant, TiO_2 and co-catalyst. However, by fixing several of these features, such as type of TiO_2 , co-catalyst and method of deposition, it is possible to identify some relevant general features. Thus, Table 1 lists reported values of ξ , for reaction (1) for different organic pollutants, using typically a fixed wt% Pt loaded P25 TiO_2 photocatalyst. In most of the studies, wt% loading (usually 1 wt% of ca. 0.5 nm radius Pt particles) was optimal and so the values of ξ may be taken as maximum values, $\xi(\max)$.

Table 1: Reported examples of P25 photocatalysed oxidation of organic pollutants by O_2 ⁴⁰⁻⁴⁴

Pt wt% ^a	Pollutant	ξ	ref
Aqueous solution			
1	Trichloroethylene (TCE)	4.8	38
0.5	BTEX (benzene, toluene, ethylbenzene and xylene)	4.8	38
1	ethanol	4.2	39
1	methanol	2.4	39
1	dichloroacetic acid (DCA)	3	40
Gas phase			
0.2	ethanol	2.2	41
0.2	benzaldehyde	1.5	42
0.2	toluene	1.3	42

a: all Pt deposited photocatalytically

In this work, ring photocatalysis in macro Pt dots has been observed and some general features established, such as, within the band between r_o and r_a , the rate of photocatalysis is uniformly enhanced, e.g. by a factor of 3.2 (for soot) to 5 (for AO7), and that r_a is directly related to r_o . If similar features are also exhibited by micro and nano dots of Pt, it is possible to generate the

following equation relating the value of $\xi(\text{max})$ to the ratio of the rate inside the RoA to that outside, γ , and the ratio of r_a to r_o , δ , i.e.

$$\xi(\text{max}) = \{\gamma 90.69(\delta^2-1)/\delta^2 + 9.31\}/100 \quad (6)$$

In deriving the above expression it is assumed that: (i) $\xi(\text{max})$ is the rate enhancement factor observed when the whole surface of the TiO_2 is covered with hexagonally packed and non-overlapping RoAs, (ii) r_a and r_o are simply related to each other *via* the expression, $r_a = \delta r_o$, and (iii) the overall enhanced rate is proportional to the number of RoAs and the fractional area of the high activity band compared to that of the whole RoA, i.e. $(\delta^2-1)/\delta^2$. The values of 90.69 and 9.31 in eqn (6) are a feature of hexagonal packing, which for a completely packed surface will cover 90.69% of the available area, leaving 9.31% free.

If, as found for soot, it is assumed that $\gamma = 3.2$ and that $\delta = 1+\alpha = 1.42$, then using eqn (6) a value for $\xi(\text{max})$ of 1.56 can be calculated, which is not dissimilar to the values for $\xi(\text{max})$ listed in Table 1 for the gas phase photocatalytic oxidation of ethanol, benzaldehyde and toluene. In aqueous solution, if γ remained at 3.2 and the radius of the ring of activation, r_a , was now 5 times that of the Pt dot, r_o , i.e. $\delta = 5$, as suggested by model studies¹¹⁻¹², then the ring photocatalysis model predicted value of $\xi(\text{max}) = \text{ca. } 2.9$, which is also similar to those values reported in Table 1 for a variety of different pollutants. These results appear to suggest that the basic features of RoA and ring photocatalysis, gained here in a study of macro Pt dots, may also be relevant to Pt nanoparticles.

Another feature of most reported examples of Pt/ TiO_2 photocatalysis is the relatively low level of metal loading (typically, ca. 1 wt% for 0.5 nm radius Pt particles on P25 TiO_2 , as indicated in Table 1) above which the rate of photocatalysis usually falls markedly, and is usually negligible above 10 wt%. Often this fall is interpreted as being due to screening of the underlying TiO_2 from

the incident light ⁴⁵⁻⁴⁷, and yet, a simple calculation based on a homogeneously dispersed array of 1 wt % loading of Pt hemispheres, radius 0.5 nm, on P25 TiO₂ (specific surface area = 50 m² g⁻¹), show only 2.8 % of the surface would be screened by such Pt particles, and that even if the loading was 10 wt%, then 72% of the TiO₂ surface would still remain free from screening. Interestingly, a simple calculation based on a ring photocatalytic model and hexagonal packing of the RoAs, reveals that a 1.3 wt% loading of Pt dots with $r_o = 0.5$ nm, would completely cover the surface of the TiO₂, assuming $\delta = 5$. Thus, ring photocatalysis would appear to provide a rationale for why the maximum activity exhibited by Pt loaded P25 TiO₂ for reaction (1) is often found to occur at ca. 1 wt %, as indicated by the results in Table 1, since increasing the loading above 1.3 wt%, would result in increasing overlap between the RoA's and the likely promotion of electron-hole recombination and concomitant loss in activity, as is observed.

4. CONCLUSIONS

Rings of high photocatalytic activity appear to surround Pt macro-sized ($r_o \geq 1$ mm radius) Pt islands, i.e. Pt dots, deposited on TiO₂ films. These rings of activation, RoA, appear upon UVA illumination of a sol-gel TiO₂ film covered with a thin layer of a pollutant, such as soot, or an adsorbed dye, such as AO7. The radius of the RoA region, r_a , described by eqn (5), appears to depend upon the nature of the pollutant, the type of metal deposited and the method of metal deposition. The rate of photocatalytic removal of the surface pollutant inside the RoA is uniform and significantly greater than that outside the RoA (typically ca. 3-5 x's). The features of the RoA's formed on Pt (macro) dot/TiO₂ films appear consistent with a simple kinetic model in which the photogenerated electrons react rapidly with ambient O₂ at the Pt dot, thereby creating a concentration gradient between the surrounding TiO₂, and the Pt dot, leaving the remaining

photogenerated holes to oxidise slowly the pollutant. Pd (macro) dots appear to exhibit similar features to Pt, whereas Au appears less effective, probably due to the lower catalytic activity for O_2 reduction of the latter. Clearly more work is required to probe the characteristics of RoA region that is formed on Pt (macro) dot/ TiO_2 films, not least of which is to see if it is also effected using Earth-abundant co-catalysts, such as Ni, say, and can be used to markedly improve the photocatalytic activities of commercial photocatalytic films and so generate new, commercially viable, products. This work also raises the question whether the general features of ring photocatalysis and RoA region formation, illustrated in Figure 1, are generic and found for very active co-catalyst island deposits ranging in size from nm to mm; an initial probe into the literature suggests it is?

5. ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

The Supporting Information (SI) section contains details about the photodeposition of Pt ink onto the surface of the sol gel films and commercial materials. RGB and greyscale data calculations are also available. (PDF)

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Author Contributions

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