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Antimicrobial activity of titania/silver and titania/copper films prepared by CVD

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ABSTRACT

We have previously reported the production of photocatalytically active films of TiO_2/Ag and TiO_2/CuO grown by atmospheric pressure thermal CVD that had high antimicrobial activity. The present study compares the activity of dual layers and co-deposited TiO_2–CuO with single layers. We also compared the BS ISO 27447:2009 method with our previously reported method for determining photocatalytic antimicrobial activity and showed that although the activity was reduced in the BS method, probably due to the lower UV irradiation used, there was still a good antimicrobial activity. The results showed that Ag–TiO_2 surfaces retained photocatalytic self-cleaning activity measured by stearic acid oxidation whereas Cu–TiO_2, both layered and co-deposited had very low activity. However, both were antimicrobial against *Escherichia coli* with activity of the Cu–TiO_2 films greatly enhanced by irradiation possibly via a photo-Fenton type reaction. The activity of the Ag–TiO_2 films against *Pseudomonas aeruginosa* and MRSA (methicillin resistant *Staphylococcus aureus*) showed reduced killing activity with an environmental isolate of *P. aeruginosa* and the MRSA showing only 3 log and 1.5 log reductions respectively. The implications for their use for reduction of surface contamination by microorganisms as part of control measures for healthcare associated infections are discussed.

1. Introduction

One of the major applications for the photocatalytic properties of TiO_2 is disinfection and this has been used for the removal/killing of microorganisms in water, in air and on surfaces [1,2]. There are a number of techniques available for coating surfaces including sol–gel approaches, sputtering and chemical vapour deposition (CVD). CVD, particularly atmospheric pressure CVD, has advantages over many of these techniques in that it requires relatively inexpensive equipment, can be scaled up to industrial production scale and is capable of producing a hard, durable and highly active product [3]. A number of studies have shown increased activity, both in oxidising activity and in antimicrobial action, of TiO_2 combined with Ag or Cu by doping or by bulk inclusion [4–10]. Previous reports show the production of highly antimicrobial coatings consisting of dual layers of Ag and CuO combined with TiO_2 [11–13] rather than surface doping. These combined the photocatalytic activity of TiO_2 [14,15] with the antimicrobial activities of Ag [16,17] and Cu [18,19]. Structures in which the Ag and CuO were layered on top of the TiO_2 had highest biocidal activity (probably because of the increased availability of Ag and CuO from the surfaces). However, coatings where TiO_2 was layered on top were most durable and also retained a much higher antimicrobial activity than single layered TiO_2. We have shown that the coatings were capable of killing both Gram-positive and Gram-negative bacteria and viruses [13,20]. Although such coatings have an obvious potential role in infection control in the healthcare sector, the food industry and in e.g. aviation, in order to get them accepted it will be necessary to show activity against relevant pathogens and under conditions found in those industries. In this report we present an extended study of the antimicrobial activity of Ag and CuO layers produced on glass by flame assisted CVD (FACVD) and overlaid with TiO_2 using thermal CVD. The recently introduced BS method for evaluating antimicrobial activity was also used. The activity of the Ag–TiO_2 films against hospital related pathogens was greatly reduced when compared to standard strains used for antimicrobial activity testing. The relevance of the studies to applications in prevention of healthcare acquired infections is discussed.

2. Materials and methods

2.1. Microorganisms and growth conditions

Escherichia coli ATCC 10536 and *Pseudomonas aeruginosa* NCIMB 10421 were obtained from the National Collection of Industrial and

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Marine Bacteria, Aberdeen, UK. *P. aeruginosa* AOH1 was obtained from water downstream of a wastewater treatment works and was from our own collection. *Staphylococcus aureus* (MRSA) NCTC 12493 was obtained from the Health Protection Agency, Manchester, UK. Bacteria were sub-cultured onto Nutrient Agar (NA, Oxoid, Basingstoke, UK) and incubated at 37 °C for 24 h. Cultures were resuspended in Nutrient Broth (NB, Oxoid) and kept on Microban® beads (TCS Ltd., Merseyside, UK) at −70 °C. Prior to use, one bead was sub-cultured onto NA and incubated at 37 °C for 24 h. Broth cultures (100 cm^3 NB in 250 cm^3 Erlenmeyer flasks) were inoculated and incubated at 200 rpm and 37 °C for 16 h in a New Brunswick G24 orbital incubator (New Brunswick Scientific, St. Albans, UK).

2.2. Production of the coatings

The Ag and Cu/CuO films were grown on 1 mm borosilicate glass (Corning Eagle 1737) using an atmospheric pressure FACVD coater with a propane/oxygen flame ratio 1:19 as previously described [21]. The substrate temperature was set at 300 °C. An aqueous solution of 0.5 M $AgNO_3$ or 0.5 M $Cu(NO_3)_2$ was nebulised into a carrier of N_2 at a rate of 3 dm^3 min^{-1} through the flame and onto the substrate. The films were removed from reactor and allowed to cool before subsequent reheating to 500 °C for TiO_2 deposition. The thermal CVD films were deposited on a custom-built atmospheric pressure CVD reactor directly onto borosilicate glass. The precursor for the TiO_2 deposition was titanium tetra-isopropoxide (TTIP; 110 °C, 0.2 dm^3 min^{-1}) transported to the reactor via a bubbler.

The copper precursor copper hexafluoroacetylacetonate ($Cu(HFAc)_2$) used for the co-deposited films was delivered via a bubbler at 105 °C and 0.2 dm^3 min^{-1}. Nitrogen was used as the carrier gas and great care was taken to ensure proper purging for an oxygen-free atmosphere. The substrate temperature was 500 °C.

Where the two deposition technologies were combined, the FACVD layers were deposited first, followed by the thermal APCVD TiO_2 layer. In the case of the co-deposited films the two precursors (TTIP and $Cu(HFAc)_2$) were delivered simultaneously, thereby demonstrating a single-step route [21].

2.3. Determination of photocatalytic antimicrobial activity

Each experiment was performed in triplicate and mean, standard deviations and *T*-tests performed using Microsoft Excel. Survival curves were plotted as the mean and standard deviations as error bars. In some cases only the upper error bars were plotted and in several cases the error bars are obscured by the data symbols.

2.3.1. BS ISO 27447:2009 method

Antibacterial activity was determined according to the method described in BS ISO 27447:2009 [22]. Cultures were centrifuged at 5000 × *g* for 10 min in a bench centrifuge and the cells were washed in de-ionised water three times by centrifugation and resuspension. Cells were resuspended in a 1:500 dilution of NB and adjusted to OD 0.1–0.2 at 600 nm in a spectrophotometer (Camspec, M330, Cambridge, UK) to give approx. 2×10^8 colony forming units (cfu) cm^{-3}. Fifty microlitres was inoculated onto each 20 mm square test sample and covered with a square of 1 mm borosilicate glass to ensure close contact between the culture and the film. The samples were placed in 50 mm diameter Petri dishes containing moistened filter paper to prevent drying out of the suspensions. The samples were irradiated with Blacklight Blue lamps with a maximum UV light intensity of 0.26 mW cm^{-2}. Plain borosilicate glass was used for controls. Samples were removed after 0, 1, 2, 4, 6 and 24 h and immersed in 20 cm^3 of sterile saline and vortexed for 60 s to resuspend the bacteria. A viability count was performed by dilution and plating on NA in triplicate and incubation at 37 °C for 48 h.

Table 1
Physical characteristics of the films produced by CVD.

Description of the film	Film thickness (nm)	Oxidation of stearic acid (cm min^{-1})
Ag FACVD	40	–
CuO FACVD	40	–
TiO_2 thermal CVD	80	0.0109
Ag (FACVD) + TiO_2 (thermal CVD)	40 + 80	0.0107
CuO (FACVD) + TiO_2 (thermal CVD)	40 + 80	0.0006
TiO_2–Cu co-deposit (thermal CVD)	100	0.0004

2.3.2. In house standard method

The method based on BS EN 13697 [23] has previously been reported [11,12] and was similar to the BS method except that cultures were re-suspended in water to 2×10^8 cfu cm^{-3}, 50 μl samples were spread out over the surface of the films which were not covered with glass but were incubated in 55 mm diameter Petri dishes kept humid by adding 2 cm^3 water. Philips high intensity UVA lamps were used to give 2.24 mW cm^{-2} for irradiation. A viability count was performed by serial dilution and plating onto nutrient agar in triplicate and incubation at 37 °C for 48 h.

2.4. Determination of photocatalytic oxidising activity

Photocatalytic activity of the films was measured by the degradation of stearic acid measured by FTIR (Bruker, Vector 22). Stearic acid (100 μl of 10 mmol dm^{-3} in methanol) was spin coated onto the sample. After drying in an oven the integrated area of the C–H stretching peaks (2800–3000 cm^{-1}) was monitored using FT-IR and plotted as a function of timed exposure to 3 mW cm^{-2} UV radiation (365 nm, black light blue lamps). The photocatalytic activity rates were calculated from straight line fits to this data, which gave numerical values for comparison. The activity of the film was defined as an integrated absorbance unit figure (cm^{-1} min^{-1}), which indicated the rate of reduction in the selected stearic acid peaks. Using a literature concentration value of 3.17×10^{15} stearic acid molecules per cm^3 per absorbance unit it would be possible to convert the integrated absorbance units obtained into the number of stearic acid molecules destroyed per cm^2 min^{-1} [24]. The technique used [25] was developed from work described previously [26].

2.5. Characterisation of the films

X-ray diffraction (XRD) measurements were performed using a Siemens D5000 diffractometer (0.5° glancing angle, Cu Kα source). Surface morphology was investigated using atomic force microscopy (NanoScope IIIa, Digital Inst. Ltd.). X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra) with an Al (monochromated) Kα radiation source was used to check the surface of the films. It was necessary to use a charge neutraliser as all the samples were insulating, mainly due to the deposition on glass. This tends to shift the peak positions up to 2 eV so the measurements were referenced to the residual C 1s signal at 285 eV. Curve fitting with CASA XP software using a mixture of Gaussian–Lorentzian functions was used to deconvolute spectra.

3. Results and discussion

3.1. Physical appearance of the film coatings

In order to understand the influence of the different structures and approaches, several types of film were produced and characterised. Multilayers of Ag and TiO_2 or CuO and TiO_2 were deposited, and a single layer of TiO_2/CuO was co-deposited (Table 1). The properties of the multi-layers were referenced to individual layers of

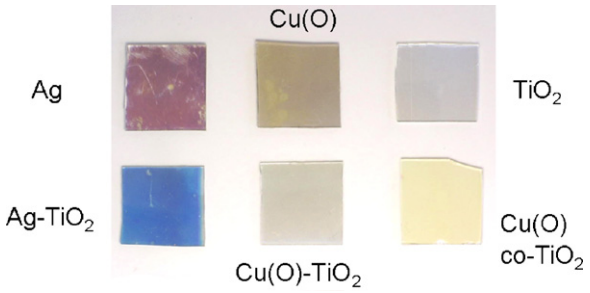

Fig. 1. Appearance of the films.

TiO_2, Ag and CuO deposited on glass under identical conditions to the multilayer composites. Dual layer films were used for majority of the antimicrobial studies. The appearance of the films is shown in Fig. 1. The Ag film was brown-red and was easily detached from the glass substrate. The CuO film was brown but was more tightly attached to the substrate. The TiO_2 film was brown in reflection, consistent with the thickness of 80 nm. The Ag–TiO_2 bilayer was a royal blue whereas the copper bilayer was light brown and the co-deposited sample was yellow-light brown.

3.2. Chemical characteristics of the film coatings

XRD (Fig. 2) showed that the TiO_2 sample was anatase and showed characteristic peaks at 25°, 48° and 55°, corresponding to the (1 0 1), (2 0 0) and (2 1 1) phases. These peaks were also observed in the multi-layer and co-deposited samples, indicating all TiO_2 structures to be anatase. For the Ag + TiO_2 multilayer, peaks corresponding to metallic cubic Ag (38° and 45° corresponding to (1 1 1) and (2 0 0) respectively) were present. Peaks were observed at 35° and 39° for the Cu(O) + TiO_2 multilayer corresponding to CuO (1 1 1) and (2 0 0) respectively. For the TiO_2–Cu(O) co-deposit no additional peaks were identified, this could either be due to the concentration of Cu in the film being below the detection limit of the system used, amorphous or that the Cu resided substitutionally within the lattice.

From XRD it is not possible to confirm whether the multilayered samples consist of two distinct layers or a mixture of materials on the surface. In order to determine the nature of the surface it was necessary to use XPS, as this is surface sensitive, only penetrating approximately the first 5 nm of the sample.

The general survey scans for all three of the samples showed no sign of any impurities except carbon. From the high-resolution scan (C 1s) this can be assigned to mainly surface species of adventitious

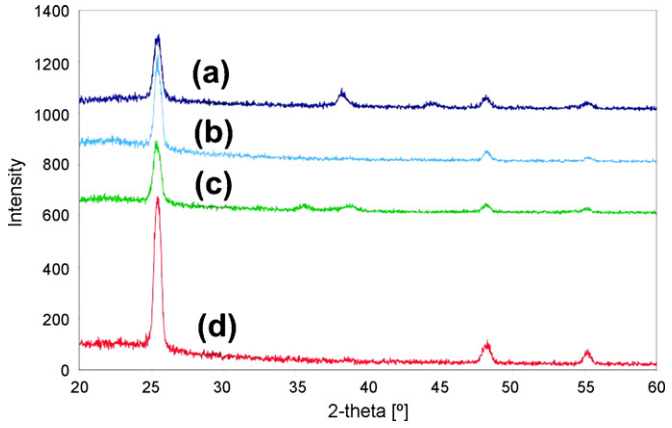

Fig. 2. XRD analysis of the films. (a) TiO_2–Ag, (b) TiO_2–Cu(O) co-deposited, (c) TiO_2–CuO layered, and (d) TiO_2.

elemental carbon at 285 eV which is used as reference for the binding energy shift. Curve fitting also confirmed the presence of two much smaller signals for C–O–H (286.5 eV) and C–C=O (288.6 eV) based organics [27].

The high-resolution Ti 2p spectra for all three samples (copper and silver containing) showed the Ti 2p at $p_{3/2}$ = 458.7 eV, with a spin orbital splitting of 5.8 eV. This along with the position of the O 1s (530.0 eV) confirmed that this was TiO_2 [28].

Next, when looking at the two copper containing samples (sequential and co-deposited) very similar signals for copper species were seen. As XPS only analyses about 5 nm of the surface, this established that the surface consists of both Cu species and TiO_2. The positions of the Ti 2p and Cu 2p were not shifted in comparison to single layers, so suggest that the species are chemically distinct.

The Cu 2p high-resolution spectra consist of the $2p_{3/2}$ and $2p_{1/2}$ along with shake-up satellite peaks and can be identified as mainly copper II oxide. The $2p_{3/2}$ is at 934.1 eV with a splitting of 19.8 eV [29] along with high intensity of the shake-up satellites (at 943 eV and 963 eV) confirm the assignment. The co-deposited film has a slightly narrower half-width (2.8 meV) for the $2p_{3/2}$ than the sequentially deposited film (3.1 meV), which is indicative of a small amount of copper I oxide [30].

Analysis of the sequentially deposited silver and TiO_2 sample showed no sign of any silver either in the survey scan or in the high resolution scan. This established that the silver atoms had not diffused through the TiO_2 film during its deposition.

Atomic force microscopy was used to examine the surface morphology (Fig. 3). It can be seen that the FACVD underlayer affected the way the subsequent TiO_2 films nucleated and grew. Comparing the AFM images of the TiO_2 grown on top of either Ag or CuO FACVD films shows that the films developed smaller particles and a texture closer to that expected for the Ag or CuO FACVD alone [16,19]. The co-deposited TiO_2/Cu(O) film demonstrated similar morphology and particle size to the TiO_2 film.

3.3. Photocatalytic activity

The oxidation of stearic acid by the TiO_2-containing films is shown in Table 1. The Ag–TiO_2 films had similar photocatalytic activity to the TiO_2 by itself, which was consistent with the XPS analysis showing that the surface was TiO_2 only. In order to enable some silver to diffuse to the surface it would be necessary to either raise the temperature of TiO_2 deposition or anneal the sample after deposition. Unfortunately, it was not possible to do the XPS analysis until after other photoactivity and biocidal tests had been completed on the current samples.

However, introduction of Cu/CuO to the TiO_2 films via laminar deposit and diffusion or co-deposition drastically reduced the photocatalytic activity. This is consistent with our previous results [13]. Previous reports of Cu enhancement of activity was proposing a mechanism based on Cu(1) to Cu(2) redox cycle. It is possible that the Cu was acting as recombination sites. Alternatively, Cu may have been substituted for Ti in the TiO_2 lattice thus drastically reduced photocatalytic activity rather than interstitially (i.e. between TiO_2 molecules) in the lattice which occurs at lower proportions of Cu. The extra Cu may also have been acting as recombination sites/centres, facilitating electron–hole recombination [24,31,32]. The detection of Cu species by XPS but not by XRD on the co-deposited sample suggests that Cu species were either amorphous or below the detection limits of the XRD. In the case of the sequentially deposited sample both techniques detected Cu oxide confirming that some had diffused to the surface. However, that which had diffused to the surface was not necessarily crystalline and could exist as crystalline material under the TiO_2 layer and amorphous on the surface. In both cases there were similar

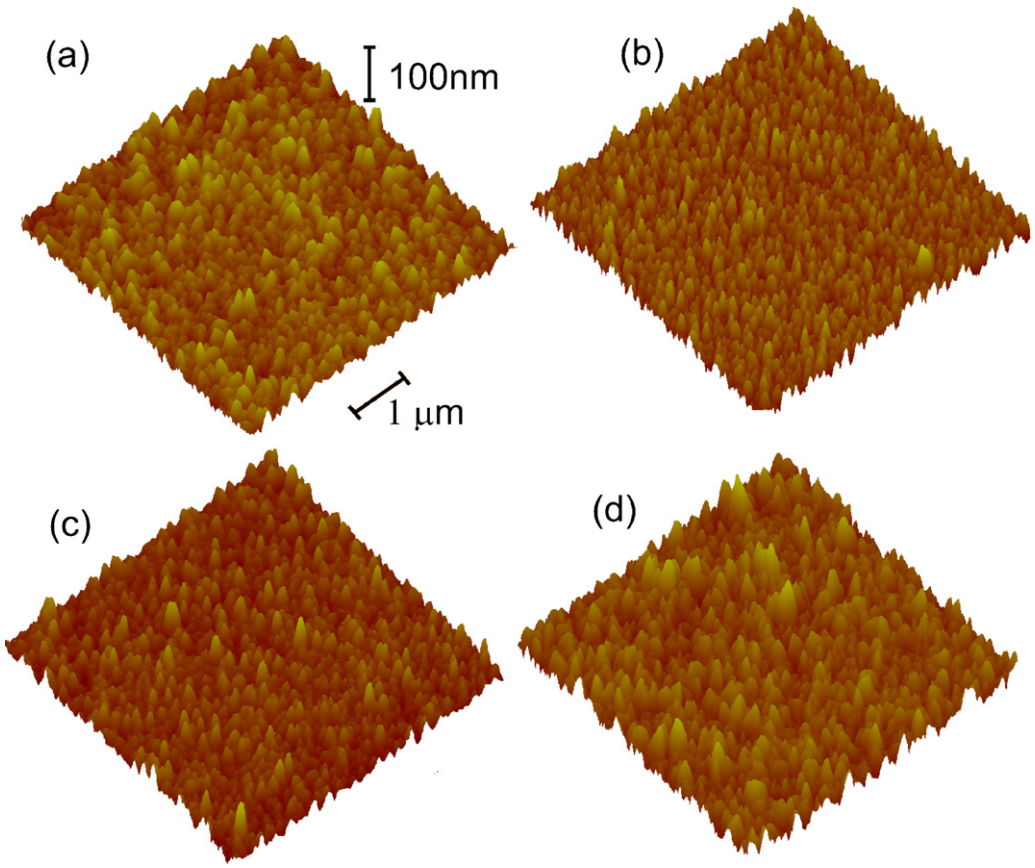

Fig. 3. Atomic force microscopy of the films. (a) TiO_2, (b) TiO_2–Ag, (c) TiO_2–CuO layered, and (d) TiO_2–Cu(O) co-deposited.

amounts of Cu on the sample surfaces, as judged from the relative intensities of the XPS signals. Further investigation is needed to find the cause of this reduction in photocatalytic activity.

3.4. Photocatalytic antimicrobial activity

3.4.1. Comparison of test methods

One of the problems with comparing studies on photocatalytic disinfection is that different workers have used different test methods. In our previous work we used a standardised method that allowed us to compare the activity of different films [11,12]. However, the recent introduction of a British Standard method [22] prompted us to compare the test results for the killing effect on *E. coli* with our previous method (Fig. 4). One clear difference was that the controls remained viable for 24 h with only a 1 log reduction whereas there was a 2 log reduction in using our method after only 6 h. It is likely that the low concentration of NB in the resuspension medium in the BS test meant that the cells were less stressed and remained viable for longer. The results showed photocatalytic killing activity was reduced from a >6 log reduction after 4 h using our own method to only a 2 log reduction with the BS method. The main cause for this was probably the reduced illumination levels which were approximately 10-fold lower. The presence of oxidisable material in the resuspension medium (1/500 dilution of NB rather than distilled water) will also compete with the bacteria for ROS. Although the use of distilled water for such tests does stress the bacterial cells, it does eliminate any variation in interference effects from ions and organic matter which are likely to be different for different surfaces e.g. plain TiO_2 or TiO_2 + Ag or CuO [33]. Indeed the activity in the presence of chloride ions (e.g. from physiological saline which is commonly used as a suspension medium for cells to eliminate osmotic effects) has been shown to be higher than that in distilled water [33,34]. However to comply with the recently introduced standard all subsequent tests were carried out using the BS method. A similar reduction in activity was seen on Ag–TiO_2 films (data not shown).

3.4.2. Comparison of the antimicrobial activity of the different films

A comparison of the activity of the different films in the dark and with illumination is shown in Fig. 5. In the dark, the Ag single layer films showed a >6 log reduction in viability of *E. coli* within

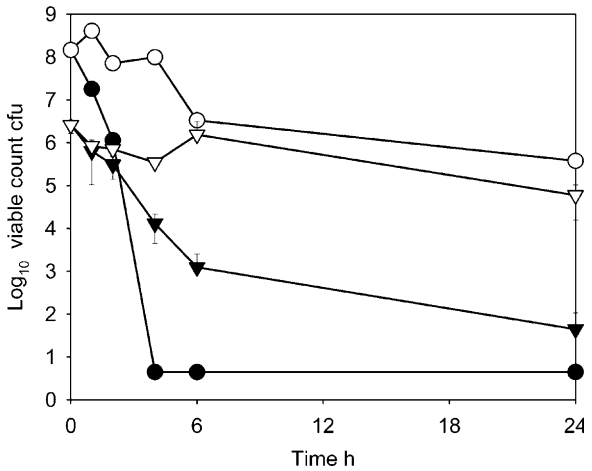

Fig. 4. Comparison of test methods for detection of photocatalytic killing of *Escherichia coli*. Key: In house test (●), control (○), BS ISO27447:2009 test (▼), control (▽).

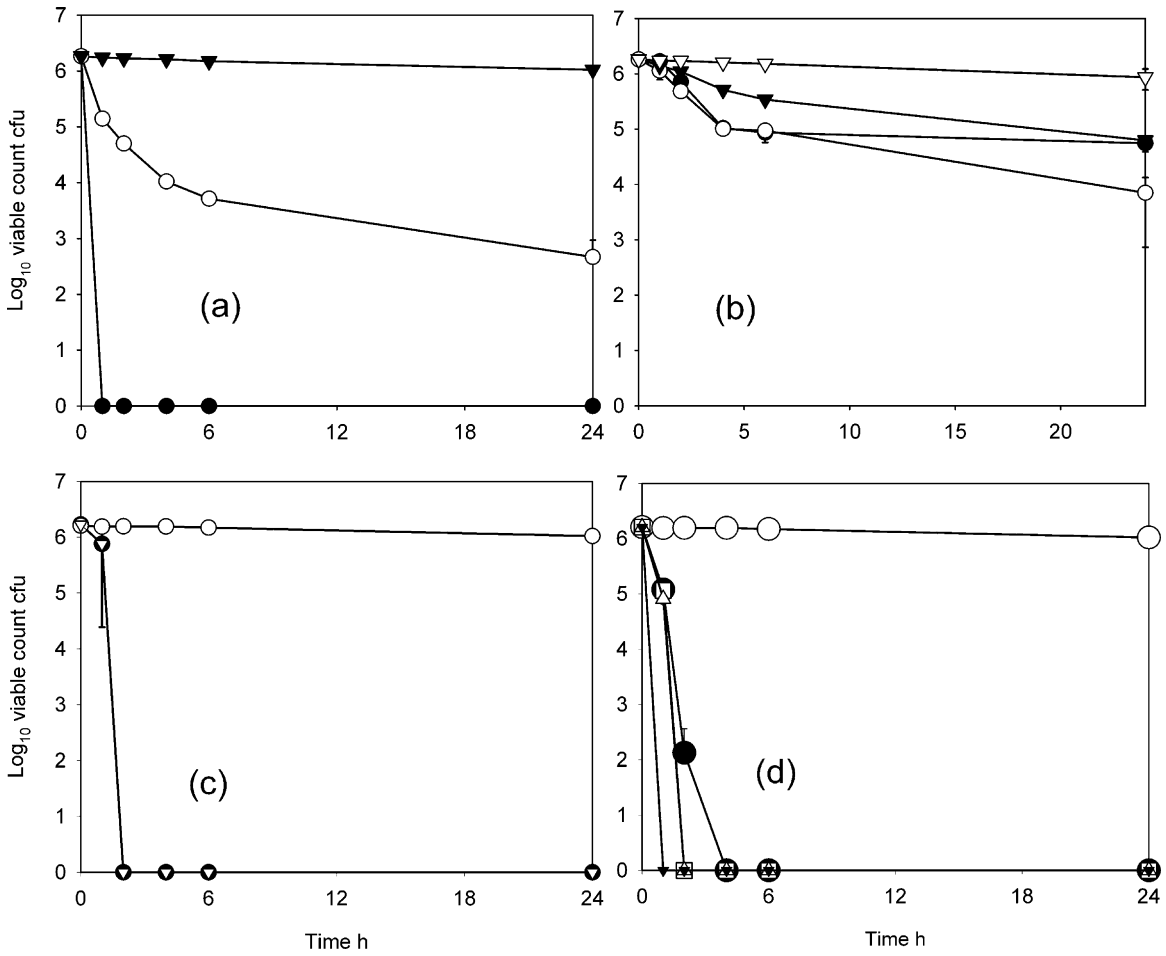

Fig. 5. Killing of *Escherichia coli* on CVD coated films. Key: Activity in the dark (a) Ag monolayer (●), Cu/CuO monolayer (○), control (▼). (b) Ag + TiO_2 (●), Cu + TiO_2 layered (○), Cu(O) + TiO_2 co-deposited (■), TiO_2 monolayer (▽), Control (▼). Activity illuminated with UVA (0.25 mW cm^{-2}). (c) Ag monolayer (●), Cu/CuO monolayer (▽), control (○), (d) Ag + TiO_2 (●), Cu + TiO_2 layered (□), TiO_2 co-deposited (▼), TiO_2 monolayer (△), control (○).

1 h (Fig. 5a). This was similar to previous reports and may be due to the toxicity of released Ag^+ despite the low concentration detected at the surface. The Cu single layer gave a 3 log reduction after 24 h (Fig. 5b) which was lower than the activity shown in our previous reports [11,12]. However, the coating was better adhered to the substrate and there may not have been as much Cu released from the surface. The activity of the dual layers in the dark was much reduced with only a 1–2 log reduction for both films after 24 h (Fig. 5c). This was probably due to the reduced availability of Ag and Cu at the surface. When illuminated by UVA the activity of the Ag films was slightly reduced with a 5 log kill after 2 h. The antimicrobial activity of the Cu films was, however, greatly enhanced and had a similar activity to the Ag film (Fig. 5c). It is possible that the production of ROS was enhanced by the irradiation or that the solubility of the Cu was increased. The activity of the TiO_2 containing films was greatly enhanced by irradiation with UVA (Fig. 5d). TiO_2 single film and Cu–TiO_2 both gave a >6 log reduction after 2 h and the Ag–TiO_2 film after 4 h. Killing on TiO_2 was probably due to the production of ROS or direct interaction between valence band holes and the bacterial cells [35–38].

The Ag–TiO_2 film had a lower activity despite showing a similar oxidising activity towards stearic acid. The XPS data showed that there was no detectable Ag on the surface. Any Ag present would be from the edges of the sample or be at concentrations below that detectable by XPS. It is possible that release of Ag^+ was inhibited or Ag at the surface may have prevented binding of the bacterial cells to the titania. Ag, at dopant levels, enhances photocatalytic activity by enhancing charge separation at the surface of the TiO_2 [39] but can also lead to the formation of ROS which may have been modified by interactions with Ag^+ (Eqs. (1)–(3)).

$$Ag^+ + O_2^{\bullet -} \rightarrow Ag^0 + O_2 \quad (1)$$

$$Ag^0 + O_2^{-} \rightarrow Ag^+ + O_2^{2-} \quad (2)$$

$$H_2O_2 + Ag^0 \rightarrow HO^- + {}^{\bullet}OH + Ag^+ \quad (3)$$

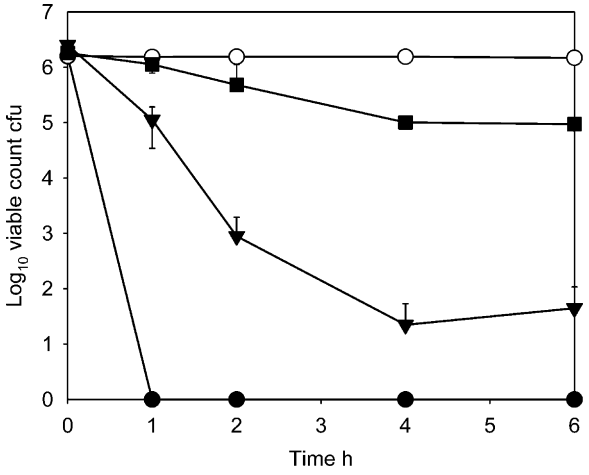

Fig. 6. Effects of light intensity on killing of *Escherichia coli* on TiO_2–Cu(O) layered film. Key: 0.25 mW cm^{-2} (●), 0.1 mW cm^{-2} (▼), dark activity (■), control (○).

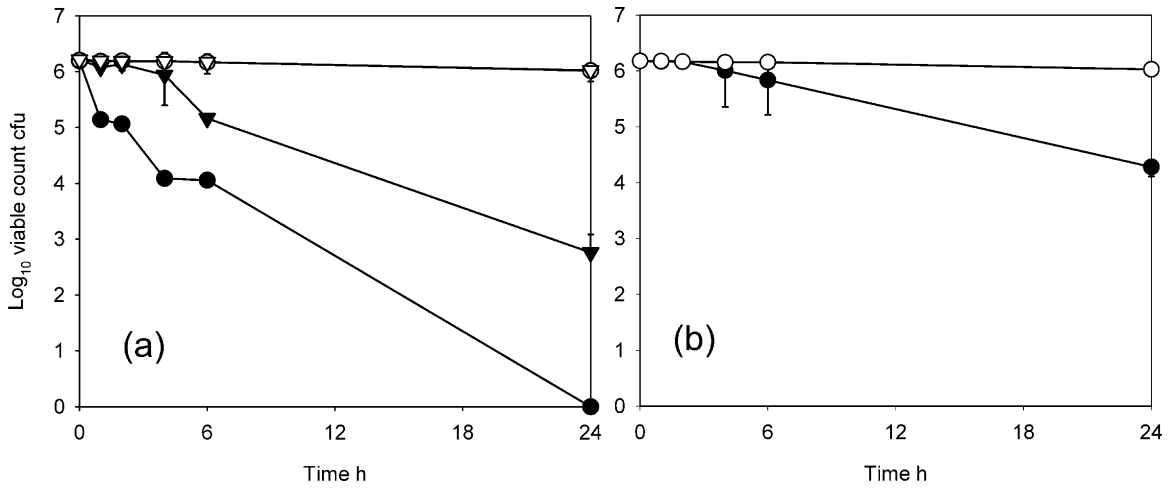

Fig. 7. Photocatalytic killing of *Pseudomonas aeruginosa* and MRSA on Ag–TiO_2 films. Key: (a) *Pseudomonas aeruginosa* NCIMB 10421 test (●), control (○); *Pseudomonas aeruginosa* AOH1 test (▼), control (▽); (b) MRSA test (●), control (○).

The Cu–TiO_2 co-deposited films were less active than the overlaid films but still gave a >5 log reduction after 24 h in the dark and a >5 log reduction within 1 h with illumination (Fig. 5c and d). The effects of light intensity on killing activity on dual layer CuO–TiO_2 are shown in Fig. 6. The rate of killing was lower at low light levels but was still higher than the activity in the dark. A similar activity to that at 0.1 mW cm^{-2} was also seen when illuminated by fluorescent lamps with a UVA content of 0.01 mW cm^{-2} (data not shown). Enhanced photocatalytic killing of *E. coli* on Cu containing TiO_2 films was shown by Sato and Taya [40]. They showed that Cu^{2+} and H_2O_2 were both produced but that neither reached high enough concentrations to kill the *E. coli* directly. They suggested that the Cu increased the photocatalytic activity of the TiO_2 hence the enhanced killing of cells bound to the TiO_2 and that Cu^{2+} also enhanced production of ROS to via a Fenton type reaction (Eqs. (4) and (5))

$$Cu^{2+} + e_{cb}{}^{-} \rightarrow Cu^{+} \quad (4)$$

$$H_2O_2 + Cu^{+} \rightarrow HO^{-} + {}^{\bullet}OH + Cu^{2+} \quad (5)$$

The low photocatalytic activity of these films may still allow production of sufficient H_2O_2 to allow these reactions to occur. Further H_2O_2 production may be produced by photo-generation as has been shown to occur in seawater containing organic matter [41]. Preliminary results show that there is also enhanced DNA damage in the presence of Cu compared to that seen on plain TiO_2 (Varghese and Foster, unpublished).

3.4.3. Activity against hospital related pathogens

The activity of the Ag–TiO_2 films was tested against two strains of *P. aeruginosa* (Fig. 7a) and methicillin resistant *S. aureus* (MRSA; Fig. 7b), both of which are important causes of healthcare acquired infections. The strains of *P. aeruginosa* were NCIMB 10421, a strain used for testing of disinfectant activity, and an environmental isolate AOH1. Fig. 7 shows that both were more resistant than *E. coli* (compare with Fig. 4) with NCIMB 10421 reduced by 2 log after 6 h and >5 log after 24 h and AOH1 by only 1 log after 6 h and 3 log after 24 h. The results show that even the disinfectant sensitive strain was harder to kill the *E. coli*, possibly because the outer membrane of *P. aeruginosa* is less permeable than that of *E. coli*. The environmental isolate was even harder to kill, possibly because it is adapted to surviving adverse conditions. The killing of MRSA was also slower than *E. coli* (Fig. 7b) although the reduction after 24 h still represents a 95% kill. MRSA is a Gram-positive organism and most studies show that Gram-positive bacteria are more resistant to photocatalytic killing, probably because they have a different cell wall structure where the membrane is protected by a thick layer of peptidoglycan [8,42–45] although some studies show either no difference of that Gram-positive bacteria are more sensitive than Gram-negatives [46–48]. The difference may be due to different affinities for the TiO_2 as well as cell-wall structure.

4. Conclusions

The results showed that the films had good biocidal activity. Although the times for a >5 log kill were longer than we have reported previously. This is probably due to the lower light levels used for irradiation (10% of previously used levels), competition for photocatalysis by the organic matter present when the recently introduced BS method for determining photocatalytic antibacterial activity was used. However the results show that the films are still capable of giving a good killing activity within a short time even at the reduced light levels in the test method used. The activity against pathogens as these lower light levels is more relevant to potential real life situations. The hospital related pathogens were more resistant than the standard disinfectant testing strains but were still reduced by 95–99.9% on the surfaces. This is equivalent to reductions seen in previous studies of non-photocatalytic antimicrobial surfaces [49]. The Ag–TiO_2 films gave a higher activity in the dark but the Cu(O)–TiO_2 films were more active when illuminated with UVA despite a much reduced photocatalytic activity. Any changes in the activity of the Ag–TiO_2 is related to the changes in the TiO_2 film caused by deposition on a film of Ag rather than glass, as little Ag had not diffused through to the top surface. Preliminary results show that the activity was also stimulated by fluorescent light. The activity of the latter films against hospital pathogens and the light activation phenomenon requires further investigation. However the activity in fluorescent light would greatly enhance their usefulness in infection control.

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