Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity

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Abstract The photocatalytic properties of titanium dioxide are well known and have many applications including the removal of organic contaminants and production of self-cleaning glass. There is an increasing interest in the application of the photocatalytic properties of TiO₂ for disinfection of surfaces, air and water. Reviews of the applications of photocatalysis in disinfection (Gamage and Zhang 2010; Chong et al., Wat Res 44 (10):2997–3027, 2010) and of modelling of TiO₂ action have recently been published (Dalrymple et al., Appl Catal B 98(1–2):27–38, 2010). In this review, we give an overview of the effects of photoactivated TiO₂ on microorganisms. The activity has been shown to be capable of killing a wide range of Gram-negative and Gram-positive bacteria, filamentous and unicellular fungi, algae, protozoa, mammalian viruses and bacteriophage. Resting stages, particularly bacterial endospores, fungal spores and protozoan cysts, are generally more resistant than the vegetative forms, possibly due to the increased cell wall thickness. The killing mechanism involves degradation of the cell wall and cytoplasmic membrane due to the production of reactive oxygen species such as hydroxyl radicals and hydrogen peroxide. This initially leads to leakage of cellular contents then cell lysis and may be followed by complete mineralisation of the organism. Killing is most efficient when there is close contact between the organisms and the TiO₂ catalyst. The killing activity is enhanced by the presence of other antimicrobial agents such as Cu and Ag.

Keywords Antimicrobial · Disinfection · Mechanism · Photocatalysis · ROS · TiO₂ · Titania

Introduction

The ability of titanium dioxide (titania, TiO₂) to act as a photocatalyst has been known for 90 years (Renz 1921), and its role in the “chalking” of paint (formation of powder on the surface) is well known (Jacobsen 1949). Interest in the application of the photocatalytic properties of TiO₂ was revived when the photoelectrolysis of water was reported by Fujishima and Honda (1972), and this activity was soon exploited both for the ability to catalyse the oxidation of pollutants (Carey et al. 1976; Frank and Bard 1977) and the ability to kill microorganisms (Matusunga 1985; Matsumaga et al. 1985). Photocatalytic surfaces can be superhydrophilic, which means that water spreads on the surface, allowing dirt to be washed off, and commercial uses include self-cleaning windows (e.g. San Gobain Bioclean™, Pilkington Active™ and SunClean™; Chen and Poon 2009) and self-cleaning glass covers for highway tunnel lamps (Honda et al. 1998). There are currently over 11,000 publications on photocatalysis. Although an early study showed no improved antimicrobial activity of TiO₂ for disinfection of primary wastewater effluent (Carey and Oliver 1980), many subsequent studies have shown the usefulness of photocatalysis on TiO₂ for disinfection of water (Chong et al. 2010). These include killing of bacteria (Rincón and Pulgarin 2004a) and viruses from water supplies (Sjogren and Sierka 1994),
tertiary treatment of wastewater (Araña et al. 2002), purifying drinking water (Wei et al. 1994; Makowski and Wardas 2001), treatment of wash waters from vegetable preparation (Selma et al. 2008) and in bioreactor design to prevent biofilm formation (Shiraishi et al. 1999). TiO₂-coated filters have been used for the disinfection of air (Jacoby et al. 1998; Goswami et al. 1997, 1999; Lin and Li 2003a, b; Chan et al. 2005). The advantage of using photocatalysis along with conventional air filtration is that the filters are also self-cleaning. TiO₂ has also been used on a variety of other materials and applications (Table 1). The potential for killing cancer cells has also been evaluated (reviewed by Blake et al. 1999; Fujishima et al. 2000).

In recent years, there has been an almost exponential increase in the number of publications referring to photocatalytic disinfection (PCD), and the total number of publications now exceeds 800 (Fig. 1). Some of the early work was reviewed by Blake et al. (1999) and sections on photocatalytic disinfection have been included in several reviews (Mills and Le Hunte 1997; Fujishima et al. 2000, 2008; Carp et al. 2004); reviews of the use in disinfection of water (McCullagh et al. 2007; Chong et al. 2010) and modelling of TiO₂ action have been published (Dalrymple et al. 2010). In this review, we explore the effects of photoactivated TiO₂ on microorganisms.

### Photocatalytic mechanism

For a more detailed discussion of the photochemistry, the reader is directed to the excellent reviews by Mills and Le Hunte (1997) and Hashimoto et al. (2005). TiO₂ is a semiconductor. The adsorption of a photon with sufficient energy by TiO₂ promotes electrons from the valence band ($e_{vb}^-$) to the conduction band ($e_{cb}^-$), leaving a positively charged hole in the valence band ($h_{vb}^+$; Eq. 1). The band gap energy (energy required to promote an electron) of anatase is approx. 3.2 eV, which effectively means that photocatalysis can be activated by photons with a wavelength of below approximately 385 nm (i.e. UVA). The electrons are then free to migrate within the conduction band. The holes may be filled by migration of an electron from an adjacent molecule, leaving that with a hole, and the process may be repeated. The electrons are then free to migrate within the conduction band and the holes may be filled by an electron from an adjacent molecule. This process can be repeated. Thus, holes are also mobile. Electrons and holes may recombine (bulk recombination) a

| Uses and applications                                      | Publication                                      |
|------------------------------------------------------------|--------------------------------------------------|
| Building materials, e.g. concrete                          | Guo et al. (2009)                                |
|                                                            | Chen and Poon (2009)                             |
| Catheters to prevent urinary tract infections              | Ohko et al. (2001)                               |
|                                                            | Yao et al. (2008c)                               |
| Coatings for bioactive surfaces                            | Ueda et al. (2010)                               |
| Dental implants                                            | Suketa et al. (2005)                             |
|                                                            | Mo et al. (2007)                                 |
| Fabrics                                                   | Gupta et al. (2008), Kangwansupamonkon et al. (2009), Wu et al. (2009a, b), Yuranova et al. (2006) |
| Food packaging films                                      | Chawengkijwanich and Hayata (2008)              |
| Lancets                                                   | Nakamura et al. (2007)                           |
| Metal pins used for skeletal traction                      | Tsuang et al. (2008)                             |
| Orthodontic wires                                         | Chun et al. (2007)                               |
| Paint                                                     | Allen et al. (2008)                              |
| Photocatalytic tiles for operating theatres               | Fujishima et al. (1997)                          |
| Plastics                                                  | Paschoalino and Jardim (2008)                    |
|                                                            | Cerrada et al. (2008)                            |
| Protection of marble from microbial corrosion             | Fujishima et al. (1997)                          |
| Surgical face masks                                       | Poulos et al. (1999)                             |
| Tent materials                                            | Li et al. (2006)                                 |
| TiO₂-coated wood                                          | Nimithtrakoolchai and Supothina (2008)           |
| TiO₂-containing paper                                     | Chen et al. (2009)                               |
|                                                            | Geng et al. (2008)                               |
non-productive reaction, or, when they reach the surface, react to give reactive oxygen species (ROS) such as $O_2^-$ (2) and $\cdot OH$ (3). These in solution can react to give $H_2O_2$ (4), further hydroxyl (5) and hydroperoxyl (6) radicals. Reaction of the radicals with organic compounds results in mineralisation (7). Bulk recombination reduces the efficiency of the process, and indeed some workers have applied an electric field to enhance charge separation, properly termed photoelectrocatalysis (Harper et al. 2000).

\[
\text{TiO}_2 + h_v \rightarrow e_{cb}^- + h_{vb}^+
\]  

(1)

\[
O_2 + e_{cb}^- \rightarrow O_2^-.
\]  

(2)

\[
h_{cb}^+ + H_2O \rightarrow \cdot OH + H^+_\text{aq}
\]  

(3)

\[
\cdot OH + \cdot OH \rightarrow H_2O_2
\]  

(4)

\[
O_2^- \cdot + H_2O_2 \rightarrow \cdot OH + OH^- + O_2
\]  

(5)

\[
O_2^- \cdot + H^+ \rightarrow \cdot OOH
\]  

(6)

\[
\cdot OH + \text{Organic} + O_2 \rightarrow CO_2, H_2O
\]  

(7)

There are three main polymorphs of TiO$_2$: anatase, rutile and brookite. The majority of studies show that anatase was the most effective photocatalyst and that rutile was less active; the differences are probably due to differences in the extent of recombination of electron and hole between the two forms (Miyagi et al. 2004). However, studies have shown that mixtures of anatase and rutile were more effective photocatalysts than 100% anatase (Miyagi et al. 2004) and were more efficient for killing coliphage MS2 (Sato and Taya 2006a). One active commercially available preparations of TiO$_2$ is Degussa P25 (Degussa Ltd., Germany) which contains approx. 80% anatase and 20% rutile. The increased activity is generally ascribed to interactions between the two forms, reducing bulk recombination. Brookite has been relatively little studied, but a recent paper showed that a brookite-anatase mixture was more active than anatase alone (Shah et al. 2008). A silver-doped multiphase catalyst was shown to have increased photocatalytic activity, but its antimicrobial activity was not reported (Yu et al. 2005a). Indoor use of photocatalytic disinfection is limited by the requirement for UVA irradiation. Modified catalysts can reduce the band gap so that visible light activates the photocatalysis. This has been shown for TiO$_2$ combined with C, N and S, metals such as Sn, Pd, and Cu, and dyes (Fujishima and Zhang 2006), but activity is generally lower than when activated with UVA. This area is currently the subject of much research.

The antimicrobial activity of UVA-activated TiO$_2$ was first demonstrated by Matsunaga and coworkers (Matsunaga 1985; Matsunaga et al. 1985). Since then, there have been reports on the use of photocatalysis for the destruction of bacteria, fungi, algae, protozoa and viruses as well as microbial toxins. TiO$_2$ can be used in suspension in liquids or immobilised on surfaces (Kikuchi et al. 1997; Sunada et al. 1998; Kühn et al. 2003; Yu et al. 2003a; Brook et al. 2007; Yates et al. 2008a, b; Ditta et al. 2008). The ability to eliminate microorganisms on photocatalytic self-cleaning/self-disinfecting surfaces may provide a useful additional mechanism in the control of transmission of diseases along with conventional disinfection methods. Copper and silver ions are well characterised for their antimicrobial activities and can also enhance the photocatalytic activity. Combinations of Cu$^{2+}$ and Ag$^+$ with TiO$_2$ therefore provide dual function surfaces (see below).

**Photocatalytic action on microorganisms**

Photocatalysis has been shown to be capable of killing a wide range of organisms including Gram-negative and Gram-positive bacteria, including endospores, fungi, algae, protozoa and viruses, and has also been shown to be capable of inactivating prions (Paspaltsis et al. 2006). Photocatalysis has also been shown to destroy microbial toxins. As far as the authors are aware, only Acanthamoeba cysts and Trichoderma asperellum conidiospores have been reported to be resistant (see below), but these have not been extensively studied. The ability to kill all other groups of microorganisms suggests that the surfaces have the potential to be self-sterilising, particularly when combined

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**Fig. 1** Number of publications on photocatalytic disinfection
with Cu or Ag. However, for the present, it is correct to refer to photocatalytic surfaces or suspensions as being self-disinfecting rather than self-sterilising. Many studies have used pure cultures, although there are reports of photocatalytic activity against mixed cultures (van Grieken et al. 2010) and of natural communities (Armon et al. 1998; Araña et al. 2002; Cho et al. 2007a).

Gram-negative bacteria
The great majority of studies have been performed with *Escherichia coli*, and there are far too many to give a complete list in this review. Some examples of different strains used and applications are shown in Table 2. Examples of other Gram-negative bacteria that are susceptible to PCD are shown in Table 3. They include cocci, straight and curved rods, and filamentous forms from 19 different genera.

Gram-positive bacteria
Most studies showed that Gram-positive bacteria were more resistant to photocatalytic disinfection than Gram-negative bacteria (Kim et al. 2003; Liu and Yang 2003; Erkan et al. 2006; Pal et al. 2005, 2007; Muszkat et al. 2005; Hu et al. 2007; Sheel et al. 2008; Skorb et al. 2008). The difference is usually ascribed to the difference in cell wall structure between Gram-positive and Gram-negative bacteria. Gram-negative bacteria have a triple-layer cell wall with an inner membrane (IM), a thin peptidoglycan layer (PG) and an outer membrane (OM), whereas Gram-positive bacteria have a thicker PG and no OM. However, a few studies show that Gram-positive bacteria were more sensitive. *Lactobacillus* was more sensitive than *E. coli* on a Pt-doped TiO$_2$ catalyst (Matsunaga et al. 1985). methicillin-resistant *Staphylococcus aureus* (MRSA) and *E. coli* were more resistant than *Microoccus luteus* (Kangwansupamonkon et al. 2009). Dunlop et al. (2010) showed that MRSA were more sensitive than an extended spectrum β-lactamase (ESBL)-producing *E. coli* strain, but less sensitive than *E. coli* K12. *Enterococcus faecalis* was more resistant than *E. coli*, but more sensitive than *Pseudomonas aeruginosa* (Luo et al. 2008). Conversely, Kubacka et al. (2008a) showed no difference in sensitivity between clinical isolates of *P. aeruginosa* and *E. faecalis*. Van Grieken et al. (2010) saw no difference in disinfection time for *E. coli* and *E. faecalis* in natural waters, but *E. faecalis* was more resistant in distilled water. These differences may relate to different affinities for TiO$_2$ (close contact between the cells and the TiO$_2$ is required for optimal activity—see below) as well as cell wall structure.

Gram-positive bacteria that have been shown to be killed by PCD are shown in Table 4 and include species of 17 different genera, including aerobic and anaerobic endospore formers. The endospores were uniformly more resistant than the vegetative cells to PCD.

**Fungi, algae and protozoa**
Fungi, algae and protozoa that have been shown to be susceptible to PCD are shown in Tables 5 and 6. These include 11 genera of filamentous fungi, 3 yeasts, 2 amoebae, 1 Apicomplexan, 1 diplomonad, 1 ciliate and 7 algae, including 1 diatom. Fungal spores were generally more resistant than vegetative forms, and *Trichoderma harzianum* spores in particular were resistant to killing under the conditions tested (Giannantonio et al. 2009). Cysts of *Acanthamoeba* showed only a 50% reduction during the treatment time and may have been killed if the treatment time had been extended (Sökmen et al. 2008).

**Viruses**
Viruses that have been shown to be killed by PCD are shown in Table 7.
Most studies were on *E. coli* bacteriophages in suspension, which have been demonstrated for icosahedral ssRNA viruses (MS2 and Qβ), filamentous ssRNA virus (fr), ssDNA (phi-X174) and dsDNA viruses (λ and T4). Other bacteriophages include *Salmonella typhimurium* phage PRD-1, *Lactobacillus* phage PL1 and an unspecified *Bacteroides fragilis* phage. Mammalian viruses include poliovirus 1, avian and human influenza viruses, and SARS coronavirus (Table 7).

**Bacterial toxins**
Photocatalytic activity has been shown to be capable of inactivating bacterial toxins including Gram-negative endotoxin and algal and cyanobacterial toxins (Table 8).

**Mechanism of killing of bacteria**
The mode of action of photoactivated TiO$_2$ against bacteria has been studied with both Gram-positive and Gram-negative bacteria. The killing action was originally proposed to be via depletion of coenzyme A by dimerization and subsequent inhibition of respiration (Matsunaga et al. 1985, 1988). However, there is overwhelming evidence that the lethal action is due to membrane and cell wall damage. These studies include microscopy, detection of lipid peroxidation products, leakage of intercellular components, e.g. cations, RNA and protein, permeability to low-molecular-weight labels, e.g. o-nitrophenyl-galactoside (ONPG), and spectroscopic studies.
Table 2 Examples of *E. coli* strains shown to be killed by photocatalytic disinfection on TiO$_2$

| Organism            | Notes                                                                 | Reference                          |
|---------------------|----------------------------------------------------------------------|------------------------------------|
| *Escherichia coli*  | WO$_3$ nanoparticle doped TiO$_2$                                     | Tatsuma et al. (2003)              |
| *Escherichia coli*  | Degussa P25 impregnated cloth filter                                 | Vohra et al. (2006)               |
| *Escherichia coli*  | Degussa P25 suspension                                                | Cho et al. (2005)                  |
| *Escherichia coli*  | Degussa P25 coated plexiglass                                         | Kühn et al. (2003)                |
| *Escherichia coli*  | Degussa P25 immobilised on glass substrate                           | Rodríguez et al. (2007)           |
| *Escherichia coli*  | Ag and CuO – TiO$_2$ hybrid catalysts                                 | Brook et al. (2007), Ditta et al. (2008) |
| *Escherichia coli*  | Degussa P25 suspension                                                | Ibáñez et al. (2003)              |
| *Escherichia coli*  | Rfc sputter was used to deposit films of 120 nm thickness on glass and steel substrates | Shieh et al. (2006)               |
| *Escherichia coli*  | Degussa P25 applied to a plastic support                             | Sichel et al. (2007a)             |
| *Escherichia coli*  | Aldrich TiO$_2$ 99.9% pure anatase                                   | Sökmen et al. (2001)              |
| *Escherichia coli*  | Aerosol deposited nanocrystalline film                               | Ryu et al. (2008)                 |
| *Escherichia coli*  | Degussa P25, suspension                                               | Huang et al. (2000)               |
| *Escherichia coli*  | Aerosil P25 suspension                                                | Maness et al. (1999)              |
| *Escherichia coli*  | Thin film TiO$_2$                                                    | Dunlop et al. (2010)              |
| *Escherichia coli*  | TiO$_2$ and ZnO suspension                                            | Liu and Yang (2003)               |
| *Escherichia coli*  | Sol–gel microemulsion with an Ag overlayer                            | Kubacka et al. (2008b)            |
| *Escherichia coli*  | Degussa P25 suspension                                                | Lan et al. (2007)                 |
| *Escherichia coli*  | Flow through reactor                                                 | Belláková et al. (1999)           |
| *Escherichia coli*  | Anatase thin film on glass                                            | Yu et al. (2002, 2003b)           |
| *Escherichia coli*  | Degussa P25 suspension                                                | Bekböl et al. (1996), Bekböl et al. (1997) |
| *Escherichia coli*  | Degussa P25 and Ag/P25 mixed suspension                               | Coleman et al. (2005)             |
| *Escherichia coli*  | Silica coated lime glass plates dip coated with TiO$_2$               | Kikuchi et al. (1997)             |
| *Escherichia coli*  | Degussa P25 suspension                                                | Sunada et al. (2003b)             |
| *Escherichia coli*  | TiO$_2$ coated air filter                                             | Sato et al. (2003)                |
| *Escherichia coli*  | Anatase thin film on glass                                            | Yu et al. (2002)                  |
| *Escherichia coli*  | Degussa P25 suspension                                                | Duffy et al. (2004)               |
| *Escherichia coli*  | Degussa P25 coated glass fibre air filter                             | McLoughlin et al. (2004a, b)      |
| *Escherichia coli*  | Degussa P25                                                          | Pal et al. (2007)                 |
| *Escherichia coli*  | Degussa P25 coated glass fibre air filter                             | Pal et al. (2008)                 |
| *Escherichia coli*  | Silica coated lime glass plates dip coated with TiO$_2$               | Rincon and Pulgarin (2003, 2004a) |
| *Escherichia coli*  | Degussa P25 suspension                                                | Marugan et al. (2008)             |
| *Escherichia coli*  | Degussa P25 suspension                                                | Fernandez et al. (2005)           |
| *Escherichia coli*  | Degussa P25 suspension                                                | Gumy et al. (2006a, b)            |
| *Escherichia coli*  | Degussa P25 suspension                                                | Quisenberry et al. (2009)         |
| *Escherichia coli*  | Thin film TiO$_2$                                                    | Dunlop et al. (2002)              |
| *Escherichia coli*  | Degussa P25 suspension                                                | Gogniat and Dukan (2007)          |
| *Escherichia coli*  | Degussa P25 suspension                                                | Kim et al. (2004)                 |
| *Escherichia coli*  | Immobilised TiO$_2$                                                  | Butterfield et al. (1997)         |
| *Escherichia coli*  | Degussa P25 suspension                                                | Benabou et al. (2007)             |
| *Escherichia coli*  | Degussa P25 and millennium PC500                                      | Guillard et al. (2008)            |
| *Escherichia coli*  | Degussa P25 suspension                                                | Robertson et al. (2005)           |
| *Escherichia coli*  | Thin films on glass substrate                                         | Choi et al. (2004)                |
| *Escherichia coli*  | Anatase thin film on glass                                            | Yu et al. (2002)                  |
Changes in cell permeability

Indirect evidence for membrane damage comes from studies of leakage of cellular components. Saito et al. (1992) showed that there was a rapid leakage of $K^+$ from treated cells of *Streptococcus sobrinus* AHT which occurred within 1 min of exposure and paralleled the loss of viability. This was followed by a slower release of RNA...
| Organism                                | Notes                                                                 | Reference                     |
|-----------------------------------------|-----------------------------------------------------------------------|-------------------------------|
| Actinobacillus actinomycetemcomitans    | TiO$_2$ coating on titanium                                            | Suketa et al. (2005)          |
| Actinomyces viscosus                    | Kobe Steel TiO$_2$ 99.98% anatase                                      | Nagame et al. (1989)          |
| Bacillus cereus                         | TiO$_2$ suspension                                                     | Cho et al. (2007a)            |
| Bacillus cereus spores                  | Colloidal suspension of TiO$_2$                                       | Armon et al. (2004)           |
| Bacillus megaterium QM B1551            |                                                                      |                               |
| Bacillus pumilis spores ATCC 27142      | TiO$_2$ anatase 99.9% slurry in Petri dish                            | Pham et al. (1995, 1997)      |
| Bacillus sp.                            | Degussa P-25 immobilised on Pyrex glass                               | Rincón and Pulgarin (2005)    |
| Bacillus subtilis vegetative cells and  | Degussa P25-coated quartz discs                                       | Wolfrum et al. (2002)         |
| endospores                              |                                                                       |                               |
| Bacillus subtilis endospores            | Aluminium foil coated with TiO$_2$                                    | Greist et al. (2002)          |
| Bacillus thuringiensis                  | 100% anatase thin film ± Pt doping                                     | Kozlova et al. (2010)         |
| Clavibacter michiganensis               | Solar + H$_2$O$_2$                                                    | Muszkat et al. (2005)         |
| Clostridium difficile                   | Evonik Aeroxide P25 thin film                                         | Dunlop et al. (2010)          |
| Clostridium perfringens spores NCIMB 6125| Degussa P-25 + UVC                                                     | Guimarães and Barretto (2003) |
| Deinococcus radiophilius               | TiO$_2$ suspension                                                     | Laot et al. (1999)            |
| Enterococcus (Streptococcus) faecalis   | Degussa P25 suspension                                                 | Herrera Melián et al. (2000)  |
| Enterococcus (Streptococcus) faecalis   | Immobilised TiO$_2$                                                   | Singh et al. (2005)           |
| Enterococcus faecalis CECT 481          | Degussa P25 suspension                                                 | Vidal et al. (1999)           |
| Enterococcus faecium                    | Degussa P25-coated Plexiglass                                         | Kühn et al. (2003)            |
| Enterococcus hirae                      | TiO$_2$ on orthopaedic implants                                        | Tsuang et al. (2008)          |
| Enterococcus sp.                        | Degussa P-25 suspension                                                | Rincón and Pulgarin (2005)    |
| Lactobacillus acidophilus               | Degussa P25 suspension                                                 | Matsunaga et al. (1985), Choi et al. (2007a) |
| Lactobacillus helveticus CCRC 13936     | TiO$_2$ suspension                                                     | Liu and Yang (2003)           |
| Lactococcus lactis 411                  | Sigma-Aldrich TiO$_2$ thin films                                      | Skorb et al. (2008)           |
| Listeria monocytogenes                  | TiO$_2$ (Yakuri Pure Chemical Company, Japan) suspension              | Kim et al. (2003)             |
| Microbacterium sp. Microbacteriaceae str. W7| Degussa P25 immobilised on membrane                                   | Pal et al. (2007)             |
| Micrococcus luteus                      | Degussa P25 thick film                                                | Wolfrum et al. (2002)         |
| Micrococcus lylae                       | TiO$_2$ suspension                                                     | Yu et al. (2005b)             |
| MRSA                                    |                                                                       |                               |
| MRSA                                    |                                                                       |                               |
| Mycobacterium smegmatis                 |                                                                       |                               |
| Mycobacterium smegmatis                 |                                                                       |                               |
| Porphyrmonas gingivalis                 |                                                                       |                               |
| Paenibacillus sp SAFN-007               | Degussa P25 immobilised on membrane                                    | Pal et al. (2007)             |
| Staphylococcus aureus                   | Degussa P25 suspension                                                 | Block et al. (1997)           |
| Staphylococcus aureus                   | TiO$_2$ thin film on steel and titanium                                | Shiraiishi et al. (1999)      |
| Staphylococcus epidermidis NCTC11047    | Ag-TiO$_2$ catalyst                                                   | Sheel et al. (2008)           |
| Staphylococcus saprophyticus            |                                                                       |                               |
| Streptococcus citricus                   |                                                                       |                               |
| Streptococcus iniae                     |                                                                       |                               |
| Streptococcus mutans                    |                                                                       |                               |
| Streptococcus mutans GS5, LM7, OMZ175   |                                                                       |                               |
| Streptococcus pyogenes ery\' cam\'      |                                                                       |                               |
| Streptococcus rattus FA-1               |                                                                       |                               |
| Streptococcus sobrinus AHT              |                                                                       |                               |
and protein. Leakage of K⁺ was also shown to parallel cell death of *E. coli* (Hu et al. 2007; Kambala and Naidu 2009). Huang et al. (2000) showed an initial increase in permeability to small molecules such as ONPG which was followed by leakage of large molecules such as β-D-galactosidase from treated cells of *E. coli*, suggesting a progressive increase in membrane permeability. Membrane damage has been shown with cells labelled with the LIVE-DEAD® BacLight™ Bacterial Viability Kit which uses the fluorescent dyes Cyto 9, which stains all cells green, and propidium iodide, which only penetrates cells with damaged membranes and stains cells red. Gogniat et al. (2006) showed that permeability changes occurred in the membrane soon after attachment of *E. coli* to the TiO₂, and we have seen similar changes (Ditta and Foster, unpublished). However, no damage was detected on a visible light active PdO/TiON catalyst until the catalyst had been irradiated (Wu et al. 2008, 2009a, b; see Fig. 2).

**Table 5** Fungi shown to be killed by photocatalytic disinfection

| Organism                           | Notes                                      | Reference               |
|------------------------------------|--------------------------------------------|-------------------------|
| *Aspergillus niger* AS3315          | Wood coated with TiO₂                      | Chen et al. (2009)      |
| *A. niger* spores                   | Degussa P25 film on quartz discs           | Wolfrum et al. (2002)   |
| *Aspergillus niger*                 | Thin films of TiO₂ on glass plates         | Erkan et al. (2006)     |
| *Candida albicans* ATCC 10231       | Degussa P25 suspension                     | Lonnen et al. (2005)    |
| *Candida albicans*                  | TiO₂-coated surfaces                       | Kühn et al. (2003)      |
| *Candida famata*                    | TiO₂ coated catheters                      | Yao et al. (2008c)      |
| *Candida vini*                      | TiO₂ thin film                             | Veselá et al. (2008)    |
| *Cladobotryum variabilis*           | TiO₂ suspension                            | Sawada et al. (2005)    |
| *Cladosporium cladosporioides*      | TiO₂-coated concrete                       | Giannantonio et al. (2009) |
| *Diaporthe actinidae*               | TiO₂ immobilised on alumina spheres        | Hur et al. (2005)       |
| *Erysiphe cichoracearum*            | Degussa P25 and Ce³⁺ doped catalysts       | Lu et al. (2006)        |
| *Epicoccum nigrum*                  | TiO₂ coated concrete                       | Giannantonio et al. (2009) |
| Fungi from spinach                  | Plastic fruit containers with TiO₂ coating | Koide and Nonami (2007) |
| *Fusarium mucedo*                   | TiO₂-coated concrete                       | Giannantonio et al. (2009) |
| *Fusarium solani* ATCC 36031        | Degussa P25 suspension                     | Lonnen et al. (2005)    |
| *Fusarium spp.* (equisetii, oxyptan, anthropilum, verticilloides, solani) | TiO₂ suspension, solar irradiation | Sichel et al. (2007b, c) |
| *Hanseula anomala* CCY-138-30       | TiO₂- and Ag-doped                         | Veselá et al. (2008)    |
| *Peronophythora litchii*            | Degussa P25- and Ce³⁺-doped catalysts      | Lu et al. (2006)        |
| *Penicillium citrinum*              | TiO₂-coated air filter                     | Lin and Li (2003a, b)   |
| *Penicillium expansum*              | TiO₂ spray coated on polypropylene film    | Maneerat and Hayata (2006) |
| *Penicillium oxalicum*              | TiO₂-coated concrete                       | Giannantonio et al. (2009) |
| *Pestalotiopsis maculans*           | TiO₂-coated concrete                       | Giannantonio et al. (2009) |
| *Saccharomyces cerevisiae*          | Aerosil P25 suspension                      | Matsunaga et al. (1985) |
| *Sacchararomyces cerevisiae*        | Pd-doped TiO₂                              | Erkan et al. (2006)     |
| *Spicellum roseum*                  | TiO₂ suspension                            | Sawada et al. (2005)    |
| *Trichoderma asperellum*            | TiO₂-coated concrete                       | Giannantonio et al. (2009) |
| *Trichoderma harzianum*             | TiO₂ suspension                            | Sawada et al. (2005)    |

Microscopic changes during PCD

TEM images of treated cells of *S. sobrinus* showed clearly that the cell wall was partially broken after cells had undergone TiO₂ photocatalytic treatment for 60 min, with further disruption after 120 min (Saito et al. 1992). The authors suggested that cell death was caused by alterations in cell permeability and the decomposition of the cell wall. SEM images of *S. aureus*, MRSA, *E. coli* and *M. luteus* showed morphological changes suggestive of cell wall disruption after UVA irradiation on apatite-coated TiO₂ on cotton fabrics (Kangwansupamonkon et al. 2009).

Damage to the cell wall of *P. aeruginosa* was shown by SEM and TEM, which showed changes in membrane structure such as “bubble-like protuberances which expelled cellular material” (Fig. 3; Amezaga-Madrid et al. 2002, 2003). They suggested that leakage of cellular material, and possibly abnormal cell division, was occurring, although the bubbles may have been due to localised
damage to the peptidoglycan layer allowing the inner membrane to bulge through the peptidoglycan layer. Sunada et al. (2003b) studied killing of E. coli on thin films of TiO₂ and showed that the outer membrane was damaged first and then the cytoplasmic membrane followed by complete degradation. Photocatalytic killing occurred without substantial visible degradation of peptidoglycan. Atomic force microscopy measurements of cells on

Table 6  Protozoa and algae shown to be killed by photocatalytic disinfection

| Organism                  | Notes                                                                 | Reference                      |
|---------------------------|----------------------------------------------------------------------|--------------------------------|
| Protozoa                  |                                                                      |                                |
| *Acanthamoeba castellanii*| Degussa P25 suspension Only 50% kill for cysts, trophozoites were sensitive | Sökmen et al. (2008)           |
| *Acanthamoeba polyphaga*  | Degussa P25 suspension                                               | Lonnen et al. (2005)           |
| *Cryptosporidium parvum*  | UV irradiation                                                        | Ryu et al. (2008)              |
| *Giardia sp.*             | Fibrous ceramic TiO₂ filter                                          | Curtis et al. (2002)           |
| *Giardia intestinalis*    | TiO₂ (anatase 99.9%) + Ag⁺                                            | Sökmen et al. (2008)           |
| *Giardia lamblia*         | TiO₂ thin film catalyst                                               | Lee et al. (2004)              |
| *Tetrahymena pyriformis*  | TiO₂ suspension                                                       | Peng et al. (2010)             |
| Algae                     |                                                                      |                                |
| *Amphidinium corterae*    | Ag–TiO₂ catalyst                                                      | Rodriguez-Gonzalez et al. (2010)|
| *Chlorella vulgaris*      | TiO₂–Pt catalyst                                                      | Matsunaga et al. (1985)        |
| *Cladophora sp.*          | TiO₂-covered glass beads                                              | Peller et al. (2007)           |
| *Chroococcus sp.* 27269   | Anatase, fluorescent light                                            | Hong et al. (2005)             |
| *Melosira sp.*            | TiO₂-coated glass beads                                               | Kim and Lee (2005)             |
| *Oedogonium sp.*          | TiO₂-coated concrete                                                  | Linkous et al. (2000)          |
| *Tetraselmis suecica*     | Ag–TiO₂ catalyst                                                      | Rodriguez-Gonzalez et al. (2010)|

Table 7  Viruses shown to be killed by photocatalytic disinfection

| Host                  | Virus                                      | Reference                      |
|-----------------------|--------------------------------------------|--------------------------------|
| *Bacteroides fragilis*| Not specified                              | Armon et al. (1998)            |
| Birds                 | Influenza (avian) A/H5N2                   | Guillard et al. (2008)         |
| *E. coli*             | Coliphage                                  | Guimarães and Barretto (2003)  |
| *E. coli*             | λvir                                      | Gerrity et al. (2008)          |
| *E. coli*             | T4                                        | Ditta et al. (2008), Sheel et al. (2008) |
| *E. coli*             | λNM1149                                    | Yu et al. (2008)               |
| *E. coli*             | φX174                                      | Belhácová et al. (1999)        |
| *E. coli*             | MS2                                        | Gerrity et al. (2008)          |
| *E. coli*             | Qβ                                         | Sjogren and Sierka (1994), Greist et al. (2002), Cho et al. (2004, 2005), Sato and Taya (2006a, b), Vohra et al. (2006), Gerrity et al. (2008) |
| Human                 | Hepatitis B virus surface antigen HBsAg | Zan et al. (2007)              |
| Human                 | Influenza A/H1N1                           | Lin et al. (2006)              |
| Human                 | Influenza A/H3N2                           | Kozlova et al. (2010)          |
| Human                 | Norovirus                                  | Kato et al. (2005)             |
| Human                 | *Poliovirus* type 1 (ATCC VFR-192)         | Watts et al. (1995)            |
| Human                 | SARS coronavirus                          | Han et al. (2004)              |
| Human                 | Vaccinia                                   | Kozlova et al. (2010)          |
| *Lactobacillus casei*  | PL-1                                       | Kakita et al. (1997, 20000), Kashige et al. (2001) |
| *Salmonella typhimurium*| PRD1                                      | Gerrity et al. (2008)          |
illuminated TiO$_2$ film showed that the outer membrane decomposed first (Sunada et al. 2003b).

TEM images showed progressive destruction of E. coli cells on Ag/AgBr/TiO$_2$ in suspension (Hu et al. 2006). Cell membrane was degraded first followed by penetration of TiO$_2$ particles into the cell and further damage. TEM of E. coli showed that there were changes to the nucleoid which became condensed, possibly due to leakage of ions out of the cell (Chung et al. 2009).

TEM of thin sections of treated cells of E. coli on a visible light-activated TiO$_2$ showed various degrees of cell disruption including plasmolysis, intracellular vacuoles ghost and cell debris (Vacaroiu et al. 2009). SEM and TEM studies showed initial swelling and rough appearance of the cells followed by scars and holes in the OM.

TEM of thin sections of treated cells of E. coli on a visible light-activated TiO$_2$ showed various degrees of cell disruption including plasmolysis, intracellular vacuoles ghost and cell debris (Vacaroiu et al. 2009).

Atomic force microscopy was used to show membrane damage to E. coli, S. aureus and Diplococcus (Streptococcus) pneumoniae on thin films of TiO$_2$ (Miron et al. 2005). Changes to treated cells of S. aureus seen by TEM included separation of cytoplasmic membrane from the peptidoglycan layer (Chung et al. 2009). Distortion of treated cells of both MRSA and methicillin-sensitive S. aureus was seen by SEM on anatase–brookite (Shah et al. 2008), again suggesting cell wall damage.

Lipid peroxidation by ROS was demonstrated by the release of MDA as a breakdown product, and there was a concurrent loss of membrane respiratory activity measured by reduction of 2,3,5-triphenyltetrazolium chloride (Maness et al. 1999). The demonstration of degradation of E. coli endotoxin without substantial degradation of peptidoglycan (Sunada et al. 1998) suggested that in the case of Gram-negative bacteria, cell disruption occurred in the order of OM→PG→IM. However, alterations to the peptidoglycan layer may not be obvious in electron micrographs as peptidoglycan is a highly cross-linked structure and

**Table 8** Microbial toxins inactivated by photocatalysis

| Toxin               | Publication                                      |
|---------------------|-------------------------------------------------|
| Brevetoxins         | Khan et al. (2010)                              |
| Cylindrospermopsin  | Senogles et al. (2000, 2001)                    |
| Lipopolysaccharide endotoxin | Sunada et al. (1998)                  |
| Microcystin-LR      | Feitz and Waite (2003)                          |
|                     | Lawton et al. (1999, 2003)                      |
|                     | Cornish et al. (2000)                           |
| Microcystins LR, YA and YR | Shephard et al. (1998)                  |
| Nodularin           | Liu et al. (2005)                               |

especially where the TiO$_2$ particles were in contact with the cells. Erdem et al. (2006) showed damage by SEM on E. coli and production of membrane breakdown products. SEM has shown changes to the outer membrane of E. coli (Li et al. 2008; Shah et al. 2008; Gartner et al. 2009). TEM of thin sections of treated cells of E. coli on a visible light-activated TiO$_2$ showed various degrees of cell disruption including plasmolysis, intracellular vacuoles ghost and cell debris (Vacaroiu et al. 2009).

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**Fig. 2** Scanning electron micrographs of photocatalytically treated E. coli: a Untreated cells. b, c Cells after 240 min. d Cells after 30 min. Catalyst TiON thin film. From Wu et al. (2010a, b)
appreciable damage may occur without destruction of its overall appearance. Localised destruction may occur where TiO$_2$ particles are in contact with the cell. This may allow protrusion of inner membrane through the cell wall as seen by Amezaga-Madrid et al. (2003), followed by total rupture of the cell wall.

Yao et al. (2007c) showed damage to cells of *Erwinia carotovora* and DNA damage, which suggested that damage to DNA was responsible for cell death. However, our own data showed that there was no DNA damage seen by COMET assay on plain TiO$_2$ surfaces even when 97% of the cells were non-viable (Varghese and Foster, unpublished data; Fig. 4). Damage to DNA does occur on TiO$_2$ (Wamer et al. 1997; Hirakawa et al. 2004; Wang and Yang 2005; Wang et al. 2005; Gogniat and Dukan 2007; Shen et al. 2008; Yao et al. 2007c; Yang and Wang 2008), but is probably a late event after rupture of the membrane and cell death.

**Killing of other microorganisms**

There have been fewer studies on the mechanism of killing of eukaryotes. Linkous et al. (2000) suggested that death of the alga *Oedogonium* sp. was due to nonspecific breakdown of cellular structures. Microscopy has shown membrane damage to the alga *Chroococcus* sp. (Hong et al. 2005). Light microscopy and SEM showed damage to cell walls of *Candida albicans* suspended over a thin film of TiO$_2$ (Kühn et al. 2003) and on TiO$_2$-coated tissue conditioner (Akiba et al. 2005). Cell wall and membrane damage to cysts were seen with light microscopy of photocatalytically treated *Giardia lamblia* (Sökmen et al. 2008). Membrane damage was also shown to occur on
treatment of the ciliate protozoan *Tetrahymena pyriformis* (Peng et al. 2010).

Killing of *Lactobacillus* phage PL1 by thin films of TiO$_2$ suspended in liquid was reported to be via initial damage to protein of the capsid by -OH, followed by damage to the phage DNA inside the particles (Kashige et al. 2001). SEM showed ghost particles and empty heads. Damage to the H and N projections of influenza virus A/H1N1 occurred on PCD and was followed by total mineralisation (Lin et al. 2006).

Spectroscopic studies

The activity of titanium dioxide on isolated phospholipid bilayers has been shown to result in disruption of the bilayer structure using X-ray diffraction (Suwalsky et al. 2005), laser kinetic spectroscopy and attenuated total reflection Fourier transform infrared spectroscopy (FTIR). Disruption was shown to be due to lipid peroxidation (Kiwi and Nadtochenko 2004; Nadtochenko et al. 2006) measured by production of malondialdehyde (MDA). Lipid peroxidation occurs when polyunsaturated fatty acids such as linoleic acid are attacked by ROS (Kiwi and Nadtochenko 2005).

FTIR spectra of treated *E. coli* confirmed the production of carboxylic acids such as MDA as products of membrane degradation. MDA was further degraded by longer irradiation times (Hu et al. 2007).

The electron decay on TiO$_2$ was studied using laser kinetic spectroscopy in the presence of phosphatidyl ethanolamine, lipopolysaccharide and *E. coli* (Nadtochenko et al. 2006). Spectroscopic studies using FTIR spectroscopy suggested that organic components bound to the TiO$_2$ were directly oxidised by reduction of the electron holes (Nadtochenko et al. 2006, 2008). This work suggested that direct oxidation of cellular components could occur without the production of ROS, but only if cells were in direct contact with the surface of the TiO$_2$. This is wholly consistent with the greater effectiveness of PCD when the cells are in contact with the TiO$_2$ rather than in suspension. Overall, the spectroscopic studies support the light microscopic studies and confirm the order of destruction being OM $\rightarrow$ IM $\rightarrow$ PG. Details of kinetic models of the killing mechanism are presented by Dalrymple et al. (2010).

The role of ROS in killing of bacteria is summarised in Fig. 5.

**Role of ROS in the killing mechanism**

Most studies show that ROS are responsible for the killing, and various authors propose that -OH are responsible (Ireland et al. 1993; Kikuchi et al. 1997; Maness et al. 1999; Salih 2002; Cho et al. 2004, 2005; Cho and Yoon 2008). Lipid peroxidation by ROS was demonstrated by the release of MDA as a breakdown product, and there was a concurrent loss of membrane respiratory activity measured by reduction of 2,3,5-triphenyltetrazolium chloride (Maness et al. 1999). The -OH scavengers, dimethylsulphoxide and cysteamine, eliminated the PCD activity of suspensions of TiO$_2$ in water (Salih 2002). However, -OH are short-lived and will probably not diffuse further than 1 $\mu$m from the surface of the TiO$_2$, especially in the presence of organic matter (Pryor 1986; Kikuchi et al. 1997). Kikuchi et al. (1997) showed that killing of *E. coli* still occurred even when the bacteria were separated from the surface by a 50-$\mu$m-thick porous membrane. However, the free radical scavenger mannitol only inhibited killing without the membrane, whereas catalase, which would degrade H$_2$O$_2$, decreased killing both with and without the membrane. This suggested that -OH and H$_2$O$_2$ were responsible for killing close to the TiO$_2$, with H$_2$O$_2$ acting at a distance. The role of other ROS, e.g. O$_2^-$, was not considered. However, no killing was seen when cells were separated from the TiO$_2$ by a dialysis membrane in a separate study (Guillard et al. 2008). Hydrogen peroxide may act at a distance if ferrous ions are present by producing -OH via the Fenton reaction (8 and 9).

$$\text{Fe}^{3+} + \text{O}_2^- \rightarrow \text{Fe}^{2+} + \text{O}_2 \quad (8)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \quad (9)$$
A study of the roles of H$_2$O$_2$ and ·OH in an immobilised TiO$_2$ thin film reactor activated by UVC using electron spin resonance suggested that ·OH were produced by direct photolysis of H$_2$O$_2$ as well as by Eqs. 3 and 4 (Yan et al. 2009).

A role for ·OH in sonocatalysis on TiO$_2$ (where the energy to bridge the band gap is provided by sound waves) was suggested by the work of Ogino et al. 2006 who showed that the killing was inhibited by the ·OH scavenger glutathione. Hydroxyl radicals produced by microwave irradiation of TiO$_2$ were shown to enhance the killing of $E$. coli (Takashima et al. 2007).

Hydroxyl radicals were shown to be the major ROS involved in killing of $C$. parvum cysts, although other ROS were also involved (Cho and Yoon 2008).

Studies with hydroxyl radical scavengers suggested that inactivation of phage in suspensions of TiO$_2$ also occurred due to bulk phase ·OH, whereas inactivation of bacteria occurred with both bulk phase and surface ·OH (Cho et al. 2004, 2005). The rate of inactivation of $E$. coli correlated with the concentration of ·OH. A role for other ROS such as H$_2$O$_2$ and O$_2^-$ was also suggested.

Studies on superoxide dismutase (SOD)-defective $E$. coli have shown that oxidative damage to the membrane combined with the turgor pressure inside the cell initially permeabilizes the cell envelope, allowing critical metabolites to escape (Imlay and Fridovich 1992). Studies on oxidative damage caused by TiO$_2$ in SOD mutants of $E$. coli showed that the inactivation rate was inversely proportional to SOD activity (Koizumi et al. 2002; Kim et al. 2004).

Kinetic models and further details of the chemistry of the killing mechanism are presented by Dalrymple et al. (2010). The role of hvb$^+$ and ROS in killing of bacteria is summarised in Fig. 5.

Importance of contact between bacteria and TiO$_2$

Many studies have shown that close contact between the bacteria and the TiO$_2$ increases the extent of oxidative damage. Studies on the disinfection of water have shown that suspended TiO$_2$ is more active than TiO$_2$ immobilised on surfaces, e.g. on thin films (Lee et al. 1997; Otaki et al. 2000; Sun et al. 2003; Gumy et al. 2006b; Marugan et al. 2006, 2008; Cohen-Yaniv et al. 2008). This is probably due to increased contact between the TiO$_2$ particles and the bacterial cells in suspension as well as an increased surface area for ROS production. A number of studies confirm the importance of such contact (Horie et al. 1996a, b, 1998; Gumy et al. 2006a; Pratap Reddy et al. 2008; Caballero et al. 2009; Cheng et al. 2009). Co-precipitation of cells and TiO$_2$ particles from suspension by alum enhanced killing of $E$. coli (Salih 2004). Certain ionic species have been shown to inhibit PCD, e.g. PO$_4^{3-}$ (Araña et al. 2002; Koizumi and Taya 2002a, b; Christensen et al. 2003; Rincón and Pulgarín 2004b; Egerton et al. 2006; Xiong et al. 2006; Marugan et al. 2008) and HCO$_3^-$ (Rincón and Pulgarín 2004b; Coleman et al. 2005; Gogniat et al. 2006), and the rate of adsorption onto the TiO$_2$ in the presence of different ions correlated with the rate of inactivation, suggesting that the inhibition was due to the prevention of binding of the bacteria to the TiO$_2$ particles. Light micrographs (Nadtochenko et al. 2005; Gumy et al. 2006b; Gogniat et al. 2006) and electron micrographs clearly show binding of the titania particles to bacterial cells (Gumy et al. 2006a, b; Saió et al. 1992; Cheng et al. 2007; Shah et al. 2008). A micrograph showing particles of TiO$_2$ attached to an $E$. coli cell is shown in Fig. 6. Contact with highly crystalline TiO$_2$ may also cause physical damage to the cells (Liu et al. 2007c; Caballero et al. 2009).

Although differences in binding of isolated O antigens to TiO$_2$ have been shown ($E$. coli O8 and Citrobacter freundii O antigens bound strongly to TiO$_2$, whereas that from Stenotrophomonas maltophilia had a low affinity for TiO$_2$; Jucker et al. 1997), differences in the susceptibility of bacteria with different O antigens have not been studied. Differences in the susceptibility of different strains of Legionella pneumophila correlated with the amount of saturated 16C branched chain fatty acids in the membrane (Cheng et al. 2007). The more hydrophobic cells of

![Fig. 6](https://example.com/fig6.png)
Flavobacterium sp. were more easily killed by PCD than E. coli (Cohen-Yaniv et al. 2008), which may also have been due to altered interactions with the TiO₂.

In an attempt to increase contact between the cells, Benabbou et al. (2007) studied the PCD of a strain of E. coli overexpressing curli, pili, which enhance adhesion to abiotic surfaces. However, the strain was more resistant than the non-piliated control, and evidence of protein degradation suggested that the pili were being degraded before the membrane was damaged and therefore protected the membrane from damage. The presence of extracellular polysaccharides interfered with PCD of biofilms of P. aeruginosa (Gage et al. 2005) and a natural biofilm (Liu et al. 2007a), but killing was seen throughout a biofilm of Staphylococcus epidermidis on a TiO₂ catalyst (Dunlop et al. 2010). The different biofilms and catalysts may explain these anomalies.

The inhibition of close contact between coliphage MS2 and TiO₂ by certain cations was shown by Koizumi and Taya (2002a, b), and the rate of inactivation was proportional to adsorption of the phage onto the TiO₂. Sato and Taya (2006a, b) showed that the presence of organic materials protected the phage by adsorbing to the surface of the TiO₂, preventing phage binding.

Cell mineralisation

Following initial cell damage and cell death, photocatalysis has been shown to be capable of complete mineralisation of bacteria on air filters using ¹⁴C-labelled cells (Jacoby et al. 1998; Wolfrum et al. 2002) and for cells suspended in water (Cooper et al. 1997; Sökmen et al. 2001). The total oxidation of Legionella by PCO was measured by total organic carbon analysis (Cheng et al. 2007). An almost complete degradation of E. coli was demonstrated on prolonged treatment on a TiO₂-activated charcoal catalyst (Li et al. 2008). Nadtochenko et al. (2008) showed total oxidation of cell organic matter by total internal reflection/FTIR. Removal of microorganisms during regeneration of photocatalytic TiO₂-coated air filters by complete removal of contaminants has also been shown by SEM (Goswami et al. 1999; Ortiz López and Jacoby 2002). Penetration of TiO₂ particles into the cells was shown using an Ag/AgBr/TiO₂ catalyst (Hu et al. 2006).

A scheme for the killing mechanism of TiO₂ on bacteria is shown in Fig. 7. We suggest that there may be initial damage on contact between the cells and TiO₂, which affects membrane permeability, but is reversible. This is followed by increased damage to all cell wall layers, allowing leakage of small molecules such as ions. Damage at this stage may be irreversible, and this accompanies cell death. As the peptidoglycan is a highly cross-linked molecule, damage may not be visibly evident at this stage or may be localised if the TiO₂ is in contact with the cells. Further membrane damage allows leakage of higher molecular weight components such as proteins, which may be followed by protrusion of the cytoplasmic membrane into the surrounding medium through degraded areas of the peptidoglycan and lysis of the cell. Degradation of the internal components of the cell then occurs, followed by complete mineralisation. The degradation process may occur progressively from the side of the cell in contact with the catalyst.

Dual function materials

Copper-deposited films show enhanced PCD activity (Sunada et al. 2003a; Foster et al. 2010; Wu et al. 2010a; Yates et al. 2008a, b). A clear synergy in photokilling of E. coli on Cu-containing TiO₂ films was shown by Sato and Taya (2006c) who showed that H₂O₂ was produced from the photocatalyst and Cu²⁺ leached from the surface, but neither reached high enough concentrations to kill the E. coli directly. They suggested that the Cu²⁺ was reduced to Cu⁺ (10) which reacted with the H₂O₂ to produce "OH via a Fenton-type reaction (11), which was responsible for killing cells in suspension and explaining why catalase reduced this activity. Inclusion of Cu also gave higher PC activity, hence the enhanced killing of cells bound to the TiO₂. In our own work, we have seen DNA damage when TiO₂/
CuO surfaces were used (Fig. 4). Thus, Cu may also kill cells by DNA damage as well as membrane damage. This is consistent with the observed enhancement of damage to DNA and protein caused by ROS (Cervantes-Cervantes et al. 2005).

\[ \text{Cu}^{2+} + \text{e}^{-}_{cb} \rightarrow \text{Cu}^+ \]  

\[ \text{H}_2\text{O}_2 + \text{Cu}^+ \rightarrow \text{HO}^- + \text{OH}^- + \text{Cu}^{2+} \]

Similar synergy has been shown between Ag and TiO2. Ag enhances photocatalysis by enhancing charge separation at the surface of the TiO2 (Sökmens et al. 2001; He et al. 2002; Hirakawa and Kamat 2005; Kubačka et al. 2008b; Liu et al. 2007b; Musil et al. 2009). Ag+ is antimicrobial and can also enhance generation of ROS (Eqs. 12, 13 and 14).

\[ \text{Ag}^+ + \text{O}_2^- \rightarrow \text{Ag}^0 + \text{O}_2 \]  

\[ \text{Ag}^0 + \text{O}_2^- \rightarrow \text{Ag}^+ + \text{O}_2^{2-} \]  

\[ \text{H}_2\text{O}_2 + \text{Ag}^0 \rightarrow \text{HO}^- + \text{OH}^- + \text{Ag}^+ \]

Conclusions

Generation of ROS by photocatalysis on TiO2 is capable of killing a wide range of organisms including bacteria endospores in water, in air and on surfaces, including various materials. The technology has the potential to provide a powerful weapon in the fight against transmission of infectious diseases, particularly in view of the development of visible light-activated catalysts.

One of the problems is that until relatively recently, there has not been an accepted standard method for the testing of the antimicrobial efficiency of photocatalytic processes. For example, many different strains of E. coli have been used (Table 2) with different growth media and test conditions. This makes it very difficult to compare results from different research groups. In the second part of this review, we will investigate the evaluation of photocatalytic killing activity.

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