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SHORTER COMMUNICATION

PHOTOCATALYTIC DISINFECTION WITH TITANIUM DIOXIDE COATED MULTI-WALL CARBON NANOTUBES

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TiO_2 photocatalysis is currently being investigated as a viable technology to combat biological warfare agents such as anthrax spores. The current challenge in the use of photocatalysis for degradation of bacterial endospores is the time (in hours, as compared to minutes for bacteria) required for disinfection. The rate of disinfection can be increased by changing the rate of recombination of photon-generated electron-hole pairs and the rate of generation of reactive species. Modified photocatalysts has been synthesized by coating titanium dioxide, in anatase polymorph, on multi-wall carbon nanotubes (around 20 nm in diameter and 2–4 microns in length), for increasing the disinfection rate of bacterial endospores. Anatase coated multi-wall carbon nanotubes were tested for disinfection of *Bacillus cereus* spores (used as surrogate for anthrax spores) and the disinfection rate was shown to be twice as compared to the commercial titanium dioxide nanopowders, Degussa P25 (primary particle size of around 25 nm). These modified photocatalysts can also be used for selective disinfection of microorganisms depending on the surface morphology of the bacterial cell wall and the shape of the photocatalysts.

Keywords: photocatalysis; bacterial endospores; titanium dioxide; carbon nanotubes.

INTRODUCTION

Endospores of bacteria are the most resistant microorganisms against all disinfection and sterilization techniques (Block, 2001). Their high degree of resistance is governed by a unique spore structure, as shown in Figure 1. Each level of spore structure provides resistance to different disinfectants. The small acid soluble proteins (SASP) in the core protect the DNA from UV radiation, whereas cortex provides heat resistance and the spore coat layers protects the spore from chemical attack (Atrih and Foster, 2002). The available disinfection/sterilization techniques have limitations that they are effective only in wet or dry state or can damage the substrate on which the disinfection/sterilization process is carried out (Block, 2001). Photocatalysis using titanium dioxide (TiO_2) particles can be used for disinfection of air and water environments. They can also be used for disinfection of surfaces, without causing any damage to the surface.

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PHOTOCATALYSIS WITH TiO_2

Titanium dioxide, when irradiated with ultraviolet (UV) light, is known to generate reactive species which help in mineralization of organic compounds. There is now a wide agreement regarding the mechanism of generation of reactive species. The first event, after absorption of UV radiation, is the generation of electron-hole pairs. As shown in Figure 2, when titanium dioxide particles are irradiated with UV light of wavelength corresponding to band gap energy of titanium dioxide, the electrons from valence band are excited to conduction band. These photon-generated electron–hole pairs can either recombine or take part in redox reactions. Majority of photon-generated electron–hole pairs recombine with dissipation of heat, as the rate of recombination is fast, occurring in few nanoseconds. Some electron-hole pairs are successful in migration to surface, where they react with adsorbed electron acceptors and donors. The migration and surface reactions are slow processes occurring from tens of nanoseconds to milliseconds. Titanium dioxide particles which are either modified or doped with other semiconductor or metals have meta-stable state which can trap electrons, thereby reducing the recombination rate (Hoffmann *et al.*, 1995).

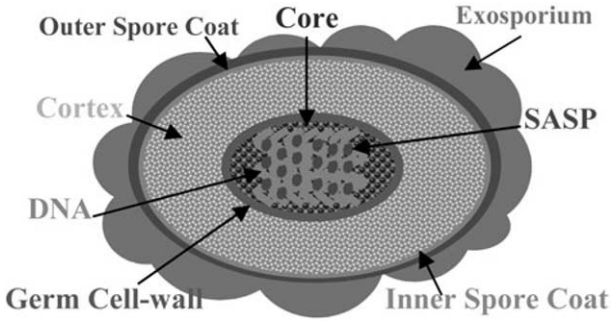

Figure 1. Structure of bacterial endospore.

Some of the reactions which may take place after irradiation, in an aqueous solution containing an organic substance (RX) are summarized below (Rincon and Pulgarin, 2003; Hoffmann *et al.*, 1995).

(1) $TiO_2 + h\nu \longrightarrow TiO_2\ (e^- + h^+)$
(2) $TiO_2\ (h^+) + RX \longrightarrow TiO_2 + RX^+$
(3) $TiO_2\ (h^+) + H_2O \longrightarrow TiO_2 + {}^{\cdot}OH + H^+$
(4) $TiO_2\ (h^+) + {}^-OH \longrightarrow TiO_2 + {}^{\cdot}OH$
(5) $TiO_2\ (e^-) + O_2 \longrightarrow TiO_2 + O_2^{\cdot}$
(6) $TiO_2\ (e^-) + H_2O_2 \longrightarrow TiO_2 + OH^- + {}^{\cdot}OH$

For degradation of organic compounds, it is necessary that the organic compounds are adsorbed on the surface of photocatalyst. In case of disinfection of microorganisms, the photocatalyst should be adsorbed on the microorganisms. Complete oxidation of organic compounds and *Escherichia coli* cells to carbon dioxide has been reported using titanium dioxide (Jacoby *et al.*, 1998).

MECHANISM OF MICROBIAL INACTIVATION BY PHOTOCATALYSIS

A better understanding of microbial inactivation has evolved since the first proposed mechanism by Matsunaga and co-workers (Matsunaga *et al.*, 1985). They proposed that the cell death was caused by decrease in respiratory activity due to photocatalytic oxidation of intracellular coenzyme A. The extent of inactivation was observed to be inversely proportional to the thickness and complexity of the cell wall. Saito *et al.* (1992) proposed that the cell death occurs due to photocatalytic disruption of cell membrane, evident from leakage of intracellular K^+ ions. Leakage of Ca^+ ions has also been observed with cancer cells. Sunada *et al.* (1998) found that endotoxin, an integral component of the outer membrane was degraded by photocatalytic action of TiO_2, which leads to membrane damage. Maness *et al.* (1999) showed that TiO_2 photocatalytic reaction causes the lipid peroxidation reaction, which results in disruption of normal activities associated with intact cell membrane, such as respiration. The loss of membrane structure was proposed to be the root cause of cell death. Lu *et al.* (2003) also showed that cell death was caused by the decomposition of the cell wall and cell membrane resulting in leakage of intracellular components, as shown in Figure 3. Since the cell death is caused by photocatalytic degradation of cell wall, the inactivation time is proportional to the complexity and density of cell wall structure (Kuhn *et al.*, 2003). Endospores, with their complex and dense shell structure, have the longest inactivation time (in hours compared to minutes for simple bacteria). The photocatalytic inactivation time can be decreased by increasing the generation of reactive species, which can be achieved by delaying the recombination process.

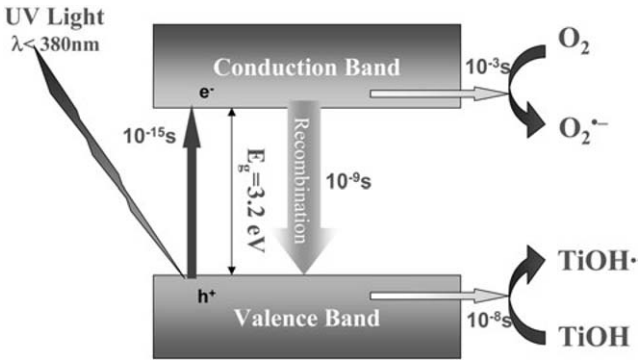

Figure 2. Steps in photoelectrochemical mechanisms.

MODIFICATION OF ELECTRONIC PROPERTIES OF TITANIUM DIOXIDE

Electronic property modification is usually done by creating an additional band (meta-stable state) near the conduction band, where the electron can remain for a longer time (Hoffmann *et al.*, 1995). The photon-generated electron-hole pairs recombine at a faster rate (10^{-9} s) than the generation of reactive species (10^{-8}–10^{-3} s) (Hoffmann *et al.*, 1995). Decreasing the recombination rate, by trapping the photon-generated electrons or holes, will increase the production of reactive species and hence the overall efficiency of photocatalysis. Several attempts have been made to increase the photocatalytic efficiency of TiO_2. Noble metals like gold, silver, platinum, palladium have been incorporated into TiO_2 either by deposition or by ion doping (Arabatzis *et al.*, 2003; Matos *et al.*, 2001; Wang *et al.*, 2002; Hu *et al.*, 2003). Although, such modifications can result in contradictory results. Experimental investigations on gold—titanium dioxide nanocomposite particles showed that the response of photocatalyst is extended to visible region with a significant decrease in their photocatalytic performance under ultraviolet radiation (Arabatzis *et al.*, 2003). Use of co-adsorbents such as silica, alumina, zeolites and activated carbon have also been explored for increasing the efficiency of photocatalysis (Matos *et al.*, 2001).

Dr Sigmund and co-workers at University of Florida have synthesized photocatalyst nanocomposites with such modifications. Multi-wall carbon nanotubes, which have

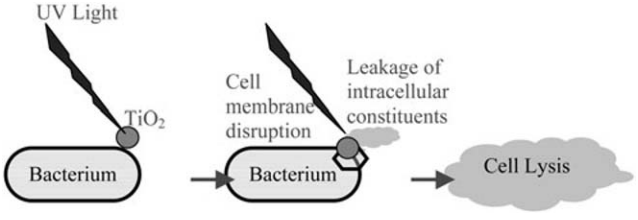

Figure 3. Photocatalytic killing of a bacterium.