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Antimicrobial properties of highly efficient photocatalytic TiO_2 nanotubes

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ABSTRACT

A rapid chlorine-based electrochemical anodization method resulted in the production of free-standing bundles of titania (TiO_2) nanotubes with high-aspect ratio (up to 100 μm long and about 20 nm in diameter). XRD and Raman spectroscopy revealed the presence of partially crystalline amorphous titania nanostructures modified with surface hydroxyl groups. Photocatalytic antimicrobial properties of these nanotubes have been investigated using *Escherichia coli* and *Staphylococcus aureus* and compared with a commercial reference sample, Evonic-Degussa P25. Titania nanotubes were found to be highly efficient in inactivating both *E. coli* (97.53%) and *S. aureus* (99.94%) in under 24 h of UV irradiation. On the other hand, commercial Evonik Degussa P-25 titania nanoparticles and control samples did not reveal antimicrobial properties for the same amount of time under either light or dark conditions. These results indicate that along with material properties, the high-aspect ratio nanotube architecture, surface hydroxyls, physico-chemical properties of TiO_2 nanotubes as well as experimental conditions of the biological investigations play a significant role in the antibacterial activity.

1. Introduction

Titanium dioxide is an extensively studied semiconductor due to its great potential in the photocatalytic degradation of organic pollutants and bacteria [1–6]. Recently, there has been a great influx of interest in using nanostructured titania for enhancing the efficiency of photocatalytic applications. In this regard, the nanotube architecture is one of the most promising morphologies for antimicrobial applications because of desirable features such as high-aspect ratio, enhanced active surface area and improved light harvesting and trapping. While titania nanotubes have been produced in the past either using a hydrothermal method or using a fluoride-based electrochemical method, a novel and efficient route for the synthesis of very long, high-aspect ratio nanotubes (up to 100 μm long and about 20 nm in diameter) using a simple chlorine-based electrochemical method has been recently demonstrated [7–9]. This procedure results in the production of free-standing bundles of nanotubes with surface hydroxyl groups. Such high-aspect ratio, surface hydroxyl rich and highly porous particles can be directly used for photocatalytic antimicrobial applications.

The photocatalytic process involves the formation of electron (e^-_{CB}) and hole (h^+_{VB}) pairs upon the irradiation of light that exceeds the band gap energy (3.2 eV) of TiO_2. Positive holes (h^+_{VB}) become trapped by water molecules in the atmosphere. The water molecule is oxidized by h^+_{VB} producing H^+ and $^\bullet OH$ radicals, which are extremely powerful oxidants [1,2]. The hydroxyl radicals then oxidize organic molecules from the surrounding environment to final products such as CO_2, mineral acids and H_2O. Electrons in the conduction band (e^-_{CB}) can be rapidly trapped by atmospheric

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oxygen. The oxygen can further be reduced by e^-_{CB} to form superoxide ($O^{2-\bullet}$) radicals that will further combine with H^+, to form peroxide radicals ($^\bullet OOH$) and hydrogen peroxide, H_2O_2. These reactive oxidation species produced during the irradiation process are able to oxidize the majority of volatile organic compounds (VOC) and organic matters such as bacteria until complete mineralization . The objective of the current investigation was to understand the antimicrobial properties of the hydroxyl group modified titania nanotubes which are produced by rapid breakdown anodization.

2. Experimental

2.1. Synthesis and characterization of titania nanotube powders

Powders of amorphous titanium dioxide (titania) nanotubes have been synthesized by DC (V = 16 V) rapid breakdown anodization [7–9] of 0.89 mm thick titanium foil (Alfa Aesar, 99.7% metal basis) for several hours in an aqueous solution containing 0.1 M ammonium chloride (Alfa Aesar, purity >99.5%). Bundles of nanotubes were continuously released in the solution from corrosion sites on the titanium foil surface, forming a white precipitate which was recovered, washed repeatedly with water and then with isopropanol, and subsequently dried on a hotplate at about 80 °C. BET (Porous Materials, Inc.) measurements were performed on approximately 0.5 g of powder which was degassed to 20 mTorr at 20 °C prior to measurements, with nitrogen at −195.76 °C used as adsorbate. Separately, bundles of nanotubes were released on a conductive substrate or directly on a transmission electron microscopy (TEM) grid for further examination by scanning electron microscopy (SEM) (Hitachi S4800) or TEM (JEOL 2010F). In addition, the powders were further analysed by Raman spectroscopy (Jobin Yvon LabRam HR800) and X-ray Diffraction (XRD) (PANalytical X'Pert Pro Philips).

2.2. Determination of antimicrobial activity

2.2.1. Preparation of organisms

Gram-negative *Escherichia coli* (ATCC 25922) and gram-positive *Staphylococcus aureus* (ATCC 6538) were chosen to conduct a pure culture study in suspension. First, sterile aliquots of nutrient broth (Oxoid) and Columbia broth (Difco) were inoculated with *E. coli* and *S. aureus*,respectively, and incubated overnight at 37 °C. Next, they were centrifuged, washed with phosphate buffered saline (PBS) and their concentration was adjusted accordingly.

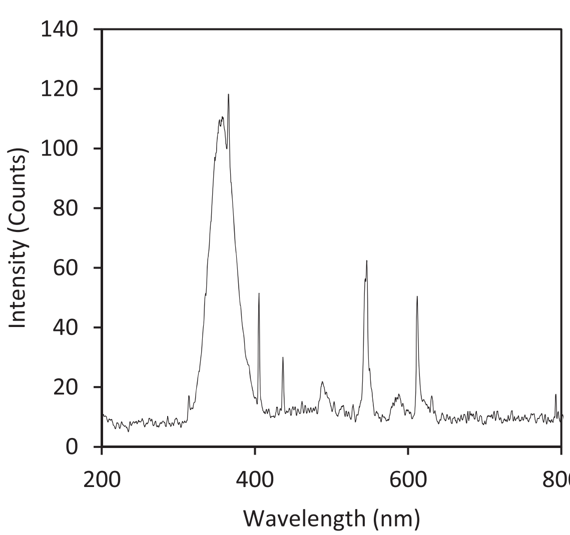

Fig. 1. Emission spectrum of the UV-A/B lamp – light source used in the experiment.

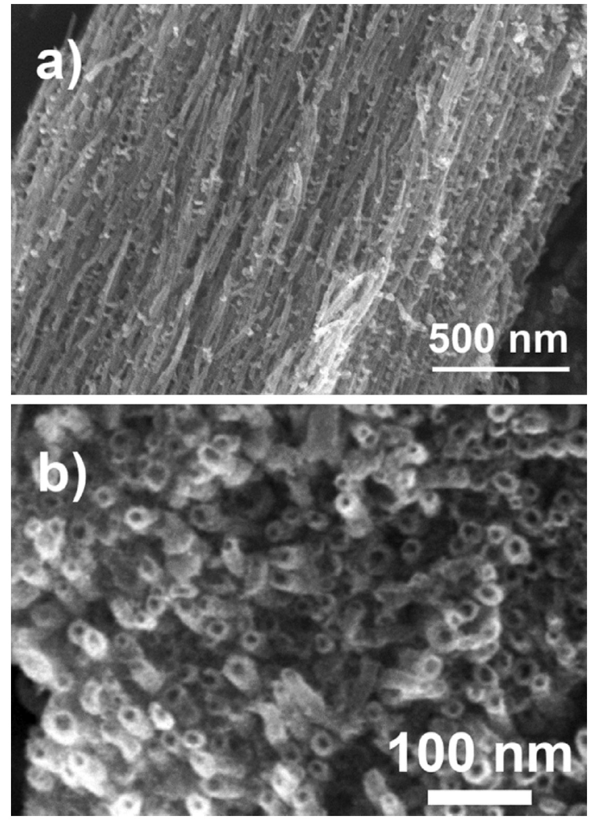

Fig. 2. SEM images of titania nanotubes-based powders; (a) side view of a microscopic grain which is in fact a compact bundle of ordered titania nanotubes; (b) top view of another grain clearly showing tightly bound nanotubes with a diameter of about 20 nm.

2.2.2. Microbiological evaluation

In order to evaluate an effect of TiO_2 nanotubes (TiO_2-NT) on the selected microorganisms, 50 mg/mL suspensions of nano-powders in Müeller-Hinton (M-H) broth were prepared. The effect of TiO_2 nanotubes on activity of *E. coli* and *S. aureus* was determined by evaluation of growth of the cultures in the presence of nano-photocatalyst compared with the growth of the culture in medium only. Commercially available photocatalyst Evonik-Degussa P25 (P25) of the same concentration served as a reference material. Sterile M-H broth or the same broth inoculated with bacteria only served as negative and positive controls, respectively. All solutions were prepared using aseptic methods. For testing, wells of sterile polystyrene plates were filled with 5 mL of previously prepared solutions. Next, bacterial suspensions were added and the final concentration in each well was adjusted to approximately 10^4 colony-forming units/mL (CFU/mL). The prepared systems were divided into two groups: one was exposed to the source of UV-AB light with the emission spectrum presented in Fig. 1, and another left without light access for a total period of 24 h. Samples from both groups were taken at 0, 1, 6 and 24 h of the experiment for further evaluation. The pour plate technique was used to determine the number of surviving organisms. For the microbiological evaluation, samples were tested in triplicate. The results were presented as the mean ± standard deviation.

3. Results and discussion

SEM imaging (Fig. 2) revealed that each microscopic powder grain is in fact a bundle of highly ordered ultra-high aspect ratio titania nanotubes, with average outer diameters around 20 nm and lengths of the order of tens of microns. The grain size is widely