Journal of Catalysis 344 (2016) 631–639

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Titania nanotube photocatalysts for effectively treating waterborne microbial pathogens

Mary Garvey [a,b,*], Eugen Panaitescu [c], Latika Menon [c], Ciara Byrne [b,d], Saoirse Dervin [b,d], Steven J. Hinder [e], Suresh C. Pillai [b,d,*]

[a] Department of Life Sciences, Institute of Technology Sligo, Sligo, Ireland
[b] Centre for Precision Engineering, Materials and Manufacturing Research (PEM), Institute of Technology, Sligo, Ireland
[c] Department of Physics, Northeastern University, Boston, MA 02115, United States
[d] Nanotechnology and Bio-Engineering Research Group, Department of Environmental Science, Institute of Technology Sligo, Ireland
[e] The Surface Analysis Laboratory, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom

ARTICLE INFO

Article history:
Received 12 September 2016
Revised 2 November 2016
Accepted 3 November 2016
Available online 24 November 2016

Keywords:
Titania nanotubes
Anatase
Rutile
Antibacterial
Pathogenic

ABSTRACT

Photocatalysts have been identified as a potential material for the efficient decontamination of lethal bacteria from drinking water. Compared to the traditional spherical powders, TiO_2 nanotube photocatalysts possess a more efficient structure due to the high-aspect ratio and effective light harvest and improved electron/hole trap properties. The impact of various calcination temperatures and phase content on the antibacterial effect on *Escherichia coli*, *Salmonella typhimurium* and *Pseudomonas aeruginosa* has been investigated. Studies show that high levels (99.9–99.99%) of bacterial inactivation were achieved for all species. Significantly higher levels of bacterial toxicity were achieved with the as prepared nanotubes and nanotubes annealed at 200 °C and 400 °C. This is explained as the higher percentages of anatase phase present in the sample. Synthesised nanotubes proved more antibacterial than titania P25 commercial nanoparticles. The order of sensitivity from most sensitive to least sensitive was found to be in the following order: *E. coli*, *P. aeruginosa* and *S. typhimurium*. In addition, bacteria were found to be more susceptible to the inactivation while in the stationary (dormant) phase of growth.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Development of innovative, environmentally benign, non-toxic and cost effective water disinfection methodologies is therefore vital to eliminate the waterborne diseases. The use of nanoparticle materials for antimicrobial activity has become widespread, due to the fact that they possess many desirable properties over their bulk material counterparts. Semiconductor titania nanoparticles (NPs) possess a number of favourable properties such as photocatalytic activity, high surface area, and nontoxicity to mammalian cells, which in addition to their inexpensive nature [1] make them ideal candidates as antimicrobials.

The presence of pathogenic organisms in water supplies has resulted in numerous incidents of water related disease. Species such as *Escherichia coli* [2], *Salmonella typhimurium* [3] and *Pseudomonas aeruginosa* have been found in water sources, where they have been linked to public safety [4]. Typically water disinfection is achieved by chemical means with the use of chlorine, ammonia and ozone and physical means such as filtration and UV light [5]. However, it has become evident that microbial species are becoming resistant to standard disinfection chemicals; furthermore they and their by-products (trihalomethanes (THMs)) are recognized as potential carcinogens [6]. Additionally, the resistance of bacterial species to standard antimicrobials and bactericides has increased due to the emergence of antibiotic resistant strains [7]. It has become clear that the development and establishment of novel water disinfection methods is essential to control waterborne disease and to ensure public safety [8]. Additionally, these methods must be non-toxic, environment friendly and cost effective for efficient water disinfection [9]. It has been established that disinfection using photocatalytic nanoparticles such as TiO_2 occurs following the production of reactive oxygen species (ROS) resulting from redox reactions occurring at the surface of photo-excited semiconductor materials [10]. Following UV exposure, a photon of energy excites electrons from the valence band to the conduction band leaving positive holes in the

* Corresponding authors at: Department of Life Sciences, Institute of Technology Sligo, Ash Lane, Sligo, Ireland.
E-mail addresses: garvey.mary@itsligo.ie (M. Garvey), pillai.suresh@itsligo.ie (S.C. Pillai).

http://dx.doi.org/10.1016/j.jcat.2016.11.004
0021-9517/© 2016 Elsevier Inc. All rights reserved.

valence band [11,12]. These excited electrons and holes can be trapped on or near the TiO_2 surface where they can react with atmospheric water and oxygen, producing ROS, typically hydroxyl radicals ($^{\bullet}OH$) and superoxide anions ($^{\bullet}O_2^-$) [13]. The formation of such ROS is detrimental to microbial species due to ROS attack on microbial cell membranes and other essential components [14]. The tube like morphology of the photocatalysts is one of the most efficient structures due to the desirable characteristics such as high-aspect ratio, improved BET surface area and high pore-volume and effective light harvest and improved electron/hole trap properties [15]. The calcination temperature, surface area and the anatase-rutile content dictate the final photocatalytic anti-microbial properties [16–18]. A number of investigations on the impact of the raw nanotubes (NTs) on various bacteria such as *E. coli* and *S. aureus* have been reported [19]. It should be noted that the anti-microbial activity is highly dependent on the phase content and textural properties of nanotubes [9,18]. To date, no systematic study on the impact of calcination temperature and related phase changes of titania nanotubes to the photocatalytic anti-microbial action on water related microbial pathogens has been reported. This paper is also novel from a microbiological aspect in that it deals with the sensitivity of the test species while in two different phases of growth (stationary and log phase). The susceptibility of microbial species to disinfectants has been known to vary depending on whether the cells are in a resting state (stationary) or actively dividing (log phase) [20]. Furthermore, the resistance of bacterial cells in the stationary phase of growth to chemical disinfection such as chlorine [21] has allowed them to persist in water even after disinfection, increasing the chlorine demand [22]. This study aimed to identify a mechanism of water disinfection which is effective for both life cycle stages of the organisms, something which is currently missing for effective water disinfection/treatment.

Therefore, studies will also determine whether life cycle stage affects their sensitivity to nanoparticle induced disinfection, by treating cells which are rapidly dividing (log phase) and cells which are not actively dividing and are dormant (stationary phase).

2. Methods

2.1. Production and characterisation of TiO_2 nanotube samples

Titania nanotubes have been synthesised using a very fast and inexpensive method involving the anodisation of titanium foil in a chloride-ion containing aqueous solution [23] [24]. Titanium foil (purity 99.7%, thickness 0.89 mm, Alfa Aesar) has been anodised at 13 V DC in a two electrode configuration in a 0.1 M aqueous solution of ammonium chloride, with the pH adjusted to 1.8–2 by addition of hydrochloric acid (all chemicals purchased from Alfa Aesar, reagent grade). Bundles of titania nanotubes were continuously produced in corrosion pits at the surface of the foil and released in the solution, forming in time a precipitate at the bottom of the container. The precipitate was recovered, washed with water and isopropanol, and then dried and sieved to remove large agglomeration, the final product being a white coloured powder where each micron-sized grain was effectively a bundle of nanotubes.

Different samples of powder were subsequently calcined in a tube furnace at various temperatures (200 °C, 400 °C, 600 °C, 800 °C) following the same routine: ramping up the temperature (10 °C/min) followed by 1 h calcination at the final temperature, and then ramping down at the same rate (10 °C/min) to room temperature.

2.2. Characterization of nanotubes

The samples were characterised by means of SEM imaging, XRD, Raman spectroscopy, and BET (porosity), and then employed in antibacterial studies.

The surface morphologies of the nanotubes were investigated using a high-resolution field emission SEM (Hitachi S-4800). X-ray diffraction patterns (XRD) for all powder samples (unheated, 200 °C, 400 °C, 600 °C, and 800 °C) were obtained using a Siemens D500 X-ray powder diffractometer with a diffraction angle range of $2\theta = 10–80°$ using Cu Kα radiation ($\lambda = 0.15418$ nm) in order to examine the impact of calcination temperature and related anatase-rutile phase changes. The spur equation was employed to determine the anatase/rutile phase content of each sample.

$$F_R = \frac{1}{1 + 0.8[I_A(1\,0\,1)/I_R(1\,1\,0)]}$$

where F_R is the quantity of rutile in mixed sample and $I_A(1\,0\,1)$ and $I_R(1\,1\,0)$ are the intensities of the main anatase and rutile peaks.

Raman spectroscopy was utilized as an additional tool to investigate the phase of each TiO_2 nanotube sample. A Horiba Jobin Yvon LabRAM HR 800 system was used. The grating that was used was 300 gr/mm. The objective lens of 100× was used. The laser line used was a 660 nm solid state diode laser standard bandwidth version with double edge filter upgrade and the acquisition time for the data was 3 s.

The textural properties of the TiO_2 nanotubes were investigated by standard N_2 gas adsorption method using a Gemini VII 2390 Surface Area Analyser (Micrometrics). The specific surfaces were calculated by the Brunauer–Emmett–Teller (BET) method. The TiO_2 nanotubes were degassed at 200 °C for one hour and the adsorption isotherms were obtained at −196.15 °C.

2.3. Bacterial test species culture and maintenance

E. coli ATCC 25922 was chosen for this study as it is currently the indicator organism for water contamination. Additional strains studied include *P. aeruginosa* ATCC 27853 and *S. typhimurium* ATCC 13311. Strains were sourced from the American Type Culture Collection and grown from storage on nutrient agar at 37 °C and identity confirmed via gram stain and standard biochemical tests prior to each experimental setup. To establish a working bacterial culture a single colony of the test strain was aseptically transferred to 100 ml sterile nutrient broth (Cruinn Diagnostics Ltd., Ireland) followed by incubation at 37 °C under rotary conditions (125 rpm) for 18 h to obtain bacteria cells in the stationary phase of growth and for 5 h to obtain bacteria in the log phase of growth. In order to determine the growth phase of each organism, a standard growth curve was constructed for a 24 h period. Following incubation test samples were centrifuged at 10,000 rpm for 10 min and the pellet re-suspended in sterile phosphate buffered saline (0.01 M phosphate buffer, containing 0.0027 M KCl and 0.137 M NaCl at a pH of 7.4) (PBS) to give a working stock of ca. 1×10^6 cfu/ml.

2.4. Antibacterial studies

Test NPs were prepared to a stock concentration of 70 ppm in deionized water; 1 ml of NP was added to 9 ml of test bacterial solution giving a NP working concentration of 7 ppm. All nanotube solutions were sonicated before use for 1 h to prevent aggregation (Elma S180 Elmasonic sonicator). Bacterial NP suspensions were then transferred to a Petri dish and exposed to UV light (Blak-Ray® 15 Watt, xx-15BLBUV, Cambridge, UK) at 365 nm for 2, 3 and 4 h under agitation. Distance from the UV lamp to the bacterial

Download English Version:

https://daneshyari.com/en/article/6455898

Download Persian Version:

https://daneshyari.com/article/6455898

Daneshyari.com