Titanium Dioxide Nanostructured Coatings: Application in Photocatalysis and Sensors

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Abstract
This paper presents some of the research work taking place at the University of Ulster investigating preparation, characterisation and application of nanostructred TiO_2. Four exemplars are used to demonstrate the potential applications of these materials i.e. photocatalytic disinfection of water containing chlorine resistant microorganisms, photocatalytic 'self-cleaning' of surfaces contaminated with protein, transducers for electrochemical biosensors and finally new opportunities presented by electrochemical growth of TiO_2 aligned nanotubes.

1.0 Introduction

Nanostructured titanium dioxide has been widely researched for application towards the photocatalytic treatment of purification of water and air, "self-cleaning" and superhydrophilic coatings for surfaces, and dye-sensitised voltaic cells. Nanoparticle TiO_2 films present a large surface area to geometric area ratio, which is useful in water and air purification and dye sensitised cells. In addition, these films also give high surface area desirable for electrochemical sensor applications. Titanium dioxide is found in three crystal forms, brookite, rutile and anatase, the latter of which is the most suitable for photocatalytic applications. Anatase TiO_2 is a wide band gap semiconductor (3.2 eV) and absorbs photons with $\lambda < 387$ nm. Band gap excitation produces electron hole pairs, which can take part in electrochemical reactions at the interface and result in the production of radical species. This photocatalytic action has been reported to degrade organic pollutants (in water and air) to CO_2 and H_2O, and kill a wide range of microoganisms. Furthermore, photocatalytic films can degrade protein material (including temperature stable proteins) adhered to their surface, and could find application in, for example, the sterilisation of surgical devices.

Nanostructured TiO_2 thick films present a high surface area, which is desirable for electrochemical sensor and biosensor applications. TiO_2 is biocompatible, non-toxic, and chemical stable under conditions found within the body, making it a suitable material for implantable biosensors. Furthermore, TiO_2 can be used for the electrochemical detection of hydrogen peroxide in the presence of oxygen. This makes nano-structured TiO_2 electrodes suitable for non-mediated biosensors utilising oxidase enzymes e.g. glucose oxidase.

Self-assembled titanium oxide nanotube arrays with maximum packing density can be formed by the anodic oxidation of titanium metal [1]. Such materials may prove to have enhanced properties for photocatalytic, sensor and other applications.

2.0 Photocatalytic disinfection of water

Cryptosporidium poses significant problems to the drinking water industry. It is ubiquitous in surface water, difficult to remove by conventional drinking water treatment processes and if ingested can cause serious illness [2]. The cost-effective removal of *Cryptosporidium* from drinking water sources remains one of the industries greatest challenges [3]. There have been many outbreaks of cryptosporidiosis all over the world associated with consumption of contaminated drinking water [4]. The largest outbreak occurred in Milwaukee, USA in 1993 with the death of 104 AIDS patients and an estimated 403,000 people becoming ill [5].

The bactericidal effect of TiO_2 photocatalysis has been widely reported [6,7] however a limited number of studies have reported the effectiveness of photocatalysis against chlorine resistant organisms. In this paper we present the photocatalytic inactivation of *Cryptosporidium parvum* oocysts

TiO_2 powder (Degussa P25) was electrophoretically immobilised onto Ti alloy substrates [8] and placed in a quartz water-jacketed reactor with the illumination source focused on the coated area (125W HPR lamp (Philips), mainline emission 365nm). An oocyst suspension was prepared by diluting fresh oocysts (Moredun Scientific) in saline solution to achieve a working concentration of $2x10^4$ oocysts per cm^3. The reactor was thermostatically controlled at 20 ± 2°C and agitation of the 10 cm^3 of oocyst suspension was provided by a small magnetic stirrer. Air sparging was achieved using a small aquarium pump, flow rate of 900 cm^3 min^{-1}. The reactor was allowed to reach equilibrium under dark conditions for 15 min prior to irradiation. A 100 µL sample was removed and the electrode illuminated. Samples were removed every 60 minutes thereafter for a period of 240 minutes. Analysis for oocyst damage was preformed using the vital dye exclusion protocol developed by Robertson et al [9].

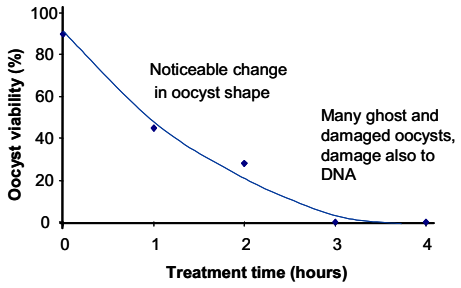
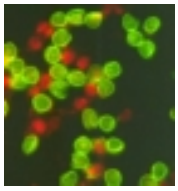
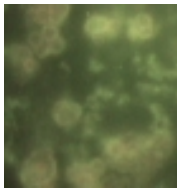


Figure 1. Photocatalytic inactivation of Cryptosporidium parvum oocysts.



Before treatment: Time = 0 mins Vital Dye Exclusion Assay indicating 90% oocyst viability



After photocatalysis: Time = 240 min Vital Dye Exclusion Assay shows extensive damage to oocysts

During the first hour observable changes in oocyst shape were observed associated with a decrease in viability (see figure 1). Following three hours treatment viability decreased to zero and fragmentation of the oocyst bodies was evident along with the presence of many ghost oocysts (oocysts missing their DNA). Further studies are being carried out confirm the loss of infectivity via in-vitro infectivity and an examination to elucidate the mechanism of disinfection will be undertaken.

3.0 Self-cleaning coatings for surface decontamination

Decontamination of surfaces is an area of current interest. Health care acquired infections (HAIs) cost the Health care sector billions of pounds every year and cause patient discomfort, prolonged hospital stays, and even death. Conventional approaches to the decontamination and sterilisation of re-usable surgical devices may not be wholly effective. While photocatalytic coatings have been reported to be 'self-cleaning' and even commercialised for this purpose e.g. Pilkington Activ self cleaning glass [10], there are few published reports dealing with photocatalytic decontamination of protein from surfaces.

In this work TiO_2 thin films were prepared using a sol gel route. Titanium IV butoxide was hydrolysed under controlled conditions with acetic acid as a catalyst. The resulting sol gel was spin coated onto glass slides and then annealed. Raman spectroscopy analysis and glancing angle XRD confirmed the presence of anatase crystal phase. Samples were contaminated with fluorescein-isothiocyanate labelled bovine serum albumin (FITC-BSA) as a model contaminant. A series of 1 µL drops of different concentrations of FITC-BSA were casted onto slides and allowed to dry. The glass slide was two-thirds coated with TiO_2, using the sol gel route, so that control spots (no TiO_2) were on the same slide. Slides were irradiated for 0 h, 6 h, 12 h and 24 h with a UVA source. Humidity was not controlled in these experiments. The fluorescence intensity measured (Fluoromax – P) and the relative protein concentration was calculated from a calibration response. Figure 2 shows the decrease in fluorescence intensity with increasing UV exposure time. These results demonstrate the photocatalytic degradation of FITC-BSA. Experiments are ongoing investigating the degradation of other protein species which are resistant against physico-chemical or biochemical treatment.

4.0 TiO_2 electrodes as transducers for biosensors utilising oxidase enzymes

Commercially available glucose biosensors utilise glucose oxidase (GOD) as the biorecognition component which is wired to the transducer

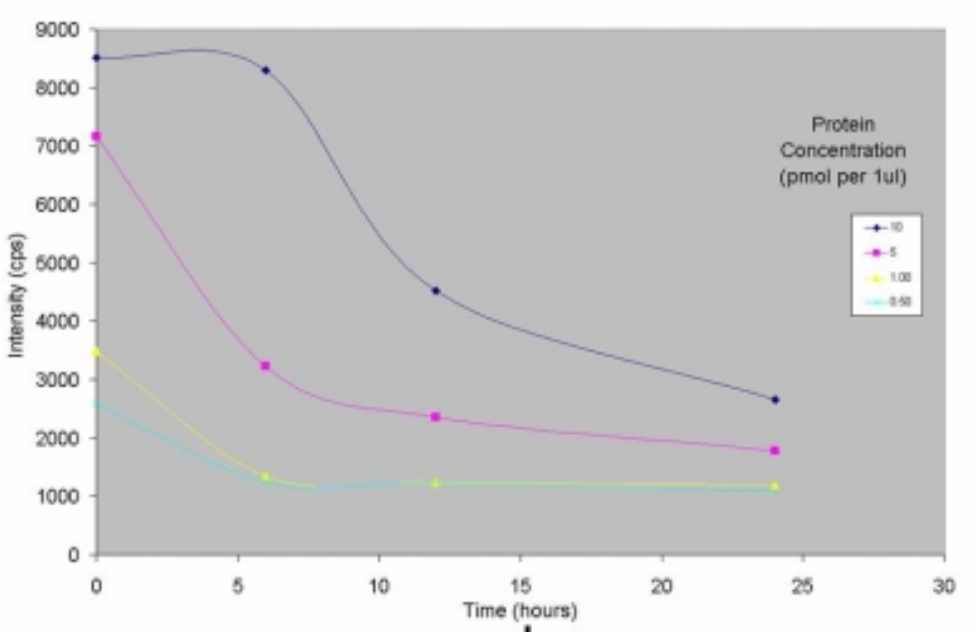


Figure 2. Photocatalytic degradation of fluorescein-isothiocyanate labelled bovine serum albumin on TiO_2 coated glass

using a mediator. However, mediated glucose biosensing may not be suitable for in-vivo sensing as mediators may be toxic or simply lost into the blood. Non-mediated glucose biosensing is possible using materials which can either be directly wired to the enzyme or which can selectively detect the H_2O_2 product in the presence of oxygen. There is an opportunity to produce a wide range of biosensors, utilising oxidase enzymes.

The use of mesoporous titanium dioxide electrodes has been reported previously for the amperometric detection of glucose via electro-reduction of released hydrogen peroxide. [11]

Electrophoretic coating may be used to produce porous nanocrystalline TiO_2 electrodes [8,12]. These electrodes have been tested for the electrochemical reduction of H_2O_2 in the presence of O_2 and the response is independent of O_2 at potentials more positive than –0.4 V vs the saturated calomel electrode (SCE). Titanium foil samples were coated with nanoparticle TiO_2 by the electrophoretic method. Electrical contact was made to an area of the Ti foil not coated with TiO_2 using copper wire and conducting epoxy. The contact and any remaining uncoated foil area were insulated using a negative photoresist.

All electrochemical analyses were carried out using a three-electrode electrochemical cell, with pH 6 phosphate buffer as the supporting electrolyte. The reference electrode was a saturated calomel (SCE), and the counter electrode was a platinum disc. Amperometric detection was carried out using a BAS LC-4C amperometric detector connected to a Lloyd instruments PL3 x-y plotter. All potentials are reported against SCE. Glucose oxidase was added to the buffer (air sparged) in free suspension, and the electrode response was measured at –0.4 V. Standard additions from a stock solution of glucose were made to the cell and the steady state current measured. The steady state current as a function of glucose concentration is shown in figure 3. The GOD oxidises the additions of glucose to produce H_2O_2, which is then reduced at the TiO_2 electrode. The electrode response was directly proportional to the glucose concentration over the 2.0 to 20.0 mM glucose.

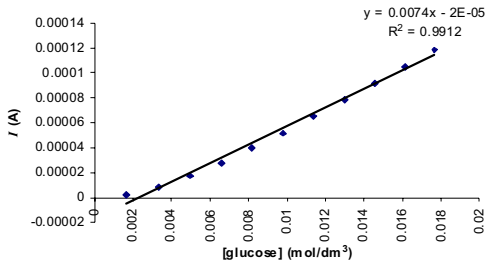


Figure 3. Electrode response to standard additions of glucose. 10 mg GOD was present as free enzyme in 30 cm^3 pH 6 phosphate buffer. The TiO_2 electrode was held at a fixed potential of -0.4 V.

5.0 Electrochemical growth of TiO_2 nanotubes on titanium metal foil

In this work the effect of HF concentration and anodisation potential were investigated. Anodisation was carried out in a one compartment cell with a titanium foil anode platinum foil cathode. Constant potential conditions were employed. The total cell volume was 100 cm^3 and electrode separation was 20 mm. The salient parameters investigated were HF concentrations 0.005%-0.5% w/v and cell potentials in the range 5.0 to 30 V. Above concentrations of 0.15% HF the Ti foil dissolved rapidly. The optimum HF concentration was found to be 0.05 % w/v.

In this system, only cell potentials above 15 V produced the nano-structuring effect and potentials greater than 30 V destroyed the nanotube formation. Sample morphology was examined using an FEI quanta SEM at an accelerating voltage of 30 kV and a beam current of 47 pA. The mean tube diameter was ca. 80 nm for the samples prepared at a cell potential of 25 V in 0.005%w/v HF (see figure 4)

Work is ongoing investigating the potential uses of TiO_2 nanotubes for photocatalysis, biosensing and other applications

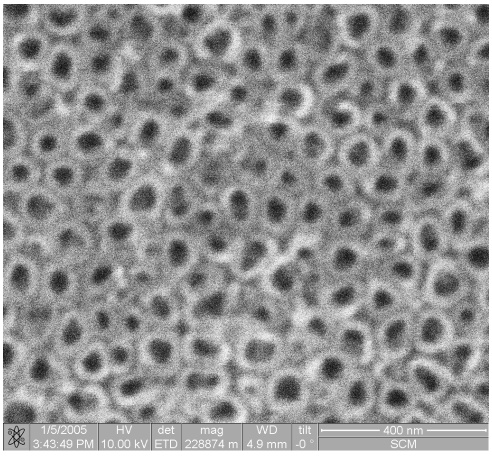


Figure 4. SEM of TiO_2 nantubes grown electrochemically on Ti foil.

7.0 Acknowledgements

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