FABRICATION OF TITANIA NANOTUBE MEMBRANES BY ATOMIC LAYER DEPOSITION USING NANOPOROUS ALUMINA AS A TEMPLATE

Peter J. Evans,1* Gerry Triani,1 Monessha Nambiar,1 Joe G. Shapter,2 Dusan Losic3
1 Australian Nuclear Science and Technology Organisation, Private Mail Bag No. 1, Menai, NSW 2234, Australia
2 Flinders University, School of Chemical and Physical Sciences, Bedford Park, Adelaide, SA 5042, Australia.
3 University of South Australia, Ian Wark Research Institute, Mawson Lakes Campus, Adelaide, SA 5095, Australia.
* Email: pev@ansto.gov.au

ABSTRACT
Conformal TiO$_2$ films have been deposited onto highly oriented porous alumina arrays to characterise membranes with controlled pore modification. A suite of tools have been used to probe the evolution of these coated porous structures. Depth profiling by secondary ion mass spectroscopy revealed the distribution of elements Ti and O deposited throughout the coated porous alumina. High resolution imaging using scanning electron microscopy confirmed the reduction in pore-size as a function of deposition cycles. Following the removal of the porous alumina template, free-standing titania nanotubes were prepared which show the pore geometry of the alumina template was preserved.

INTRODUCTION
Vertically oriented, highly ordered titania nanotube (TNT) arrays are versatile nanostructured materials that can be readily integrated into micron-sized devices. TNT arrays are characterised by remarkable optical, photocatalytic, chemical and charge transport properties enabling a variety of advanced applications for sensors, dye sensitized solar cells, hydrogen generation by water photoelectrolysis, electrochromic devices, self-cleaning surfaces, microfluidics, molecular separation, drug delivery, and tissue engineering (Ghichov et al 2009, Losic et al 2010, Sinn Aw et al 2011). In particular

Scheme 1: A scheme for the fabrication of titania nanotube membranes using atomic layer deposition and porous alumina as the template
TNT’s are recognised as promising biomaterial with proven biocompatibility that are being explored as adhesion and growth support platforms for bone and stem cells, for the prevention of bacterial adhesion, drug delivery and enhancing blood clotting (Losic et al 2009).

Among several synthetic strategies for the preparation of nanotube arrays, electrochemical anodization is far by the most practical method for the fabrication of titania nanotubes, on account of its simplicity, low cost, and self-ordering process. This method allows large-scale aerial fabrication of highly ordered TiO$_2$ nanotube arrays from different starting materials such as Ti foils, alloys of Ti, or Ti films (Ghichov et al 2009, Losic et al 2011). The dimensions of such nanotubes can be controlled by anodization condition such as voltage and electrolyte composition however the process parameter range is limited, which restricts the size (diameters and length) for use in applications such as membrane separation of small molecules or pore diameter controlled growth of stem cells (Losic et al 2009). This paper presents an alternate synthetic approach for preparation of titania nanotubes using a surface mediated process which enables control of the pore diameter based on atomic layer deposition (ALD) using nanoporous alumina (PA) structure as the template. This concept is presented in scheme 1.

ALD is a surface mediated deposition process for the preparation of conformal coatings using sequential pulsing of reactive precursors to deposit metal oxide films. This non-line of sight deposition process relies on self-limiting reactions between the incoming precursor and the surface. Films grow in a digital layer by layer method thereby offering unique control over uniformity and thickness. In porous structures, precursors can be dosed to prepare ALD layers thus allowing pores within the membrane to be tailored for highly selective molecular separation. PA templates provide a stable support for the preparation of titania nanotubes with desired crystal structure and dimensions.

**EXPERIMENTAL METHODS**

Porous alumina was prepared by two step anodization of Al foil (Alfa Aessar) in 0.3 M oxalic acid using our previously described methods (Losic et al 2011). The pore diameters and pore length of PA were controlled by anodization condition (voltage and time). Once fabricated, PA’s were placed in a laboratory built ALD reactor with vertical precursor flow to the vacuum pumping port. Both titanium tetrachloride and water were pulsed independently through separate channels under a nitrogen gas flow of 50 sccm using a shower head attachment. The PA was placed on a hot stage platform held at 200°C. The pulsing sequence for the deposition of titania was as follows 0.3 seconds pulse of TiCl$_4$ followed by a 4 second purge pulse of nitrogen. In order to complete one ALD cycle, a water pulse of 0.4 sec was followed by a 8 second purge pulse of nitrogen. Conformal titania films were grown at 200°C using the following number of cycles; 200,400,600 and 700. The morphology and chemical composition of the PA membranes before and after ALD deposition of titania were investigated using a suite of
characterisation techniques to elucidate the structure and chemical composition of the membrane.

RESULTS AND DISCUSSION

SEM micrographs (Fig. 1a-c) show the typical structure of a fabricated titania nanotube/PA composite membrane prepared by ALD deposition. These images confirm a typical topography of membrane showing an array of highly ordered nanopore/nanotube titania structures with pore diameters 80-100 nm and 20 µm in length (Fig. 1a-b). SEM images taken after titania deposition (Fig 1b) confirm a very thin titania layer on the wall inside of PA pores. The EDAX analysis of PA before and after deposition confirmed that the deposited layer is composed of titania. In order to investigate the effect of pore reduction by ALD, several membranes with larger pore diameters were prepared offering easier SEM characterization. The influence of ALD deposition cycles on the morphological changes of AAO was investigated with particular emphasis on the reduction of the size of pore diameters over the entire surface area of the membrane. Our results show that by depositing ALD cycles between 200 cycles to 700 cycles it is possible to control the thickness of deposited layer of titania inside of pores and therefore control diameter of nanotube composite membrane.

![Fig. 1 SEM images of titania nanotube/PA composite membrane prepared by atomic layer deposition of titania on porous alumina template showing a-b) low and high resolution image of cross-section of membrane, and c) the top surface](image)

Chemical depth profiling was undertaken to investigate the level of penetration and uniformity of film deposition through the PA membrane thickness by TOF-SIMS. This analysis confirmed the presence of Ti peak across whole PA structures, which is in agreement with EDAX results.

Finally, free-standing titania nanotubes were obtained after completely dissolving the AAO template with CuCl₂/HCl solution to reveal that the morphology and pore structure of the PA template was preserved. These nanotubes were liberated in solution demonstrating an alternate fabrication step, which can be readily adapted for use in drug delivery applications. The formed titania nanotubes are amorphous but can be easily transformed into catalytically active polymorphs rutile and anatase through annealing. Future studies will investigate the photocatalytic and self-cleaning properties of these prepared membranes.
In conclusion, the fabrication of aligned titania nanotube arrays using a combination of PA as the template followed by ALD provides an adaptable technology platform for tailoring materials with specific pore size diameter in membranes. Results showed the titania coating was not only inside of pores but extended over the entire pore structure of the PA. The dimensions of titania nanotubes (diameters and length) were controlled by the number of ALD cycles applied. This synthetic strategy can be applied to the preparation of a wide variety of different metal oxides that exhibit specific catalytic, optical or magnetic properties.

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BRIEF BIOGRAPHY OF PRESENTER
Dr Peter Evans
Australian Nuclear Science and Technology Organisation
Institute of Materials Engineering

Dr Evans is a senior research fellow with IME and has worked on the development of the atomic layer deposition platform for over 10 years. ANSTO were the first research group in Australia to adopt the ALD technology platform where the primary focus has been on deposition of complex oxide surfaces and interfaces on polymer structures. Dr
Evans has over 20 publications in the field of atomic layer deposition including two process patents.