

Controlling the surface functionalities of nanoporous alumina membranes

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Abstract— A new approach for controlling and to functionalise nanoporous anodic alumina oxide (AAO) membranes is described. Our approach is predicated on the remarkable stability of the silanised AAO surface during anodisation. Well ordered nanoporous AAO membranes with different external surface properties compared to the internal pore surface properties were prepared and characterised.

Keywords— alumina membranes; anodisation; silanisation

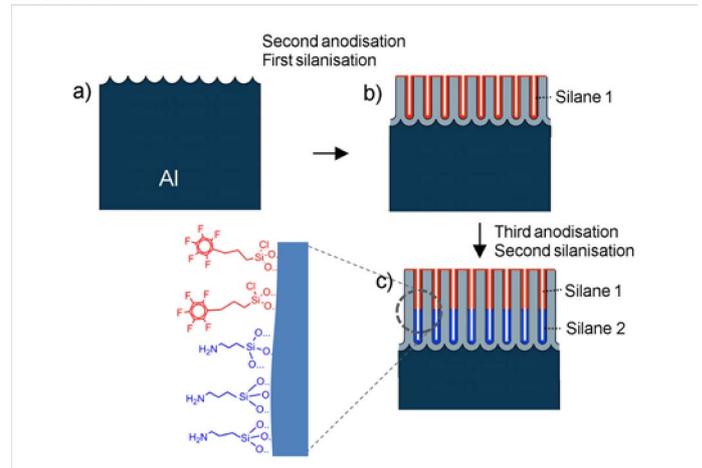
I. INTRODUCTION

Control over surface properties of mesoporous materials can govern its interaction with various analytes with regard to potential application such as separation and detection of chemical and biological species [1-3]. Self organised nanoporous anodic alumina oxide (AAO) membranes fabricated by electrochemical anodisation have become popular and attractive mesoporous materials in recent years with respect to their structure, properties and applications. Controlling surface chemistry of AAO membranes is of considerable interest, because it can alter their functionality, advancing their properties and applications [4]. Several modification techniques including silane chemistry [5], plasma polymerisation [6], and polymer grafting [7, 8] have been reported where only single chemical functionality were introduced. In our previous work, we have shown the fabrication methods to control surface chemistry of AAO membranes with two functionalities, one at the pore opening and the second inside of pores [9]. The method is based on incorporating different silanes by combining the anodisation and silanisation process. Herein, we report a further advance of this fabrication approaches with aim to achieve the spatially controlled surface chemistry inside of pores and advance selectivity properties of AAO membranes. The highly sensitive analytical technique of energy-dispersive X-ray spectroscopy (EDX) and time-of-flight-secondary ion mass spectrometry (TOF-SIMS) were used for the characterisation of fabricated membrane.

II. METHODOLOGY

AAO membranes were fabricated through a typical mild anodisation and two-step anodisation process following

previous reported procedures [10]. The functionalisation procedures employed in this work could allow fabricating layered membranes with multifunctional surface chemistries. Pentafluoro phenyldimethylpropylchlorosilane (PFPTES), 3-aminopropyltriethoxysilane (APTES) and N-triethoxysilylpropyl-O-polyethylene oxide urethane (PEG-silane) were selected and used to chemically functionalise the pore channels inside the membrane. The fabrication process to control surface chemistry of nanoporous AAO membranes is illustrated in cross-sectional schematics in scheme 1. Characterisation by scanning electron microscope (SEM) and EDX spectra were collected on a Philips XL 30 FEGSEM and EDAX Genesis, respectively. TOF-SIMS analysis were performed using physical electronics Inc PHI TRIFT IITM, with a 200 nm beam from an unbunched mono-atomic LMIG Au⁺ source. Transport experiments were carried out using custom-designed cells in which the membrane was clamped between feed and permeate cells. The hydrophobic dye, pinacyanol chloride (PCN) and the hydrophilic dye, rose bengal (RB) were used to probe the transport properties of the membranes.



Scheme 1. Fabrication of layered AAO membranes and controlling surface chemistry in pore channels. (a) Aluminium substrate after first anodisation, (b) AAO membrane after second anodisation and first silanisation with PFPTES, (c) after third anodisation and second silanisation with APTES.

III. RESULTS AND DISCUSSION

A. Scanning Electron Microscopy (SEM)

The structure of prepared AAO membranes were characterised by scanning electron microscopy (SEM) and shown in Fig. 1. Fig. 1a is a top view of the membrane after the first silanisation and second anodisation. The pores are hexagonally aligned with the mean pore diameter of about 30 nm and an interpore distance of approximately 80 nm. This result confirms that anodisation is possible on a silane-modified AAO surface. The bottom surface of a free-standing membrane (Fig. 1b) shows a hexagonal array of pores with an average diameter and interpore distance of 30-45 nm and 100 nm, respectively. A typical cross-sectional view (Fig. 1c) of the membranes shows the typical non-intercrossing, straight and cylindrical pores of AAO.

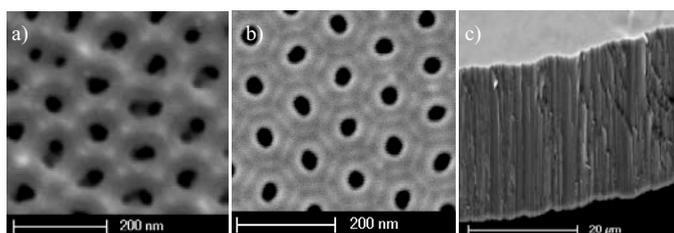


Figure 1. SEM images of fabricated AAO membranes. (a) Top view AAO surface after first silanisation and second anodisation. (b) Bottom view of AAO surface after removing of Al substrate and pore opening. (c) Cross-sectional image of AAO membrane.

B. Energy-dispersive X-ray Spectroscopy (EDX)

The energy-dispersive X-ray spectroscopy (EDX) analysis on cross section of top layered membrane showed there were silica, carbon, fluorine and chlorine elements, which correspond to fluorinated silanes (FPFTES) (Fig. 2a). These results highlight that FPFTES was still immobilised on all top layers and survived after third anodization. Fig. 2b shows EDX spectra of the bottom layer of the layered membrane illustrating silica and nitrogen peaks which was functionalised by APTES.

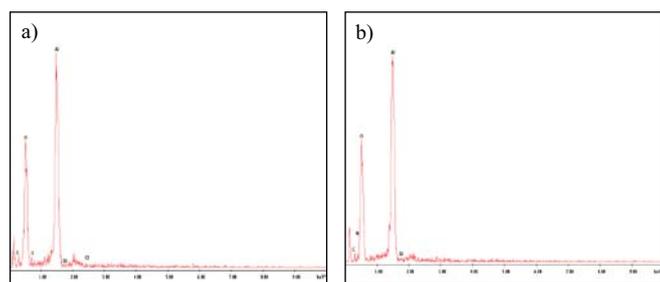


Figure 2. Cross-section energy-dispersive X-ray spectroscopy (EDX) spectras of the AAO membrane. (a) Top layer of AAO membrane functionalised with FPFTES shows silica, carbon, fluorine and chlorine elements correspond to fluorinated silane (FPFTES), (b) bottom layer of membrane functionalized with APTES with nitrogen and silica peak.

C. Time-of-flight-secondary ion mass spectrometry (TOF-SIMS)

TOF-SIMS is a surface sensitive, ultra-high vacuum mass-spectroscopic technique capable of acquiring elemental and molecular information. It offers several advantages including high mass resolution combined with high spatial resolution for imaging on conducting or non-conducting samples. TOF-SIMS clearly distinguished regions in the membrane cross-section analysis, exhibiting differences in chemical composition as shown in Fig. 3. The surface sensitivity provides clear distinction of boundaries, minimising the distortion due to depth effects. Fig. 3a shows the total negative ion yield (TIY) of cross-sectional analysis on layered AAO membrane with PFPTES functionalised on top and APTES on the bottom of the membrane, whereas fluorine ion image is shown in Fig. 3b. The image in Fig. 3c shows two different colors of negative ion which correspond to fluorine (red) and nitrogen (green) fragments differentiating PFPTES and APTES functionalised regions on the top and bottom of AAO membrane, respectively.

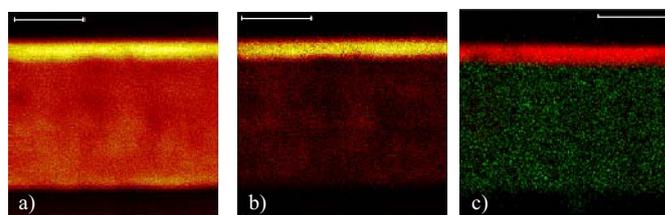


Figure 3. Cross sectional TOF-SIMS negative ion images. (a) The total ion yield (TIY) shows the AAO membrane cross-section analysis. (b) Fluorine ion image on top of the membrane. (c) F and N fragments clearly differentiate the functionalisation of PFPTES (red) and APTES (green) respectively. Bar = 10 microns

D. Transport studies on fabricated membrane

To demonstrate the practical application of our surface modification approach for development of membranes with controlled chemical selectivity, we fabricated the membrane with sharp contrast of hydrophobicity layers using combination of PFPTES and PEGs-silane. This was done to tune wettability and selectivity of the membrane towards chemical solutes of different interfacial properties (polarities). The transport and selectivity characteristics of this membrane were investigated using two different dyes: pinocyanol chloride (PCN) and rose bengal (RB), which have hydrophobic and hydrophilic properties respectively. Figure 4 shows the flux rate of both dyes as a function of time through AAO membranes with layered surface chemistry functionalised with different portion of PFPTES and PEG-silanes (1:0.25). The trend lines indicate that thicker hydrophobic layer favouring the transport of hydrophobic dyes, whereas transport of hydrophilic dye was considerable slower. Our results on the layered surface chemistry of nanoporous alumina membrane demonstrate that the flow rate of the molecules based on their chemical properties (hydrophobicity/hydrophilicity) can be tuned by controlling the thickness of surface chemistry inside pore channel.

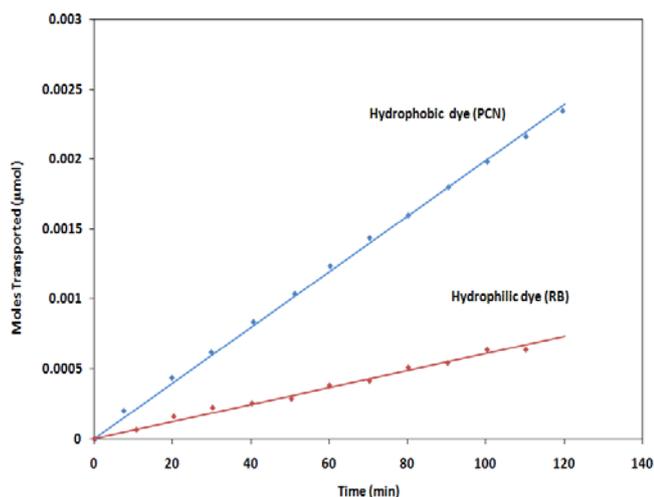


Figure 4. Transport studies and comparison of hydrophobic (PCN) and hydrophilic (RB) dye through layered membrane

IV. CONCLUSION

In conclusion, we have developed a simple and facile technique for spatially controlling the surface chemistry inside the pores of AAO membranes. Multifunctional membranes produced by this technique were chemically robust and showed selectivity towards the transport of small molecular compounds, rendering these multifunctional membranes useful components of future molecular separation.

ACKNOWLEDGMENT

The authors gratefully acknowledge Australian Research Council for the support on this project. AMMJ thanks the Malaysian government a postgraduate scholarship.

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