Gold nanotube membranes; Fabrication of controlled pore geometries and tailored surface chemistries

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Abstract— **This study concerns the fabrication, chemical modification and characterisation of gold nanotube membranes using porous alumina (PA) membranes as templates. Electroless deposition was used to finely coat membranes with gold, forming gold nanotubes within the pores. PA templates were fabricated with straight and shaped pores thus allowing the fabrication of a wide range of gold nanotube geometries. The gold deposition process provides control over the pore size of the membrane, where pore sizes can be reduced to molecular dimensions. Chemical sensitivity was introduced into the membrane through the addition of self assembled monolayers (SAMs) of thiols. Characterisation of thiol assembly within the pores of the membrane was investigated using confocal Raman.**

Keywords- Gold nanotube membrane, porous alumina, thiol, Raman spectroscopy.

I. INTRODUCTION

Nanoporous membranes have shown great promise in the field of chemical separations due to their porosity, high surface area and rich surface chemistry. Our group has prepared gold nanotube membranes based on the work by C. Martin et al [1]. where electroless gold deposition is used to coat the surfaces and pores of porous templates [2]. The electroless deposition process involves finely coating porous membranes with gold to form gold nanotubes within the pores (Fig. 1 (a)) [1, 3-7]. This approach provides control over the pore size of the membrane, where pore sizes can be reduced to molecular dimensions thus enabling size based molecular separation [8].

Porous alumina (PA) has been chosen as a suitable template to form gold nanotube membranes. The structure of PA consists of a very ordered array of vertically aligned cylindrical pores [9, 10]. PA has attracted significant interest in applications such as template synthesis, molecular separation, sensing, and drug delivery [11-13]. In particular, the use of PA as a template for nanostructures has been extensively studied. PA templates have been employed in the fabrication of a variety of nanostructures such as nanowires, nanotubes and nanoparticles [14, 15].

Another attractive feature of PA membranes is the ability to precisely control the geometry of the pores. During the anodization process it is possible to fabricate pores with modulated diameters along the length of the pore (Fig. 2(b)). PA with shaped pore geometries have considerable potential as

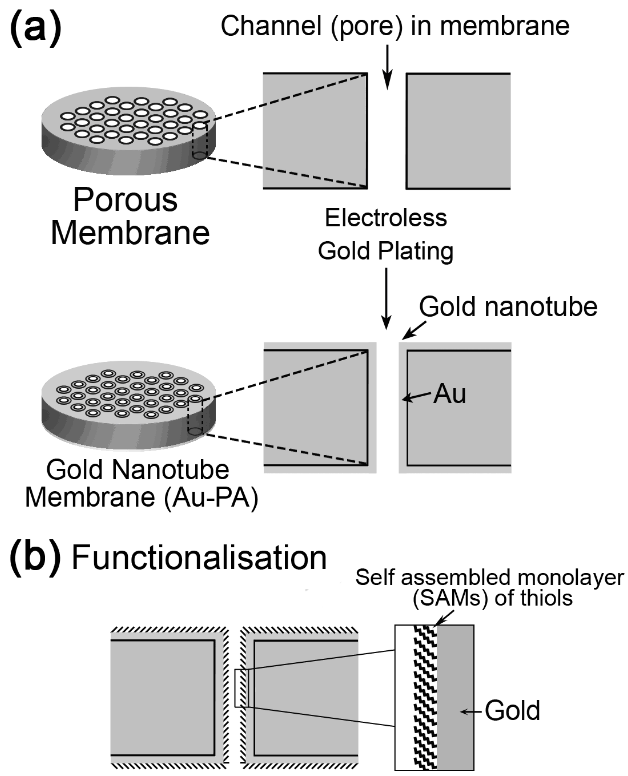

Figure 1. Schematic of the electroless plating process used to form gold nanotubes membranes (a) and subsequent functionalisation with self assembled monolayers of thiols (b).

templates for the production of shaped nanotubes with unique properties and can be used in advanced molecular filtration devices [16, 17]. However, for use as molecular filtration devices, the pores size of shaped PA membranes are still too large (50 – 200 nm). Thus through applying the electroless gold deposition process on shaped PA membranes the pore sizes can be reduced to <10 nm while still maintaining the shaped pore structure.

The membranes can be made chemically sensitive through functionalisation with self assembled monolayers (SAMs). Thiol chemistry is used to form SAMs on gold nanotube membranes (Fig. 1 (b)). It has been demonstrated that an enhancement of transport selectivity can be achieved by exploiting chemical features of the membrane as well as the molecule to be selectively transported [18]. Functionalisation of gold nanotube membranes provides an approach for performing complex separations and overall provides an enhancement in areas such as separation, stability and biocompatibility [19].

II. Experimental

A. *Fabrication of porous alumina membranes*

Porous alumina membranes were fabricated using a two step anodization process on high purity aluminium foil (0.3 M oxalic acid, 60-80V, 0^oC). This procedure produced porous alumina membranes with highly ordered cylindrical pores (Fig. 2(a)). In addition, shaped pore geometries along the length of the channel were produced by using different combinations of electrolytes and applied voltage/current signals during anodization (Fig. 2(b)).

B. *Fabrication and functionalisation of gold nanotube membranes*

The electroless plating method consists of several steps; sensitisation of the membrane with tin ($SnCl_2$, 0.026M), activation with silver ($AgNO_3$, 0.035M) and the deposition of gold ($Na_3Au(SO_3)_2$, $7.9x10^{-3}$M). Metal deposition commences at the pore walls creating hollow nanotubes within the pores. The schematic of this process is shown in Fig. 1. The electroless deposition method is applied to PA membranes. Through varying the shape and size of the pores in the membrane, and the thickness of the membrane a variety of nanotube geometries can be obtained.

Gold nanotube membranes were functionalised with the thiol mercaptobenzoic acid (MBA). The membranes were immersed in a 1 mM solution for 48 h, then thoroughly rinsed in ethanol and dried in air. This procedure results in a monolayer of MBA over the gold surfaces of the membrane.

C. *Characterisation of gold nanotube membranes*

Scanning electron microscopy (SEM) was used to characterise the electroless deposition of gold onto the porous template (Philips FESEM XL30). Deposition of gold within the pores of the membrane was verified through dissolving the PA template to reveal the gold nanotubes. Functionalisation of gold membranes with the Raman active thiol, MBA, was investigated with confocal Raman spectroscopy (632 nm laser, 100µW power, x100 objective).

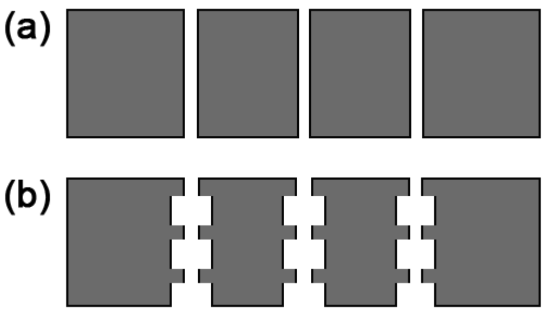

Figure 2. Examples of pore geometries that can be obtained during the fabrication of porous alumina (PA) membranes.

III. Results and Discussion

A. *Formation of gold nanotube membranes*

Porous alumina templates were fabricated with straight channel pores and with shaped pores. SEM images of the PA membranes fabricated are shown in Fig. 3. The PA membranes were fabricated with a thickness of 20 – 30 µm (Fig. 3(a)). The surface of the PA membrane displays a very ordered array of pores with a narrow pore size distribution (Fig. 3(b)). Fig. 3(c & d) are cross sectional images of the straight channel and shaped PA membranes respectively. The straight channel PA membrane is seen to have a high degree of order with very low tortuosity. The shaped PA membrane clearly demonstrates the control that the anodization conditions have on the pore structure, producing any pore geometries required.

The surface morphology of gold nanotube membranes based on PA membranes with an original pore diameter of 80 nm is presented in Fig. 4. Through coating the porous membrane with gold a significant decrease in the pore diameter is seen in comparison with uncoated membranes (Fig. 4 inset). Due to the reduction in the pore diameter of the membrane size selective separations can be performed.

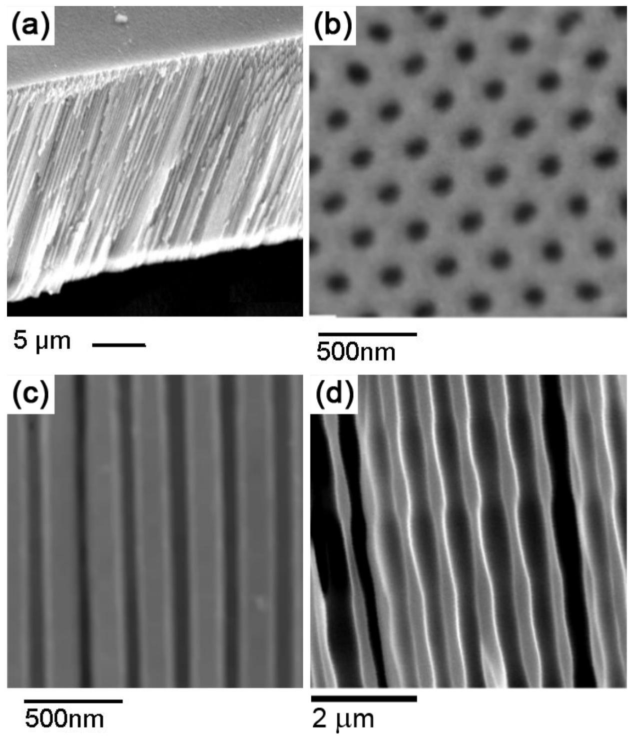

Figure 3. SEM images of fabricated porous alumina membranes. (a) Cross section of PA membrane. (b) The surface of a PA membrane. (c) Cross section of a straight channel PA membrane. (d) Cross section of a shaped pore PA membrane.

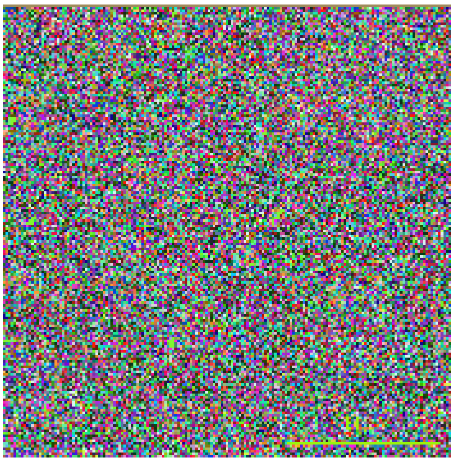

Figure 4. SEM image of PA membrane after electroless gold deposition. Inset: Uncoated PA membrane.

In order to verify gold deposition occurred within the pores of the membrane and to ensure deposition extended through the entire length of the pore, the PA template was dissolved to reveal the standing array of gold nanotubes (Fig. 5). The gold nanotubes were obtained by coating straight channel PA membranes. Furthermore, these nanotube structures provide additional opportunities for application in areas such as sensing, catalysis and nanoelectronics [22].

B. Membranes with shaped pore geometries and shaped gold nanotubes

PA membranes constructed with shaped pore geometries were plated with gold to produce shaped gold nanotube membranes. Dissolution of the PA membrane was performed in order to achieve liberated gold nanotubes. These gold nanotubes replicated the contours of the shaped PA membranes. Through varying the shape of the pores formed during anodization, a variety of nanotube geometries were formed. Figure 6 presents the PA templates (Fig. 6 (a) & (c)) which were used to form the gold nanotubes shown in Fig. 6 (b) & (d)) respectively. These nanotubes clearly display the degree of control of the PA pore structure that can be obtained during PA fabrication.

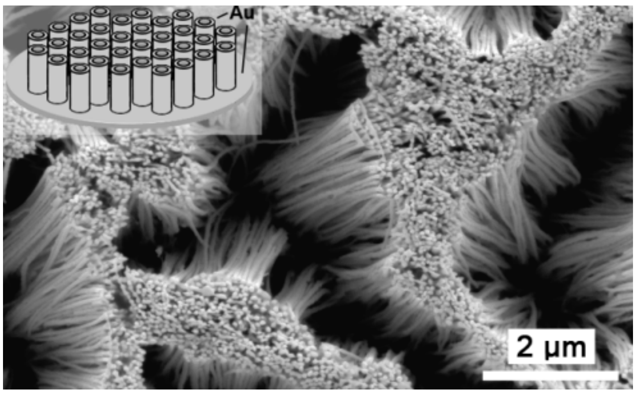

Figure 5. SEM image of an array of standing gold nanotubes after removal of the PA template.

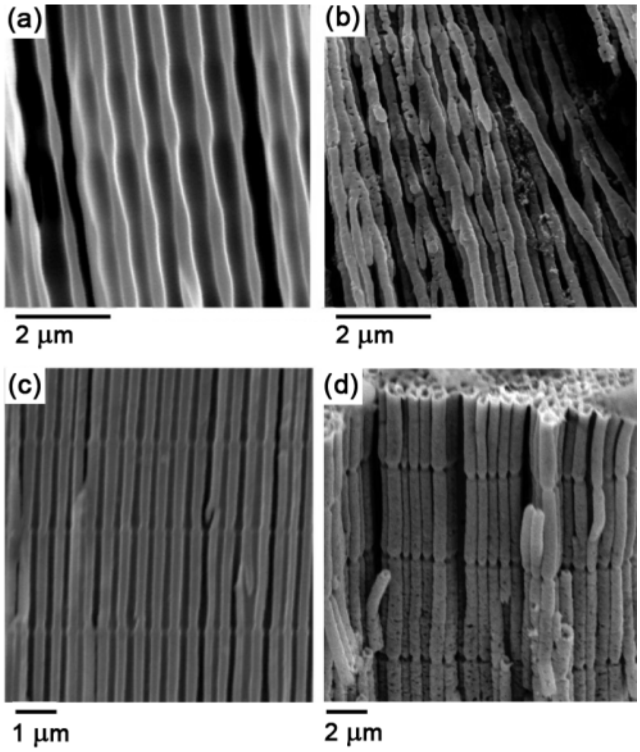

Figure 6. SEM images of liberated shaped gold nanotubes (b) & (d) fabricated from the PA templates (a) & (c) respectively.

C. Raman spectroscopy of self assembled monolayers on gold nanotube membranes

Raman spectroscopy was employed to verify thiol deposition on the face and within the pores of the gold nanotube membranes. The Raman spectrum of pure MBA (Fig. 7(a)) is compared to the spectrum of a monolayer of MBA inside the pores of a gold nanotube membrane (Fig. 7(b)). The surface enhanced Raman spectroscopy (SERS) effect occurs for the functionalised gold membrane. The SERS effect allows the detection of the monolayer of MBA on the gold surface. The two spectra are similar thus verifying the attachment of MBA to the gold surface of the membrane. Differences between the bulk MBA spectrum and the spectrum of MBA on gold is due to a difference in the selection rules arising from the SERS effect causing some bands to appear in one spectrum and not the other [23].

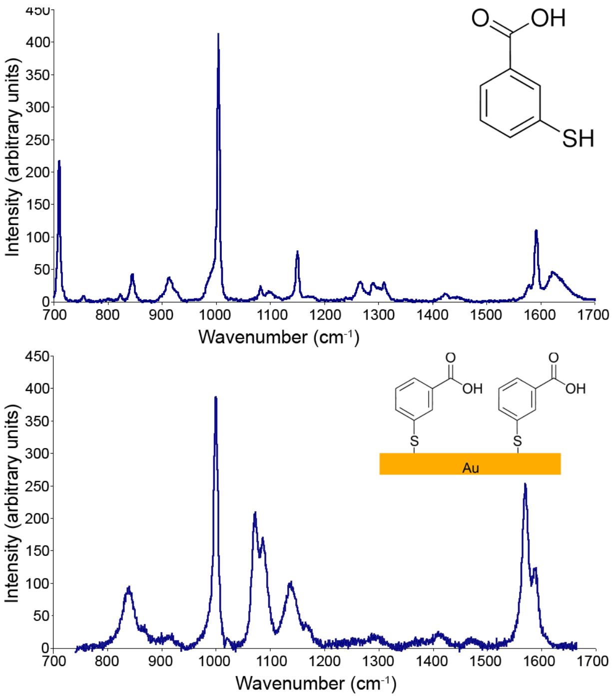

Figure 7. Raman spectra of (a) pure mercaptobenzoic acid (MBA) and (b) a monolayer of MBA attached to gold taken from a cross section of the membrane 10 µm from the surface.

IV. Conclusions

Gold nanotube membranes were successfully synthesized using the template-based electroless deposition technique, forming gold nanotubes within the pores of a porous alumina template. Porous alumina membranes were fabricated with straight pores and complex pore geometries. These PA membranes have the potential to provide unique template based materials. Furthermore gold nanotube membranes based on PA have the potential to be used as advanced molecular filters. The functionalisation of gold nanotube membranes with SAMs of MBA was demonstrated. Raman spectroscopy confirmed the attachment of thiol monolayers within the pores of the membrane.

Acknowledgment

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