Tailoring the surface properties of nanotube membranes for controlled separations

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DECLARATION

I certify that the work presented in this thesis is, to the best of my knowledge and belief, original unless otherwise acknowledged. The material in this thesis has not been submitted, either in whole or in part, towards another degree at this or any other institution.

Leonora Velleman

LIST OF PUBLICATIONS

The following is a list of peer-reviewed publications arising from the author's Doctor of Philosophy degree. The thesis is based around publications 3 – 8.

1. L. Dumée, **L. Velleman,** K. Sears, J. Schütz, N. Finn, M. Duke, S. Gray. Control of porosity and pore size of metal reinforced carbon nanotube membranes. *6th conference of the Aseanian Membrane Society* & *7th International Membrane Science and Technology Conference AMS6/IMSTEC10*, Sydney, Australia, 2010, submitted.

2. **L.Velleman,** C.J. Shearer, A.V. Ellis, D. Losic, N.H. Voelcker, J.G. Shapter, Fabrication of self-supporting porous silicon membranes and tuning transport properties by surface functionalisation. Nanoscale, 2010, DOI: 10.1039/c0nr00284d.

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7. **L. Velleman**, J.G. Shapter, and D. Losic. Template fabricated gold nanotube membranes: a nucleation and growth study. *15th AINSE Conference on Nuclear and Complementary Techniques of Analysis* 326 - 329 November 2007 Melbourne.

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LIST OF SYMBOLS AND ABBREVIATIONS

ALD	Atomic layer deposition
APTES	Aminopropyltriethoxy silane
Au	Gold
Au-PC	Gold coated polycarbonate
Au-PA	Gold coated porous alumina
$Au_{(ext-pore)}PC$	Gold coated polycarbonate on the interfaces and inside pores
$Au_{(pore)}PC$	Gold coated polycarbonate only within the pores
$Au_{(ext)}PC$	Gold coated polycarbonate only on the interface
BG	Bromocresol green
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
DT	1-Decanethiol
EDAX	Energy dispersive analysis X-ray spectroscopy
EDC	1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride
EY	Eosin yellow
FIB	Focussed ion beam
FO	Forward osmosis
FTIR	Fourier transform infrared spectroscopy
LCST	Lower critical solution temperature
MBA	Mercaptobenzoic acid
MV	Methyl viologen
NEXAFS	Near Edge X-ray Absorption Fine Structure
NHS	N-hydroxy succinimide
NS	Nickel sulphate
PA	Porous alumina
PC	Polycarbonate
PCN	Pinacyanol chloride
PDMS	Polydimethylsiloxane
PF	Potassium ferricyanide
PFDS	Perfluorodecyldimethylchlorosilane
PFDT	Perfluorodecanethiol

PNIPAAM	Poly(*N*-isopropylacrylamide)
RB	Rose bengal
RhB	Rhodamine B
RO	Reverse osmosis
Rubpy	tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate
SAM	Self assembled monolayer
SEM	Scanning electron microscopy
Si	Silica
Si-PA	Silica coated porous alumina
SIMS	Secondary ion mass spectrometry
SERS	Surface enhanced Raman scattering
TEM	Transmission electron microscopy
TMA	Trimethyl aluminium
UV-Vis	Ultraviolet – Visible
XPS	X-ray photoelectron spectroscopy

ABSTRACT

Membrane-based separation is a rapidly developing technology which offers many advantages over other separation techniques. However, existing membrane technology requires further research into improving efficiencies which involves flux enhancement, improved selectivity, sufficient long term stability and anti-fouling properties. The fabrication of membrane materials capable of performing highly controlled molecular separations can be achieved by developing nanoporous materials with controllable structural, physical and chemical properties. Recently there has been increased interest in the functionalisation of membrane surfaces in order to enhance the stability and transport properties of membranes. However, current research into the characterisation of functional layers within porous materials is lacking. Further insight into how surface modifications may impact the transport properties of porous membranes is essential for the development of membrane materials.

This thesis presents an approach for tailoring porous materials with surface functionalities and controlling pore architecture to provide controlled transport properties. Membranes such as polycarbonate and porous alumina membranes were used in these studies due to their ordered pore architectures. Further structural modification of the membranes was carried out in order to reduce the pore diameter of the membranes. Pore size reduction was achieved using two methods; electroless deposition of gold and atomic layer deposition (ALD) of silica. The pore size of the membranes was altered systematically by adjusting the number of ALD cycles or by adjusting gold deposition time.

The surface properties of the membranes were tailored in order to provide controlled molecular transport. It is important to determine how surface modifications may impact the transport properties of porous membranes in order to devise more efficient separation processes. Desired chemical properties were imparted to the membranes by modifying the membrane surfaces with self assembled monolayers (SAMs). Predominantly, hydrophobic SAMs were used as it presented a simple technique to demonstrate changes to the transport properties of membranes due to

introduced surface functionalities. The transport properties of fluoro-derivatised membranes (1H,1H,2H,2H-perfluorodecanethiol) towards hydrophobic and hydrophilic molecules was compared with a membrane modified with an analogous alkanethiol; 1-decanethiol to demonstrate the influence that a slight variance in surface modification can have on the transport properties of the membrane. The effects of the controlled positioning of functional groups on the transport properties of the membrane were investigated. Several hybrid membrane structures based on polycarbonate membranes were created in which gold was deposited on different areas on the membrane; on one of the membrane interfaces, within the pores of the membrane and completely coating all surfaces of the membrane. Gold-thiol chemistry was exploited in which the thiols only assembled on the gold coated regions of the membrane thus providing controlled positioning of functional regions. Lastly, silica coated PA membranes were functionalised with perfluorodecyldimethylchlorosilane (PFDS) to demonstrate that the transport and selectivity properties of silica composite PA membranes can be varied by functionalisation using silane chemistry.

The investigation of the coverage and reproducibility of SAMs within porous matrices is of utmost importance in the design of filtration membranes and sensing platforms. The surface enhanced Raman scattering (SERS) effect was employed to confirm and characterise the formation of SAMs of 3-mercaptobenzoic acid (mMBA) on the surfaces of the gold coated alumina membranes.

To explore more sophisticated surface functionalisation, stimuli responsive membranes were produced. The transport properties of the gold nanotube membranes were controlled through the reversible switching of adsorbed fluorinated azobenzene layers. The fluorinated, hydrophobic end group of the azobenzene chain produces a transition between hydrophobic and less hydrophobic surface properties when switching from the *trans* to the *cis* state. The selective mediation of a hydrophilic probe dye across the membrane was investigated.