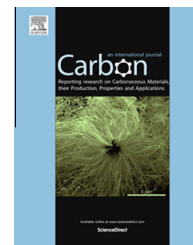


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Carbon nanotube-nanoporous anodic alumina composite membranes with controllable inner diameters and surface chemistry: Influence on molecular transport and chemical selectivity

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ABSTRACT

This work presents the fabrication of carbon nanotube composite membranes with controllable nanotube dimensions (inner diameters and lengths) and surface chemistry and explores their influence on the transport properties and chemical based transport selectivity. These membranes were prepared by growing of vertically aligned multiwalled carbon nanotubes (MWCNTs) inside nanoporous anodic alumina membranes (NAAMs) through a catalyst-free chemical vapour deposition (CVD) approach. The deposition time during CVD process and the length of NAAMs were used to control nanotube dimensions. The thermal annealing and wet and dry oxidation processes were used to control the surface chemistry of inner walls of nanotubes from highly graphitic-hydrophobic to oxygen rich and hydrophilic. The structural features and chemical composition of the prepared membranes are characterised by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The influence of the nanotube dimensions and surface chemistry on molecular transport properties of prepared membranes are assessed by analysing the transport of two model molecules with different hydrophilic–hydrophobic and charge properties. The obtained results reveal that the diffusional flux of model molecules through CNTs-NAAMs can be controlled by nanotube dimensions and surface chemistry of graphitic surface and these parameters can be used to tailor their chemical based molecular separation for specific applications.

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1. Introduction

Separation processes based on membrane technology have been established for many years as a favourable strategy

across many industries including chemical, food, pharmaceutical and waste and drinking water purification. Advancing membrane's performances for these applications such as energy efficiency, low operating costs, improved selectivity,

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and high operational stability has attracted enormous research activities in past 50 years [1,2]. Among the plethora of available commercial membranes and membrane materials usually based on polymers and ceramics, carbon nanotubes (CNTs)-based membranes have been recently explored with great interests due to their exceptional properties, including outstanding transport properties from their smooth hydrophobic graphitic walls, ordered and vertically aligned nanotube structures with high aspect ratio, and chemical and thermal stability [3,4]. So far, several theoretical and experimental studies have successfully demonstrated outstanding transport and selective properties of CNTs membranes for a broad range of gases and molecules [3–7]. Their applications for water desalination, gas separations, nanofiltration of biological mixtures, transdermal drug delivery, ultra-sensitive sensing and energy storage suggested CNTs membranes as a new frontier in membrane separation technology.

Traditionally, vertically aligned CNTs membranes have been produced by two approaches using silicon nitride and polymer matrices. The major disadvantage of these methods is the use of expensive laboratory facilities, time consuming and low throughput fabrication processes limited to laboratory scale [3,8,9]. Another drawback of these synthesis methods is the difficulty of controlling the geometric features of CNTs structures and ability to tailor their transport and selectivity properties required for specific molecular separations. Template direct synthesis, however, makes it possible to overcome that inherent limitation by growing CNTs inside templates with precisely controlled geometry. Among various templates, nanoporous anodic alumina membranes (NAAMs), consisting of hexagonal close packed cell arrangement with nanopores, have been extensively used to prepare highly ordered nanostructures including CNTs [10,11]. Pioneering works by Kyotani et al. demonstrated that these nanoporous alumina membranes can also be used as a host material to grow CNTs by catalyst-free chemical vapour deposition method [12,13]. The resulting composite membranes (CNTs-NAAMs) present hexagonally arranged arrays of CNTs of controlled inner diameter and length. Moreover, this method not only provides a precise control over the nanotubes' geometry but also enables selective surface chemistry modification of the inner wall surface of CNTs while keeping the outer surface chemistry unaltered (i.e. asymmetric surface chemistry inner-outer surface). To establish direct correlation between the dimensional features of CNTs-NAAMs and their inner surface chemistry with the transport performance is of critical importance for advancing their properties for separation applications. Recently, our group [14] demonstrated the fabrication of CNTs-NAAMs by catalyst-free CVD approach inside NAAMs using non-degradable grocery plastic bags as a carbon source and showed their transport performance. Nevertheless, more research must be carried out in order to explore the influence of the dimensional features of CNTs and inner surface chemistry of CNTs-NAAMs on their transport and selectivity properties related for their applications for chemical based separations.

In this paper, we present a study on the transport and selectivity performance of CNTs-NAAMs as a function of the dimensional features of CNTs (i.e. inner diameters and

lengths) and their internal surface chemistry. The aims of this work are: (i) to demonstrate the fabrication of CNTs membranes with controllable dimensions (i.e. pore diameters and length), (ii) to demonstrate the tailoring interfacial properties of the inner walls of CNTs by simple functionalization processes, and (iii) to explore the influence of CNTs dimensions and surface chemistry on their transport and selectivity properties. These studies will improve our understanding how to control the transport and chemical selectivity of CNTs membranes and design advanced membranes for addressing specific problems for separation of biomolecules with the same molecular size but different interfacial properties. A schematic illustration of the fabrication process of CNTs-NAAMs and subsequent surface chemistry modification is shown in Fig. 1.

CNTs-NAAMs were prepared using catalyst-free CVD approach using a mixture of toluene and ethanol. The dimensional features of CNTs-NAAMs were precisely engineered by the anodization conditions of NAAMs and the deposition time during the CVD process. The thermal annealing, hydrogen peroxide and plasma oxidation were used as simple processes to control the surface chemistry of inner walls of nanotubes from highly graphitic-hydrophobic to oxygen rich and hydrophilic. The molecular transport properties of prepared CNTs-NAAMs were explored by studying the diffusion of two model dye molecules with different hydrophobic-hydrophilic and charge properties.

2. Experimental details

2.1. Materials

High purity aluminium (Al) foils (0.32 mm, 99.999%) was obtained from Goodfellow Cambridge Ltd, UK. Copper chloride (CuCl_2), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), chromium trioxide (CrO_3), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), ethanol 99.7% ($\text{C}_2\text{H}_6\text{O}$), toluene 99.8% (C_7H_8), hydrogen peroxide (H_2O_2), hydrofluoric acid (HF), Rose Bengal ($\text{C}_{20}\text{H}_4\text{Cl}_4\text{I}_4\text{O}_5\text{-(RosB)}^{2-}$) and Tris(2,20-bipyridyl) dichlororuthenium(II) hexahydrate ($\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_6\text{Ru}\cdot 6\text{H}_2\text{O}\text{-(Ru(BPY)}_3\text{)}^{2+}$) were purchased from Sigma Aldrich (Australia) and used as received. High purity deionized (DI) water (resistivity 18.2 M Ω cm) from a Milli-Q water purification system was used in all the solutions used in this study.

2.2. Fabrication of nanoporous anodic alumina membranes (NAAMs)

Al foils were cut into small pieces of 15 mm \times 15 mm and used as substrates to prepare NAAMs by electrochemical anodization process as reported elsewhere [10,15,16]. Briefly, Al foils were first cleaned under sonication (10 min) in ethanol followed by water and then electro-polished in a mixture of HClO_4 and $\text{C}_2\text{H}_6\text{O}$ 1:4 (v:v) at 20 V for 3 min and then dried under a nitrogen stream. NAAMs were prepared through a two-step anodization process using 0.3 M $\text{H}_2\text{C}_2\text{O}_4$ as electrolyte solution. The first anodization step was performed at 40 V and 5 $^\circ\text{C}$ for 20 h in a two electrode electrochemical cell, where electropolished Al foils act as anode and a platinum

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