Synthesis, characterisation and applications of carbon nanotube membranes containing macrocycles and antibiotics

Luke Joshua Sweetman

University of Wollongong
UNIVERSITY OF WOLLONGONG

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SYNTHESIS, CHARACTERISATION AND APPLICATIONS OF CARBON NANOTUBE MEMBRANES CONTAINING MACROCYCLES AND ANTIBIOTICS

A thesis submitted in fulfilment of the requirements of the award of the degree

DOCTOR OF PHILOSOPHY

From

UNIVERSITY OF WOLLONGONG

By

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B NanotechAdv(Hons)

School of Chemistry

August, 2012
Certification

I, Luke Joshua Sweetman, declare that this thesis, submitted in fulfilment of the requirements for awarding the degree of Doctor of Philosophy, in the School of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Luke Sweetman
August, 2012
Abstract

This thesis explores the development of novel carbon nanotube membranes (buckypapers, BPs) incorporating antibiotic and macrocyclic ligands as dispersants. Membranes were obtained by vacuum filtration of dispersions containing the functional dispersants, or the surfactant Triton X-100 (Trix), and either single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). The homogeneity and stability of SWNT dispersions was first evaluated using a combination of UV-vis-NIR spectrophotometry, optical microscopy and Raman spectroscopy.

Microanalytical data and energy dispersive X-ray spectra were obtained for the SWNT buckypapers, and provided evidence for retention of dispersant molecules within the structure of the membranes. The electrical conductivities of the SWNT membranes varied between 30 ± 20 and 220 ± 60 S cm⁻¹, while goniometry revealed they all possessed hydrophilic surfaces (contact angle = 28 - 89°). The mechanical properties of SWNT buckypapers prepared using both macrocyclic ligands and antibiotics were shown to be comparable to that of a benchmark material prepared using SWNTs and Trix. Analysis of images obtained using scanning electron microscopy (SEM) showed that the surface morphology of the buckypapers was dependant on the identity of the dispersant, and the type of CNTs used to prepare the sample, with the average surface pore size varying between 7 ± 3 and 80 ± 20 nm. The surface area of SWNT buckypapers was determined through BET analysis of nitrogen adsorption-desorption isotherms, and found to vary between 30 ± 1 and 790 ± 4 m² g⁻¹. The length of sonication was shown to influence the porosity of SWNT buckypapers, which were also characterised using cyclic voltammetry and thermogravimetric analysis. The results of analysis by these methods revealed that the physical properties of the buckypapers
membranes were highly dependent on their composition and the conditions used during their preparation.

The permeability towards water of selected SWNT and MWNT buckypapers was explored using a custom made dead-end filtration setup. The permeability of membranes prepared using SWNTs was found to be strongly dependant on the identity of the dispersant used to produce the buckypaper (25 – 2400 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)), and in some cases rivalled that of commercial microfiltration membranes (1900 – 7000 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)). Transport of water through SWNT membranes was found to occur much more rapidly than with MWNT buckypapers made using the same dispersant.

The ability of buckypapers containing SWNTs or MWNTs, and either Trix or the antibiotic ciprofloxacin, to filter aqueous suspensions containing the bacterium Escherichia coli (\(E.\ coli\)) was examined. Analysis of the filtrates obtained after these experiments revealed that MWNT buckypapers were more effective at removing the bacteria from solution, and that incorporation of ciprofloxacin resulted in near complete removal of \(E.\ coli\) by both types of membranes.

The ability of MWNT buckypapers to remove metal ions and a radionuclide from solution was also investigated. These buckypapers proved to be ineffective for recovery of cesium or strontium from acidic solution, however, significant quantities of molybdenum, present as the molybdate ion, MoO\(_4^{2-}\) could be adsorbed. Experiments performed using molybdate containing the radioisotope \(^{99}\)Mo, showed that buckypapers became saturated with adsorbed molybdate after relatively short periods of time (c.a. 4 h). Furthermore, up to 2.6 mmol MoO\(_4^{2-}\) g\(^{-1}\) could be recovered.
Acknowledgments

First and foremost I would like to thank my primary supervisor Assoc. Prof. Stephen Ralph. Your passion and enthusiasm for chemistry is inspirational, and has driven me to persist even when things were not going my way in the lab. Thanks also for the many opportunities you have given me to join you on adventures both locally and abroad. I would also like to thank my co-supervisor Assoc. Prof. Marc in het Panhuis for his guidance and for sharing his extensive knowledge of carbon nanotubes. This has been an invaluable asset for both Steve and myself throughout the entirety of this study.

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<th>Description</th>
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<tr>
<td>MWNT-NH₂</td>
<td>Amine functionalised multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>ANSTO</td>
<td>Australian Nuclear Science and Technology Organisation</td>
</tr>
<tr>
<td>β–CD</td>
<td>β-cyclodextrin sulfated</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner and Halenda</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
</tr>
<tr>
<td>BP</td>
<td>Buckypaper</td>
</tr>
<tr>
<td>BSA</td>
<td>Bovine serum albumin</td>
</tr>
<tr>
<td>C₄S</td>
<td>4-sulfonic calix[4]arene</td>
</tr>
<tr>
<td>C₆S</td>
<td>4-sulfonic calix[6]arene</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>Dᵇᵘⁿ</td>
<td>Carbon nanotube bundle diameter</td>
</tr>
<tr>
<td>MWNT-COOH</td>
<td>Carboxyl functionalised multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>Cipro</td>
<td>Ciprofloxacin</td>
</tr>
<tr>
<td>σ</td>
<td>Conductivity</td>
</tr>
<tr>
<td>R₉</td>
<td>Contact resistance</td>
</tr>
<tr>
<td>CPM</td>
<td>Counts per minute</td>
</tr>
<tr>
<td>cc</td>
<td>Cubic centimetre</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>°</td>
<td>Degrees (angle)</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
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# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DAPI</td>
<td>4',6-diamidino-2-phenylindole</td>
</tr>
<tr>
<td>$K_d$</td>
<td>Distribution coefficient</td>
</tr>
<tr>
<td>$\varepsilon_{\text{Break}}$</td>
<td>Ductility</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>$E. \text{coli}$</td>
<td>Escherichia coli</td>
</tr>
<tr>
<td>F</td>
<td>Farad</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>HiPCO</td>
<td>High pressure carbon monoxide disproportionation</td>
</tr>
<tr>
<td>HK</td>
<td>Horvath-Kawazoe</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma-mass spectrometry</td>
</tr>
<tr>
<td>$d_{\text{BET}}$</td>
<td>Internal pore size (determined by BET)</td>
</tr>
<tr>
<td>pI</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>l</td>
<td>Length</td>
</tr>
<tr>
<td>L</td>
<td>Litre</td>
</tr>
<tr>
<td>LEP</td>
<td>Liquid entry pressure</td>
</tr>
<tr>
<td>LSZ</td>
<td>Lysozyme</td>
</tr>
<tr>
<td>LB</td>
<td>Luria-Bertani</td>
</tr>
<tr>
<td>$f$</td>
<td>Membrane Flux</td>
</tr>
<tr>
<td>$A_{\text{BET}}$</td>
<td>Membrane surface area (determined by BET)</td>
</tr>
</tbody>
</table>
m Metre
min Minute
mol Mole
M Molar concentration (mol L⁻¹)
MWNT Multi-walled carbon nanotube
MW Molecular weight (g mol⁻¹)
N Newton
NMR Nuclear magnetic resonance
Ω Ohm
ppm Parts per million
Pa Pascal
PVDF Polyvinylidene fluoride
PTFE Polytetrafluorethylene
TSP meso-tetra(4-sulfonatophenyl) porphyrin
PI Propidium iodide
PTS Pthalocyanine tetrasulfonic acid
rpm Revolutions per minute
SEM Scanning electron microscopy
υ Scan rate
s Second
S Siemen
SWNT Single-walled carbon nanotube
DSEM Surface pore size (determined by SEM)
σBreak Tensile strength
TGA Thermogravimetric analysis
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
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<tbody>
<tr>
<td>$R_T$</td>
<td>Total resistance</td>
</tr>
<tr>
<td>$T$</td>
<td>Toughness</td>
</tr>
<tr>
<td>Trix</td>
<td>Triton X-100</td>
</tr>
<tr>
<td>UV-vis-NIR</td>
<td>Ultraviolet-visible-near infra-red</td>
</tr>
<tr>
<td>$V$</td>
<td>Volts</td>
</tr>
<tr>
<td>$W$</td>
<td>Watt</td>
</tr>
<tr>
<td>(w/v)</td>
<td>Weight per volume</td>
</tr>
<tr>
<td>wt. %</td>
<td>Weight percent</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus</td>
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1

Introduction

This chapter gives an overview of the current state of knowledge of carbon nanotubes, including their properties, methods of processing, and potential applications. Also included are the aims of this project.
1.1 Chemical Separations:

The past few decades have seen chemical separation techniques become an integral feature of the scientific and industrial landscapes.\textsuperscript{1-3} In general, a chemical separation can be classified as any process whereby a mixture is broken down into two or more individual components with different composition. An enormous range of techniques are available to achieve a chemical separation depending on the composition of the mixture, including adsorption, chromatography, distillation, electrophoresis, dialysis and filtration.\textsuperscript{4} However, all separation techniques have the same end goals, which are to maximise the speed of the process and the volume of material which can be separated, whilst minimising energy input to make the process as economically viable as possible.

Of all the separation techniques, adsorption and filtration are by far the most simple and thus the most widely used approaches. The adsorption approach to chemical separation relies on the ability of a material to bind tightly to solutes, insoluble particles or even living organisms present in a solution that it is immersed in. Once the material is subsequently physically removed from the solution, any components of the solution that were sufficiently tightly adsorbed are recovered. A variety of different types of physical and chemical interactions can occur between an adsorbent material and the components of a solution, including dipole-dipole forces, hydrogen bonding, π–π stacking interactions and covalent bonding. Separation using adsorbent materials is commonly used in water purification and will be explored in more detail in section 1.1.3.

The earliest recorded filtration methods date back some 4000 years to the ancient Chinese, who used a variety of fabrics and metal colanders in wine making processes.\textsuperscript{5}
Approaches similar to this still exist today, however in more recent times the ability to separate not only heterogeneous mixtures, but also homogeneous mixtures of miscible liquids or gases has been realised. One technique that has emerged into a pre-eminent position in this ever growing field is membrane filtration. Membrane based separation methods are already widely used in fields such as water purification (e.g. desalination), milk fractionation and deacidification of fruit juices, and will be discussed further in the sections below.6

1.1.1 Membrane filtration:
A membrane can be considered as a selective barrier between two phases. The role of a membrane is to regulate the passage of components in one phase whilst retaining others in an adjacent phase.1 Such a simple concept obviously has advantages over many other chemical based separation methods. Perhaps of greatest importance in light of current climate issues, is the appreciably lower energy consumption of membrane filtration compared to most other separation techniques. In addition, many of the materials used for membrane separations are considerably more environmentally benign than those used in other separation techniques, and have the potential to be re-used after cleaning, thus helping to overcome wastage issues. The high durability and flexibility of membrane materials ensures there is enormous scope for developing novel separation systems for applications involving large quantities of complex mixtures. For these key reasons industry has rapidly adopted many membrane separation approaches to replace other more cumbersome techniques. Annual sales of synthetic membranes were quoted as being over US $2 billion in 2003 alone, with annual growth rates of the order of 5%, while in some sectors it was as high as 12-15% p.a.1
Membrane filtration is a broad field often subdivided into four different areas based on the size of the pores present in the membrane material. These four areas are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Figure 1.1). Each of these techniques rely on the existence of a pressure gradient to induce transport of molecules across a membrane barrier. In RO all the components present in a mixture are retained other than the solvent. This is in direct contrast with each of the other filtration techniques where macromolecules or particles are retained depending on their size. For example, microfiltration membranes are designed to retain micron sized particles with diameters between $0.5 - 10 \, \mu m$, whilst UF targets macromolecules or particles that are around $100 - 500 \, \text{nm}$ in diameter. As a result microfiltration membranes generally find greatest use for pre-filtration of solutions prior to further purification using other techniques such as UF or RO. Ultrafiltration is used most prolifically in the food industry, and in particular the dairy industry for concentration of whey protein and milk protein standardisation.

![Figure 1.1: Classification of membrane filtration techniques according to the size of the pores present in the membrane material. Figure adapted from reference 7.](image-url)
The term nanofiltration was introduced in the early 1980’s and has been classified as a process intermediate between reverse osmosis and ultrafiltration. Nanofiltration rejects particles which have diameters of the order of one nanometre, and has already proved highly successful for wastewater purification, separation of pharmaceuticals and in the food industry. Nevertheless, problems still exists with the technology used for NF and other membrane filtration techniques. Areas that are currently attracting significant interest include improving chemical and mechanical stability of membrane materials and preventing membrane fouling. Despite these issues, the advantages of using membrane technology will continue to ensure these methods remain in high use within the industrial separations sector.

The effectiveness of a filtration membrane for any application is dependent on its selectivity and permeability towards the analytes of interest. The selectivity of a membrane can be defined as its ability to remove a specific component from a mixture, whilst allowing the passage of others. The rate of flow of solvent across a membrane is commonly referred to as its permeability or flux rate ($f$). The flux rate can be calculated using the relationship shown in Equation 1.1, which shows that it is directly proportional to the mass or volume transport across the membrane per unit time ($J$), and is inversely proportional to the membrane surface area ($A$) and pressure difference applied across the membrane ($\Delta P$). The flux rate can be compared between membrane materials, regardless of the conditions used for measurement.

$$f = \frac{J}{A\Delta P}$$

**Equation 1.1**

The permeability of membranes varies markedly in response to differences in their composition, pore structure and the way they are prepared. Typical values for the
applied pressures used in conjunction with the various membrane filtration processes, and the permeabilities exhibited by commercial membranes under these conditions, are shown in Table 1.1. This data shows that membranes with larger pore sizes require a much lower pressure range for operation and provide a much higher flux of solvent.3

Table 1.1: Typical permeabilities and operating pressures for pressure driven membrane separation processes.13

<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Pressure range (bar)</th>
<th>Permeability (L m⁻² h⁻¹ bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>0.1 - 2.0</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>1.0 - 5.0</td>
<td>10 - 50</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>5.0 – 20</td>
<td>1.4 - 12</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>10 – 100</td>
<td>0.05 - 1.4</td>
</tr>
</tbody>
</table>

1.1.2 Membrane separation mechanisms:

The process by which a membrane separates the components of a mixture may involve one or more mechanisms, including size exclusion, adsorption and electrostatic interactions.15 Size exclusion is believed to be the main rejection mechanism for removal of molecules, and occurs when the physical size of an analyte is too great to allow its passage through the pores present in the membrane (Figure 1.2). Consequently the molecular weight, structure, size, geometry and hydrodynamic radius of the components of a mixture all play a role in determining the extent of their removal.16 There are a number of models that have been developed using these physical parameters, coupled with the membrane pore size, to predict whether or not analytes will be retained by this mechanism.17, 18 However, empirical calculations of this type are often complicated by the fact that the pores present in filtration membranes, and the components of a mixture, seldom have uniform shapes or sizes.
Although size exclusion is considered the predominant mechanism by which a membrane separates the components of a mixture, the overall process is also influenced by other membrane-mixture interactions. Adsorption is one such phenomenon and is often governed by the relative hydrophilicity or hydrophobicity of the membrane surface, and extent of hydrogen bonding and other interactions between solutes and the membrane. For example, the hydrophobic components of a mixture are more able to adsorb onto the surface and throughout the internal pore structure of a conventional hydrophobic polymer membrane, than other more hydrophilic components. This results in a higher level of rejection of hydrophobic analytes. In this case adsorption will continue until all the hydrophobic sites available on the surface and in the pores of the membrane have been saturated with hydrophobic components of the mixture. Thereafter there will be a lower level of rejection of these hydrophobic components.\textsuperscript{19} Hydrogen bonding between hydrophilic components of a mixture and a hydrophilic membrane can also produce a similar effect, as well as a significant drop in water flux. This occurs as a result of competition for hydrogen bonding sites on the membrane surface between water molecules and hydrophilic analytes.\textsuperscript{20}
Electrostatic interactions are another major factor influencing the ability of a membrane to separate charged solutes present in a mixture. The magnitude of these interactions is dependent on the size of the positive or negative charge present on the analytes, which are in turn influenced by factors such as solution pH and ionic strength. In addition, the pH of the feed solution in contact with a membrane can also affect the surface charge present on the latter, hence altering its retention properties.\(^{21}\) A number of studies have reported an increase in rejection of negatively charged organic solutes due to repulsive electrostatic interactions with a negatively charged membrane surface.\(^{22, 23}\) Conversely, positively charged solutes in a mixture will experience lower rejection due to electrostatic charge attraction towards a negatively charged membrane (Figure 1.3).

![Figure 1.3: Effect of a negative membrane surface charge on rejection of solutes with different overall charges.](image)

**1.1.3. Adsorbents:**

Adsorption of small molecules or ions by a material is another common technique employed within the chemical separations sector. One of the first adsorbent materials to be used industrially was activated carbon, which was originally used in the United States for the elimination of taste and odour from contaminated water sources.\(^{24}\) A variety of activated carbons can be produced from sources such as coconut shells, wood char, petroleum coke, lignite, coal and peat, to yield materials possessing graphitic and
highly porous structures with diameters of the same order as molecular dimensions.\textsuperscript{24, 25} Activated carbons undoubtedly remain the most popular and widely used adsorbents for the purification of wastewater due to their extremely high surface areas (up to 2000 $\text{m}^2\text{g}^{-1}$), high removal capacity, ability to remove a wide range of pollutants and very fast uptake kinetics. However, despite these outstanding properties, activated carbons are often expensive, non-selective and non-reusable once their capacity is reached. There is therefore a drive towards the use of new, lower cost adsorbents, including zeolites, molecular sieves, clay minerals and biosorbents such as algae, bacteria and chitosan.\textsuperscript{24, 26, 27} The ability to adsorb analytes is not limited to microporous materials, but also extends to many conventional polymer membranes. Some nanofiltration membranes, for example, have been shown to remove trace organic pollutants by hydrophobic adsorption mechanisms, while others are able to reject polar compounds owing to unfavourable electrostatic interactions.\textsuperscript{19, 22}

In more recent times, the development of new composite adsorbents incorporating functional and/or responsive components such as conducting polymers has received growing interest. For example, the recovery of the precious metal gold from aqueous solutions containing AuCl$_4$ was successfully achieved using polypyrrole, polyaniline composites where these polymers had been deposited on either reticulated vitreous carbon or common fabrics.\textsuperscript{28-33} Recovery was attributed in some cases to an adsorption phenomena facilitated by ion exchange reactions with dopant ions at the polymer surface, or in other instances to redox reactions, in which the metal ion is reduced to the zero-valent state by the conducting polymer, resulting in a highly oxidised polymer surface. In the case of the redox mechanism, the acidic medium used provided a means for spontaneous reduction of the oxidised polymer to its original redox state, thus
allowing the recovery process to continue. Significant levels of silver and platinum recovery have also been achieved using polypyrrole coated textiles.\textsuperscript{30, 34}

Materials functionalised with large supramolecules have proven successful for the recovery of metal ions from solution. For example, mesoporous silica containing the macrocyclic ligand cyclam anchored to its surface has been used to successfully recover copper(II) from aqueous solution.\textsuperscript{35} The efficiency of this material was shown to be highly sensitive to the solution pH, with basic conditions resulting in the greatest level of copper retention. This was unfortunately achieved at the cost of some degradation of the adsorbent material, with high pH solutions resulting in leaching of copper(II) cyclam moieties from the silica substrate.

### 1.2 Carbon Nanotubes:

Although significant advances in separation technology have been achieved, there is still scope for further separation applications to be developed if new, innovative materials can be produced. The current challenge is to overcome the typical situation where improvements to permeability generally have the undesirable effect of lowering selectivity.\textsuperscript{36-39} One material that is rapidly emerging as a promising component of membranes or adsorbent is carbon nanotubes (CNTs).\textsuperscript{40-42} This new form of carbon was discovered by Iijima in 1991,\textsuperscript{43} and possesses exceptional electrical and thermal conductivity, as well as unprecedented mechanical strength and rigidity (\textbf{Table 1.2}). This endows CNTs with the potential to tolerate high pressures, thus allowing very high flux rates to be produced using membranes composed of CNTs.\textsuperscript{42, 44, 45} The resistance of CNTs to high temperatures and harsh chemical environments will also enable them to be used in extreme industrial environments (pH or temperature) where conventional
polymer membranes or adsorbents would be unsuitable. Carbon nanotubes also possess unprecedented electrical and thermal conductivity, which can be attributed to their highly symmetric sp² hybridized structure. Consequently, there have been a myriad of proposed applications for CNT based materials, ranging from high strength conducting composites to hydrogen storage, sensors and actuators.

Carbon nanotubes are a unique allotrope which possess a structure similar to that of graphene and graphite, in that they also consist of a large number of carbon atoms bonded to each other so that they form numerous hexagons. While graphene sheets consist of a single plane of hexagonally linked carbon atoms, CNTs consist of graphene cylinders, with both ends which can be capped with fullerene (C₆₀) hemispheres. Carbon nanotubes exist as either single or multiple concentric graphene planes wrapped around a common axis, with diameters ranging between 0.5 – 100 nm, and lengths extending up to 100 mm. Depending on the number of graphene cylinders present, CNTs can be classified into one of three categories. These are single-walled carbon nanotubes (SWNTs), which consist of a single cylinder, double-walled carbon nanotubes (DWNTs), which are comprised of two cylinders, and multi-walled carbon nanotubes (MWNTs), which are formed when three or more individual graphene cylinders are present in the one system. In addition, it is also possible for each concentric graphene sheet to possess a different chirality, which is typically described

Table 1.2: Comparison of the properties of individual single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) to those of conventional materials.

<table>
<thead>
<tr>
<th>Property</th>
<th>CNTs</th>
<th>Conventional Materials</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>3500 W m⁻¹ K⁻¹ (SWNTs)</td>
<td>2000 W m⁻¹ K⁻¹ (Diamond)</td>
<td>52</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>0.9 TPa (MWNTs)</td>
<td>207 GPa (Steel)</td>
<td>53, 54</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>150 GPa (SWNTs)</td>
<td>900 MPa (Steel)</td>
<td>54, 55</td>
</tr>
<tr>
<td>Carrier mobility</td>
<td>10⁶ cm² V⁻¹ s⁻¹ (SWNTs)</td>
<td>1350 cm² V⁻¹ s⁻¹ (Silicon)</td>
<td>56, 57</td>
</tr>
<tr>
<td>Electrical Current Density</td>
<td>&gt; 10⁹ A cm⁻² (MWNTs)</td>
<td>&lt; 10⁷ A cm⁻² (Copper)</td>
<td>58</td>
</tr>
</tbody>
</table>

Conductivity values reported represent electrical or heat flow along the length of the CNTs (not across).
by a chiral vector defined by \( n \) and \( m \) as shown in Figure 1.4. This chiral vector dictates the molecular orbital pattern and density of states within each graphene sheet and thus controls whether each cylinder is metallic or semiconducting in nature. In general, if \( n-m \) is a multiple of 3 the individual tube sheet will display metallic electronic properties, whereas if \( n-m \) is not a multiple of 3 it will behave as a semiconductor.\(^6\) Thus, SWNTs typically contain a mixture of semiconducting and metallic nanotubes, whilst MWNTs are always metallic despite having some semiconducting sheets.

![Figure 1.4: A single graphene sheet showing how the chiral vector is defined.\(^6\)](image)

Four main techniques exist for the production of CNTs. These are arc discharge, laser ablation, ball milling and chemical vapour deposition. In this study, investigations were performed using both SWNTs and MWNTs which were produced using a chemical vapour deposition (CVD) technique. This method involves the decomposition of a carbon-containing carrier gas such as carbon monoxide onto a substrate, typically in the presence of a metal containing catalyst under very high temperature and pressure.\(^6\) The CVD approach provides advantages over other methods of CNT preparation, as it rapidly provides materials with higher purity and in greater quantity.\(^6\) These benefits are due to the continual replacement of the carbonaceous gas flowing into the reaction chamber, rather than the etching of a carbon target or electrode.
Throughout this work, MWNTs were obtained from Nanocyl™, who utilise a CVD method of production, whereas SWNTs were obtained from Unidym™. The latter company produce their materials using a modified CVD method known as the high pressure carbon monoxide disproportionation (HiPCO) process. This method involves the catalytic growth of SWNTs using carbon monoxide gas as the source of carbon and Fe(CO)$_5$ as a metal-containing catalyst. As these two species are injected into a heated reactor, Fe(CO)$_5$ decomposes and subsequently re-condenses into larger iron clusters onto which SWNT growth can nucleate (Figure 1.5). This process is described by the chemical equation shown in Reaction 1.1, known as the Boudouard process. During this reaction carbon monoxide undergoes disproportionation to produce SWNTs and carbon dioxide gas. The pressure and furnace temperature control the size, diameter distribution and amount of CNTs produced. Due to this high degree of control, and the ability of the process to be fully automated, HiPCO remains the predominant technique for the continuous production of SWNTs today.

\[
\text{CO} + \text{CO} \xrightarrow{\text{Fe}} \text{CO}_2 + C_{\text{(SWNT)}}
\]  

Reaction 1.1

![Figure 1.5: Schematic overview of the HiPCO process for synthesising the SWNTs used in this study.](image)
1.3 Processing Carbon Nanotubes:

While their unheralded properties make CNTs attractive for a number of possible applications including membrane filtration, their inability to be readily processed into useful bulk materials has proven a major stumbling block for researchers worldwide. Perhaps the most popular approach to overcoming this problem is to disperse the CNTs in a solvent, and manipulate the material in the liquid state. However, this is not a trivial task as CNT production methods result in the formation of nanotubes in a highly aggregated state by virtue of strong intermolecular interactions between individual tubes and their very high surface area to volume ratios.\textsuperscript{67, 68} Consequently, CNTs are inherently hydrophobic and insoluble in water and only sparingly soluble in selected organic solvents.\textsuperscript{69}

Functionalisation of CNTs using either covalent or non-covalent methods has proven a popular method for allowing them to be dispersed into solution. Covalent functionalisation involves the chemical modification of the CNT surface with various moieties such as amino or carboxylic acid groups (Figure 1.6(a)).\textsuperscript{70, 71} The presence of these functional groups can provide anchor points for the attachment of larger groups, which can significantly alter the hydrophobicity and hence wetting behaviour of the nanotube surface, resulting in higher solubility in various solvents.\textsuperscript{71} Despite the utility of the covalent functionalisation method, a major drawback of this approach is that considerable damage to the sp\textsuperscript{2} hybridised carbon structure can occur as a result of the harsh chemical methods required to introduce these functional groups. This results in the formation of what are known as functionalised CNTs and gives rise to a dramatic, and permanent change in properties.\textsuperscript{72, 73}
An alternative method for the dispersion of CNTs involves non-covalent functionalisation. This approach involves the modification of the nanotube surface by the adsorption of an amphiphilic dispersant molecule such as a surfactant or large polymer molecule. For example, Chen et al. reported the non-covalent functionalisation of SWNTs using 1-pyrenebutanoic acid, succinimidyl ester, where adsorption was facilitated by a $\pi-\pi$ stacking mechanism. This process involves the sharing of $\pi$ electrons between those in the aromatic rings of the pyrene, and the basal graphitic plane of the CNTs (Figure 1.6b). These dispersants are subsequently able to provide steric or electrostatic repulsions that are capable of overcoming strong inter-tube forces. At the same time, the dispersant experiences strong hydrophilic forces such as hydrogen bonding or dipole-dipole interactions with solvent molecules, enabling solubilisation of the CNTs to take place.

An aqueous dispersion is usually obtained through application of ultrasonic energy to a suspension of CNTs in a solution containing a suitable dispersant. Ultrasonic energy utilises acoustic waves at frequencies well beyond human hearing (18 – 20 kHz). The effect of ultrasonic energy on materials arises primarily from a phenomenon known as

Figure 1.6: Structures of: (a) a SWNT covalently modified with amine and carboxyl groups; and (b) a SWNT non-covalent functioned by $\pi-\pi$ stacking with 1-pyrenebutanoic acid, succinimidyl ester.}

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**Figure 1.6:** Structures of: (a) a SWNT covalently modified with amine and carboxyl groups; and (b) a SWNT non-covalent functioned by $\pi-\pi$ stacking with 1-pyrenebutanoic acid, succinimidyl ester.74
Cavitation refers to the collapse of micrometer sized bubbles created by the proliferation of acoustic waves in liquids, which grow through diffusion and coalescence. This process enables the concentration of low-density air bubbles into bubbles with much higher and less stable densities which, upon collapse result in extreme conditions that can induce profound changes at a solid-liquid interface.

Collapse at a solid surface will result in considerable damage by the shock waves produced, whereas collapse near the surface will result in a microjet of solvent hitting the solid with great force. Strain rates of up to $10^9$ s$^{-1}$ are theoretically predicted for radial elongational flow around a cavitation bubble, which are capable of cutting particles. In the case of CNT dispersions, ultrasonic energy has already been shown to cause bond breaking and thus shortening of carbon nanotubes and dispersant molecules. When employing a sonication horn as used in this study, the extent of scission of the nanotubes is strongly dependent on the sonication time used and thus the energy imparted (Figure 1.7). Therefore it is imperative to ensure that the sonication regime used does not provide excessive energy which may damage the CNTs. This will be explored in more detail in chapter 3.

![Figure 1.7: Effect on the Average length of MWNTs (0.9 wt. %) dispersed in sodium dodecyl sulphate (1.2 wt. %) of: (a) sonication time ($T_{US}$) and (b) acoustic energy ($E_{US}$).](image)

Chapter One: Introduction
1.4 Carbon Nanotube Dispersions:

Extensive studies have shown that a large range of surfactants and polymers are capable of effectively dispersing CNTs via a non-covalent mechanism.\textsuperscript{72, 79-82} In contrast, there have been limited studies into the suitability of other classes of small molecules, such as macrocycles and antimicrobial agents for dispersing CNTs.\textsuperscript{72, 83, 84} Each of these classes of small molecules have their own unique properties which could potentially be added to those of the nanotubes, thereby creating new classes of materials that may be suitable for a variety of novel applications. There is ample literature precedent for this strategy, as composite materials consisting of conducting polymers such as polypyrrole (PPy) and macrocyclic ligands have been studied previously.\textsuperscript{85-89} For example, PPy membranes containing the conducting polymer doped with sulfonated cyclodextrins and calixarenes have been prepared and shown to display variable permeability towards a variety of metal ions.\textsuperscript{86, 90} Transport across these membranes was facilitated by electrochemically cycling PPy between its reduced and oxidised forms, and through complexation equilibria involving the metal ions and macrocycle dopants. Electrodes composed of PPy doped with $\beta$-cyclodextrin have also been prepared and proposed for use in sensing applications. For example, electrochemically deposited films comprised of PPy doped with $\beta$-cyclodextrin, present on a platinum substrate have shown high selectivity towards the detection of dopamine, with a limit of detection of only $3.2 \times 10^{-6}$ M.\textsuperscript{88} It was believed that the sensing properties of this composite could be attributed to the formation of an inclusion complex between the cationic dopamine and the negatively charged macrocyclic ligand.

The following sub-sections review the work that has appeared in the literature describing the preparation and properties of CNTs which have been non-covalently
functionalised with different classes of dispersants. Each of these classes of compounds will be the subject of further investigation throughout this study.

1.4.1 Surfactants:

Surfactants have proven to be highly effective dispersing agents for CNTs due to their unique amphiphilic nature. The term surfactant is a general name given to molecules that have the ability to accumulate at the interface between two insoluble phases and modify the interfacial surface tension, such as that between CNTs and water. Surfactants generally possess a long non-polar hydrocarbon chain and a polar head group, and can thus act as a bridge between a hydrophobic and a hydrophilic phase. Surfactants are classified according to the charge of the polar head group as cationic, anionic, zwitterionic or non-ionic.

The use of both ionic and non-ionic surfactants for dispersing CNTs has been successfully demonstrated. One non-ionic surfactant that has proven highly efficient at dispersing CNTs in aqueous solution is octylphenolesulfonate, also known as Triton X-100 (Trix). The mechanism by which Trix disperses CNTs is thought to involve \( \pi \)-stacking between the aromatic ring system of the surfactant molecule and double bonds present on the CNT surface. Adsorption interactions are also believed to occur when ionic surfactant molecules such as sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (NaDDBS) disperse CNTs. In both cases, it is postulated that the hydrophobic region of the surfactant molecule adsorbs onto the graphite surface by van der Waals interactions, and the hydrophilic part orients itself towards the aqueous phase giving rise either to a monolayer or a half-cylinder structure on the surface. Several different mechanisms by which surfactant molecules adsorb...
ont the surface of CNTs according to this commonly accepted model are shown in Figure 1.8. However, another model has also recently been proposed.\textsuperscript{81}

It has been demonstrated that surfactants can successfully produce dispersions containing up to \textit{c.a.} 0.2 \% (w/v) CNTs. Such dispersions typically have surfactant concentrations between 0.5 – 2 \% (w/v), which translates to an optimum nanotube : surfactant ratio between 1 : 5 and 1 : 10 (wt:wt).\textsuperscript{81, 95-97} Wang \textit{et al.} showed the cationic surfactant hexyl-α,β-bis(dodecyldimethylammonium bromide) (C\textsubscript{12}C\textsubscript{6}C\textsubscript{12}Br\textsubscript{2}) could be used to produce MWNT dispersions that were stable for over four months, and contained 0.1 \% (w/v) CNTs.\textsuperscript{98} Similarly, Jiang and co-workers used quantitative methods to show that dispersions produced using SDS still contained 85\% of the CNTs in solution after 500 h (c.a. 3 weeks).\textsuperscript{97} While some initial precipitation of CNT material occurred during the first 150 h after preparation of the dispersion, after this period no further settling took place throughout the duration of the study. This example illustrates the excellent stability that can be achieved with CNT dispersions.
produced using surfactants after initial removal of undispersed material. High dispersion stability is of vital importance to ensure that the CNTs remain individualised, and to prevent any compromising of their extraordinary properties. Thus, due to inherent stability, and the significant quantity of CNTs which can be incorporated into dispersions using surfactants, these solutions are typically used to produce stand-alone films. The latter materials are commonly used as platforms for further modification by intercalation of other molecules such as polymers for use as high strength composite materials, or as electrodes for investigating electrochemical interactions between various analytes and the nanotube surface.95, 99

1.4.2 Biomolecules:
The term biomolecule refers to large molecules that are made from naturally occurring monomer units, and which are found in living organisms. A wide variety of these biomolecules, including proteins, carbohydrates and deoxyribonucleic acid (DNA) have been investigated for their ability to disperse CNTs via a non-covalent mechanism. Lysozyme (LSZ) and bovine serum albumin (BSA) are just two examples of proteins that have proven highly successful for solubilising CNTs in water.100-102 The use of protein dispersants is of particular interest due to their lack of toxicity compared to surfactant and other dispersant molecules, and because they enable the CNTs to be identified by other proteins or macromolecules, thus facilitating their use for biological applications.100

The mechanism by which proteins disperse CNTs is believed to involve electrostatic interactions, and is thus highly dependent on the charge distribution present along the length of the molecule and solution pH.100, 103 For every protein there is a specific pH at
which its net charge will be zero. This pH value is commonly referred to as the isoelectric point (pI), and varies with the amino acid composition of the protein. Near the pI, CNT dispersions have been shown to be unstable as there are insufficient repulsive forces between individual protein-adsorbed CNTs to prevent reaggregation.\textsuperscript{100, 103} Conversely, the further solution pH is from the pI of the protein, the greater the charge present along its length (Figure 1.9a). This increases the ability of the protein to produce highly stable CNT dispersions. For example, Nepal \textit{et al.}\textsuperscript{98} investigated the ability of proteins such as LSZ and BSA (pIs of 10.7 and 4.7, respectively) to disperse SWNTs (Figure 1.9b). When the pH of the solution used to disperse the CNTs was close to the pI of the protein, a clear solution was obtained due to the lack of suspended nanotubes. However, when the pH was moved away from the pI, the dispersions obtained were generally considerably darker, indicating a much greater concentration of stabilised SWNTs was now present in solution.\textsuperscript{100} This investigation also showed that by using solutions with a concentration of protein of just 1 mg mL\textsuperscript{-1} it was possible to obtain aqueous dispersions in which the concentration of SWNTs was between 0.13 and 255.3 mg L\textsuperscript{-1}.

\textbf{Figure 1.9:} The effect of: (a) pH on the charge along the polymer backbone of LSZ, as determined by its zeta potential and (b) solution pH on the ability BSA and LSZ to disperse SWNTs in water. The pIs for BSA and LSZ are 4.7 and 10.7, respectively.\textsuperscript{100}
Carbohydrates such as chitosan and gellan gum have also been shown to be highly effective at dispersing CNTs in water via a similar mechanism to that exhibited by proteins.\textsuperscript{104} These polysaccharides are typically protonated or deprotonated in aqueous solution, thus allowing their adsorption onto the surface of CNTs, preventing re-aggregation by a combination of electrostatic repulsion and steric hindrance.\textsuperscript{105} For example, chitosan has been shown to produce solutions with loadings of 0.5\% (w/v) SWNTs. This was achieved using chitosan concentrations between 0.25 and 1.5\% (w/v), and a dispersant : nanotube ratio of at least 1 : 1 (wt:wt).\textsuperscript{106} Similar dispersions prepared using MWNTs have been shown to display very high stability (up to 12 months).\textsuperscript{107}

Deoxyribonucleic acid has also been shown to disperse CNTs by a number of research groups.\textsuperscript{102, 108, 109} The ability of single stranded DNA (ssDNA) to bind to the surface of CNTs has been attributed to the presence of the heterocyclic bases, which can participate in π–π interactions with the nanotubes, and results in further exposure of the polar nucleic acid backbone to solvent molecules.\textsuperscript{102} Dispersions produced using ssDNA or salmon sperm DNA have been shown to have maximum CNT loadings between 1 and 4 mg mL\(^{-1}\), and nanotube : DNA ratio of c.a. 1 : 1 (wt:wt).\textsuperscript{102, 107}

The ability to produce CNT dispersions using biomolecules is of great interest owing to their potential to be used in biological applications. The majority of research in this area has focused on utilising the high conductivity of CNTs within a variety of constructs including thin films, hydrogels and porous sponges. These materials have shown promise in a range of potential applications such as biosensors, drug delivery agents and as scaffold materials for tissue engineering.\textsuperscript{101, 106-108} Materials synthesised from
dispersions of CNTs produced using biomolecules also exhibited substantial mechanical strength compared to other CNT composites. This enhancement is believed to be due to the ability of the large polymer chains to entangle between the network of nanotubes, thereby providing additional reinforcement.\textsuperscript{110, 111} For example, Whitten \textit{et al.} used SWNT dispersions produced using chitosan and salmon sperm DNA to prepare thin films which exhibited tensile strengths 5 – 10 times greater than that of identical films prepared using SWNTs and Triton X-100.\textsuperscript{112} The surfaces of films produced using the biopolymers were also shown to support growth of large numbers of L-929 mouse fibroblast cells.

\textit{1.4.3 Macrocycles:}

Macrocycles are large cyclic molecules of particular interest in the field of host-guest chemistry. One of the main objectives of host-guest chemistry is to synthesise molecules capable of selectively binding specific guest analytes such as metal ions, anions and small organic molecules.\textsuperscript{113, 114} In order to achieve this a macrocycle must typically possess an intramolecular cavity with a similar size to that of the guest molecule of interest, and be able to bind to the desired guest molecule by a combination of weak intermolecular interactions such as hydrogen bonding, π–stacking interactions and van der Waals forces. Owing to the predominance of these relatively weak interactions in the overall binding mechanism, host-guest interactions are generally reversible.\textsuperscript{113}

A myriad of macrocyclic molecules have been the subject of host/guest studies in recent times,\textsuperscript{115-118} however there have only been a small number of studies which have focused on their ability to disperse CNTs.\textsuperscript{119-125} Of these, three classes of macrocycles,
namely porphyrins, calixarenes and cyclodextrins have been the subject of preliminary investigations. The molecular structures of examples of each of these classes of molecules are shown in Figure 1.10. Each of these are amphiphilic in nature and therefore capable of forming a micelle-like supramolecular structure.\textsuperscript{126} This property coupled with the extensive sp\textsuperscript{2} bonding present in some instances in their highly conjugated structures, makes them highly suitable for dispersing CNTs. The formation of composite materials in which macrocycles are non-covalently attached to CNTs also provides a means to increase the ability of the latter to interact with a myriad of guest analytes. This could be achieved through the guest molecule binding to the internal cavity of the macrocycle or as a result of the ability of the latter to trap molecules in the core of their micelles.\textsuperscript{124}

![Figure 1.10](image-url)

**Figure 1.10:** Molecular structures of: (a) 4-sulfonic calix[6]arene hydrate, (b) β-cyclodextrin sulfated, (sodium salt) and (c) phthalocyanine tetrasulfonic acid.

In 2003 Murakami *et al.* was the first to investigate the use of a metal porphyrin complex as a dispersant for SWNTs. These workers found it was possible to produce dispersions in organic solvent, using zinc protoporphyrin (ZnPP – Figure 1.11a), and that a strong interaction existed between the porphyrin and the SWNTs.\textsuperscript{119} Evidence of this strong interaction was provided by fluorescence spectroscopy, which showed that the fluorescence resulting from the ZnPP was quenched when coupled with SWNTs in solution. This was believed to be a result of efficient energy transfer between the ZnPP complex and the nanotubes.
In more recent times the use of water soluble porphyrin derivatives to disperse CNTs in aqueous solution has been demonstrated. For example, *meso*-(tetrakis-4-sulfonatophenyl) porphine (Figure 1.11b) was shown to disperse SWNTs effectively in aqueous solution using ultrasonication, when the nanotubes were present at very low loadings (0.0004% (w/v)). The stability of the dispersions was attributed to physical adsorption of porphyrin molecules onto the sidewalls of the SWNTs, via π–π stacking and van der Waals interactions. UV-vis spectrophotometry confirmed that the dispersions contained SWNTs coated by porphyrin aggregates adsorbed onto their debundled surfaces. After further examination it was concluded that it was the free base form of the porphyrin that selectively binds to SWNTs and renders them soluble.

Figure 1.11: Molecular structures of: (a) zinc protoporphyrin, and (b) *meso*-(Tetrakis-4-sulfonatophenyl)porphine.

Cyclodextrins and calixarenes have also been investigated for their ability to disperse nanotubes via ultrasonication, using CNT concentrations of up to 0.2% (w/v) and 0.1% (w/v), respectively. For example, dispersions containing up to 0.2% (w/v) MWNTs could be successfully prepared using aqueous 2% (w/v) β-cyclodextrin (β–CD) solutions and sonication times of 10 min. These dispersions contained a maximum of 2 mg of MWNTs and were immediately drop cast onto electrode surfaces to form films. Therefore the stability and interactions within these dispersions have yet
to be fully investigated. These electrodes were subsequently investigated for their ability to specifically detect various biomolecules including uric acid, ascorbic acid, guanine and adenine. A marked increase in electrochemical currents were observed for all analytes using the modified electrodes, demonstrating their significantly improved sensitivity. It was believed that this was due to the formation of inclusion complexes between the \( \beta\text{–CD} \) bound to the nanotube surface and the biomolecules, which resulted in a significant increase in the apparent concentration of analyte present at the interface with the modified electrode.

1.4.4 Antibiotics:

The term antibiotic was first coined by Selman Waksman in 1942 and refers to a class of compounds that are capable of inhibiting the growth of bacteria and fungi, or killing them outright. Most antibiotics are derived from natural products, however an increasing number are now synthesised in the laboratory (synthetic) or modified from existing compounds (semi-synthetic). Antibiotics can be classified into two main categories; broad spectrum and narrow spectrum antibiotics. Narrow spectrum antibiotics specifically target gram-negative or gram-positive bacteria, whilst broad spectrum antibiotics can affect both categories. The structures of an example of each class of antibiotic are shown in Figure 1.12.

![Molecular structures of: (a) penicillin G, a narrow spectrum antibiotic, and (b) the broad spectrum antibiotic tetracycline.](image_url)
The presence of double bonds, as well as hydrophobic and hydrophilic functional groups in their structures, has led to a number of investigations into the potential of CNTs and graphite as potential absorbent materials for antibiotics in aquatic environments. These have shown that CNTs are highly efficient at removing the antibiotics tetracycline, sulfapyridine and sulfamethoxazole, which was attributed to π–π stacking interactions with the graphene surface of the nanotubes. Prior to this the use of antibiotics to disperse CNTs using a non-covalent mechanism had only been explored by Kumar and co-workers. These studies showed that MWNTs could be successfully dispersed using acidic aqueous solutions containing ciprofloxacin, with the aid of ultrasonication (10 min). Stable dispersions could be obtained using 5 mM ciprofloxacin and 0.1% (w/v) MWNTs, however these solutions only contained a maximum of 4 mg MWNTs. These dispersions were drop cast onto glassy carbon electrodes and then used to immobilise proteins such as myoglobin and cytochrome C. These highly biocompatible surfaces provided a useful platform to study direct electron transfer reactions with the proteins, and also facilitated their use as biosensors for the detection of H₂O₂.

1.5 Carbon Nanotube Membranes:

The synthesis of macroscopic materials from CNTs is of great interest to those who wish to utilise their unique properties. The past few years has seen researchers focus on examining two main classes of such materials: vertically aligned CNT membranes and CNT buckypaper membranes (Figure 1.13). Each class of materials is prepared by distinctly different methods, and has different structures and properties, both of which will be explored in the sections that follow.
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Figure 1.13: SEM micrographs of: (a) an aligned CNT forest deposited via CVD onto a substrate, and (b) a buckypaper produced from SWNTs using the dispersant Trix. 133, 134

1.5.1 Aligned CNT membranes:

As the name suggests, aligned carbon nanotube membranes consist of highly ordered vertically aligned arrays of individual CNTs (Figure 1.13a). Aligned CNT membranes possess a very regular pore structure consisting of very narrow internal cavities within individual tubes (if opened), which are of the order of < 5 nm, as well as interstitial voids between the tubes, which are typically c.a. 5 – 30 nm in diameter.135-137 The pore structures of these membranes therefore are capable of separating small organic or inorganic molecules from each other via a size exclusion mechanism.

Aligned CNT membranes are made by either embedding CNTs into a matrix, or growing them directly onto a substrate, utilising a CVD technique. The former method, typically requires a flat surface such as quartz or silicon, which contains transition metal catalyst particles deposited on its surface to serve as the sites where CNTs are formed.132, 138 Alternatively the substrate can be a porous material such as anodised alumina.132 In this case the aligned CNTs that grow on the surface of the substrate can then be treated with a range of polymer binders (such as polystyrene) or with silicon nitride, to fill in the interstitial voids between the individual CNTs.132, 139 After the growth of CNTs the substrate can then be removed by chemical etching methods using
reagents such as hydrofluoric acid or sodium hydroxide, leaving a forest of CNTs whose internal cavities can then be exposed by oxidation using a water generated plasma.\textsuperscript{139}

An alternative to producing aligned CNT membranes is to synthesise a membrane without a supporting matrix. Again a flat or microporous substrate such as quartz or alumina is required. This method does produce CNT forests that are as highly aligned as those made by the previous method.\textsuperscript{132, 140} This technique does not include sealing of the interstitial pore spaces. Therefore the final material can contain larger voids which can extend up to tens of nanometres in diameter throughout its structure. Once complete, the removal of the CNT film from the substrate using chemical means as described previously can again be employed, to leave behind a free-standing material.

\textit{1.5.2 Buckypapers:}

Although aligned CNT membranes have a number of properties which make them very attractive for specific applications such as nanofiltration, there are two major drawbacks associated with these materials. Firstly, the aligned forest of CNTs must often be removed from an underlying substrate, which can involve vigorous chemical etching methods using reagents such as hydrofluoric acid. Secondly, the ends of the CNTs must be opened, which also requires harsh conditions such as plasma oxidation. Both steps are quite complex to optimise and costly to perform. Furthermore there are significant risks involved in using the dangerous chemical reagents and conditions involved.

An alternative to producing aligned CNT membranes for different applications is to use the self-supported mats of entangled CNTs known as buckypapers (BPs) shown in
Figure 1.13b. These materials are made by first producing dispersions of CNTs, and then filtering the dispersion either using vacuum or positive pressure onto a porous polymer filter. Once dry, these thin films can be removed from the underlying polymer support to produce a thin free-standing film. It is possible to produce buckypapers on a larger scale than aligned CNT membranes, and their preparation relies on much simpler, and inexpensive procedures. Buckypapers possess a highly disordered structure, consisting of CNTs bound together by intermolecular forces, such as van der Waals forces and $\pi-\pi$ interactions, at intertube junctions. The internal structure of BPs consists of a combination of small and large pores which correspond to the spaces within and between bundles of CNTs, respectively. However, the pore size distributions of BPs are dominated by the presence of larger pores with diameters of 100 nm or above.

Due to the wide range of conditions available to produce BPs, including variations in the type of CNTs used, the identity of the dispersant used during preparation (if any), the solvent, and the sonication conditions employed, it is possible to produce an enormous range of these materials. Surprisingly, studies have shown that the pore structure of MWNT buckypapers produced using organic solvents (with no dispersant) vary very little in response to changes in the amount of sonication time and the solvent used. When considering aqueous dispersions however, it has been shown that the type of dispersant used and sonication time play an important role in determining the properties of the BP membrane created. Short sonication times ($\leq 15$ min) have been shown to result in BPs featuring morphologies with highly aggregated SWNTs, whereas longer sonication times ($\geq 30$ min) generally resulted in BPs with a much finer pore structure due to greater de-aggregation of nanotubes in the initial dispersions. However,
use of increased sonication times can severely reduce the conductivity and mechanical properties of the final BPs produced, due to defect sites being created within the sp² hybridised structure of the nanotubes as a result of prolonged exposure to ultrasonic energy. The choice of dispersant can also play an even more significant role in determining the porosity and properties of BPs made from aqueous solution. The use of larger dispersant molecules such as chitosan or gellan gum, in place of smaller dispersants such as the surfactant Triton X-100, was found to result in BPs with much larger pore diameters and an overall rougher surface morphology. The presence of these larger biopolymers also gave rise to much lower electrical conductivities and improved mechanical properties as a result of absorption onto the surface of the CNTs. This was due to impaired electron transfer between adjacent nanotubes, and providing entanglement of the bulky polymer chains between CNTs.

In recent times buckypapers have been proposed for a range of potential applications such as supercapacitors, electrodes and high strength light weight composites. These specific investigations have been inspired by the high conductivity of BPs, which have been shown to be of the order of 10⁵ S m⁻¹, and their very high specific surface areas which are of the order of 500 m² g⁻¹. Buckypapers have also been shown to possess high Young’s moduli of up to 2.3 GPa, breaking stresses of up to 33 MPa, and ductility ranging from 1 – 2.5%, ensuring that they are robust enough for use as electrodes.

An emerging area of BP research is that of use in membrane separation based applications. As pore sizes in buckypaper membranes are dominated by large pores,
these materials may be suitable for filtration of larger molecules such as proteins. The following section provides a general overview of the work that has already appeared in the literature describing the potential use of BPs and aligned CNT membranes for separation applications.

1.6 Filtration using Carbon Nanotube Membranes:

Carbon nanotubes have been shown by molecular dynamics simulations to be extremely permeable towards gases. 42, 152 This was proposed to be due in part to the intrinsic smoothness of the surfaces of the nanotubes, which minimises interactions between gas molecules and the CNTs. The permeability of water through CNTs within a membrane has also been predicted to be very high, owing to the existence of ordered hydrogen bonding networks between solvent molecules, and formation of weak attractive interactions between water molecules and the smooth CNT surface, which results in almost frictionless flow. 132, 153, 154 Experimental permeability measurements performed using aligned CNT membranes have exceeded all of these predictions for both gas and liquid transport. These studies have shown that flux rates across aligned DWNT membranes composed of nanotubes with diameters less than 2 nm surpass predicted permeability values by more than a factor of 10 for gases, and up to 5 orders of magnitude for water. 42, 153

Aligned CNT membranes have already proven quite successful for separating a range of mixtures. 132,135 For example, Srivastava et al. showed that membranes composed of radially aligned MWNTs (Figure 1.14) could selectively remove the higher molecular weight hydrocarbons from a crude petroleum sample. 135 Similar studies have also
shown that membranes composed of aligned MWNTs permit the passage of \([\text{Ru}(\text{bipy})_3]^{2+}\) and small gold nanoparticles with diameters \(\leq 5\) nm, but excluded larger gold nanoparticles with diameters of 10 nm or greater.\textsuperscript{155} It has also been shown that modifying the surface of nanotubes present in an aligned membrane using plasma oxidation and acid treatment, or through attachment of a protein such as streptavidin, make it possible to regulate the rate of passage of compounds such as \([\text{Ru}(\text{NH}_3)_6]^{3+}\) and methylviologen by several orders of magnitude.\textsuperscript{136,155,156}

![Figure 1.14:](image)

\(1\ \text{mm}\)

The permeability of buckypapers towards a wide range of gases such as \(\text{H}_2, \text{He}, \text{O}_2, \text{N}_2, \text{CH}_4\) and \(\text{CO}_2\) has also been investigated and shown to be highly dependent on the applied pressure. The fluxes obtained varied between 3 and \(12 \times 10^{-9}\) \(\text{m}^2\ \text{s}^{-1}\) for BPs produced from MWNTs dispersed in organic solvents (DMF and acetylacetone), and was shown to be strongly dependent on the effective size of the gas molecules.\textsuperscript{144,157}

Thin buckypaper / cellulose fibre composites have also been used to separate airborne particulates, with the membranes achieving removal efficiencies in excess of 99.9% for particles having diameters of the order of approximately 300 nm.\textsuperscript{158} Desalination of water using a membrane distillation technique and BPs produced from isopropanol has also been shown by Dumée \textit{et al.}\textsuperscript{14} This process utilised the vapour pressure gradient
existing across the hydrophobic membrane to transport purified hot saline solution to a
cold permeate, and resulted in 99% salt rejection and very high flux rates
of \( \sim 12 \text{ kg m}^2\text{ h}^{-1} \).

### 1.7 Antibacterial Properties of CNT membranes:

The cytotoxicity of CNTs is an area of ever growing interest and remains a highly
controversial topic.\textsuperscript{159} Data concerning the potential toxicity of different classes of
CNTs still remains quite scarce, and has to date been obtained from in vitro studies
focused primarily on mammalian and algal cells, rather than bacterial cells.\textsuperscript{160, 161}. Limited studies have been performed on the \textit{in vivo} effects of implanted CNTs. One
early investigation examined the effect of introducing 5 mg/kg SWNTs into the
intratracheal region of rats. This resulted in produced an increased mortality rate within
24 hours compared to control rats with a mixture of catalyst particles (cobalt and nickel,
2 - 3 \( \mu \text{m} \) particle size) and graphite particles (3 – 10 \( \mu \text{m} \))\textsuperscript{162, 163}. It was later determined
that the aggregation of material in the major airways of the rat, and not direct cytotoxic
effect of the SWNTs were the cause of the increased mortality.

Based on the results of these conflicting studies, researchers have proposed three
possible cytotoxic mechanisms: oxidative stress, metal toxicity and physical penetration
of the cell membrane.\textsuperscript{164, 165} Oxidative stress occurs as a result of oxidation of crucial
proteins and enzymes through interaction with the CNT surface. This may give rise to
severe membrane disruption via lipid peroxidation, resulting in cell inactivation.\textsuperscript{164, 166}
Metals are able to induce toxicity by producing reactive oxygen species which can also
cause oxidative stress as described above.\textsuperscript{167} At elevated concentrations, metal species
such as those used for the catalytic growth of CNTs can bind to and inactivate enzymes,
resulting in impaired cellular function. Of all three proposed cytotoxic mechanisms, physical penetration of membranes by CNTs is believed to be the prevailing pathway of cellular inactivation, and occurs as a result of the cylindrical geometry and high aspect ratio of the CNTs.

In recent times, studies on the interactions between CNTs and microbes have been slowly emerging. The results of these studies suggest that the antimicrobial activity of nanotubes is due to a combination of oxidative stress and physical piercing. Direct metal toxicity is believed to play only a very minor role in bacterial toxicity, as methods of CNT purification only leave behind trace amounts of metal particles in the final product (< 0.8 % (w/v)). The major factor causing death of bacterial cells is believed to be irreversible damage to the outer membrane wall, which causes release of intracellular material. This phenomena was first observed by Kang et al., who observed a 5-fold increase in the amount of DNA found in Escherichia coli (E. coli) suspensions in contact with SWNTs. This was verified in a later study which showed that SWNTs were much more effective at damaging bacterial membranes than MWNTs, due to a greater degree of interaction made possible by the higher aspect ratio for the former materials.

In light of these strong bactericidal effects, interest in producing CNT membranes which can both remove and kill bacteria present in contaminated solutions has slowly emerged. In 2004, Srivastava et al. reported for the first time that a membrane composed of aligned MWNTs could be used to filter E. coli suspensions. These membranes completely removed all viable bacteria, as subsequent culturing of the filtrate did not result in the growth of any bacterial colonies (Figure 1.15). This result
was most probably due to the bacteria being prevented from passing across the membrane by a size exclusion mechanism, and not to the anti-bacterial activity of the CNTs.

Figure 1.15: Plates of culture colonies of E. coli: (a) obtained prior to filtration across an aligned MWNT membrane, and (b) from the filtrate obtained after filtration of the same suspension of bacteria.135

Following the above work, Brady-Estévez and co-workers showed that similar results could be achieved using buckypaper membranes.44 Initial studies using SWNT BPs produced from dimethylsulfoxide dispersions showed complete removal of E. coli. This was demonstrated by a combination of SEM imaging of the surface of the BPs, and a fluorescence based assay of the surface of the BPs performed using propidium iodide (PI) and SYTO-9. The latter assay showed that c.a. 80% of bacteria were killed upon retention on the membrane surface.

Subsequent work has also shown MWNT and SWNT-MWNT composite BPs also possess antibacterial activity and the ability to filter bacteria efficiently.169 These studies have been performed not only using the gram negative bacterium E. coli, but also gram positive bacteria such as Staphylococcus epidermidis (S. epidermidis).169 The number of the latter bacteria killed was noted to be significantly lower with both types of membrane filters, which was attributed to the much thicker cell wall of S. epidermidis.
inhibiting physical penetration of the CNTs. In addition, the successful removal of viral particles using CNT membranes has also been achieved,\textsuperscript{45,135} and the ability to use an electrical stimulus to enhance removal of both bacteria and virus particles has been demonstrated.\textsuperscript{170} The latter result was believed to be due to oxidation of the pathogens, either directly when in contact with a CNT anode, or indirectly as a result of the production of an aqueous oxidant such as Cl\textsubscript{2} \textsuperscript{-}, HO\textsuperscript{-} or SO\textsubscript{4} \textsuperscript{-} at the CNT surface.

Despite the increased interest in using BP membranes for removal of pathogens, to the best of our knowledge no one has investigated the use of BPs produced from aqueous dispersions of CNTs for this purpose. In a recent study, Bai and co-workers investigated the antibacterial activity of surfactant modified MWNTs in aqueous solution.\textsuperscript{171} Their results showed a significant reduction in cell numbers, and a substantial delay for the bacterium Streptococcus mutans to reach exponential growth phase of between 4 – 6 h. These workers, however, only investigated the antibacterial properties of surfactant modified MWNT dispersions, and not of the corresponding BP membranes. There is therefore still a need to explore the antibacterial potential of BP membranes produced using dispersants such as surfactants or antibiotics.

1.8 Adsorption of Radionuclides by CNTs:

Although radioisotopes play a vital role in both the energy and medical sectors, the generation of unwanted waste products remains an ongoing dilemma for these nuclear industries. Such products are typically present in radioactive liquid waste streams, where the issue of safe disposal remains a significant challenge. The radionuclides \textsuperscript{137}Cs and \textsuperscript{90}Sr constitute the majority of the isotopes present in these waste streams, and give
rise to high levels of radioactivity. These problematic isotopes are often sequestered using a small volume of a suitable adsorbent material, such as an inorganic ion-exchanger, thereby allowing the bulk of the effluent to be disposed of as low-level waste. This not only provides a safer means of disposal, but also represents a significant cost saving for industry. In the radiopharmaceutical industry, technetium-99m ($^{99m}$Tc) is perhaps the most widely used isotope for diagnostic imaging of patients. Technetium-99m is a metastable radionuclide, and is produced as a result of $\beta^-$ decay of molybdenum-99 ($^{99}$Mo), which has a half life of c.a. 66 hours. The $^{99m}$Tc decay product is separated from the precursor $^{99}$Mo by selective elution from an ion-exchange resin, often referred to as a technetium-99m generator.

The need to further improve methods for recovering radionuclides such as those mentioned above has sparked interest in a myriad of new adsorbent materials. In the last 5 – 10 years, studies have been slowly emerging that reveal the potential of CNTs for the recovery of radionuclides. For example, Wang et. al. showed that sorption of $^{243}$Am by MWNTs could be achieved at room temperature (20 ± 2°C). The adsorption efficiency of the nitric acid treated MWNTs towards $^{243}$Am was shown to be $\geq 40$ mg g$^{-1}$, and was attributed to a surface complexation mechanism. Since this time the uptake of a variety of other radionuclides of including Th and Eu, Ce, Sr and U have also been reported. These studies all concluded that conditions such as solution pH, concentration of CNTs, and the degree of functionalisation (oxidation) of the nanotubes all dictated the sorption capacity of the MWNTs used.

To the best of our knowledge all previous studies examining the uptake of radionuclides by CNTs have solely focused on MWNT powders, rather than buckypapers composed
of MWNTs. Furthermore, the ability of MWNTs that have been non-covalently functionalised with macrocyclic ligands or other classes of molecules to recover radionuclides has yet to be examined.

1.9 Research Objectives:

Although buckypaper membranes have already shown considerable promise for a number of applications, the range of materials used in these studies has been limited. This is because most of the buckypapers were produced from dispersions made using an organic solvent (i.e. with no dispersant present), or from aqueous solutions usually containing a limited range of surfactant or biopolymer dispersants. There are now many examples of composite materials which combine both an inherently conducting polymer and a functional or responsive chemical compound, that display the properties of both components (section 1.4). Therefore there is good reason to expect that it may be possible to achieve the goal of preparing highly functional or responsive composite materials composed primarily of CNTs, but which also contain molecules capable of either selectively recognising metal ions or small organic molecules, or killing microorganisms.

The main objectives of this thesis were thus as follows:

1.) To prepare dispersions containing SWNTs using dispersant molecules capable of conferring molecular recognition or antimicrobial properties.

2.) To characterise the resulting dispersions using optical microscopy, UV-vis-NIR spectrophotometry and Raman spectroscopy.
3.) To prepare SWNT buckypapers from the above dispersions, and characterise their physical and morphological properties.

4.) To explore the permeability towards water of SWNT and MWNT buckypapers containing various macrocyclic ligand molecules.

5.) To compare the bacterial filtration properties of SWNT and MWNT buckypapers containing antibiotic molecules to each other, and that of the corresponding buckypapers containing Trix.

6.) To investigate the ability of MWNT buckypapers prepared using different types of MWNTs and, in some instances, macrocyclic dispersants, to recover a radionuclide ($^{99}$Mo) by an adsorption mechanism.
1.10 References:


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159. B. S. Harrison and A. Atala, Biomaterials 2007, 28, 344-353.
162. B. S. Harrison and A. Atala, Biomaterials 2007, 28, 344.


2

Experimental Procedures

This chapter provides details about the general experimental procedures used in this work.
2.1 Chemicals:

All chemical reagents were used as received from suppliers, without any further purification or modification. For the majority of this project purified SWNTs (85+% C purity) purchased from Unidym™, lot# P0348 was used unless otherwise stated. Two other batches of purified SWNTs from Unidym™, namely lot# P0261 and lot# P02150 were also used. Nanotubes were also sourced from Nanocyl™, including SWNTs (70+% C purity) batch no. 100618 and thin MWNTs (95+% C purity) batch no. 081010. Carboxyl and amine functionalised MWNTs were purchased from Nanocyl (batch no. MEL110514 and LMWA-P-NH2, respectively).

Triton X-100 (Trix); sulfated β-cyclodextrin and sodium salt (β−CD) were purchased from Sigma-Aldrich. Both meso-tetra(4-sulfonatophenyl) porphyrin dihydrogen chloride (TSP) and phthalocyanine tetrasulfonic acid (PTS) were obtained from Frontier Scientific. The calixarene dispersants 4-sulfonic calix[4]arene hydrate (C4S) and 4-sulfonic calix[6]arene hydrate (C6S) were supplied from ACROS and Alfa Aesar, respectively. The hydrochloride salt of ciprofloxacin (cipro) and the acid sulfate salt of berberine were acquired from MP Biomedicals LLC and City Chemical LLC, respectively.

The metal salts used in buckypaper uptake experiments were sodium molybdate dihydrate (99.5%), strontium nitrate (99.995%) and cesium nitrate (99%). These were acquired from Sigma Aldrich and the Australian Nuclear Science and Technology Organisation (ANSTO). The 99Mo radionuclide used in further recovery experiments was also provided by ANSTO, and was obtained by nuclear fission of 235U. The molybdenum was provided in the form of 99MoO42−, which was chemically separated
from synthetic by-products using a combination of chromatographic and boil-down processes.

Unless otherwise specified, all solutions were prepared using Milli-Q water (18.2 MΩcm). Other solvents used in this study included methanol (99.8%, Merck), ethanol (absolute, AJAX), acetone (AJAX) and nitric acid (70%, AJAX).

2.2 Experimental Methods:

The general experimental methods used to prepare and characterise samples are summarised below under the headings: Preparation of dispersions, buckypaper preparation, characterisation of buckypapers and performance testing of membranes.

2.2.1 – Preparation of Dispersions:

All dispersions in this study contained between 0.1 – 1% (w/v) dispersant, and 0.007 - 0.1% (w/v) CNTs in a typical volume of 15 mL. To enable dispersion of the nanotubes energy was added to the system most commonly via a high energy (400 W) sonication horn (Branson 450, Ultrasonics). However, on some occasions a low energy 50 Hz sonication bath (FXP4, Ultrasonics) or homogeniser (WiseTis® digital homogeniser, HG-15D) was used.

When high energy sonication was used, the following parameters were employed with the sonication horn: Power amplitude = 30% (~20 W output per pulse), probe diameter = 10 mm, pulse duration = 0.5 s, pulse delay = 0.5 s. In all sonication experiments, the mixtures subjected to sonication were immersed in a water-ice slurry to prevent evaporative losses (Figure 2.1). Dispersions produced using the sonication bath
were prepared by immersing the mixture of reagents in the bath, which was then switched on for pre-determined time intervals. The water and ice in the bath was changed every 1 – 2 hours to minimise excessive heating of the mixture of reagents. Dispersions produced using the homogeniser were prepared by varying the velocity of the stirrer from 10,000 – 27,000 rpm over the course of a 5 minute cycle to prevent overheating.

2.2.2 – Buckypaper Preparation:

Dispersions were formed into buckypaper membranes using vacuum filtration. Depending on the filtration apparatus used, two different sized buckypapers were obtained. Small, circular buckypapers (~40 mm diameter) were prepared using Aldrich or Millipore glass filtration units with sintered glass frits (Figure 2.2a). Dispersions were drawn through commercial membranes (polytetrafluoroethylene (PTFE), 5µm pore, diameter, Millipore) in these filtration units by using a vacuum pump (CVC2, Vacuubrand) typically operating between 30 - 50 mBar. The filter funnel containing the dispersion was covered to prevent evaporative losses. Once filtration was complete, the buckypapers were washed with 100 mL of Milli-Q water followed by 20 mL of
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Figure 2.2: Images of the filtration cells used to produce buckypaper membranes throughout the course of this study. (a) the small filtration setup used to produce 40 mm diameter circular membranes, and (b) the large filtration setup used to create large rectangular membranes (4 cm x 7.5 cm).

methanol whilst still in the filtration unit. After this washing procedure, the damp buckypaper attached to the commercial membrane was left to dry under ambient conditions (c.a. 21°C) on a lab bench between absorbent paper sheets overnight (~15 hours). The dry buckypaper was then peeled away from the filtration membrane to leave a free standing film.

Large buckypapers used for water permeability experiments were prepared using a custom made rectangular (4 cm x 7.5 cm) filtration cell containing an internal sintered glass frit measuring 5.5 cm x 8 cm (Figure 2.2b). Dispersions were filtered onto large sheets of polyvinylidene fluoride (PVDF) membrane (0.22 µm pore diameter, Millipore), then washed and dried using an analogous procedure to what was outlined earlier for the smaller membranes. Typically, small buckypapers contained at least 30 mg of CNTs, whereas the larger rectangular buckypapers contained 90 mg. All buckypaper samples were stored at room temperature in sealed glass or plastic petri dishes (c.a. 21°C).
2.3 Characterisation Techniques:

A large number of characterisation techniques were utilised to investigate both CNT dispersions and buckypaper membranes. For each technique a brief overview of the conditions used is described in the sections below.

2.3.1 – UV-vis-NIR Spectrophotometry:

UV-vis-NIR spectra of solutions and CNT dispersions were obtained using a double beam UV-vis-NIR spectrophotometer (Cary 500) operating between 300 – 1400 nm. All samples were appropriately diluted with Milli-Q water prior to analysis to fit within the absorbance limits of the detector, and placed into 1 cm pathlength quartz stoppered cuvettes. All spectra were collected at room temperature (~21°C) unless otherwise stipulated.

2.3.2 – Raman Spectroscopy:

Raman spectroscopy was obtained of a range of CNT dispersions and buckypaper samples using a Jobin Yvon Horiba spectrometer (HR800). All spectra were obtained using a 632.8 nm laser source and a 950 line diffraction grating, and were recorded between 150 and 2500 cm⁻¹. Spectra of CNT dispersions were obtained by casting small volumes (~10 µL) from the top of the sample onto glass microscope slides. All spectra were analysed and processed using LabSpec software provided with the instrument.

2.3.3 – Mass Spectrometry:

Mass spectra were obtained using a Waters electrospray ionisation mass spectrometer (Quattro Micro™). Spectra were acquired between m/z 100 and 1000, in both positive and negative ion modes. Data acquisition was controlled using the Micromass
Masslynx™ software system with each spectrum being reported as an average of a minimum of 30 scans.

**2.3.4 – Nuclear Magnetic Resonance Spectroscopy:**

Nuclear magnetic resonance (NMR) spectroscopy was used to investigate the stability of the dispersants in solution. In this work, proton NMR (¹H NMR) spectra were acquired on samples dissolved in deuterium oxide (D₂O, 99.9 atom % D, Aldrich) using a Varian 500-MHz VNMR spectrometer. A peak of 4.79 ppm, assigned to the HOD, was used as the reference for all ¹H NMR spectra.¹ All spectra were recorded by Miss Kimberley Davis.

**2.3.5 – Microscopy and EDX Spectroscopy:**

Dispersions of CNTs were imaged via optical microscopy using a microscope equipped with a digital camera (Z16 APO LED1000, Leica). Images were obtained by drop casting a small volume of dispersion onto a glass slide. Buckypapers were imaged using scanning electron microscopy (SEM) either with a field emission SEM located at the University of New South Wales (UNSW) electron microscopy unit (S-900, Hitachi) or a field emission SEM, located at the University of Wollongong (UoW) electron microscopy facility (JSM-7500FA, JEOL). The operating voltages of the SEM units at UNSW and UoW were 4 kV and 5 kV, respectively. The latter instrument was operated with the assistance of Mr. Tony Romeo. In all cases samples were cut into small strips and mounted onto a small conductive stub using carbon tape or by wedging the sample between a screw mount on the stub itself. All materials were sufficiently conductive to enable images to be obtained without having to first coat them with a metallic or carbon layer.
Images were analysed using Image Pro Plus software to ascertain quantitative information concerning the size of surface pores. Energy Dispersive X-Ray (EDX) spectroscopy was performed in conjunction with imaging using the SEM at UoW to provide information on the identity of elements present on the surface of buckypaper samples.

2.3.6 – Contact Angle Determination:

The hydrophobicity of a material is commonly measured by determining the contact angle of a water droplet on its surface. The contact angles of all buckypapers were determined using the sessile drop method and a goniometer fitted with a digital camera (SCA20, Data Physics). The contact angles of 2 μL water (Milli-Q, Millipore) droplets on the surface of the buckypapers (Figure 2.3) were calculated using the accompanying Data Physics software (SCA20.1). The mean contact angle was calculated using the results obtained from measurements performed on 5 different water droplets on the same buckypaper sample.

![Figure 2.3: Schematic illustration of the contact angle (Θ) of a water droplet on the surface of a material.](image)

2.3.7 – Electrical Measurements

The conductivity of buckypaper samples was determined using a standard two-point probe method.\(^2\) In short, buckypapers were cut into rectangular strips approximately

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3 mm wide and 3 - 5 cm long. The strips were fixed using high purity silver paint (SPI) onto a small piece of copper tape (3M) adhered to a glass slide. Another glass microscope slide was clamped onto the slide containing the buckypaper strip using bulldog clips to ensure the sample was secure, and apply a constant force. Electrical leads were used to connect the copper tape overhanging the glass slide to a digital multimeter, while a waveform generator was used to apply electrical potentials to the buckypaper samples, and measure the resulting current outputs. The full setup used for performing two-point probe conductivity measurements is illustrated in Figure 2.4.

![Figure 2.4: Photograph of the setup used to connect a buckypaper membrane strip to the multimeter and waveform generator used in the two-point probe conductivity method.](image)

Experiments were performed by applying a triangular waveform with potential limits of -0.05 and 0.05 V to the sample using a waveform generator (33220A, Agilent) operating at a frequency of 5 mHz. The induced current flow was measured using a multimeter (34410A, Agilent) connected within the simple circuit, and attached to a personal computer recording data points every 1.0 s. This enabled current - voltage plots to be constructed which could then be used to determine sample resistance for the length of sample used, enabling the calculation of sample and contact resistance. Using these resistance values, the conductivity could be calculated by accounting for the sample
thickness, which was measured using a digital micrometer (IP65, Mitutoyo) as outlined further in chapter 4.

### 2.3.8 – Tensile Testing

The mechanical integrity of samples was determined using a Shimadzu EZ-S universal testing device and buckypaper samples cut into small rectangular strips measuring approximately 15 mm x 3 mm and mounted into a small paper frame (Figure 2.5). The length of the sample between the top and bottom clamps was kept constant at 10 mm. The paper frame was cut between the clamps prior to testing, and the mounted samples were then stretched in tension using a 10 N load cell until failure. All results were recorded via an attached personal computer using the Trapezium X software package provided with the instrument, and analysed using Microsoft Excel to yield the corresponding stress-strain curves. These stress-strain curves were used to determine the Young’s modulus, tensile strength, ductility and toughness of samples.

![Figure 2.5: Buckypaper sample mounted in a re-enforcing paper window, and mounted between the two clamps of the tensile testing instrument prior to analysis of its mechanical properties.](image)

### 2.3.9 – Cyclic Voltammetry

Cyclic voltammetry (CV) experiments were conducted using a standard three electrode cell, with a platinum mesh auxiliary electrode, a Ag/Ag⁺ reference electrode and a
buckypaper membrane as the working electrode. The electrochemical capacitance was then measured after submersing the electrodes in a solution of 1.0 M NaNO₃, by using a potentiostat (Voltalab®, PSTO50, Radiometer Analytical) to apply potentials over the range 200 – 600 mV, at scan rates between 25 – 100 mV s⁻¹. As the solution contained a non-Faradic electrolyte (i.e. it contained no redox active species), the electrochemical capacitance could be determined from the difference between the measured cathodic and anodic currents.

2.3.10 – Thermogravimetric Analysis

The thermal stability of buckypaper samples was examined by thermogravimetric analysis (TGA) using either a thermogravimetric analyser located at the University of Wollongong (Q500, TA Instruments), or an instrument located at ANSTO (TAG – 2400, SETRAM instrumentation). Samples were tested in air, and were examined over the temperature range 0 - 1000 °C using a ramp rate of 10 °C min⁻¹.

2.3.11 – Nitrogen Adsorption-Desorption Analysis

Adsorption-desorption isotherms were obtained at ANSTO using a surface area analyser (ASAP 2010 or ASAP 2400, Micromeritics®) operating at 77 K. Prior to analysis, residual gas trapped within samples was removed under vacuum at a temperature between 90 - 250°C, depending on the thermal stability of the sample of interest. The resulting isotherms were analysed using the Horvath-Kawazoe (HK) and Barrett, Joyner and Halenda (BJH) methods to determine the distribution of small and large pores, respectively.³,⁴ In addition, multipoint Brunauer, Emmett, and Teller (BET) analysis of the isotherms was used to calculate the specific surface area of the samples.⁵
2.3.12 – Microanalysis

Microanalysis was performed on the CNT starting material and buckypapers by the microanalytical unit of the Research School of Chemistry at the Australian National University, Canberra. Prior to analysis, buckypaper were ground into a find powder using a mortar and pestle.

2.4 Performance testing of Membranes

The suitability of buckypaper membranes for different applications was investigated using the procedures outlined in the following sections.

2.4.1 Permeability Experiments

The permeability of BPs towards water was measured using a custom-made dead-end filtration cell setup (active area enclosed by rubber o-ring = 6.5 cm x 3.5 cm), which uses compressed air to force a feed solution across a membrane (Figure 2.6). Initially, a pressure of 0.069 bar was applied to induce water transport across the BPs. The volume of water passing across the membrane was monitored for 10 min using an analytical balance connected to a personal computer, and then the pressure increased incrementally and the process repeated. This yielded a series of permeability plots which could be used to determine the membrane specific flux as outlined in chapter 5. All permeability experiments were performed in the Environmental Engineering Laboratories at the University of Wollongong.
2.4.2 Bacterial Testing:

*Escherichia coli* (*E. coli*) JM109 was selected as the model bacterium throughout the course of this study. A single colony of *E. coli* was inoculated into 5 mL of Luria-Bertani (LB) broth and grown at 37°C for 16 hours with shaking at 200 rpm. The overnight culture (1 mL) was used to inoculate 20 mL of pre-warmed LB broth, which was subsequently incubated at 37°C with shaking until an OD$_{600}$ of 0.5 (mid-exponential growth phase) was obtained. For filtration experiments, 1 mL of freshly prepared cells was suspended in a sterile saline solution (0.9 % (w/v) NaCl) giving a final cell concentration of c.a. 10$^4$ mL$^{-1}$. Prior to testing, BP membranes were sterilised by soaking in 70% ethanol and thoroughly washed with sterile saline to remove any remaining ethanol solution. Bacterial suspensions were filtered through dry BPs using either a 25 mm diameter polycarbonate syringe filter holder (*Figure 2.7a*), or a commercial vacuum filtration apparatus (*Figure 2.7b*).

**Figure 2.6:** Dead-end filtration cell used in water permeability experiments: (a) side view, and (b) top view after removing the upper half of the Perspex chamber.
Figure 2.7: Photographs of the apparatus used to perform bacterial filtration experiments: (a) syringe filter holder assembly, and (b) a commercial vacuum filtration apparatus.

Small circular buckypapers (~40 mm diameter) had to be cut in order to fit within the syringe filter holder (25 mm diameter), and were then sealed in place by a rubber o-ring. The entire assembly was then sterilised by drawing 70% ethanol through the syringe holder and buckypaper, and allowing the latter to soak for 15 min. The buckypaper was then extensively washed with sterile saline solution, before a 5 mL suspension of *E. coli* was drawn up into the syringe and subsequently forced through the filter holder containing the sterilised buckypaper membrane by hand. In the case of vacuum filtration experiments, the glass filter holder and flask used was first sterilised using an autoclave. The small circular buckypapers were then placed in the filter holder and allowed to dry under vacuum (200 – 300 mbar) prior to filtration of a 50 mL suspension containing *E. coli*. Initially suspensions were filtered under high vacuum (60 mbar) in order to expedite the filtration procedure. However, this resulted in fracturing of the buckypaper surface and poor filtration efficiency. Thereafter all experiments were performed under a gentle vacuum (200 – 300 mbar) using buckypapers kept in their original filter holder assembly to ensure that maximum rejection was achieved.
To determine the extent of removal of *E. coli*, a dilution series was prepared from the filtrate by plating onto LB agar and incubating overnight at 37°C. The numbers of colonies present after this period of time were then counted by direct visual inspection. The viability of *E. coli* on buckypaper membranes was examined using a live / dead assay as developed by Brady-Estevez et. al. Post filtration experiments, buckypapers were either stained with propidium iodide (PI) followed by counter staining with SYTO-16, or stained with PI followed by counter staining with 4',6-diamidino-2-phenylindole (DAPI). These experiments were performed with the assistance of Dr. Elise Stewart and Dr. Jason McArthur of the University of Wollongong. Staining was performed by the addition of a small volume of the chosen dye (50 µL) in the dark. Stains were allowed to develop for c.a. 5 min before rinsing with Milli-Q water. This process was then repeated for the counter stain, before the buckypaper was again being rinsed and then stored in the dark until imaging was performed using a Zeiss AxioImager fluorescence microscope (A1m) equipped with an AxioCam camera and an HB100 mercury lamp. Microscope control and image acquisition was facilitated by AxioVision software (version 4.8.1). The viability of cells was determined by analysis of micrographs using the Image J software package as described in chapter 5.

### 2.4.3 Uptake of Radionuclides

The ability of different buckypapers to recover radionuclides of interest to the Australian nuclear industry was investigated using two approaches. In some instances, recovery experiments were performed using cold (i.e. non-radioactive) samples of the element of interest. Small rectangular sections of MWNT buckypaper membranes prepared as described in section 2.2.2, were cut into sections measuring approx. 1cm x 2 cm and weighing 10 – 15 mg. These samples were then submerged in a 5 mL solution
containing between 0.1 - 1 ppm of the element of interest. These simulated waste solutions also contained nitric acid at a concentration between 0.1 – 6 M. Submerged samples were shaken for 1 – 2 days using a rotating stage set at approximately 100 rpm. Once the adsorption period was complete, the remaining solution was removed and any remaining particulate material excluded using a 0.22 µm syringe filter. Filtered solutions were analysed using an Agilent, HP4500 inductively coupled plasma – mass spectrometer (ICP-MS) in order to quantify the amount of the element remaining in solutions. The extent of removal was then determined by measuring the difference between this concentration and that of the stock solution, and expressing the result as a percentage of the concentration of the stock solution.

Recovery experiments involving the radionuclide $^{99}$Mo were performed by a similar technique. Buckypaper samples were cut into small rectangular strips and submerged in a 0.1 M nitric acid solution containing a small quantity of $^{99}$MoO$_4^{2-}$. The exact volume of the radioisotope solution added varied depending on its activity, as it was important that the latter remained in the linear region of detection of the Perkin Elmer gamma counter (Wallac Wizard 2). The solutions were agitated at 300 rpm for approximately 2 hours before being separated from the BPs using a syringe filter as described previously. The concentrations of the radioisotope remaining in the filtrate, and in the stock solution, were subsequently measured using the gamma spectrometer. The percent recovery of the radioisotopes was then calculated as described previously.
2.5 References:


This chapter discusses the synthesis and characterisation of a range of SWNT dispersions prepared using novel classes of dispersants. These results provide the basis for subsequent work exploring the synthesis, properties and applications of buckypapers, described in later chapters.
3.1 Introduction:

One of the most common methods used to obtain useful materials incorporating CNTs involves processing the latter into a solution or dispersion. However, CNTs tend to form large aggregates in solution, as their solubility in common solvents is often very low. In this chapter, the preparation of SWNT dispersions using the surfactant Triton X-100 (Trix) as well as a variety of macrocyclic ligands and antibiotic molecules is discussed. This entails firstly the optimisation of the sonication regime employed, followed by an examination of the stability of the dispersions and the strength of the dispersant-SWNT interactions. Some aspects of the work described in this chapter were published in the following articles:


3.2 Dispersion of SWNTs using Triton X-100:

Although sonication using an ultrasonic horn can be used to successfully prepare CNT dispersions, excess sonication can be detrimental. Sonication for extended periods may lead to structural defects and considerable shortening of the nanotubes as a result of the damage caused by the shock waves generated by the collapse of cavitation bubbles near the nanotube surface.\(^1\), \(^2\) Moreover, this can lead to a considerable reduction in the
number of sp$^2$ hybridised carbons present, which can adversely affect the properties of the CNTs$^3$. Sonication can also lead to pH changes which suppress interband electronic transitions of semiconducting SWNTs$^4$. Similarly, it well known that the breakdown of dispersant molecules such as carbohydrates and other polymeric species as a result of sustained periods of sonication can occur$^5$-$^7$. Consequently, it is important to ensure sonication is kept as brief as possible. Therefore a study to determine the optimum period of sonication required for adequate dispersion of the CNTs was undertaken. In this chapter all experiments were performed using SWNTs purchased from Unidym (lot# P0348).

Optimisation of the sonication time required to prepare stable dispersions using Trix was initially explored using UV-vis-NIR spectrophotometry and samples containing 5 mg (0.03% (w/v)) of SWNTs in a 1% (w/v) solution of the surfactant. Spectra were obtained after different periods of sonication and are shown in Figure 3.1. A gradual increase in absorbance at all wavelengths with increased sonication time was observed, indicating an increase in the quantity of SWNTs dispersed in solution. To examine this in more detail, the absorbance at a single wavelength corresponding to a specific absorbance peak was selected and plotted against sonication time (Figure 3.1 - inset). This plot clearly shows an initial dramatic increase in absorbance with increasing sonication time. However, after 10 min the increase in absorbance became more gradual. After 30 min sonication (~36 kJ of acoustic energy) the absorbance of the solution entered a “plateau” region. This region corresponds to sonication times where further dispersion of SWNTs into solution is negligible. Sonication beyond this timeframe would expose the nanotubes to increased amounts of energy, which would likely lead to further degradation of the nanotubes and a concomitant decrease in the
physical properties of the resulting dispersion.\textsuperscript{2} Therefore 30 min was selected as the optimum sonication time for preparing SWNT-Trix dispersions using the amounts and concentrations of reagents described above.

Similar results were obtained when the above experiment was repeated using samples containing the same concentration of Trix, but different amounts of SWNTs (Figure 3.2). This confirmed that a sonication time of 30 min was sufficient to maximise production of dispersed SWNTs. This sonication time was therefore used to prepare SWNT/Trix dispersions for comparison to those prepared using novel dispersant molecules discussed in the following sections.

\textbf{Figure 3.1:} Effect of sonication time on the UV-vis-NIR spectra of dispersions prepared using a sample containing 5mg (0.03\% (w/v)) SWNTs and 1\% (w/v) Trix. The inset shows how the absorbance of a discrete van Hove singularity (at 810 nm) varied as a function of time.
Figure 3.2: Comparison of the effect of increasing sonication time on the absorbance at 810 nm of dispersions prepared from samples containing different quantities of SWNTs and 1 % (w/v) Trix.

The spectra shown in Figure 3.1 display a large series of absorption features between 300 and 1000 nm. To ensure these were solely due to the dispersed SWNTs, a spectrum of a solution containing only 1% (w/v) Trix was also recorded, and found to show no measurable absorbance in this region (Appendix 1). The series of absorption features present in Figure 3.1 are related to the van Hove singularities, which are a product of the pseudo one-dimensional nature of individualised CNTs. In this form the normal continuum of electronic states of carbon transforms into a discrete succession of regularly spaced energy levels. Upon excitation at the appropriate energy (wavelength) it is possible to observe a transition between these quantised energy levels. For carbon nanotubes, selection rules specify that two energy states, located symmetrically either side of the Fermi level, are involved (i.e. the valence band and conduction band). The energy required to excite the SWNTs between these states is dependent on the properties of the nanotubes themselves, including whether they are metallic or semiconducting, their diameter, chirality vector and overall morphology.
3.3 Preparation of Novel SWNT Dispersions:

In order to optimise the conditions for producing other dispersions, a similar UV-vis-NIR investigation to that described in the previous section was performed using samples containing 5 mg SWNTs and various novel dispersant molecules. However, before these dispersions were analysed by UV-vis-NIR spectrophotometry, the absorption spectra of the dispersant molecules themselves were obtained. Significant absorption bands were found to be present in the UV-vis-NIR spectra of solutions containing meso-tetra(4-sulfonatophenyl) porphyrin dihydrogenchloride (TSP), phthalocyanine tetrasulfonic acid (PTS), berberine and ciprofloxacin (cipro - Figure 3.3). However, no significant absorption was noted within the spectra of solutions containing Trix, β–CD and C6S dispersants (Appendix 1).

Figure 3.3: UV-vis-NIR spectra of strongly absorbing molecules used to disperse SWNTs. The concentrations of the dispersants were 0.01% (w/v) for ciprofloxacin, 0.005% (w/v) for berberine, and 0.001% (w/v) for TSP and PTS.

The spectrum of Berberine has absorption bands centred at ~350 and 425 nm attributable to π–π* transitions,\(^\text{11}\) while cipro has also been reported to exhibit three
characteristic electron transitions at $c.a.\ 225\ nm$, $293\ nm$ and $325\ nm$.\textsuperscript{12} Although these absorption bands were expected to overlap with the van Hove singularities in a sample of dispersed SWNTs, they do not appear to have significantly impacted on the $300$ – $1000\ nm$ region of interest in this study. The remaining dispersants, however, have very intense and broad spectral features which would interfere with the absorption bands arising from dispersed SWNTs. TSP and PTS display intensely absorbing peaks near $400\ nm$ and $650\ nm$ assigned as the Soret and Q-band(s), respectively.\textsuperscript{13}

Inspection of Figure 3.3 confirms that the region above $800\ nm$ of the UV-vis-NIR spectra for solutions containing cipro, berberine, PTS and TSP would be suitable in order to avoid significant interference from these dispersant molecules. A series of experiments was therefore performed using selected dispersants, to determine whether the sonication time of $30\ min$ previously shown to be optimal for preparing SWNT dispersions with Trix was also suitable for the novel dispersants. Figure 3.4 shows the effect of sonication time on the UV-vis-NIR spectra of dispersions prepared using samples containing $5\ mg\ (0.03\%\ (w/v))$ of SWNTs and different dispersants. In all cases there was an overall increase in absorbance at all wavelengths with increasing sonication time, indicating greater dispersion of the SWNTs was taking place.

When the absorbance at $810\ nm$ in the spectra shown in Figure 3.4 was plotted against sonication time, the results shown in Figure 3.5 were obtained. In each of the resulting graphs, the increase in absorbance slows dramatically after $30\ min$ sonication, indicating that there was no significant increase in dispersion of the SWNTs beyond this time. Hence a $30\ min$ sonication time was again considered optimal for maximising dispersion of the SWNTs, whilst ensuring minimal mechanical damage. This sonication
Figure 3.4: UV-vis-NIR spectra of dispersions prepared from samples containing 5 mg (0.03 % (w/v)) SWNTs and: (a) 1% (w/v) cipro, (b) 1% (w/v) C6S, (c) 1% (w/v) β−CD, (d) 0.1% (w/v) PTS, (e) 0.5% (w/v) berberine and (f) 0.1% (w/v) TSP.

time was therefore used for the preparation of all SWNT dispersions used to make BP membranes, unless otherwise stipulated. It should also be noted that the maximum absorbance shown in Figure 3.5 for each of the dispersions varied considerably depending on the identity of the dispersant used. Dispersions produced using cipro and TSP showed the highest absorbance (1.22 and 1.15, respectively), indicating that these dispersants were the most successful for dispersing SWNTs. On the other hand, the low absorbance of the SWNT/berberine and SWNT/β−CD dispersions (0.86 and 0.70, respectively) indicates that these molecules have a poorer ability to disperse SWNTs.
Figure 3.5: Effect of increasing sonication time at 810 nm of SWNT dispersions prepared using various dispersants.

Figure 3.6 presents the absorption spectra for each type of dispersion after they had been subjected to 30 min sonication. The absorption bands present can be classified into one of three distinct classes of electronic transitions attributable to either metallic or semiconducting SWNTs. These three classes of electronic transitions regions are classified as $M_{11}$ (metallic transitions), $S_{11}$ or $S_{22}$ (semiconducting transitions), and are characteristic of the specific classes of SWNTs present in the dispersion. With the exception of the spectra arising from dispersions containing $\beta$–CD, it is apparent that all three types of electronic transitions associated with semiconducting and metallic SWNTs are present in each of the dispersions. In the case of dispersions produced using $\beta$–CD, a largely featureless spectrum was obtained which indicates that there were few individual nanotubes in solution. The spectrum of the dispersion produced using C6S showed mainly transitions due to metallic SWNTs. This suggests that C6S may preferentially disperse the metallic SWNTs into solution.
Figure 3.6: Absorption spectra of dispersions containing 5 mg (0.03% (w/v)) SWNTs and 1% (w/v) dispersant (0.5% (w/v) for berberine), showing the regions where electronic transitions arising from the presence of metallic and semiconducting CNTs occur. All dispersions were produced using 30 min sonication time.

An examination of the various dispersions produced was undertaken using optical microscopy to see if their physical appearance correlated with what would be predicted based on their UV-vis-NIR spectra. Figure 3.7a shows that SWNT dispersions prepared using Trix and a sonication time of 30 min appeared homogeneous, with no solid aggregates apparent. In contrast, dispersions produced using β–CD and 4-Sulfonic Calix[4]arene hydrate (C4S) showed signs of significant CNT aggregation (Figures 3.7b and c). This indicates that these particular macrocyclic ligands were not as effective at dispersing the SWNTs. This is consistent with the relatively featureless UV-vis-NIR spectra shown in Figure 3.4c for SWNT/β–CD dispersions, which did not shown any evidence of well resolved bands attributable to van Hove singularities.

In contrast, the spectra of SWNT/Trix dispersions shown in Figure 3.1 contain many clearly discernible van Hove singularities, indicating that the surfactant had a
pronounced ability to de-aggregate bundles of SWNTs and stabilise individual nanotubes. In view of the poor results obtained using C4S, it is perhaps initially surprising that the larger calixarene, C6S, proved to be very adept at dispersing SWNTs. This is revealed by the optical micrograph of a SWNT/C6S dispersion shown in Figure 3.7d, which shows no sign of any nanotube aggregates. The well dispersed sample of SWNT/C6S obtained is consistent with the presence of van Hove singularities in the corresponding UV-vis-NIR spectrum shown in Figure 3.4b, and may be the result of the larger and more flexible cavity of the C6S ligand trapping individual SWNTs in its hydrophobic interior. Alternatively, the presence of the two additional aromatic ring systems in C6S may have resulted in extra \( \pi- \) stacking interactions with the sp\(^2\) hybridised carbon atoms present in the SWNTs.\(^{15}\) These types of interactions are also likely to have played a significant role in the formation of well dispersed solutions containing SWNTs when TSP or PTS were also present (Figures 3.7e and f, respectively). It is surprising, however, that the UV-vis-NIR spectra of these dispersions (Figures 3.4f and d respectively) did not contain any van Hove singularities.

The two antibiotic molecules, ciprofloxacin and berberine, were shown to differ significantly in their ability to disperse SWNTs. The presence of cipro resulted in a relatively homogenous dispersion, as evident by the absence of large aggregates in solution (Figure 3.7g). Berberine, however, did not produce a stable dispersion as shown by the high degree of clumping of SWNTs present in solution (Figure 3.7h). It should be noted that this may have been due in part to the lower concentration of berberine used (0.5 mg mL\(^{-1}\)) which was the solubility limit of the dispersant in aqueous solution. However, decreasing the quantity of SWNTs present in the initial sample to only 1 mg had no significant impact on the quality of the final dispersion obtained with
Chapter Three: Non-covalent Functionalisation of SWNTs

Figure 3.7: Optical micrographs (10x magnification) of dispersions containing 5 mg SWNTs (0.03% (w/v)) and different low molecular mass dispersants: (a) Trix, (b) β-CD, (c) C4S, (d) C6S, (e) TSP, (f) PTS, (g) cipro and (h) berberine. All dispersants were present at 1% (w/v) concentration with the exception of TSP and PTS which were present at 0.1% (w/v) concentration. All dispersions were prepared using 30 min sonication time.
both berberine and ciprofloxacin. Despite the very different dispersions obtained with the two antibiotics, both gave UV-vis-NIR spectra that showed well resolved van Hove singularities (Figure 3.4a and e), although this was even more apparent with the dispersions containing ciprofloxacin. Therefore, ciprofloxacin was determined to be a much better antibiotic dispersant compared to berberine for SWNTs, and was thus the only one chosen for studies focussed on the antibacterial properties of BPs that are discussed in chapter 5.

3.4 Stability of SWNT-Dispersions:

In order to prepare CNT materials that combine the unique properties of the molecules chosen to disperse SWNTs, and of the SWNTs themselves, it is imperative that the sonication process used for preparing dispersions does not result in any degradation of either component. In the previous section, results were presented from experiments designed to ensure that the minimum sonication time necessary to prepare suitable dispersions were always used, and therefore avoid damage to the SWNTs. However, it has also been reported that sonication of larger molecules sometimes used as dispersants, such as chitosan and gellan gum, results in degradation of their structure. In addition there have been numerous studies which have examined the effects of ultrasonic energy on the structures of smaller molecules such as those used in this work. However, none of these reports explored whether or not such treatment affected their ability to disperse CNTs. It was therefore decided to use different spectroscopic techniques to see if the brief periods of exposure to ultrasonic energy used to prepare SWNT dispersions caused any degradation of selected, low molecular mass dispersants.
Figure 3.8a shows the positive ion ESI mass spectrum of the antibiotic ciprofloxacin (MW = 331.3) prior to sonication. The dominant feature of the spectrum are ions of high abundance at m/z 332.3 which are attributable to intact, protonated ciprofloxacin molecules [M+H]^+. In addition, ions of low abundance are also present at m/z 166.8 which can be assigned to doubly charged ciprofloxacin ions, [M+2H]^{2+}. After the solution of ciprofloxacin was sonicated for 1 hour under identical conditions to those employed to prepare SWNT dispersions, the mass spectrum was again obtained. If degradation of the dispersant molecule had occurred, additional ions would have been expected to be present, attributable to the breakdown products. However, none of these were present in significant amounts in the resulting spectrum (Figure 3.8b) which is essentially identical to that of the compound prior to sonication. Therefore it can be concluded that no significant breakdown of ciprofloxacin occurred, and the antibacterial effectiveness of the solution was preserved.

![Figure 3.8](image_url)

Figure 3.8: Positive ion ESI mass spectra of ciprofloxacin: (a) prior to sonication, and (b) after one hour sonication using the same conditions employed to produce SWNT/cipro dispersions.
activity of this dispersant should be retained when present in a SWNT dispersion or buckypaper.

A similar investigation was performed using $^1$H NMR spectroscopy and the TSP dispersant. Mass spectrometry could not be used on this occasion as the presence of a large number of charged sites on the macrocycle resulted in a complex and broad distribution of ions within the mass spectrum. The $^1$H NMR spectrum of TSP was found to be unaffected by sonication for one hour (Figure 3.9). Both the spectrum obtained prior to, and after sonication, revealed only three sets of peaks due to the high symmetry of the molecule, at 9.1, 8.8 and 8.5 ppm. These peaks are assigned to protons ortho to the sulfonic acid group in the benzene rings, the protons in the meta position with respect to the sulfonic acid group in the benzene rings, and the pyrrole hydrogen atoms, respectively. No signal was observed for the pyrrole hydrogen atoms due to these having been exchanged with deuterium from the D$_2$O solvent. Once again, it can be concluded that the sonication regime employed for producing SWNT dispersions did

**Figure 3.9:** $^1$H NMR spectrum of TSP before sonication and after sonication for one hour, together with a schematic showing the assignment of the peaks in the spectra.
not provide sufficient energy to break the covalent bonds within the small dispersant molecule, and thus its molecular recognition properties should be retained upon incorporation into a SWNT dispersion or BP.

The ability to prepare functional buckypaper materials is also heavily dependent on the stability of the nanotube dispersions. This is because the vacuum filtration process used to prepare buckypaper membranes can take several days, depending on the amount of CNTs used, the identity of the dispersant and the underlying support membrane. An unstable dispersion will result in deposition of CNTs during the course of filtration, which may detrimentally impact on the morphology, composition and overall properties of the final material. In order to examine the stability of dispersions the UV-vis-NIR spectra of SWNT dispersions containing each of the dispersant molecules was collected between 0 – 8 days after sonication (Appendix 1). The absorbance of a discrete van Hove transition (810 nm) was then selected and monitored as a function of time (Figure 3.10).

![Figure 3.10: Effect of time on the stability of SWNT dispersions, as reflected in the change in absorbance at 810 nm.](image)

**Figure 3.10:** Effect of time on the stability of SWNT dispersions, as reflected in the change in absorbance at 810 nm.
In the case of dispersions produced using Trix, β−CD, cipro, PTS and TSP, absorbance was found to decrease by approximately 10% after one day. This trend continued for each of the above dispersants, but was most noticeable in the cases of Trix and ciprofloxacin. Dispersions produced using these molecules showed a decrease in absorbance of more than 50% after 3 days. However, after this period of time had elapsed the absorbance remained relatively constant. These results indicate that during the first 3 days after preparation of the dispersions, there was significant deposition of non-stabilised CNT material from solution. As a consequence it was essential to ensure that the vacuum filtration procedure used for preparing BPs was always completed within 1 day in order to obtain materials that were homogeneous, and ensure that samples exhibited reproducible morphologies. In contrast, the absorbance of dispersions produced using PTS and TSP did not vary significantly over a period of one week. This indicates that these dispersions were stable, perhaps as a result of the large number of aromatic rings present in the structures of the dispersants to facilitate π−π interactions with the SWNTs.

In order to produce buckypaper membranes, much larger quantities of SWNTs than just 5 mg must be dispersed into solution and processed by vacuum filtration. It was therefore important to see if increasing the amount of SWNTs present in dispersions significantly affected their stability. This was examined by comparing the effect of time on the absorbance arising from a specific van Hove singularity of dispersions produced from samples containing 1, 5 and 15 mg (0.007, 0.03 and 0.1% (w/v), respectively) of SWNTs, and 1% (w/v) Trix. These results are presented in Figure 3.11, and show in all cases a drop in absorbance, and hence the amount of dispersed SWNTs, occurred across
Figure 3.11: Effect of time on the stability of SWNT/Trix dispersions, as revealed by the change in absorbance of a specific van Hove transition in the UV-vis-NIR spectrum. All absorbance values have been normalised with respect to the absorbance at 810 nm immediately after sonication (day = 0).

the entirety of the time period of the experiment. These results reinforce the need to prepare buckypaper samples quickly post-sonication.

3.5 Raman spectroscopy:

Raman spectroscopy is a powerful tool which can be used to investigate the chemical and electronic environment of CNTs both in the solid state, and when dispersed in aqueous solution. The characteristic features of the Raman spectrum are dependent on both the structure and type of the CNTs, and the extent of their interaction with surrounding molecules. A Raman spectrum of the SWNTs (batch no. P0348) used to prepare the majority of dispersions described in this thesis is presented in Figure 3.12, and shows four major spectral features between 100 and 2000 cm\(^{-1}\) when using an excitation wavelength of 632 nm. The broad band located at ~1310 cm\(^{-1}\) is called the D-band, and arises from the presence of amorphous graphitic carbon impurities found in the starting SWNT material, as well as defect sites along the side-walls of the nanotubes.
containing sp³ hybridised carbon atoms. The band at ~1585 cm⁻¹ is known as the G-band, and is due to the presence of a highly organised sp² carbon, such as that found for pyrolytic graphite. In close proximity to this feature is another peak at approximately 1550 cm⁻¹, which is assigned as the G’ band, and is characteristic of SWNTs produced from the HiPCO process.

The ratio of the G/D peak intensities is commonly used to deduce the proportion of SWNT to amorphous carbon material present in a sample, with higher ratios reflecting a higher proportion of sp² hybridised carbon present, and CNTs of higher graphitisation. In addition, by monitoring the G/D intensity ratio as a function of time it is possible to obtain further information about the stability of SWNT dispersions. Raman spectroscopy was therefore used to determine the degree to which SWNTs were retained in dispersions prepared using novel dispersants. This was accomplished for dispersions produced using Trix, C6S, cipro, berberine and β-CD. Due to the high degree of intrinsic fluorescence associated with solutions containing PTS or TSP, Raman spectra could not be obtained for dispersions produced using these molecules.
using the 632.8 nm laser source. The G/D intensity ratio was calculated for each of the remaining dispersions both immediately after their preparation, and after standing for 24 h, and is presented in Table 3.1. There was no significant shift in the position of either of the G or D bands between the dispersions on the one hand, and the solid SWNTs on the other.

**Table 3.1:** Normalised G/D intensity ratio (normalised to P0348 SWNT) of peak intensities for SWNT dispersions produced using 15 mg (0.1% (w/v)) SWNTs and 1% (w/v) dispersant immediately after dispersion preparation (initial) and after 24h. Errors associated with the initial G/D intensity ratios were calculated from standard deviation of triplicate measurements (initial). This relative error was therefore also assigned to the G/D intensity ratios measured after 24 hours.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalised G/D intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>P0348 SWNTs</td>
<td>1.00 ± 0.18</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>1.05 ± 0.23</td>
</tr>
<tr>
<td>SWNT/β−CD</td>
<td>1.18 ± 0.22</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>1.65 ± 0.05</td>
</tr>
<tr>
<td>SWNT/Cipro</td>
<td>2.23 ± 0.09</td>
</tr>
<tr>
<td>SWNT/Berberine</td>
<td>0.91 ± 0.27</td>
</tr>
</tbody>
</table>

The G/D intensity ratio of dispersions prepared using β−CD, Trix and berberine were initially very similar to that of the starting SWNT material. In contrast, dispersions prepared using C6S and cipro initially showed much higher G/D intensity ratios. This can be attributed to a preferential retention of SWNTs, over that of the amorphous carbon impurities in the starting material. Upon standing for 24 h, the G/D intensity ratio of most dispersions either decreased or remained constant. For the samples which showed a decrease in G/D intensity ratio, this result indicates that precipitation of SWNTs had taken place, consistent with earlier observations made using UV-vis-NIR spectrophotometry (Figure 3.10). The one exception to the above trend was found with dispersions produced using Trix, which showed a substantial increase in G/D intensity ratio on standing, suggesting that it was the amorphous carbon material that was principally depositing as the sample aged.
As was shown using UV-vis-NIR spectrophotometry, increased periods of sonication resulted in a greater dispersion of SWNTs (Figure 3.4). However, it is well known that sustained sonication can substantially impact on the structure and therefore the properties of carbon nanotubes. For example, prolonged sonication could lead to a higher proportion of amorphous carbon in dispersions and consequently a lower G/D intensity ratio. This hypothesis was tested by examining the effect of increasing sonication time on the G/D intensity ratio of dispersions prepared containing 15 mg (0.1% (w/v)) SWNTs and 1% (w/v) C6S. The results of this study are shown in Figure 3.13.

Figure 3.13: Effect of increasing sonication time on the G/D intensity ratio of SWNT/C6S dispersions.

Over the 15 – 60 min sonication time frame investigated, there was no significant variation between the G/D intensity ratios of dispersions measured immediately after their preparation. This suggested little additional mechanical damage occurred to the SWNTs over this period of time. However, after being allowed to stand for 24 h, there was a significant decrease (~ 15%) the in the G/D intensity ratio of the dispersion prepared using a 15 min sonication time. Much smaller decreases of c.a. 10 – 15% were observed for the two SWNT/C6S dispersions exposed to ultrasonic energy for a longer
period of time. This is not surprising, as the larger energy input should allow greater
debundling of the SWNTs, and hence facilitate greater adsorption of dispersant onto
their exterior surfaces, resulting in greater dispersion stability. These results also
suggest that during the timeframe of this experiment, no significant mechanical
degradation of the SWNTs had occurred.

One of the most informative features of the Raman spectra of SWNTs is the radial
breathing mode (RBM) region, which can also be used to determine the state of
aggregation of the nanotubes. The series of RBM peaks arise due to the inphase motion
of carbon atoms in the radial direction, with the energy of the RBM peaks being
inversely proportional to the diameter of the SWNTs. An estimate of the diameter of
the SWNTs can be obtained based on the RBM frequency ($\omega$), as shown in
Equation 3.1.

$$d(nm) = \frac{223.75 nm cm^{-1}}{(\omega - 14)}$$  \hspace{1cm} \text{Equation 3.1}$$

It has been well documented that the dispersion of SWNTs by non-covalent means can
result in a shift in the position of the Raman vibrational modes in the RBM region. The extent of this shift depends on whether the nanotubes are well separated, or still in
contact with each other (i.e. highly bundled). In highly bundled samples, the large
extent of intertube contact maintains strong van der Waals forces between the
nanotubes, resulting in energy losses and lowering the frequency of the RBM peaks. By
separating the nanotubes through formation of a stabilised dispersion, these forces are
reduced and the inphase motion of the carbon atoms in the radial direction is hindered
only as a result of the adsorption of dispersant molecules. This results in a shift in the
position of the RBM peaks for a dispersion relative to those for the SWNTs from which it is prepared. Therefore by measuring the spectral shift of particular Raman peaks in the RBM region for SWNT dispersions, it is possible to obtain information on the extent of interaction between the dispersant and the nanotubes, and the degree of debundling.

To examine this in greater detail, the RBM region of the Raman spectra of different SWNT dispersions were compared to that of the SWNT starting material (Figure 3.14). The spectrum of the SWNTs contained four main peaks at 194.2 cm\(^{-1}\), 217.2 cm\(^{-1}\), 257.0 cm\(^{-1}\) and 282.8 cm\(^{-1}\), corresponding to SWNTs with diameters of 1.2 nm, 1.1 nm, 0.9 nm and 0.8 nm, respectively.

![Figure 3.14](image.png)

**Figure 3.14:** Comparison of the RBM region of the Raman spectra of a range of different SWNT dispersions to each other and that of the SWNT starting material.

All dispersant molecules induced a shift to higher frequency for all RBM peaks. Similar shifts have been observed previously for SWNT dispersions containing large polymeric species such as poly(styrene-\(\beta\)-isobutylene-\(\beta\)-styrene) and chitosan, and explained as being the result of a high degree of debundling and strong dispersant / nanotube interactions.\(^{25,26}\) These shifts are collated in Table 3.2, and suggest that there is an
interaction between each of the dispersants and the SWNTs. This is most likely a consequence of the dispersant coating the surfaces of nanotubes after the SWNT bundles have been separated during ultrasonication.

3.6 Alternative approaches to the preparation of dispersions:

Two alternative methods to high power sonication were investigated for their effectiveness at producing SWNT dispersions using a non-covalent functionalisation approach. These methods involved the use bath sonicator and a high speed homogeniser. Previous work by others has shown that the use of these techniques in conjunction with a high energy ultrasonication probe can produce high quality CNT dispersions.\textsuperscript{27, 28} However, there are only few reports which use of bath sonication or a high speed homogeniser by themselves for preparing CNT dispersions.\textsuperscript{29, 30} These much milder techniques would deliver less mechanical shear stress and therefore should help to reduce damage to the sp\textsuperscript{2} hybridised structure of the CNTs responsible for their unique properties.

The use of a bath sonicator to produce proved unsuccessful, with the resulting solutions containing large aggregates apparent to the naked eye. Furthermore, significant amounts of solid material settled on the bottom of the reaction vessel within half an hour of ceasing sonication. The UV-vis-NIR spectrum of a sample containing 5 mg (0.03\% (w/v)) SWNTs and 1\% (w/v) Trix, which was subjected to bath sonication for 12 hours,
is compared to that of an identical sample subjected to high power tip ultrasonication for 30 min in Figure 3.15. The UV-vis-NIR spectrum of the solution obtained after bath sonication contains no readily discernible features attributable to van Hove singularities, confirming that there was negligible separation of CNT bundles under these conditions.

![Figure 3.15: Comparison of UV-vis-NIR spectra of solutions prepared by subjecting a sample containing 5 mg (0.03% (w/v)) SWNTs and 1% (w/v) Trix to: (a) bath sonication and (b) high energy probe sonication.](image)

Attempts to disperse SWNTs via the use of a high speed homogeniser also yielded very poor results even after applying the maximum speed of the instrument (200,000 rpm) for 30 min. Since the use of either a bath sonicator or high speed homogeniser homogeniser failed to produce suitable dispersions, neither method was pursued further explored within this thesis.

### 3.7 Conclusion:

SWNTs were successfully dispersed using high energy probe sonication and a variety of small dispersant molecules with unique properties which may induce functionality into the resulting systems. Optical microscopy and UV-vis-NIR spectrophotometry confirmed that many of the dispersants used were effective for processing of SWNTs in
aqueous solution, thereby facilitating the preparation of buckypapers containing molecular recognition agents and antibiotics. The optimum sonication time was determined by UV-vis-NIR spectroscopy to be 30 min for all dispersants. Previous investigations into the preparation of SWNT dispersions using sulfated β-CD or C6S used a sonication time of only 10 min.\textsuperscript{15, 31} This discrepancy can be attributed to the larger quantities of CNTs used to produce dispersions detailed here. A sonication time of only 10 min was also used previously for preparing SWNT dispersions containing the antibiotic ciprofloxacin.\textsuperscript{32} However, there was no discussion of whether the sonication procedure employed had been optimised in this report.

The stability of SWNT dispersions produced using macrocyclic or antimicrobial dispersants has, to the best of our knowledge not been reported on previously. Most studies using these systems have typically drop cast the dispersions immediately after preparation to form films for electrochemical studies. Many of the dispersions produced using these molecules were shown in the current work to deposit significant amounts of carbonaceous material during the first 2 days after their preparation. This indicated that in order to prepare homogeneous buckypapers with optimal properties it was necessary to vacuum filter the dispersions promptly. Varying the amount of SWNTs present in the samples used to prepare dispersions was found to not affect the experimental conditions that needed to be used, or the properties of the final dispersion.

Raman spectra of dispersions contained RBM peaks which were shifted to higher frequency compared to the SWNT starting material, confirming the existence of significant interactions between the SWNTs and dispersant molecules. The ratio of the intensities of the Raman G and D bands was initially significantly higher in the case of dispersions produced using ciprofloxacin and C6S, than for the SWNT starting material.
This suggests that these dispersants were initially the most adept at selectively binding to the SWNTs over the amorphous carbon impurities present in the initial SWNT soot. However the G/D intensity ratio decreased dramatically after 24 h, indicating that these dispersants were not as effective as Trix for conferring stability on the dispersions. This observation correlates well with the results obtained by UV-vis-NIR spectrophotometry, and again strongly emphasises the need for rapid filtration of dispersions when producing BPs.

Electrospray ionisation mass spectra and $^1$H NMR spectra of selected macrocyclic dispersant molecules that had been subjected to sonication showed no evidence of degradation. This is in stark contrast to what has been reported for larger biopolymer species such as chitosan, which were shown to decrease in molecular weight by up to 85% for each hour of sonication time, under comparable conditions.33 Hence, the functionality of the macrocyclic and antibiotic molecules used as dispersant in the current study should be retained in the dispersions, and also the buckypapers they are used to produce. This should result, for example, in buckypapers that can be used for selective molecular based separations.
3.8 References:


Synthesis and Characterisation of Buckypaper Membranes

This chapter discusses the preparation and characterisation of buckypaper membranes containing a range of functional dispersant molecules.
4.1 Introduction:

In order for a material to be useful in a separations application, it should ideally possess a range of properties including a high porosity, large surface area, good chemical and thermal stability, and mechanical integrity. In this chapter, the properties of buckypapers obtained from dispersions described in chapter three are presented and discussed in relation to the above criteria. Parts of this chapter describing the properties of buckypapers obtained using macrocyclic dispersants have been published as part of the following article:


4.2 Preparation of Buckypapers:

A wide range of buckypapers (BPs) were successfully obtained from aqueous dispersions produced using Triton X-100 (Trix), Calix[6]arene (C6S), β-cyclodextrin (β–CD), phthalocyanine tetrasulfonic acid (PTS), meso-tetra(4-sulfonatophenyl) porphyrin dihydrogenchloride (TSP), ciprofloxacin (cipro) and berberine and the optimum sonication time and concentrations identified in chapter 3. Both small and large buckypapers could be made using SWNTs or MWNTs, however this chapter will focus primarily on the characterisation of membranes created from SWNTs. To the best of our knowledge, the synthesis and characterisation of BPs incorporating supramolecular complexing agents and antibiotics has been hitherto unexplored. All
buckypapers in this study were subjected to a simple washing procedure after preparation to remove loosely adsorbed dispersant molecules. This left behind free-standing films such as the case for the SWNT/Trix buckypapers shown in Figure 4.1. In their dried state, the buckypapers were sufficiently robust to be handled and trimmed to any desired size and shape for characterisation studies. The following sections describe the systematic examination of the structure and properties of these membranes, which was conducted prior to evaluating their ability to act as membranes or adsorbents.

Figure 4.1: Digital photographs of: (a) a large SWNT/Trix buckypaper, and (b) a small SWNT/Trix buckypaper.

4.3 Membrane Composition:

All buckypapers were extensively washed after their preparation, to remove loosely bound dispersant molecules. However, it was anticipated that even after this washing procedure, some dispersant molecules would remain bound to the MWNTs as a result of effectively being trapped within the membrane. In order to confirm this hypothesis a number of different approaches were pursued. The simplest approach to accomplish this was to dry the buckypapers to constant mass at 110°C, and compare this to the mass of MWNTs used to prepare the initial dispersions (~30 mg). Table 4.1 presents the dried masses for several MWNT membranes examined in the current study. Assuming that all
of the MWNT starting material was retained during the filtration process, a mass gain of between 8.5 – 16.1% was observed for all buckypapers, which could only be attributed to the presence of dispersant molecules after the drying process.

**Table 4.1:** Comparison of the dry mass of selected MWNT buckypaper membranes to the mass of the MWNTs used in their preparation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of MWNTs (mg)</th>
<th>Mass of BP (mg)</th>
<th>Mass gain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/β–CD</td>
<td>27.9 ± 0.5</td>
<td>30.5 ± 0.5</td>
<td>8.5 ± 0.7</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>30.2 ± 0.5</td>
<td>36.0 ± 0.5</td>
<td>16.1 ± 0.7</td>
</tr>
<tr>
<td>MWNT/cipro</td>
<td>26.4 ± 0.5</td>
<td>31.4 ± 0.5</td>
<td>15.9 ± 0.7</td>
</tr>
</tbody>
</table>

Microanalytical data were also obtained for the SWNT starting material used for preparing the buckypapers, as well as for the buckypapers themselves (**Table 4.2**). The results obtained for the SWNT starting material showed that it contained no sulfur and only very small amounts of fluorine and nitrogen. This was important to establish, as each of the dispersant molecules contained one or more of these types of atoms. Therefore retention of dispersant molecules in a buckypaper should result in greater elemental percentages being obtained for one or more of these elements. Inspection of the data in **Table 4.2** shows that this was the case for most of the buckypapers examined.

**Table 4.2:** Microanalytical data for SWNT buckypapers and SWNT starting material. The error in each case is ± 0.1%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Unidym SWNTs (P0348)</td>
<td>85.1</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>78.3</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>76.9</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>79.1</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>64.5</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>68.9</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>76.2</td>
</tr>
<tr>
<td>SWNT/berberine</td>
<td>64.2</td>
</tr>
</tbody>
</table>
Retention of antibiotic molecules in the SWNT/cipro buckypaper was confirmed by a small but significant increase in fluorine content, and an even larger increase in the amount of nitrogen present. For a SWNT/berberine buckypaper, the nitrogen analysis result was one of the largest values obtained, suggesting that even more of this antibiotic was retained. This was a surprising result in view of the poor quality of SWNT/berberine dispersions, relative to SWNT/cipro dispersions, noted earlier in this thesis (section 3.3).

Incorporation of TSP and PTS in SWNT/TSP and SWNT/PTS buckypapers, respectively was confirmed by nitrogen and sulphur analyses that were significantly greater than that of the SWNT starting material. This was particularly true for the latter buckypaper, and indicates that these aromatic molecules were not only very effective for dispersing SWNTs, but remained bound to the nanotubes afterwards as well.

Retention of C6S and β−CD in their respective SWNT buckypapers was also confirmed by the sulphur elemental analyses obtained for these materials. In the case of the SWNT/β−CD buckypaper examined, the sulfur analysis was found to be only 0.45%. While this is still greater than the value of 0.01% obtained for the SWNT starting material, it is significantly less than the values obtained for any of the other buckypapers prepared using a sulfur-containing dispersant. This observation may be attributable to the poorer ability of β−CD to disperse SWNTs prior to buckypaper preparation.
The results presented in Table 4.2 also reveal that all BP samples contained significantly lower carbon contents than the SWNT starting material. This is also attributable to incorporation of the dispersant molecules, which contained a lower percentage of carbon, and a higher percentage of other elements, than what is found for the SWNT starting material. Taken together, the microanalytical results conclusively show the presence of dispersant molecules within SWNT buckypaper samples, thereby raising the prospect of having access to materials with a range of molecular recognition properties for nanofiltration and other applications.

Buckypapers were also analysed using Energy Dispersive X-ray Spectroscopy (EDX) in an attempt to confirm the presence of elements that could only be attributed to incorporation of dispersant molecules within the membranes. The EDX spectrum of the SWNT starting material (Figure 4.2a) shows peaks corresponding to the elements chlorine and iron, in addition to that arising from carbon. The presence of iron is not surprising as iron catalysts are used during synthesis of SWNTs via the HiPCO process. Chlorine may have been introduced into the original sample of SWNTs as a result of the purification process used, in which the catalytic iron particles are typically removed by treatment with an acid such as HCl.

Not surprisingly, EDX analysis of all BP samples showed an identical series of peaks indicating the presence of carbon, iron and chlorine from the SWNT starting material. Furthermore, a peak was also identified in the EDX spectrum of many buckypaper samples (Figure 4.2 b-c) due to the presence of titanium. This was attributed to
degradation of the titanium sonicator tip used to prepare the initial dispersions from which the buckypapers were produced (Figure 4.2d). The EDX spectra of SWNT/β-CD, SWNT/PTS and SWNT/TSP buckypapers all showed a peak at ~2.3 keV attributable to sulfur (Appendix 2). This therefore provides further strong support for the inclusion of these sulfur-containing dispersants in the buckypapers. The EDX spectrum of the SWNT/cipro buckypaper showed a peak at ~ 0.65 keV, which overlapped with the peak attributed to iron at ~ 0.7 keV, and is representative of the inclusion of fluorine. This again supports the incorporation of the fluorine-containing ciprofloxacin molecules within the buckypaper sample.

The extent of interaction between the SWNTs and dispersants in buckypaper samples was investigated using Raman spectroscopy, as was performed previously for the corresponding dispersions. As described in section 3.5, the ratio of the intensity of the band at ~ 1585 cm\(^{-1}\) (G band) to that of the band at ~ 1310 cm\(^{-1}\) (D band) is determined
Chapter Four: Synthesis and Characterisation of Buckypaper Membranes

by the proportion of sp\(^2\) hybridised carbon relative to sp\(^3\) amorphous carbon within a sample.\(^1\) The ratio of these peak intensities was determined for all buckypaper samples using Raman spectroscopy, and is summarised in Table 4.3. The G/D intensity ratio for all buckypaper samples are well below those obtained for the SWNT starting material. This can be attributed to defects in the nanotube structure introduced as a result of the sonication process. The G/D intensity ratios of the buckypaper membranes are also significantly lower than that of the corresponding dispersions from which they were made. This is most likely due to the incorporation of amorphous carbonaceous material that had precipitated during the formation of the dispersion, into the final buckypaper.

Table 4.3: Comparison of the G/D intensity ratios for selected SWNT buckypapers and SWNT starting material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalised G/D intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0348 SWNTs</td>
<td>1.00 ± 0.18</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>0.68 ± 0.14</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>0.72 ± 0.09</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>0.86 ± 0.18</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>0.59 ± 0.14</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>0.59 ± 0.09</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>0.5 ± 0.05</td>
</tr>
<tr>
<td>SWNT/berberine</td>
<td>0.45 ± 0.18</td>
</tr>
</tbody>
</table>

Measurement of the position of the radial breathing mode (RBM) frequencies in the Raman spectrum of a buckypaper sample provides insight into the chemical environment surrounding the nanotubes. Shifts in the RBM peaks of a buckypaper to higher frequencies has been attributed to interactions with the surface of the nanotubes, resulting in constriction of their diameters and raising the energy of the radial breathing mode relative to that in the corresponding dispersion. Examination of the RBM of the buckypaper samples revealed that some dispersants produced a significant shift to higher frequency. This is illustrated in Figure 4.3 which compares the RBM region of a
SWNT/C6S dispersion and buckypaper to each other, and that of the SWNT starting material, while Table 4.4 presents the shifts in the specific RBM at 218 cm\(^{-1}\) for several buckypapers. Significant shifts in the RBM to higher frequencies can be attributed to the loss of loosely adsorbed dispersant molecules on the SWNT surfaces, thus resulting in less restriction of radial expansion of the CNTs.

**Table 4.4:** Comparison of the shift in position of the RBM peak frequency at 218 cm\(^{-1}\) for selected buckypapers, to that of the SWNT starting material (P0348).

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Shift in peak at 218 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>1.8</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>4.3</td>
</tr>
<tr>
<td>SWNT/β–CD</td>
<td>0.81</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>0.73</td>
</tr>
</tbody>
</table>

**Figure 4.3:** Comparison of the RBM region of the Raman spectrum of a SWNT/C6S dispersion to that of a SWNT/C6S buckypaper, and the SWNT starting material.
4.4 Surface morphology and Pore Structure:

The surface morphology of buckypaper samples was examined using scanning electron microscopy (SEM). In each case, a randomly entangled mat of SWNTs was observed, with the diameter of the pores and other surface features highly dependent on the preparative conditions employed, and in particular, the identity of the dispersant used. Examination of the SEM image of a SWNT/Trix buckypaper (Figure 4.4a) revealed a highly porous surface structure, and similar overall morphology to that reported elsewhere for this material.2

It is clear from this image that the membrane possesses a large number of irregularly sized pores, with software image analysis (see section 2.3.5 for details) revealing an average surface pore diameter of 23 ± 7 nm (Table 4.5). This agrees well with previous studies which showed that the surface pore sizes of buckypapers containing SWNTs vary between 10 – 100 nm in diameter.3,4 In contrast, the SEM image of a MWNT/Trix buckypaper showed a different surface morphology (Figure 4.4b). Image analysis of the MWNT/Trix buckypaper gave an average surface pore diameter of 80 ± 20 nm (Table 4.5), which is comparable to that obtained previously for similar BPs produced.
using MWNTs.\textsuperscript{5, 6} The variation in morphology between buckypapers containing SWNTs or MWNTs may be explained by the larger diameter of the latter nanotubes, which results in a less efficient packing of nanotube bundles, and gives rise to larger membrane pores.

**Table 4.5:** Surface pore diameters ($D_{\text{SEM}}$) of buckypapers imaged by SEM. Pore diameters were calculated by using image analysis software (Image Pro Plus) and micrographs taken at 70K magnification.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>$D_{\text{SEM}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>80 ± 20</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>23 ± 7</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>27 ± 14</td>
</tr>
<tr>
<td>SWNT/$\beta$-CD</td>
<td>49 ± 38</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>29 ± 17</td>
</tr>
<tr>
<td>SWNT/berberine</td>
<td>53 ± 38</td>
</tr>
</tbody>
</table>

When BPs were prepared using macrocyclic dispersants, additional changes in surface morphology were observed. The SEM micrograph of a SWNT/$\beta$-CD membrane (Figure 4.5a) revealed a surface morphology consisting of large bundles of nanotubes, with the diameters of the bundles often exceeding 100 nm, and pore sizes considerably larger than those found for the SWNT/Trix membrane. This finding is perhaps not surprising considering the poorly dispersed SWNT suspension used to produce the buckypaper, which is shown in Figure 3.7b. Image analysis of the SWNT/$\beta$-CD buckypaper gave an average surface pore diameter of 49 ± 38 nm (Table 4.5). This large range of pore diameters is what would be expected given that a large percentage of the SWNTs were not thoroughly debundled in the dispersion used to prepare this BP. On the other hand, the SWNT/C6S buckypaper was debundled to a greater extent (Figure 4.5b), and possessed a similar morphology to that of a SWNT/Trix buckypaper. This is consistent with the hypothesis that solutions containing highly dispersed CNTs
generally give BPs containing smaller bundles of nanotubes and therefore smaller pore openings on their surfaces. This is supported by a comparison of the surface pore diameters for these materials, which were $23 \pm 7$ nm and $27 \pm 14$ nm for SWNT/Trix and SWNT/C6S buckypapers, respectively.

Buckypapers prepared from dispersions containing the PTS and TSP dispersants gave slightly different surface morphologies shown in Figures 4.5c and 4.5d, respectively. The almost featureless SEM images obtained for these materials was surprising, as it
was anticipated that the highly debundled nanotube dispersions used to produce these buckypapers would lead to a surface morphology similar to that of the SWNT/Trix and SWNT/C6S buckypapers. Image analysis of the SWNT/TSP buckypaper gave an average surface pore diameter of only $7 \pm 3$ nm, which was the smallest obtained for any buckypaper. In the case of a SWNT/PTS buckypaper, image analysis could not be used to obtain an estimate of the average surface pore diameter, owing to the very small size of the surface features imaged.

The surface morphology of buckypapers produced using antibiotic dispersants resembled what was expected based on the differences in the dispersions they were prepared from. For example, the SEM image of the surface of a SWNT/berberine buckypaper (Figure 4.6a) possessed noticeably larger bundles or aggregates of tubes, than the corresponding BP containing ciprofloxacin (Figure 4.6b). In addition, image analysis revealed an average surface pore size for the former BP of $53 \pm 38$ nm, which is almost twice as great as that for the SWNT/cipro buckypaper, which was $29 \pm 17$ nm.

Figure 4.6: SEM micrographs of different buckypapers imaged at 70K magnification: (a) SWNT/berberine and (b) SWNT/cipro. Both BPs were prepared from dispersions containing 0.1% (w/v) SWNTs and either 0.5% (w/v) berberine or 1% (w/v) ciprofloxacin using a sonication time of 30 min.
(Table 4.5). This is consistent with the greater degree of dispersion of the SWNTs that was achieved using the ciprofloxacin dispersant (section 3.2.1).

There is conflicting evidence in the literature concerning the effect of increasing the sonication time used for preparing dispersions to be used for making BPs, on the final pore size distribution and surface features of the latter. Investigations performed by Smajda et al. included varying the sonication time used for making MWNT dispersions in DMF between 10 - 50 min, and found this had no significant effect on the pore diameter distribution of the resulting BPs.\(^5\) In contrast, a later study showed dramatic changes in surface morphology occurred for SWNT buckypapers containing biomolecular dispersants, if sonication time was altered.\(^7\) To further explore this disparity between literature results, the sonication time employed to produce SWNT/C6S dispersions used for preparing BPs was varied, and the effect on surface morphology evaluated by SEM. **Figure 4.7** shows the SEM micrographs of SWNT/C6S BPs produced from dispersions made with sonication times of 15, 30 and 60 min. The BP produced using a very short sonication time of 15 min appeared to show slightly larger bundles and aggregates of SWNTs across its surface, together with fewer pore openings, than either of the BPs produced from dispersions made using longer sonication times. These results are consistent with those obtained from UV-vis-NIR investigations into the effect of increasing sonication time on the degree of dispersion of SWNTs, reported in section 3.3. In the latter section it was determined that a sonication time of 30 min was optimal for achieving debundling of the SWNTs in the presence of C6S. While it was suspected that sonicating for 60 min may result in shortening or damage to the SWNTs, no clear evidence of this was found by SEM.
SEM images of the cross section of a SWNT/Trix buckypaper are shown in Figure 4.8. The formation of the highly layered structure apparent in this image has been attributed to the nature of the deposition process, with deposition of the first nanotubes forming a mat that behaves as a ‘chattering valve’ throughout the remainder of the filtration process. During this process nanotubes initially deposit rapidly onto the underlying substrate to form a compact layer, which causes the next layer of deposited nanotubes to settle more slowly and form a loose interlayer. At this point the compact layer begins to react to the material deposited on top of it, by elastically relaxing, thereby forming a much more open, porous structure, and resulting in a greater pressure, restarting the
cycle of events. This continual rearrangement of deposited layers, causes a marked
difference in packing between the layers, hence explaining the layered structure
observed by SEM.

![Figure 4.8](image1.png)

**Figure 4.8:** SEM micrographs of the cross-section of a SWNT/Trix buckypaper made using 0.1\% (w/v)
SWNTs and 1\% (w/v) Trix, imaged at: (a) 1.9K and (b) 20K magnification.

In section 3.6 it was reported that bath sonication produced highly unstable dispersions
containing numerous, large aggregates of SWNTs. It is therefore not surprising that BPs
produced from such ‘dispersions’ contained large, highly entangled, bundles of SWNTs
(Figure 4.9).

![Figure 4.9](image2.png)

**Figure 4.9:** SEM micrograph of a SWNT/Trix buckypaper made using a dispersion containing 30 mg
SWNTs and 1\% (w/v) Trix, which was obtained using bath sonication for 12 hours. Image was collected
using 70K magnification.
4.5 Nitrogen Adsorption-Desorption Isotherms:

To develop further understanding about the internal pore structure of the buckypaper samples, nitrogen adsorption-desorption isotherms were obtained and analysed. Prior to analysis, samples were de-gassed under vacuum at 200°C to remove any loosely adsorbed dispersant molecules, as thermogravimetric analysis (TGA) confirmed the stability of all samples at this elevated temperature. Analysis of the results obtained revealed that all SWNT buckypapers exhibited a general type IV isotherm with hysteresis at higher relative pressures. Representative isotherms obtained for several SWNT buckypapers are shown in Figure 4.10. Hysteresis occurs in porous materials as a result of differences between the rate of filling and removal of the adsorbent, which occurs by a capillary condensation mechanism. The results obtained with all SWNT buckypapers confirmed the presence of a large proportion of mesopores (2 – 50 nm), consistent with the SEM results.

![Figure 4.10](image_url)
The changes in N$_2$ adsorption/desorption below P/P$_0 = 0.1$ can be attributed to the presence of micropores with diameters < 2 nm. These are believed to be the interstitial pores, which consist of channels between individual nanotubes within CNT bundles.$^5, ^{10}$ Barrett, Joyner, and Halenda (BJH) and Horvath-Kawazoe (HK) analysis of the N$_2$ isotherms was used to calculate the pore size distribution within the BPs.$^{11, 12}$ HK analysis enabled calculation of the distribution of small pores (< 2 nm), while the BJH method allowed estimation of the larger pores. Combining the two sets of results yielded pore size distribution curves such as those shown for SWNT/C6S and SWNT/β–CD buckypapers in Figure 4.11. There was good agreement in the crossover region between both analysis methods at approximately 2 nm for all BPs.

The distribution of pore sizes shown in Figure 4.11 reveal a large peak at ~0.7 nm, which can be attributed to the interstitial pores. A broad distribution of peaks is also present in both cases between 1 and 100 nm, which is attributed to larger pores whose openings were observable via SEM. Numerical integration of the curves in Figure 4.11 revealed that these larger interbundle pores are responsible for 76% of the total free volume of the SWNT/C6S buckypaper, and 93% for the SWNT/β–CD buckypaper. When this analysis was repeated using data for the other SWNT buckypaper samples, the results presented in Table 4.6 were obtained. The interbundle pore volumes ranged between 76 – 95% amongst different buckypaper samples.
The specific surface area (\(A_{\text{BET}}\)) of the SWNT buckypapers was calculated by the Brunauer, Emmett and Teller (BET) method, and found to vary between 30 – 800 m\(^2\)g\(^{-1}\) (Table 4.6). These values are in close agreement with those reported previously for other CNT membranes. For example, similar SWNT buckypapers have been shown to possess specific surface areas of 611 m\(^2\)g\(^{-1}\) and 642 m\(^2\)g\(^{-1}\) using dispersions obtained using Trix and ethanol, respectively.\(^{10}\) In general, the buckypapers prepared using lower molecular mass dispersants exhibited the largest surface areas (\(A_{\text{BET}} > 350\) m\(^2\)g\(^{-1}\)). The one exception to this general rule was SWNT/PTS, which displayed a much smaller surface area (\(A_{\text{BET}} = 30\) m\(^2\)g\(^{-1}\)) comparable to that found when high molecular mass dispersants were used (e.g. \(A_{\text{BET}}\) for SWNT/lysozyme = 31 m\(^2\)g\(^{-1}\)).\(^{13}\) Average internal pore diameters calculated using the BET method ranged from 0.2 – 2.7 Å in diameter (Table 4.6). In general, these values are smaller than those determined by SEM (Table 4.5), as secondary and back scattered imaging does not reveal the interstitial pores. Due to the relatively small contribution of interstitial pores to the overall pore volume revealed by BJH/HK analysis, they should not significantly impact upon the filtration characteristics or performance of the buckypapers. By neglecting the contribution due to interstitial pores, \(A_{\text{BET}}\) can also be used to calculate an approximate nanotube bundle
diameter \( (D_{\text{bun}}) \) for each buckypaper, by using Equation 4.1 and a value for the theoretical CNT bundle density \( (\rho_{\text{CNT}}) \) of 1500 kg.m\(^{-3}\). The values calculated using Equation 4.1 are summarised in Table 4.6 and yield nanotube bundle diameters between 0.3 and 9.0 Å. These values are rather small when compared to what was observed in the SEM images, and should be considered a lower limit.

\[
A_{\text{BET}} = \frac{4}{\rho_{\text{CNT}}D_{\text{bun}}} \quad \text{Equation 4.1}
\]

Table 4.6: Surface areas \( (A_{\text{BET}}) \), average internal pore diameters \( (d_{\text{BET}}) \), average bundle diameters \( (D_{\text{bun}}) \), and interbundle pore volumes derived from data obtained from nitrogen adsorption-desorption isotherms for large SWNT buckypapers.

| Buckypaper   | \( A_{\text{BET}} \) \((\text{m}^2\text{g}^{-1})\) | \( d_{\text{BET}} \) \((\text{nm})\) | \( D_{\text{bun}} \) \((\text{nm})\) | Interbundle Pore Volume (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>790 ± 4</td>
<td>4.0 ± 0.4</td>
<td>3.4 ± 0.1</td>
<td>84 ± 5</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>580 ± 3</td>
<td>4.0 ± 0.4</td>
<td>4.6 ± 0.1</td>
<td>76 ± 5</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>690 ± 4</td>
<td>4.0 ± 0.4</td>
<td>3.9 ± 0.1</td>
<td>93 ± 6</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>30 ± 1</td>
<td>27 ± 3</td>
<td>90 ± 3</td>
<td>78 ± 5</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>360 ± 4</td>
<td>2.0 ± 0.2</td>
<td>7.4 ± 0.1</td>
<td>#</td>
</tr>
</tbody>
</table>

\(^a\) Interbundle pore volume could not be calculated for the SWNT/TSP buckypaper as too few data points were collected to perform HK analysis for smaller pore diameters.

Another important property a membrane must possess if it is to be used for filtration applications is a reproducible pore structure. That is, different samples of the same membrane must have a similar surface area and pore structure. To our knowledge, there has been no prior work performed which looked at the consistency of buckypaper internal pore structure using BET, which provides quantitative information about the entire pore network. Therefore two different SWNT/Trix membranes were analysed by
this method, with the results obtained summarised in Figure 4.12 and Table 4.7. Both the surface area and average pore diameters were found to be similar between the duplicate samples analysed. This indicates that the method used for preparing these membranes produced BPs with a similar morphology. This finding is critical as it ensures that when solutions are exposed to the BP membranes they will experience similar interactions.

**Table 4.7:** Comparison of the surface area ($A_{\text{BET}}$) and average internal pore diameter ($d_{\text{BET}}$) of two different SWNT/Trix buckypapers.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>$A_{\text{BET}}$ (m$^2$/g)</th>
<th>$d_{\text{BET}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix (1)</td>
<td>790 ± 4</td>
<td>4.0 ± 0.4</td>
</tr>
<tr>
<td>SWNT/Trix (2)</td>
<td>840 ± 6</td>
<td>5.0 ± 0.4</td>
</tr>
</tbody>
</table>

**Figure 4.12:** Pore size distributions for two SWNT/Trix buckypaper samples derived by BJH analysis of nitrogen adsorption-desorption isotherms.

An important issue encountered when fabricating CNTs into membranes or other constructs is the inherent variability between different batches of nanotube soot starting material. As most purified samples of CNTs are still limited to relatively small batch sizes using current commercial production methods, this variation can often result in quite different structures and hence properties for the final fabricated products. This was
again highlighted by the results of BET analysis performed on SWNT/Trix buckypapers prepared using different batches of SWNTs (Table 4.8).

The impact of sonication time on the internal structure of the buckypaper was also examined using a SWNT/Trix buckypaper. As was evident from SEM, use of short sonication periods resulted in a more highly aggregated morphology as there had been less energy available to break up nanotube bundles in the solution state. Table 4.8 shows there is a marked decrease in the BET surface area of ~ 500 m$^2$/g, and an ~ 2 nm increase in average internal pore size upon decreasing the sonication time from 30 to 15 min when using the same batch of SWNTs, agreeing with this hypothesis. Taken together, these results again highlight the importance of ensuring that the synthesis conditions employed remain consistent in order to provide a fair comparison of sample properties.

Table 4.8: Surface area ($A_{\text{BET}}$), average internal pore diameter ($d_{\text{BET}}$), average bundle diameter ($D_{\text{bun}}$), and intertube pore volumes calculated from data obtained from nitrogen adsorption-desorption isotherms derived for three different SWNT/Trix membranes.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>$A_{\text{BET}}$ (m$^2$/g)</th>
<th>$d_{\text{BET}}$ (nm)</th>
<th>$D_{\text{bun}}$ (nm)</th>
<th>Interbundle Pore volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix (SWNT batch #P0261, 30 min sonication)</td>
<td>400 ± 1</td>
<td>7 ± 0.7</td>
<td>6.7 ± 0.1</td>
<td>97 ± 6</td>
</tr>
<tr>
<td>SWNT/Trix (batch #P0348, 30 min sonication)</td>
<td>840 ± 6</td>
<td>4 ± 0.4</td>
<td>3.4 ± 0.1</td>
<td>84 ± 5</td>
</tr>
<tr>
<td>SWNT/Trix (batch #P0348, 15 min sonication)</td>
<td>350 ± 3</td>
<td>6 ± 0.6</td>
<td>7.6 ± 0.2</td>
<td>87 ± 6</td>
</tr>
</tbody>
</table>
4.6 Physical Properties of Buckypapers:

The density of SWNT buckypapers ($\rho_{\text{paper}}$) is a fundamental, but important property that can also be used to calculate the interbundle free volume ($V_f / V_T$) of these materials, which is a measure of their porosity. Table 4.9 presents both the densities and interbundle free volumes, calculated according to Equation 4.2, for the various BPs examined. All BPs possessed low densities due to the inefficient nature of nanotube bundle packing. The calculated interbundle free volumes ranged between 2 - 60%, indicating that the porosities of the buckypapers vary widely. This is consistent with the variations in surface morphology and surface pore diameters revealed by SEM, which were discussed in section 4.2.2. For example, Table 4.9 suggests that the SWNT/$\beta$–CD buckypaper was the most porous examined. The SEM micrograph of this BP, shown in Figure 4.5a, revealed the presence of very thick bundles and aggregates of nanotubes on the materials surface, which formed a web-like structure containing surface pores that were large and variable in size. This was confirmed by image analysis of the SEM micrograph, which gave an average surface pore diameter of 49 ± 38 nm. This was larger than what was found for any other SWNT buckypaper, apart from that composed of SWNT/berberine, which was also produced from a very poorly dispersed solution of SWNTs that contained large aggregates of nanotubes.

$$\frac{V_f}{V_T} = 1 - \frac{\rho_{\text{paper}}}{\rho_{\text{CNT}}}$$

Equation 4.2

Perhaps the most striking interbundle free volume in Table 4.9 was that calculated for a SWNT/PTS buckypaper, which was only 2.0 ± 0.3%. This value is consistent with the
Table 4.9: Densities and interbundle free volumes of buckypapers produced using dispersions containing 30 mg (0.1% (w/v)) SWNTs and selected dispersants.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>ρ_{\text{paper}} (kgm^{-3})</th>
<th>\text{V}_F / \text{V}_T (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>1000 ± 100</td>
<td>33 ± 3</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>700 ± 70</td>
<td>53 ± 5</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>600 ± 60</td>
<td>60 ± 6</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>1500 ± 200</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>1200 ± 100</td>
<td>18 ± 2</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>700 ± 100</td>
<td>54 ± 5</td>
</tr>
</tbody>
</table>

SEM micrograph presented in Figure 4.5c for a SWNT/PTS buckypaper, which showed a surface morphology consisting of tightly packed bundles of nanotubes, and very few surface pore openings with a significant size. In fact, image analysis of the SWNT/PTS surface could not be used to obtain a value for the average surface pore diameter, owing to the lack of pore openings on the surface. The reason for this structure is unclear, however it is likely to be due to how the highly planar PTS molecules adsorb to the surface of the SWNTs during BP formation.

For many separation applications, it is important that the membrane or adsorbant being used exhibits a high degree of thermal stability. For this reason, the effect of temperature on SWNT buckypapers was analysed by TGA by applying temperatures between 25 - 1000°C to all samples. Representative TGA traces are shown in Figure 4.13. In all cases, a small loss of mass was observed when the sample was heated to 100°C, which can be attributed to the evaporation of residual water trapped within the BP. The TGA trace illustrated in Figure 4.13a shows that between 100°C and 250°C, the mass of the SWNT/Trix sample remained relatively constant. Above 250°C there was then a sharp decrease in mass. This occurred at a much lower temperature compared to when the SWNTs alone were examined (Appendix 2), confirming the
Retention of the less thermally stable dispersant molecules (Trix) within the BP membrane.\textsuperscript{15} Loss of mass between 250°C and 500°C is assigned to loss of the dispersant followed by the SWNTs themselves.\textsuperscript{2} Consequently the maximum operating temperature to ensure minimal degradation of these SWNT membranes was determined to be 250°C. The TGA traces shown in \textbf{Figure 4.13b-d} for SWNT buckypaper incorporating macrocyclic dispersants, reveals that these membranes exhibited significantly greater thermal stability. This is indicated by the majority of the sample remaining intact until a temperature of \( \sim 350°C \) was reached. Above 400°C in all cases, a more dramatic decrease in mass was observed, which is attributed to CNT decomposition. The residual mass remaining after the temperature had been raised to \( \sim 700°C \) can be attributed to the presence of metallic iron catalyst particles that were used to prepare the CNTs, and were not removed during their purification.

\textbf{Figure 4.13:} TGA traces for SWNT buckypaper membranes: (a) SWNT/Trix, (b) SWNT/C6S, (c) SWNT/\( \beta \text{--} CD \) and (d) SWNT/TSP.
Table 4.10 summarises the approximate temperatures at which decomposition of the dispersant molecules and SWNTs in a buckypaper sample commenced (degradation temperature). The degradation temperatures for all buckypapers containing small macrocyclic dispersants were very similar (350 – 380°C).

Table 4.10: Summary of the degradation temperatures of SWNT buckypapers determined by TGA.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Degradation Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>250</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>350</td>
</tr>
<tr>
<td>SWNT/β–CD</td>
<td>380</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>350</td>
</tr>
</tbody>
</table>

4.7 Mechanical Properties of Buckypapers:

Robust mechanical integrity is an important property BP membranes must exhibit if they are to be used for membrane separation applications. This is because the membrane must be able to survive the application of a wide range of pressures and flow rates for extended periods of time, and possibly high working temperatures as well. An investigation of the mechanical properties of the BPs was therefore undertaken using the tensile test method described in section 2.3.8. Typical stress-strain curves are displayed in Figure 4.14, and reflect the mechanical properties of the SWNT buckypaper samples. All plots show an initial linear stress-strain relationship indicative of elastic deformation. However, minimal plastic deformation was observed due to very little deviation from this linear relationship at higher strains, which suggests a highly brittle failure mechanism. Fracture was observed at very low strains of approximately 1 – 3% in all cases.
The mechanical properties determined from the stress-strain curves were the Young’s modulus (E), tensile strength (σ\text{Break}), breaking extension or ductility (ε\text{Break}) and toughness (T). Table 4.11 summarises the mechanical parameters of the various BPs produced using different dispersants. The values obtained for each of the four parameters fall within relatively narrow ranges, and are generally comparable to those obtained previously for buckypapers prepared from SWNTs or MWNTs. For example, buckypapers obtained from dispersions containing SWNTs and surfactants have been shown to possess Young’s moduli that fall between 0.5 – 2.3 GPa, tensile strengths within the range 4.7 – 33 MPa and ductility ranging from 1 – 2.5%.\textsuperscript{3, 14, 16, 17} These ranges are very similar to those obtained for the materials prepared as part of the work described in this thesis, which were Young’s moduli = 0.6 – 2.3 GPa, tensile strength = 6 – 20 MPa, and ductility = 0.9 – 3.2 %.

\textbf{Figure 4.14:} Representative stress-strain curves for SWNT buckypaper membranes prepared from Trix, C6S, PTS, TSP or β–CD dispersants. The diagram also illustrates how the parameters used to evaluate the mechanical properties of samples in this study were derived.
Table 4.11: Summary of mechanical properties of SWNT buckypapers prepared from dispersions containing 30 mg (0.1% (w/v)) SWNTs and different dispersants.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>$E$ (GPa)</th>
<th>$\sigma_{\text{Break}}$ (MPa)</th>
<th>$\varepsilon_{\text{Break}}$ (%)</th>
<th>$T$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>1.7 ± 0.3</td>
<td>20 ± 10</td>
<td>3.2 ± 0.5</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>0.98 ± 0.04</td>
<td>18 ± 4</td>
<td>2.4 ± 0.8</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>SWNT/β−CD</td>
<td>0.6 ± 0.1</td>
<td>6 ± 3</td>
<td>1.7 ± 0.7</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>2.0 ± 0.3</td>
<td>15 ± 6</td>
<td>1.3 ± 0.3</td>
<td>0.05 ± 0.03</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>1.3 ± 0.6</td>
<td>13 ± 9</td>
<td>1.1 ± 0.3</td>
<td>0.07 ± 0.05</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>1.1 ± 0.2</td>
<td>7 ± 2</td>
<td>0.9 ± 0.3</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>SWNT/berberine</td>
<td>0.8 ± 0.4</td>
<td>13 ± 4</td>
<td>2.6 ± 0.7</td>
<td>0.19 ± 0.03</td>
</tr>
</tbody>
</table>

The similarity between the mechanical properties of the buckypapers examined here may be due to the similar size of the dispersants present in the membranes. Consistent with this hypothesis are the results of a recent study which showed that the tensile strength of buckypapers made from SWNTs was significantly improved only when high molecular mass dispersants, such as proteins or polysaccharides, were incorporated into the membranes.7

The results of SEM analysis of buckypaper samples, which were presented in section 4.4, indicated that the degree of debundling of SWNTs evident in the membranes was strongly influenced by the sonication time used to prepare the initial dispersions. In order to investigate whether the extent of debundling evident in the SEM images affected the mechanical properties of membranes, a series of SWNT/C6S buckypapers were prepared from dispersions made using a range of sonication times between 15 and 60 min, and subjected to tensile testing. The results of these experiments are summarised in Table 4.12, and show that varying the sonication time used to prepare the initial dispersion had little impact on the mechanical properties of the final BPs. Increasing the concentration of β–CD present in SWNT/β–CD dispersions used to
produce SWNT/β–CD buckypapers also had little effect on the mechanical properties of the latter membranes (Table 4.13).

**Table 4.12:** Mechanical properties of SWNT/C6S buckypapers produced from dispersions prepared using 1% (w/v) C6S and 0.1% (w/v) SWNTs, but different sonication times.

<table>
<thead>
<tr>
<th>Sonication Time (min)</th>
<th>E (GPa)</th>
<th>$\sigma_{\text{Break}}$ (MPa)</th>
<th>$\varepsilon_{\text{Break}}$ (%)</th>
<th>T (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.4 ± 0.3</td>
<td>23 ± 7</td>
<td>2.0 ± 0.6</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>1.0 ± 0.4</td>
<td>18 ± 4</td>
<td>2.4 ± 0.8</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>60</td>
<td>1.2 ± 0.4</td>
<td>17 ± 9</td>
<td>1.3 ± 0.6</td>
<td>0.10 ± 0.07</td>
</tr>
</tbody>
</table>

**Table 4.13:** Mechanical properties of SWNT/β–CD BPs produced from dispersions containing 0.1% (w/v) SWNTs and various concentration of dispersant. Sonication time = 30 min for all BPs.

<table>
<thead>
<tr>
<th>[β–CD] (% (w/v))</th>
<th>E (GPa)</th>
<th>$\sigma_{\text{Break}}$ (MPa)</th>
<th>$\varepsilon_{\text{Break}}$ (%)</th>
<th>T (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6 ± 0.1</td>
<td>6 ± 3</td>
<td>1.7 ± 0.7</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>3</td>
<td>0.5 ± 0.1</td>
<td>4 ± 2</td>
<td>1.7 ± 0.4</td>
<td>0.03 ± 0.02</td>
</tr>
<tr>
<td>5</td>
<td>1.0 ± 0.4</td>
<td>10 ± 4</td>
<td>1.4 ± 0.4</td>
<td>0.09 ± 0.04</td>
</tr>
</tbody>
</table>

### 4.8 Hydrophobicity of Buckypapers:

In order to evaluate the use of BPs as potential filtration membranes an understanding of their ability to interact with solvent molecules needs to be developed. A popular method for investigating these interactions is to determine the wettability of the membrane surface with the solvent of interest, which is most commonly water. One of the most common ways for accomplishing this is to determine the contact angle for the membrane / solvent system. The contact angle is defined as the angle between the tangential line to a liquid drop placed on the surface of the membrane. In the case of measurements performed using water droplets, small contact angles (< 90°) indicate that the surface of the material is hydrophilic, while large angles (> 90°) show that the material is hydrophobic in nature. The contact angles for all SWNTs buckypapers examined in this work were measured using 2 µL water droplets delivered via a syringe, as shown in Figure 4.15.
Chapter Four: Synthesis and Characterisation of Buckypaper Membranes

Figure 4.15: Images of 2 µL water droplets added to the surface of different buckypapers: (a) SWNT/TSP and (b) SWNT/berberine.

The contact angles of water on SWNT buckypapers varied between 28 - 94°, indicating that their surfaces are in general hydrophilic in nature (Table 4.14). This agrees well with the results of a similar study by Whitten et al., who reported a water contact angle of 82° for SWNT buckypapers produced from dispersions containing the surfactant Trix.16 In contrast, work by Dumée et al. showed that buckypapers produced from organic solvents such as 2-propanol displayed a higher contact angle of 113.3°.6 Therefore the buckypapers produced as part of the current work are more hydrophilic than those produced from organic solvents, but similar to those produced previously using SWNTs and surfactants. It has been well documented that the process of purification of SWNTs often introduces hydrophilic functional groups such as –OH or -COOH groups, which offset the inherent hydrophobic nature of CNTs.19 In addition, since many of the dispersants used in the current work contain polar, charged functional groups such as sulfonic acid residues, it is not surprising that the contact angles measured are generally lower those reported previously for buckypapers.
Table 4.14: Contact angles of 2 µL water droplets on SWNT buckypapers.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>54 ± 4</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>89 ± 8</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>49 ± 7</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>56 ± 4</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>28 ± 7</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>62 ± 7</td>
</tr>
<tr>
<td>SWNT/berberine</td>
<td>94 ± 4</td>
</tr>
</tbody>
</table>

A series of experiments were performed to determine whether it is possible to alter the preparation conditions used for preparing a buckypaper in order to increase its wettability, as this might make the membrane more suitable for nanofiltration applications. The BP chosen for this study was prepared using β-CD as the dispersant. It was proposed that increasing the concentration of β-CD in the original solution used for preparing SWNT/β-CD dispersions might result in a greater number of the hydrophilic dispersant molecules bound to the SWNTs in the buckypaper ultimately produced, and therefore a decrease in contact angle. Similarly, decreasing the amount of SWNTs in the initial dispersion would result in a greater proportion of dispersant molecules present with the ability to coat the SWNT surfaces and therefore might produce more hydrophilic buckypapers. The results of these experiments are summarised in Table 4.15, and show that altering the SWNT : dispersant ratio did not have a significant effect on the wettability of the membranes produced. This suggests that other factors, such as the intrinsic morphology induced into the buckypapers as a result of variations in the molecular structure of the dispersant are more important.
Table 4.15: Contact angles for SWNT/β−CD buckypapers produced from dispersions prepared using different concentrations of β−CD and SWNTs.

<table>
<thead>
<tr>
<th>Dispersion Preparation Conditions</th>
<th>Buckypaper Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% w/v β-CD/ 30 mg SWNTs</td>
<td>49 ± 7</td>
</tr>
<tr>
<td>3% w/v β-CD / 30 mg SWNTs</td>
<td>50 ± 9</td>
</tr>
<tr>
<td>3% w/v β-CD / 15mg SWNTs</td>
<td>60 ± 10</td>
</tr>
<tr>
<td>5% w/v β-CD / 30 mg SWNTs</td>
<td>60 ± 10</td>
</tr>
</tbody>
</table>

It has been recently shown that increased sonication time results in lower contact angles for BP membranes prepared using large biopolymer dispersants. With the smaller dispersant molecules used in this work, an opposite trend was observed (Table 4.16). In the case of the SWNT/C6S buckypapers, increasing the sonication time from 15 to 30 min resulted in an increase of 19° in the contact angle, which is believed to be due to greater debundling of nanotubes on the surface of the BP. This would result in a greater buckypaper surface area in contact with the solvent, and therefore an increase in the contact angle. Further increasing the sonication time from 30 to 60 min, however, resulted in no significant change in the contact angle measured.

Table 4.16: Contact angles of SWNT/C6S buckypapers prepared from dispersions produced using different sonication times.

<table>
<thead>
<tr>
<th>Sonication time (min)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>68 ± 8</td>
</tr>
<tr>
<td>30</td>
<td>89 ± 8</td>
</tr>
<tr>
<td>60</td>
<td>83 ± 6</td>
</tr>
</tbody>
</table>

4.9 Electrical Properties of Buckypapers:

Despite carbon nanotubes theoretically being one of the most conductive materials known, the construction of highly conductive composites encompassing them in a matrix has posed a major challenge. A highly conductive membrane would be advantageous for filtration processes, as this may enable a means of engendering
additional solute selectivity through the application of an electrochemical potential.\textsuperscript{20, 21} In order to determine the conductivity of BP membranes produced in this study, a 2-point probe method was employed. By applying the method described in section 2.3.7, a series of I-V plots such as those shown in Figure 4.16 were constructed for each buckypaper sample. The linear relationship between current and applied potential obtained for each discrete length of buckypaper examined indicates that the membranes were displaying ohmic behaviour. The electrical resistance for each length of buckypaper examined was then calculated as the inverse of the slope of each individual linear plot. The calculated resistances were found to decrease as the length of the buckypaper being examined was decreased, as expected.

![Figure 4.16: Sample I-V plots for a SWNT/cipro buckypaper membrane obtained using the 2-point probe conductivity method and a range of membrane lengths between 0.9 – 2.5 cm.](image)

The calculated resistances obtained for each length of buckypaper are known to incorporate both the resistance of the BP itself, as well as the resistance associated with
making electrical contact between the testing equipment and the sample. This is described by the relationship shown in Equation 4.3 where $R_T$ is the total resistance of the system, as calculated from the inverse of the slope of each of the plots shown in Figure 4.16. $A$ represents the cross-sectional surface area of the sample being measured (in cm$^2$), $l$ is the length of the buckypaper sample (in cm) and $R_C$ represents the contact resistance.

$$R_T = \frac{1}{\sigma A} l + R_C$$  \hspace{1cm} \text{Equation 4.3}$$

The true buckypaper conductivity ($\sigma$), was obtained from plots of total resistance against sample length, such as that shown in Figure 4.17. All plots displayed a linear relationship, thus enabling calculation of the contact resistance ($R_C$) from the y-intercept, and the sample conductivity from the slope. The contact resistance for all samples remained consistent at c.a. 250 $\Omega$ (Table 4.17).

![Figure 4.17: Effect of varying buckypaper length on total sample resistance for a SWNT/cipro buckypaper. The linear relationship observed is described by equation 4.3, and allows calculation of the true sample resistance and thus buckypaper conductivity from the slope of the plot.](image)
The conductivity of SWNT/Trix buckypapers was determined to be 85 ± 2 S cm⁻¹, which is in good agreement with values reported by Blighe et al. for SWNT buckypapers obtained using solutions containing polystyrene in N-methyl-2-pyrrolidone, of c.a. 100 S cm⁻¹. The values obtained for the other BPs containing alternative dispersants are summarised in Table 4.17.

Table 4.17: Electrical conductivities of SWNT buckypapers measured using the 2-point probe method.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Conductivity (S cm⁻¹)</th>
<th>R_c (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>85 ± 2</td>
<td>251 ± 5</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>48 ± 10</td>
<td>250 ± 2</td>
</tr>
<tr>
<td>SWNT/β−CD</td>
<td>170 ± 20</td>
<td>252 ± 3</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>220 ± 60</td>
<td>259 ± 8</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>30 ± 20</td>
<td>230 ± 10</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>70 ± 20</td>
<td>258 ± 5</td>
</tr>
<tr>
<td>SWNT/berberine</td>
<td>30 ± 20</td>
<td>240 ± 30</td>
</tr>
</tbody>
</table>

These results show that incorporation of different dispersant molecules had a significant effect on buckypaper conductivity. Previously, buckypapers produced using biopolymer dispersants and the same batch of SWNTs were found to exhibit electrical conductivities ranging between 3.9 ± 0.4 S cm⁻¹ for SWNT/gellan gum buckypapers to 52 ± 3 S cm⁻¹ for SWNT/lysozyme buckypapers. In these buckypapers, it was noted that electrical conductivity decreased as the molecular weight of the dispersant increased. This was attributed to greater coating of the CNT surfaces by larger biopolymer dispersants, which impedes tube-to-tube electronic transitions. As the majority of the dispersants used in the current work are considerably smaller than the biopolymers used in this earlier study, it was anticipated that higher conductivities would be obtained. However, only the SWNT/β−CD and SWNT/PTS buckypapers displayed conductivities (170 ± 20 S cm⁻¹ and 220 ± 60 S cm⁻¹, respectively) which were significantly larger than those for BPs containing the biopolymers. The deviation
from this previous trend may be a result of different binding mechanisms being used by different classes of dispersants to adsorb to the surface of the SWNTs. Alternatively, variations in the morphology of the BPs may play a more significant role. In this context it is worth noting that SEM showed the surface morphology of SWNT/TSP and SWNT/PTS buckypapers to consist of much more tightly packed assemblages of SWNTs, giving rise to markedly lower surface pore sizes. This may result in lower electron tunnelling barriers in the case of these two types of BPs, and contribute to them exhibiting the highest conductivities reported in Table 4.17.

In previous studies, the length of the sonication process used to make CNT dispersions has been shown to have a significant impact on the electrical properties of the BP membranes made from the resulting solutions. A similar investigation was performed here using the calixarene dispersant and sonication times between 15 and 60 min. The conductivities of the SWNT/C6S buckypapers obtained are presented in Table 4.18, and show a significant decrease in conductivity with increased sonication time. This could be caused by the increasing mechanical stresses the CNTs are subjected to as a result of increased sonication. This would result in shortening of the nanotubes present within the BP, thus increasing the number of tube-to-tube junctions and hence increasing resistance across the membrane.

*Table 4.18:* Effect of increasing sonication time on the electrical conductivity of SWNT/C6S buckypapers.

<table>
<thead>
<tr>
<th>Sonication Time (min)</th>
<th>Conductivity (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>300 ± 100</td>
</tr>
<tr>
<td>30</td>
<td>48 ± 10</td>
</tr>
<tr>
<td>60</td>
<td>20 ± 10</td>
</tr>
</tbody>
</table>
Chapter Four: Synthesis and Characterisation of Buckypaper Membranes

4.10 Electrochemical Capacitance:

The use of CNT modified microelectrodes for conducting electrochemical investigations has been extensively examined over the past two decades. However, to date there have been few reports on the electrochemical characteristics of buckypapers, such as their charge storage capability. In addition, to the best of our knowledge there have been no studies investigating the use of BP electrodes modified with low molecular mass dispersants such as porphyrin or cyclodextrin molecules for performing electrochemical studies. Therefore, the electrochemical response of selected buckypaper samples was investigated using cyclic voltammetry. Figure 4.18 shows typical cyclic voltammograms (CVs) obtained using a SWNT/C6S buckypaper working electrode immersed in aqueous 1.0M NaNO₃. The CVs exhibit a pseudo rectangular shape indicative of a capacitive material. This shape is maintained even at very high sweep rates, indicating rapid charge-discharge behaviour ideal for a capacitive substrate.

![Cyclic voltammograms obtained using a SWNT/C6S buckypaper immersed in aqueous 1.0 M NaNO₃. The scan rate was varied between 25 – 100 mV s⁻¹.](image)

The electrochemical capacitance (C) of buckypapers is related to the difference in current between the cathodic and anodic regions (ΔI) at a specific potential, and the scan...
rate ($\nu$), by \textbf{Equation 4.4}. Therefore for each buckypaper $\Delta I$ was determined at five different scan rates and the data obtained plotted as shown in Figure 4.19. This enabled the capacitances shown in Table 4.19 to be obtained from the slope of the plots and the mass of the buckypaper electrode used as the working electrode.

$$C = \frac{1}{2} \times \frac{\Delta I}{\nu}$$ \textbf{Equation 4.4}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.19.png}
\caption{Effect of scan rate ($\nu$) on the difference between the cathodic and anodic currents at 400 mV observed during CV experiments performed using a SWNT/C6S buckypaper.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Buckypaper & Capacitance (F g$^{-1}$) \\
\hline
SWNT/Trix & 13 ± 1 \\
SWNT/C6S & 20 ± 1 \\
SWNT/β–CD & 20 ± 1 \\
SWNT/TSP & 7 ± 1 \\
SWNT/cipro & 17 ± 1 \\
\hline
\end{tabular}
\caption{Electrochemical capacitance of SWNT buckypapers determined by cyclic voltammetry.}
\end{table}

The capacitances obtained varied between 7 ± 1 and 20 ± 1 F g$^{-1}$. These values are lower than that reported for a similar buckypaper prepared using unmodified SWNTs and a surfactant of c.a. 50 F g$^{-1}$. This may be due to the dispersants used in the current work significantly modifying the morphology of the membranes, as was shown
previously by SEM. This would have in turn affected the surface area and conductivity of the BP electrodes.

4.11 Conclusion:

This chapter reported for the first time the successful preparation of free-standing buckypapers from dispersions containing SWNTs and β–CD, C6S, TSP or PTS macrocyclic dispersants, or berberine or cipro antibiotic dispersants. The morphology of all membranes was confirmed by a combination of SEM and nitrogen adsorption-desorption analysis. SEM revealed that the morphology of the membranes varied significantly in response to changes in the identity of the dispersant used, and was also dependent on the sonication time used to prepare the initial dispersion. Surface pore diameters were shown to be between 7 – 80 nm depending on membrane composition, with the MWNT/Trix buckypaper proving to possess the largest and greatest number of pores at the surface. These results were confirmed by those obtained from analysis of nitrogen adsorption-desorption isotherms, which also showed that the buckypapers had high surface areas (360 – 690 m²g⁻¹), and their internal structures were dominated (> 75%) by the presence of large interbundle pores between CNTs measuring > 2 nm. The results of density measurements also revealed that the membranes were extremely porous, and possessed a very high proportion of free space (2 – 60%). Taken together, these results suggest that the SWNT/PTS buckypaper, which possessed the largest internal pore diameter and smallest surface area (27 ± 3 nm and 30 ± 1 m²g⁻¹), may have the highest permeability as the extent of interaction between an analyte solution and the membrane would be small.
The composition of the buckypapers was investigated using a combination of microanalysis, EDX and Raman spectroscopy, which provided evidence that the dispersant molecules were retained in the membrane structure. The incorporation of these molecules was shown to influence the physical properties of the BPs, including their hydrophobicity (contact angle = 28 - 94°) and electrical properties (\(\sigma = 30 - 220 \text{ S cm}^{-1}\)). These results suggested that all buckypapers possessed a relatively hydrophilic surface, with SWNT/TSP proving most hydrophilic (contact angle = 28°), which indicates that it may require the lowest onset pressure (Liquid entry pressure) to induce transport of aqueous solution across the membrane surface. Electrical conductivity measurements on the other hand show that the SWNT/PTS buckypaper (\(\sigma = 220 \text{ S cm}^{-1}\)) may be suitable as an electrode platform for electrochemical applications. No correlations were observed between the properties of the buckypapers, and those of the dispersants themselves (such as mol. wt.), as was shown previously for SWNT buckypapers containing large biopolymer dispersants.\(^7\) The reason for this is, at present, uncertain, but may be because of different mechanisms used by the small dispersant molecules to adsorb to the SWNTs, compared to the large biopolymers.

Most buckypapers displayed similar mechanical properties, with the exception of SWNT/β–CD which displayed a low Young’s modulus and tensile strength of 0.6 ± 0.1 GPa and 6 ± 3 MPa, respectively. Despite this all buckypapers were sufficiently robust to be used for experiments designed to investigate their suitability for separation applications. This is explored in the following chapters.
4.12 References:


5
Membrane Filtration

This chapter compares the permeability towards water of buckypaper membranes containing different dispersant molecules, each other, and to that of selected commercial polymer membranes. In addition, the ability of buckypaper membranes to remove E. coli from aqueous solutions, and subsequently kill the bacteria whilst on the buckypaper surface was examined.
5.1 Introduction:

Although membrane-based separations are now commonplace within the industrial and scientific communities, there is still a need to find new membrane materials which can overcome technical problems associated with fouling, short service lifetimes and low chemical selectivity.¹ The results presented in chapter 4 showed that buckypapers displayed good mechanical, electrical and thermal properties which make them ideal candidates as a membrane material. While the permeabilities of buckypapers composed of MWNTs or SWNTs towards water have been reported previously,², ³ the materials examined were prepared using very small quantities of CNTs and without a dispersant. Furthermore the buckypapers examined were not removed from the underlying polyvinylidene (PVDF) support that the initial CNT dispersions were filtered through. The results in this chapter provide further information on the permeability of buckypapers towards water, in the form of measurements made using mechanically robust free-standing SWNT buckypaper membranes. These results were published in the article below:


A number of studies have shown that BPs made from CNT dispersions prepared in dimethylsulfoxide are highly effective at removing bacteria from aqueous solutions.³⁻⁷ In the second half of this chapter, the ability of buckypapers containing the antibiotic ciprofloxacin to remove E. coli is investigated. The efficiency of these membranes was
examined by a combination of bacterial filtration experiments and fluorescence based assays.

5.2 Permeability of Buckypapers:

The permeability of SWNT buckypapers containing different dispersants towards water was measured using a custom-made dead end filtration cell setup, which used compressed air to force a feed solution across a membrane. Initially, a pressure of 0.069 bar was applied to induce transport of water across all BPs. If this was insufficient the applied pressure was increased until transport commenced. The mass of water passing across the membrane was monitored for 10 min using an analytical balance, and then the pressure increased incrementally and the process repeated. This yielded a series of linear permeability plots for SWNT buckypapers containing a range of different dispersant molecules (Figure 5.1a – e) and a commercial PVDF membrane tested under the same conditions (Figure 5.1f). Each of the BPs investigated proved to be permeable to water at only relatively low pressures (< 1 bar). Furthermore, the water transport behaviour of the BPs resulted in permeability plots that were very similar in overall appearance to each other, and that obtained using the commercial 0.22 μm pore diameter PVDF microfiltration membrane tested, despite the BPs possessing pore sizes less than 100 nm.

The slope of each of the plots in Figure 5.1 afforded the flux rate \( J \) for the membrane at a specific applied pressure. As expected, the flux rate increased as a function of applied pressure for all buckypapers until failure occurred. The pressure required to initiate water transport across the membrane varied markedly depending on the composition of the buckypaper. The most significant variation was found between the
Figure 5.1: Water permeability plots for selected buckypapers and commercial membranes obtained using applied pressures between 0.07 and 1.52 bar: (a) SWNT/Trix, (b) MWNT/Trix, (c) SWNT/β–CD, (d) SWNT/C6S, (e) SWNT/PTS and (f) PVDF Durapore® membrane (0.22 µm). The straight lines represent a linear fit to the experimental data obtained.

SWNT/Trix and MWNT/Trix buckypapers, which required 0.07 and 1.28 bar, respectively to induce water flow. The higher pressure required to initiate transport of water across the MWNT/Trix membranes, and smaller volumes of water that passed across these membranes with time clearly indicate that its permeability was much lower than that of the SWNT/Trix buckypapers. Membrane rupture occurred when the applied pressure was raised to between 0.7 – 1.4 bar for all buckypapers (Table 5.1).
By plotting the flux rate \((J)\) for each buckypaper as a function of the applied pressure, the graphs shown in Figure 5.2 were obtained. The slopes of these plots were then used to calculate the membrane specific flux \((f)\) for each BP by applying Equation 1.1, and dividing the gradients by the cross-sectional area exposed to the solvent enclosed by the sealing rubber o-ring within the transport cell.

**Figure 5.2:** Effect of applied pressure on the flux rate of different CNT buckypaper membranes and a commercial membrane: (a) SWNT/Trix, (b) MWNT/Trix, (c) SWNT/β−CD, (d) SWNT/C6S, (e) SWNT/PTS and (f) PVDF Durapore® membrane (0.22µm). The straight lines represent a linear fit to the experimental data obtained.
Table 5.1 presents the specific flux for each BP examined. The average permeability of three SWNT/Trix buckypapers was 80 ± 5 L m⁻² h⁻¹ bar⁻¹, which is almost three times greater than the average permeability determined for five MWNT/Trix buckypapers under identical conditions, (24 ± 4 L m⁻² h⁻¹ bar⁻¹). The greater permeability of the SWNT/Trix buckypapers is, perhaps, surprising in view of their significantly smaller surface pores and internal pores, compared to those present in the MWNT/Trix membranes. For example, SEM showed that the average surface pore sizes of the MWNT/Trix and SWNT/Trix membranes were 80 ± 20 nm and 23 ± 7 nm, respectively. This suggests that other factors, including, inherent differences between MWNTs and SWNTs may be more important in determining membrane permeability. In addition, BET analysis showed the surface area of a SWNT/Trix buckypaper was 160% greater than that of a MWNT/Trix membrane. This suggests that a greater number of water molecules are in contact with the surface of a SWNT/Trix buckypaper, which may facilitate faster transport through surface pores.

Table 5.1: Membrane flux (f), failure pressure, Liquid Entry Pressure (LEP) and permeance (i.e. permeability / thickness) of CNT buckypapers and commercial membranes analysed in this study (Membrane thicknesses used for these calculations are shown in Appendix 4).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Membrane Flux (f) (L m⁻² h⁻¹ bar⁻¹)</th>
<th>Failure Pressure (bar)</th>
<th>Liquid Entry Pressure (bar)</th>
<th>Permeance (x 10⁵ L m⁻³ h⁻¹ bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>25 ± 2</td>
<td>1.1 ± 0.6</td>
<td>0.2 ± 0.2</td>
<td>5.0 ± 0.4</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>83 ± 5</td>
<td>1.2 ± 0.3</td>
<td>0.7 ± 0.5</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>2400 ± 1300</td>
<td>1.0 ± 0.5</td>
<td>0.4 ± 0.3</td>
<td>600 ± 300</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>1000 ± 500</td>
<td>0.69</td>
<td>0.2</td>
<td>200 ± 100</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>160 ± 50</td>
<td>1.1 ± 0.5</td>
<td>0.5 ± 0.4</td>
<td>24 ± 7</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>800 ± 100</td>
<td>1.38</td>
<td>0.9</td>
<td>180 ± 20</td>
</tr>
<tr>
<td>PTFE - 0.22 µm</td>
<td>1900 ± 300</td>
<td>-</td>
<td>-</td>
<td>160 ± 30</td>
</tr>
<tr>
<td>PTFE - 5 µm</td>
<td>7000 ± 1000</td>
<td>-</td>
<td>-</td>
<td>530 ± 80</td>
</tr>
</tbody>
</table>

*Data taken from Millipore specification data sheet
† Value obtained from previous studies performed by Boge et al.⁴,⁵-six
‡ Membrane flux values obtained from one membrane. The error was determined in these cases from the standard deviation of the plots in Figure 5.2
The above permeability results may be compared with those reported previously for SWNT and MWNT membranes prepared from dispersions synthesised using the organic solvent DMSO. These buckypapers were left on the underlying 5 µm PVDF membrane on which they were deposited during the filtration process, and were found to display permeabilities towards water of 13800 ± 320 and 11900 ± 435 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively.\(^2\), \(^3\), \(^6\) These permeabilities are much greater than those exhibited by any of the BPs prepared in this work, which may be due in part to the smaller amounts of CNTs used in the preparation of membranes by these workers (3 - 8 mg).\(^2\), \(^3\), \(^6\) In contrast, buckypapers prepared as part of the work described in this thesis contained approximately 90 mg of CNTs, and displayed thicknesses of c.a. 50 µm, compared to 2 - 6 µm in the case of the membranes examined in the earlier studies.\(^6\) Consequently, solvent molecules had to cross a much greater distance in the case of the BPs prepared as part of the current study, and hence would have experienced a greater number of interactions with the membrane matrix, thus resulting in the significantly lower permeabilities observed.

Varying the dispersant used to prepare SWNT buckypapers revealed significant increases in permeability towards water. The most dramatic increase in permeability was exhibited by SWNT/PTS buckypapers, which displayed an average membrane flux of 2400 ± 1300 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), which is almost 30 times greater than the value obtained for the SWNT/Trix buckypapers. The average membrane flux for the SWNT/PTS buckypapers was larger than that of commercial 0.22 µm PTFE membranes (1900 ± 300 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)), but less than that of 5.0µm PTFE membranes (7000 ± 100 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)). Therefore replacement of the surfactant Trix with the PTS dispersant imparts a more permeable structure on the buckypaper.
Further evidence of the impact varying the dispersant used to prepare a buckypaper can have on its aqueous permeability is provided by inspection of the membranes fluxes for SWNT/TSP, SWNT/β−CD and SWNT/C6S buckypapers in Table 5.1. These were 1000 ± 500, 160 ± 50 and 800 ± 100 L m⁻² h⁻¹ bar⁻¹, respectively. The smallest increase in permeability (relative to a SWNT/Trix buckypaper) was a factor of two displayed by the SWNT/β−CD buckypaper, whereas the remaining two membranes were at least ten times more permeable than SWNT/Trix. For the SWNT buckypapers prepared using low molecular mass dispersants, there was no discernible correlation between membrane flux and either average surface pore size (determined by SEM) or the BET-derived average internal pore size ($D_{BET}$). Despite this, it is worth noting that the most permeable buckypapers prepared as part of this project, which were those composed of SWNT and PTS, possessed an average internal pore size of 27 nm. This is at least five times greater than that of any of the other SWNT membranes examined. The presence of significantly larger internal pores in the SWNT/PTS buckypapers would be expected to facilitate faster trans-membrane transport of water molecules.

The permeability of the buckypapers towards water was found to increase linearly with decreasing membrane surface area, as determined by BET. The linear fit in Figure 5.3 suggests that the membrane flux is inversely proportional to membrane surface area according to Equation 5.1, where $c$ and $J_0$ are constants.

$$J = c \frac{1}{A_{BET}} + J_0,$$

Equation 5.1

It is likely that $J_0$ could represent the limiting membrane flux attainable with this type of membrane, which is likely to be highly dependent on the preparation
conditions employed to prepare the buckypaper, i.e. sonication and filtration conditions. The inverse dependence on $A_{BET}$ is consistent with the hypothesis that a membrane with lower surface area will have larger pores on its surface, which would be expected to increase membrane flux. However, further research is necessary to test this hypothesis.

![Figure 5.3: Effect of surface area ($A_{BET}$) on permeability towards water of SWNT buckypaper membranes.](image)

**5.3 Effect of Using Different Batches of SWNTs:**

The values of membrane flux reported in Table 5.1 for the SWNT/TSP and SWNT/C6S buckypapers were obtained using a single buckypaper. In contrast, the values reported for each of the other buckypapers are the average of results obtained from measurements performed on two or more membranes. Additional values could not be obtained for SWNT/TSP and SWNT/C6S buckypapers as the entire initial batch of SWNTs (Unidym, lot# P0348) which were used to prepare these membranes had been used in experiments. New batches of the same SWNTs were purchased from Unidym (lot# P2150), however, attempts to prepare large, mechanically robust SWNT membranes using the conditions previously employed for TRIX as well as alternate
dispersants were unsuccessful. In the case of SWNT/Trix buckypapers, increasing the dispersant concentration from 1% (w/v) to 2% (w/v), raising the SWNT content from 90 mg to 250 mg and doubling the sonication time used to prepare the initial dispersions to 60 min, all still resulted in BPs which fractured upon drying (Figure 5.4). This was an unexpected series of results, as microanalysis of the initial samples of Undiym SWNTs and SEM analysis of buckypaper fragments themselves revealed no significant differences (Table 5.2 & Figure 5.5, respectively).

Table 5.2: Microanalytical data for three batches of SWNTs used in this thesis. The error in each case is ± 0.1%.

<table>
<thead>
<tr>
<th>SWNT batch</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Unidym (lot# P2150)</td>
<td>84.0</td>
</tr>
<tr>
<td>Unidym (lot# P0348)</td>
<td>85.1</td>
</tr>
<tr>
<td>Nanocyl (batch no. 100618)</td>
<td>70.7</td>
</tr>
</tbody>
</table>

Figure 5.4: Large SWNT/Trix buckypaper membranes produced using alternate batches of SWNTs: (a) Unidym lot# P02150 and (b) Nanocyl batch no. 100618. In image (a) each sample corresponds to different conditions used (all contained 1% w/v Trix): (i) 90 mg SWNTs, 30 mins sonication, (ii) 180 mg SWNTs, 30 mins sonication, (iii) 180 mg SWNTs, 60 mins sonication, (iv) 180 mg SWNTs, 15 min sonication. In image (b) buckypapers contain: (i) 90 mg SWNTs and (ii) 180 mg SWNTs, and were produced using a sonication time of 30 mins and 1% (w/v) Trix.

The root of this problem stems from small, but significant variations in the properties of different batches of carbon nanotubes ostensibly produced by exactly the same procedure. It is well known that it is not possible to completely control the chemical and
electrical properties of CNTs at the point of assembly (synthesis). Thus, although the elemental and surface morphology of these buckypapers appeared similar, their properties still varied significantly in some key, but yet unidentified aspects. Consequently it is not surprising that fracturing occurred with BPs produces using the new batches of SWNTs.

Perhaps not surprisingly, buckypapers produced using Trix and nanocyl SWNTs (batch no. 100618), which were shown by microanalysis to have a significantly lower carbon content (Table 5.2), fractured to a greater extent (Figure 5.4b), due to the lower proportion of carbon nanotubes. As a consequence of these problems, further investigations of the aqueous permeability of large SWNT buckypaper membranes could not be performed within the time constraints of this project.

![Figure 5.5: SEM micrographs of SWNT/Trix buckypapers made using Unidym SWNTs (a) lot # P0348; and (b) lot # P2150. Both images taken at 70K magnification and were made from dispersions containing 1% (w/v) Trix and 0.1% (w/v) SWNTs sonicated for 30 mins.](image)

5.4 Comparison of Permeability with MWNT Membranes:

As was shown in Table 5.1, the aqueous permeability of MWNT/Trix buckypapers differed markedly to that of SWNT/Trix buckypapers. To further investigate this
observation, the aqueous permeability of a range of SWNT buckypapers containing different macrocycles was compared to that of MWNT buckypapers containing the same dispersants. The permeabilities of the latter membranes were determined by Mr. Leighton Alcock, who was working on a parallel project.\textsuperscript{8} Table 5.3 compares the permeabilities of the two sets of buckypapers, and clearly shows that the membrane fluxes for all MWNT buckypapers were significantly lower than that of their SWNT counterparts. This was most apparent in the case of the buckypapers containing PTS dispersant, where the SWNT membranes exhibited an average permeability of $2400 \pm 1300$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$, while for MWNT/PTS the value obtained was only $18 \pm 2$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$.

<table>
<thead>
<tr>
<th>SWNT Membrane</th>
<th>Membrane Flux (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>MWNT Membrane</th>
<th>Membrane Flux (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT/Trix</td>
<td>83 $\pm$ 5</td>
<td>MWNT/Trix</td>
<td>25 $\pm$ 2</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>$2400 \pm 1300$</td>
<td>MWNT/PTS\textsuperscript{*}</td>
<td>18 $\pm$ 2</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>1000 $\pm$ 500</td>
<td>MWNT/TSP\textsuperscript{*}</td>
<td>20 $\pm$ 3</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>800 $\pm$ 100</td>
<td>MWNT/C6S\textsuperscript{*}</td>
<td>16 $\pm$ 5</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Values provided by L. Alcock.\textsuperscript{8}

It is also apparent from Table 5.3 that the permeabilities of the MWNT buckypapers did not vary greatly in response to changing the dispersant present in the membrane, with the membrane fluxes obtained ranging from $16 \pm 5$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$ (for MWNT/C6S) to $25 \pm 2$ L m$^{-2}$ h$^{-1}$ bar$^{-1}$ (for MWNT/Trix). The lack of variation in the permeability of the MWNT buckypapers containing different dispersants is somewhat surprising considering the large changes observed with SWNT buckypapers. However, in this context it is important to note that while the macrocyclic dispersants were shown by microanalytical data to have been successfully incorporated into the MWNT buckypapers, SEM analysis of these membranes revealed only minor differences in their
surface morphology (Figure 5.6). This contrasts dramatically with what was observed with the SWNT buckypapers (section 4.4), and suggests that all the MWNT buckypapers may have had very similar internal and surface pore structures, which could account for the similarity between their aqueous permeabilities.

Figure 5.6: SEM micrographs of: (a) a MWNT/Trix buckypaper, and (b) a MWNT/C6S buckypaper at 70K magnification. Images reproduced from reference 8.

5.5 Bacterial Filtration:

To date, no studies have been performed to investigate the use of free standing buckypaper membranes for removing bacteria from aqueous solutions. In the following sections, the results of filtration experiments designed to evaluate the effectiveness of buckypaper membranes comprised of either SWNTs or MWNTs, and Trix or the antibiotic ciprofloxacin, for this purpose are presented. In addition, the viability of cells trapped on the surface of the buckypaper membranes was examined by treating them with fluorescent probes, and subsequently using an image analysis technique.

5.5.1 Filtration Experiments:

Initial investigations into the ability of SWNT and MWNT buckypapers to filter bacteria from an aqueous solution were conducted using small circular pieces of
membrane placed in a hand held syringe unit (described in section 2.4.2). The colour of
the filtrates collected using a MWNT/Trix buckypaper and this method suggested that
most of the bacteria had been collected by the membrane. After culturing the filtrate
using Luria-Bertani (LB) agar plates, the number of bacterial colonies that grew was
determined to be 89 ± 9 % of that obtained by treating a sample of the initial bacterial
suspension in an identical fashion. This value was lower than what was expected, as
literature studies have stated that buckypaper membranes are able to completely remove
*E. coli* from aqueous solution.6, 9 The comparatively poor performance displayed by the
MWNT/Trix buckypaper here when used with this syringe filtration method may be
attributed to the use of a positive pressure to filter the suspension, as opposed to the
vacuum filtration procedure described in the literature. 6, 9 The large amount of force
applied to the membrane surface when using the syringe method may have resulted in
minor disturbances to how the BP was seated in the syringe holder during the filtration
process, thus allowing some bacteria to pass across the membrane/filter holder
assembly.

It was therefore decided to instead use a gentle vacuum (200 – 300 mbar) to filter
suspensions containing *E. coli* as described in section 2.4.2. Two membranes were
initially investigated using this modified procedure. These were a SWNT/Trix
buckypaper and a MWNT/Trix buckypaper. Images of agar plates that were treated with
the initial bacterial suspension, as well as the filtrates obtained after filtration through
the CNT buckypapers are shown in **Figure 5.7**. Comparison of colony numbers grown
from the initial bacterial suspension with those grown from the filtrates obtained using
the SWNT/Trix and MWNT/Trix buckypapers showed that > 99% of *E. coli* was
removed by both of these membranes. This indicates that the slow filtration procedure
Chapter Five: Membrane Filtration

Figure 5.7: Images of LB plates after overnight culture of 100 µL of: (a) Initial E. coli suspension, (b) filtrate obtained after passing an E. coli suspension across a MWNT/Trix membrane, and (c) filtrate obtained after passing an E. coli suspension across a SWNT/Trix membrane (colonies coloured with a black marker).

employed in this experiment was highly successful. Consequently, this method was employed for all remaining bacterial filtration experiments performed with various buckypapers, as well as with a commercial filtration membrane. The results of triplicate measurements are reported in terms of log removal as calculated by Equation 5.2, where $x$ is the percentage removal of bacteria from the initial suspension.

$$\text{Log Removal} = - \log_{10} (100 - x) + 2$$  \hspace{1cm} \text{Equation 5.2}

The log removal values obtained are shown in Table 5.4. Larger log removal values correspond to a greater proportion of E.coli removed from the initial suspension. Compared to the commercial 5 µm pore diameter PTFE membrane, all CNT
buckypapers demonstrated a considerably greater ability to retain *E. coli*, as would be expected due to the much larger pores present in the commercial membrane. Inspection of the data also shows that both BPs containing MWNTs were more effective than their SWNT counterparts containing the same dispersant. This was a surprising result, in view of the superior antibacterial properties of pure SWNTs compared to MWNTs noted previously.\(^5\) This variation is likely due to a combination of factors, including differences in rejection of bacteria by the BPs owing to the size of the cells compared to the pore size of the membrane, and toxicity imparted onto the bacteria through contact with the nanotubes themselves or the dispersant. Incorporation of cipro instead of Trix into both types of BPs resulted in a substantial reduction in the number of *E. coli* colonies growing in the filtrates. In the case of MWNT/cipro, no viable bacteria were present in the filtrate for each of the three samples analysed, suggesting this membrane is the most effective for removal of *E. coli*.

Table 5.4: Effectiveness of different membranes for removing *E. coli* from aqueous suspensions. Reported removal values obtained from triplicate filtration experiments performed under identical conditions.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Log removal of <em>E. coli</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>5.00 ± 0.01</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>2.96 ± 0.01</td>
</tr>
<tr>
<td>MWNT/cipro</td>
<td>#</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>4.70 ± 0.01</td>
</tr>
<tr>
<td>5 µm PTFE membrane</td>
<td>0.99 ± 0.02</td>
</tr>
</tbody>
</table>

\(^5\) Complete removal of bacteria observed.

5.5.2 Fluorescence Imaging Analysis:

The extent of inactivation of *E. coli* cells trapped on the surface of the above buckypaper membranes was assessed using the fluorescence-based viability assay outlined in section 2.4.2. In short, once the bacterial filtration experiments were completed, the surfaces of the buckypaper membranes were stained using a combination of either propidium iodide (PI) and SYTO-16, or PI and 4',6-diamidino-2-phenylindole
(DAPI), and then imaged using fluorescence microscopy. Representative fluorescence micrographs of MWNT/Trix and MWNT/ciprofloxacin buckypapers treated in this manner are shown in Figure 5.8.

![Figure 5.8](image.png)

**Figure 5.8**: Fluorescence images of: (a) a MWNT/Trix buckypaper stained with PI (red) and SYTO-16 (green) taken at 50x magnification and (b) a MWNT/cipro buckypaper stained with PI (red) and DAPI (blue) taken at 20x magnification. In these images, green or blue fluorescence indicates the presence of live cells, while red fluorescence corresponds exclusively to dead cells.

DAPI and SYTO-16 interact with the DNA present in both live and dead cells, and result in the green and blue fluorescence, respectively, as evident in these images. Propidium iodide on the other hand cannot pass across intact cell membranes and is therefore excluded from live cells. In contrast, when a bacterial cell dies, its membrane loses its integrity. This allows PI to enter the cell and results in a red fluorescence. In Figure 5.8 the presence of dead cells is indicated by red fluorescence owing to incorporation of PI, whereas the green or blue regions of the images are attributable to viable bacteria that have incorporated SYTO-16 or DAPI remaining on the buckypapers. It is apparent immediately that the proportion of red fluorescent areas relative to those fluorescing green in the MWNT/Trix membrane in Figure 5.8a is much lower than the proportion of red fluorescent areas relative to those fluorescing blue in Figure 5.8b for a MWNT/cipro buckypaper. Therefore it can be qualitatively
concluded that there are a greater proportion of live cells on the surface of the MWNT/Trix membrane compared to the MWNT/cipro membrane.

Quantitative analysis of the fluorescent images of the BP membrane surface was performed using software analysis, in accordance with the area-based estimation method outlined by Kang et al. 9 In short, each of the colour images shown in Figure 5.8 was split into two separate images showing the individual fluorescence attributable to each dye staining the buckypaper surface. These images were then converted to 8-bit greyscale images in which the colour intensity is converted into a 256 increment scale with 0 corresponding to completely black, and 255 corresponding to completely white. The software package enabled the distribution of the brightness of the pixels within the image to be determined, as shown in Figure 5.9 for a MWNT/Trix buckypaper.

![Figure 5.9: Relationship between the distribution of the brightness of pixels within a MWNT/Trix BP (light intensity between 0 & 255) and the cumulative fraction of pixels within the 8-bit greyscale micrograph showing the fluorescence of the SYTO-16 dye.](image)

From the resulting curves, a threshold intensity value was chosen for all images, from which a binary black and white image was produced to most closely match that of the original image. For example, Figure 5.10a and b show the greyscale images derived
from the SYTO-16 and PI fluorescent areas present on the surface of a MWNT/Trix buckypaper, while Figures 5.10c and d show the corresponding binary images that were subsequently obtained from these greyscale images. In the latter images, the white pixels represent areas of fluorescence. Therefore by determining the ratio of black to white pixels in the image the percentage of the membrane area that was fluorescing as a result of the presence of either live or dead bacteria could be calculated. By comparing these values for the two dyes for each buckypaper sample, the percentage of inactivated bacteria could be determined.

Figure 5.10: Greyscale fluorescence micrographs of MWNT/Trix buckypaper membranes stained with: (a) PI and (b) SYTO-16. The corresponding binary images of the PI and SYTO-16 stained buckypapers determined using the image J software package are shown in (c) and (d), respectively.

In contrast to what was observed for the filtrates, the SWNT membranes outperformed their MWNT counterparts containing the same dispersant, when it came to directly killing *E. coli*. For the MWNT/Trix sample shown in Figure 5.10, the image area stained by the PI dye (i.e. dead cells) was determined to be 4.7%, whereas 8.9% of the
image area was stained by the SYTO-16 dye (i.e. all cells). Thus, the percentage of dead
cells on the surface of the membrane was determined to be 53%. This process was
performed for all buckypaper samples, with the final results obtained summarised in
Table 5.5. Both SWNT and MWNT buckypapers displayed much higher bactericidal
properties when the dispersant used to prepare the buckypaper was ciprofloxacin. This
was particularly true for the MWNT buckypapers, for which the percentage of dead
bacteria on the membrane surface increased from 58 ± 13% for MWNT/Trix, to 100%
for MWNT/cipro. The high proportion of dead bacteria on the surface of all membranes
(≥ 58%) is believed to be due to irrecoverable damage to the outer cell wall of the
bacterium. The greater toxicity of the SWNTs (revealed by comparing the bactericidal
properties of the SWNT/Trix and MWNT/Trix buckypapers), may be attributed to their
smaller diameter compared to that of MWNTs. This results in SWNTs having a greater
ability to interact with the cell walls of the bacteria, including physically piercing the
barrier.10

Table 5.5: Comparison of the bactericidal properties of different buckypapers towards E. coli.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Dead bacteria of surface (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>58 ± 13</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>73 ± 18</td>
</tr>
<tr>
<td>SWNT/cipro</td>
<td>98*</td>
</tr>
<tr>
<td>MWNT/cipro</td>
<td>100*</td>
</tr>
</tbody>
</table>

* Due to the poor quality of fluorescent images obtained for these samples, the percentage of dead
bacteria on the surface of the BP was determined from one sample only.

In addition to performing image analysis of the BP surfaces, the filtrates obtained after
filtering the bacterial solutions through SWNT/cipro and MWNT/cipro membranes was
stained and imaged. In order to obtain images, a sample of the filtrate was centrifuged
and the pellet resuspended in a small volume of sterile saline prior to casting onto a
poly-L-lysine coated microscope slide. The sample was then dried in air and stained
with a combination of PI and DAPI as previously described. No cells were found to be
present in the filtrate obtained using the MWNT/cipro membrane, however, a small number of cells were detected in the filtrate obtained using the SWNT/cipro buckypaper (Figure 5.11a). When compared to an image of the initial suspension of *E. coli* treated in an identical manner (Figure 5.11b), it is clear that the number of bacteria in the filtrate was considerably reduced as a result of exposure to the SWNT/cipro membrane. These results are consistent with those presented in section 5.5.1 obtained from vacuum filtration experiments, where fewer colony numbers grew from the filtrates obtained using MWNT membranes compared to filtrates obtained using the corresponding SWNT buckypapers. This confirms the view that MWNT buckypapers are more effective for both removing and killing *E. coli* under the conditions used in this study.

Figure 5.11: Fluorescence micrographs of: (a) an initial *E. coli* suspension in saline prior to use in a filtration experiment, and (b) the filtrate obtained after passing the suspension through a SWNT/cipro buckypaper. Both samples have been stained with DAPI and PI.

### 5.6 Conclusion:

Single-walled carbon nanotube buckypaper membranes incorporating a range of functional dispersant molecules were found to be permeable to water when subjected to low applied pressures. The permeability of the membranes was found to be strongly dependent on the identity of the dispersant used to produce the buckypaper. However, in most cases they remained significantly less permeable towards water
than commercial polymer membranes. The most permeable buckypapers were the SWNT/TSP and SWNT/PTS membranes, which displayed membrane fluxes of 1000 ± 500 and 2400 ± 1000 L m⁻² h⁻¹ bar⁻¹, respectively. These values are lower than those previously reported for SWNT and MWNT buckypapers made from CNT dispersions prepared in organic solvents.², ³, ⁶ This may be attributed in part to the larger quantity of nanotubes present in the stand-alone buckypapers used in the current work, which resulted in thicker membranes that would be expected to slow the passage of solvent molecules.

Buckypapers produced using the surfactant Trix proved to be effective at removing the bacterium *E. coli* from aqueous solutions, with membranes containing MWNTs proving to be more efficient than those composed of SWNTs containing the same dispersant molecules. Incorporation of the antibiotic ciprofloxacin into either SWNT or MWNT buckypapers resulted in a marked improvement in the extent of removal of the bacterium. This was primarily attributed to the antibiotic retaining its antibacterial activity after being trapped within the membrane or after subsequently leaching into the filtrate produced by these experiments. The results of fluorescence image analysis showed that SWNT buckypapers containing the dispersant Trix were more effective at inactivating bacteria on their surface than their MWNT counterparts. This result agrees with those reported by Kang et al., who attributed the greater toxicity of SWNTs compared to MWNTs to the more profound ability of the smaller diameter and shorter length CNTs to physically damage the outer bacterial cell wall.⁹
5.7 References:

6

Adsorption of Radionuclides

The uptake of a radionuclide relevant to the radiochemical industry, by adsorption onto selected MWNT buckypapers is investigated in this chapter.
6.1 Introduction:

The nuclear industry continues to be faced with the issue of recovering radionuclides both safely, and economically. At present, the most successful strategy employs the use of materials such as inorganic ion-exchangers, which can extract a variety of these problematic isotopes from liquid waste streams. Carbon nanotubes have recently shown promise as an adsorbent for the recovery of radionuclides such as Am, Th, Eu, Ce, Sr and U.1-5 In this chapter, the ability of MWNT buckypapers containing selected macrocyclic ligands to recover cesium, strontium or molybdenum ions is presented. These metal ions provide many of the hazardous isotopes present in these waste streams, and give rise to high levels of radioactivity.6 A more detailed investigation of the uptake of the radionuclide $^{99}$Mo is also provided.

6.2 Uptake of Inactive Isotopes:

The uptake of inactive isotopes of cesium ($\text{Cs}^+$), strontium ($\text{Sr}^{2+}$) and Molybdenum ($\text{Mo}^{6+}$) by buckypapers prepared using MWNTs was measured using an ICP-MS technique described in section 2.4.3. All buckypapers were prepared from dispersions containing either Triton X-100 (Trix) or one of the following macrocyclic ligands: Calix[6]arene (C6S), $\beta$–cyclodextrin ($\beta$–CD), phthalocyanine tetrasulfonic acid (PTS) and $\text{meso}$-tetra(4-sulfonatophenyl) porphyrin dihydrogenchloride (TSP). These dispersions were obtained using the optimum sonication time and concentrations identified in chapter 3. In addition, buckypapers prepared from MWNTs containing carboxylic acid (MWNT-COOH) or amine (MWNT-NH$_2$) functional groups, dispersed using the surfactant Trix, were also examined.
As radionuclide solutions are often highly acidic in nature it is imperative to understand the effect of pH on the stability of the adsorbent as well as the extent of uptake of the isotope of interest. In order to determine the extent of extraction as a function of pH, small pieces of MWNT/TSP and MWNT/C6S buckypaper membranes weighing 15 mg in total were submerged in solutions containing 0.1 ppm Cs\(^+\), Sr\(^{2+}\) or Mo\(^{6+}\), and nitric acid with a concentration between 0.1 – 6 M. After agitation for c.a. 48 hours, the pieces of buckypaper were removed and the concentration of analyte remaining in solution measured using ICP-MS. Comparison to the initial concentrations of each of the three metal ions revealed that only Mo\(^{6+}\) was recovered to a significant extent in any of the solutions, and then only when the concentration of nitric acid in the solution was 0.1 M. For the other two metal ions, and in solutions with nitric acid concentrations > 0.1 M, the percent uptake observed was < 1%. In contrast, the percent uptake of Mo\(^{6+}\) by the MWNT/TSP (~50%) and MWNT/C6S (~31%) samples immersed in solutions containing 0.1 M nitric acid indicated that these materials were worth investigating further.

Despite the poor level of uptake in most cases, all buckypapers showed no visible signs of degradation after testing, illustrating that they display some stability to an acidic environment. Leaching of highly coloured porphyrin molecules from MWNT/TSP buckypapers was apparent throughout the above experiments in solutions containing high nitric acid concentrations (> 1 M). In view of this observation, and the lack of metal ion uptake from solutions with acid concentrations above 0.1 M, the remainder of the uptake experiments described in this chapter were performed only using solutions containing 0.1 M nitric acid.
In order to provide further evidence for the affinity of the buckypapers towards Mo\textsuperscript{6+}, a further series of preliminary experiments were performed using ICP-MS and solutions containing only molybdate ions. The results of these experiments, which was performed using a total of 15 mg of buckypapers, are presented in Table 6.1. Significant removal of Mo\textsuperscript{6+} by the MWNT/PTS, MWNT/C6S and MWNT/TSP samples was observed.

Table 6.1 also presents distribution coefficients (K\textsubscript{d}), defined as in Equation 6.1, for each of the systems investigated. In this equation, C\textsubscript{O} is the initial concentration of molybdate ions, C\textsubscript{f} is the final concentration of molybdate ions, V is the volume of solution in contact with the membrane, and M is the membrane mass. Distribution coefficients are commonly used to reflect the extent of uptake of an analyte by an adsorbent, with higher K\textsubscript{d} values indicating a greater extent of removal. These values are more commonly reported in the literature, as they enable comparison between samples by effectively normalising the extent of removal with respect to weight of the sample used.\textsuperscript{5-7}

\[
K_d = \frac{(C_O - C_f)}{C_f} \times \frac{V}{M}
\]

Equation 6.1

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Mo\textsuperscript{6+} Uptake (\textmu mol g\textsuperscript{-1})</th>
<th>K\textsubscript{d} (mL g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/PTS</td>
<td>0.062 ± 0.009</td>
<td>80 ± 10</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>0.103 ± 0.002</td>
<td>140 ± 5</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>0.18 ± 0.01</td>
<td>290 ± 50</td>
</tr>
<tr>
<td>MWNT/Trix</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.1: Recovery of Mo\textsuperscript{6+} from solutions containing 0.1 ppm molybdate ion selected by MWNT buckypapers. All experiments were performed using 15 mg buckypaper adsorbent.

Three of the four buckypapers studied recovered significant amounts of molybdate ion. In view of this result, it was decided to continue investigating the uptake of this metal ion by buckypapers, but this time using a radioisotope of molybdenum (\textsuperscript{99}Mo).
6.3 Uptake of Radioactive Molybdenum (\textsuperscript{99}Mo):

The extent of uptake of \textsuperscript{99}Mo by small pieces of buckypaper was measured using gamma spectroscopy and the procedure outlined in section 2.4.3. The gamma spectrum of \textsuperscript{99}Mo (as Mo\textsubscript{O}\textsubscript{4}\textsuperscript{2-}) in 0.1 M nitric acid contained a small peak at 739.5 keV and another much more intense peak at 140 keV. For the purpose of the investigations described in this chapter, the less intense peak at 739.5 keV was used because the decay product (\textsuperscript{99m}Tc) also emits gamma radiation with energies that overlap with the more intense \textsuperscript{99}Mo peak. Prior to each molybdenum uptake experiment, a calibration curve was constructed to ensure that the intensity of the emitted gamma radiation, which is reflected in the number of counts per minute (CPM) provided by the spectrometer as an output, showed a linear relationship with respect to \textsuperscript{99}Mo concentration (Appendix 3). In addition, the molybdenum solution used for each individual uptake experiment was diluted using 0.1 M HNO\textsubscript{3} by an amount depending on its activity. This ensured that all buckypapers were exposed to a consistent level of radioactivity, and that measurements made by the spectrometer were within its optimal working range (0 – 30000 CPM).

The results of a preliminary experiment performed to assess the ability of different buckypapers to recover \textsuperscript{99}Mo from a solution containing 13 ± 1 ng L\textsuperscript{-1} radionuclide and 0.1M HNO\textsubscript{3} are shown in Table 6.2. The percent uptake of \textsuperscript{99}Mo varied between 27 – 87\% (K\textsubscript{d} = 23 – 330 mL g\textsuperscript{-1}), with the most efficient materials proving to be the three buckypapers that were prepared using Trix as the dispersant, i.e. MWNT/Trix, MWNT-COOH/Trix and MWNT-NH\textsubscript{2}/Trix. The result achieved using MWNT/Trix was surprising, considering the lack of uptake exhibited by this material in the previous experiment performed using non-radioactive molybdate.
**Table 6.2:** Uptake of $^{99}$Mo from 5 mL of a solution containing an approximate $^{99}$Mo concentration of 13 ± 0.1 ng L$^{-1}$ by various buckypapers and the MWNT starting materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Removal of $^{99}$Mo (%)</th>
<th>$K_d$ (mL g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNTs (081010)</td>
<td>68 ± 2</td>
<td>208 ± 4</td>
</tr>
<tr>
<td>MWNT-COOH</td>
<td>51 ± 1</td>
<td>109 ± 2</td>
</tr>
<tr>
<td>MWNT-NH$_2$</td>
<td>55 ± 1</td>
<td>112 ± 2</td>
</tr>
<tr>
<td>MWNT/Trix</td>
<td>83 ± 4</td>
<td>330 ± 6</td>
</tr>
<tr>
<td>MWNT-COOH/Trix</td>
<td>87 ± 3</td>
<td>303 ± 3</td>
</tr>
<tr>
<td>MWNT-NH$_2$/Trix</td>
<td>85 ± 2</td>
<td>245 ± 3</td>
</tr>
<tr>
<td>MWNT/TSP</td>
<td>62 ± 2</td>
<td>111 ± 2</td>
</tr>
<tr>
<td>MWNT/β-CD</td>
<td>80 ± 20</td>
<td>190 ± 3</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>27 ± 1</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>MWNT/PTS</td>
<td>54 ± 2</td>
<td>57 ± 1</td>
</tr>
</tbody>
</table>

*Table 6.2* also shows that each of the three buckypaper materials containing Trix proved to be more effective at recovering $^{99}$Mo from the acidic solution than the MWNT starting material from which they were prepared. This shows that the process of dispersing the CNTs and producing a buckypaper can, at least in the case of this particular dispersant, produce a material that is more effective at recovering $^{99}$Mo than the raw MWNTs. In contrast, replacing Trix with one of the macrocyclic dispersants generally resulted in a buckypaper that exhibited poorer molybdenum uptake than the MWNT starting material. This may be attributable in part to differences in the internal pore structure of the buckypapers, as well as the identity of the dispersant. *Figure 6.1* shows that in general buckypapers possessing higher surface areas, such MWNT-COOH/Trix and MWNT/Trix (376 m$^2$ g$^{-1}$ and 303 m$^2$ g$^{-1}$, respectively) recovered a larger proportion of the available $^{99}$Mo than those with a lower surface area such as MWNT/PTS and MWNT/C6S (182 m$^2$ g$^{-1}$ and 246 m$^2$ g$^{-1}$, respectively). This suggests that removal of $^{99}$Mo is due to a large extent to adsorption onto the surface of the MWNTs within the membranes, rather than to interactions with the dispersant molecules themselves.
As outlined in section 6.1, the ability of an adsorbent to withstand degradation in low pH media is a critical property that must be possessed by a material if it is to be used for the uptake of metal ions from nuclear waste streams, since the latter are often highly acidic. The data presented in Table 6.3 shows how the ability of selected MWNT buckypapers to extract $^{99}$Mo from a solution with a concentration of $5.4 \pm 0.5$ ng L$^{-1}$, varied as a function of nitric acid concentration. When the concentration of nitric acid was 0.01 M, a significant level of uptake was observed for all three types of buckypapers investigated. Once again the MWNT/Trix and MWNT-NH$_2$/Trix buckypapers displayed a very similar level of $^{99}$Mo uptake, resulting in $K_d$ values of $380 \pm 30$ mL g$^{-1}$ and $390 \pm 30$ mL g$^{-1}$, respectively. The most surprising aspect of the results presented in Table 6.3 is that the MWNT/C6S buckypaper, which showed the poorest ability to recover $^{99}$Mo in the preliminary set of results shown in Table 6.2, displayed the greatest ability to do so when the nitric acid concentration was 0.01 M. Increasing the concentration of nitric acid in solution resulted in the level of uptake of the radionuclide rapidly decreasing for each of the buckypapers examined, which is
consistent with results reported in other studies which have examined uptake of molybdenum using inorganic ion exchangers.\textsuperscript{9, 10} The reason for the decrease in efficiency of $^{99}$Mo recovery in solutions with lower pH values is most likely due to increasing protonation of the molybdate ion, which would be expected to reduce its ability to interact with defects on the surfaces on the CNTs, the amine groups in the MWNT-NH$_2$, or the dispersant molecules by ion-dipole interactions.

\textbf{Table 6.3:} Effect of varying nitric acid concentration on the uptake of $^{99}$Mo by selected MWNT buckypapers.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Distribution Coefficients for the uptake of $^{99}$Mo ($K_d$: mL g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01 M HNO$_3$</td>
</tr>
<tr>
<td>MWNT/Trix</td>
<td>380 ± 30</td>
</tr>
<tr>
<td>MWNT/C6S</td>
<td>3000 ± 1000</td>
</tr>
<tr>
<td>MWNT-NH$_2$/Trix</td>
<td>390 ± 30</td>
</tr>
</tbody>
</table>

The effect of time on the extent of uptake of $^{99}$Mo by several MWNT buckypapers was also investigated in order to determine the minimum time required to achieve maximum uptake of the radionuclide. The results of this experiment are presented in Figure 6.2, which shows that uptake of $^{99}$Mo occurs very rapidly, with most of the radionuclide recovered after just one hour exposure to any of the buckypapers. After four hours there was no further significant increase in the extent of uptake of $^{99}$Mo by most of the buckypapers examined. This indicates that after four hours the buckypapers had become saturated with $^{99}$Mo, which is consistent with previous reports using ion-exchange adsorbents that displayed maximum uptake of molybdenum after 2 – 5 h, irrespective of the pH of the solution employed during testing.\textsuperscript{9, 11} Figure 6.2 also shows that the uptake of $^{99}$Mo by the MWNT-NH$_2$/Trix buckypaper decreased from c.a. 80\% after 1 h, to approximately 60\% after 4 h, and remained relatively constant thereafter. In view of the highly unusual nature of this result, it was essential to perform a similar experiment again to see if this behaviour was reproducible.
Chapter Six: Adsorption of Radionuclides

Figure 6.2: Effect of time on the uptake of $^{99}$Mo from a solution (5 mL) containing a molybdenum concentration of 7.1 ± 0.7 ng L$^{-1}$ by selected MWNT buckypapers.

The rapid uptake of molybdenum shown in Figure 6.2 indicates that the time intervals used for the other experiments reported in this chapter would have been sufficient to allow maximum recovery of the metal ion from solution to take place. However, in order to obtain a more detailed understanding of the initial rate of $^{99}$Mo uptake, a second set of experiments was performed in which the kinetics of the process was more closely monitored between 0 – 4 h with selected buckypapers. The results of these experiments are presented in Figure 6.3, and show that the majority of metal ion uptake took place between 0 – 1 h, during which the rate of uptake was approximately linear with respect to time. Beyond the 1 h time point, the rate of molybdate uptake decreased significantly in most cases and/or approached a plateau value, which may be indicative of the onset of buckypaper saturation, which was suggested to occur after c.a. 4 hours in the previous experiment. Figure 6.3b shows that the MWNT-COOH/Trix buckypaper displayed the fastest and most efficient uptake behaviour, with a maximum level of $^{99}$Mo uptake of c.a. 75% (315 mL g$^{-1}$) achieved after only 2 hours.
Figure 6.3: Effect of time on the uptake of $^{99}$Mo from a solution (5 mL) containing a concentration of 7.1 ± 0.7 ng L$^{-1}$ by: (a) MWNT/Trix (b) MWNT-COOH/Trix, (c) MWNT/PTS and (d) MWNT-NH$_2$/Trix buckypapers.

In contrast to the behaviour exhibited by the other buckypapers, Figure 6.3d shows that the MWNT-NH$_2$/Trix buckypaper displayed an unusual kinetic profile in which there was an initial period of rapid MoO$_4^{2-}$ uptake during the first hour, followed by a decrease in the amount of molybdenum uptake. This result mirrors closely that shown in Figure 6.2 for the MWNT-NH$_2$/Trix buckypaper, and is highly unusual in that it suggests after an initial phase of rapid molybdenum uptake, there is then a slow release of the metal back into the surrounding solution. At present we do not have an explanation as to why this material should exhibit this behaviour.

The maximum capacity of an adsorbent for an analyte of interest, such as $^{99}$Mo, is an important property when considering the suitability of a material for future applications. Therefore a suite of experiments were conducted to determine the capacity of selected...
buckypapers, by constructing a series of equilibrium isotherms using data obtained from uptake experiments performed using solutions containing non-radioactive MoO$_4^{2-}$ at concentrations between 1 – 20000 ppm, which had been spiked with a small amount of $^{99}$Mo as a radiotracer. Recovery experiments were performed in this manner, as it was not possible to obtain $^{99}$Mo concentrations that spanned this entire range. By measuring the extent of uptake of the radiotracer using gamma spectroscopy, the total number of moles of MoO$_4^{2-}$ that had been recovered could be determined by assuming the uptake of the tracer was directly proportional to that of MoO$_4^{2-}$. A series of equilibrium isotherms obtained from preliminary experiments is presented in Figure 6.4.

![Figure 6.4](image_url)

**Figure 6.4:** MoO$_4^{2-}$ adsorption isotherms for selected buckypapers determined using solutions (5 mL) containing different concentration of non-radioactive MoO$_4^{2-}$ and a small amount of $^{99}$Mo radiotracer.

While there is a noticeable amount of scatter in the isotherms obtained for some buckypapers, at higher total molybdate concentrations it can still be discerned that all of the materials tested were becoming saturated when the total concentration of molybdenum in the initial solution approached 5000 ppm. In addition, Figure 6.4 suggests that the capacity of the MWNT/PTS buckypaper was significantly less than that of the other materials tested.
In order to gain a more detailed understanding of the adsorptive capacity of these materials, the above experiment was repeated using a MWNT-COOH/Trix buckypaper and MWNT-COOH starting material, and solutions where the total molybdenum concentration was in the range 25 - 7500 ppm. The results of these experiments are presented in Figure 6.5, and show that there was an almost linear dependence of molybdenum uptake on total molybdenum concentration at low values of the former quantity. At molybdenum concentrations above 1000 ppm, however, the extent of uptake did not increase as dramatically and eventually reached a plateau at c.a. 2.5 and 1 mmol g$^{-1}$, for the MWNT-COOH and MWNT-COOH/Trix buckypaper, respectively.

Figure 6.5: MoO$_4^{2-}$ adsorption isotherms for: (a) MWNT-COOH starting material and (b) a MWNT-COOH/Trix buckypaper determined using solutions (5 mL) containing different concentrations of non-radioactive molybdenum and a small amount of $^{99}$Mo radiotracer. Data in both cases is fitted with both Langmuir and Freundlich isotherm models.
In an attempt to identify the mechanism of adsorption of molybdenum onto the carbon nanotubes, the experimental data shown in Figure 6.5 were compared to binding isotherms derived using the Langmuir and Freundlich isotherm models.

The Langmuir isotherm is described by Equation 6.2:

\[ C_{ads} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \]  

Equation 6.2

In this equation, \( C_{eq} \) (ppm) and \( C_{ads} \) (mmol g\(^{-1}\)) are the concentrations of molybdenum in the liquid and solid phase, respectively, whereas \( q_{max} \) and \( b \) are Langmuir constants related to the maximum uptake by the solid and the energy or affinity of the adsorbent, respectively. The Langmuir model of adsorption assumes that metal ions are chemically adsorbed onto a discrete number of well-defined sites on the adsorbent, and that there is no interaction between these ions. It is also assumed that each of the sites available on the adsorbent has the ability to hold only one ion, and that all sites are energetically equivalent in nature.\(^7\)

On the other hand, the Freundlich isotherm is described by Equation 6.3:

\[ C_{ads} = C_m C_{eq}^{\frac{1}{n}} \]  

Equation 6.3

In this model, \( C_m \) and \( n \) are Freundlich parameters related to adsorption capacity and intensity, respectively. In contrast to the Langmuir model, the Freundlich model can accommodate situations where multiple molecules bind to the same region of adsorbent (i.e. multilayer coverage), and the bound surface molecules interact with each other.\(^12\)
The fitting of both theoretical isotherm models to the experimental data was achieved using the Microsoft Excel solver function, which seeks to optimise the best fit by varying the mathematical constants within the respective models. For both materials, the adsorption data obtained experimentally was determined to be better described by the Langmuir, rather than the Freundlich expression (Table 6.4). This suggests that the molybdate ions were adsorbing onto the surface of the CNTs to form a monolayer, and that there was little multi-layer coverage occurring.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mmol g$^{-1}$)</td>
<td>$b$</td>
</tr>
<tr>
<td>MWNT-COOH</td>
<td>3.06</td>
<td>0.0012</td>
</tr>
<tr>
<td>MWNT-COOH/Trix</td>
<td>1.26</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

Inspection of the values shown in Table 6.4 reveals that the values of the constants $b$ and $1/n$, which are derived from the Langmuir and Freundlich models, respectively, were very similar for the two materials examined. As each of these constants is related to the energy of interaction between the adsorbent and molybdate ions, this suggests a similar binding mechanism occurred with both the MWNT-COOH starting material and MWNT-COOH/Trix buckypaper. This is consistent with the hypothesis that adsorption of molybdate ions onto the nanotube surface plays the dominant role in the binding mechanism, and that the dispersant present in the buckypaper does not contribute significantly. According to the Langmuir model, the saturation capacity of the MWNT-COOH starting material and MWNT-COOH/Trix buckypaper for molybdate ions, $q_{\text{max}}$, was determined to be 3.06 and 1.26 mmol g$^{-1}$, respectively. These values are in good agreement with an analogous value determined for uptake of molybdate by an
antimonate ion exchanging material examined by El-Naggar et al., which was c.a. 2 mmol g\(^{-1}\).\(^9\)

### 6.4 Conclusion:

The adsorption of a select group of metal ions onto multi-walled carbon nanotube membranes incorporating the surfactant Trix, or macrocyclic ligands as dispersant molecules, was investigated under acidic conditions. Studies performed using inactive isotopes of molybdenum, cesium and strontium revealed that there was no measurable uptake of the latter two species, whilst adsorption of molybdate ions onto the surface of the buckypapers varied between 0.062 – 0.18 µmol g\(^{-1}\) (80 – 290 mL g\(^{-1}\)). Preliminary experiments performed using a radioactive isotope of molybdenum (\(^{99}\)Mo) showed that an uptake of up to 83% of the molybdenum in solution by a buckypaper could be achieved in some instances. Under these conditions, buckypapers containing the dispersant Trix outperformed those containing the macrocyclic dispersants, probably due to the higher surface area of the former materials. Buckypapers prepared using MWNTs functionalised with carboxyl or amine groups, and the surfactant Trix, showed molybdenum uptake which closely matched that exhibited by the MWNT/Trix buckypaper, and were again significantly greater than those shown by buckypapers prepared using macrocyclic dispersants.

Uptake experiments performed using solutions containing a range of concentrations of the \(^{99}\)Mo radionuclide showed that the MWNT buckypapers had capacities between 0.5 – 2.6 mmol g\(^{-1}\), which agrees well with results obtained in previous studies that examined recovery from solution of molybdenum by ion exchange materials.\(^9,\)\(^11\) All CNT materials examined displayed fast molybdenum uptake kinetics, with saturation
typically achieved within 4 hours. The buckypapers exhibited appropriate stability under the acidic conditions employed during the testing procedure. Therefore, these materials are promising candidates for the uptake of radioactive molybdenum from nuclear waste streams, and likely to be the subject of ongoing investigation.
6.5 References:

7

Conclusion and Future Directions

In this chapter, the results achieved throughout the course of this project are summarised, and their significance assessed. A short discussion of how this work might be continued is also included.
7.1 Conclusions:

The ultimate goal of this study was to develop novel carbon nanotube membranes which could be used for a variety of separations. The preceding chapters addressed the development of membranes using SWNTs and MWNTs from dispersions that incorporated a range of macrocyclic or antibiotic dispersants. The results presented in this thesis show that it was possible to prepare dispersions of SWNTs using these unique dispersant molecules. However, the homogeneity of these dispersions varied depending on the dispersant used. Evidence of interactions between the nanotubes and dispersant molecules was obtained by Raman spectroscopy, suggesting that the dispersant might be retained in buckypapers produced from these dispersions.

Buckypapers were successfully prepared using the optimised dispersion conditions determined from UV-vis-NIR spectrophotometry. Further evidence of the retention of dispersant molecules was provided by microanalytical results and EDX spectra of the corresponding SWNT membranes prepared using these compounds. However, visual inspection of buckypapers prepared using the highly coloured PTS and TSP dispersants after they were placed in contact with water revealed at least some of the dispersant that the latter molecules were probably only loosely retained. While the buckypapers prepared as part of this project exhibited sound mechanical integrity (Young’s modulus = 0.6 – 2 GPa) and a hydrophilic surface (contact angle = 28 - 89°), their strength is still wanting in some respects when compared to current commercial membranes. For example, the ductility of the buckypapers varied from = 0.9 – 3.2%, while the ductility for PTFE used to produce commercial membranes is in excess of 50%.1
The use of buckypapers prepared from SWNTs and novel dispersants in a typical dead-end membrane filtration setup revealed encouraging permeability towards water (83 – 2400 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) at low applied pressures (< 1 bar) due to the highly porous nature of each of these membranes. Although these values are considerably less than those reported previously for buckypapers prepared using organic solvents,\(^2\)\(^3\) it must be remembered that the latter materials consisted of very thin layers of CNTs deposited on a highly porous commercial PVDF membrane, which conferred mechanical integrity on the entire composite. The permeabilities reported here therefore represent the first values obtained for mechanically robust, free-standing buckypaper membranes.\(^4\)

Membranes composed of either SWNTs or MWNTs incorporating the antibiotic ciprofloxacin were also shown to remove a model bacterium (\textit{E. coli}), and were much more efficient at removing bacteria than those prepared using Trix or a commercial polymer membrane (PVDF). Surprisingly, buckypapers prepared from MWNTs were shown to be much more effective than those made from SWNTs when it came to removing bacteria from solution, whereas fluorescence imaging revealed that SWNT buckypapers were much effective at inactivating bacteria.

Membranes composed of MWNTs and various dispersants were shown to selectively adsorb molybdenum from acidic solutions containing molybdate as well as cesium and strontium ions. The recovery of the radioisotope \(^{99}\)Mo from solution could be achieved in good capacity (0.5 - 2.6 mmol g\(^{-1}\)), agreeing well with results obtained using other adsorbent materials currently under investigation.\(^5\) The buckypaper membranes also displayed rapid uptake of molybdenum (< 4 hours), and excellent stability to the harsh chemical environments used.
7.2 Future Work:

The scene has now been set for detailed investigation into the ability of buckypapers to act as selectively permeable membrane filters to take place. Despite this, however, several key issues need to be addressed in order to further progress the ability of these materials to function in a commercial setting. Perhaps the greatest drawback of these materials thus far is their highly brittle nature. Therefore it is clear that future work should focus in part on improving the mechanical properties of the buckypapers so that full advantage of the high degree of permeability they exhibit towards water can be fully taken advantage of through operating at much higher pressures. There are several possible approaches to tackling this issue, including producing buckypapers from dispersions containing both a dispersant such as PTS or cipro, which has been selected to impart a specific functional property on the material, and a small amount of a biopolymer such as chitosan or bovine serum albumin. Previous work has shown that incorporation of biopolymer dispersants in SWNT buckypapers significantly improves their mechanical properties.6,7 Other methods for improving mechanical properties of the buckypapers could include post-preparative intercalation of synthetic polymers,8 and allowing them to remain attached to the suitable support membrane upon which they are initially prepared.

Developing methods for increasing the number of dispersant molecules incorporated within these buckypapers should also be investigated, as this might lead to further changes to their chemical and physical properties that prove useful for particular applications. This might be achieved, for example, by covalently attaching dispersant molecules to either MWNT-NH₂ or MWNT-COOH. It would therefore be very informative to see if the enhanced permeability exhibited by SWNT buckypapers
containing dispersant molecules such as PTS is retained if the latter could be covalently
attached to the nanotubes.

There is still a great deal to be learnt about the potential use of buckypapers described in
this thesis for membrane filtration applications, or as adsorbents for specific analytes of
interest. Consideration of the sizes of both the surface pores and internal pore structures
indicates that the buckypapers are unlikely to be suitable for selective separation of
small molecules on the basis of subtle differences in their sizes and shapes. Although
this may be achievable as a result of differences in interactions between membrane-bound
dispersant molecules, and analytes, or through post-synthetic modification of the
pores, it is in the area of ultrafiltration that buckypapers are perhaps initially most likely
to prove useful. Experiments should therefore be conducted where the ability of the
membranes to allow selective transport of one biomolecule over another(s) is examined,
or perhaps concentration of biomolecule samples in the presence of salt and other small
molecules.

Finally, although MWNT buckypapers were shown to possess the ability to selectively
recover molybdenum from acidic solutions, the potential use of these materials for the
nuclear waste industry requires further evaluation. This would require an examination of
the recovery of $^{99}$Mo from a more realistic waste solution containing a large number of
other fission products. This could be accomplished, for example, by exposing the
buckypapers to solutions obtained from digested, irradiated uranium plate. Discussions
are currently being held with collaborators at ANSTO to enable this experiment to take
place in the near future.
7.3 Final Statement:

This thesis has, for the first time shown that free-standing buckypapers produced from aqueous dispersions which incorporated macrocyclic and antibiotic molecules can potentially be used in a variety of separation scenarios. It is hoped that this contribution will further add to the understanding of the rapidly expanding field of separations science, and may one day lead to a viable membrane encompassing CNTs which fully realises the potential that these materials offer.
7.4 References:


Appendices

In this section, supplementary information supporting the results within this thesis are presented.
Appendix 1: UV-vis-NIR spectra

Figures A1 and A2 display UV-vis spectra to support the results presented in chapter 3.

**Figure A1**: UV-vis spectra of solutions (1% (w/v)) containing molecules used as dispersants for preparing buckypapers.

**Figure A2**: UV-vis spectra of (a) SWNT/Cipro and (b) SWNT/C6S which were measured initially after sonication, and then after standing for between 1 – 8 days after sonication. Each dispersion contained 5 mg (0.03% (w/v)) SWNTs in a 1% (w/v) dispersant solution. This data was used to construct Figure 3.10.
Appendix 2: Further Buckypaper Characterisation

Figure A3 shows the other EDX spectra of SWNT buckypapers prepared from macrocyclic dispersants and antibiotics which were not shown in chapter 4. Figure A4 shows the TGA trace for the SWNTs used to prepare the buckypapers described in chapter 4.

**Figure A3:** EDX spectra of (a) a SWNT/PTS buckypaper, (b) a SWNT/cipro buckypaper and (c) a SWNT/TSP buckypaper.

**Figure A4:** TGA trace for HiPCO SWNTs (lot# P0348) used to prepare the majority of buckypapers shown in chapter 4.
Appendix 3: $^{99}$Mo Gamma Counting

Figure A5 is a screen shot of the gamma spectrum obtained during a typical $^{99}$Mo uptake experiment. The very intense peak on the left (140 keV) represents the $^{99}$Mo peak which overlaps with the peak from the decay product ($^{99m}$Tc) which also emits gamma radiation in this region. The highlighted blue window shows the location of the smaller peak at 739.5 keV which was used for quantitative work. Figure A6 shows a typical calibration curve for the $^{99}$Mo stock solution obtained prior to performing an uptake experiment.

**Figure A5:** A screen shot showing the gamma spectrum of a diluted $^{99}$Mo solution used to perform recovery experiments.

**Figure A6:** A typical calibration curve obtained using the $^{99}$Mo stock solution prior to uptake experiments.
Appendix 4: Buckypaper Thickness

**Table A1:** Thickness of buckypapers used for water transport experiments shown in Table 5.1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/Trix</td>
<td>49 ± 5</td>
</tr>
<tr>
<td>SWNT/Trix</td>
<td>36 ± 4</td>
</tr>
<tr>
<td>SWNT/PTS</td>
<td>41 ± 5</td>
</tr>
<tr>
<td>SWNT/TSP</td>
<td>41 ± 4</td>
</tr>
<tr>
<td>SWNT/β-CD</td>
<td>66 ± 5</td>
</tr>
<tr>
<td>SWNT/C6S</td>
<td>44 ± 4</td>
</tr>
<tr>
<td>PTFE - 0.22 µm</td>
<td>120 ± 10</td>
</tr>
<tr>
<td>PTFE - 5 µm</td>
<td>130 ± 10</td>
</tr>
</tbody>
</table>