Purification, Dispersion and Separation of Single Walled Carbon Nanotubes

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A thesis submitted to Imperial College London for the Degree of Doctor of Philosophy.

February 2009

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Abstract

In this thesis, the purification, dispersion and separation of Single Walled Carbon Nanotubes (SWNTs) are explored. The motivation for this work arose from the basic desire to understand and further develop the underlying chemistry of SWNTs, thus enabling the extraordinary properties of SWNTs to be used to their full potential. Achieving highly pure SWNT samples on which further chemistry can be undertaken is of critical importance; purification must be able to be performed in a reliable and repeatable manner. As such, a new method of SWNT purification was developed. This method introduced a new base washing step that removed a significant fraction of the impurities created during the standard acid reflux purification. This finding has implications for many existing reports on nanotube chemistry. Separation of SWNTs by their electronic properties is extremely important if SWNTs are to fulfil their potential in a wide range of applications, from optoelectronics to molecular sensing. In order to separate metallic and semiconducting SWNTs, two novel methods were developed, both of which are relatively cheap and easily scalable. First, SWNTs were reduced in liquid ammonia containing an alkali metal. The reduced tube salts were then spontaneously dissolved in dry solvents to form stable dispersions which were found to contain primarily metallic SWNTs; hence, separation was achieved. The second method investigated the separation of SWNTs reduced by electrochemical means. When a voltage was passed through a SWNT sample in a suitable electrolyte, SWNTs were reduced and therefore dissolved. These dissolved SWNTs were deposited as a thin carbon film, in which metallic SWNTs were found to preferentially present; once again, separation was achieved.
The work described in this thesis was carried out in the Department of Chemistry, Imperial College London between March 2005 and August 2008. Except where specific reference is made, the material contained in this thesis is the result of my own work. This thesis has not been submitted in whole or in part for the reward of a degree at this or any other university.

Siân Fogden
2009
Acknowledgments

Firstly I would like to thank my supervisor, Dr. Milo Shaffer for his guidance over the course of my PhD, without his extensive knowledge of everything connected to carbon nanotubes this thesis would simply not exist. Special thanks go to Dr. Chris Howard for his collaboration with the liquid ammonia work and for many incredibly helpful nanotube discussions. Importantly, I wish to thank the EPSRC and Thomas Swan for funding.

Many thanks go to those people who helped me collect the analytical data crucial for my work, Dr. Ben Cottam and Richard Winchester for the TEM images, Dr. Boris Thomas and Dr. Raquel Verdejo for the SEM images, Dr. Mike Tran and Dr. Kingsley Ho for the XPS data and Tawfique Hasan for the PL data. I also want to thank the whole of the nanotube group, past and present for your extensive help with this project.

I am hugely indebted to all of my friends who have been really wonderful to me though my PhD life, especially Lucy, Ben, Ana and Matt. I know that it has not been easy for you at times but the emotional support and constant encouragement you have provided me with has been fantastic, I am very lucky to have such wonderful friends. I feel that I also should thank all of the great friends I made though cricket, you have helped to keep me sane through the course of my time at Imperial!

A special mention should go to David and Caroline who have been incredibly kind to me in the last year of my PhD, thank you.

To my family; Mum, Dad, Bryn and Jessica, thank you for always being there for me when I needed to talk and for your unwavering support and encouragement, without which there is no way that I could have finished my PhD. You are amazing.
To Mum and Dad
Thanks for everything
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This thesis lead to the following peer review publications and patents:

**Peer Reviewed Journal Publications:**


**Patents:**

1. M. Shaffer, S. Fogden, C. Howard and N. Skipper, Separation Method. Filing Date: 10\textsuperscript{th} Dec 2008, Application No. 0822526.0.

### Acronyms

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<th>Acronym</th>
<th>Description</th>
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<tr>
<td>AD</td>
<td>Arc Discharge</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>ARC</td>
<td>Arc Evaporation of Metal-Doped Carbon Electrode</td>
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<tr>
<td>BWF</td>
<td>Breit-Wigner-Fano</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
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<tr>
<td>CCF</td>
<td>Carboxylated Carbonaceous Fragment</td>
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<tr>
<td>CE</td>
<td>Counter Electrode</td>
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<tr>
<td>CoMoCAT</td>
<td>Cobalt and Molybdenum Catalyst</td>
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<td>CS</td>
<td>Carbon Solutions</td>
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<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
<td>DC</td>
<td>Direct Current</td>
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<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
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<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<td>DWNT</td>
<td>Double Walled Carbon Nanotube</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
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<tr>
<td>GCMS</td>
<td>Gas Chromatography Mass Spectrometry</td>
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<tr>
<td>HiPCO</td>
<td>High-Pressure Carbon Monoxide Conversion</td>
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<tr>
<td>HOPG</td>
<td>Highly Ordered Pyrolytic Graphite</td>
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<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>JACS</td>
<td>Journal of the American Chemical Society</td>
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<td>MS</td>
<td>Mass Spectrometry</td>
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<td>MWNT</td>
<td>Multi Walled Carbon Nanotube</td>
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<tr>
<td>NIR</td>
<td>Near Infrared</td>
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<tr>
<td>NMP</td>
<td>N-methylpyrrolidone</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<td>PEG</td>
<td>Polyethyleneglycol</td>
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<tr>
<td>PL</td>
<td>Photoluminescence Spectroscopy</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethene</td>
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<tr>
<td>RBM</td>
<td>Radial Breathing Mode</td>
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<tr>
<td>RE</td>
<td>Reference Electrode</td>
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<tr>
<td>SCE</td>
<td>Standard Calomel Electrode</td>
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<tr>
<td>SDS</td>
<td>Sodium Dodecyl Sulphate</td>
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<td>SEM</td>
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<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
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<tr>
<td>STPB</td>
<td>Sodium Tetraphenylborate</td>
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<td>SWeNTs</td>
<td>South Western Nanotechnologies</td>
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<td>SWNT</td>
<td>Single Walled Carbon Nanotube</td>
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<tr>
<td>TBAH</td>
<td>Tetrabutylammonium Hexafluorophosphate</td>
</tr>
<tr>
<td>TBATFB</td>
<td>Tetrabutylammonium Tetrafluoroborate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>TGA</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>WE</td>
<td>Working Electrode</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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1 Introduction

1.1 Introduction to Nanotechnology

Many of the distinguishing concepts in nanotechnology were first mentioned in 1959 by the physicist Richard Feynman in his talk "There's Plenty of Room at the Bottom" [1]. However, the term ‘nanotechnology’ only came into common use amongst scientific circles in the 1980s [2], when the development of nanoscale characterisation techniques, such as Transmission Electron Microscopy, catalysed a huge increase in the volume of nanoscale research. The use of nanotechnology is, however, far from new; its early use can be seen as far back as the 4th century AD with the Roman ‘Lycurgus Cup’ (Figure 1.1). The glass contains gold nanoparticles, which result in different colours being seen when the cup is viewed under different lights.

![Figure 1.1 The Lycurgus Cup [3].](image)

Currently, nanotechnology has many different applications, ranging from the active ingredient in sun screen (titanium dioxide nanoparticles) to a strengthening component in tennis rackets and golf clubs (carbon nanotubes) and an antimicrobial agent in wound dressings (nanocrystalline silver).

Although all of these applications are interesting and important, the potential applications of nanotechnology could be even more exciting. The science of solar
cells is currently being revolutionised by nanotechnology to produce highly efficient and yet inexpensive cells to satisfy the world energy demand [4]. Drug delivery is an area where nanotechnology could possibly be used to greatly increase the effectiveness of current medicines, by targeting specific sites within the body [5]. Nanotechnology also has the power to help fulfil Moore's Law [6] (where computer power must double every two years) to produce better supercomputers.

1.2 Introduction to Carbon Nanotubes

Carbon nanotubes are one of the most exciting chemical discoveries of recent times, offering an opportunity for an entirely new material system to be developed [7]. Nanotubes are an allotrope of carbon, like graphite and diamond, and they have unique physical and electronic properties [8]. These properties range from a higher axial thermal conductivity than diamond [7] and greater axial mechanical strength than steel (orders of magnitude by weight) [9], to larger current capacity than copper [10]. It is due to these and other unique properties that carbon nanotubes are likely to be of great importance in the future of materials. Carbon nanotubes have already attracted a lot of interest from within the scientific community, with the numbers of papers published growing exponentially each year. As research into nanotubes continues, many more possible uses for this fascinating material are being discovered. There are many potential biological applications; ranging from their use as biosensors, by attaching enzymes to their exterior [11], to exploiting their ability to act as filters to build artificial livers [12]. The electronics industry is also interested in using nanotubes to make nano-scale circuitry by exploiting their versatile electronic properties and small size. The desire to exploit the properties of individual nanotubes at a macroscopic scale has driven the development of nanotube-reinforced composites.
[13]. To pick one last example, amongst many options, their large surface area and relative inertness make them ideal to use as a catalytic support [14].

1.3 The Discovery of Carbon Nanotubes

The discovery of multi walled carbon nanotubes (MWNTs) is commonly attributed to Iijima et al. who observed tubular structures in 1991, when using High Resolution Transmission Electron Microscopy (HRTEM) to study the products of a new method of synthesising fullerenes [15]. However, they were probably discovered much earlier; with papers published in the 1950s showing tubular carbon structures. Radushkevich et al. published a paper in 1952 which contained electron microscopy images of structures resembling carbon nanotubes (Figure 1.2) [16, 17].

![Figure 1.2 Electron microscopy images from 1952 of possible carbon nanotubes [17].](image)

In fact, it is possible that MWNTs have been described in papers as far back as 1890, when Schutzenberger described the formation of carbon threads [18]. However, in 1890 the equipment was not available to characterise these threads, and it is only with
the benefit of hindsight that the possibility that these threads were MWNTs can be suggested.

Although Iijima et al. may not have actually discovered the first MWNT, the importance of his 1991 paper, published in the journal *Nature*, should not be overlooked. This paper initiated the explosion in MWNT research, following the discovery of fullerenes in 1985. With this paper it was recognised that MWNTs bridge the gap between the continuum and molecular domains, and that this specific molecular structure might have important implications. SWNTs were first reported in 1993 by both Iijima [19] and Bethune [20] independently, after they introduced a cobalt catalyst into the arc system. Herein, we focus on SWNTs.

### 1.4 The Synthesis of Single Walled Carbon Nanotubes

The methods of synthesising carbon nanotubes can be grouped into two categories: the first category involves high temperatures and these techniques include the arc evaporation of metal-doped carbon electrodes (ARC) [8, 21], and laser ablation of a metal doped carbon target [23, 24]. The second category involves more moderate temperatures and is undertaken by the decomposition of a carbon containing gas, in the presence of a metal catalyst [8, 25-27].

Each different synthesis method produces SWNTs of different types and levels of impurity. These impurities include metal catalytic particles, amorphous carbon and graphitic nanoparticles.
1.5 The Idealised Structure of Single Walled Carbon Nanotubes

An idealised SWNT consists of a hollow tube of sp$^2$ hybridised carbon atoms, usually terminated by hemispherical (fullerene) end caps [26, 28]. SWNTs can be thought of as elongated fullerenes formed by the addition of rings of carbon atoms circumferentially around the fullerene molecule. A SWNT may be modelled by rolling up a sheet of graphite along a given vector (Figure 1.3); each lattice vector generates a different nanotube with different properties [29].

![Figure 1.3](image)

**Figure 1.3** Vector diagram showing how a SWNT can be formed from a graphite sheet [30].

Nanotubes can be defined by a chiral angle, $\theta$, and a chiral vector, $C_h$, given by *Equation 1.1*, where $a_1$ and $a_2$ are the unit vectors in a 2D graphite lattice, and $n$ and $m$ are integers [26].

\[
C_h = na_1 + ma_2 \equiv (n,m)
\]

*Equation 1.1*

The chiral vector $C_h$ connects two crystallographically equivalent sites on a 2D graphite sheet [e.g. (0,0) and (5,2)], while the chiral angle is the angle it makes with respect to basis vector $a_1$. 
A SWNT is formed by rolling up the graphite sheet to allow the ends of the chiral vector to connect. There are three possible SWNT structures:

- **Zigzag** SWNTs are formed if either \( n \) or \( m \) is equal to zero, giving a chiral angle of 0°. The circumference of the nanotubes will have a zigzag pattern.

- **Armchair** SWNTs are formed when \( n = m \), giving a chiral angle of 30°. The circumference of the nanotube will have an armchair pattern.

- **Chiral** SWNTs are formed when \( n \neq m \neq 0 \) and have a chiral angle between 0° and 30°. They contain a screw axis parallel to the axis of the tube.

These three SWNT types are illustrated in **Figure 1.4**. The armchair and zigzag morphology of the SWNTs, a) and b) respectively, can be seen around the end circumference of the SWNT models. The helical character of the chiral SWNT can be seen in c) of **Figure 1.4**; they are called chiral as they can exist as enantiomers [31-33].

![Figure 1.4](image_url)

**Figure 1.4** The three types of SWNTs a) armchair b) zigzag c) chiral [34, 35].
The hemispherical end caps can only occur if curvature perpendicular to the axis of the SWNT is introduced. Just as in the structure of fullerenes, pentagons incorporated into the hexagonal framework allow this curvature [8, 26]. The nanotube diameter $d_t$ can also be written in terms of the integers $(n,m)$ using \textit{Equation 1.2}.

$$d_t = C_h / \pi = (\sqrt{3})a_{CC}(m^2 + mn + n^2)^{1/2} / \pi \quad \text{Equation 1.2}$$

Where $a_{CC}$ is the nearest neighbour C-C distance (1.421 Å in graphitic structures) and $C_h$ is the length of the chiral vector $C_h$. The chiral angle $\theta$ is given by \textit{Equation 1.3}.

$$\theta = \tan^{-1}\left[ (\sqrt{3})m/(m + 2n) \right] \quad \text{Equation 1.3}$$

\textbf{1.6 The Properties of Single Walled Carbon Nanotubes}

The electronic properties of SWNTs, which are central in the author’s future work, will be discussed at length in the following section. For completeness, the mechanical properties of SWNTs are mentioned subsequently, but they are less relevant to this thesis.

\textbf{1.6.1 Electronic Properties of Single Walled Carbon Nanotubes}

SWNTs can either be metallic or semiconducting depending on their diameter and chirality. Armchair SWNTs are always metallic, while two thirds of zigzag and chiral SWNTs are semiconducting and one third are metallic [10]. The electronic structure of SWNTs can be obtained from graphite, its parent material; graphite is a semimetal because transitions between the valence and conduction bands only occur close to the corners of the graphite Brillouin zone. The point at which the valence and conduction bands touch is called the K-point (\textbf{Figure 1.5}).
Figure 1.5 a) The unit cell (dotted rhombus), containing sites A and B where carbon atoms are located, b) the Brillouin zone (shaded hexagon) of a graphene or 2D graphite layer. \( a_1 \) and \( b_i \) (i=1,2) are basis vectors and reciprocal lattice vectors, respectively. The high symmetry points \( \Gamma, K \) and \( M \) are indicated, c) the calculated constant energy contours for the conduction and valence bands of a 2D graphene layer in the first Brillouin zone using the \( \pi \)-band nearest neighbour tight binding model. The valence and conduction bands touch in the \( K \) points. Solid curves show the cutting lines for the (4,2) nanotube, but translated to the first Brillouin zone of 2D graphite, the dark points indicating the connection points [36].

When graphite is rolled up to form a nanotube a periodic boundary condition is imposed along the tube circumference in the \( C_h \) direction. This quantum confinement quantizes the electron momentum in the circumferential direction. SWNTs will only be metallic when one of the allowed wave vectors coincides with the K point (Figure 1.6a). This leads to metallic conductance occurring when \( q \) (in Equation 1.4) is an integer, where \( n \) and \( m \) are the integers which specify the specific nanotube [31].

\[
(n - m) = 3q \\
\text{Equation 1.4}
\]

So, for armchair SWNTs, where \( n = m \), this equation shows that all the SWNTs will be metallic, whereas only one third of zigzag, \( (n \text{ or } m \text{ is equal to zero}) \) or chiral \( (n \neq m \neq 0) \) will be metallic.

This effect can also be seen by looking at the density of states (DOS) of the SWNTs. The DOS quantifies how close-packed the energy levels are within the SWNT system and are calculated from the graphene structure using a variety of tight binding models, all of which have been shown to match experimental data [29, 37]. Examples of the
DOS for different types of SWNT are shown in Figure 1.6. The peaks in the DOS are due to quantum confinement effects and are called van Hove singularities.

Figure 1.6 a) Allowed $k$-vectors of the (5,5), (7,1) and (8,0) tubes (grey lines) mapped onto the graphite Brillouin zone, b) Density of states for the (5,5) armchair, (7,1) chiral and (8,0) zigzag SWNTs [33].

In Figure 1.6, it can be seen that the (5,5) armchair SWNT (0.68 nm in diameter) will be metallic: there is no band gap in the DOS. The (7,1) chiral SWNT (0.59 nm in diameter), will be metallic at room temperature but contains a small band gap due to curvature effects (trigonal warping), which is only noticeable at low temperatures. The (8,0) zigzag SWNT (0.63 nm in diameter) has a large band gap in the DOS and the tube will be semiconducting.
The band gap of semiconducting SWNTs is inversely proportional to their diameter. As the diameter increases, the quantum confinement becomes less significant and the electron character tends towards that of the semimetal graphite. For small semiconducting SWNTs, less than 1nm in diameter, $\sigma-\pi$ rehybridization associated with the high curvature begins to decreases the band gap (eventually by up to 50%). For very small SWNTs which would normally be metallic, the $\sigma-\pi$ rehybridization can cause a small band gap to appear, making them semiconducting.

The Kataura plot (Figure 1.7) shows the various energies of optical transitions between the van Hove singularities in the valance and conductive bands in the density of states, plotted as a function of SWNT diameter. Strong optical transitions between the van Hove singularities only occur when the energy of the incident light matches transitions between two peaks that are mirrored [36]. The cross-transitions (e.g. $E_{12}$) have been observed but are very weak.

This plot is used in Raman, UV/Vis/NIR and fluorescence spectroscopy to relate spectroscopic data to the SWNT structure. When analysing the data created using these techniques it is often useful to mark on the area of a particular transition; for example, a $M_{11}$ label would indicate a transition between the first van Hove singularities of metallic tubes, whereas the $S_{22}$ would indicate the transition between the second van Hove singularities of semiconducting tubes.
Figure 1.7 Kataura plot generated for SWNTs up to 2nm in diameter. The black points represent metallic tubes, the white points represent semiconducting tubes. In this plot two different tight binding models are shown, represented by the circles and the crosses. The black and white circular points represent the most up to date values [37].

When the experimentally observed electronic transition energy, $E_{ii}$, is plotted as a function of the radial breathing mode (RBM) frequency, $\omega_{\text{RBM}}$, (2n+m) geometric (family) patterns can be seen to appear (Figure 1.8). This interesting phenomenon allows family maps to be produced, allowing for easier identification of (m,n) indices [38]. SWNTs can thus be divided into three different classes according to whether “(2n + m) MOD 3” = 0, 1 or 2, when the number 0, 1 and 2 are the remainder when the (2n +m) is divided by 3. In these classes, 0 is metallic and 1 and 2 are two different semiconducting types. Further details are available in the literature [29].
The measured current carrying capacity of a SWNT has been found to be approximately 1 billion A/cm² which is greatly superior to a copper wire which cannot reach 1 million A/cm² without suffering electromigration [10, 39]. If metallic and semiconducting nanotubes are joined, the junction formed behaves as a diode, permitting electricity to flow in one direction only [31].

With these miniature diodes and other components made similarly, it may one day be possible to replace (or augment) silicon chips. Not only could this make circuitry much smaller, but the impressive thermal conductivity of the SWNT may mean that many more circuits could be packed into a small space without overheating.

However, these possibilities remain in the future of SWNT research as problems with purification, separation of individual (m,n) species, and integration into devices remain unsolved.

The theoretical electronic properties assume a perfect SWNT structure. However, SWNTs are rarely perfect and it has been shown that a small number of point defects

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**Figure 1.8** $E_{ii}$ vs RBM plot. Solid, open, and crossed symbols stand for $n,m$ SWNTs with “$(2n + m) \text{ MOD } 3 = 0$ metallic, 1 or 2 semiconducting SWNTs, respectively. The grey lines connect SWNTs within the same $2n+m$ family. The $2n+m$ numbers are displayed close to each family [38].
in their structure can greatly alter their inherent properties [40]. Goldsmith et al. demonstrated that when SWNTs were functionalised the sp\(^2\) structure changed to the sp\(^3\) structure and the conductance of the SWNTs decreased dramatically [40]. It is also known that SWNT functionalisation bleaches electronic transitions [38]. Thus it is important to minimise functionalisation of the SWNT structure when electronic properties are to be studied or exploited.

1.6.2 Thermo-Mechanical Properties of Single Walled Carbon Nanotubes

SWNTs have unique mechanical properties. The Young’s Modulus (tube axis elastic constant) of a SWNT has been found to be \(~\)1TPa, over 5 times the Young’s modulus of steel (\(~\)200 GPa) [7, 31, 41]. SWNTs have a density of approximately 1.35 g/cm\(^3\) and although this value to known to vary with diameter it is still, for the most part, less than one fifth of the density of steel [9]. To date, the tensile strength of SWNTs bundles has been found experimentally to be between 13 and 52 GPa [42], but theoretically it could be as high as 150 GPa. This figure greatly surpasses the tensile strength of steel at 0.5 to 2.5 GPa, graphite at 2.5 GPa and carbon fibre at 5 GPa [31]. SWNTs also possess excellent thermal properties, being stable up to 1500°C in a vacuum. They also have a thermal conductivity ranging from 200 to 6000 W/mK depending on quality and alignment, giving some SWNTs a higher thermal conductivity than diamond (900 – 2300 W/mK) [7, 31]. SWNTs are therefore one of the strongest, toughest and stiffest known fibres [43]. However, as with the electronic properties, problems arise when trying to exploit these nanoscale objects on a macroscopic level.
1.7 Current and Future Applications of Carbon Nanotubes

There are many possible applications for carbon nanotubes, some of which have already been brought to the market. Currently, most of the existing commercial applications for these materials focus on their use in composites. They are currently incorporated into high end tennis racket and bike frames, where they are used because of their high strength and low weight. Their electric properties are used to increase spray painting efficiency by incorporating them into plastics [9, 44].

When SWNTs can be reliably and completely separated into their metallic and semiconducting fractions then many more possible applications will be realised. For example, semiconducting tubes must alone be used to produce good field-effect transistors since any metallic tubes present will short the device, and their possible use as an active component in solar cells relies on just semiconducting SWNTs being present. On the other hand, metallic nanotubes must alone be present if low resistance materials for transparent conductors are to be produced [45].

1.8 Aims and Objectives of the Project

In this thesis, the purification, dispersion and separation of Single Walled Carbon Nanotubes (SWNT) are all explored. The motivation for this work arose from the basic desire to understand and further develop the underlying chemistry of SWNTs, thus providing the building blocks which could allow their extraordinary properties to be used to their full potential. Firstly, a new method of SWNT purification was developed. Achieving highly pure SWNT samples on which further chemistry can be undertaken is of critical importance; purification must be able to be performed in a reliable and repeatable manner. In short, the new approach followed the standard literature purification technique with an additional base washing step.
Following on from this purification work, two different methods were undertaken to form good dispersions of SWNTs, allowing them to be separated by their electronic properties and/or size.

The first of these methods involved dissolved metal reduction. This reaction involved the reduction of SWNTs by an alkali metal in liquid ammonia. The reduced tube salts were spontaneously dissolved in dry solvents to form stable dispersions. The degree of separation of different SWNTs in the spontaneously dissolved portion was investigated.

The second method investigated was similar to the method outlined above; however, the SWNTs were electrochemically reduced. By passing a voltage through a SWNT sample in a suitable electrolyte the SWNTs were reduced and therefore dissolved, allowing once again the degree of separation to be investigated.
1.9 References


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2 Literature Review

2.1 Introduction

The purpose of this thesis is to study the purification, dispersion and separation of single walled carbon nanotubes. As such, this chapter contains an overview of the current literature based on these topics. First, a summary of the currently purification literature is given. As the author used two different methods to try to disperse and separate the SWNTs by their electronic properties, a literature review relevant to each method is given; dissolved metal reduction and electrochemistry. Lastly, the current routes to the separation of SWNTs by their electronic properties are discussed.

2.2 Purification of SWNTs

2.2.1 Defects and Impurities in SWNT samples

As-synthesised SWNTs are generally impure, with each different synthesis method producing a different type and level of contaminant [1]. These initial impurities include metal catalytic particles, amorphous carbon, and graphitic nanoparticles [2]. It should also be understood that nanotubes are rarely perfect and often contain many defects. Purification of SWNTs to remove the initial impurities often introduces extra defects. Examples of these defects, both those formed during synthesis and those introduced during purification, are illustrated in Figure 2.1. These defects include heptagons and pentagons (instead of the usual hexagonal carbon bonding) which occur along the length of the nanotube and cause local Gaussian curvature [3], sp3-hybridised defects (R= -H and -OH), defects caused by oxidatative damage (-COOH groups) and the open ends of the SWNTs which are often terminated with -COOH groups [4]. It has long been a (potentially unattainable) goal of SWNT research to
find a single, reliable, and repeatable method of purification applicable to every different type of SWNT.

**Figure 2.1** Typical defects in a SWNT A) five or seven membered rings B) sp$^3$-hybrised defects (R= -H and -OH) C) framework damaged by oxidative conditions, leaving a hole lined with -COOH groups, and D) open end of the SWNT, terminated with -COOH groups [4].

### 2.2.2 Purification Techniques

Purification of SWNT samples is problematic for several reasons:

- Metal nanoparticles are often encapsulated within the SWNTs, so removing them means destroying an area of the tube [2].
- The high SWNT aspect ratio induces strong Van der Waals forces between the nanotubes themselves, which forms bundles of tubes, and between the nanotubes and the amorphous carbon.
- The reactivity of amorphous carbon and graphitic nanoparticles is very similar to the reactivity of the SWNTs themselves.
- Harsh purification techniques can introduce defects into the SWNTs [2].
Many different methods have been attempted to remove these impurities whilst leaving the SWNTs with minimal surface defects. Purification is usually based on competitive oxidation and current purification techniques can be grouped into six categories; liquid phase oxidations [1, 2], gas phase oxidations [5, 6], chemical functionalisation [2], filtration and chromatography techniques [2, 7], microwave heating [8] and electrochemical oxidation [9]. The following discussion focuses mainly on the liquid phase oxidations which are the common factor in the majority of purification regimes and have been the primary focus of the author’s research. Although each purification technique will be discussed individually, it is common for two or more purification techniques to be used in combination with one another, as detailed at the end of the section.

2.2.2.1 Liquid Phase Oxidation Techniques

There are many types of liquid phase oxidations applied within the nanotube field to remove catalytic particles and carbonaceous impurities, these include using; HCl, HNO₃, H₂SO₄/HNO₃, KMnO₄ and H₂O₂ [2]. All of these techniques are often, but not always, undertaken under reflux conditions.

Liquid phase oxidation techniques are a relatively easy and simple way to remove metal catalyst particles, as the particle catalyses local oxidation of the carbon encasing it [10]. The metal particle is then dissolved in the oxidising acid, allowing it to be removed from the sample by washing. Acids such as HCl, which are not capable of oxidising carbon, can still be used to remove the metal catalyst particle but before they are used another, stronger oxidation is usually undertaken to breach the carbon shell. The advantage of HCl is that minimal further damage to the SWNT carbon structure occurs. This oxidation increases the volume of the particle which cracks the
nanotube wall, freeing the metal and allowing it to dissolve and hence be washed out of the SWNT sample [11]. This method is often used for SWNT purification as the more aggressive oxidation is stopped before the metal particle is completely exposed thus decreasing the probability that other areas of the SWNT will be oxidised.

It is also understood that many oxidative treatments will attack both the carbonaceous impurities and the SWNTs themselves. However, due to heightened reactivity, these impurities react quicker than the SWNTs. Many different studies have been undertaken to find the most advantageous reaction conditions for removal of the amorphous carbon without introducing many defects into the SWNTs. SWNT samples synthesised by different methods react differently to each type of oxidative purification and all purification techniques have introduced some amount of oxygenated functional groups onto the SWNT surface [2]. It is worth noting here that oxygenated groups added to SWNTs can be useful for further reactions but can damage the intrinsic properties. Of all of the purification techniques available, refluxing in nitric or nitric/sulphuric acid is the most common and also the subject of the author’s work.

Acid treatments have long been used on carbon materials including carbon fibres [12]. The use of acid treatments on MWNTs was first reported by Esumi et al. [13], who showed that MWNTs could be purified by using a mixed acid reflux which consisted of a 1:3 ratio of nitric acid and sulphuric acid, under reflux conditions [13], followed by a water wash. This method works well due to the formation of the highly reactive nitronium ion, \( \text{Equation 2.1} \) in the presence of \( \text{H}_2\text{SO}_4 \), which is a very strong oxidising agent.

\[
\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{NO}_2^+ + \text{H}_2\text{O}
\]

\( \text{Equation 2.1} \)
The weight loss from the sample is attributed to loss of both impurities and SWNTs. Esumi et al. also showed that this mixed acid reflux introduced a higher concentration of oxygenated groups onto the outside of the nanotubes than the nitric acid reflux.

For SWNTs, either a similar short mixed nitric/sulphuric reflux [13] or a longer (more dilute) nitric acid reflux are commonly used [1]. The simple nitric acid reflux was popularised by Smalley’s paper on ‘Fullerene Pipes’ in 1998 [14]. He described the purification of nanotubes, by a 2.6 M nitric acid reflux, followed by filtration using distilled water. The popularity of this technique is not only due to its reasonable effectiveness at removing impurities, but also its straightforward nature and relative inexpensiveness. Many different groups have investigated the most favourable reaction conditions for the nitric acid reflux. The most complete of these studies was undertaken by Haddon’s group, which concluded that the most effective reflux conditions were either 3 M NHO₃ for 12 hours or 7 M NHO₃ for 6 hours. All the samples were subsequently washed to neutral with distilled water [1].

It is well known that these oxidations can damage the framework of the nanotubes, introducing chemical defects into the nanotube structure [2]. On the other hand, it has only recently been realised that these treatments also produce molecular debris which can remain adsorbed onto the nanotube walls, and that this debris is not removed by conventional water washing.

Rinzler et al. first proposed the use of a dilute base wash during purification, however the main incentive was in changing the diameter distribution rather than quantifying the effects on purify [15]. Last year, Verdejo et al. showed that when the common nitric/sulphuric acid purification regime is undertaken for MWNTs, there is a significant fraction of oxidation debris that is only removed using a dilute base wash [16]. Salzman et al. reported similar results for SWNTs; however, a range of
complicated and more aggressive conditions were used in the initial purification, and subsequent removal, of the oxygenated carbonaceous debris. Specifically, the purification used microwave treatment in 16% HCl, reflux in 8 M nitric acid for 24 h, followed by reflux in 8 M sodium hydroxide (NaOH) for 48 h, and finally a HCl wash [17]. The basic (NaOH) reflux/washing cycle was performed three times to achieve maximum purification.

2.2.2.2 Gas Phase Oxidation Techniques

Gas phase oxidation is the process of heating SWNTs in air, oxygen, carbon dioxide, water vapour or other oxidative gases. It again relies on the principle of selective oxidation, whereby the amorphous carbon is oxidised more quickly than the SWNTs themselves. This attack results in a peelback effect of the amorphous carbon layers. Although this method can be preferable to liquid oxidation, in that it leads to less functionalisation of the SWNT surface, the metal catalyst particles are still left encapsulated within the SWNT and overall yields following on from this method are very low. A HCl wash is often undertaken after gas phase oxidation; this dissolves the catalyst particles after the removal of the surrounding amorphous carbon [2].

SWNTs grown in different ways have been shown to require different gas phase oxidation techniques. SWNTs grown using pulsed laser vapourisation were shown by Zimmerman et al. to be purified by heating to 500°C in a gaseous mixture of Cl₂, H₂O and HCl [5]. Although CVD grown SWNTs have been shown to be purified by simple oxidation in air at 470°C, wet Ar-O₂ oxidation at 180-300°C is more successful at removing the impurities without destroying the tubes [10].
2.2.2.3 Chemical Functionalisation

The purification of SWNTs was found as a by-product of some chemical functionalisation techniques. Georgakilas et al. showed that azomethine ylides, formed when molecules such as 2-(heptamino)acetic acid react with aldehydes such as formaldehyde, preferentially functionalise SWNTs rather than the amorphous carbon contained within a SWNT sample [18]. The impurities could then be removed from the SWNT sample by a precipitation process which takes advantage of the lower solubility of the unfunctionalised amorphous carbon material. After separation, the functional groups can be removed using thermal treatment. Although chemical functionalisation is an alternative to oxidation, often the functionalisation process itself is quite complicated and by modifying the tubes, the intrinsic properties, which rely on sp² hybridisation, are disrupted.

2.2.2.4 Filtration and Chromatography Techniques

Filtration and chromatography can be used to purify SWNTs. However, before either can be undertaken, a good dispersion of the SWNTs must first be achieved [2]. SWNT purification through filtration is simply achieved by size separation. Bandow et al. used a cationic surfactant to purify SWNTs using microfiltration [7]. The paper showed significant removal of metal nanoparticles, carbon nanospheres, polycyclic aromatic carbons, and fullerenes.

High performance liquid chromatography, coupled with size exclusion chromatography, is often used to purify SWNTs by separating them into fractions of different sizes [19-22]. The chromatography columns are packed with material containing pores of specific sizes. The SWNTs will flow down the column, with the smallest molecules taking the longest path. Hence the bigger the molecule, the faster
it will flow through the column. Chromatography is very useful for obtaining small quantities (typically <1mg) of SWNTs with different lengths and diameters. It is also good at removing any impurities within the SWNT samples which are significantly different in size and shape to the SWNTs. However, it does not remove any amorphous carbon attached to the SWNT itself or any catalyst particles contained within the SWNTs.

### 2.2.2.5 Microwave Heating

Microwave heating in air followed by a HCl wash is a very successful method of removing the metal catalytic particles from within the SWNT sample [8]. The advantage occurs because the microwaves couple with the metal particles and significantly increase the local temperature. This effect causes oxidation and ultimately destruction of the carbon layers surrounding the metal and allows the metal to be easily removed by the HCl wash. However, microwave heating does not remove the amorphous carbon impurities, so other types of purification techniques must be undertaken and microwave energy is also known to introduce defects into SWNTs. Due to these factors microwave oxidation is not a very common oxidation technique.

### 2.2.2.6 Electrochemical Oxidation

The possibility of using electrochemistry as a tool for purifying SWNTs has yet to attract much interest from the scientific community, with only a small number of papers being published on the topic. Fang et al. showed that it is possible to purify SWNTs by taking advantage of the fact that carbon material with fewer defects usually shows a lower rate of electrochemical
oxidation, hence, SWNTs showed a higher electrochemical oxidation resistance than amorphous carbon [9]. Fang et al. used cyclic voltammetry (CV) from 1.3 V to 0.78 V to perform oxidation treatment in KOH to eliminate most of the amorphous carbon and to expose the catalyst particles, which can then be easily removed by HCl washing. The redox peaks increased with CV cycle number as the peaks were attributed to the redox activity of the metal catalyst particles partially exposed following amorphous carbon removal. Thus, as more amorphous carbon was removed and more particles were exposed, the intensity of the CV peaks increased until all of the amorphous carbon had been removed. Thus, electrochemical oxidation can give a good indication for judging the extent to which the amorphous carbon has been removed, thus limiting the loss and damage of the SWNTs themselves. Although this technique shows a large amount of promise within the SWNT purification field, it has to be assumed that, like other oxidative techniques, the walls of the SWNTs will be functionalised.

2.2.2.7 Vacuum Annealing

Vacuum annealing is used to repair damage to the SWNT structure, introduced during purification processes. It can also be used to remove functional groups that have become attached to the SWNT during purification. By heating the SWNTs between 350-1000°C under vacuum of 10^{-3} to 10^{-6} mbar, the SWNTs can gain enough energy to rearrange to their lowest energy state, thus reforming the highly ordered SWNT structure. This rearrangement produces by-products which are removed by the vacuum [23, 24].
2.2.2.8 Combinations of Purification Techniques

Although in Sections 2.2.2.1-2.2.2.7, the current SWNT purification techniques have been discussed individually, they are most commonly used in conjunction with one another, often involving vacuum annealing as the final step [25]. As previously stated, gas phase oxidations are often followed by an HCl wash and then an annealing step. Chiang et al. showed that HiPCO SWNTs could be purified by a gas mixture of 20% O$_2$ in Ar followed by a concentrated HCl wash and finishing with an annealing step at 800°C in Ar for 1 hour [11]. Some groups use a nitric acid reflux, followed by a wet air oxidation and then a vacuum annealing step to purify their SWNTs [2]. Wet air oxidation can be used in subsequent steps with an HCl wash in-between. In short, each research group has their own specific method that they consider purifies SWNTs to the highest degree. Although many different purification techniques do exist, it is often costly in both time and material to try many different techniques to purify the SWNTs. Due simply to their similar chemistry to the amorphous carbon, achieving large amounts of highly pure SWNT samples is still an ongoing challenge.

2.3 Liquid Ammonia Reduction

2.3.1 Introduction

Research into SWNTs is hampered by their minimal solubility in common organic solvents [26]. Even when ‘good’ solutions are produced; either at low concentrations or in the presence of surfactants, the tendency of SWNTs to reaggregate, particularly into bundles, should not be underestimated. Only when stable solutions of individual SWNTs can be produced will reliable functionalisation and separation be achieved. Solutions of SWNTs are also desirable for fundamental characterisation and
applications. It has therefore been a long standing goal of SWNT research to produce homogeneous dispersions of individual SWNTs.

Penicaud et al. completed work on the dispersibility of reduced SWNTs using sodium naphthalene in THF as a reducing agent. These reduced SWNTs spontaneously dissolved in polar, aprotic solvents, resulting in individual SWNTs which could be readily functionalised with oxygenated groups to give water soluble SWNTs [27, 28]. Martinez-Rubi et al. demonstrated the controllable nature of this reaction by reacting the reduced tubes with diacyl peroxides and showing that the functionalisation level could be controlled through repetitive application of the redox reaction [29].

Recently, metal ammonia solutions began to be recognised as a good solvent for functionalisation of SWNTs. Liquid ammonia is usually formed by condensing gaseous ammonia into a reaction tube cooled to -45°C in an acetone-dry ice bath. Alkali metals dissolved in liquid ammonia produce strongly reducing solutions as they readily give up their single outer-shell electrons to form solutions of unpaired electrons (Equation 2.2). These unpaired (solvated) electrons can be seen as an intense blue colour within the solution (Figure 2.2), due to the tail of a very broad optical absorption band in the near IR with a maximum near 1500 nm [30, 31]. In liquid ammonia, hydrogen bonding takes place which creates cavities within the liquid ammonia structure in which the solvated electrons can reside [32, 33].

\[
\text{Li} + n\text{NH}_3 \rightarrow \text{Li}^+ + e^-(\text{NH}_3)_n
\]  

Equation 2.2
Figure 2.2 Solvated electrons from a bead of Sodium Potassium alloy in anhydrous liquid ammonia [34].

If nothing is added to the ammonia, these blue solutions decompose to give hydrogen and sodium amide (NaNH₂), however this reaction is quite slow and a better electron accepter will always be preferentially reduced. Any functional group with a low energy π* orbital into which the electron can enter will be reduced in these solutions. Conjugated systems can be reduced in liquid ammonia via the Birch reduction (Figure 2.3). In this reaction, the electron will go into benzene’s lowest lying antibonding orbital, forming a radical anion. When this anion reacts with an alcohol the benzene is hydrogenated [32].

Figure 2.3 The Birch Reduction [32].
In an analogous fashion, solvated electrons can be transferred to SWNTs (Equation 2.3). Functionalisation on these reduced SWNTs has then been carried out, as discussed in Section 2.3.2 [35].

\[ \text{e}^-(\text{NH}_3)_n + C \rightarrow n\text{NH}_3 + C^- \]  \hspace{1cm} \text{Equation 2.3}

In a liquid ammonia reduction analogous to those used for SWNTs, Howard et al. showed that C\textsubscript{60}\textsuperscript{5-} could be dispersed in liquid ammonia by the formation of 3 giant solvation shells around the fullerene anions [36].

2.3.2 Liquid Ammonia Reactions

The interaction and functionalisation of SWNTs in ammonia has only recently been studied and only a few papers have been published on the topic. Pekker et al. prepared hydrogenated SWNTs by reducing 200 mg of pristine SWNTs with 100 mg of Li metal in 20 mL of liquid ammonia, then adding 5 mL of dry methanol; a reaction analogous to the Birch reduction [37]. A similar reaction was previously reported for the hydrogenation of fullerenes [38]. The mechanism for the hydrogenation of SWNTs in liquid ammonia, as proposed by Pekker, starts with the formation of the carbanion complex (Equation 2.3), followed by the formation of a hydrogenated carbon derivative by the reaction with methanol, causing the carbanion to decompose (Equation 2.4).

\[ \text{C}^- + \text{CH}_3\text{OH} \rightarrow \text{CH} + \text{CH}_3\text{O}^- \]  \hspace{1cm} \text{Equation 2.4}

The formation of hydrogen also competes with this reaction (Equation 2.5).

\[ \text{C}^- + \text{CH}_3\text{OH} \rightarrow \text{C} + \text{CH}_3\text{O}^- + \frac{1}{2}\text{H}_2 \]  \hspace{1cm} \text{Equation 2.5}

Subsequently, additional hydrogen will be evolved due to the reaction of the excess ammoniated electrons with methanol (Equation 2.6) [37].

\[ \text{e}^-(\text{NH}_3)_n + \text{CH}_3\text{OH} \rightarrow n\text{NH}_3 + \text{CH}_3\text{O}^- + \frac{1}{2}\text{H}_2 \]  \hspace{1cm} \text{Equation 2.6}
In this paper, Pekker et al. used tubes manufactured by pulsed laser vaporization (PLV) and by analysing thermogravimetric-mass spectrometry (TG-MS) data, found that the strongly-bound hydrogen evolved from the sample at around 500°C to indicate a hydrogen content of C_{11}H.

Liang et al. carried this reaction one step further and reductively alkylated 20 mg (1.6 mmol) of HiPCO SWNTs using 231 mg (33 mmol) of lithium metal in 60 mL liquid ammonia [39], followed by the addition of 6.4 mmol of an alkyl halide. These functionalised nanotubes then showed a high degree of solubility in common organic solvents such as chloroform, THF and DMF. AFM was used to show that complete debundling had occurred. Liang, theorised that the initial debundling of the carbon nanotubes occurred due to the extensive intercalation by lithium. This process leads to the lithium ions being inserted between negatively charged tubes [39]. TG-MS was used to show that depending on the alkyl halide used, the alkyl group/carbon ratio ranged from 1:17 for CH_{3}(CH_{2})_{3}I to 1:35 for THP-O-(CH_{2})_{3}I.

To further understand the mechanism behind the charge transfer induced lithiation of SWNTs, Gu et al. performed in situ Raman studies of SWNTs in liquid ammonia as lithium was added [40]. In this reaction, 100 mL of liquid ammonia was condensed onto 50 mg (4.3 mmol) of HIPCO SWNTs and the Raman spectra of the SWNTs was measured as 40.7 mg (5.9 mmol) of lithium metal was added in 1-5 mg increments. This reaction showed that charge transfer from the liquid ammonia solvated lithium to the SWNTs led to intercalation of lithium into the SWNT ropes, as well as the semi-covalent lithiation of the SWNTs. As electrons transferred from the alkali metal to the SWNTs, a downshift and a broadening of the G-band was seen in the Raman spectra due to the electron occupancy in the π* orbital, in addition the RBMs disappeared [40]. The study used only a 785 nm laser which is known to excite semi-
conducing SWNTs. The increase in the D-band in the Raman spectrum when lithium is added to the liquid ammonia indicates that the electron transfer between the lithium metal and the SWNTs is not purely ionic but a mixture of ionic and covalent, with the electron being most likely shared between the lithium and the carbon. After lithiation of the SWNTs, 1.5 mL (6.1 mmol) 1-iodododecane was added to the solution and was shown to fully dodecylate all of the individual tubes [40]. Chattopadhyay et al. then showed that using the liquid ammonia reduction (4.1 mmol HiPCO SWNTs, 41 mmol lithium and 300 mL ammonia), water-soluble PEGylated SWNTs were produced on adding 12.5 mmol ω-bromocarboxylic acid to the liquid ammonia to form SWNTs functionalised with carboxylic acids, removing the ammonia, and then reacting the nanotubes with amine-terminated polyethyleneglycol (PEG) chains in DMF (Figure 2.4) [35].

Figure 2.4 Reaction mechanism for the formation of water-soluble PEGylated SWNTs [35].

Chattopadhyay et al. went on to show that reduced SWNTs could be reacted with aryl and alkyl sulphide, by a single electron transfer mechanism, to yield a transient radical anion that dissociates to yield carbon-centred free radicals and mercaptides [41]. It is these free radicals that add to the sidewalls of the nanotube or recombine with the SWNT radical anions (Figure 2.5).
The first paper to exploit the difference in chemical relativities between metallic and semiconducting SWNTs, with respect to sidewall functionalisation via reductive alkylation, was published at the start of 2008 by Wunderlich et al. [30]. In this work, 30 mg of HiPCO SWNTs (2.5 mmol) were reduced using 23 mg sodium (1 mmol) in 100 ml liquid ammonia and subsequently alkylated with 0.12 mL (1 mmol) of 1-iodobutane (no attempt was made in this paper to quantify the yield of the reaction). Following the interpretation of the Raman, Fluorescence and UV-vis-nIR data, SWNTs with smaller diameters were found to be more reactive than tubes with larger diameters. The reaction was also found to favour functionalisation of metallic over semiconducting tubes. Wunderlich proposed a slightly different reaction pathway to account for this selective alkylation which starts with the electron transfer of solubilised electrons onto the SWNTs, generating charged nanotube reaction intermediates, which are exfoliated due to electrostatic repulsion and are homogenously dispersed as individual species in the liquid ammonia. The smaller diameter SWNTs react first because they have a higher degree of charge located on...
them as their small size leads to a higher degree of pyramidalization, which distorts the trigonal planar molecule towards tetrahedral and therefore leads to more effective stabilisation of the negative charge. The preferred charging and therefore functionalisation of the metallic tubes can be explained by the accessibility of the density of states just above the Fermi level. When the tubes were hydrogenated instead of alkylated, via the use of ethanol addition following the liquid ammonia removal, the degree of functionalisation was found to be considerably lower (seen by a smaller D-band increase in the Raman spectrum) and no pronounced tube selectivity could be seen. This lower degree of functionalisation was due to the ethanol addition being undertaken in the solid state so the reaction occurred in bulk rather than at the individual nanotube level [30].

As more papers are published on the reduction of SWNTs in liquid ammonia, different reaction conditions and mechanisms for the reduction are described. Only when significantly more research has been undertaken into the area will the best reaction conditions be achieved and a conclusive and widely accepted reaction mechanism be found.

2.3.3 Conclusions

SWNTs have been shown to be reduced by solvated electrons produced by an alkali metal present in liquid ammonia under strictly dry conditions. Current literature suggests that this reduction forms an initial SWNT dispersion by either the intercalation of Li\(^+\) ions between the SWNTs or by inter-tube repulsion following the reduction, or a mixture of both mechanisms. This dispersion of reduced SWNTs then allows for the functionalisation of the SWNTs with a variety of different chemical species. When this functionalisation is completed in the ammonia itself, smaller
diameter and metallic SWNTs were found to be the most reactive, thus allowing for the separation of SWNTs based on their electronic properties. However, no work has been reported on the separation of different types of SWNT without functionalisation and it is this work that will be explored fully in the current thesis.

2.4 Electrochemistry involving SWNTs

2.4.1 Introduction

Many of the potential applications for the unique properties of carbon nanotubes rely on a good understanding of their redox properties, which can be achieved through electrochemistry. For example, Barisci et al. attempted to use carbon nanotubes as electromechanical actuators [42], where they undergo a dimensional change as a result of an electrical charge injection [43]. This effect can only be optimised when their electronic properties have been fully studied and understood [43]. Many other potential applications of carbon nanotubes also rely on a fundamental yet practical understanding of their redox properties. These issues are particularly important for use in field emission devices, nanoelectronics, hydrogen storage, sensors and the electrochemical storage and production of energy [9]. Many techniques have been developed to study the electronic properties of carbon nanotubes such as Raman, UV/vis/nIR and fluorescence spectroscopy. However, only a small amount of work has been undertaken on the redox properties of carbon nanotubes and the effects on their electronic structure. The most fundamental way of testing these properties is by using electrochemistry and, as it is the focus of the author’s work, the current literature on the electrochemistry and redox properties of carbon nanotubes is discussed in the following section.
2.4.2 Electrochemical Characterisation of SWNTs

The first electrochemical characterisation of SWNTs was undertaken by Liu et al. in 1999 [44]. Thin films of carbon nanotubes were made by evaporating a solution of carbon nanotubes, made by sonicating in aqueous SDS, and used as the working electrode in a 3 terminal electrochemical cell. Over the potential range of 1 to -1 V, the Cyclic Voltammogram (CV) of the SWNTs was compared to the CVs produced using an analogous method to produce films of C\textsubscript{60}. C\textsubscript{60} is known to have many distinct features in its CV due to specific electron transfer events (Figure 2.6), whereas the CV obtained for carbon nanotubes was relatively featureless (Figure 2.7). This response is most likely the result of the wide distribution of different SWNT species, producing a CV containing the average of many closely spaced electron transfer events into each nanotube type [44]. It should be noted that a larger capacitive response is seen for the SWNTs than the platinum wire alone, most likely due to the larger surface area of the SWNT electrode.

![Figure 2.6 CVs of a C\textsubscript{60} film cast as a suspension from acetone on a Pt electrode in MeCN containing 0.1 M TBAPF\textsubscript{6}. Scan rate, 50 mV/s [44].](image-url)
Figure 2.7 Cyclic voltammograms of a Pt electrode with and without a SWNT film cast from acetone in MeCN containing 0.1 M TBAPF₆. Scan rate, 50 mV/s [44].

Following on from this paper, Barisci et al. published two papers in 2000 on the electrochemical characterisation of SWNTs [42, 43]. The first showed broad redox responses when a bucky paper working electrode was cycled between ±0.8 V in an aqueous solution (Figure 2.8 NTP3, NTP5). These redox responses were attributed to the presence of oxygen-containing functional groups on the nanotubes, introduced during acid purification; annealing the material at 900°C eliminated these responses due to the removal of the oxygen-containing groups (Figure 2.8 NTP5A) [42].

Figure 2.8 Cyclic voltammograms for bucky papers NTP3 (as produced), NTP5 (as-produced and heated to 70°C) and NTP5A (as produced, heated to 70°C and then vacuum annealed at 900°C) in 1.0 M NaCl, scan rate 50 mV s⁻¹. The location of the redox couple is indicated (A and A') [42].
Barisci’s second paper focused on non-aqueous electrochemistry. No redox features were seen in a broad potential range (±1.5 V) using the common and relatively inert electrolyte tetrabutylammonium tetrafluoroborate (TBATFB), unless LiClO$_4$ was added (Figure 2.9). The CV in acetonitrile containing this Li compound exhibited a defined reduction peak at -0.7 V and a smaller oxidation response at -0.2 and 0.5 V when ran from ±0.8 V. These peaks were attributed to lithium insertion into the interstitial sites on the nanotube bundles [43].

![Cyclic voltammogram of a nanotube paper in acetonitrile solutions of 0.1 M LiClO$_4$ and 0.1 M TBATFB, scan rate 50 mV/s (reference electrode Ag/Ag$^{+}$) [43].](image)

Kavan et al. went on to show that in dry and oxygen-free solutions, the electrochemistry of the SWNTs is controlled by capacitive charging in the range of ±1.5 V. Electrochemical charging of the SWNTs were traced by reversible changes in the intensity and frequency of the RBM in the Raman spectra, along with the bleaching of the electronic transitions between the Van Hove singularities in the vis-nIR regions. As expected, it was found that the bands associated with metallic tubes were more sensitive to electrochemical doping as the extra electrons could be more easily inserted into the conduction band just above the Fermi level [45].
peaks assigned by Barisci et al. to Li insertion were reassigned by Kavan et al. as Faradic pseudocapacitance associated with trace humidity: a dry cell with none of these peaks was exposed to air and the peaks could be seen to appear (Figure 2.10).

![Figure 2.10](image)

**Figure 2.10** TR-SWCNT: Cyclic voltammogram on Pt electrode in 0.2 M LiClO$_4$+ acetonitrile (water content 10 ppm), scan rate 0.1 V/s. (Curve 0) Blank Pt electrode. (Curve 1) Freshly assembled cell measured in a drybox. (Curves 2 and 3) The closed cell removed from a drybox and exposed to air for 1 day (2) or 3 days (3). TR-SWCNT weight 0.036 mg [45].

Strano et al. found that following the acidification of solutions containing surfactant dispersed SWNTs, H$^+$ ions react with the nanotube’s sidewalls, hence localising the valence electrons of the nanotubes [46]. This localisation was measured by a loss of absorption intensity for transitions corresponding to the first van Hove singularity, the quenching of fluorescence from the nanotubes, and the reduction in the RBMs in the Raman spectrum. Interestingly, this reaction was only seen to take place in the presence of air. It is proposed by Strano that the O$_2$ catalyses the reaction of H$^+$ with the nanotube side wall. Using this method, metallic tubes were found to react first followed by successive protonation of nanotubes with increasing band gap as the solution is increasingly acidified [46]. Zheng et al. took this work a step further and showed that this pH effect is probably due to the oxidation of SWNTs by dissolved
oxygen at negative potentials and their subsequent reduction at alkaline pHs [47]. Zheng et al. also showed that the reduction potential of carbon nanotubes increased with increasing band gap. Hence, tubes with larger diameter will be reduced first [47].

The absolute potential of the Fermi level in individual, isolated, tubes was estimated to be between 4.1 eV and 5 eV (vs vacuum) from the electrochemical potential dependence of Raman intensity of isolated SWNTs by Okaaki et al. [48]. These values are slightly smaller than previously documented values (4.8 – 5.1 eV, vs vacuum), probably due to the Okaaki’s measurement of individual tubes. Through this work it was found that the work function of a nanotube becomes larger, in a manner inversely proportional to the diameter of the SWNT. The properties of metallic tubes were seen to be more dependent on their size than semiconducting tubes, as measured by the bleaching of the SWNT RBMs; smaller diameter SWNTs were bleached more easily under potential control, indicating that they are easier to reduce, hence have a lower Fermi level.

![Potential energy diagram of the electronic states for individual SWNTs. From left to right: (9, 7), (11, 4) semiconducting nanotubes with diameters 1.10 nm and 1.06 nm respectively and (13, 10), (15, 6) metallic nanotubes with diameters 1.59 nm and 1.49 nm respectively [48].](image)

**Figure 2.11** Potential energy diagram of the electronic states for individual SWNTs. From left to right: (9, 7), (11, 4) semiconducting nanotubes with diameters 1.10 nm and 1.06 nm respectively and (13, 10), (15, 6) metallic nanotubes with diameters 1.59 nm and 1.49 nm respectively [48].
It is well established that as the diameter increases, the band gap decreases. However, Okaaki suggests that as the band gap increases, the absolute Fermi level decreases; in other words, as the diameter increases the absolute Fermi level increases (Figure 2.11). Hence, it is easier to reduce smaller diameter metallic and semiconducting tubes. Although no definitive explanation is given in this paper, it is proposed that \( \sigma-\pi \) mixing increases with decreasing SWNT diameter, leading to a downshift of the Fermi level [48]. It is also proposed that the difference in the mixing ability of metallic and semiconducting tubes accounts for the differences seen in the Fermi levels. This Fermi level change was seen for individual tubes; when bundles of tubes were studied by the same method, no dependence on diameter of the Fermi level was seen, presumably as the work function is averaged across the bundle [49]. As shown previously, individual, narrow diameter tubes required a more positive bias for oxidative doping than large diameter tubes, but the bundled tubes were found to have a consistent Fermi energy [49]. This difference in the Fermi level for different SWNTs has ramifications for the author’s work (Chapters 6 and 7), in that smaller diameter metallic tubes have a lower Fermi level and therefore are the most easily reduced.

All of the examples listed above use immobilised SWNTs, which play the role of an active electrode. When assessing the properties of SWNTs immobilised on substrates or in bucky papers, the redox properties of the carbon nanotubes might be affected by the close proximity of the conducting substrate or by the inter-tube bundling in the bucky paper. To minimise such interactions and thus truly look at the redox properties of carbon nanotubes themselves, Paolucci et al. studied solutions of isolated SWNTs [50]. There is an inherent difficulty in this approach, as stable
solutions of isolated SWNTs must be produced; to this end, the SWNTs were functionalised with pyrrolidino compounds and dispersed in THF (Figure 2.12).

![Figure 2.12 SWNT functionalised with a pyrrolindo compound [50].](image)

When CV data were collected under dry conditions, using tetrabutylammonium hexafluorophosphate (TBAH) in tetrahydrofuran as the electrolyte and a SCE reference electrode, the current density increased monotonically with overpotential (Figure 2.13).

![Figure 2.13 CV curves for saturated THF solutions of SWNTs where current density is measured as a factor of overpotential. Data collected at 1Vs⁻¹ and 295 K. Working electrode Pt disc of 5 mm diameter. Double-headed arrows represent the energy band gap for a series of (n,m) SWNTs. Potentials are referred to SCE [50].](image)
This behaviour is associated with the progressive filling of the empty electronic states (cathodic branch) or emptying of filled states (anodic branch) of the SWNTs. At higher overpotentials (-1.1 V and +1.3 V), the sharp increase in current relates to the increase in the proportion of different nanotube types which are able to be reduced/oxidised [50]. Although it is briefly mentioned in this paper, very little heed is given to the fact that the dispersion protocol uses functionalisation which inherently destroys the electronic properties of the tubes. It has been previously discussed by Goldsmith et al. that just a few functionalisation sites greatly affect the properties of the tubes [51] (Section 1.6). It is therefore quite probable that the functionalisation affects the individual properties of the SWNTs.

### 2.4.3 Electrochemical Functionalisation

As well as studying the fundamental electrochemical properties of SWNTs, electrochemistry has also been used to functionalise the tubes. The first example of such work, by Bahr et al., used a bucky paper working electrode for the electrochemical reduction of aryl diazonium salts [52]. It was found that small diameter SWNTs (less than 0.7nm) were functionalised first, due their higher reactivity attributed to their higher curvature strain. Functionalisation of SWNTs in this manner with bulky salts also increases the solubility of SWNTs in organic solvents [52]. Although it is highly likely Bahr also preferentially functionalised metallic SWNTs, no mention of this is given; the Raman data shows only the excitation of semiconducting SWNTs.

Other papers showed different examples of how radical species could be produced at the surface of the nanotube by electrochemistry. These radical species then attach to the carbon lattice. Importantly, these reactions were shown to work under both
anodic and cathodic conditions depending on the coupling agent used [53]. Balasubramanian et al. furthered this work by comparing the D/G ratio in the Raman spectrum following the electrochemical coupling. No increase in the relative intensity of the D-band in the oxidative case was found; hence, the SWNTs were assumed to be coated with a polymeric layer without forming covalent bonds. In the reductive case, the D-band was seen to greatly increase, implying that chemical bonds were formed. This distinction indicates that SWNTs are more easily reduced than oxidised [54]. Wang et al. demonstrated electrochemical nitration of SWNTs by performing CV of a SWNT bucky paper in an aqueous solution of potassium nitrite [55]. The nitro groups were intended to hydrogen bond to organic polymers to form nanocomposites with potentially enhanced mechanical strength.

In their 2007 Science paper, Goldsmith et al. showed that SWNT conductance could be used to as a real time indicator of functionalisation [51]. Individual SWNT circuits were fabricated and electrolytes containing a variety of different compounds were tested. In every electrolyte tested, the conductance was stable across a range of different electrochemical potentials, but after a certain oxidative threshold (different for each electrolyte studied), reaction occurred and the conductance decreased to zero. Due to the 1D conductance of the SWNT only a small number of modification sites are needed to greatly affect the conductance. Oxidation in bases and weak acids was found to be electrochemically irreversible whereas oxidation with strong acids is essentially reversible. Using the devices fabricated during the course of Goldsmith’s research, the redox behaviour was found to be indistinguishable for semiconducting and metallic tubes, the conductance decreased to zero at the same applied voltage of both types of tubes, probably due to the liquid gate being very effective at moving the Fermi level into the valence band at the large oxidative potentials used. After the
electrochemical functionalisation, it appeared that ethers, rather than the expected carboxylic acid groups, were the primary surface functionality [51], a result that is also seen by Tran et al. [56].

The redox properties can also be used to functionalise SWNTs even if no direct electrical current is applied. Choi et al. showed that SWNT spontaneously reduce metal nanoparticles, which were then deposited onto the SWNT surface [57]. Using metal ions known to have different reduction potentials, the redox potential of an individual SWNT was found to be +0.5 V vs the standard hydrogen electrode (SHE) which is in rough agreement with the redox potential found by other means [58]. This method could template pure metal nanowires by removing the SWNT by oxidation [57]. Using the process described by Choi [57], only metal ions with a reduction potential higher than the carbon nanotubes can be reduced onto the nanotube surface; this process allows gold and platinum to be deposited but not Cu$^{2+}$ or Ag$^+$. Qu et al. overcame this problem by supporting the nanotubes on a metal substrate with a lower reduction potential than the metal ion to be reduced into nanoparticles [59].

Metal catalyst particles, present in the SWNT sample after synthesis, are also known to influence the electrochemical response of carbon nanotubes; iron impurities were shown by Kruusma et al. to oxidise to Fe$_3$O$_4$ which can be seen in the electrochemical oxidation of hydrazine and the electrochemical reduction of hydrogen peroxide [60]. This data shows the importance of purification of the SWNTs before the redox process are investigated.

SWNTs grown on an inert support can also be used as an electrode material with very low background currents. This result opens up the possibility of applying SWNTs as trace level CV electrodes [61-64].
Carbon nanotube based chemically-modified microelectrodes can be used in biosensor electronic applications. Randomly dispersed arrays of SWNTs increase the efficiency of redox reactions. If large biomolecules are physically-adsorbed or covalently-immobilized onto the SWNTs, direct electrical communication between electrodes and the active site of redox-active enzymes can be achieved, thus allowing the development of enzyme biosensors without mediators [65].

2.4.4 Electrochemical Dissolution

Research into SWNTs is hampered by the minimal or complete lack of solubility in common organic solvents. Hence it has been a long standing goal to produce homogeneous dispersions of SWNTs. To this end Kim et al. used an electrochemical method to disperse carbon nanotubes in nitric acid. Bias voltages between 0.4 and 1.1 V were passed through a thin film of purified SWNTs. These nanotubes were then dispersed in the nitric acid electrolyte via NO₃⁻ intercalation to form a good dispersion of carbon nanotubes. It was found that heat treatment could remove these intercalated NO₃⁻ groups [66].

2.4.5 Electrochemical Purification

Fang et al. used electrochemistry to purify SWNTs [9]. By using a SWNT working electrode consisting of the nanotube sample sandwiched between two platinum webs, CVs were run from -1.3 to 0.78 V in potassium hydroxide. This process removed amorphous carbon and exposed the metal catalyst particles which could be removed by a subsequent HCl wash. They found redox peaks associated with the Fe and Ni impurities and by looking at the intensity change in these peaks, the end of the purification could be observed [9].
2.4.6 Electrochemical Deposition

Abe *et al.* produced thin films of SWNTs from well-dispersed SWNT solutions (made by sonicating SWNTs in H$_2$SO$_4$/HNO$_3$ to make them hydrophilic, washing them to remove the acid, and redispersing them in anhydrous N,N-dimethylformamide) by passing a DC electric field of 1.5 V between two conducting substrates placed a few millimetres apart within the SWNT solution. Using this highly efficient electrodeposition method, uniform films could be produced with a thickness ranging from a few hundred nanometres to a millimetre, on various conducting substrates at room temperature without involving any other material [67]. No data is given in this paper to see if the film is representative of the starting SWNT solution or if a certain type of SWNT would be deposited (as expected and utilised by the author in this thesis).

2.4.7 Conclusions

Due to the large number of different diameter nanotubes present in any given sample, research into their redox behaviour is fundamentally difficult. Using SWNT bucky paper working electrodes, some groups have identified broad redox peaks present in the sample. Electrochemistry is often used more to functionalise, disperse, and purify the SWNTs and further research must be undertaken into the fundamental properties of individual and bundled SWNTs before the redox behaviours can be fully understood.
2.5 Separation by Electronic Properties

2.5.1 Need for Separation

Current synthesis methods produce bundles of SWNTs with many different diameters and chiralities [68] (the electronic properties of SWNTs are discussed fully in Sections 1.5 and 1.6 [69]). This heterogeneity limits many potential applications of carbon nanotubes. Therefore, before the excellent electronic properties of carbon nanotubes can be used to their full potential; in molecular electronics, optoelectronic and molecular sensing [70], there must be made available a cheap and scalable approach that allows for separation of nanotubes by their electronic character. The importance of being able to separate the different SWNT types for the future prospects of the material should not be underestimated. For example, semiconducting tubes must alone be used to produce good field-effect transistors since any metallic tubes present will short the device. On the other hand, metallic nanotubes must alone be present if low resistance materials for transparent conductors are to be produced [71]. Separation by (m,n) values is highly desirable, but even separation into metallic and semiconducting fractions would be extremely beneficial.

The post production separation of metallic and semiconducting nanotubes has received a lot of interest in the last few years with many groups pursuing this goal, using various strategies based on either physical; dielectrophoresis [72], density gradient ultracentrifugation [70] and chromatography [73], or chemical; diazonium salts [71, 74], ozonolysis [75], ‘nano tweezers’[76], reduction with sodium and subsequent alkylation [30], amine functionalisation [68, 77, 78], controlled electrical breakdown [79], Br functionalisation [80] and pyrene functionalisation [78], means. It should also be noted that a number of groups (such as Li [81] and Lolli [82]) went right back to the synthesis methods to try and produce samples with a high degree of
particular nanotubes, thus providing synthetic separation. More details on all of these current separation techniques are given below.

### 2.5.2 Selective Synthesis

The first, and still most successful selective synthesis came with the development of the CoMoCAT process [82, 83]. In this chemical vapour deposition (CVD) process, a highly selective cobalt and molybdenum catalyst induces tight diameter control; Lolli *et al.* showed that samples of specific chiralities could be produced by varying the reaction temperature, gaseous feed, and the catalyst support used [82]. Commercially, South Western Nanotechnologies (SWeNTs) produce these CoMoCAT SWNTs, containing mostly semiconducting (6,5) nanotubes; they are produced using a high temperature (about 800°C), a SiO$_2$ catalyst support and CO feed gas [82, 84]. Li *et al.* also showed a selective synthesis method for (6,5) tubes [81]. Using a bimetallic FeRu catalyst during methane CVD they showed that they could predominately produce the (6,5) tubes at the lower temperature of 600°C. By increasing the temperature to 850°C they found that the dominant semiconducting species were (8,4), (7,6) and (7,5) [81]. In both the Lolli [82] and Li [81] cases, although the samples contained predominantly semiconducting tubes, metallic tubes were also observed. It is tempting to think that these selective synthesis methods will continue to improve until complete control over the particle size of the catalyst will be obtained and hence just one type of SWNT can be grown. The likely futility of such an approach comes to light when considering that the difference in diameter of the (10,10) metallic and (9,11) semiconducting tube is only 0.03 Å. Most likely, the variation in thermal energy at the temperature required for growth will always tend to
produce mixed products even from identical catalyst particles [80]. Hence, the post synthesis separation methods are likely to remain of critical importance. However, it is impossible to rule out radically different synthetic approaches that might emerge in the future.

2.5.3 Physical Methods of Post Synthesis Separation

2.5.3.1 Dielectrophoresis

Alternating current dielectrophoresis has been shown to separate metallic and semiconducting nanotubes in suspension [72]. This method takes advantage of the difference of the relative dielectric constants (or polarisability) of the two species with respect to the solvent. Using this method, metallic nanotubes were attracted to a microelectrode array whilst the semiconducting tubes remained in the solvent [72]. Although this method produces reasonably well enriched metallic samples (roughly 80% enrichment), the method is limited by the high cost of the microelectrode, the very small sample size, and problems associated with producing good quality initial solutions. Further work has shown that, by varying the electric field frequency, either semiconducting or metallic SWNTs can be deposited [85]. In conjunction with other methods, dielectrophoresis has been used to create very small quantities of almost chirality pure SWNTs. A version of this method is also used to generate single SWNT devices directly.

2.5.3.2 Density Gradient Ultracentrifugation

Density gradient ultracentrifugation sorts carbon nanotubes by both their diameter and electronic type. This approach utilises the differences in the buoyant densities (mass per volume) among different SWNT structures. During ultracentrifugation, the
centripetal force sediments the SWNTs towards their buoyant densities and spatially separates them in the gradient [70]. Through initial surfactant wrapping of the SWNTs, Arnold et al. showed different fractions of nanotubes could be obtained [70]. However, once again, a good dispersion of nanotubes must be produced before centrifugation. Also, only after multiple cycle ultracentrifugation is significant separation by electronic properties seen. This extensive use of ultracentrifugation will hinder the commercial viability of this process due to its costly and time consuming nature.

Preliminary wrapping of the SWNTs in DNA before ultracentrifugation was undertaken previously by Arnold et al. to produce SWNTs separated by diameter [86]. This method, using DNA, showed no separation by electronic properties and the costly nature of DNA, and the problem of removing it following the diameter separation, implies limited use for this method.

2.5.3.3 Gel Electrophoresis and Chromatography

Heller et al. used gel electrophoresis and column chromatography to yield fractions of carbon nanotubes separated simultaneously by both diameter and length [73]. Sonication was used to cut a sample of HiPCO SWNTs into various fractions. It was found that sonication cuts nanotubes in proportion to the time of ultrasonic treatment. Gel electrophoresis separates nanotubes primarily by length, as the shortest nanotubes move most quickly through the gel. It was also found that shorter nanotubes also process a 30% larger diameter than the as received sample. This trend was also found using column chromatography. This trend is counterintuitive and actually is the opposite to that found by other groups; Heller suggested that larger diameter tubes were more easily cut because they contained more inherent defects from the synthesis.
process, or that smaller diameter tubes are less prone to the mechanical cutting of sonication due to the extra stability imparted by the end caps [73].

2.5.4 Chemical Methods of Post Synthesis Separation

2.5.4.1 Diazonium Salts

In 2003, Strano et al. showed that diazonium salts selectively functionalise metallic over semiconducting tubes suspended in aqueous solution [74]; the reaction mechanism is seen in Figure 2.14.

![Figure 2.14](image)

**Figure 2.14** A) Diazonium reagents extract electrons, evolve N₂ gas and leave a stable C-C covalent bond with the nanotube surface. B) The extent of electron transfer is dependent on the density of states in that electron density near E_F leads to higher initial activity for metallic nanotubes. (C) The arene-functionalized nanotube may now exist as the delocalized radical cation, which could further receive electrons from neighbouring nanotubes or react with fluoride or diazonium salts [74].

This predominant functionalisation of metallic tubes is due to the availability of electrons near the Fermi level to stabilise a charge transfer transition state preceding bond formation. After the selective functionalisation, a simple heat treatment in inert gas removed the aryl compound from the sidewall of the nanotube therefore restoring the properties of the nanotubes [74]. Although the obvious selective functionalisation could be seen in this Science paper, no real attempt was made to separate the metallic from semiconducting tubes.
In 2006, Kim et al. showed that selective diazonium salt functionalisation could be taken one step further to actually produce SWNT samples enriched with metallic nanotubes [71]. This step was achieved following the diazonium salt functionalisation, by deprotonation in alkaline solution to induce a negative charge on the SWNT which then could be separated by electrophoretic means [71]. This method is limited by small sample sizes and the need to functionalise the SWNTs before any separation can be undertaken.

2.5.4.2 Ozonolysis

Banerjee et al. showed that smaller diameter SWNTs were shown to react preferentially in ozonolysis reactions. The effect is attributed to the high curvature of the outer convex surface, causing the hybrid-\pi orbitals on the tubes exterior to become exposed, therefore allowing bonding with incoming addends more easily [75]. Although this method shows good diameter selectivity it shows no electronic selectivity.

2.5.4.3 Nano Tweezers

Nano Tweezers have been used to separate SWNTs by their chirality. Peng at al. showed that chiral ‘gable-type’ diporphyrin molecules bind with different affinities to left and right handed helical nanotube isomers to form complexes with unequal stability [76]. These complexes can then be readily separated. Samples of optically active SWNTs were obtained by extracting either the left or the right handed SWNTs [76]. Although this separation method is relatively simple and works very well at separating isomers, no separation of SWNTs by their electronic properties was reported. Although not discussed in detail in this thesis, the need to separate
nanotubes by their chirality is an interesting problem and the theory behind it is discussed by Strano in his 2007 *Nature* note – ‘sorting left from right’ [87].

### 2.5.4.4 DNA Wrapping

Zheng *et al.* found that SWNTs could be dispersed in water when they were sonicated in the presence of single stranded DNA. DNA binds to carbon nanotubes through π-stacking, resulting in helical wrapping of the surface (*Figure 2.15*) [88].

![Figure 2.15 Model of a SWNT wrapped by DNA. The bases (red) orient to stack with the surface of the nanotube, and extend away from the sugar-phosphate backbone (yellow). The DNA wraps to provide a tube within which the carbon nanotube can reside, hence converting it into a water-soluble object [88].](image-url)

These dispersed carbon nanotubes can then be separated into fractions with different electronic structure by ion exchange chromatography. When the DNA attaches to the SWNTs the phosphate groups on the DNA create a negative charge density on the SWNT surface. Metallic tubes elute first from the anion exchange column because of their reduced effective charge [88].
2.5.4.5 Bromine Functionalisation

Chen et al. found that Br functionalisation followed by high speed centrifugation can enrich either metallic or semiconducting SWNTs [80]. Just as in the case of the diazonium salts, the metallic SWNTs were found to react with the Br first due to easier charge transfer between the bromine and the nanotube. It was found, after high speed centrifugation, that the more highly functionalised metallic tubes collected in the sediment whereas the less functionalised semiconducting tubes stayed in the supernatant and could be removed [80]. Although this method is interesting, only enrichment, not separation was reported.

2.5.4.6 Controlled Electrical Breakdown

Collins et al. produced devices containing purely semiconducting nanotubes by using current-induced electrical breakdown to eliminate individual metallic SWNTs [79]. They connected a rope of SWNTs between two electrodes and by appropriate biasing, a large current was generated though the metallic tubes, leading to their oxidation and destruction, leaving behind just the semiconducting SWNTs [79]. This method is effective for generating simple devices containing solely semiconducting nanotubes, for applications such as field effect transistors, but it is not viable as a bulk separation method.

2.5.4.7 Amine Functionalisation

Density functional theory gave rise to the suggestion that amines will be more strongly absorbed onto metallic than semiconducting nanotubes [89]. Maeda et al. took advantage of this suggestion in his 2005 paper in JACS where it was shown that it was possible to concentrate metallic HiPCO nanotubes by first dissolving them in a
tetrahydrofuran solution of amine, where the amines would be more strongly absorbed onto the metallic tubes [68]. Centrifugation was then used to pull out the semiconducting tubes with only weak amine attachment, leaving the metallic tubes in the supernatant solution. By measuring the change in RBMs, a sample containing 87% more metallic nanotubes than the as-received sample was produced by repeatedly undertaking the dispersion-separation process (it should be noted that for reasons outlined in Section 3.6, giving an absolute value to the metallic enrichment is highly unreliable) [68]. Following on from this paper, in 2006, Maeda went on to show that the same process also works for CoMoCAT SWNTs [77]. Also in 2005, Kim et al., undertook a study of the underlying mechanism involved in the amine functionalisation of preferentially metallic SWNTs. He discussed the influences of redox processes on the separation, which is more fully discussed in Chapter 2.4 [90].

### 2.5.4.8 Pyrene Functionalisation

Wang et al. showed that metallic nanotubes could be separated from their semiconducting counterparts by the use of 1-docosyloxymethyl pyrene as a planar aromatic agent [78]. This pyrene preferentially functionalised the semiconducting SWNTs which were therefore solubilised; the insoluble metallic fractions being removed by centrifugation. The metallic fraction was then incorporated into conductive polymer thin films and shown to significantly increase the conductive properties [78].
2.5.4.9 Reduction with Sodium and Subsequent Alkylation

The 2008 paper by Wunderlich et al. is the first paper to conduct a selectivity investigation into reductive alkylation [30]. The paper itself is discussed in full in Section 2.3. However, from a separation perspective, during the reduction with sodium metal in liquid ammonia and the subsequent alkylation, SWNTs with either smaller diameters and/or metallic character react preferentially. Interestingly, the diameter dependence weakened and the electronic dependence disappeared, if hydrogenation, rather than alkylation, was the chosen reaction following nanotube reduction. The preferred reduction of metallic tubes is expected due to the accessibility of the empty density of states just above the Fermi level. The preferred functionalisation of the small diameter SWNTs has been attributed to their higher degree of pyramidalization, which stabilises the negative change [30]. The work shown in the liquid ammonia reduction chapter (Chapter 5) of this thesis also shows this type of selectivity.

2.5.5 Conclusions

There have been many different methods shown to separate SWNTs by their electronic properties with varying degrees of success. Selective synthesis has yet to provide samples of one SWNT type, whilst post synthetic methods are marred by high costs and problems with scalability. Currently the best method for separation without property degradation, is probably density gradient centrifugation, although the quantities used are tiny. The literature has failed, as of yet, to find a fully repeatable, reliable and scalable approach to SWNT separation which preserves their unique structure.
2.6 References


3 Analytical Techniques

3.1 Introduction

A wide range of analytical techniques are currently employed in the study of SWNTs. Most of these techniques are common in the broader chemistry field but they are limited by or adapted to the nature of the SWNTs. Individually, the analyses give limited information about the structure, morphology and purity of a given SWNT sample. However, when used in conjunction with one another, much qualitative information can be obtained. Quantitative standardisation measurements still remain elusive, although it is the subject of considerable effort [1].

The problems encountered with the purification and dispersibility of SWNT samples, as discussed in Chapter 2, also present particular difficulties when undertaking most current analytical techniques. It is often difficult to establish whether the measured properties relate to the SWNT themselves, or to the impurities present within the sample. The subtle variations of SWNT properties can also be difficult to distinguish from the background in many techniques. The low dispersibility of SWNT samples greatly hinders many analytical techniques (such as UV/Vis/NIR, TEM, AFM and photoluminescence) and completely prohibits other techniques such as Mass Spectrometry (MS) which rely on good dispersion to provide accurate results. The metallic nature of the tubes and the impurities contained within them (metal catalyst particles) also prohibit Nuclear Magnetic Resonance (NMR) measurements.

This chapter briefly outlines each commonly used analytical technique, including Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), Raman Spectroscopy, Thermogravimetric analysis (TGA), UV/Vis/Near-
Infra Red Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Photoluminescence Spectroscopy (PL), Cyclic voltammetry (CV) and Zeta Potential.

3.2 Atomic Force Microscopy

The AFM technique was invented in 1986 by Binnig, Quate and Gerber [2]. It is a useful technique for analysing the morphology and purity of SWNTs. Using AFM it is possible to measure the diameter and lengths of SWNTs and qualitatively assess the content of impurities contained within a sample [3]. The AFM is a scanning-proximity probe microscope which operates by measuring the forces between a tip and a sample placed nearby [4]. As the tip, which is attached to a cantilever, is moved over the sample, it flexes, and this flexing is measured by reflecting a laser beam off the cantilever onto a split photo diode [5].

For delicate samples such as SWNTs, tapping mode AFM is used. Using tapping mode, the tip is alternately placed in contact with the surface and then removed, to avoid problems associated with friction, adhesion, electrostatic forces and other difficulties that plague conventional AFM scanning methods. During tapping mode AFM, a piezoelectric crystal drives oscillation of the tip near its resonant frequency. When the tip passes over a bump in the surface, the cantilever has less room to oscillate, and the amplitude decreases. Conversely, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases, approaching the maximum free air amplitude. It is from this change in amplitude that tapping AFM images are produced. More information on the inner workings of the AFM can be found in S. Cohen’s book Atomic Force Microscopy/scanning tunneling microscopy [5]. Unlike traditional microscopes, scanned-probe systems do not use lenses. Therefore, the size of the probe, rather than diffraction effects, limits the
resolution. It should be noted at this point, that because the tips are not atomically sharp, the horizontal dimensions of features narrower than the AFM tip itself are often misrepresented in the images and the images can be spatially convoluted [6].

A typical AFM of a SWNT sample is shown in Figure 3.1, where the lighter the colour of the image, the higher the feature on the surface of the sample.

![Figure 3.1 A typical AFM image, Image size (x,y): 1.1µm x 1.1µm, z scale:0-5nm [7].](image)

A Nanoscope IV Digital Instruments AFM machine was used by the author to produce all AFM images, using phosphorous doped silicon tips (Veeco). A scan rate of 1 Hz was used with 256 sample lines with the reverse trace used to produce the images.

Samples are usually prepared for AFM by dispersion in a suitably volatile solvent followed by spin coating onto an atomically flat surface. Unless otherwise stated in the methodology, AFM samples were prepared by sonicating approximately 1 mg of dry SWNT material in 5 mL 1,2-dichlorobenzene for 5 minutes then leaving to stand overnight. The supernatant solution was then decanted and over the course of 30
seconds, 10 drops were spin-coated onto a freshly cleaved mica surface, and the sample span at 8000 rpm for another 2 minutes. This surface was then immobilised on a metal puck using double sided sellotape. This method of sample preparation relies heavily on the quality of the initial dispersion, in providing an accurate picture of the true content of the sample.

3.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a very powerful technique for imaging SWNTs. Most TEM machines have a resolution down to ~0.2 nm, allowing individual SWNTs to be imaged. Using TEM it is possible to clearly see the structure, morphology and purity of SWNT samples. The images obtained are able to show the impurities present in a SWNT sample, both wrapped round the SWNTs themselves and contained within the sample as a whole. Figure 3.2 shows a TEM image that includes both the nanotube walls and the amorphous carbon [3, 8, 9].

![Figure 3.2](image)

**Figure 3.2** A TEM image of two double walled carbon nanotubes (DWNT) which show the individual tube walls along with the amorphous carbon.
The walls can be seen as lines of contrast: both SWNTs in the example below are laying flat on the surface of the supporting grid, and can be seen as lines running diagonally along the image.

A TEM works by shining a beam of (more or less) monochromatic electrons through a specimen. Whatever electrons are transmitted through the specimen are projected onto a phosphor screen allowing the image to be seen by the user and detected by a CCD camera. For information about the complexities of contrast formation in different imaging modes see the excellent series of books by Williams and Carter entitled *Transmission Electron Microscopy. A Textbook for Materials Science* [10].

High resolution TEM, used for SWNT imaging, is also known as phase contrast imaging as the contrast is due to differences in the phase of electron waves scattered through the thin specimen. The exact image formation mechanism in phase contrast imaging is somewhat complex and some care should be taken over the interpretation of the images. However, in most images the darker areas can be taken as the graphite walls [10-13]. All TEM images are bright field images taken using a JEOL JEM 2010 operating at 200 kV by Ben Cottam or Richard Winchester.

Just as for AFM, TEM samples were first prepared by producing a solution of SWNTs by sonication in a suitable solvent (such as 1,2-dichlorobenzene, THF or DMF). A drop of this solution is then placed onto a holey carbon film (300 mesh copper grid, *Agar*) and left to dry over night. Once again, the quality of the initial SWNT dispersion will greatly affect what information can be gleaned from the sample. Another problem of using TEM to image SWNTs, is that the SWNT structure can be destroyed by the electron beam, so any high resolution images must be taken quickly and with great care. Ideally 120 kV, instead of 200 kV, should be
used when imaging SWNTs, however this condition was not always possible on our microscope set up.

To achieve statistically significant TEM data, a large number of images must be taken at different magnifications and as many different areas of the sample should be sampled as time and money constraints will allow.

3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) can be a useful analytical technique for imaging SWNTs. However, an image created by SEM is not of high enough resolution to enable individual SWNTs to be resolved from bundles, although, individually separated tubes can be imaged. A typical SEM image can be seen in Figure 3.3.

Figure 3.3 Two SEM images of SWNTs produced by Thomas Swan and purified using acid reflux and base washing (see Chapter 4 for more details) at two different magnifications.
The principles underlying the SEM are similar to TEM in that an electron beam is directed at the specimen. However, the method of creating an image has more in common with the AFM, as the electron beam is rastered across the sample, instead of passing through it. The image is usually formed by collecting the secondary electrons that are generated when the primary beam hits the sample. However, the image can also be generated using the signal from backscattering of the primary beam [3, 4, 9, 14].

All SEM images were taken using a LEO Gemini 1525 FEGSEM by Raquel Verdejo Marquez and Boris Thomas. The samples were prepared by fixing a small amount of sample to SEM pin stubs with silver paint. This approach provides a more statistically significant view of the sample than TEM or AFM, as larger areas can be easily examined with no potentially selective liquid phase dispersion step required.

### 3.5 Fourier Transform Infrared Spectroscopy

A simple Infrared (IR) spectrum is obtained when a photon of infrared radiation is absorbed and a molecule is promoted to a higher vibrational state. By measuring the IR intensity that passes through without being absorbed, a spectrum can be recorded. An FTIR spectrometer makes use of the interference effects between two rays from a broad band source and detects an interferogram, a signal that oscillates in time [15].

FTIR spectra can show information about functional groups which are attached to the surface of SWNTs. However, good FTIR spectra of SWNTs are very difficult to obtain as the SWNTs absorptions are broad and the concentration of functional groups are low. In addition, the high absorbance (blackness) of SWNTs means that samples containing enough SWNTs to assess their functional groups often do not allow
enough IR radiation to be transmitted for a spectrum to be recorded. Samples need to be produced that give a high signal to noise ratio.

In this study, all FTIR spectra were taken using a Perkin-Elmer 1720 machine. FTIR samples were prepared by grinding a small amount of sample into 0.2 g of pre-ground potassium bromide (KBr) powder and then drying in a vacuum oven overnight (at 150°C and 76 cmHg). The samples were then pressed into a pellet 1 cm in diameter at a load of 9 tonnes for 15 minutes. This method of sample preparation was shown to produce the best FTIR spectra. However, producing totally uniform samples of individual SWNTs is difficult and reproducibility is a common problem.

### 3.6 Raman Spectroscopy

Raman spectroscopy is one of the most powerful tools for the characterisation of SWNTs. It is a fast and non-destructive method of sample analysis. Raman scattering in nanotubes results from the inelastic scattering of light from the nanotube, leading to an increase or decrease in the energy of the incident light due to an emission or absorption of a phonon present in the nanotube [3]. A typical Raman spectrum of a SWNT sample is shown in Figure 3.4. A review of the electronic properties of SWNTs is given in Section 1.6.1 and understanding these properties is key to the interpretation of SWNT Raman spectra.

The radial breathing modes (RBM) of the SWNT can be seen at ~200 cm$^{-1}$ (Figure 3.5). These RBMs occur due to the symmetric in-phase displacement of the carbon atoms in the radial direction. From the position of these peaks, the size of the SWNT can be determined, since this peak frequency is inversely proportional to diameter; the higher the frequency of the peak, the smaller the size of the SWNTs [16, 17].
Figure 3.4 A typical SWNT Raman spectrum, obtained by the author, of SWNTs as-received from Carbon Solutions, using a red (633 nm) laser.

Many different research groups have modelled the exact relation between the RBM frequency and the diameter of the SWNT. Although each model produces slightly different equations for this correlation, Equation 3.1 is the most commonly used, where \( d \) is the diameter of the SWNT in nm and \( \omega_{rbm} \) gives the frequency of the RBM in cm\(^{-1}\).

\[
\omega_{rbm} = \frac{214.4}{d} + 18.7
\]

Equation 3.1
Many RBMs overlap with one another, so often the diameter associated with a given peak can occur as a range instead of a discrete value.

The Defect band (D-band) is seen at about $\sim1350$ cm$^{-1}$ and the Graphite band (G-band) is seen at $\sim1580$ cm$^{-1}$. The D-band is observed when there is a symmetry-breaking perturbation on the hexagonal sp$^2$ bonded lattices for graphite and nanotubes, and it is therefore associated both with defects in the tubes themselves, and graphitic impurities within the sample as a whole. The G-band is associated with the tangential vibrational modes in the SWNTs. The line shape of the G-band can give insight into the type of nanotubes within the sample. The G-band of metallic SWNTs is not symmetrical and can be fitted to a Breit-Wigner-Fano (BWF) line shape. We observe this shape when the electronic density of states at the Fermi level has a finite value; therefore it is only seen for metallic tubes. The G-band of metallic tubes contains two features: a $G^+$ (peaked at $1590$ cm$^{-1}$) feature associated with carbon atom vibration along the nanotube axis, and a $G^-$ (peaked at $1570$ cm$^{-1}$) associated with vibrations of carbon atoms along the circumferential direction [18].

The relative intensity of the G/D bands gives an indication of the purity of the sample, as the D-band is associated with disordered carbon and the G-band in associated with the in plane vibrations within the graphite layer. The band at $\sim2700$ cm$^{-1}$ is called the D* or G’ band and is an overtone of the D-band and G-band [3, 8, 16, 17].

Importantly, only a small fraction of a given polydispersed SWNT sample will be excited by a given wavelength. There are a large number of different laser frequencies used to study the Raman spectra, they generally fall into the category of Green ($\sim514$nm, 2.3eV), Red ($\sim633$nm, 1.96eV) or Near-Infrared ($\sim785$nm, 1.58eV). As discussed fully in Section 1.6.1, SWNT tube diameter can be correlated with the diameter dependent transition energies between the van Hove singularities due to the
periodic boundary conditions that are imposed along the rolling vector, resulting in
the Kataura plot (Figure 1.7). This plot shows which SWNTs will be excited by a
given laser wavelength due to the efficiency of resonant energy transfer. It can also
clearly be seen whether metallic or semiconducting SWNTs are excited [3, 19].
Micro-Raman spectra was taken in house using a LabRam Infinity Raman Instrument
using a red laser light at 633 nm with an absolute power of 8 mW at the sample (used
at 100 % power), or a green laser at 514 nm with an absolute power of 42 mW at the
sample (used at 25 % power) or a Renishaw InVia spectrometer equipped with a high-
power 785 nm NIR laser (used at 100 % power) using 50 times optical magnification
with a spot size of the order of 10 microns. Each spectrum was taken using 2 repeats
of 30 second detection times. Unless explicitly stated Raman spectra were taken with
the sample resting on a glass cover slide. In Chapter 6 and Chapter 7 Raman spectra
were also taken following the sample deposition on Platinum or HOPG.
Raman spectroscopy requires almost no sample preparation, so it makes it a good
 technique for quickly assessing the bulk properties of the sample. The only important
consideration is that the samples must be dry and free of fluorescent contaminants to
achieve the best spectra. Although Raman spectroscopy of solutions is very common
in chemistry, when dealing with SWNTs, any method that requires a good, uniform
solution to be made in order for reproducible and significant results to be obtained
must be treated with caution. Hence, Raman spectra of the solid SWNTs are often
used to produce good, reproducible results which are statistically significant, due to
the large spot size exciting many nanotubes in a relatively large area, especially when
multiple laser lines are used in conjunction with one another.
3.7 Thermogravimetric Analysis

TGA is often used in SWNT research as a simple and relatively inexpensive way to assess the stability of SWNTs to combustion (if heated in air) or the functional group content of the SWNTs (if heating in an inert gas such as nitrogen). Differences in combustion rate and the remaining ash are also used to assess the purity and residual metal catalyst content within the sample, respectively.

The TGA accurately weighs the mass of a sample as the temperature of the sample is increased, under a controlled atmosphere, and hence produces a plot of percentage weight change versus temperature. TGA is commonly undertaken in either air or pure nitrogen but other gases can be used [20-22].

Higher SWNT oxidation temperatures are usually associated with purer, less defective samples. It should be noted that small SWNTs will oxidise at a lower temperate due to their high curvature strain [23].

All of the TGA experiments were carried out using approximately 1 mg of sample in a Perkin Elmer Pyris 1 TGA using a heating rate of 10°C/min from 50-800°C in air. It was found to be important to use a consistent initial sample mass to obtain reproducible results. As the oxidation temperature is known to depend on heating rate, the heating rate was kept constant throughout all of the experiments. In all samples the oxidation temperature was taken as the maximum in the derivative weight curve [23].

As TGA can be used to evaporate solvent from a given sample to assess solubility it requires very limited sample preparation. Dry samples were most often used in this thesis, as the easiest means to control the weight of SWNT material used. Although the solvent can be easily evaporated from the sample by holding the sample at an appropriate temperature until no further weight loss occurs. TGA is a very useful
technique in SWNT research as its highly controllable nature and large sample size offer a higher degree of reproducibility.

3.8 UV/Vis/Near-Infrared Spectroscopy

UV/Vis/Near-IR spectroscopy can be used to probe the van Hove singularities in the electronic density of states of SWNTs (Figure 3.6). As with Raman spectroscopy, an understanding of the electronic properties of SWNT is essential in understanding UV/Vis/Near-IR spectra (see Section 1.6.1). The interband transitions in the electronic structure of SWNTs can be seen when the energy of the incident light matches the transition between two peaks in the van Hove singularities that are mirrored. The peaks will only be clearly resolved when the SWNTs are debundled. Hence, UV/Vis/Near-IR spectroscopy can be used qualitatively to indicate that there are individual, debundled SWNTs within a given sample. SWNT suspension stability can be measured by comparing the area under a given SWNT peak with the baseline [23]. These interband transitions can also only be seen when the SWNTs are not functionalised; the conversion of significant numbers of sp² to sp³ carbon atoms destroys the confinement of electrons in the circumferential direction [24]. Lack of peaks in the UV/Vis/Near-IR spectra is often used to infer functionalisation [25, 26]. The difference between the size of a given transition peak and the baseline can also be used as an evaluation of purity [9], although the results are difficult to interpret as they are highly influenced by the concentration of the sample and probably the nature of the SWNTs themselves.

It should also be noted that, just as in Raman spectroscopy, tubes of different chirality and diameter have transitions at different wavelengths. When analysing absorbance data, it is often useful to mark on the area of particular transitions, for example an
“M\textsubscript{11}” label would indicate a transition between the first van Hove singularities of metallic tubes, whereas “S\textsubscript{22}” would indicated the transition between the second van Hove singularities of semiconducting tubes (Figure 3.6).

All spectra were taken using a Perkin Elmer Lambda 950 from 200-2000 nm. All samples were baseline corrected using a control of 1.25 mg of sodium cholate hydrate in 5 ml of deuterated water (D\textsubscript{2}O). The spectra were collected in absorbance mode with a data interval of 1 nm and an integration time of 0.32 seconds. UV/Vis/Near-IR spectroscopy can be obtained either from SWNT films or from SWNTs in solution. Whichever route is chosen, debundled SWNTs must be present in the sample otherwise the interband transitions between the Van Hove singularities will not be clearly seen. Unless explicitly stated in the methodology, samples were prepared by first dissolving, by shaking, 1.25mg of sodium cholate hydrate in 5 ml of deuterated water (D\textsubscript{2}O) then adding 1mg of SWNTs. The mixture was then sonicated using a sonic probe for 5 minutes before being left to stand overnight. After this time,
the top fraction in which no visible particulates could be seen was decanted and it was this fraction that was both used for UV/Vis/Near-IR spectroscopy and photoluminescence measurements. Thus all of the problems with SWNT dispersibility are inherent in this technique. The use of ‘dry’ solvents when undertaking UV/Vis/Near-IR measurements is also of importance, as water has many strong absorbance peaks in this range. Deuterated water is commonly used as a solvent as it has a large solvent window; however, due to the hydrophobic nature of SWNTs, surfactants must be used. As an alternative, N-methylpyrrolidone (NMP) can be used to make a good dispersion of SWNTs via sonication, but its smaller solvent window (only up to 1000 nm) means that it is not the solvent of choice.

3.9 X-ray Photoelectron Spectroscopy

XPS supplies information about the chemical structure of carbon nanotubes [8, 27-29], and is often used to obtain evidence of surface modification, given the difficulties of using more conventional chemical characterisation. It is a very powerful tool for determining the oxygen to carbon ratio within a sample, as well as element bonding environments. It can also show the percentage and bonding environments of other elements contained within catalyst particles or other impurities.

In XPS, X-rays are used to eject electrons from the inner core of atoms. From the kinetic energy of the ejected photons, and the incident X-rays, the core ionization energy of the atom can be deduced. These ionization energies are characteristic of individual atoms rather than overall molecules. However, the molecular environment of the atoms will cause small but detectable shifts in the XPS and therefore the environment of the atoms can, in theory, be deconvoluted [30]. In practice, the low
degree of functionalisation and heterogeneous nature of SWNT samples can cause problems, as discussed in Section 4.2.5.

XPS was obtained with an ESCS300 XPS machine, using a monochromatised AlKα/CrKβ x-ray source (hν = 1486.7/5946.7 eV), selectable aluminium or chromium targets and a high power rotating anode with a maximum power rating of 8 kW. The source was focused into a line 6 mm x 0.5 mm on the sample. Drying of SWNT samples in a vacuum oven overnight (at 150°C and 76 cmHg) is required before XPS is undertaken. All XPS was collected by Mike Tran and Kingsley Ho at the National Centre for Electron Spectroscopy and Surface Analysis at the Daresbury Laboratory.

As XPS is a surface characterisation technique, only atoms up to approximately 3 nm from the surface are probed. Thus, only the properties of the surface of a SWNT bundle are seen, not the bulk properties.

### 3.10 Photoluminescence

In broad terms, photoluminescence (PL) occurs when a molecule is excited by absorbing a photon of similar or lower frequency, depending on the internal relaxation pathway available. As the molecule returns to a lower energy state, it re-emits a photon. In SWNTs, photoluminescence most commonly occurs when a photon is absorbed by the E_{22} band (although it can be absorbed by a higher energy band) and emitted from the E_{11} band (Figure 3.7).
Figure 3.7. Diagram of the photoluminescence process in a SWNT structure. Schematic density of electronic states for a single nanotube structure. Solid arrows depict the optical excitation and emission transitions; dashed arrows denote non-radiative relaxation of the electron (in the conduction band) and hole (in the valence band) before emission [31].

Only semiconducting SWNTs can be seen in photoluminescence since metallic tubes relax fully without emission [32]. PL measurements can be taken in a variety of solvents but individual nanotubes must be present for good PL spectrum to be produced, as the PL of semiconducting SWNTs will be quenched by interaction with metallic tubes. Hence, this technique is even more susceptible to the problems of producing good dispersions than UV/Vis/Near-IR spectroscopy [33]. In 2002, O’Connell et al. and Bachilo et al. both published papers in Science showing, not only the first well-defined PL spectra of individual nanotubes, but that these spectra could then be indexed to different tubes [31, 34]. They show that using the Kataura plot, individual, semiconducting SWNTs in the PL spectra can be assigned. PL is a powerful technique for the assignment of population density of semiconducting SWNTs within a given SWNT sample. A classic example of the PL spectrum seen for HiPCO SWNTs is shown in Figure 3.8. As PL intensity depends on the
population of SWNTs within a sample; the higher the peaks in the spectrum, the higher the population density of the SWNTs.

**Figure 3.8** PL spectra of the author’s HiPCO SWNTs sample.

All PL measurements were collected at the University of Cambridge in collaboration with Tawfique Hasan using a HORIBA Jobin Yvon excitation-emission spectrofluorometer (Fluorolog-3) equipped with a xenon lamp excitation source and an InGaAs detector (Symphony solo) cooled by liquid nitrogen. The PL maps were measured by scanning the excitation wavelength from 440 to 850 nm with 6 nm steps and a 30 s exposure for an emission range from 900 to 1400 nm. The samples for PL measurement were prepared in the same way as for UV/Vis/Near-IR spectroscopy by dissolving, by shaking, 1.25 mg of sodium cholate hydrate in 5 ml of deuterated water (D$_2$O), then adding 1mg of HiPCO SWNTs. The mixture was sonicated using a sonic probe for 5 minutes, before being left to stand overnight.
After this time, the top fraction, in which no visible particulates could be seen, was decanted and used for PL measurements.

3.11 Cyclic Voltammetry

Cyclic Voltammetry (CV) is a useful technique for studying the redox properties of SWNTs. Cyclic voltammetry is a potentiodynamic electrochemical measurement; the voltage applied to a working electrode in solution is swept across a range of values and resulting current plotted, give the cyclic voltammogram. The current flow in a CV cell is limited by the rate in which the electrochemically active species can diffuse towards and away from the working electrode [35]. CV in which the potential is swept in both the negative and positive ranges, is commonly undertaken for substances that have reversible redox chemistry. For example, in the potassium ferrocyanide cell the ferricyanide ion is reduced to ferrocyanide (*Equation 3.2*), hence it produces distinct oxidation and reduction peaks (*Figure 3.9*) [35, 36].

\[
\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-} \quad \text{Equation 3.2}
\]

In this standard reaction couple, the experiment begins at a highly negative potential (A). At this potential, after a suitable period of time, all of the Fe(CN)$_6^{3-}$ near the working electrode will reduced to Fe(CN)$_6^{4-}$ and only small current will pass, as the concentration of reducible species around the working electrode will be low once the CV begins. From this starting point, as the potential is swept towards the standard electrode potential of the couple (E$^\circ$), a larger current will begin to flow (B) as the Fe(CN)$_6^{4-}$ is oxidised back to Fe(CN)$_6^{3-}$. After the value of E$^\circ$ is passed, a maximum will be reached (C) once enough of the iron near the electrode has been oxidised, so that the reaction will be limited by molecular diffusion to the electrode surface. The
diffusion limit means that the current becomes small at high positive potentials and when the current reaches a plateau (D) the cell is swept back to negative potentials. The same reaction mechanism occurs in this reduction pathway, with F being the point where the reduction reaction starts to be limited by diffusion.

Figure 3.9 CV of the potassium ferrocyanide cell, scan rate 50 mV/s, letters explained in the text [36].

Peaks in both directions will only be seen for reversible reactions; an irreversible reaction will give a peak in one direction only. In an ideal system containing a reversible reaction, the oxidation and reduction peaks should be separated by 59 mV for a 1 electron process (a value obtained by application of the Nernst equation), their ratio should be near unity and their position should not change with scan rate [35]. Scan rate will change the height of a given CV peak: the quicker the scan rate the smaller the peak, as the diffusion limit is reached earlier. Common scan rates range from 25 – 500 mV/s, within SWNT research 50 mV/s is often used [37]. The shape of the peaks in reversible reactions can give information about the electrochemical process [38].
Reversible reactions only truly occur when the electron transfer process at the surface of the electrode is in equilibrium. When the scan rate is set too high (so not enough diffusion can occur) or when a system containing poor electron kinetics is investigated the system cannot remain in equilibrium. Both of these factors have an effect on the position and shape of the peaks in the CV. Although both oxidation and reduction peaks can still be seen, the oxidation peak will be shifted to more positive potentials and the reduction peak to more negative potentials. The peaks will also not be as high in current or as sharp. It should be noted that when the scan rate is lowered, a reversible reaction may turn into an irreversible reaction as the oxidised or reduced species may have enough time to undergo further chemical reactions and thus be removed from redox activity [38]. Often a range of different scan rates must be used to fully examine a given redox active species.

As well as the choice of experimental conditions the selection of solvent and electrolyte is also of paramount importance. Although water is commonly used as an electrochemical solvent [38], the electrochemical processes investigated in the author’s work require dry and oxygen free solvents. Full details of the nonaqueous solvents used are given in Chapter 6: Electrochemistry.

The information given above shows how the CV for a standard couple should be interpreted. For SWNTs, however, this interpretation is notoriously difficult. Due to the large number of SWNTs present within a given sample, CVs are often seen to be broad and featureless due to the large number of overlapping electron transfer events [39]. When peaks are produced they are often found to be due to intercalation, functional groups or impurities within the sample [40-42]. As such, the CVs given in the electrochemistry chapter have been interpreted with the utmost of care.
All CVs were taken by the author using a Solartron potentiostat (SI 1287 and FRA 12556). A three terminal electrochemical cell was used in all experiments (this cell contained a working, counter and reference electrode).

### 3.12 Zeta Potential

Zeta potential ($\zeta$-potential) is the name given to the measurement of the electrokinetic potential in colloidal systems. When colloidal particles are dispersed in a solution they are electrically charged due to their ionic characteristics and dipolar attributes. Each dispersed particle is surrounded by oppositely-charged ions called the fixed layer (Figure 3.10). Outside this layer is an area called the ion diffusion layer, containing varying compositions of ions of opposite polarities; the whole area is electrically neutral. When a voltage is applied, particles are attracted to the electrode of the opposite polarity, accompanied by the fixed layer and part of the diffuse double layer, or internal side of the conceptual "sliding surface". Zeta potential is considered to be the electric potential of this inner area, including the "sliding surface". As this electric potential approaches zero, particles tend to aggregate. The greater the magnitude of a given zeta potential, the more stable the suspension of particles [43, 44].

![Figure 3.10](image)

**Figure 3.10** A pictorial representation of the migration occurring in a $\zeta$-potential machine [44].
Not only can $\zeta$-potential measure the stability of a solution, it also provides a means to characterise the surface charge density of the dispersed particles. In the SWNT field, $\zeta$-potential is often measured as a function of pH; with a more negative $\zeta$-potential indicating a SWNT sample functionalised with a higher degree of acidic groups, as ionization of acid groups leads to the presence of a negative charge on the SWNT surface [45, 46].

In the current work, samples for zeta potential measurements were prepared by sonicating 1 mg of the required SWNT sample in 40 ml of deionised H$_2$O containing 6 mg of KCl. The solution was left to stand overnight and the supernatant decanted and used for the measurements. All zeta potential measurements were collected using a Brookhaven Instruments Corporation PALS Zeta Potential Analyser, Version 3.48. The measurement of each sample at a given pH was repeated 6 times and the mean taken after any outliers were excluded. The pH was varied between 2 and 10 using an automated setup using KOH and HNO$_3$. Problems with the solution quality were apparent when performing these measurements and this fact should be taken into consideration when interpreting the results.
3.13 References


13. Lincoln, Transmission Electron Microscope, Centre for Materials Research and Analysis University of Nebraska.


44. Nition, Zeecom, Zeta potential analyzer, What is Zeta potential?.


4 Purification of SWNTs; the Problem with Oxidation Debris

4.1 Introduction

As detailed in Chapter 1, SWNTs exhibit extraordinary mechanical and electronic properties suggesting their importance in the future of materials. However, before SWNTs can be exploited to their full potential they must be purified in a reliable and repeatable manner. As-synthesised SWNTs are generally impure, with each different synthetic method producing a different type and level of contaminant [1]; including metal catalytic particles, amorphous carbon, and graphitic nanoparticles [2]. It has long been a goal (which may actually be unattainable) of SWNT research to find a single method of purification applicable to all types of SWNT. The various techniques used to purify SWNTs were given in Chapter 2. Motivated by the need to produce highly purified SWNT samples in a cheap, scalable, and reliable manner, this chapter explores an improved method of purification. This purification is achieved by following a standard mixed or nitric acid reflux, with a dilute base and HCl wash (at room temperature) and relates to the recent suggestion that commonly-used purification techniques actually create oxidation debris which is not removed from the sample by conventional water washing.

Rinzler et al. first proposed the use of a dilute base-wash during purification, as a means of affecting the diameter distribution rather than the purity [3]. Monthioux et al. dispersed acid-refluxed nanotubes by sonication in a base containing 0.5% Triton X-100 surfactant [4], although the different reflux conditions were comprehensively discussed, the effects of the base-washing were not discussed [4]. Similarly, both Gromov et al. [5] and Wiltshire et al. [6] used base-washing as part of their purification regime, but without examining its specific role. Last year, Verdejo et al.
showed that when the common nitric/sulphuric acid purification regime is undertaken for multi-walled carbon nanotubes, there is a significant fraction of oxidation debris that is only removed using a dilute base-wash [7]. Salzman et al. reported similar results for SWNTs, however, more complex and aggressive conditions were used for both the purification and subsequent removal of the ‘oxygenated carbonaceous debris’. Specifically, they used microwave treatment in 16% HCl, reflux in 8 M nitric acid for 24 h, followed by reflux in 8 M sodium hydroxide for 48 h and finally a HCl wash [8]. The basic reflux/washing cycle was performed three times to achieve maximum purification.

For the current study, a range of samples were used, synthesised by both arc-discharge (AD) and Catalytic Vapour Deposition (CVD). The purity increase is quantified using Raman spectroscopy, TEM, AFM, SEM, XPS and zeta potential measurements. The need for a final HCl wash is emphasised using TGA, and the nature of the impurities removed is analysed with FTIR.

4.2 Experimental Details

Four different SWNT samples were used in this study. Two were produced by Thomas Swan Ltd using CVD, one in their manufacturing facility (TS1), the other in their laboratory (TS2); both were classed as Elicarb SW samples. A third sample was produced by Carbon Nanotechnologies Inc., using HiPCO CVD (HiPCO), and was purchased as ‘raw SWNTs’. Carbon Solutions provided the fourth sample, which was manufactured using Electric Arc Growth and purchased pre-purified using the manufacturer’s “P2” procedure (CS); thought to involve an air oxidation and subsequent HCl wash. All other chemicals used were of analytical grade and were purchased from Aldrich, Fisher, or VWR and used as-received.
For comparative purposes, both a mixed nitric/sulphuric acid reflux (henceforth referred to as mixed acid reflux) and a nitric acid reflux were performed on TS1 and CS. In the literature, both types of reflux have been used regularly to purify CVD and arc-grown SWNTs [2, 9, 10]. However, only the more common nitric acid reflux has been performed on the HiPCO and TS2 CVD SWNTs [1, 11-16].

The oxidation treatments were carried out as follows: 0.2 g of the nanotubes were refluxed at around 120°C in a 500 ml round-bottomed flask either in 30 ml concentrated nitric acid (65%, Fluka, puriss. p.a. plus) for 6 h, or in 7 ml of 3:1 concentrated sulphuric (98%, Aldrich, A.R. grade) and nitric acid (65%) for 30 mins. This procedure was carried out in a fume cupboard. First, the weighed nanotubes were placed in the round-bottomed flask and the acid added. Then, the reflux condenser was attached and the flask lowered into the cold oil bath (with the condenser running). The oil bath was heated to the required temperature then left for the required amount of time (Figure 4.1), before removing the flask and cooling naturally.

![Figure 4.1 Schematic of SWNT reflux [17.](n/a)](n/a)

Following the reflux, both samples were treated similarly: after the sample had cooled, it was diluted with 300 ml of deionised water by slow addition to the flask. The diluted acid/nanotube mixture was then washed with further deionised water,
over a 0.2 \( \mu \text{m} \) PTFE Whatman filter membrane, using vacuum filtration, until the filtrate was colourless and reached the pH of the deionised water (~5.5). The pH of the sample was tested from the drop formed at the bottom of the filter. Samples were reserved for characterisation at this step. Subsequently, the SWNTs were washed with approximately 500 ml of 0.01 M sodium hydroxide (BDH, AnalaR grade). The base-washing produced a brown-coloured filtrate and was continued until the filtrate ran clear. The solution was once again, washed with deionised water until the filtrate reached a neutral pH. Finally, the SWNTs were washed with approximately 500 ml of 0.01 M hydrochloric acid (BDH, AnalaR grade) and then washed to neutral once again with deionised water. These samples are termed ‘base-washed’ in the remainder of this thesis.

### 4.3 Results and Discussion

It is very common in SWNT research to complete a mineral acid reflux purification step before any further chemical reactions or property investigations are attempted. It is assumed that this reflux purifies the SWNT to such an extent that further work can be undertaken reliably; however, the work detailed in this chapter shows that this assumption is incorrect.

A mineral acid reflux not only allows for tube purification by removal of catalyst particles and amorphous carbon, but it also creates molecular debris which can remain adsorbed onto the nanotube walls after conventional water washing. The extra base-washing step was performed on the acid-refluxed SWNT samples in order to convert any acid groups present within the sample to their conjugate base and hence to solubilise any partially oxidised fragments remaining as contaminants [7, 8]. The removal of additional impurities was confirmed clearly by the yellow/brown colour of
the filtrate produced after the base-washing. The filtrate produced during the base-washing was darker brown in colour after the more aggressive mixed acid reflux, compared to the nitric acid reflux. It is worth emphasising that ‘purified’ SWNT samples have commonly been used without this additional washing step. Figure 4.2 shows an example of the waste produced after each washing phase. The base-washing waste samples are taken from the first 100 ml of filtrate produced. The greater concentration of debris is expected after the mixed acid reflux due to the production of the nitronium ion (NO$_2^+$).

\[ \text{H}_2\text{SO}_4 + \text{HNO}_3 \rightleftharpoons \text{HSO}_4^- + \text{NO}_2^+ + \text{H}_2\text{O} \quad \text{Equation 4.1} \]

The nitronium ion is more oxidising than the nitric acid alone [18], and ultimately generates a greater quantity of partially oxidised carbonaceous fragments during the acid reflux, which are then released during the base-wash.

Figure 4.2 Sample vials containing examples of the waste from TS1 (a) initial washing following acid reflux, (b) final washing following acid reflux, (c) base-washing after mixed acid reflux, (d) base-washing after nitric acid reflux, (e) HCl wash following the base-washing.
4.3.1 Raman Spectroscopy

The Raman data in Figure 4.3 shows that all SWNT samples are purer after base-washing compared with acid reflux alone as judged by the G:D ratio (Figure 4.3b). In all but the HiPCO case, the purity after base-washing is higher than the purity of the starting material. In the case of the HiPCO SWNTs, the ratio decreases after acid reflux and then increases slightly after base-washing, however, it does not reach the level of the raw material. This slight reduction can be attributed to a number of factors: including the increased sensitivity of the smaller diameter HiPCO SWNTs to the acid due to their higher elastic strain, the relatively low concentration of carbonaceous impurities in the starting material, and the exceptionally high concentration of catalyst particles encapsulated within the SWNTs, which may cause local damage upon removal.
As discussed in Section 3.6, the peak frequency of the RBM is inversely proportional to the diameter of the SWNT. As each different laser excites a different nanotube, the average diameters of the raw material (Table 4.1) calculated from one laser line must be taken only as a rough guide.

<table>
<thead>
<tr>
<th>SWNT Type</th>
<th>Average Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiPCO</td>
<td>1.07 ± 0.02</td>
</tr>
<tr>
<td>TS2</td>
<td>1.32 ± 0.04</td>
</tr>
<tr>
<td>TS1</td>
<td>1.36 ± 0.05</td>
</tr>
<tr>
<td>CS</td>
<td>1.60 ± 0.02</td>
</tr>
</tbody>
</table>

*Table 4.1* The calculated diameters of the as-received SWNTs from their red (633nm) Raman spectra.

From the Kataura plot, which is explained in Section 1.6, mainly metallic tubes are excited in the HiPCO, TS1 and TS2 samples at 633nm. However, this laser primarily excited the semiconducting CS tubes. To check that the changes in G/D band were consistent when different laser frequencies are used, the results were repeated using...
an Infrared laser at 785nm. This laser excites semiconducting HiPCO SWNTs, semiconducting and metallic TS1 and TS2 SWNTs, and metallic CS SWNTs. Despite the change in excitation, the G/D ratios followed the same trend, indicating that the purity changes are representative of the sample.

4.3.2 Atomic Force Microscopy

AFM provides an alternative assessment of the purity of the samples; the images showed that the as-received SWNTs contain many impurities, with the level of impurities decreasing after acid reflux and again after base-washing; examples are shown in Figure 4.4.

![Tapping mode AFM images of TS1 SWNTs, (a) as-received, (b) after mixed acid reflux, (c) after mixed acid reflux and base-washing. Z-scale is 0-100nm.](image)

4.3.3 Transmission Electron Microscopy

High Resolution TEM images showed that, in all cases, the as-received SWNTs are multi-component material containing a significant proportion of amorphous carbon, nanoparticles and catalytic particles, with these impurities surrounding the SWNTs themselves and as separate agglomerates within the samples (Figure 4.5a). These results are consistent with other published data [4]. After the acid treatment, the clumps of impurities can be seen to have changed in consistency. However, the
SWNTs can still be seen to be wrapped in amorphous material (Figure 4.5b). After base-washing, areas of clean nanotube surfaces were generated, and the overall quantity of amorphous material was seen to decrease (Figure 4.5c). The TEM images also show that in the TS1 sample, some double-walled nanotubes were also present amongst the predominately single-walled carbon nanotubes.

Figure 4.5 High Resolution TEM images of TS1 SWNTs, (a) as-received, (b) after mixed acid reflux and (c) after mixed acid reflux and base-washing.
4.3.4 Scanning Electron Microscopy

SEM of the purified samples showed a change in the make-up of the impurities within the sample. **Figure 4.6** shows a set of SEM images taken for TS1 samples. In the as-received material both SWNTs (probably bundles) and impurities can be seen, after the acid reflux then base-wash, the samples appear to contain a higher fraction of SWNTs. Unfortunately quantification of such images is notoriously difficult [2].
Figure 4.6 SEM images of TS1 at two different magnifications a/d) the sample as-received b/e) after mixed acid reflux c/f) and after base-washing.
4.3.5 X-ray Photoelectron Spectroscopy

Many groups, such as Fang et al. [19] and Okpalugo et al. [20], have analysed XPS data for the C1s peak, in an attempt to determine the relative fractions of sp² and sp³ carbon within the SWNTs, as well as the different carbon-oxygen bonding environments (C-O, C=O, and COO) [19, 20]. The XPS spectra for the author’s SWNT samples were remarkably similar to those in the literature: a reasonably symmetrical O1s peak and a C1s peak, with a long and significant tail towards lower binding energies (Figure 4.7). At this point it should be noted that due to the time and expense of undertaking XPS measurements, only three of the six sample sets produced during this study were measured; specifically CS nitric, CS mixed and HiPCO nitric SWNTs. Although apparently satisfactory fits could be obtained, the process overfitted the available data. No reliable and unambiguous peak fitting could be obtained for the C1s. This difficulty is due to two factors; the first being that the peak concerned with the sp² carbon (~284.6 eV) and the peak concerned with the sp³ carbon (~285 eV) are very close in binding energy, and hard to resolve. The second problem occurred when trying to fit the carbon to oxygen bonding environments within the tail of the C1s peak. The breadth of the peak relates not only to the variety of carbon oxygen bonding environments but also to the C-C shake-up tail. The shake-up feature relates to the effect that the sudden creation of a core hole has on the other electrons within the atom. In SWNTs, the shake-up effect excites a large number of electrons at the Fermi level. The number of excited electrons diverges near ΔE=0, so the shake-up peak manifests itself as a tail added to the photoelectron peak towards higher binding energy, which produces an asymmetric line-shape. As this shake-up contribution occurs throughout the binding energies that the carbon-oxygen bonding environments would be expected, the intensities of the carbon to oxygen binding
peaks tend to be overestimated. The problem is exacerbated by the low carbon-oxygen ratio which reduces the intensity of the peaks of interest. It is suspected that much of the C1s fitted in the literature should be examined with caution.

Figure 4.7 XPS C1s peak of a) CS as-received, b) CS after nitric acid reflux, c) CS after nitric acid reflux and base-washing, d) CS mixed acid reflux, e) CS mixed acid reflux and base-washing, f) HiPCO as-received, g) HiPCO after nitric acid reflux, and f) HiPCO after nitric acid reflux and base-washing.
For these reasons, the author simply used the total C1s peak area and did not interpret the C1s peak any further. Attempts to analyse the peak quantitatively did not produce any reliable data. On the other hand, the O1s peak gives a clearer signal and was fitted using the standard literature methods [12, 21] (Figure 4.8). The standard components within these methods were seen as a C-O peak at ~533.3 eV, a C=O peak at ~531.6 eV and a H$_2$O peak at ~534.7 eV. The peaks were fitted from the XPS data using the CasaXPS program. This fitting could be completed in a more reliable fashion; as the peaks are significantly separated, all oxygen peaks are relevant, and the oxygen peak does not suffer from an equivalent problem with shake-up tails. However, it was the author’s experience that the fitting of these peaks was still ambiguous in some cases; care should be taken when interpreting the results.

The values obtained through peak fitting for all the sample sets studied is summarised in Table 4.2. It should be noted that after the acid reflux both of the CS samples contain a nitrogen peak, with the concentration of nitrogen within the sample being over twice as large for the nitric acid reflux than the mixed acid reflux (0.4% for CS mixed and 1.0% CSP2 nitric). However, the HiPCO SWNT sample does not contain any nitrogen. The residual nitrogen content in the majority of samples may be due to the nitration of the amorphous carbon impurities which are seen at higher levels within the CS SWNT sample.
**Figure 4.8** XPS fitting of the O 1s peaks a) CS as-received, b) CS after nitric acid reflux, c) CS after nitric acid reflux and base-washing, d) CS mixed acid reflux, e) CS mixed acid reflux and base-washing, f) HiPCO as-received, g) HiPCO after nitric acid reflux, and f) HiPCO after nitric acid reflux and base-washing.
The data shows that the CS and HiPCO as-received samples both contain a small amount of oxygen in a rough 1:1 C-O:C=O ratio. In absolute terms, the CS sample contains twice as much oxygen (1.9 %) as the HiPCO sample (0.9 %) and this value can be correlated to the Raman spectroscopy of CS, which shows a higher impurity percentage. After the reflux process, the oxygen content for each sample increases dramatically. For CS, the oxygen content increase is much more marked after mixed acid reflux than after nitric acid reflux, 12.5% and 6.9% respectively. This difference is expected, as the mixed acid has a much greater oxidative effect than the nitric acid alone, due to the nitronium ion formation. The oxygen content of the HiPCO SWNT sample also increases significantly after acid reflux: the sample contains 13.5 % more oxygen after the reflux than before. Although only a nitric acid reflux was undertaken...
on these HiPCO tubes, their small size and high curvature make them more susceptible to the oxidative acid than the larger diameter CS SWNTs.

For the CS samples, following both the mixed and nitric acid reflux, the ratio of C-O to C=O remained roughly 1:1. Although peak-fitting to the HiPCO data indicated a threefold increase in the C-O:C=O ratio after nitric acid reflux, not too much significance should be placed on this result; as can be seen from Figure 4.8g, the XPS spectrum from this sample produced exceedingly noisy results.

After base-washing, the total oxygen content is unchanged in the HiPCO nitric acid and CS mixed acid samples, and increases in the CS nitric acid sample. This result is not as expected; the oxygen content was expected to decrease when the highly oxygenated impurities were removed from the sample by the base-washing process. However, this result can be understood when the sodium present in the sample is taken into account as after each of the base-wash steps sodium was measured within the sample. This sodium will be present as either sodium hydroxide or sodium carboxylate. In the O1s peak, sodium hydroxide will be seen at 532.8 eV and sodium carboxylate at 531 eV [21, 22]. To try to fit the raw data to include these two extra peaks and hence to achieve a quantitative analysis of the sodium related groups would be a gross over interpretation of the data. Figure 4.9 shows an example of a typical O1s peak fitted to three, four or five peaks, depending on which functional groups were selected, and indicates the unreliable nature of the absolute individual intensities. If the peaks are just fitted to contain the NaOH peak (not the COONa peak), then a significant contribution from NaOH is seen in each sample; accounting for the inflated oxygen content (Figure 4.10). Due to the sodium peaks present in the base-washed samples, the individual C-O, C=O and H2O values given in Table 4.2 are exaggerated and have not been interpreted any further. Sodium was only thought
to be present within the sample, as the samples sent for XPS analyses were those that had been base-washed but not HCl washed. It is thought that if the final sample (following the HCl wash) was analysed then there would be no sodium present and a lower oxygen content. Unfortunately due to research constrains these extra XPS samples could not be analysed.

![Figure 4.9](image1.png)

**Figure 4.9** An example of possible peak fitting to the O1s XPS peak for CS after nitric acid reflux and base-washing: a) fitted to 3 peaks, b) fitted to 4 peaks c) fitted to 5 peaks.

![Figure 4.10](image2.png)

**Figure 4.10** XPS fitting of the O1s peaks including NaOH peak a) CS after nitric acid reflux and base-washing, b) CS mixed acid reflux and base-washing, c) HiPCO after nitric acid reflux and base-washing.
4.3.6 Thermogravimetric Analysis

TGA analysis in air shows the stability of the materials to combustion; the temperature of combustion was determined from the maximum in the differential of the mass loss curve (Figure 4.11). Ideally, purer SWNT samples have a higher temperature of combustion [3, 14, 23], however, stability after the initial oxidation depends on the relative effects of removing amorphous carbon and introducing further defects. Overall, the peak combustion temperatures after full purification were not significantly different to those for the initial starting material. However, the TGA data does indicate the need for the final acid washing step; in all cases, the combustion temperature is lower after the initial treatment with base but increases again after the final acid wash. The decrease in the decomposition temperature may be attributed to the presence of more thermally sensitive conjugate salts which are converted back to the original acidic functionalities by the final acid wash.

Figure 4.11 Summary of combustion temperatures extracted from TGA data.
The TGA data also indicates purity in terms of the non-combustible fraction. For unpurified samples, the residue usually relates to metal catalyst particles within the sample. As can be seen in Table 4.3 each different SWNT type, as-supplied, has a different initial ash content ranging from 5% for TS2 to 33% for HiPCO. In all cases, the residual weight fraction decreases after the initial acid reflux which dissolves any exposed metal and allows it to be removed from the sample. After the base-washing step, this weight is found to increase significantly due to the presence of sodium within the sample. In all but the HiPCO case this weight returns to around the same value as the initial acid treated sample after the final HCl wash. Clearly, the final HCl washing step is useful for removing the sodium ions from the samples, although no further catalyst particles are removed. For the HiPCO sample the residual weight following the final acid reflux is half that of the first acid reflux, indicating that more catalyst particles are washed from the sample.

<table>
<thead>
<tr>
<th></th>
<th>As-received</th>
<th>Acid reflux</th>
<th>Base-washed</th>
<th>HCl washed</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS1 – Mixed</td>
<td>7</td>
<td>4</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>TS1 – Nitric</td>
<td>7</td>
<td>2</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>TS2 – Nitric</td>
<td>5</td>
<td>1</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>CS – Mixed</td>
<td>19</td>
<td>11</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>HiPCO – Nitric</td>
<td>33</td>
<td>10</td>
<td>12</td>
<td>4</td>
</tr>
</tbody>
</table>

*Table 4.3* Residual weight from the TGA data.

### 4.3.7 Zeta Potential Measurements

Zeta potential ($\zeta$-potential) is used to show the surface charge density of nanotubes, in the simplest terms a more negative $\zeta$-potential indicates a more acidic sample, as ionization of acid groups leads to the presence of a negative charge on the SWNT surface. However, $\zeta$-potential is also a function of pH and is often more complex.
The $\zeta$-potentials of TS1 after just the nitric acid reflux and after subsequent base-washing are shown in Figure 4.12.

**Figure 4.12** Graph showing zeta potential as a function of pH for the TS1 SWNT samples after nitric acid reflux and nitric acid reflux followed by the base and HCl washes, lines are sigmoidal fit of data.

In the more basic pH range, the difference between the samples is clearly seen as the plateau value changes from -36 mV for the nitric acid reflux alone, to -22 mV following the base-washing. The reduced surface charge indicates that many acid groups apparently introduced by the acid reflux are washed from the sample during the base-washing. At acidic pHs, the $\zeta$-potential of the base-washed sample is slightly more negative than the acid-refluxed sample alone (-7 mV compared to -2 mV) and has a slower inflection, suggesting that stronger acids remain on the SWNTs following the base-washing. This suggestion is consistent with the hypothesis that oxidised debris contains weakly acidic groups. These groups do not ionise in the distilled water, but do ionise in the dilute base, raising the solubility of the debris molecules.
4.3.8 Chemical Composition of Impurities

Following on from the purity increase seen in the SWNT sample itself, attempts were made to identify the chemical composition of the waste produced. To this end XPS, GCMS, Raman, TEM, NMR and FTIR were undertaken. Only FTIR spectroscopy was able to give any meaningful results. TEM simply showed that the sample contained amorphous carbon, Raman showed that there were some aliphatic and aromatic components to the sample, whereas the other techniques either produced results that were too complex to analyse or were limited by the insolubility of the product in common solvents such as THF, DMF, DCB, acetone, water and ethanol.

FTIR spectra were used to establish, qualitatively, the nature of the groups contained within the base-washing waste. All of the FTIR spectra from each different type of nanotube and reflux produced similar spectra (an example is shown in Figure 4.13) which are indistinguishable from that reported previously for MWNT treatments [7]. The peak at 3600-3200 cm\(^{-1}\), is due to O–H stretching vibrations: although the samples were dried, –OH will remain in the form of both hydroxyl groups and chemisorbed water; the shape of the band particularly suggests the latter [24]. The peaks present at 2960, 2930 and 2850 cm\(^{-1}\) are due to aliphatic C–H stretches, probably associated with debris from amorphous carbon [25]. The peak at 2500 cm\(^{-1}\) is most likely due to the stretching vibrations of chelated –OH groups found on the highly oxygenated carbonaceous fragments [26], although a broad peak from the –OH group of sulfonic acid can be found in the same region [27]. The presence of the conjugated salts of the oxidation products are evidenced in the form of carboxylate ion peaks (1620, 1450 cm\(^{-1}\)), C–O stretches at 1040-1150 cm\(^{-1}\), and sodium alkoxides at 880 cm\(^{-1}\) [12, 25, 28, 29]. The peak at 1610 cm\(^{-1}\) may also be linked to water or to aromatic C=C [8]. These observations are consistent with proposals that the oxidation
debris (or ‘carboxylated carbonaceous fragments’ (CCFs) [8]) contains partially oxidised carbonaceous fragments terminated by a variety of oxygen-containing groups [7, 29], which are converted to carboxylate and phenoxide functionalities under basic conditions. Although intercalation effects have been invoked in harsher basic treatments [8], under the mild conditions used here only pH based effects are likely to be relevant.

![FTIR spectra](image)

**Figure 4.13** FTIR spectra of the filtrate produced during the base-washing the CS SWNT after mixed acid reflux.

### 4.3.9 Yield Data

The yield for the reaction varies greatly depending on the nature of the initial acid reflux. For example, using a pure nitric acid reflux, the average yield of TS1 was 82% dropping to 77% following base-washing, indicating that acid-refluxed SWNTs contain around 6 wt% debris. Following mixed acid reflux however, the yield is just 33%, dropping to 10% after base-washing. As commented above, the mixed acid is much more oxidative, destroying a greater fraction of the sample. However, it is worth noting that, in both cases, the debris content is equal to around one third of the
amount of carbon consumed during the reflux. This result is consistent with the suggestion that the debris consists of partially oxidised fragments of both SWNTs and carbonaceous impurities.

4.4 Conclusions

The results obtained from the variety of characterisations detailed above, confirm that the commonly applied mixed and nitric acid purification treatments of SWNTs create a significant level of oxidation debris which is not removed from the sample by the simple water washing. This debris can be mostly removed by a simple, mild, base-washing step to leave a higher purity SWNT sample. The washing can be performed at room temperature in dilute base. Treatment converts the acidic groups on both the impurities and SWNTs to their conjugate salt, increasing the solubility of both the impurities, and the SWNTs, in water. Subsequent treatment with dilute acid reproto
tonates the groups remaining on the SWNT surface, if required. This purification method is cheap and relatively easily scalable (it contains no centrifugation, the limiting factor in many other purification regimes) and yield data suggests that the nitric acid reflux is the better method for a range of different types of SWNTs. Removal of the debris is crucial if direct covalent functionalisation of the SWNT is required and should be taken into account when using surface acid groups as sites for further functionalisation.
4.5 References


5 Characterisation of Materials

5.1 Introduction

The rest of the work detailed in this thesis (Chapters 6 and 7), is concerned with two different, yet connected, techniques to separate SWNTs by their electronic properties. The first of these novel techniques involves the reduction of SWNTs in liquid ammonia, and the second involves reduction via electrochemistry. Both of these methods allow for the separation of semiconducting and metallic SWNTs. Rigorous characterisation of the SWNT material to be used in both reactions is of paramount importance. Only by gaining a full understanding of the materials used can the results be analysed in a meaningful way. This chapter gives an account of the three different SWNT materials used in the separation work. ARC grown SWNTs were used when attempting the liquid ammonia reduction work, CoMoCAT tubes were used in both the liquid ammonia reduction and electrochemical work, and HiPCO SWNTs were used solely in the electrochemistry work.

Although there are many different techniques commonly used to characterise SWNTs, only ones that shed light on the purity or the electronic configuration of the SWNT sample are given here. Also, due to time and financial constraints, not all of the nanotubes have been analysed by all of the techniques. However, each of the following three sections gives a good insight into each of the SWNTs that are used in the following work.
5.2 Characterisation of ARC SWNTs

ARC SWNTs are produced by the evaporation of metal-doped carbon electrodes at high temperatures. The ARC SWNTs were purchased from Carbolex (SE grade), and used as-received.

The electronic properties of ARC tubes can be analysed by Raman spectroscopy, as shown below. Due to the limitations of this technique, it would have been advantageous to analyse the SWNTs using UV/Vis/NIR or PL spectroscopy. However, due to the impure nature of the ARC sample, as well as the large diameter no UV/Vis/NIR or PL spectra were successfully recorded for the ARC tubes. The purity of the ARC SWNTs is also assessed using Raman, AFM and TGA.

5.2.1 Raman Spectroscopy of ARC SWNTs

As discussed fully in Section 3.6, Raman spectroscopy is generally a convenient tool to study the electronic properties of SWNT samples. It is known from the literature that the position of the RBM can be used to calculate the diameter of an individual SWNT, which can be correlated with the diameter dependent transition energies between the van Hove singularities using the Kataura plot. However, the large size of ARC SWNTs, and their narrow diameter distribution, limits the fraction of the sample that can be probed with common laser lines. The Kataura plot is used on a practical level to assign the peaks seen in the Raman spectra. When analysed with the red laser, (Figure 5.1) two radial breathing mode peaks can clearly be seen.

Using the equation:

\[ \omega_{rbm} = \left( \frac{214.4}{d} \right) + 18.7 \]

Equation 5.1

the diameter (d) in nm of each SWNT excited using this red laser can be calculated from the wave number (\( \omega_{rbm} \)) of the RBM in cm\(^{-1} \), Table 5.1. By looking at the
Kataura plot, it can be seen that using the red laser line only metallic nanotubes are excited ($M_{11}$ transition). Using the charts published by Wang et al. and other literature assignments such as Lian et al., the individual SWNTs were assigned possible (n,m) values [1, 2].

![Raman spectrum](image)

**Figure 5.1** Raman spectrum of ARC grown SWNTs using the red laser (633 nm), showing RBMs occurring due to $M_{11}$ transitions.

<table>
<thead>
<tr>
<th>Peak (cm$^{-1}$)</th>
<th>Transition</th>
<th>SWNT diameter (nm)</th>
<th>(m.n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>146</td>
<td>$M_{11}$</td>
<td>1.53</td>
<td>(15,6) (13,10)</td>
</tr>
<tr>
<td>159</td>
<td>$M_{11}$</td>
<td>1.40</td>
<td>(10,10) (13,7)</td>
</tr>
</tbody>
</table>

**Table 5.1** Assignment of peaks seen in spectrum of ARC grown SWNTs, using the red Raman laser (633 nm) [1, 2].

By looking at the whole Raman spectrum of ARC SWNTs (Figure 5.2), the metallic nature of the SWNT in resonance with the red laser is also confirmed by the G-band which shows a Breit-Wigner-Fano (BWF) line shape, indicative of metallic tubes.
This spectrum also shows that these ARC tubes are relatively pure; they show a small D-band compared to the size of the G-band, having a G/D ration of 40.

![Raman spectrum of ARC grown SWNTs using the red laser (633 nm).](image)

**Figure 5.2** Raman spectrum of ARC grown SWNTs using the red laser (633 nm).

To complement the data found with the red laser, a green laser (532 nm) was then used to characterise the ARC SWNTs. Again, two clear peaks could be seen in the RBM spectrum (**Figure 5.3**) and the diameter of each SWNT correlating to each peak was calculated using *Equation 5.1* (**Table 5.2**). The Kataura plot showed that only semiconducting SWNTs were excited using the green laser (*S*_33 transition); using the charts published by Wang and other assignments in the literature, the individual SWNTs were then assigned with *(n,m)* values.

<table>
<thead>
<tr>
<th>Peak (cm⁻¹)</th>
<th>Transition</th>
<th>SWNT diameter (nm)</th>
<th>(m,n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td><em>S</em>_33</td>
<td>1.49</td>
<td>(14,7) (12,11)</td>
</tr>
<tr>
<td>164</td>
<td><em>S</em>_33</td>
<td>1.36</td>
<td>(14,6)</td>
</tr>
</tbody>
</table>

**Table 5.2** Assignment of peaks seen in spectrum of ARC SWNTs, using the green Raman laser (532 nm).
Figure 5.3 Raman spectrum of ARC grown SWNTs, using the green laser (532 nm), RBM in resonance with $S_{33}$ transitions.

Figure 5.4 Raman spectrum of ARC grown SWNTs, using the green laser (532 nm).

When the whole Raman spectrum is analysed (Figure 5.4), the semiconducting nature of the SWNT excited by the green laser can also be seen in the G-band; the sharpness being indicative of semiconducting tubes. This sample is also seen to be extremely pure having a G/D ratio of over 100.
As the red laser solely probes metallic SWNT and the green laser solely probes semiconducting SWNTs, neither laser provides any significant results regarding the separation of metallic and semiconducting SWNTs since neither laser addresses both species. Due to the relatively large diameter of these ARC grown SWNTs no commonly used laser manages to probe both species.

### 5.2.2 TGA Analysis of ARC SWNTs

TGA analysis in air shows the stability of the ARC SWNTs to combustion (Figure 5.5); the temperature of combustion is determined from the maximum in the differential of the mass loss curve (Figure 5.6). ARC SWNTs have two distinct differential peaks at 405°C and 473°C, indicating that the sample contains two different material fractions. The ARC SWNTs have a high ash content, approximately 30%, indicating that a high number of catalyst particles are contained within the sample.

![TGA of ARC SWNTs](image)

**Figure 5.5** TGA of ARC SWNTs, run in air at 10°C/min.
5.2.3 AFM of ARC SWNTs

AFM indicated, qualitatively, that the ARC (Figure 5.7) tubes have a large quantity of impurities, occurring mainly in large clusters.

Figure 5.6 Derivative of ARC SWNT TGA (Figure 5.5) run in air, at 10°C/min.

Figure 5.7. Tapping mode AFM images of ARC SWNTs, Z-scale is 0-200nm.
5.2.4 ARC SWNT Conclusions

The Raman spectra show metallic and semiconducting SWNTs within the sample. As each laser only excited a single electronic type of SWNT, neither laser can be used to assess the possible separation of metallic from semiconducting SWNTs. The relatively large G/D ratio gives the impression that the ARC tubes themselves contain few defects and the sample as a whole only contains a limited amount of amorphous carbon. However, the double burn peaks in the TGA spectra show that the sample is multi-component and the high final ash content indicates that the sample contains many catalyst particles. The high level of impurities seen in the AFM images also confirms these findings, as the aggregated nature of the impurities is more consistent with carbon and catalyst nanoparticles.

5.3 Characterisation of CoMoCAT SWNTs

CoMoCAT SWNTs (purchased from South Western Nanotechnologies) were chosen because they are grown with a relatively small diameter range, leading to only a limited number of (m,n) types within the as-received material. Although these materials have been well characterised in the literature, and the published work shows that the semiconducting (6,5) SWNTs have the highest population density, the sample used by the author was fully characterised before any work was undertaken. Differences were found between the sample used in this project and the data published in the literature. An overview of the synthesis method used to produce them is given in Section 2.5.2.

The population density of the tubes present within the CoMoCAT sample was assessed with red, green and NIR Raman spectroscopy, photoluminescence and
UV/Vis/NIR. The purity was assessed with Raman spectroscopy, AFM, TGA and TEM.

### 5.3.1 Raman Spectroscopy of CoMoCAT SWNTs

To fully characterise the CoMoCAT SWNTs using Raman Spectroscopy; red, green and NIR laser lines were used (Section 3.6 should be consulted for an overview of Raman spectroscopy).

The red laser Raman spectrum is included as **Figure 5.8**. The diameters of the SWNTs corresponding to each peak are listed in **Table 5.3**, together with an assignment of the individual SWNTs [3, 4]. The red laser excites both metallic and semiconducting SWNTs, and is therefore very useful for the studying possible CoMoCAT separation reactions.

![Raman spectrum of CoMoCAT SWNTs as-received, using the red (633 nm) laser line. Boxed regions show areas governed by a given transition, the shaded box shows an area when the M11 and S22 transition overlap.](image)

**Figure 5.8** Raman spectrum of CoMoCAT SWNTs as-received, using the red (633 nm) laser line. Boxed regions show areas governed by a given transition, the shaded box shows an area when the M11 and S22 transition overlap.
<table>
<thead>
<tr>
<th>$\omega_{RBM}$</th>
<th>d (nm)</th>
<th>(m,n)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>191</td>
<td>1.25</td>
<td>(13,4)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9,9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(14,2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12,6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(15,0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10,7)</td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>1.10</td>
<td>(12,3)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11,5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8,8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13,1)</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td>0.93</td>
<td>(7,7)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10,3)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11,1)</td>
<td></td>
</tr>
<tr>
<td>281</td>
<td>0.83</td>
<td>(7,5)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8,4)</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>0.79</td>
<td>(8,3)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6,5)</td>
<td></td>
</tr>
<tr>
<td>334</td>
<td>0.70</td>
<td>(6,4)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td>381</td>
<td>0.60</td>
<td>(5,4)</td>
<td>$S_{11}$</td>
</tr>
</tbody>
</table>

*Table 5.3* Assignment of the peaks in CoMoCAT red spectra [1, 3-6].

*Figure 5.9* Raman spectrum of CoMoCAT SWNTs, as-received, using the red (633 nm) laser.

When the whole Raman spectrum is analysed (*Figure 5.9*), the mixed semiconducting and metallic nature of the SWNTs excited by the red laser can also be seen in the G-band. The sharpness is indicative of semiconducting tubes, whereas the slight BWF
line shape shows metallic tubes. The G/D ratio of 16 shows that this sample contains a significant level of impurities, either as defects within the SWNT themselves or as graphitic nanoparticles or amorphous carbon within the sample.

The green laser Raman spectrum (Figure 5.10) tends to excite small to medium metallic tubes and large diameter semiconductors; the assignments and diameters are summarised in Table 5.4. Although this sample gives a spectrum with a poor signal to noise ratio, by cross referencing with the current literature assignments the correct peaks can be assigned. This laser can also be used to look for any possible separation of metallic and semiconducting peaks by looking at the change of intensity of the relative peaks.

![Raman spectrum of CoMoCAT SWNTs, as-received, green laser (532 nm).](image)

**Figure 5.10** Raman spectrum of CoMoCAT SWNTs, as-received, green laser (532 nm).
<table>
<thead>
<tr>
<th>$\omega_{RBM}$</th>
<th>d (nm)</th>
<th>(m,n)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>1.46</td>
<td>(15,5)</td>
<td>$S_{33}$</td>
</tr>
<tr>
<td>177</td>
<td>1.35</td>
<td>(14,4)</td>
<td>$S_{33}$</td>
</tr>
<tr>
<td>202</td>
<td>1.17</td>
<td>(12,3)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8,8)</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>1.07</td>
<td>(10,7)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>242</td>
<td>0.97</td>
<td>(10,4)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>257</td>
<td>0.91</td>
<td>(7,7)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>264</td>
<td>0.89</td>
<td>(8,5)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>286</td>
<td>0.82</td>
<td>(9,3)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>299</td>
<td>0.78</td>
<td>(7,4)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>306</td>
<td>0.76</td>
<td>(6,5)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td>328</td>
<td>0.71</td>
<td>(6,4)</td>
<td>$S_{22}$</td>
</tr>
</tbody>
</table>

*Table 5.4* Assignment of the peaks in the CoMoCAT green laser spectrum.

**Figure 5.11** Raman spectrum of CoMoCAT SWNTs, as-received, using the green (532 nm) laser line.

By analysing the complete Raman spectra (**Figure 5.11**), the G-band also indicates the mixed nature of the sample, and the G/D ratio of 15 shows a significant level of impurities.

Due to the $S_{11}$ and $S_{22}$ transitions (**Table 5.5**), the NIR 785 nm laser (**Figure 5.12**) only excites semiconducting SWNTs, and therefore this laser line will not be used to assess any metallic and semiconducting separation.
Figure 5.12 Raman spectrum of CoMoCAT SWNTs, as-received, using the NIR (785 nm) laser line.

<table>
<thead>
<tr>
<th>$\omega_{\text{RBM}}$ (cm$^{-1}$)</th>
<th>d (nm)</th>
<th>(m,n)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>254</td>
<td>0.92</td>
<td>(9,4)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10,3)</td>
<td></td>
</tr>
<tr>
<td>262</td>
<td>0.90</td>
<td>(7,6)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td>301</td>
<td>0.75</td>
<td>(6,5)</td>
<td>$S_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8,3)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5 Assignment of the peaks in CoMoCAT 785 nm spectra.

Based on the Raman data, the CoMoCAT SWNTs clearly contain a number of different SWNTs, both metallic and semiconducting.

5.3.2 UV/Vis/NIR of CoMoCAT SWNTs

UV/Vis/NIR spectroscopy is discussed in Section 3.8. It is known from the literature that the peaks at 550 nm and 1050 nm in the UV/Vis/NIR spectra of CoMoCAT SWNTs (Figure 5.13) correspond to the $S_{22}$ and $S_{11}$ transitions of (6,5) SWNTs. This feature dwarfs the other nanotube features, including the metallic peaks.
However, this method can see both nanotube types and therefore will be highly effective at looking at possible separation. The fact the semiconducting peaks are so much larger than the metallic peaks is an indication that the as-received CoMoCAT sample contains mostly semiconducting SWNTs.

5.3.3 Photoluminescence of CoMoCAT SWNTs

As discussed in Section 3.10, PL occurs due to $E_{22}$ (or $E_{33}$ ext) absorption and $E_{11}$ emission [6], so only semiconducting SWNTs are shown in PL. From the position of the peaks in the 2D excitation-emission spectrum it is possible to assign the individual tubes that are present in a given sample. The photoluminescence data (Figure 5.14) shows that the semiconducting tubes present, are predominately (6,5). The detailed assignment is given in Table 5.6 [6, 7] where an estimate of intensity is given by scaling all of the peaks against the most intense peak (6,5). It should be noted that the peak at $E_{22}$ 515 nm and $E_{11}$ 980 nm is a phonon sideband of the intense (6,5) peak.
Figure 5.14 The PL spectrum of as-received CoMoCAT SWNTs, used during this study.

<table>
<thead>
<tr>
<th>Emission, nm $E_{11}$</th>
<th>Excitation, nm $E_{22}$</th>
<th>Assignment</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>960</td>
<td>665</td>
<td>(8,3)</td>
<td>18</td>
</tr>
<tr>
<td>981</td>
<td>568</td>
<td>(6,5)</td>
<td>100</td>
</tr>
<tr>
<td>1026</td>
<td>648</td>
<td>(7,5)</td>
<td>18</td>
</tr>
<tr>
<td>1120</td>
<td>575</td>
<td>(8,4)</td>
<td>30</td>
</tr>
<tr>
<td>1125</td>
<td>650</td>
<td>(7,6)</td>
<td>23</td>
</tr>
<tr>
<td>1132</td>
<td>555</td>
<td>(9,2)</td>
<td>22</td>
</tr>
</tbody>
</table>

*Table 5.6* Assignment of the peaks in CoMoCAT PL spectra.
5.3.4 TEM of CoMoCAT SWNTs

Transmission Electron Microscopy (TEM) is a very powerful technique for imaging SWNTs and it is explained in detail in Chapter 3.3. Using TEM, it is possible to see clearly the structure, morphology and purity of SWNT samples. High Resolution TEM images showed that, in all cases, the as-received SWNTs are multi-component materials containing a significant proportion of amorphous carbon, nanoparticles and catalytic particles. These impurities are present around the SWNTs themselves and as separate agglomerates within the samples (Figure 5.15), a result that is consistent with previously published observations.
5.3.5 TGA of CoMoCAT SWNTs

TGA analysis of CoMoCAT SWNTs shows two distinct burn events (Figure 5.16). In measuring from the differential of the curve, these events can be seen to occur at 440°C and 750°C. This shows that CoMoCAT samples are multi component materials. CoMoCAT SWNTs have a moderate ash content of approximately 15%, indicating that a significant number of catalyst particles are contained within the sample.

Figure 5.15 High Resolution TEM images of CoMoCAT SWNTs.
5.3.6 CoMoCAT SWNT Conclusions

Raman spectroscopy showed that the sample contained a significant level of impurities with a range of different SWNTs present; the red and green laser excites both metallic and semiconducting SWNTs allowing analysis of the separation attempts.

UV/Vis/NIR views metallic and semiconducting SWNT concurrently but highlights the large percentage of semiconducting (6,5) SWNTs in the CoMoCAT sample. PL measurements confirmed the predominate (6,5) tubes.

TEM also showed that there were many impurities present, although few identifiable catalyst particles could be seen. TGA confirmed a multi component system containing 15 % catalyst particles.

CoMoCAT tubes contain over twice as many impurities as ARC SWNTs although they have under half the amount of catalyst particles. However, the key advantage in the analysis of CoMoCAT tubes lies in Raman spectroscopy; simultaneous metallic and semiconducting RBM signals can be seen with the available lasers.
5.4 Characterisation of HiPCO SWNTs

HiPCO SWNTs were purchased from Carbon Nanotechnologies as the as-produced grade and used as-received. They were manufactured using the decomposition of a carbon containing gas (CO), in the presence of a metal catalyst (Fe), at moderate temperatures [8].

5.3.1 Raman spectroscopy of HiPCO SWNTs

A Raman spectrum collected at 633 nm, is shown in Figure 5.17. Using the Kataura plot it is possible to see easily that below approximately 205 cm$^{-1}$, peaks are associated with the $M_{11}$ transitions, however above this value, the peaks are associated with the $S_{22}$ transitions. The red laser is therefore a very good method for assessing the relative population of metallic and semiconducting tubes within the HiPCO sample, since both classes are excited (Table 5.7). The semiconducting and metallic regions are indicated on the Raman plot (Figure 5.17).

Figure 5.17 Raman spectrum of HiPCO SWNTs, as-received, using the red (633 nm) laser.
<table>
<thead>
<tr>
<th>Peak (cm(^{-1}))</th>
<th>Transition</th>
<th>SWNT diameter (nm)</th>
<th>(n,m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>M(_{11})</td>
<td>1.15</td>
<td>(15,0) (14,2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(10,7)</td>
</tr>
<tr>
<td>204</td>
<td>M(_{11})</td>
<td>1.10</td>
<td>(8,8)</td>
</tr>
<tr>
<td>216</td>
<td>S(_{22})</td>
<td>1.04</td>
<td>(9,7) (14,0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(10,6) (13,2)</td>
</tr>
<tr>
<td>243</td>
<td>S(_{22})</td>
<td>0.96</td>
<td>(8,6) (9,5)</td>
</tr>
<tr>
<td>255</td>
<td>S(_{22})</td>
<td>0.88</td>
<td>(10,3) (9,4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(7,6) (10,2)</td>
</tr>
</tbody>
</table>

*Table 5.7* Assignment of peaks seen in the HiPCO SWNTs, as-received, using the red (633 nm) laser.

When analysing the complete Raman spectrum ([Figure 5.18](#)), the G-band also suggests the presence of both metallic and semiconducting tubes given the slight BWF line shape. The G/D ratio of 15 also shows that the HiPCO sample contains a significant level of impurities.

![Figure 5.18](#) Raman spectrum of HiPCO SWNTs using the red laser (633 nm).

To further characterise the material, a green (514 nm) Raman laser line was used ([Figure 5.19](#)). Using the Kataura plot it was observed that the green laser predominantly excites large diameter semiconducting and middle to small diameter metallic tubes. This time, many different peaks of comparable intensity could be seen.
in the spectrum. As for the red laser, the diameter of the SWNTs was calculated and the (m,n) values assigned (Table 5.8). It can be clearly seen that, with the green laser, mostly metallic SWNTs are excited. Above 195 cm\(^{-1}\), all of the peaks correspond to the M\(_{11}\) transition. At 187 cm\(^{-1}\), one S\(_{33}\) transition can be seen. The green laser can therefore give some indication of the separation of metallic and semiconducting tubes.

![Raman spectrum of HiPCO SWNTs](image)

**Figure 5.19** Raman spectrum of HiPCO SWNTs, as-received, using the green (514 nm) laser.

<table>
<thead>
<tr>
<th>Peak (cm(^{-1}))</th>
<th>Transition</th>
<th>SWNT diameter (nm)</th>
<th>(n,m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>187</td>
<td>S(_{33})</td>
<td>1.20</td>
<td>(15,1) (10,8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(14,3) (11,7)</td>
</tr>
<tr>
<td>206</td>
<td>M(_{11})</td>
<td>1.09</td>
<td>(10,7)</td>
</tr>
<tr>
<td>215</td>
<td>M(_{11})</td>
<td>1.04</td>
<td>(12,3) (8,8)</td>
</tr>
<tr>
<td>228</td>
<td>M(_{11})</td>
<td>0.98</td>
<td>(9,6)</td>
</tr>
<tr>
<td>246</td>
<td>M(_{11})</td>
<td>0.91</td>
<td>(7,7) (11,2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(12,0)</td>
</tr>
<tr>
<td>263</td>
<td>M(_{11})</td>
<td>0.85</td>
<td>(8,5)</td>
</tr>
<tr>
<td>269</td>
<td>M(_{11})</td>
<td>0.83</td>
<td>(9,3)</td>
</tr>
</tbody>
</table>

**Table 5.8** Showing the diameter and (n,m) values of the tubes excited using the green laser.

The G-band in **Figure 5.20** also indicates that the SWNTs excited by the green laser are predominantly metallic, given the clear BWF line shape. The G/D ratio of 13 also
shows that the HiPCO sample contains a significant level of impurities, a fact also confirmed by the sloping background which is present due to the fluorescence of impurities.

![Raman spectrum of HiPCO SWNTs using the green laser (532 nm).](image)

**Figure 5.20** Raman spectrum of HiPCO SWNTs using the green laser (532 nm).

The IR laser at 785 nm excites only semiconducting tubes. From the RBMs seen in the IR Raman spectrum (**Figure 5.21**), a number of different peaks can be seen and their (n,m) values are assigned in **Table 5.9**. As no relative measure of metallic and semiconducting SWNTs is possible, this laser line was not used to analyse SWNTs following the separation process.
**Figure 5.21** Raman spectrum of RBM of HiPCO SWNTs, using the NIR (785 nm) laser.

<table>
<thead>
<tr>
<th>Peak (cm$^{-1}$)</th>
<th>Transition</th>
<th>SWNT diameter (nm)</th>
<th>(n,m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>206</td>
<td>$S_{22}$</td>
<td>1.09</td>
<td>(12,4) (14,0)</td>
</tr>
<tr>
<td>216</td>
<td>$S_{22}$</td>
<td>1.04</td>
<td>(9,7) (10,6)</td>
</tr>
<tr>
<td>227</td>
<td>$S_{22}$</td>
<td>0.99</td>
<td>(10,5) (13,0)</td>
</tr>
<tr>
<td>234</td>
<td>$S_{22}$</td>
<td>0.96</td>
<td>(11,3) (12,1)</td>
</tr>
<tr>
<td>245</td>
<td>$S_{22}$</td>
<td>0.91</td>
<td>(8,6) (10,3)</td>
</tr>
<tr>
<td>259</td>
<td>$S_{11}$</td>
<td>0.86</td>
<td>(9,4) (7,6)</td>
</tr>
<tr>
<td>267</td>
<td>$S_{11}$</td>
<td>0.84</td>
<td>(10,2) (11,0)</td>
</tr>
</tbody>
</table>

*Table 5.9* The diameter and (n,m) values of the tubes excited using the NIR (785 nm) laser.
5.4.2 UV/Vis/NIR of HiPCO SWNTs

UV/Vis/NIR measurements of the HiPCO tubes were undertaken to complement the Raman (Figure 5.22) data, as they are less sensitive to resonance effects (Section 3.8). The different regions of the spectra associated with different types of SWNTs can again be taken from the Kataura plot and are illustrated on the graph. UV/Vis/NIR spectroscopy is very powerful analysis tool because it shows both the metallic and semiconducting SWNTs without strong resonance effects. However, due to overlap between the transitions it is difficult to assign the individual peaks to particular nanotubes.

![UV/Vis/NIR spectrum of HIPCO SWNTs, as-received.](image)

**Figure 5.22** UV/Vis/NIR spectrum of HIPCO SWNTs, as-received.
5.4.3 Photoluminescence of HiPCO SWNTs

The PL spectrum of the HiPCO sample can be seen in Figure 5.23. By correlating the emission and excitation frequency with that given in the Bachilo paper, the individual SWNTs were assigned (Table 5.10). An estimate of intensity is given by scaling all of the peaks against the most intense peak (8,6).

Figure 5.23 The PL spectra of the as-received HiPCO SWNTs used during this study.

<table>
<thead>
<tr>
<th>Emission, nm $E_{11}$</th>
<th>Excitation, nm $E_{22}$</th>
<th>Assignment</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>960</td>
<td>670</td>
<td>(8,3)</td>
<td>12</td>
</tr>
<tr>
<td>990</td>
<td>575</td>
<td>(6,5)</td>
<td>23</td>
</tr>
<tr>
<td>1040</td>
<td>650</td>
<td>(7,5)</td>
<td>40</td>
</tr>
<tr>
<td>1062</td>
<td>745</td>
<td>(10,2)</td>
<td>42</td>
</tr>
<tr>
<td>1110</td>
<td>730</td>
<td>(9,4)</td>
<td>88</td>
</tr>
<tr>
<td>1124</td>
<td>590</td>
<td>(8,4)</td>
<td>48</td>
</tr>
<tr>
<td>1131</td>
<td>655</td>
<td>(7,6)</td>
<td>95</td>
</tr>
<tr>
<td>1194</td>
<td>725</td>
<td>(8,6)</td>
<td>100</td>
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<tr>
<td>1202</td>
<td>800</td>
<td>(11,3)</td>
<td>78</td>
</tr>
<tr>
<td>1261</td>
<td>680</td>
<td>(9,5)</td>
<td>58</td>
</tr>
<tr>
<td>1269</td>
<td>645</td>
<td>(10,3)</td>
<td>46</td>
</tr>
<tr>
<td>1264</td>
<td>790</td>
<td>(10,5)</td>
<td>68</td>
</tr>
<tr>
<td>1283</td>
<td>730</td>
<td>(8,7)</td>
<td>60</td>
</tr>
<tr>
<td>1332</td>
<td>795</td>
<td>(9,7)</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 5.10 Assignment of the semiconducting SWNTs from the PL spectra [6].
5.4.4 AFM of HiPCO SWNTs

AFM of the HiPCO tubes (Figure 5.24) shows that there is only a small amount of impurities contained within the sample, which occur mainly in large clusters. Catalyst particles can also be seen.

Figure 5.24 Tapping mode AFM images of HiPCO SWNTs, Z-scale is 0-75 nm.
5.4.5 TEM of HiPCO SWNTs

High Resolution TEM images of the as-received HiPCO SWNTs (Figure 5.25) showed a multi-component material containing a large number of catalyst particles and impurities surrounding the SWNTs.
5.4.6 TGA of HiPCO SWNTs

TGA analysis of HiPCO SWNTs shows one distinct burn event (Figure 5.26), with a peak rate at 440°C. This indicates that HiPCO samples primarily contain a single material and can therefore be considered to only contain a small amount of amorphous carbon and graphitic nanoparticles. However, HiPCO SWNTs have a high ash content, approximately 33%, indicating that a large number of catalyst particles are present. Catalyst particle oxidation accounts for the small weight increase seen to begin at 215°C.
5.4.7 HiPCO SWNT Conclusions

The HiPCO SWNT sample contains a wide range of different nanotubes, with a relatively small average diameter of 0.9 nm. The overlap between the excitation of the metallic and semiconducting SWNTs in the red and green Raman lasers make them suitable for studying separation. Although the Raman shows a significant level of impurities, the AFM and TEM show that the samples are reasonable pure except for the large number of catalyst particles, also highlighted in the TGA data. This indicates that the impurities are largely surrounding the nanotubes so they cannot be easily detected in AFM or TEM.
## 5.5 Summary

<table>
<thead>
<tr>
<th></th>
<th>ARC SWNTs</th>
<th>CoMoCAT SWNTs</th>
<th>HiPCO SWNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Raman</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Associated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>transitions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red (633nm)</td>
<td>$M_{11}$</td>
<td>$M_{11}$</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
</tr>
<tr>
<td></td>
<td>$S_{22}$</td>
<td>$S_{22}$</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td>Green (532nm)</td>
<td>$S_{33}$</td>
<td>$M_{11}$</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_{33}$</td>
<td>$S_{33}$</td>
</tr>
<tr>
<td>NIR (785nm)</td>
<td>Not taken</td>
<td>$S_{11}$</td>
<td>$S_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S_{22}$</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td><strong>Diameter range (nm)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red (633nm)</td>
<td>1.40 – 1.53</td>
<td>0.60 – 1.25</td>
<td>0.88 – 1.15</td>
</tr>
<tr>
<td>Green (532nm)</td>
<td>1.36 – 1.49</td>
<td>0.71 – 1.46</td>
<td>0.83 – 1.20</td>
</tr>
<tr>
<td>NIR (785nm)</td>
<td>Not taken</td>
<td>0.75 – 0.92</td>
<td>0.84 – 1.09</td>
</tr>
<tr>
<td><strong>G/D ratio</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red (633nm)</td>
<td>40</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>Green (532nm)</td>
<td>100</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td><strong>TGA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burn events (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>405</td>
<td>440</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>Ash content (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>15</td>
<td>33</td>
</tr>
<tr>
<td><strong>AFM</strong></td>
<td>Visual purity assessment</td>
<td>Large number of impurity clusters</td>
<td>Not imaged</td>
</tr>
<tr>
<td><strong>UV/Vis/NIR</strong></td>
<td>Associated transitions</td>
<td>Suitable dispersion not produced</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$S_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$S_{22}$</td>
</tr>
<tr>
<td><strong>PL</strong></td>
<td>Largest population density</td>
<td>Suitable dispersion not produced</td>
<td>(6,5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TEM</strong></td>
<td>Visual purity assessment</td>
<td>Suitable dispersion not produced</td>
<td>Multi-component</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 5.11* Summary of Raman, TGA, AFM, UV/Vis/NIR, PL and TEM of ARC, CoMoCAT and HiPCO SWNTs.
5.6 References


6 Liquid Ammonia Reduction

6.1 Introduction

Alkali metals dissolved in liquid ammonia produce strongly reducing solutions containing solvated electrons. These electrons can be transferred to SWNTs causing spontaneous debundling [1]. As detailed in Chapter 2, it has been shown that it is possible to functionalise these tubes using, for example, hydrogenation and alkylation. At the start of the author’s research on this topic, the influence of the SWNTs electronic properties on the dissolution or reaction process had not been reported. Since then, only one paper, published in 2008, showed that certain SWNTs were functionalised more readily than others. To the author’s knowledge, no research has studied the possibility that the initial reduction process is selective. This chapter reports work investigating the possibility of separating SWNTs using liquid ammonia reduction, without functionalisation. All of the work reported to date using liquid ammonia reduction performs the subsequent functionalisations whilst the SWNTs are still dissolved in the liquid ammonia [2,3]. To handle liquid ammonia requires specialist equipment and knowledge as ammonia is not only highly corrosive, but also highly toxic. The alkali metals used in these reactions are also difficult to handle as they react violently with water and oxygen, so must be manipulated in an inert atmosphere.

In this chapter, the liquid ammonia reduction is carried out in isolation to generate a SWNT salt by slowly removing the ammonia to leave a dry powder of charged SWNTs containing an alkali metal. This salt can be further processed using standard organic chemistry techniques to allow the separation of SWNTs by their electronic
properties, or to carry out functionalisation reactions using different solvents. Electrochemistry of the dissolved tubes was also attempted.

All the liquid ammonia work was undertaken in collaboration with Dr. Chris Howard at University College, London. Dr. Howard had originally designed and built a rig to allow ammonia to be condensed on a mixture of C\(_{60}\) and lithium metal with the complete exclusion of air [4, 5]. His paper published in JACS showed that C\(_{60}\)\(^5\)-solutions could be formed in liquid ammonia by the formation of 3 giant solvation shells around the fullerene anions. All the condensations detailed in this chapter were undertaken using this rig, without any further modifications.

### 6.2 Experimental Details

Two different types of SWNTs were used in the study, synthesised by two different methods. The first type, grown using the arc evaporation of metal-doped carbon electrodes (ARC) were purchased from Carbon Solutions and used as-received. The second was purchased from Southwestern Nanotechnologies, grown using the decomposition of a carbon-containing gas, in the presence of a metal catalyst containing cobalt and molybdenum (CoMoCAT), and also used as-received. The materials are described in detail in Chapter 5.

In the beginning of this work, each reaction was undertaken with a roughly 1:20 ratio of carbon atoms to alkali metal atoms. This ratio was chosen based on Dr. Howard’s previous experience that C\(_{60}\) dissolved best with 3 electrons per molecule. After the success of the reaction had been confirmed, different ratios were used and full details are given in the text. The reaction was undertaken in a custom-built, high pressure glass reaction tube, containing a glass to metal joint, manufactured by Caburn, which allows a needle valve to be fitted (Figure 6.1). Into this clean and dry reaction tube
(dried in a vacuum oven at about 80°C for at least 4 hours), the required amount of SWNTs (either ARC or CoMoCAT) were accurately weighed. The SWNTs were then out-gassed by first pumping down the glass reaction tube using a Leybold turbo pump, until the pressure reached $10^{-6}$ mbar and heating in a tube furnace at 400°C for 48 hours; the tube was continually pumped during this time to remove any gas released.

![High pressure glass reaction tube](image1)

**Figure 6.1** High pressure glass reaction tube.

After this time, the needle valve was closed and the reaction tube transferred into a glove box with an argon atmosphere. The required amount of sodium was then accurately weighed and transferred to the reaction tube. Making sure that the needle valve was securely closed, the reaction tube was then removed from the glove box and attached to the specially designed liquid ammonia rig (**Figure 6.2**). The liquid ammonia rig contains a Leybold turbo pump and a gas rig capable of withstanding pressures of up to ~15 bar, **Figure 6.3** and **Figure 6.4**. The rig was designed so that small amounts of ammonia could be released safely from the high pressure lecture bottle containing ammonia (Aldrich at 99.9% purity). The rig is constructed from stainless steel Swagelok® components with PTFE seats on the valves.
The rig contains four different lecture bottles: one used to store ammonia, another used to store deuterated ammonia, ND$_3$, (which is not used in this project) and two used as buffers (150 cc and 300 cc). The also rig contained four different valves:

Valve 1 - isolates the pump from the rig.

Valve 2 - isolates the ammonia lecture from the rig.

Valve 3 – isolates the deuterated (ND$_3$) lecture from the rig.

Valve 4 – isolates the sample from the rig.

A pressure transducer is also fitted to the rig and the rig itself is maintained under vacuum to reduce the risk of contamination.
With the reaction tube attached to the rig and the needle valve closed, the connecting stainless steel tubing was pumped down by opening valves 1 and 4. After the pressure in this tube reached \(<10^{-5}\) mbar, the needle valve to the reaction tube was opened and the reaction tube was pumped down to \(10^{-7}\) mbar, for 12 hours at room temperature. After this time, a propanol, dry ice bath was made by adding small
amounts of dry ice to propanol until the bath reached the required temperature of between -43 °C and -53 °C. Care was taken to keep the bath between these values as the ammonia does not condense at higher temperatures and freezes at lower temperatures. The reaction tube was submersed in this bath.

The rig was created to condense approximately 0.12 moles of ammonia gas in 0.024 mole aliquots. The ideal gas equation (*Equation 6.1*) was used to calculate the pressure of ammonia used in the reaction.

\[
\Delta P = \frac{nRT}{V} \quad \text{Equation 6.1}
\]

The pressure in Pascal’s (\(P\)) is in a known volume in m\(^3\) (\(V\)) (the 300cc buffer), \(R\) is the molar gas constant (8.314 m\(^2\)kgs\(^-2\)mol\(^-1\)K\(^-1\)), \(T\) is the temperature of the gas in Kelvin and \(n\) is the number of moles.

Hence, 10 bar of ammonia was condensed into the reaction vessel in 2 bar aliquots.

The gas was stored in the 150 cc buffer and decanted into the 300 cc buffer before condensing onto the sample. First, valve 1 was closed; isolating the rig from the pump, then valve 4 was closed; isolating the sample from the pump. The 300 cc buffer was then opened by gradually opening the valve in its top. The first of the aliquots was then removed from the 150 cc buffer by slowly opening the valve in its top. After the pressure reached approximately two bar, the valve on top of the 150 cc buffer was closed and the exact value of the pressure noted. This ammonia is then condensed onto the SWNT and alkali metal mixture by slowly opening valve 4; the condensation process draws the ammonia from the 300 cc buffer onto the sample. When the pressure within the rig had stabilised, the pressure was noted and valve 4 was closed again. The difference between the two pressures determines how much ammonia had been condensed onto the sample. The process was then repeated 5 times to condense further 2 bar (0.024 mol) aliquots until a pressure of approximately
10 bar had been added to the sample. After the final aliquot was added, valve 4 was left open so that the pressure within the reaction tube could be monitored.

Upon addition of the first aliquot of ammonia, the intense blue colour of solvated electrons could be seen [1]; after this point the experimental conditions determined the outcome of each process, and details are given in the text at each point. When the process was complete, the ammonia was removed from the reaction tube by cryopumping. This process was undertaken by submersing the 150 cc buffer in liquid nitrogen, being careful to only submerse the bottom half so as not to freeze the valve. After about 2 minutes, any remaining ammonia in the 150 cc buffer was frozen. In order to isolate the sample from the rig, valve 4 was then closed and the valve to the 150 cc buffer opened, to condense any ammonia within the rig. Valve 4 was then very slowly opened to cryopump the liquid ammonia from the sample, until the vapour pressure in the rig reached about 0.03 bar. At this rate, the ammonia was drawn off over approximately 3 hours; this slow rate avoids bubbling in the solution.

After all of the ammonia was returned to the holding buffer, the valves to both holding buffers were closed. Valves 4 and 1 were then opened to allow the reaction tube to be pumped for 12 hours to remove any remaining ammonia. Once “dry”, the reaction tube was removed from the liquid ammonia rig and passed back into the argon atmosphere glove box.

In this glove box, the charged SWNTs were separated into two weighed quantities and transferred to two specially-made Schlenk tubes containing Young’s taps (Figure 6.5).
The Schlenk tubes were then attached to a Schlenk line which allows for the manipulation of liquid under an inert atmosphere (Figure 6.6) and using standard Schlenk line techniques, organic solvents were introduced (Figure 6.7).

First, two Schlenk tubes containing the nanotube powder and the dry solvent respectively were attached to the Schlenk line via ground glass joints. The tubing attached to the joint was then pumped filled three times via the Schlenk line to remove any trace of air from around the Young’s tap. Keeping a positive pressure of nitrogen, the Young’s taps were then removed from each Schlenk tube and replaced with a suba seal. A clean, dry, hot cannula (double-ended stainless steel needle) was then put through the suba seal into the flask containing the solvent and a positive
pressure of nitrogen was allowed to flow out through the cannula to remove any traces of air, whilst using a heat gun to desorb water. After 2 minutes, the open end of the cannula was inserted into the Schlenk tube containing the nanotube powder. The dry solvent was then transferred from the flask to the Schlenk tube by turning off the flow of nitrogen to the Schlenk tube, pushing the cannula down into the solvent and placing an exit needle in the suba seal at the top of the Schlenk tube. The positive pressure of nitrogen on the solvent causes it to flow up the needle and into the Schlenk tube containing the SWNT salt. After the required amount of solvent had been transferred, the cannula was pulled out of the solvent, the nitrogen was turned back on to the Schlenk tube and the exit needle removed. The cannula was then removed first from the Schlenk tube and then from the Schlenk flask. After this point both the suba seals were removed and the Young’s taps screwed back on.

Figure 6.7 Addition of dry solvent to reduced SWNTs.
The majority of the work used dry THF (dried in house on a solvent drying column, 0.58 ppm as reported from the technician’s Karl Fisher measurements) or dry DMF (Aldrich, anhydrous 99.8%). The solvents were chosen as they had previously been shown to act as good solvents for nanotube salts by authors such as Penicaud [6]. Following the spontaneous dissolution of the SWNT fraction, experiments were undertaken using different quenching agents. Electrochemical experiments were also undertaken in an attempt to quench the charge on the SWNT without using chemical means. All details of these process are given in the text.

6.3 Analytical Results for ARC SWNTs

The liquid ammonia reduction was first attempted with ARC-grown SWNTs as these were the choice of SWNTs in the liquid ammonia functionalisation work in the literature. Initially, 20 mg SWNT and 2 mg sodium were used. When the liquid ammonia was added to the mixture, a blue colour was observed. The nanotubes were then seen to dissolve in the liquid ammonia with eventual loss of the blue colour of solvated electrons; a clear indication of the charging of the SWNTs. Although no high quality photographs of this process were taken during the author’s work, in his previous work, Dr. Howard managed to take photographs of ARC SWNTs in the liquid ammonia (Figure 6.8). Figure 6.8a shows the formation of the blue colour upon addition of the liquid ammonia where the SWNT powder can clearly be seen to be undissolved, Figure 6.8b shows that the SWNTs then dissolve into the ammonia and the blue colour can still be seen, Figure 6.8c shows that eventually the blue colour disappears and the SWNTs stay dissolved in the ammonia.
When the dry powder of the charged nanotubes was transferred to the Schlenk tubes, care was taken to completely exclude air, both during the transfer and the subsequent manipulation (oxygen and moisture both quench charged tubes [6]). When using dry THF as a ‘solvent’, the SWNTs remained at the bottom of the Schlenk tube; no dispersion was apparent.

In contrast, dry DMF was seen to swell the nanotubide powder, leading to spontaneous dissolution. Figure 6.9 shows the swelling and dissolution of SWNTs upon addition of DMF, which began immediately on the addition of solvent (in <1 min) and continued steadily for 12 hours, after which time a black solution was seen. It is worth emphasising that no stirring, and more importantly, no ultrasound was used at any stage of the process.
Figure 6.9 Spontaneous dissolution of a powder of ARC SWNTs following a liquid ammonia reduction, into 10 cm$^3$ dry DMF after a) 1 minute, b) 10 minutes, c) 30 minutes, d) 1 hour, e) 12 hours.

Although DMF and THF are both polar, aprotic solvents, DMF may allow the spontaneous dissolution of the SWNT due to its resonance structure (Figure 6.10) allowing for the stabilisation of both the negative charge on the nanotube itself and the positive sodium ion (Figure 6.11).

Figure 6.10 Resonance forms of DMF.
Figure 6.11 Schematic representation of the possible stabilisation that DMF can bring to the reduced SWNTs.

This spontaneous dissolution of SWNTs is a very exciting result, as the dissolution of SWNTs in common solvents such as DMF has long been a goal of SWNT research. Often, solutions are formed following intense sonication, which is known to damage the unique structure of the SWNTs, or following surfactant wrapping or functionalisation. The liquid ammonia reduction method produces a good dispersion in DMF by utilising electrostatic repulsion between the charged SWNTs to overcome the van der Waals forces that hold the SWNTs together. It should be noted that when DMF is added to as-received ARC SWNTs, no spontaneous dissolution occurs.

After the SWNT sample was left to fully dissolve in the DMF, the dissolved fraction was removed using standard Schlenk line techniques and the undissolved fraction was then opened to air and left to dry in a fume cupboard. The reduced weight of this sample showed that 40% of the SWNTs had been dissolved into the DMF.

Raman spectroscopy was used to assess if functionalisation of the ARC SWNTs had occurred after the spontaneous dissolution. Following the quenching in air, the G/D ratio was seen to decrease by half (Figure 6.12) showing that a significant number of
carbon atoms in the SWNT wall had changed from sp² to sp³ hybridisation; this effect is consistent with functionalisation, most likely with oxygen groups along the surface of the nanotubes. It is also possible that functionalisation within the liquid ammonia itself might occur. If the ammonia was to decompose during the reduction process then NH₂⁻ may be formed by the reaction sequence given in *Equation 6.2*.

\[
\text{Na} + \text{NH}_3 \rightarrow \text{Na}^+ + \text{e}^- \cdot \text{NH}_3 \rightarrow \text{Na}^+ + \text{NH}_2^- + \frac{1}{2}\text{H}_2 \quad \text{Equation 6.2}
\]

This may lead to functionalisation with NH₂ groups on the nanotube surface, causing a change from sp² to sp³ hybridisation and hence a decrease in the G/D ratio. However, this is thought to be unlikely due to the short time scale of the reduction reaction; ammonia containing dissolved alkali metals has been shown to be stable for 72 hours in an air free environment. Therefore no significant decomposition should occur during the liquid ammonia reduction.

![Figure 6.12](image) Raman data of ARC SWNTs, showing as-received (solid line) and quenched in air (dotted line) using a red (633 nm) laser.
A slight increase in the metallic contingent of the G-band suggests an increase in the metallic character of the sample. However, as detailed in Chapter 5, when looking at the RBMs, neither red nor green Raman laser lines provide information regarding the separation of metallic and semiconducting ARC SWNTs. Therefore, following the work on the electrochemical deposition of the ARC SWNTs, the work was repeated with CoMoCAT tubes which are more easily analysed using the readily available red and green Raman lasers and UV/Vis/NIR spectroscopy.

6.3.1 Electrochemical Deposition

To assess the electrochemical properties of the charged SWNT solution a 3-electrode electrochemical cell was set-up using platinum working, reference, and counter electrodes and attached to a Solartron potentiostat (SI 1287) (further details provided in Chapter 7). The cell was kept dry at all times to prevent the quenching of the charged nanotube species. A cyclic voltammogram (CV) was then run over the range of +3 to -4 V. Although this potential range would be considered very large in standard electrochemical experiments and in fact even exceeds the solvent window of DMF, it was used because the big differences seen between the control and SWNT CV meant that the SWNT redox events were more important than the solvent degradation and information could still be obtained. During the CV, the potential of the working electrode was swept from 0 V to +3 V then cycled between +3 and -4 V, at 50 mV/s, for 5 cycles, ending at 0 V, the cell was stirred during each CV. The scan rate of 50 mV/s was chosen as it is the standard scan rate used in most previous electrochemical work on SWNTs [7-9] and produced clear spectra in this work. No extra electrolyte was added to the reaction mixture, just simply the charged SWNTs containing sodium ions and dry DMF. Oxidation and reduction peaks were clearly
seen (Figure 6.13), whereas the control reaction, using just the dry DMF, showed no such peaks (Figure 6.14) and a significantly lower current. The two sharp peaks in the control CV are artefacts caused by a mixture of the low current and the stirring of the electrochemical cell.

**Figure 6.13** CV of reduced ARC SWNTs in dry DMF, at 50 mV/s, 5 cycles. Red arrows indicate the cycle direction.

**Figure 6.14** CV of dry DMF, 50 mV/s for 1 ½ cycles. Red arrows indicate the cycle direction.
The CV of the reduced SWNTs shows a number of oxidation and reduction peaks; there appear to be 3 of each with significant hysteresis. This CV was seen to be stable over many cycles, indicating reversible electron transfer events. The reversible nature of these electron transfers is what would be expected from SWNT redox events as electrons can be transferred to and from the nanotubes without fundamentally altering the SWNT structure. The distinct nature of the peaks occurs as the spontaneously dissolved fraction contains a discrete number of nanotubes, thus producing discrete peaks. It should be taken into account that although it is thought the redox events present in the CVs are due to the SWNT themselves, there may also be a contribution from residual transition metal catalyst particles, poly aromatic hydrocarbons and fullerenes.

Following on from this work, electrodeposition of the SWNTs was attempted by holding the working electrode at 2 V for 2½ hours whilst stirring. The cell was held at the highest potential oxidation peak in an attempt to deposit all of the suspended species. During the potentiostatic deposition, the current rises as the SWNT deposit grows on the working electrode (Figure 6.15). After this time, the working electrode was removed from the black solution and a gel type network of SWNTs was clearly seen to have deposited (Figure 6.16). The growing volume (and hence surface area) of this gel deposit probably accounts for the increasing deposition current. Ultimately, if there is any selectivity in either the dissolution or deposition process, this method will provide a means of collecting a certain fraction. To show that deposition only occurs when a current is passed, the cell was set-up and left to stir for 2½ hours without passing a current; this experiment produced no deposition (Figure 6.16c).
Figure 6.15 Potentiostatic deposition at 2 V, current density of the spontaneously dissolved ARC SWNT fraction.

Figure 6.16 Photographs of the electrochemical processing of ARC SWNTs following the liquid ammonia reduction; a) electrochemical cell used to deposit the SWNT onto the WE after being held at 2V for 2 ½ hours, b) close up image of this deposit, c) wire dipped in electrochemical cell and stirred for 2 hours with no current flow.
6.3.2 ARC Conclusions

This work showed that ARC SWNTs could be reduced in liquid ammonia to produce a dispersion of nanotube anions. This SWNT salt can be dried and re-dispersed in DMF as long as air and moisture are avoided. Although this dispersion has been demonstrated at a microgram level, larger quantities could be processed straightforwardly, given sufficient ammonia handling experience and facilities. Redox features of the SWNTs were then identified and the possibility of electrodeposition demonstrated. Next, the same reaction was attempted with CoMoCAT SWNTs, whose more distinctive RBMs make them easier to analyse using Raman spectroscopy.

6.4 Analytical Results for CoMoCAT SWNTs

6.4.1 Initial Separation Results

Following the dissolution success of the ARC SWNTs, the same reaction was attempted with CoMoCAT SWNTs. As previously mentioned, CoMoCAT tubes allow the study of metallic and semiconducting SWNTs using the two available lasers; red (633 nm) and green (532 nm) (a full discussion of CoMoCAT characterisation is given in Chapter 5). An initial reaction was attempted using 20 mg SWNTs and 2 mg Na metal. Initially, a vivid blue colour solution formed which disappeared over time as the SWNT powder swelled to approximately 10 times the original volume. In this case, the SWNTs did not dissolve into the ammonia to make a black solution. This lack of apparent dissolution is likely due to the greater length of the CoMoCAT SWNTs, meaning that the individual tubes will be more entangled.
When dry DMF was added to the dry powder, following the liquid ammonia reduction, the CoMoCAT SWNTs were seen to swell and spontaneously dissolve into the DMF (Figure 6.17).

The liquid ammonia reduction and the subsequent DMF addition were performed using the same techniques as the ARC case. The CoMoCAT SWNTs swell more than the ARC tubes upon DMF addition but the dissolution progresses at a slower rate; after 12 hours the swollen powder can still be distinguished from the dissolved fraction, indicating that a smaller percentage of the SWNTs have dissolved at this stage. Once again this can be attributed to the greater length of the CoMoCAT SWNTs compared to the ARC SWNTs. The CoMoCAT samples are also extremely sensitive to air, causing immediate aggregation. It should be noted that when DMF is added to as-received CoMoCAT SWNTs no swelling or dissolution is seen. By measuring the weight loss of the undissolved fraction (remaining undissolved after 48 hours) after further drying, it was found that only 5% of the CoMoCAT SWNTs dissolve.
A portion of the spontaneously dissolved fraction was removed from the tube and deposited onto a cover slip, causing the tubes to be quenched in air. After all of the solvent had evaporated, the 633 nm Raman spectra clearly shows a decrease in the intensity of the peaks correlating to the semiconducting SWNTs, relative to the metallic nanotubes (Figure 6.18). From the characterisation work detailed in Section 5.3 it is known that the semiconducting tubes represented 75% of this CoMoCAT sample, however after this dissolution their intensity is insignificant within the spectra indicating a very strong separation. The peak at 152 cm\(^{-1}\) stays at the same intensity, due to the significant contribution from the metallic (7,7) tubes.

![Figure 6.18 Raman spectra](image)

Figure 6.18 Raman spectra [red (633 nm) laser] in the RBM region for as-received CoMoCAT SWNTs (solid line), the spontaneously dissolved CoMoCAT fraction (dashed line) and the spontaneously dissolved CoMoCAT fraction following vacuum annealing (dotted line). The shaded area represents the cross-over between the metallic and semiconducting SWNTs.
<table>
<thead>
<tr>
<th>$\omega_{\text{RBM}}$</th>
<th>d (nm)</th>
<th>(m,n)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>191</td>
<td>1.25</td>
<td>(13,4)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9,9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(14,2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12,6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(15,0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10,7)</td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>1.10</td>
<td>(12,3)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11,5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8,8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13,1)</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td>0.93</td>
<td>(7,7)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10,3)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(11,1)</td>
<td></td>
</tr>
<tr>
<td>281</td>
<td>0.83</td>
<td>(7,5)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8,4)</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>0.79</td>
<td>(8,3)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6,5)</td>
<td></td>
</tr>
<tr>
<td>334</td>
<td>0.70</td>
<td>(6,4)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td>381</td>
<td>0.60</td>
<td>(5,4)</td>
<td>$S_{11}$</td>
</tr>
</tbody>
</table>

**Table 6.1** The measured $\omega_{\text{RBM}}$ with associated diameter, (m,n) indices and transition type as seen from the peaks observed in the red Raman spectra (633 nm) [10-13].

To exclude the possibility of differential or selective functionalisation, vacuum annealing was undertaken. Vacuum annealing is often used in SWNT research to restore the original properties of SWNTs following functionalisation, by removing the functional groups such as alcohols, ethers, esters, and acid groups. Vacuum annealing was performed on the sample at 500°C and $10^{-6}$ mbar for 24 hours, after which time the Raman spectra could be seen to stay the same; a good indication that real separation by selective dissolution had occurred. It is important to note that the Raman spectrum shown in **Figure 6.18** is representative of the whole spontaneously dissolved fraction. To check reproducibility, 10 spectra where recorded of each sample and all of the Raman spectra taken from the spontaneously dissolved fraction were identical.
The green Raman laser line similarly shows the relative decrease in intensity of the semiconductor peaks relative to the metallic peaks, a result that persists after vacuum annealing (Figure 6.19). The peaks are subtly different after vacuum annealing compared to the spontaneously dissolved fraction. However, this result should not be over analysed as problems with the fluorescent background leads to the peaks observed using the green laser being less reproducible than those seen using the red laser.

**Figure 6.19** Raman spectra [green (532 nm) laser] in the RBM region for as-received CoMoCAT SWNTs (solid line), the spontaneously dissolved CoMoCAT fraction (dashed line) and the spontaneously dissolved CoMoCAT fraction followed by vacuum annealing (dotted line).
<table>
<thead>
<tr>
<th>$\omega_{\text{RBM}}$</th>
<th>d (nm)</th>
<th>(m,n)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>242</td>
<td>0.97</td>
<td>(10,4)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>257</td>
<td>0.91</td>
<td>(7,7)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>264</td>
<td>0.89</td>
<td>(8,5)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>286</td>
<td>0.82</td>
<td>(9,3)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>299</td>
<td>0.78</td>
<td>(7,4)</td>
<td>$M_{11}$</td>
</tr>
<tr>
<td>306</td>
<td>0.76</td>
<td>(6,5)</td>
<td>$S_{22}$</td>
</tr>
<tr>
<td>328</td>
<td>0.71</td>
<td>(6,4)</td>
<td>$S_{22}$</td>
</tr>
</tbody>
</table>

*Table 6.2* The measured $\omega_{\text{RBM}}$ with associated diameter, (m,n) indices and transition type as seen from the peaks observed in the green Raman spectra (532 nm).

UV/Vis spectroscopy was also used to assess the fraction of metallic and semiconducting SWNTs within the sample. UV/Vis clearly shows a reduction in the size of the semiconducting peaks following the dissolution in the DMF. The first van Hove transition of the metallic species can be seen in the 350-500 nm range, the low intensity of the peaks in the as-received sample shows the small fraction of SWNTs. The second van Hove transitions of the semiconducting SWNTs can be seen in the 480-700 nm range. In this range, the largest peak at 560 nm relates to (6,5) SWNTs, known to be the largest fraction in CoMoCAT samples. Following the spontaneous dissolution of the charged tubes, the intensity of all the peaks in the semiconducting region can be seen to greatly decrease (Figure 6.20).
Figure 6.20 UV/Vis spectra of as-received CoMoCAT SWNTs (black line) and the spontaneously dissolved fraction (red line).

This selective dissolution matches the selective functionalisation observed by Wonderlich et al. [1], as it is easier to reduce metallic SWNTs due to the availability of the conductance band above the Fermi level. The approach is a relatively simple, scalable and non destructive method to separate SWNTs by their electronic properties. SEM, undertaken on the spontaneously dissolved fraction, showed that the sample contained predominantly nanotube material (Figure 6.21).
Although the results above show that there is clear separation of the SWNTs after the liquid ammonia reduction and DMF dissolution; when the undissolved fraction following DMF dissolution was quenched in air and analysed, a wide range of SWNT spectra were seen both with the red (Figure 6.22) and green lasers (Figure 6.23). In
both cases, spectra varied between that of the as-received material to that of the dissolved fraction. The apparent enrichment of metallic tubes could therefore also be seen in this undissolved fraction.

**Figure 6.22** RBM region of the undissolved fraction using 633 nm laser, all spectra collected from a single sample.

**Figure 6.23** RBM region of the undissolved fraction using 532 nm laser, both spectra collected from a single sample.
This complete mix of nanotube species seen within a variety of areas of the same undissolved sample, along with the enrichment of metallic tubes, gives an indication that either during the liquid ammonia reduction process or in the DMF itself the nanotubes are separated by their electronic character; producing areas of specific SWNT types.

When the pure nanotube salt was analysed, following liquid ammonia reduction but before DMF addition, by quenching with air, a similar mixture of RBM spectra were seen. This result suggests that the separation must occur in the liquid ammonia. To test the hypothesis further and to exclude the possibility that the quenching reaction itself is responsible for selective degradation of semiconducting SWNTs, the salt was decomposed without quenching. A sample of the nanotube salt was maintained air free and the metal was removed by pumping at $1 \times 10^{-6}$ whilst heating to $200\degree C$ for 12 hours. The sodium condensed at the far end of the sample tube, visible as a metallic coating (Figure 6.24). Following removal of the metal from this sample, the Raman spectra once again showed the mixture of as-received and sorted characteristics discussed above.

![Figure 6.24 The liquid ammonia reduced SWNTs following metal removal.](image)

However, after this sample was dissolved in N-Methylpyrrolidone (NMP) by sonication for 15 minutes to destroy the bundles, the Raman spectra were essentially identical over the whole sample and returned almost to that of the starting material (Figure 6.25). A rising background remains due to NMP trapped within the sample. It should be noted that that Raman spectra shown in Figure 6.25 is representative of
the whole sample; when 10 spectra were recorded, no significant differences were observed.

![Figure 6.25](image)

**Figure 6.25** Raman spectrum [red (633 nm) laser] in the RBM region for CoMoCAT SWNTs with metal removed under air free conditions, dissolved into NMP and deposited onto a cover slip.

This evidence supports the proposed mechanism that the metallic tubes are reduced most easily in the liquid ammonia, repel one another and attempt to break free of the bundles that constrain them. Sometimes the metallic SWNTs can break free of the bundles and hence disperse in the DMF or ammonia, but in other cases they are still partially entangled. When the solvent is removed from the sample, the metallic tubes tend to form areas of higher concentration, so that the enrichment is still seen using Raman spectroscopy. Extensive grinding with a pestle and mortar still leads to the mixed Raman spectra; indicating that the semiconducting SWNTs are constrained within bundles which are not affected by macroscopic grinding. However, by removing the metal and redissolving the tubes the local segregation is removed, the
as-received spectra is essentially recovered, confirming that the semiconducting tubes remained in the bulk of the sample.

### 6.4.2 Metal to Carbon Ratio

In all the previous work, 2 mg of sodium was added to 20 mg of SWNTs, giving a ratio of 1 metal atom to 20 carbon atoms. To investigate the possibility of increasing the yield of the reaction and changing the reaction selectivity, two different metal:carbon ratios were investigated. First the amount of metal used was doubled, giving a carbon:metal ratio of 10. In this case, the same process was seen in the liquid ammonia; the initial blue colour was lost during extensive swelling of the CoMoCAT SWNTs. The SWNT salt was then seen to dissolve into the DMF. On analysis of the spontaneously-dissolved, undissolved, and bulk fractions, the Raman results were similar to the 2 mg metal sample; a huge enrichment of metallic tubes was seen in the dissolved fraction. However, the increase in metal content allowed for a larger percentage dissolution, reaching 14 wt%. On increasing the carbon:metal ratio to 4, the same process was seen to occur in the liquid ammonia, but no dissolution occurred upon DMF addition. This may be due to the high level of charge causing a more favourable ionic crystallisation energy than the solvation energy, therefore dissolution will not occur. Further reactions need to be performed to determine the metal to carbon ratio that allows for maximum SWNT dissolution in DMF.

### 6.4.3 Scale Up

To move any chemical research out of the laboratory and into the manufacturing world, scale-up is of optimum importance. Although specialist knowledge is needed in working with liquid ammonia, the method offers the possibility of relatively easy
scale-up due to avoidance of centrifugation, sonication, or other volume-limited steps.

As an initial test, a larger scale reaction was attempted. In this case, 48 mg of CoMoCAT SWNTs were used with 9.6 mg of sodium metal. The reaction sequence in the liquid ammonia occurred just as before and the SWNTs were seen to dissolve into the DMF, a yield of 15 wt%. A much larger reaction needs to be undertaken to truly check the reaction scale-up; however, a new experimental rig would need to be designed and built.

6.4.4 Functionalisation Following Liquid Ammonia Reduction

The degree of functionalisation produced by quenching the charged SWNTs following the liquid ammonia reduction is also an important factor when considering the practical relevance of the reaction. Assuming the charge is fully delocalised along the length of the tube, it seems unlikely that simply the addition of charge will create defects in the nanotube structure, unless functionalisation with the ammonia itself occurs, as discussed in Section 6.3. It is thought that this reaction mechanism is unlikely due to the short time scale of the reduction in the liquid ammonia; liquid ammonia has been shown previously to be stable for days under air free conditions with no decomposition taking place. However, exposing the sample to air, which will quench the charge on the sample (most likely due to reaction with oxygen groups in the air) will, in turn, functionalise the SWNTs. After the SWNT reduction, spontaneously dissolved and undissolved fractions were exposed to air, and the G/D Raman ratio measured. In each case, a decrease in the G/D ratio showed that a significant number of carbon atoms in the SWNT wall had changed from sp² to sp³ hybridisation; this effect is consistent with functionalisation, most likely with oxygen
groups along the surface of the nanotubes. The spontaneously dissolved fraction always contained a large number of defects as they are the most charged tubes.

To investigate this functionalisation effect, different chemical quenching agents were used. The tubes were quenched with air, water and methanol, by either direct exposure to the dry sample or by adding to the dissolved fraction in DMF (Figure 6.26).

![Chemical sequence for quenching process following the liquid ammonia reduction.](image)

**Figure 6.26** Chemical sequence for quenching process following the liquid ammonia reduction. Labels in bold type show the points where the G/D ratio was measured.

Each different quenching agent changed the G/D ratio slightly; the full results are given in the Table 6.3. The difference between quenching the spontaneously dissolved fraction still dissolved in the DMF, and the same fraction following DMF removal, was also investigated. The difference between dissolved and bulk quenching was observed by Wunderlich et al., who showed that when charged SWNTs are quenched in a bulk format, charge transfer between the SWNTs means
that only SWNTs on the outside of the bulk will be functionalised due to quenching [1]. After the DMF was removed from the spontaneously dissolved fraction by direct pumping and the solvent-free sample was exposed to air, the G/D ratio was seen to be twice that of the spontaneously dissolved fraction quenched while still dissolved in DMF. This apparent decrease in the amount of functionalisation in the bulk format is a good indication that individual tubes can be seen in the DMF.

<table>
<thead>
<tr>
<th>Point in separation process</th>
<th>Quenching agent</th>
<th>SWNT/Na (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20/2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48/9.6</td>
</tr>
<tr>
<td>As-received</td>
<td>N/A</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>SWNT salt</td>
<td>Air</td>
<td>Not taken</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Not taken</td>
</tr>
<tr>
<td>Undissolved fraction</td>
<td>Air</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Dissolved fraction</td>
<td>Air</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Not taken</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>Not taken</td>
</tr>
<tr>
<td></td>
<td>DMF removed</td>
<td>Not taken</td>
</tr>
<tr>
<td></td>
<td>and air</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>quenched</td>
<td></td>
</tr>
</tbody>
</table>

*Table 6.3* The G/D ratio of different CoMoCAT fractions with different metal contents and quenching agents. Red Raman laser used (633 nm).

### 6.4.5 Electrochemical Deposition

To both increase the effectiveness of the electrochemical separation and to investigate the possibility of forming separated species without functionalisation, attempts were made to use the electrochemical equipment developed in *Chapter 7* to oxidatively
deposit the SWNTs. Under dry conditions the spontaneously dissolved fraction of the dry DMF solution was transferred to an electrochemical cell, using the same methods as detailed for the ARC work.

Once again, a 3-electrode electrochemical cell was set-up and the CV was run using the same conditions as in the ARC case (Section 6.3.1). This CV also showed distinct peaks (Figure 6.27), which were not seen in the control CV (Figure 6.14). It is thought that these peaks are due to oxidation and reduction events, however they may also have a contribution from residual transition metal catalyst particles, poly aromatic hydrocarbons and fullerenes.

![Figure 6.27 CV of charged CoMoCAT SWNTs in DMF at 50 mV/s for 5 scans, the red arrow indicate the direction of the cycle.](image)

Although clear peaks could be seen in both the CV of the charged ARC SWNTs and the charged CoMoCAT SWNTs salt, closer inspection shows clear differences between the two voltammograms (Figure 6.28). The clearest difference between the two voltammograms can be seen in the extra oxidation and reduction peaks of ARC
SWNTs at 2.1 V and -2.1 V, respectively. This oxidation peak at a higher potential indicates that the charge on the ARC SWNTs is more stable than that on the CoMoCAT SWNTs which also accounts for the extra dispersibility in DMF and the more stable solution it forms (it takes longer to crash out on exposure to air).

Figure 6.28 CV in DMF at 50 mV/s for 5 scans a) Charged ARC SWNT salt, b) Charged CoMoCAT SWNT.

Nevertheless, to keep consistency between the two samples, the CoMoCAT cell was again held at 2 volts for 2 ½ hours whilst stirring; the SWNTs were deposited on the working electrode (Figure 6.29).

Figure 6.29 CoMoCAT SWNTs deposited on the working electrode, held at 2 V for 2½ hours.

When these SWNTs were analysed with the red Raman laser they were found to have the same RBM intensity as the spontaneously dissolved fraction as a whole. No further separation had taken place following the deposition. This outcome is expected as the voltage (2 V) used is much higher than the 1st oxidation peak; any further
separation could only be achieved at lower voltages. The G/D ratio of these electrochemically-deposited tubes was 6, suggesting either high degree of functionalisation of the SWNTs themselves or a higher level of impurities present.

6.4.6 CoMoCAT Conclusions
Liquid ammonia reduction has been shown to be a useful method for creating powders of charged SWNTs that can be spontaneously dissolved in dry DMF. The spontaneously-dissolved fraction is shown to consist mainly of metallic SWNTs. This separation approach is scalable, thus allowing large quantities of metallic SWNTs to be produced. If developed, the process could have far reaching influences on the future development of the material.

6.5 Further work
The conclusions drawn from the successful separation of SWNTs leave huge scope for future work. The first step would be further variation of the metal:carbon ratio used in the initial ammonia reduction to give the maximum percentage-dissolved yield. The type of alkali metal used may also change the outcome of the reduction and should be investigated. Although a small scale-up experiment was undertaken by the author, much larger volumes need to be investigated to prove that this method of separation could work on an industrial level. The amount of liquid ammonia present may also have an important influence on the ability of the nanotubes to debundle, disentangle and therefore dissolve. The two other areas that warrant investigation are the possibility of functionalising the reduced SWNTs with any required groups by selective active quenching agents and conversely the possibility of quenching the charge with as little functionalisation as possible, for example by vacuum annealing.
6.6 References


7 Electrochemical Enrichment and Separation

7.1 Introduction

The need to separate SWNTs by their electronic properties has been known for some years. The work detailed in this chapter describes a completely new method of SWNT enrichment and separation using electrochemical means. The underlying principle of this electronic separation technique is currently used as a cheap and scalable electrochemical purification process in, for example, the purification of copper; here it is adapted to reduce carbon nanotubes, thus producing individual nanotube species which can be selectively deposited by oxidation.

Current literature indicates that it is possible to disperse charged nanotubes: several groups investigated nanotube dispersions by reducing the tubes with an alkali metal in liquid ammonia [1-3] or by oxidising/protonating in fuming sulphuric acid [4]. The work detailed in this chapter exploits the redox behaviour of carbon nanotubes by electrochemistry, using a bucky paper (a thin sheet of carbon nanotube paper formed by filtering a good SWNT dispersion) as the working electrode. When the cell containing the electrolyte (sodium tetraphenyl borate) is held at negative potentials, the SWNTs are reduced, repel one another and overcome the van der Waals forces that hold them together. They therefore leave the bucky paper as individually separated nanotubes and disperse into the electrolyte. These reduced nanotubes can then be electrochemically deposited on the counter electrode as a thin carbon nanotube film.

The ease by which certain nanotubes are initially reduced, and subsequently deposited, depends on their electronic character; a fact that is fully explored as a means of enrichment and separation in this chapter.
The electrochemical work was preformed in a dry, oxygen free environment as it is known that any air and moisture within the system will react with the SWNTs, quenching any charge on the SWNTs [5]. As such, standard organic chemistry Schlenk line techniques were combined with the electrochemical methods, as described below.

Firstly, this chapter will briefly discuss how the potentiostat used during all of the electrochemical experiments was tested, using the standard potassium ferrocyanide cell. Then the work moves on to show how the dryness of the cell, designed by the author, was tested using the electrochemical generation of a sodium anthracinide. From this starting point, the redox properties of the carbon nanotubes were probed using cyclic voltammetry (CV) and the separation of the SWNTs by their electronic properties was carried out. This chapter ends by giving examples of the future work which could be undertaken in this area.

### 7.2 Testing the Potentiostat

All electrochemistry experiments undertaken in this thesis used a Solartron potentiostat (SI 1287 electrochemical interface and FRA 12556). Before any electrochemical reactions were undertaken the potentiostat was calibrated and tested to assess its working condition, using a Solartron Instruments 12861 ECI test module. After following the automated calibration procedure, all results were found to be within the manufacturer’s guidelines.

Following this successful calibration, testing of the potentiostat was then undertaken using the potassium ferrocyanide cell. This redox couple is often used to illustrate a reversible cyclic voltammetric response, as the ferricyanide ion is reduced to
ferrocyanide, producing distinct oxidation and reduction peaks in the resulting voltammogram [6].

The three component cell was set-up using a glassy carbon electrode as the working electrode, silver/silver chloride (Bioanalytical RE-5B) as the reference electrode, and platinum as the counter electrode. The electrolyte, potassium ferricyanide, 0.01 M, (Aldrich ACS reagent) was in a solution of aqueous potassium nitrate, 0.1 M, (VWR AnalaR NORMAPUR). The reduction reaction of this cell can be seen in Equation 7.1.

\[
\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}
\]

Equation 7.1

This system was shown to produce the cyclic voltammogram (CV) expected from the literature (Figure 7.1).

![Figure 7.1 A CV collected for the standard ferricyanide couple, 25 mV/s.](image)

7.3 Designing and Testing a Dry and Air Free Electrochemical Cell

As discussed in Section 3.3, the air and moisture free electrochemistry has yet to be fully explored, despite the other methods [7] indicating that interesting redox events occur within a broader potential window than aqueous systems allow. For these
reasons, the author designed an electrochemical cell which could be used ‘air free’. A three electrode cell (Figure 7.3) was used, initially employing platinum wire as both the counter electrode and as a pseudo-reference electrode. Platinum is commonly used in electrochemical systems as a counter electrode due to its unreactive nature. Later in the work this platinum reference electrode was substituted for a piece of Highly Ordered Pyrolytic Graphite (HOPG), to allow for easier spectroscopic characterisation of the SWNTs. Although the use of platinum as a pseudo-reference electrode is known [8], it is not common. However, for the purposes of these experiments, common reference electrodes such as the silver/silver chloride system or the calomel electrode contain small amounts of water, so are unsuitable for use in this dry environment. A quasi-reference electrode could have also been used, however, they are not thought to be much more accurate than Pt wire and are difficult to manufacture and maintain [9-12]. To explore the redox and dissolution properties of the carbon nanotubes, a piece of SWNT bucky paper was attached to a platinum wire as the working electrode.

These rather delicate electrodes were inserted into a 25 ml three necked round bottom flask, the working electrode (WE) inserted into the central neck, and the counter electrode (CE) and reference (RE) into one of the side arms. A small, glass coated, stirrer bar was placed in the bottom of the cell to counter any problematic mass transport effects that may occur during the reaction. Initially, a solution of dry tetrahydrofuran (THF) (dried in-house using a solvent drying column, 0.58 ppm as reported from the technician’s Karl Fisher measurements) and sodium tetraphenylborate (STPB) (Aldrich A.C.S.) (Figure 7.2) was chosen as the electrolyte, however, dimethylformamide (DMF) (Aldrich, anhydrous 99.8%) was used instead of THF in the later work.
STPB was chosen as the electrolyte instead of more common electrolytes such as LiClO$_4$ because it was expected that the positive sodium ion, along with the phenyl groups, would stabilise the charged SWNTs. STPB was dried before use by dissolving it in dry methanol and using dry ether to reprecipitate it. The solvents were removed under reduced pressure, and the resulting STPB was heated to 80°C for 4 hours. A photograph of this cell can be seen in Figure 7.3.

**Figure 7.2 Sodium tetraphenylborate (STPB).**

**Figure 7.3 Photograph of the electrochemical cell.**
During all of the experiments carried out using this cell set up, standard Schlenk line techniques were used to make sure that the cell was air free. Any air contained within the system would quench any radicals formed. All of the glassware was dried overnight at 150°C to remove any adsorbed water and the cell containing just the glass coated stirrer bar was pump filled three times with dry nitrogen to make sure that there was no oxygen present. The cell was then kept under a positive pressure of nitrogen during all of the experiments. Before any experiments using the SWNTs were carried out, the dryness of the cell was tested by completing the electrochemical generation of sodium anthracinide. From the literature it is known that a dry solution of anthracene, containing a suitable sodium salt (STPB being a perfect example of this) should generate the strongly coloured (purple/green depending on report) anion of sodium anthracinide at sufficiently negative potentials, as anthracene is reduced. This reaction is known to only work in a dry environment as any oxygen present will inhibit the sodium anthracinide formation as reaction with the oxygen will occur [13, 14].

For this test, the cell described above was used, replacing the SWNT working electrode with a glassy carbon working electrode (5 mm in diameter). The electrolyte contained THF and STPB as to be used in the SWNT work as well as dry anthracene. Anthracene (Aldrich, ReagentPlus) was dried by recrystallisation from dry toluene. Then 2.5 mM of anthracene and 250 mM of STPB were dissolved into 20 mL dry THF by stirring [14].

The CV of the electrochemical cell containing just STPB and THF indicated one electrochemical event at -2.5 V, which is probably due to solvent degradation at this large voltage (Figure 7.4a). When anthracene was added to the cell a clear reduction
peak was seen at -2.4 V. This peak was largest after the first cycle and decreased with each subsequent cycle (Figure 7.4b).

![Graphs showing CV taken at 50 mV/s for 5 cycles: a) Control sample containing STPB in THF b) STPB and anthracene in THF. Red arrows indicate cycle direction, blue arrow indicates cycle trend.]

This result is expected, as the anthracene surrounding the working electrode is reduced and the process becomes limited by mass transport. As in the control sample,
the peak probably due to solvent degradation can also be seen. After the cell was held at -2.6 V for 5 minutes, the blue colour of sodium anthracinide could be seen deposited onto the working electrode. This solid sodium anthracinide was deposited, rather than in solution, because it undergoes quasi-radical electro-polymerization [15]. The formation of this sodium anthracinide is a good indication of the air-free nature of the cell and the ability to reach significantly low potentials to reduce SWNTs.

7.4 SWNT Electrochemistry

Having demonstrated the working condition of the electrochemical system, it was decided to attempt the electrochemical separation using 2 different types of CVD grown SWNTs; HiPCO (Carbon Solutions) and CoMoCAT (South Western Nanotechnologies). HiPCO SWNTs contain a relatively small population range with diameters from 0.88 nm to 1.15 nm; within this range the population is quite diffuse. CoMoCAT SWNTs have a wider population range, with diameters from 0.53 to 1.48 nm, however, there are fewer individual SWNT types. Before any electrochemical work was attempted, each material was characterised to establish the nature of the tubes in each sample and the relative abundances (Section 5.4). The electrochemistry of each SWNT type is discussed in turn.

7.4.1 Electrochemistry of HiPCO SWNTs

7.4.1.1 Producing a HiPCO Bucky Paper Working Electrode

Although it was hoped that the electrochemical process itself would debundle the SWNTs, it is still important to produce a high quality bucky paper containing unentangled SWNTs. Bucky papers prepared from well-dispersed solutions are more
homogenous, mechanically stable, and are more likely to offer reproducible (electrochemical) results.

Bucky papers were fabricated by dispersing 50 mg of SWNTs in 100 ml of 1,2-dichlorobenzene (DCB), by sonicating for 2 minutes using a Branson Sonifier 150 sonic probe, shaking for 30 seconds and repeating 5 times. The dispersion was left to stand overnight and the supernatant subsequently collected. To improve the yield of dispersion another 100 ml of DCB was then added to the sediment and the dispersion process undertaken again. These two supernatant portions were combined and filtered to dryness though a 0.2 µm Whatman cellulose acetate filter membrane by vacuum filtration. The filter paper was then left to dry in air overnight, before the SWNTs were carefully removed from the filter paper, to leave a free standing bucky paper. A piece (around 50 mm²) of this bucky paper was attached to a piece of platinum wire by using a needle to make a hole through which the wire was threaded (Figure 7.5).

![Figure 7.5 Photograph of HiPCO bucky paper working electrode.](image)

### 7.4.1.2 Attempting the electrochemistry using THF

The electrochemical cell was set-up and run as follows: 10 mg of sodium tetraphenyl borate (purified as described in Section 7.3) was added to a clean, dry, 25ml three neck round-bottom flask containing a 6 mm glass-encased magnetic stirrer bar. Using standard Schlenk line techniques, the flask was placed under a nitrogen atmosphere using a pump fill cycle whilst heating the flask and contents using a heat gun (at
~150°C). After the flask had cooled, 7 ml of pre-dried THF was transferred into the flask under nitrogen and the solution was stirred for 2 minutes.

The bucky paper working electrode was threaded through a 37/24 suba seal (by first making a hole with a needle), dried using a heat gun and, whilst maintaining a positive pressure of nitrogen in the cell, inserted into the central arm of the reaction cell. This working electrode was lowered in order that the bucky paper was part submerged into the electrolyte, without the electrolyte directly touching the platinum wire.

The counter electrode and reference electrodes, both consisting of individual pieces of platinum wire threaded through a single 25/33 suba seal, were heated using the heat gun, and inserted through the remaining side arm of the flask, into the electrolyte. All electrodes were then attached to the potentiostat and clamped to prevent any short-circuit. A photograph of this cell is shown in Figure 7.3.

All of the electrochemical experiments were undertaken under a positive pressure of nitrogen. As a first control, the cell was run containing just THF (no STPB electrolyte) in the potential range of ±4 V, at 288 mV/s, for five cycles using glassy carbon as the working electrode. As expected, no current was seen to pass (Figure 7.6) and therefore the need for the electrolyte was confirmed. For consistency with the later SWNT CVs this control was stirred, however, it should be noted that identical CVs were produced independently of stirring the solution.
Figure 7.6 CV from glassy carbon working electrode at 266 mV/s in THF without STPB.

As a second control experiment, STPB was added to the THF. When the glassy carbon working electrode was cycled from ±4 V, at 288 mV/s, for five cycles, two distinct events appeared at -1.5 V and 0.7 V. The shape of these peaks indicates the onset of an irreversible reaction [16]. Running the CV through such a range exceeded the THF solvent window, the largest reported being 1.8 V to -3.6 V. The exact potentials used in the CV experiments are ambiguous as a pseudo reference was used. However, the nature of the peaks indicates that these events were probably associated with the degradation of the solvent or electrolyte or possibly the reduction of sodium which is expected at -2.7 V (Figure 7.7); the solvent window for this system is only therefore between -1.5 V and 0.7 V. Smaller peaks associated with further redox events can be seen in the central region and are probably associated with a small amount of impurities contained within the THF. It should be noted that, for consistency with the SWNT data produced below, this CV was stirred.
When a CV using the SWNT bucky paper working electrode was run at 266 mV/s in the solvent window measured above (-1.5 V and 0.7 V) no features were seen. However, when an extended scan was run from ±4 V, at 266 mV/s, clear features were seen, being very different to those seen in the control sample (Figure 7.8). By taking into consideration the overall background current seen in the control sample, very broad oxidation and reduction peaks can be seen within the SWNT CV. Although unconventional, all of the CVs were run whilst the cell was being stirred; in more conventional CV experiments the electrolyte is not stirred so mass transport effects can clearly be seen. Without this stirring the diffusion limit made the reaction prohibitively slow (the large size of individual SWNT allows them to be compared to molecules), and although it is expected that over a long enough time frame all the reactions will take place, when the CVs were recorded without stirring no peaks due to the SWNTs were ever seen.
Figure 7.8 CV from SWNT bucky paper 266 mV/s, average of 20 scans, STPB in dry THF.

The data indicates the reversible nature of the redox properties of the SWNTs: They are reduced at negative potentials and re-oxidised at positive potentials. The shape of the graph also indicates the air free nature of the cell, since neither of the H₂O or O₂ related redox events are apparent. The redox peaks are very broad, as expected given the range of different SWNTs within the sample; the discreet redox events associated with each type of SWNT appear as a broad peak. Although this CV showed quite distinguishable peaks, they do not show the classic redox appearance, due in part to the very low concentrations of SWNTs within the sample and the stirring destroying any mass transport effect that normally give rise to the distinctive CV shape.

In an attempt to produce more distinct redox peaks, the scan rate of the reaction was decreased. The initial scan rate of 266 mV/s was chosen as scan rates of roughly this value are often used in the literature and it gave a convenient time scale for a single CV of approximately 15 minutes. After a full literature review, a decreased scan rate of 50 mV/s was chosen [17, 18]. However, at this slow scan rate, when the cell was cycled from ±4 V, at positive potentials the CV became very noisy and to the point
that no sensible data could be taken from it, so the cell was only cycled from 0 V to
-3 V, where CV data could be seen (Figure 7.9).

**Figure 7.9** CV from SWNT bucky paper at 50 mV/s. Red arrows show cycle direction.

In the negative potential range both oxidation and reduction peaks are seen. Although
this CV seemed to give promising results as it was significantly different from those
control CVs seen before, when a control of this slower scan rate CV was run from 0 V

**Figure 7.10** CV from glassy carbon working electrode at 50 mV/s. Red arrows indicate cycle
direction, blue arrows indicate cycle number.
to -3 V, using a glassy carbon working electrode instead of a SWNTs working electrode a very similar CV was obtained (Figure 7.10).

This CV indicates that at this low scan speed the peaks are due, not to the redox properties of the SWNTs, but rather due to the degradation of the solvent, the electrolyte, the reduction of sodium (although this is expected at lower voltages) or the reduction of catalyst particles.

As a test to see if the peak at -1.8 V, seen during the slower scan rate, was due to the degradation of solvent or had a nanotube contribution, an attempt was made to disperse the SWNTs by holding the cell at -2 V. Even after 2 hours at -2 V, no swelling of the bucky paper working electrode could be seen, the electrolyte did not change colour at all, and (using Raman spectroscopy) no SWNTs or carbonaceous material could been found on the working electrode. This indicates that the peak was due to either solvent degradation, electrolyte degradation or sodium reduction and thus another electrolyte system must be investigated if the dispersion of SWNTs is going to be successfully performed.

7.4.1.3 Electrochemistry using DMF as the Solvent

Due to the failure of the cell containing THF to disperse the SWNTs, N,N-dimethylmethanamide (DMF) was used instead. The selection of DMF was stimulated by the Penicaud paper, in which the SWNTs are reduced in sodium naphthalide and THF, but then dried and spontaneously dissolved in DMF. Although DMF and THF are both polar, aprotic solvents, DMF is thought to favour the spontaneous dissolution of the SWNT due to its resonance structure (Figure 7.11) allowing for the stabilisation of both the negative charge on the nanotube itself and the positive sodium ion (Figure 7.12).
Figure 7.11 Resonance forms of DMF.

Figure 7.12 Example of the stabilisation that DMF can bring to the reduced SWNTs.

Exactly the same electrochemical set up was used as before, only the THF was substituted for dry DMF. DMF is known to have a wide potential window, ranging from 2.3 to -3 V and there is some indication that this range may be expandable dependent on the electrolyte used [10, 16].

Due to the inaccurate nature of the platinum reference electrode it is hard to determine the absolute voltage at any given point in the CV data obtained. As such, to try and give the widest range possible, CV was undertaken by cycling the voltage between -4 and 3 V at 266 mV/s. Under these conditions, when using a HiPCO bucky paper WE, reduction and oxidation peaks could be seen (Figure 7.13). These peaks were observed using the HiPCO bucky paper WE, but not in the control sample, which used a piece of platinum wire in place of the bucky paper. Although peaks can be
identified they are not very clear and although they may be due to the SWNTs present, they may also be due to sodium reduction or solvent degradation. The control sample does also not produce a completely featureless spectrum and the shape of the CV coupled with the slope of the line indicates some redox events, probably associated with a very small amount of residual moisture or oxygen present in the sample. DMF is known to scavenge water from the atmosphere, therefore it must be handled with extreme care to keep it dry; it is almost impossible to exclude water completely.

In DMF, both the reduction and oxidation peaks are very broad and therefore it is difficult to assign a value to either peak. Once again, when slower scan rates were used, CVs from the control and from the SWNTs were found to be nearly identical. The features may be assigned to solvent degradation, STPB degradation or sodium reduction. This is because, even in the dry conditions used in this reaction, the wide

Figure 7.13 CV from SWNT bucky paper working electrode at 266 mV/s and a control run at the same scan rate substituting the bucky paper for a piece of platinum wire. STPB in dry DMF used.
potential range used to study the nanotubes redox potentials is probably exceeding the expected range of the solvent [10, 16]. In an attempt to investigate the possibility of spontaneous dissolution, and to test to see if the peaks seen are due to the SWNTs or due to some other factor, the cell was held at -2.5 V for 30 minutes. The potential was chosen as the maximum of the reduction peak seen in the spectra, whilst still within the solvent degradation window. After about 1 minute of this potentiostatic hold, the bucky paper could be seen to swell and after about 10 minutes the electrolyte became grey in colour. A stream of nanotubes could just be seen leaving the working electrode and dispersing in the electrolyte. This colour change is shown in the photographs in Figure 7.14. Once again, the cell was stirred during the runs, otherwise a much smaller current was seen to pass and although the bucky paper was still seen to swell, no SWNTs were seen to leave the paper in a reasonable time frame. No swelling of the bucky paper was seen if the cell was stirred without the application of a voltage.

Figure 7.14 Shows the electrochemical cell a) before, b) after 20 minutes holding at -2.5 V.

After 30 minutes, the reaction was stopped, the cell exposed to air, and the working, counter and reference electrodes were removed from the electrolyte. Raman spectroscopy showed that SWNTs were deposited on the counter electrode and that
there was some selectivity, both in the initial dispersion and on the electrode itself, as discussed below. **Figure 7.14** shows the use of HOPG as the counter electrode, although it should be noted that equal results were produced when using a platinum counter electrode. No swelling of the bucky paper or colour change of the solution was seen when the cell was held at positive potentials.

In order to establish the exact point at which SWNT reduction occurred, the cell was held at progressively lower voltages for 15 minutes at a time. It was found that only when the potential was -1.2 V or lower was there significant swelling of the electrode or colour change within the solution. The SWNTs dispersed in solution and deposited on the counter electrode were analysed using Raman spectroscopy, UV/Vis/NIR and photoluminescence.

### 7.4.1.4 Electrochemical Enrichment Results for HiPCO SWNTs

After the electrochemical reaction, the cell was exposed to air, the counter electrode removed, and a sample of electrolyte containing SWNTs deposited onto a glass cover slip and left to dry overnight to remove the DMF; the RBMs were then studied by Raman spectroscopy.

As shown in **Section 5.4**, when using a red laser line, the original HiPCO SWNTs show five RBM peaks. Below approximately 205 cm\(^{-1}\) the peaks are associated with the M\(_{11}\) transition, above this value the peaks are associated with the S\(_{22}\) transitions. When analysing the RBM Raman spectra, it is important to view the peak sizes relative to one another, since absolute intensity is strongly dependent on a number of factors; including sample surface scattering, the laser power used and the time used to acquire the spectrum. Therefore, all spectra were normalised for comparison.
**Figure 7.15** shows the RBMs of the HiPCO SWNTs as-received and the fraction that dissolved in the electrolyte.

In the as-received sample, the two most prominent features are the two semiconducting peaks at 216 cm\(^{-1}\) and 252 cm\(^{-1}\). A small metallic peak can be seen at 196 cm\(^{-1}\). In comparison, the material dissolved into the electrolyte shows an enrichment of the metallic relative to the semiconducting tubes. This preference is extremely promising and is consistent with the expected behaviour; it should be easier to reduce metallic SWNTs due to two complementary factors; specifically, the slightly lower value of the Fermi level in metallic tubes [19], and the availability of the conductance band above the Fermi level. In separation work based on the functionalisation of SWNTs, this preference for metallic tubes has been demonstrated previously in the literature [20-22] and in the author’s own liquid ammonia reduction work (*Chapter 6*). However, to the author’s knowledge it has never been shown before with electrochemistry alone.

![Raman spectra](image.png)

**Figure 7.15** Raman spectra, obtained using the red laser (633 nm), comparing the HiPCO SWNTs as-received, and following the dispersion in the electrolyte.
Analysis of the RBMs of the SWNTs deposited on the counter electrode shows an enrichment of metallic and small diameter semiconducting SWNTs, compared to both the as-received material and that dissolved into the electrolyte (Figure 7.16). This enrichment will occur because the metallic and small diameter SWNTs will be the most easily oxidised as they contain the highest energy first van Hove singularity.

![Figure 7.16 Raman spectra, obtained using the red laser (633 nm), comparing HiPCO SWNTs dispersed in the electrolyte and deposited on the counter electrode.](image)

To provide further confirmation, a green, 514 nm Raman laser line was also used which mostly excites large diameter semiconducting S_{33} and small diameter metallic M_{11} tubes. Using this green laser, these HiPCO samples give spectra with a poor signal to noise ratio. However, as discussed in Section 5.5, by cross referencing with the current literature peak assignments the correct peaks can be assigned. In the dissolved fraction (Figure 7.17), the peaks for both the metallic and large diameter semiconducting tubes can still be seen. In this reductively dissolved fraction, small diameter metallic tubes appear to be dissolved first, due to their lower Fermi level [19], allowing them to gain extra electrons more easily (Section 2.4.2).
Figure 7.17 Raman spectra, obtained using the green laser (532 nm), comparing HiPCO SWNTs as-received and dispersed in electrolyte.

For the deposited fraction, the green laser shows (Figure 7.18) that the large semiconducting SWNT have remained in solution, with metallic tubes deposited preferentially. Once again, this effect can be attributed to metallic SWNTs being the most easily oxidised.

Figure 7.18 Raman spectra, obtained using the green laser (532 nm), comparing HiPCO SWNTs dispersed in electrolyte and deposited on the counter electrode.
The results using the green laser are consistent with the results from the red laser. The Raman data thus indicates a redox selective dissolution/deposition process. Raman spectroscopy is useful for its sensitivity, but it is beneficial to support it with other, larger volume techniques.

Although PL measurements cannot show metallic enrichment within a given sample (only semiconducting SWNTs can be measured), measurements were attempted to assign any semiconducting SWNTs left within the sample. When the SWNTs dispersed in the electrolyte were dried and redispersed in D$_2$O containing sodium cholate hydrate, as detailed in Chapter 5.4, unfortunately only a very weak PL signal was obtained (Figure 7.19).

![Figure 7.19](image)

Figure 7.19 The PL spectra of the HiPCO SWNTs, dispersed into the electrolyte following electrochemistry.

This effect may be due to the enriched fraction of metallic tubes, quenching the fluorescence from any semiconducting tubes that are present. Or it may be that the concentration of tubes in this sample was simply too low for the detector to measure. The PL spectrum shows very weak features in the region where HiPCO peaks should
exist, however none can be quantified (Figure 7.19). PL measurements were also attempted on the SWNTs deposited onto the counter electrode, but due to the small quantity of SWNTs, no PL data was obtained.

UV/Vis/NIR spectra were collected using the same sample produced for PL (Figure 7.20). The spectra were normalised to allow an effective comparison, as the concentration of SWNTs in the sample produced from the SWNTs dissolved into the electrolyte was much less than the sample produced using the as-received material, an effect also seen in PL.

![Figure 7.20 UV/Vis/NIR spectra of HIPCO SWNTs as-received and after reduction and dispersion in electrolyte.](image)

It was much harder to produce a viable sample following the electrochemistry; due to problems with sample redissolution, the absolute absorbance of this sample was much lower. However, the enrichment of metallic tubes is apparent with the $M_{11}$ transition increasing in intensity relative to both the $S_{11}$ and $S_{22}$ transitions. There is also a slight blue shift in the peaks after electrochemistry, which is known to occur if the
SWNTs bundle; a slight increase in bundling is consistent with the lack of PL spectrum due to quenching after dissolution and drying.

7.4.1.5 HiPCO Conclusions

An electrochemical method has been developed which shows that it is possible to enrich SWNTs by electronic type using their electrochemical redox properties. It has been shown that during electrochemical reduction, metallic SWNTs are reduced first, most likely due to two factors; their slightly lower Fermi level and the availability of the conductance band above the Fermi level. Metallic and small diameter semiconducting tubes have been shown to be oxidised first and deposited onto the counter electrode due to their highest energy first van Hove singularity. The work on this project could be greatly expanded and the possibilities for future work will be discussed at the end of the chapter.

7.4.2 Electrochemistry of CoMoCAT SWNTs

Following on from the successful separation of HiPCO SWNTs, the electrochemistry and separation of CoMoCAT SWNTs was investigated. CoMoCAT SWNTs (purchased from South Western Nanotechnologies) were chosen for further studies because they are grown with a relatively small diameter range leading to only a limited number of (m,n) types within the as-received material.

7.4.2.1 Electrochemistry using CoMoCAT SWNTs

To generate the working electrode, a bucky paper of the CoMoCAT tubes was produced. Unfortunately, when applied to CoMoCAT tubes, the method developed for HiPCO bucky papers produced films that fragmented when removed from the
filter paper. In order to maintain a suitable electrode, the CoMoCAT bucky paper was used in the reaction whilst still attached to the filter paper, hung from a platinum wire. When the control reaction described in Figure 7.13 was performed using this set up the CV was seen to be identical to the one seen in Figure 7.13; the presence of the filter paper in the electrochemical cell did not seem to affect the reaction. The same cell set up was used as for the HiPCO tubes, using DMF as a dry solvent and STPB as the electrolyte, and an air-free cell with a platinum pseudo-reference and counter electrode. Whilst stirring, distinct peaks, which were not present in the control (Figure 7.13), could be seen in the CV spectra of the CoMoCAT tubes, when run at the slowest of the rates investigated previously, 50 mV/s (Figure 7.21). These peaks were seen to be largest in the first CV cycle. The symmetric peaks indicated the reversible nature of the peaks seen in this CoMoCAT electrochemistry, with the onset of the reduction peak seen at approximately -1.2 V (a figure comparable to the onset described in the HiPCO electrochemistry work).

Figure 7.21 CV of CoMoCAT SWNTs run at 50mV/s, 5 cycles in DMF with STPB. Red arrows indicate the cycle direction, blue arrows indicate the change in peak position from the 1st to 5th cycle.
The height of the reduction and oxidation peaks can be seen to change dramatically in Figure 7.21. In both cases the current is seen to decrease with each scan. This is expected due to the nature of the bucky paper working electrode. In the first scan (starting at -0.1 V and cycling to -5 V then to 5 V) the largest reduction peak can be seen, this will be due to the highest number of unentangled reducible SWNTs on the surface of the bucky paper working electrode which will be able to leave the paper upon reduction. The high number of SWNTs that are still entangled within the paper after reduction will account for the high oxidation peak. As each cycle progresses, more SWNTs will be able to leave the bucky paper, so both the oxidation and reduction peaks will decrease.

The electrochemical cell was then held at -3 V, a slightly larger voltage than that used in the HiPCO case due to the difference in the reduction peak position between the two samples, for 30 minutes. Although a small stream of nanotubes was seen to leave the paper during this time, the electrolyte did not change colour. Nevertheless, nanotubes could be seen to be deposited onto the counter electrode (Figure 7.22). The potentiostatic holds were shorter for this sample due to the fragility of the working electrode and its tendency to detach from the platinum wire.

![Figure 7.22](image.jpg)

**Figure 7.22** Photograph of the counter and reference electrode after holding a cell containing a CoMoCAT WE at -3 V for 30 minutes.

Raman spectroscopy was attempted using the red, green and NIR laser lines. Unfortunately, meaningful spectra were only obtained for the separated SWNTs using
the red laser (Figure 7.23). No spectrum could be obtained from the green line due to high background noise which did not allow the weak signal seen for the thin nanotube film to be distinguished.

Using the red laser a clear enrichment of metallic SWNTs could be seen in the SWNTs deposited onto the counter electrode. Due to the small amount of SWNT material seen in the electrolyte and in the counter electrode deposit it can be assumed that it is mostly metallic SWNTs that have been reduced from the WE. Metallic SWNTs are easiest to reduce due to the slightly lower value of the Fermi level in metallic tubes and the availability of the conductance band above the Fermi level. No data was collected for the CoMoCAT SWNTs dispersed in the electrolyte as the dissolved concentrations were very low. The low concentration of SWNTs in the electrolyte and on the counter electrode meant that UV/Vis/NIR and photoluminescence data could not be undertaken.

![Raman spectra](image)

**Figure 7.23** Raman spectra comparing CoMoCAT SWNTs deposited on the counter electrode (red line) relative to the as-received sample (black line), using the red laser (633 nm). The transitions associated with each peak are written in the box, with the hatched box being a mixture of metallic and semiconducting tubes.
7.4.2.2 CoMoCAT Conclusions

This work shows that an electrochemical approach can be used to separate SWNTs by their electronic properties. Two different nanotube samples were used to show that the metallic nanotubes contained within them can be preferentially reduced and deposited.

Using Raman spectroscopy it is shown that, metallic tubes are reduced most easily and deposited first from solution. As with the liquid ammonia reduction work, this effect is as expected due to the slightly lower value of the Fermi level in metallic tubes and the availability of the conductance band above the Fermi level. Unlike many of the other methods detailed, this method is cheap and continuous. It also is potentially highly scalable to produce large quantities of separated nanotubes. The processes for the purification of copper where an impure copper anode is dissolved by oxidation and deposited onto the cathode by reduction is analogous in many ways to this SWNT work and suggests that industrial scale up should be practical. The nanotubes produced by this novel separation approach will have immediate application in such fields as solar cells, transistors and sensing.

7.5 Future Work

The work detailed in this chapter may hail the beginning of an exciting new era in SWNT research. Given the evidence that SWNTs can be selectively dissolved and deposited, much more research must be undertaken to find the precise conditions under which the selectivity is optimised. It is expected that, with more research, samples fully separated by their electronic properties and size might be produced. For example, by using an array of electrodes set to different voltages, nanotubes with different electronic structures could be deposited independently of one another;
producing a cheap and scalable method for the electrochemical separation of SWNTs by their electronic properties.

Different solvent and electrolyte systems should be studied; in fact, the need for a molecular electrolyte could be challenged, as when the SWNTs are charged they conceptually form their own electrolyte. The need to produce excellent bucky papers is also paramount and an investigation into methods of producing bucky papers that could be used in a continuous process is of optimum importance [23, 24].
7.6 References


8 Conclusions

SWNTs are one of the most exciting chemical discoveries of recent times, offering an opportunity for an entirely new material system to be developed. Devices made from individual SWNTs can harness the unique properties of these tubes. However, bulk applications for such devices are hampered by problems with impure samples containing SWNTs with a mixture of electronic properties. The ‘Holy Grail’ of SWNT research would be to find a method of completely purifying SWNTs, allowing them to be subsequently separated based on their individual chiralities and length. The most obvious solution to this problem would involve a revolution in their synthesis; but this has yet to be conceived. Therefore, post synthesis approaches to this problem, such as those detailed in this thesis, are of optimum importance. There are many different purification strategies detailed in the literature although all contain inherent flaws and are unlikely to be able to provide the whole solution. Separation has been demonstrated in the literature using many different techniques but despite this, until 2008, no technique could provide samples with significant separation, yield and scale. In 2008, density gradient ultracentrifugation made a huge step forward and for the first time separated SWNTs can be purchased at $500/mg. However such high costs and small scale make this an unrealistic product to attempt to bring to the wider market. Only when fully scalable separation routes, such as those demonstrated in this thesis, are fully researched and taken forward to produce separated SWNTs, will products containing nanotubes be truly able to be brought to market. The importance of this should not be underestimated. SWNTs may, for example, be used in radical new solar cells which could be used to help supply the world’s future energy needs.