The Production of Single-Walled Carbon Nanotubes
By a CVD Method and their Characterisation by Various Techniques

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Submitted in Partial Fulfilment of the Requirements of the Degree of Doctor of Philosophy, January 2007
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Acknowledgement

I would firstly like to thank deeply my supervisor Prof. Keith Ross for his help and insight resolving many of the problems encountered throughout this work. He has given me the freedom to work on problems and approaches of most interest to me. I have also to thank Keith for financial support, which is giving me the chance to continue my study.

I am pleased to thank the people from the group, past and present, for the friendly atmosphere and help. Peter Georgiev, Dan Bull and Juan Fernandez.

I would like to thank Dr. C. A. Faunce for his assistance with the SEM and TEM observations.

Finally I would like to thank Alessandra Giannasi for measuring the Raman spectra of the SWNT samples.
Abstract

In this work, Chemical Vapour Deposition (CVD) was used to prepared Single-Walled carbon nanotube (SWNT) samples. In developing the production techniques a large number of parameters were varied during the course of work resulting in the successful repeatible growth of single-walled carbon nanotubes. Methane was used as a carbon-carrier gas decomposed at 950°C over a catalyst material consisting of 1.5% and 2% by wt Fe chemically deposited on a MgO support. The activity of the catalyst and the surround atmosphere were controlled by varying the flow ratio of Ar and H\textsubscript{2} gases as well as the flow of the carrier gas. Metallic catalyst particles together with the support material were treated by consecutive acid treatments in HNO\textsubscript{3} and HCl at 50°C to reduce their concentration.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to show the presence of nanotubes and also to measure the diameter of SWNT bundles and the size of carboneous materials. Images of SEM and TEM show a large number of nanotubes in the samples.

Raman scattering was used to probe the electronic properties and hence derive the diameters of the SWNT. For this reason, Raman spectra of SWNT samples were measured in the radial breathing mode (RBM) and Tangential mode (TM) ranges using three different laser lines. Raman spectra show a diameter distribution of nanotubes ranging from 0.97 to 1.45 nm.

Microgravimetric measurements of nitrogen and hydrogen adsorption were then applied to these samples to evaluate the specific surface areas Brunauer, Emmett and Teller (BET) and H\textsubscript{2} storage capacities of the samples and also derive information about the diameter of the pores in the samples by analysing the hysteresis loop in the
\( \text{N}_2 \) isotherm. The BET measurements show a different surface area for samples 350 \( \text{m}^2/\text{g} \) for sample 1 and 227 \( \text{m}^2/\text{g} \) for sample 2. Because there is a direct relationship between the surface area and hydrogen adsorption so the different storage capacity are shown for samples 0.5\%wt for sample 1 and 0.25\%wt for sample 2.
Chapter 1. Introduction

1.1 Importance of hydrogen-material systems

Today there is a growing need for alternative and clean energy that can replace our growing dependence on fossil fuels for vehicular propulsion. Hydrogen may be such an energy vector because it is the most abundant element in the universe 75 % (1) and also emits no pollutants when burned. However, an efficient storage method is needed for hydrogen, before it can become a replacement for gasoline.

1. As Gaseous, liquid or solid hydrocarbons, e.g. CH₄,
2. Through Nuclear fusion and fission processes
3. As a future synthetic fuel produced by the dissociation of H₂O or e.g. decomposition of CH₄ using an appropriate primary energy.

Hydrogen (and its isotopes deuterium and tritium) is the simplest element of the periodic table with just one electron. Hydrogen exists as a gas in the form of molecular H₂, and as a liquid below 21K and a solid below 14K.

Hydrogen vehicles generally use the hydrogen in one of two methods: Internal Combustion Engine or Fuel cell conversion. In combustion, the hydrogen is burned in engines in the same method as traditional gasoline cars. In fuel cell conversion, the hydrogen is turned into electricity through reaction with oxygen inside the fuel cell which then provides power to an electric motor. The only by-product from the spent hydrogen in both methods is water.
1.2 Hydrogen storage

There are four main technologies used for hydrogen storage: Physical storage, chemical storage in hydrogen carriers (e.g. methanol, ammonia), metal hydrides, and gas-on-solid adsorption (physical and chemical) (2).

Among the above methods for hydrogen storage, gas compression is only useful for pressures above 50 MPa at room temperature and liquefaction has the disadvantage of requiring a very low temperature. Storage by chemisorption in chemical and complex metallic hydrides of light elements is inconvenient because it is not easily reversible and desorption needs high temperatures. Thus hydrogen adsorption appears to be preferable method for storage at pressures under 20 MPa in a temperature range between 77 to 300 K. Physical adsorption is suitable for use with fuel cells because it is reversible (3). The very low boiling point of H$_2$ (20K) makes it necessary to apply temperatures of around 70K to achieve sufficient amounts of adsorbed H$_2$. The United States Department of Energy (DOE) (4) has set the target H$_2$ storage capacity of such an adsorbent to 6.5 wt %, which equals 720 ml (STP)/g in order for a vehicle to have an acceptable driving range. Because the interaction forces between hydrogen molecules and the adsorbent surface are physical in nature, the interaction is mainly determined by the specific surface, pore structure and mean pore diameter, and less on the nature of the bulk of the adsorbent material. It has been claimed that physisorption is the most promising hydrogen storage method for meeting the goals of the United States Department of Energy (DOE) (5). Carbon nanotubes may be a possible solution to the storage of hydrogen in fuel cell powered vehicles due to their low density, high strength, and hydrogen adsorption characteristics. Early work in this area focused on the H$_2$ adsorption properties of various activated Carbon materials (6).
1.3 Activated Carbon

Activated Carbon is a carbonaceous material in which most of the volatile non-carbon constituents are removed by thermal or chemical methods leaving the material with high surface area. Activated carbon show a limited affinity for water via capillary condensation. Activity is often expressed in terms of total surface area per unit weight, usually in square meters per gram. Activated carbons are the most investigated materials for gas storage applications. Hydrogen storage capacities of 6wt% are obtained at liquid nitrogen temperature and a few tens of bar pressure (7,8). For the surface area to be useful in adsorption it must have a large pore structure to admit the adsorbate molecules. The smallest diameter pores, the micropore structure, are the highest adsorption energy sites. Microporosity is helpful in adsorbing lower molecular weight gases.

Unfortunately, the vast majority of the sites for adsorption could not stabilize hydrogen above cryogenic temperatures. The adsorption energy of H₂ molecules on available surfaces are only effective at 80K or below (9).

1.4 Carbon Structure

The electronic structure of a carbon atom is $1s^2 2s^2 2p^2$. Three possible hybridisations of carbon are, sp when one of the 2s orbital and one of the 2p orbitals combine, sp² if one 2s orbital and two 2p orbitals combine or sp³ which result from combining one 2s orbital and three 2p orbitals. The best known carbon structures are graphite and diamond. Chemically they are identical, both being composed of only carbon, but physically they are very different. In graphite each carbon atom is bonded to three carbon atoms covalantly to give trigonal geometry. The bond angle in graphite is 120°. The Hybridization of the carbon atom in graphite is sp². Three valence electrons of each
carbon atom are bonded to three other carbon atoms while the fourth electron is free to move in the structure of graphite. The carbon atoms in the graphite layer form a hexagonal network with a C-C bond length of 1.42 Å. In graphite these rings form flat layers. These individual layers are sometimes referred to as “graphene” sheets. These layers stack parallel together, one above the other, and are 3.35 Å apart, and are held together by weak Van der Waals forces only. The stacking of the layers could be A.B.A.B, the hexagonal form or A.B.C.A.B.C, the rhombohedral form but the former is the more stable structure. These layers can slide easily over one another and thus it is very soft. The fourth electron of each carbon atom forms delocalized π-bonds, which spread uniformly over all carbon atoms. Hence graphite conducts electricity parallel to its plane. The surface area per gram of one plane of graphite, if only one side of the plane is accessible, is 1315 m²/g. The crystal structure of hexagonal graphite is shown in Fig 1.1

Fig 1.1 Crystal structure of Graphite
On the other hand, diamond is made of a three-dimensional network of \( \sigma \) bonds providing a very rigid and stable structure. The crystal structure is based on f.c.c lattice with a lattice parameter \( a=3.567 \, \text{Å} \) and atoms at \((0,0,0)\) and \((1/4,1/4,1/4)\). Hybridisation of carbon atoms in diamond is \( \text{sp}^3 \) implying that the 2s wave function is combined with three 2p wave functions to give four hybrid orbital in a tetrahedral arrangement. The diamond structure, which has a tetrahedral 4 coordination, is shown in Fig 1.2.

![Fig 1.2 Crystal structure in Diamond](image)

A third class of carbon compounds has recently been discovered (10). These are called fullerenes. Fullerenes are molecules composed entirely of carbon, taking the form of a hollow sphere, ellipsoid, tube or ring. The structure of Fullerenes is similar to graphite, being composed of a sheet of linked hexagonal rings, but they also contain pentagonal rings, which prevent the sheet from being planar. The first stable fullerene is \( \text{C}_{60} \) with sixty carbon atoms and a diameter of \( 7\,\text{Å} \) (Fig 1.3). The crystal structure of \( \text{C}_{60} \) is f.c.c with a lattice constant \( a=14.17\,\text{Å} \). There are two tetrahedral and one octahedral interstitial
sites per molecule of $C_{60}$. Only the octahedral site is large enough ($r=2.06\text{Å}$) to accommodate a hydrogen molecule.\(^{(11)}\)

![Fig 1.3 Structure of C60 molecule](image)

Cylindrical fullerenes are often called nanotubes. It is interesting that the $sp^2$ hybridisation which forms a planar structure in two dimensional graphite also forms planar local structure in the closed polyhedra (0-dimensional) of the fullerene and in a (1-D) cylinders called carbon nanotubes. Different kinds of carbon are listed in table 1.1.

<table>
<thead>
<tr>
<th>Kind of carbon</th>
<th>$C_{60}$</th>
<th>nanotube</th>
<th>graphite</th>
<th>diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension</td>
<td>0-D</td>
<td>1-D</td>
<td>2-D</td>
<td>3-D</td>
</tr>
<tr>
<td>Hybridisation</td>
<td>$sp^2$</td>
<td>$sp^2$</td>
<td>$sp^2$</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.72</td>
<td>1.2-2</td>
<td>2.26</td>
<td>3.51</td>
</tr>
<tr>
<td>Bond length (Å(^0))</td>
<td>1.40 (c-c)</td>
<td>1.44 (c-c)</td>
<td>1.42 (c-c)</td>
<td>1.54 (c-c)</td>
</tr>
<tr>
<td>Electronic properties</td>
<td>semiconductor</td>
<td>metal or semiconductor</td>
<td>semimetal</td>
<td>insulating</td>
</tr>
</tbody>
</table>
1.5 Sorption of hydrogen

The interaction of hydrogen with the surface of a solid can be physisorption of hydrogen molecules or chemisorption into hydrogen atoms. The force field at the solid surface, which is called the adsorbent, causes the hydrogen molecules to be adsorbed to the surface. Interaction between adsorbate and solid surface in physisorption is similar to Van der Waals bonding, due to fluctuations of the charge distribution on one molecule (fluctuating dipole-induced dipole). Hydrogen sorption via physisorption is a reversible process, i.e. all of the adsorbed hydrogen on the surface of material can be released by decreasing the H\textsubscript{2} pressure or increasing the temperature.

1.6 Adsorption of hydrogen in carboneous materials

Gas adsorption depends on different factors such as: the specific surface area of the materials, the purification of the adsorbent before adsorption, and the porosity of the material (i.e. whether the surface is accessible). Hence porous carbon, due to its high surface area and pore volume is a good adsorbent of hydrogen but high hydrogen adsorption is only found at very low temperature such as liquid nitrogen temperature; 77K because of the low heat of adsorption. The main difference between graphite and carbon nanotubes is the curvature of the graphene sheets and the cavity inside the tubes. In ropes of nanotubes hydrogen can be stored in the inner tube cavities and in the interstitial volume between the nanotubes. Then the storage density can be higher than for a planar graphene surface. Nanotubes with micropore sizes having diameters less than 5nm, are known to adsorb much more hydrogen than graphite because in these pores the potential fields from opposite walls overlap so the attractive force on adsorbate molecules is increases as compared with a flat carbon surface. (12).
The hydrogen storage capacity of carbon nanotubes against surface area was measured at room temperature and 77K by Zuttel et al and Nijkamp et al respectively Fig 1.4. The hydrogen storage capacity of carbon nanotubes against surface area was measured at room temperature and 77K by Zuttel et al and Nijkamp et al respectively Fig 1.4. (12)

Fig 1.4 Hydrogen gas adsorption measurement on carbon nanotubes against the BET surface area at 298K with the fitted line (circle) and at 77K (triangle).

Nijkamp et al performed hydrogen adsorption measurements at 77K in the pressure range 0 to 1 bar and Hydrogen uptake at room temperature was performed by electrochemical measurements. The electrochemical hydrogen absorption is reversible. As Fig 1.4 shows, the amount of hydrogen uptake is proportional to the BET surface area of the carbon nanotubes.

The hydrogen uptake of carbon nanotubes against pressure at room temperature shows a linear form at low pressure. This linear relationship according to Henry's Law occurs in a
very low coverage region where the only interaction is between molecules and surfaces and the interaction between adsorbed molecules is neglected. At higher pressures, coverage increases and so does intermolecular interaction so that the hydrogen uptake at high pressure becomes slightly curved. Hydrogen capacity is enhanced at 77K and shows a Type I isotherm. In the high-pressure region, hydrogen adsorption increases only slowly because, the surfaces are approaching saturation. Hydrogen sorption at 77K is also reversible with respect to pressure because the only interaction is physisorption (13).

Adsorption of hydrogen in single-walled carbon nanotube occurs on sites with different binding energies. By performing a quantitative examinations on rope of single-walled nanotube (SWNT) at 10 MPa and 77K, Williams et al (14,15) found that interstitial sites have the strongest average attractive potential energy (-1443 K) followed by grooves sites (-1088 K), inner (-758 K) and outer (-603 K) cylindrical surface of nanotubes.

The influence of the rope diameter on the specific surface area was investigated by Williams et al. (16). They computed surface area in different adsorption sites: interstitial (cylindrical shape formed by three tubes at the interior of the rope); endohedral (inside SWNT); and outer (along the outer cylindrical surfaces of nanotubes). in SWNT ropes as a function of the diameter of the ropes under these conditions: Ropes were composed of one to 37 nanotubes, the Van der Waals radius of carbon was taken to be 1.7Å . As Fig 1.5 shows, by increasing the rope diameter, the surface area in the interstitial channel $S_{\text{inter}}$ slowly increases, the surface area in the endohedral $S_{\text{endo}}$ is constant for all diameter and $S_{\text{outer}}$ approaches zero.
Fig 1.5 Dependence of surface area of different sites and total surface area on the diameters of ropes (13).
Chapter 2. Structure and classification of nanotubes

2.1 Introduction

A single layer of graphite is called two dimensional graphite or a graphene layer. The stacking of these layers occurs in two ways, hexagonal and rhombohedral (17). The most common stacking sequence of the graphite crystal is hexagonal with a ABAB stacking order. The crystal lattice parameters are $a_0 = 0.245$ nm and $c_0 = 0.6708$ nm. Hexagonal graphite thermodynamically is the stable form of graphite. The other graphite structure is rhombohedral with the stacking order ABCABC. In this case, the crystal lattice parameters are $a_0 = 0.2256$ nm and $c_0 = 1.006$ nm. Rhombohedral graphite is thermodynamically unstable. The density of perfect graphite is 2.26 g/cm³. Most graphite material has lower densities due to the structural imperfections such as porosity, lattice vacancies and interstitials and dislocations. The properties of graphite such as electrical, mechanical and thermal behaviour are anisotropic. These properties show differences between the ab directions (within the plane) and the c direction (perpendicular to the plane) (18).

Electrical properties Graphite can be considered to be a semi-metal. It is a conductor in the basal plane and an insulator in the direction normal to the basal plane. The highest filled valence band overlaps with the lowest empty conduction band. So the fourth valence electron forms a partially filled conduction band in the basal planes. Therefore they can easily move in a potential field. In the c direction, the space between the planes is large and the electrons are not able to move from one plane to another. As a result the electrical resistivity in this direction is high.
**Mechanical properties:** the sp² covalent bond between the carbon atoms in the basal plane of the graphite crystal is much stronger than the Van der Walls interaction between the planes of graphite.

**Thermal properties:** The thermal conductivity of graphite is influenced by the anisotropy of the graphite crystal. In a perfect graphite crystal, in the basal plane, the mean free path for phonon scattering, $L$, which appears in the thermal conductivity, as described by the Debye equation $K = b C_p v L$, where $b$ is a constant, is high so the thermal conductivity in the $ab$ direction is high. In the direction perpendicular to the basal plane, the $c$ direction, the conductivity is lower because the coupling of the lattice vibration in the $c$ direction is lower than in the $ab$ direction.

The Unit Cell and the Brillouin Zone of two-dimensional graphite is shown in Fig 2.1 and 2.2 respectively. $a_1$ and $a_2$ are the unit vectors in real space and $b_1$ and $b_2$ are the reciprocal lattice vectors. The direction of the unit vectors, $b_1$ and $b_2$, of the reciprocal lattice are rotated by 30° from the $a_1$ and $a_2$. Three points $\Gamma$ (centre), $K$ (corner) and $M$ (centre edge) in Fig 2.2 are the three high symmetry points where energy dispersion relations are calculated for the triangle $\Gamma MK$ (19).

![Fig 2.1 dotted rhombus shows the unit cell of two dimensional graphite](image1)

![Fig 2.2 shaded hexagon show brillouin zone of two dimensional graphite](image2)
Graphene sheets have two electronic bonds, $\sigma$ and $\pi$, which respectively belong to the covalent bonds and the weak Van der Waals interaction between the graphene sheets. The $\pi$ bonds are close to the Fermi surface so electrons can be excited optically from the valence $\pi$ to the conduction $\pi^*$ bond. This transition occurs at K points of the Brillouin zone where the energy gap between valence and conduction bonds is zero.

2.2 Carbon nanotube

The third class of carbon, which was first discovered by Iijima (10), is called the carbon nanotube (CNT). Carbon nanotubes are formed by one or more seamless cylindrical shells of graphite sheets, with an inner diameter starting from 0.7 nm up to several nm and a length of ten to one hundred $\mu$m. Nanotubes are divided into single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). Tubes formed by only one single graphite layer are called single wall nanotubes. Tubes consisting of multiple concentric graphite layers are called multi-wall nanotubes. The diameter of SWNT varies from 0.7 to 3 nm, whereas MWNTs show typical diameters of 30 to 50 nm. The SWNT and MWNT are shown in figures 2.3 and 2.4 respectively.
The helicity of the nanotubes is usually described by the chiral vector, which indicates how the graphene sheet is rolled up along a lattice vector with components \((n,m)\). The values of the integers \(n\) and \(m\) identify the general geometry of SWNT.

The chiral vector of the nanotube, \(C_h\), which specifies the structure of a SWNT can be expressed by unit vectors of the hexagonal lattice

\[
C_h = na_1 + ma_2
\]  

Where \(a_1\) and \(a_2\) are unit vectors in the two dimensional hexagonal lattice, and \(n\) and \(m\) are integers. Another important parameter is the chiral angle, \(\theta\), which is the angle between \(C_h\) and \(a_1\), and is given by

\[
\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}
\]  

The tubes with \(n = m\) and a chiral angle of 30 are named "Armchair". Tubes when either the \(n\) or the \(m\) is zero and the chiral angle is zero are named "zigzag". All others with chiral angles intermediate between 0 and 30, are known as "chiral" nanotubes. These three forms of single-walled carbon nanotubes are shown in Fig 2.5. The diameter of the carbon nanotube \(d_t\) is given by

\[
d_t = \frac{a}{\pi} \sqrt{m^2 + n^2 + mn}
\]  

where \(a = 2.49\AA\) is a lattice constant
The Unit cell of a carbon nanotube in real space is given by the OAB B rectangle, which contain the chiral vector $C_h$ and the translational vector $T$ in Fig 2.6. The Translational vector, the shortest repeat distance along the nanotube axis, is the unit vector of a one dimensional nanotube which is parallel to the nanotube axis and is normal to chiral vector in the unrolled hexagon lattice.

$$T = t_1 a_1 + t_2 a_2$$

Where $t_1 = 2m+n/d_R$ and $t_2 = -2n+m/d_R$. $d_R$ is the greatest common divisor of $(2m+n)$ and $(2n+m)$. 

Fig 2.5 Classification of single-walled carbon nanotube (20)
The number of hexagons per unit cell is given by

\[ N = \frac{2(m^2 + n^2 + nm)}{d_R} \]

Therefore the number of carbon atoms in each unit cell is 2N.

Vectors in reciprocal space corresponding to T and C_h are the vectors \( \mathbf{K}_2 \) along the nanotube axis and \( \mathbf{K}_1 \) in the circumferential direction. The vectors \( \mathbf{K}_1 \) and \( \mathbf{K}_2 \) are obtained from the relation

\[ \mathbf{R}_i \cdot \mathbf{K}_j = 2\pi \delta_{ij} \]

where \( \mathbf{R}_i \) and \( \mathbf{K}_j \) are respectively the lattice vectors in real and reciprocal space. So \( \mathbf{K}_1 \) and \( \mathbf{K}_2 \) are given by
The parameters of carbon nanotubes are summarised in table 2.1.

### Table 2.1 parameters of carbon nanotubes

<table>
<thead>
<tr>
<th>Symbol</th>
<th>name</th>
<th>formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>length of unit vector</td>
<td>(a = 3a_{c-c}, \quad a_{c-c} = 1.44) Å</td>
</tr>
<tr>
<td>(a_1, a_2)</td>
<td>unit vectors</td>
<td>(\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a, \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a)</td>
</tr>
<tr>
<td>(b_1, b_2)</td>
<td>reciprocal lattice vectors</td>
<td>(\left(\frac{1}{\sqrt{3}}, 1\right)\frac{2\pi}{a}, \left(\frac{1}{\sqrt{3}}, -1\right)\frac{2\pi}{a})</td>
</tr>
<tr>
<td>(C_h)</td>
<td>chiral vector</td>
<td>(C_h = na_1 + ma_2)</td>
</tr>
<tr>
<td>(L)</td>
<td>length of chiral vector</td>
<td>(L = a\sqrt{n^2 + m^2 + nm})</td>
</tr>
<tr>
<td>(d_t)</td>
<td>diameter</td>
<td>(d_t = L / \pi)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>chiral angle</td>
<td>(\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}})</td>
</tr>
<tr>
<td>(T)</td>
<td>translational vector</td>
<td>(T = t_1a_1 + t_2a_2)</td>
</tr>
<tr>
<td>(T)</td>
<td>length of (T)</td>
<td>(T = \frac{\sqrt{3}L}{d_R})</td>
</tr>
<tr>
<td>(N)</td>
<td>number of hexagons in nanotube unit cell</td>
<td>(N = \frac{2(n^2 + m^2 + nm)}{d_R})</td>
</tr>
</tbody>
</table>
2.3 Different adsorption sites of nanotube

Single-walled carbon nanotubes tend to agglomerate and form a bundle. Ropes or bundles of (SWNT) are opportunity to study the interaction of molecules and atoms with a physical surface. Bundle structure of SWNTs produce four different sites in which gas molecules can adsorb Fig.2.7: on the external bundle surface, in a groove formed at the contact between tubes on the outside of the bundle, within an interior pore of an individual tube and inside an interstitial channel formed at the contact of three tubes in the bundle (22).

Fig 2.7 Schematic picture of a rope of 19 single-walled carbon nanotubes with different adsorption sites (23).
2.4 Electronic structure of nanotubes

Although graphene is a zero gap semiconductor, carbon nanotubes can be metals or semiconductors depending on the diameter and helicity of the tubes \((n,m)\). Therefore there is a connection between the electronic properties and geometric structure of the carbon nanotubes. The electronic structure of graphene near the Fermi energy is given by occupied \(\pi\) band and empty \(\pi^*\) band. These two bands have linear dispersion and meet each other at the K point at the Fermi Level in the Brillouin zone, Fig 2.8. So these two bands are degenerate at the K points.

![Energy dispersion along the high symmetry directions of the 2D Brillouin Zone](image)

By applying the periodic boundary condition in the circumferential direction of Graphite sheet when forming a tube, the wave vector \(K_1\) becomes quantized while the wave vector \(K_2\) in the direction of the axis remains continuous. So not all values of \(k\) states of the planar graphite sheet are allowed. The allowed \(k\)'s depends on the diameter and helicity of the tube. If the allowed \(k\) include the point K, the carbon nanotube is metallic, otherwise it is a semiconductor \((24,25)\). The general rules for electronic properties of single-walled carbon nanotubes are: armchair \((n,n)\) tubes are metallic while zig-zag \((n,0)\)
and chiral \((n,m)\) tubes with \(n-m=3i\), where \(i\) is a non zero integer, are metallic otherwise the tubes are all semiconducting.

### 2.5 Energy dispersion relations for electrons in two dimensional graphite

Block functions which are constructed from atomic orbitals of carbon atoms at \(A\) and \(B\) in Fig 2.1 are the basis functions for two dimension graphite (25).

\[
\Phi_j(K, r) = \frac{1}{\sqrt{N}} \sum_{\tilde{R}} \exp(iK \cdot \tilde{R}) \cdot \varphi_j(r - \tilde{R}) \quad j = 1, \ldots, n
\]

\(\tilde{R}\) is a position of atom, \(\varphi_j\) is an atomic wave function in state \(j\) and \(n\) is the number of atomic wave functions in the unit cell. In order to obtain the energy dispersion relations, the secular equation must be solved for high symmetry points.

\[
\det [H - ES] = 0
\]

where \(H\) is a Hamiltonian of the system and

\[
H_{jj}(K) = \langle \Phi_j | H | \Phi_j \rangle, \quad S_{jj}(K) = \langle \Phi_j | \Phi_j \rangle
\]

are transfer integral matrices and overlap integral matrices. By considering only nearest neighbour interactions

\[
H_{AA} = H_{BB} = \varepsilon_{2p}
\]

And for \(H_{AB}\), consider three nearest neighbour \(B\) atoms relative to \(A\) atom.
\[ H_{AB} = t \{ \exp(i \mathbf{K} \cdot \mathbf{R}_1) + \exp(i \mathbf{K} \cdot \mathbf{R}_2) + \exp(i \mathbf{K} \cdot \mathbf{R}_3) = tf(k) \} \tag{2.13} \]

where

\[ t = \langle \varphi_A(r-R)|H|\varphi_B(r-R \pm \frac{a}{2}) \rangle \tag{2.14} \]

\[ f(k) = \exp\left(\frac{ik_x a}{\sqrt{3}}\right) + 2 \exp\left(\frac{ik_x a}{2 \sqrt{3}}\right) \cos\left(\frac{k_y a}{2}\right) \tag{2.15} \]

By using equation (2.15) the overlap integral matrix is given by

\[ S_{AA} = S_{BB} = 1 \tag{2.16} \]

\[ S_{AB} = Sf(k) = S^*_{BA} \tag{2.17} \]

Therefore the form of H and S is given by

\[
H = \begin{pmatrix}
\varepsilon_{2p} & tf(k) \\
tf(k)^* & \varepsilon_{2p}
\end{pmatrix} \tag{2.18}
\]

\[
S = \begin{pmatrix}
1 & sf(k) \\
sf(k)^* & 1
\end{pmatrix} \tag{2.19}
\]

By solving the secular equation, the eigenvalues \( E(\mathbf{K}) \) are obtained.

\[
E_{g2D}(\mathbf{K}) = \frac{\varepsilon_{2p} \pm t\omega(\mathbf{K})}{1 \pm s\omega(\mathbf{K})} \tag{2.20}
\]
\[ \omega(\mathbf{k}) = \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2} } \]  

The + and − signs in 2.20 show the bonding \( \pi \) energy and anti-bonding \( \pi^* \) energy. Therefore the energy dispersion relation for two dimensional graphite in the case of \( \varepsilon_{2p} = 0 \) and \( s = 0 \) is given by

\[ E_{g2D}(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2} } \]  

2.6 Energy dispersion relations for nanotubes

The electronic structure of SWNTs can be obtained from the two dimensional energy dispersion relation of graphite by applying one dimensional limitations in their electronic states, which causes Van Hove singularities in the nanotube density of states. The two dimension energy dispersion relation of graphite is.

\[ E_{g2D}(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2} } \]  

By applying the periodic boundary condition for armchair nanotubes, the allowed wave vectors in the circumferential direction are given by

\[ k^m_x = \frac{m \cdot 2\pi}{n \cdot \sqrt{3}a}, \quad (m=1,\ldots,2n) \]
by substitution of the $k_{x}^{m}$ into equation (2.23) the one dimensional energy dispersion relation for armchair nanotube can be written as

$$E_{m}^{a}(\kappa) = \pm \gamma_{0} \left\{ 1 \pm 4 \cos \left( \frac{m\pi}{n} \right) \cos \left( \frac{\kappa a}{2} \right) + 4 \cos^{2} \left( \frac{\kappa a}{2} \right) \right\}^{\frac{1}{2}} \quad 2.25$$

$$-\pi < ka < \pi$$

The energy bands of zigzag nanotubes like armchair tubes can be obtained by substituting the periodic boundary condition on $k_{y}$ as

$$K_{m} = \frac{2\pi}{n} a \quad (m = 1, \ldots, 2n) \quad 2.26$$

in to the two dimensional dispersion relation of graphite eq (2.23)

$$E_{m}^{n}(\kappa) = \pm \gamma_{0} \left\{ 1 \pm 4 \cos \left( \frac{\sqrt{3} \kappa a}{2} \right) \cos \left( \frac{m\pi}{n} \right) + 4 \cos^{2} \left( \frac{m\pi}{n} \right) \right\}^{\frac{1}{2}} \quad 2.27$$

$$-\frac{\pi}{\sqrt{3}} < ka < \frac{\pi}{\sqrt{3}}$$

where $\gamma_{0}$ is a nearest neighbor carbon-carbon interaction energy and $k$ is a wave vector along the nanotube axis, \( a=2.49\AA \)

In armchair nanotubes, the energy bands are degenerate at the zone boundary where \( ka=\pi \). By applying the energy dispersion relation to (5,5) armchair nanotube it is found that the valence and conduction bands cross each other at the K point at the Fermi Level Fig 2.9a (26). Therefore there is a degeneracy point between valence and conduction
bands at point K. So the (5,5) nanotube is a metallic. It has also been shown that the other armchair nanotubes also have a degeneracy between the highest valence band and the lowest conduction band at $k = \pm 2\pi/3a$ where the bands cross the Fermi Level.

Calculations of one dimensional electron dispersion relation for (9,0) and (10,0) zigzag nanotubes are shown in Fig 8b and 8c respectively. As this figure shows there is no energy gap between valence and conduction band at $k = 0$ for the (9,0) nanotube, so the (9,0) zigzag nanotube is metallic but the (10,0) nanotube shows an energy gap at $k = 0$ therefore this nanotube is semiconducting. For the (n,0) zigzag nanotubes the general form nanotube is metallic if $n$ is multiple of 3 otherwise it is semiconducting (25,27).

![Fig 2.9 Electronic bond structure of nanotubes (a) armchair (5,5), (b) zigzag (9,0), (c) zigzag (10,0).](image)
2.7 Defects in carbon nanotubes

The presence of defects changes the density of state around the Fermi Level and therefore change the properties of the carbon nanotubes. The defects can be classified in four main groups: topological (non hexagonal rings), re-hybridization (sp²-sp³ intermediate bonding), incomplete bonding defects (vacancies, dangling bonds, dislocations) and doping with elements other than carbon. (28). Among the above defects, pentagon and heptagon are the main defect in carbon nanotubes.

The presence of ring sizes other than hexagon, such as pentagons and heptagons in the graphene sheet creates topological changes that can be thought of as a local defect. A single heptagon or pentagon is a point defect and it is present only close to the tips. This defect can changed the electronic properties of tubes. Attaching a pentagon and heptagon to each other forms another common defect. This pair creates a small local change in the width of the nanotube and may also create a change in the helicity (29). Detection of this defect experimentally is difficult but observation of the carbon nanotubes becoming gradually thicker can be assigned to a very large number of these pair defects (30). Stone and Wales (31) showed that a dipole consisting of a pair of pentagon-heptagon rings can be created by rotating a C-C bond in the hexagonal network by 90°, such a dipole is called a Stone-Wales defect. These pairs could be connecting two nanotube (cylindrical) with different diameters leading to the metal-semiconductor, metal-metal or semiconductor-semiconductor devices.

When atoms are continuously removed from the surface of the hexagonal lattice, for example through irradiation or evaporation during growth, vacancies are created which form a cluster and could change into large holes in the structure of nanotube. By
removing these holes, the surface of original tube can reconstruct in to a cylinder of smaller diameter (32).
3.1 Introduction

Carbon nanotubes can be synthesised by different methods (33). The most common CNT synthesis methods are Laser Vaporisation of graphite and Arc-discharge (34) and High pressure carbon monoxide, which are high temperature processes and Chemical Vapour Deposition (CVD) which is medium temperature method (35). In the high temperature methods, the catalyst and carbon are evaporated simultaneously. In arc discharge, vapour is formed by arc discharge between two carbon electrodes and in the Laser Vaporisation, vapour is formed by directing the laser beam on to a volume of carbon. In contrast, in the CVD method, carbon is obtained from the decomposition of hydrocarbons by small metallic (catalytic) particles on the substrate. Although these two methods use a different range of temperature, they show some similarities.

1-For making the SWNT, these methods all use transition and rare earth metals.

2-In each method, SWNT can be found as isolated tubes or as bundles having a range of diameter from 0.7 to 3 nm.(33).

High temperature methods have the advantage of producing high quality nanotubes. The disadvantage of these methods is that a high temperature needed, This limits scope for any scaling-up of the process. Furthermore, the final product of these methods contains by-products and amorphous carbon which must be removed by purification. The CVD method has advantages for scale-up and commercial production and also the quantity of by-products is lower than for the other methods.
3.2 Laser vaporization

In the laser vaporization method (36), a pulsed laser is used to vaporise a graphite target inside a furnace at 1200°C. The furnace is filled with helium or argon gas in order to keep the pressure at 500 Torr. After forming, the vapour expands and cools rapidly. As the vaporised species cool, small carbon molecules condense to form clusters. The catalysts also begin to condense and attach to carbon clusters and prevent their closing into cage structures. Using this method, both MWNT and SWNT could be synthesised (37). Which is formed depends on whether pure graphite or graphite mixed with transition metals such as Co, Ni, Fe is used. In the first case, MWNT and in the second case SWNT could be synthesised. The product of Laser Vaporisation contains carbon nanotubes and carbon nanoparticles. Single wall carbon nanotubes, where formed in this way are bundled together in ropes.

3.3 Arc-discharge

The arc-discharge method produces both multi-wall and single-wall nanotubes. In this method two graphite rods electrodes are used as cathode and anode to generate an arc by a high dc current in a helium or argon atmosphere (38). A direct current of 50 to 100 amps and 20 volts provides a high temperature discharge between the two electrodes. The discharge vaporises the anode rod and forms a small rod shape deposit on the cathode rod. Carbon nanotube and amorphous carbon both form at the cross section of the anode rod so this method does not produce clean nanotubes. If both electrodes contain pure graphite, MWNT could be synthesised, For producing SWNT, the anode has to be doped with metal catalyst such as Co, Ni, Fe.
3.4 High Pressure Carbon Monoxide

A high pressure carbon monoxide process can be used to produce SWNT from reactions of iron in carbon monoxide (in the gas phase) at high pressure. In this method a gas phase catalyst is used, the catalyst and hydrocarbon gas are introduced into a furnace. This process is relatively clean and can also produce SWNT in large quantities (39). In this process, SWNT grow in high pressure and high temperature of flowing CO gas on clusters of iron which are formed by adding Fe to the gas flow in the form of Fe(CO)$_5$. Upon heating Fe(CO)$_5$ decomposes and the iron clusters are formed. These clusters act as nuclei where SWNT nucleate and grow.

3.5 Chemical vapour deposition (CVD)

In early research on nanotube production, it seemed that the CVD method was useful for synthesising MWNT but not SWNT. In 1996, Dai et al (40) and Fonseca et al (41) showed that the CVD method could fairly produce SWNT. Dai suggested that small sized catalytic metal particles are necessary for the growth of SWNT, They used (Fe, Mo, Co, Ni) as metal particles on Si and Al supports in the temperature range 800-1200°C. They also used methane instead of acetylene or ethylene because of kinetic stability at high temperature. Dresselhaus (42) and Rao (43) developed this new technique. In the Dresselhaus model, SWNT are synthesised from a mixture of benzene and ferrocene in a hydrogen gas flow and nanoparticles are formed by thermal decomposition of organometallic compounds. This process used two furnaces. Ferrocene [Fe(C$_5$H$_5$)$_2$] is vaporized at low temperature (200-400°C) in hydrogen in the first furnace, hydrocarbon (benzene) and the catalyst are decomposed in the second furnace at 900-1200°C. In Rao’s method, SWNT were synthesised by pyrolysis of mixtures of acetylene with (Fe, Co, Ni) or metallocene Fe(CO)$_5$ at
1100°C, while Fe(CO)₅ is pyrolyzed with acetylene in the same furnace as in the Dresselhaus method.

Colomer et al synthesised SWNT by decomposition of ethylene on supported metal catalyst (44). As a metallic compound, they used Co, Ni and Fe and their binary and ternary mixtures and used Silica or Alumina as a support. They showed that the best yield was obtained by using a Fe-Co mixture on Alumina. In the case of Silica, the SWNT are coated with a thick layer of amorphous carbon.

Chemical vapour deposition (CVD) of carbon nanotubes contain deposits of hydrocarbons (methane, acetylene, benzene,…) on metal catalyst (Co, Ni, Fe,…) (44). In the CVD method, first the transition metal particles (Fe, Co, Ni,…) are deposited on the support catalyst which constitution a dispersion of metal particles. Then the catalyst on its support is placed in a quartz boat. The boat is placed in the CVD furnace and then a mixture of hydrocarbon and hydrogen is introduced into the reaction chamber. During the reaction, nanotubes are formed by the decomposition of the hydrocarbon at temperatures of 700-900°C.

3.6 The Mechanism of SWNT growth

The growth mechanism of nanotubes is not well understand. In fact, it may depend on which method is used. Although different methods operate in different temperature ranges, they show similarities between synthesised samples. For all methods, transitions metals are necessary for the growth of SWNT because they are often found at the tip inside the nanotube or also somewhere in the tube. Also the structure of SWNTs produced from different methods are similar, SWNT can be found isolated or in bundles and the diameter range are between 0.7 to 3 nm. The growth of the
nanotubes is probably normal to the substrate surface because the gradient of carbon concentration is in this direction. Carbon first deposits on the surface of the metal particle and diffuse through and or over the metal particle to precipitate at the opposite side in the form of nanotubes (45). There are several important conditions for successfully growing SWNT such as suitable catalyst particles, the minimum size of the catalyst particle must be 0.7 nm. In the CVD method, the catalyst is required to break the bonds of the carbon feedstock molecules to produce carbon atoms and also to act as a solvent for carbon atoms. A suitable temperature is required (minimum temperature is 823 K (46) and maximum is 1473 K (47). Several mechanisms have been proposed for the process involved.

Scooter model: This was proposed for the first time as a growth mechanism of SWNT from evaporated carbon from a solid surface (laser vaporization and Arc-discharge methods) (48). This model assumes that atoms of the catalyst attach to a graphene sheet to prevent the closing of the graphene sheet and have leading to the formation of tubes (49).

Root growth mechanism: in this model, carbon atoms are involved in a diffusion-segregation process, which happen on the surface of the catalytic particle. The carbon atoms are then added to the root of the growing tube (50).

Metal-Catalytic growth mechanism: according to this model, carbon vapour dissolves in the metal clusters and then extra carbon precipitate in the form of nanotube (51). There are two different situations, depending on the size of catalytic particle. When carbon atoms precipitate from particles larger than the tube diameter, this process suggests root-growth mechanism. When the diameter of the metal particle is the same size or smaller than the tube diameter the SWNT growth is explained by the presence of dangling bonds at the tip which act as a attraction site for carbon atoms.
3.7 Review of the growth mechanism

Yudusaka et al proposed a mechanism for growing SWNT synthesised using pulsed laser (YAG) ablation (52). In this process, the laser heats the surface of the target and then molten carbon and catalyst are ejected from the surface. As the molten particles cool, dissolved carbon segregates from the metal and the SWNT grow. Growth mechanism that were proposed by Kataura et al (53) consist of three steps: in the first step (high temperature state), nucleation of carbon clusters start and some of them are melted in metal particles. In the second step, the system is cooled down (medium temperature state) and melting of carbon clusters stop and metal particles are covered with the carbon clusters. Then SWNT start to grow. Kokai et al (54) suggested that carbon-metal particles melted at ablation temperature, when the metal particle are saturated with carbon, segregation occurs at about 1593K.

Kanzow et al (55) proposed a mechanism for growing SWNT where they are synthesised using CVD. The model contains four steps: in the first step hydrocarbon molecules are adsorbed on different parts of the surface of small metal particles. Carbon-hydrogen bands are broken and in the second step carbon diffuses into the bulk material. When the surface of the particle is saturated, carbon is precipitated at the metal surface. If the extra carbon on the surface does not diffuse fast, the process of growth is stopped because the particle becomes completely encapsulated with amorphous carbon. A Diffusion model has been described by Tibbets for producing MWNT by the CVD method (56). In this model, metal-metal hydrocarbon particles diffuse across the surface of the catalytic particle, allowing the carbon to precipitate in contact with the previous deposit. A similar model for SWNT formation was first proposed by Saito (57). The first growth step in this model is the formation of a liquid nanoparticle of metal, supersaturated with carbon. The extra carbon then starts to
segregate towards the surface. All the methods proposed for growing the SWNT are based on a Vapour-liquid-solid (VLS) model which was developed by Wagner and Ellis (58) for the formation of whiskers. According to the VLS model, carbon and atoms that are in the vapour phase form a liquid metal-carbide particle and when this particle becomes supersaturated with carbon, solid phase SWNT are grown (59).

Classical Molecular Dynamic (60) with the Brenner potential (61), tight-binding molecular dynamics simulation (62) and quantum-molecular-dynamics have supported the mechanisms proposed by experimental observations such as the Scooter Model, the Diffusing Model and the Root Growth Model.

3.8 Electron Microscopy

Electron microscopy is applied to the investigation of ropes of single-walled carbon nanotubes in samples. This is a method for proving the formation, shape, structure and purity of nanotubes. By using high resolution TEM, diameter of ropes and SWNT can be measured.

3.8.1 Scanning electron microscopy

SEM is the most important electron-optical instrument for the investigation of the surface of bulk materials. SEM uses electrons for imaging. The advantages of the SEM with respect to light microscopy are greater magnification and much greater depth of field. The construction of a SEM can be described in terms of three components: electron column, vacuum system and signal detection. The Electron column consists of an electron gun, which generates electrons with an energy range between 0.1-30 KeV and two or more electron lenses, for demagnifying the electron
beam and scanning coils. Most SEM can produce an electron beam at the sample with size less than 10 nm (63).

As an incident electron beam strikes the sample, electrons interact elastically and inelastically with the sample and then electrons with different energies are emitted from the surface in the region where the beam is incident. For studying more than a single location, an image beam is moved from place to place by using of scanning system. Interactions of the beam with a sample are shown in Fig 3.1.

![Interaction Volume Diagram](image)

**Fig 3.1 inelastic interaction of electron beam with material. Emitted electrons and rays from surface are shown.**

Emitted electrons from the surface of materials contain backscattered primary electrons, secondary electrons, characteristic X-rays and Auger electrons. The majority of the scattered particles are secondary electrons, which formed in multiple inelastic scattering processes. In the SEM, images can be classified as follows

- Secondary electrons: these electrons are produced by the inelastic interactions between the sample and the incident electron beam. These low-energy (less than
50 ev) electrons are emitted from near the sample surface. These electrons provide the best resolution because the exit depth is very small < 10nm.

- Back-scattered electrons: these electrons are produced by the elastic interactions between the sample and the electron beam. These high energy electrons (range from the energy of the primary electrons to about that of the secondary electrons) can exit from much deeper than secondary electrons. The information depth of backscattered electrons is 0.1-1μm depending on the density of the specimen and the electron energy.

- Auger electron: These electrons are produced after the secondary electrons. In a secondary electron process, a lower energy electron is emitted from the atom and then an inner shell vacancy is filled by a electron from a higher shell. Auger electrons exit carrying the excess energy. Auger electrons have low energies, up to 1 or 2 Kev so are emitted from a depth < 3nm.

- X-rays: Since a lower energy electron is emitted from the atom during the secondary electron process, a higher energy electron can fill this vacancy. As the electron fill the vacancy, energy is emitted usually as a X-rays.

### 3.8.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) operates on the same basic principles as the light microscope but with electrons instead of light. Because the wavelength of the electron is much lower than that of light the resolution is much higher than for the light microscope. Thus, a TEM can show the finest details of internal structure.

In a TEM, a electron is emitted in the electron gun by thermionic, Schottky or field emission. Electro-magnets in the TEM column focus the electrons. These electrons
are focused into a very thin beam by a double condenser lenses. They then, pass through the specimen. In order for electrons to pass through the specimen, it must be very thin usually less than 100nm. Depending on the density of the material, some of the electrons are scattered and lost from the beam. Unscattered electrons, focused by the objective lens, hit a fluorescent screen at the bottom of the microscope and give rise to an image of the specimen. The remaining lenses in the TEM are the intermediate lens and the projector lens. The intermediate lens is used to control magnification. The projector lens forms a real image on the fluorescent screen.

3-9 Experimental Techniques for synthesising a SWNT samples

In the present work, the Chemical Vapour Deposition (CVD) technique was used to prepared the samples. In developing the production technique, many parameters were varied. Efforts at reproducing good yields indicated which were the most critical experimental parameters and how carefully they had to be controlled. Table 3.1 shows the summarised conditions of producing carbon nanotubes. The value of parameters are obtained by assuming that the amount of catalyst +support and location of boat in reactor to be constant in each run.

The conditions report are the best tested but the range of possible parameter choice is so large that they probably only represent a local optimum.
Table 3.1: summary of conditions for producing carbon nanotube samples

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<thead>
<tr>
<th>T room 500°C</th>
<th>T 950°C</th>
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<th>t (minute)</th>
<th>result SWNTs</th>
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<tr>
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For the first time I used a catalyst material consisting of 1.5% and 2% by wt Fe chemically deposited on MgO support. The catalyst materials for the CVD process were prepared by mixing 6g of magnesium oxide (MgO) powder with a surface area of 10 m²/g and 0.65g (Sample 1) or 0.87g (Sample 2) of iron nitrate, Fe(NO₃)₃·9H₂O, in methanol solution. The solution was then sonicated for about 20 minutes and then the methanol was removed using a rotary evaporator. The catalyst was then dried at 140 °C overnight and ground into a fine powder. The syntheses of the SWNTs were carried out in a horizontal reactor consisting of a quartz tube, 640 mm long and 50 mm in diameter. Fig 3.2.
3g of the catalyst + catalyst support were placed in a quartz boat in the centre of the reactor tube. This was then heated in a gas mixture of Ar / H₂ at a flow rate of 100 / 100 Sccm as the temperature was raised linearly to 500°C.

At this temperature, the iron nitrate had decomposed into iron oxide (mixed Fe⁴⁺/Fe⁺). In order to form elemental iron nano particles, which can serve as nuclei for nanotube growth, the catalyst was then reduced at a higher temperature in hydrogen flowing through at a rate of 100 Sccm (64). Then, at a reaction temperature of around 950 °C, a mixture of Ar / CH₄/H₂ was passed through the system at flow rates of 200/40/100 Sccm for 30 minutes. The furnace was then switched off and allowed to cool (unaided) to ambient temperatures. In order to remove the support material and the metal particles, the samples were then treated by acid. They were first placed in dilute HCl acid for two days. They were then transferred into dilute HNO₃ for three days they were then filtered under vacuum, using a 0.2 μm filter paper, and then rinsed with deionised water. After the acid treatment, all the catalyst
support and any accessible catalyst had been removed. It should be noted that this process was not able to remove particles that had become entirely coated with amorphous carbon. Finally the resultant material was dried at 140 °C overnight.

3.10 Characterisation of samples by SEM and TEM

The purified samples were characterised using SEM (JOEL JSM 6400) and TEM (JEOL 3010). With the present catalysts and CVD conditions, a large number of SWNTs bundles are observed in both samples. The SEM images at different points are all very similar to each other. Fig.3.3-3.4 shows the presence of SWNTs bundles with a range of diameters throughout the image, and these images were typical of the whole sample. The diameters of the bundles lie between 10 and 70 nm (Fig 3.5). It will also be noted that there are many dark dots. These are due to metal particles encapsulated within the nanotubes and also, shaded zones, attributed to amorphous carbon (58). The samples for the TEM were prepared by sonicating about 3mg of material in alcohol, One drop was then put on the Lacey-Carbon-coated CU grid. Fig 3.6 clearly shows the different part of the TEM image of the SWNTs bundles, where each bundle contains several tubes. The size of the bundles, here range from 5.3 to 16 nm, and the lengths are up to tens of micrometers. The difference in bundle size between the two images (SEM, TEM) may be related to the sonication of samples prior to examination with the TEM. The diameters of SWNTs within these bundles are estimated to be 1.05nm. Besides the bundles of SWNTs, the individual SWNTs with average diameters of 1.5 nm are observed. The TEM image in Fig 3.7 also shows that the average size of the catalyst particles coated by amorphous carbon is about 7nm.
Fig 3.3 SEM images of a CVD prepared acid-treatment carbon sample. These images show the presence of SWNT bundles throughout the sample. Dark spots are due to carboneous materials.
Fig 3.4 same as in the previous figure but for the different part of the sample.
Fig 3.5 Higher magnification SEM image of sample in Fig 3.3 and 3.4, which shows clearly the size of the SWNT bundles in the sample. As can be seen, the diameter of the bundles lie between 10 and 70 nm.
Fig 3.6 High-resolution TEM images of different areas of the carbon sample, showing SWNT presence throughout. The range of diameters of bundles are from 5.3 to 16 nm. Dots spots are due to metal particles encapsulated in the nanotubes and amorphous carbon.
Fig 3.7 High-resolution TEM image of the carbon sample, clearly showing the size of the catalyst particles coated by amorphous carbon to be about 7nm.
Chapter 4. Thermodynamic of adsorption

4.1 Adsorption

When a gas is in contact with a solid, part of it is taken up by the solid. The molecules of gas can either enter inside the solid (absorption) or remain on the surface (adsorption). When both of these processes occur simultaneously on the surface, the process is termed sorption. The solid that adsorbs gas is called the adsorbent, and the adsorbed gas on the surface is called the adsorbate. It is not easy to tell whether the gas is inside the solid or only at the surface because most practical absorbents are very porous with large internal surfaces. The gas adsorption processes can be used to determine the surface area of most absorbents. Adsorption processes can be divided into two categories: physical and chemical adsorption. In physisorption (physical adsorption) the attraction of molecules to the surface is very weak, via Van der Waals forces so molecules are not limited to specific sites and can cover the surface. Chemisorption occurs by chemical bonding of the gas with surface so in chemisorption, the adsorbed molecules are more localized on the surface than physical adsorption (H₂ → 2H ). In addition chemisorption in contrast with physisorption is irreversible. The fractional coverage of a surface is defined by the quantity \( \theta \).

\[
\theta = \frac{\text{number of occupied adsorption sites}}{\text{total number of possible sites}}
\]

At any temperature, the adsorbate in the gas phase and on the surface are in a dynamic equilibrium, that is, the chemical potentials of the gas and the adsorbate are equal. The
chemical potential of the gas depends on its pressure, and the chemical potential of the adsorbate depends on the coverage \( \theta \). Thus the coverage at a given temperature is a function of the applied adsorbate pressure. The variation of \( \theta \) with \( p \) at a given \( T \) is called an adsorption isotherm. The adsorption process is generally reversible, but, under some conditions the shapes of the isotherms for adsorption and desorption may be different. This is called hysteresis. Hysteresis loops can be used to determine the structure and size of pores in the absorbent.

Adsorption isotherms are classified into six types based on Brunauer, Deming, Deming and Tellers proposal (65). This classification is shown in Fig 4.1. Type I isotherms which are fitted by the Langmuir equation, are reversible and as \( p/p_0 \) approaches 1, adsorption reaches a limit value. Sorption isotherms on microporous materials are often of Type I. Type II isotherms are due to nonporous or macroporous adsorbent where unlimited monolayer-multilayer adsorption can occur. The knee of the isotherm is called point B which indicates that monolayer coverage is complete and multilayer adsorption begins. Type III isotherms indicates that the adsorbate-adsorbent interactions are weak and adsorbate-adsorbate interactions are important. Types IV isotherms are due to mesoporous material. The characteristic of this isotherm is the hysteresis loop, which is related to condensation with the pore. The initial part of this isotherm can be related to monolayer-multilayer adsorption like Type II and the flat part of the hysteresis indicates complete pore filling. Type V isotherms show pore condensation and hysteresis. The initial part of this sorption isotherm relates to adsorption isotherms type III, which indicates weak attractive interaction between adsorbent and adsorbate. Type VI isotherms represent stepwise multilayer adsorption on a uniform nonporous surface (66).
Fig 4.1 classification of sorption isotherms. From (65)

4.2 Adsorption Isotherm

Langmuir in 1918 proposed a model for describing the kinetics of adsorption. This model is based on two basic assumptions. First, each site on the surface can adsorb one molecule and when all of the sites are occupied no further adsorption is possible. The second assumption is that all sites are equivalent and the energy of an adsorbed molecule is independent of the presence of other molecules. The first assumption is the monolayer assumption, which limits the number of adsorbed molecules and gives the saturation value. This condition is fulfilled when the time of adsorption for molecules in a second layer is short compared to the time of adsorption in the first layer. The equilibrium that
may exist between gas adsorbed on a surface and molecules in the gas phase is a dynamic
equilibrium in which the rates of adsorption and desorption are equal. The rate of
adsorption is dependent on the pressure and the number of vacant sites. And the rate of
desorption is dependent on the number of occupied sites. The Langmuir isotherm gives us
the expression for the number of particles adsorbed in a system with respect to pressure
for a constant temperature and an ideal gas.

The enthalpy of a system is

\[ H = U - T \, S \]  \hspace{1cm} 4.2

where \( U \) is the internal energy, \( T \) is the temperature and \( S \) is the configurational. Entropy, given by

\[ S = K \ln W \]  \hspace{1cm} 4.3

Where \( K \) is the Boltzman constant and \( W \) is the number of possible configurations of the
system. If the number of sites on the surface is \( N \) and the concentration of occupied sites
is \( \Theta \), then the number of possible configurations would be

\[ W = \frac{N!}{N(1-\Theta)!N\Theta!} \]  \hspace{1cm} 4.4

Therefore, the entropy becomes
\[ S = K \ln \frac{N!}{N(1-\Theta)!N\Theta!} \]  

Using Stirling approximation \( \ln N! = N \ln N - N \), the entropy becomes

\[ S = -KN \left[ \Theta \ln \Theta + (1-\Theta) \ln (1-\Theta) \right] \]

The entropy per site would be given by

\[ s = \frac{S}{N} = -K \left[ \Theta \ln \Theta + (1-\Theta) \ln (1-\Theta) \right] \]

And the enthalpy per molecule is \( h = u - Ts \). The chemical potential of the adsorbate is given by

\[ \mu = \frac{dh}{d\Theta} = \frac{du}{d\Theta} - T \frac{ds}{d\Theta} \]

\[ \mu = \frac{du}{d\Theta} + KT \ln \frac{\Theta}{1-\Theta} \]

The chemical potential of an ideal gas is

\[ \mu = \mu^0 + KT \ln \frac{P}{p_0} \]

Putting both expressions together, and considering \( u = -q\Theta, \mu^0 = 0 \). q is sites energy, \( p_0 \) is saturated vapour pressure.
\[
\ln \frac{p}{p_0} = -\frac{q}{KT} + \ln \frac{\Theta}{1 - \Theta} \quad \text{(4.11)}
\]

Or

\[
\Theta = \frac{p}{p_0 e^{\frac{-q}{KT}} + p} \quad \text{(4.12)}
\]

Equation 4.12 can be written as

\[
\Theta = \frac{kp}{1 + kp} \quad \text{(4.13)}
\]

where \( k = \frac{e^{\frac{q}{KT}}}{p_0} \) so the amount of coverage depends on \( q \) (heat of adsorption) and temperature \( T \). This means that, in a given pressure, coverage increases by increasing the \( q \) and decreases by increasing the temperature as is shown in Fig 4.2.

For a system where there are two types of site with different probabilities, a double Langmuir model suggests

\[
\Theta = \Theta_1 + \Theta_2 \quad \text{(4.14)}
\]

Where \( \Theta_1, \Theta_2 \) are the fraction of sites of type 1 and type 2 respectively occupied.
Fig 4.2 Coverage variation with heat of adsorption. As can be seen the coverage is increased by increasing the value of heat of adsorption.

### 4.3 Different methods of measuring adsorption/desorption

Each method assumes a different relationships between the heat of adsorption and the coverage. Langmuir assumes that heat of adsorption is constant with coverage, the Temkin method assumes that $q$ decreases linearly with increasing coverage and the Freundlich method assumes that $q$ decreases exponentially with increasing coverage.

*Langmuir theory*, according to kinetic principles the rate of adsorption is given by

$$\text{rate of adsorption} = K_a p (1 - \theta) \quad 4.15$$

where $K_a$ is the adsorption constant and $\theta$ is the fraction of surface covered with adsorbate. The rate of desorption is given by
rate of desorption = $K_d\theta$  

$K_d$ is desorption constant. At equilibrium these two rate are equal so

$$K_d p(1-\theta) = K_d \theta$$

The above equation can be written as

$$K_p = \frac{\theta}{1-\theta}$$

Where $K = K_a / K_d$ is a langmuir constant. If $K$ is replaced by the generalized Arrhenius expression

$$K = K_0 \exp\left[\frac{q}{RT}\right]$$

All three theories can be represented by the equation 4.18. $K_0$ is constant, $T$ the adsorption temperature and $q$ is heat of adsorption. Langmuir assumed that $K$ is constant therefore $q$ must be a constant.

*Temkin method*, in this method, assuming that $q$ decreases linearly with increasing coverage

$$q = q_0 (1-\lambda \theta)$$
Here $q_0$ is a constant, equal to the heat of adsorption at zero coverage and $\lambda$ is proportionality constant. After substitution for $K$ and $q$ in to the equation (4.18) we obtain

$$K_0 \exp q_0 \left[ \frac{1 - \lambda \theta}{RT} \right] = \frac{\theta}{p(1 - \theta)} \quad 4.21$$

after taking logarithms and rearranging, thus yields

$$\theta + A \ln \left[ \frac{\theta}{1 - \theta} \right] = A \ln p + B \quad 4.22$$

where $A = RT / q_0 \lambda$ and $B = (A \ln K_0 + 1 / \lambda$. If $A$ is very small and especially when $\theta$ approaches 0.5 the factor $A \ln (\theta / 1 - \theta)$ can be neglected, so equation (4.22) can be written as

$$\theta = A \ln p + B \quad 4.23$$

since $\theta = V/V_m$ where $V$ is the volume of gas adsorbed and $V_m$ is the volume of gas required to complete a monolayer then

$$V = V_m A \ln p + V_m B \quad 4.24$$

The Temkin method predicts that plotting $V$ against $\ln p$ is a straight line at intermediate coverage (between 0.2 and 0.8) Fig 4.3.
Fig 4.3 Illustrative Temkin plot for three isotherms at low, intermediate and high temperatures. (67)

*Freundlich method*, assumed that the heat of adsorption decreases exponentially with increasing coverage.

\[ q = -q_m \ln \theta \]  

4.25

Here \( q_m \) is a constant equal to the heat of adsorption at \( \theta = 0.3679 \). For this method equation (4.18) is given by

\[ K_0 \exp \left( -\frac{q_m \ln \theta}{RT} \right) = \frac{\theta}{p(1-\theta)} \]  

4.26

By taking logarithms and rearranging we get
\[ \ln \theta + c \ln \left[ \frac{\theta}{1-\theta} \right] = c \ln p + D \] 

Here \( c = \frac{RT}{q_m} \) and \( D = c \ln K_0 \) are constants. The magnitude of \( c \) is often small. In addition, as with the Temkin method, at intermediate coverage the factor \( c \ln (\theta/(1-\theta)) \) can be neglected and therefore equation (4.27) becomes

\[ \ln \theta = c \ln p + D \] 

a plot of \( \ln V \) against \( \ln p \) should yield a straight line.

### 4.4 Classification of pore sizes

The pore systems of solids are of many different kinds. The individual pores may vary both in size and in shape within a given solid and between one solid and another. The widths \( W \) of the pores (the diameter of a cylindrical pore or the distance between the sides of a slit-shaped pore) are of most interest. According to the international union of Pore and Applied Chemistry (68), pores may be classified by their internal pore width. In Micropores, where the width is less than \( \sim 20 \AA \), the interaction potential is higher than in wider pores because of the proximity of the walls. Hence, the amount adsorbed (at a given relative pressure) is correspondingly enhanced. In Mesopores where the width is between 20 and 500\( \AA \), adsorption does not only depend on the fluid-wall attraction but also on the interaction between fluid-molecules thus leading to capillary condensation. In
Macropores the width is more than 500Å, and the widths of the pores are so large that they can be considered as nearly flat surfaces.

4.5 Adsorption in mesopores

Sorption in mesopores not only depends on fluid-wall interaction but also on the attractive interaction between fluid molecules. So the most important phenomena happening in mesopores are multilayer adsorption, phase transitions (pore condensation) and sorption hysteresis. At a critical thickness of the multilayers, pore condensation occurs in cores of pore \((a = r-l, a \text{ radius of core}, r \text{ radius of pore and } l \text{ is thickness of multilayer})\). Fig 4.4 shows adsorption process in mesopores.

![Adsorption isotherm for adsorption/desorption of a fluid in a single mesopore of cylindrical shape.](image)

Point A indicate that formation of monolayer is completed and multilayer adsorption starts at point B. When the thickness of multilayer reaches a critical thickness (point C),
capillary condensation occurs in the core of the pore (transition from C to D). The flat part of the isotherm means the pore is completely filled with liquid. Pore evaporation occur at pressure less than pore condensation pressure (point E). The difference is due to the vapour pressure over a coverage surface. There is a relation between the shape of the hysteresis loop and the size distribution and geometry of pores. Empirical classification of the hysteresis loop is based on the classifications of de Boer (69) as shown in Fig 4.5.

![Relative Pressure](image)

**Fig 4.5 Classification of hysteresis loops. From (69)**

Type H1 relates to porous materials containing cylindrical pores, for type H2, hysteresis is related to disordered material where the pore size distribution and the shape are not well defined. Type H3 shows that there is no limiting on adsorption which give rise to slit-shape pores. Type H4 is related to narrow slit pores including micropores.
The width of the hysteresis loop depends on pore size and temperature so that it decreases with decreasing pore size and increasing of temperature.

4.6 Physical adsorption gases

The effect of the pore structure (mesopores), on multilayer adsorption is to convert an isotherm of Type II into Type IV or a Type III into Type V (70). This occurs because the finite pore width places a limit on the extent of multilayer formation before the pore becomes filled with liquid-like condensate, and this will occur with the formation of a highly curved miniscus which results in a depression of the liquid vapour pressure below its normal value. Adsorption-desorption hysteresis also results because pores are filled and emptied by different processes. Emptying occurs by evaporation from the liquid miniscus which retreats down the pore in the process. In practice, except sometimes with micropores (diameter less than about 1nm) physical adsorption with capillary condensation usually gives an isotherm with a hysteresis loop. This is because in adsorption the miniscus is cylindrical \( r_{m,\text{ads}} = 2r_{m,\text{eff}} \) and in desorption the miniscus is spherical \( r_{m,\text{des}} = r_{m,\text{eff}} \).

\[
r_{m,\text{ads}} = 2r_{m,\text{des}} \quad 4.29
\]

Then capillary evaporation occurs at a lower pressure than capillary condensation for a given amount of adsorption and causes the hysteresis loop in the isotherm. Methods which are used for the analysis of pore structure from physical sorption isotherms depends on the use of either desorption or adsorption parts of the hysteresis loop.
4.7 Calculation of pore size

On the desorption branch, the vapour is in equilibrium with liquid in the pores. The Kelvin equation, is the classical expression, which relates the vapour pressure of a liquid to the radius of curvature of its surface, \( r \) is given by (71)

\[
\ln \frac{p}{p_0} = -\frac{2\gamma V_L}{RT} \frac{1}{r_m}
\]

Here \( p/p_0 \) is the relative pressure of the vapour in equilibrium with a meniscus having a radius of curvature \( r_m \), and \( \gamma \) and \( V_L \) are the surface tension and molar volume respectively, of the liquid adsorptive. Using the Kelvin equation, it is possible to calculate the minimum radius of pores, in which capillary condensation occurs, from the relative pressure at the lower limit of the hysteresis loop. The Kelvin equation leads to values of the core size rather than the pore size. The conversion of an \( r_m \) to a pore size involves recourse to a model of pore shape, and also knowledge of the angle of contact \( \theta \) between the capillary condensate and the adsorbed film on the walls. When capillary condensation occur along as isotherm, the pore walls are already covered with adsorbed film with a thickness \( t \). Starting at the top end of the desorption branch, removal of a small quantity of adsorbate corresponding to a volume \( \Delta V \) of liquid occurs at a certain relative pressure, and corresponds to a certain pore size which can be calculated from the Kelvin equation.

The pore size distribution is characterised by the collection of values of \( \Delta V \) and the corresponding pore sizes. However, the problem is complicated by the fact that the pore wall is covered by a multilayer of adsorbate, where the thickness is a function of the
relative pressure. The pore size parameter, which is evaluated from the Kelvin equation, is thus less than the true pore size. Several empirical relations have been proposed to represent the variation of adsorbed layer thickness with relative pressure in the range of $0.3 < p/p_0 < 1$, and one is worth noting here (70), remembering that it refers to adsorbed nitrogen at 77K, we have

$$\log \frac{P}{P_0} = 0.034 - \frac{13.99}{t^2}$$

4.31

Starting at a point where all the pores are full of liquid. Assume start at nth step which starts at a relative pressure $p/p_0)_a + \Delta$ and finish at a $p/p_0)_a - \Delta$. The value $p/p_0)_a$ is thus at the mid point of the step. The volume emptied by the process of going from $(p/p_0 + \Delta)$ to $(p/p_0 - \Delta)$ can be related to the pore volume by the geometrical relation

$$\Delta V = \frac{(r_K + \Delta t)^2}{r_p^2} \cdot V_p$$

4.32

The problem is complicated by the fact that the reduction in layer thickness in the pores, which were already emptied, also contributes to $\Delta V$. Therefore the pore volume is $\Delta V_a$ where $A_p = \frac{2V_p}{r_p}$ and $r_K = r_m$. In the above equation, the first term is related to capillary evaporation and the second term is related to a correction. For each desorption step the average diameter of the pore which undergoes capillary evaporation is calculated from the Kelvin equation and the empirical equation.
\[ r_p = r_k + t \]  
\[ \log \frac{P}{P_0} = 0.034 - \frac{13.99}{r^2} \]  
\[ \log \frac{P}{P_0} = -\frac{4.14}{r_k} \]

\( \Delta r \) is the change in layer thickness in each desorption step and \( \Delta V_n \) is the volume desorbed in each step.

### 4.8 Physical adsorption of gas on SWNT

Gas adsorption is one of the experimental methods for characterisation surface areas and pore sizes in porous materials which can cover a wide range of pore sizes from 0.35 nm up to >100 nm. The amount adsorbed on a solid depend on temperature, pressure and the interaction energy between the adsorbate and the solid surface, so at constant temperature and equilibrium pressure, the weight of gas adsorbed on a unit weight of solid is given by

\[ W = F(P, E) \]

A plot of \( W \) against \( P \) is assigned to the sorption isotherm.\(^{(72)} \). There are two ways that hydrogen can be adsorbed on a material surface: physical adsorption (physisorption) and chemisorption. In physisorption, \( \text{H}_2 \) keeps its molecular identity but in chemisorption, \( \text{H}_2 \) molecules dissociate and hydrogen is stored in the atomic form \(^{(73)} \).
Hydrogen adsorption in carboneous materials corresponds to the amount of hydrogen which is adsorbed on the surface of solid carbon due to van der Waals interactions between the carbon atoms and hydrogen molecules (74). For physisorption, hydrogen adsorption in nanotubes is maximised when the nanotubes have highly uniform micropores sizes, high surface area and attractive surface potentials (75). At a definite temperature, the amount of hydrogen adsorbed is a function of pressure. When the pressure decrease the hydrogen is released so the process of adsorption (physisorption) is reversible with pressure. Bundles of SWNT have at least three different kinds of adsorption sites: Grooves, the region in which two tubes in the outer surface of the bundle meet; the outer surface of individual tubes; and the interstitial channels (ICs), the space formed by three tubes in the interior of bundle. If the SWNT is open-ended a further type of adsorption site could be within an interior of a tube. The interstitial channel would have the highest binding energy and followed by the grooves, the outer surface site would have the lowest binding energy (76).

4.8.1 Review of hydrogen adsorption on nanotubes

In 1997 Dillon et al were first to report on hydrogen adsorption by SWNT’s. The range of hydrogen storage on 0.1 to 0.2 wt % of SWNT in the sample was estimated to be between 5 and 10 wt % at 273K and 0.05 MPa pressure. (77). In 1998 Chambers et al found that the hydrogen storage capacity of carbon nanotubes was 11.26 wt % at room temperature and 11.35 MPa pressure (78). Darkrim et al computed hydrogen adsorption in SWNT in two arrangements of open carbon nanotubes by simulation. In the simulation,
gas was allowed to be adsorbed inside and outside the tubes. At 10 MPa and 77K, the simulation predicted 11.24 wt% hydrogen adsorption in SWNT. This result is in agreement with the experimental adsorption in SWNT, which was performed by Ye et al at 77k and 10 MPa pressure. (79). Ye et al performed hydrogen adsorption isotherms on an SWNT sample at 80K temperature and 0.32 MPa pressure. The BET surface area of the SWNT sample was 285 m²g⁻¹. The hydrogen uptake was 0.33 wt% for SWNT and 2.35 wt% for high surface area Saran carbon with 1600 m²g⁻¹ surface area. At higher pressure (7 MPa) and at 80K the adsorbed hydrogen on SWNT reached 7.7 wt%. (80).

Absorption of hydrogen in a tubular pore was calculated by Rzepka et al. They found that the maximum amount of hydrogen at 300K and 6MPa pressure was 0.6 wt% and that at 77K temperature, was about 6 wt%. (81). Liu et al reported hydrogen adsorption on samples containing 50 wt% nanotubes. The amount of hydrogen uptake was from 2.4 to 4.2 wt% at 298K and 12 MPa pressure. (82). Chen et al reported that hydrogen uptake of 14 wt% to 20 wt% can be obtained by doping MWNT by Li or K at 0.1 MPa pressure. Hydrogen sorption for K-doped tubes took place at room temperature but for Li-doped tubes, the temperature required had to be increased (473-673 K). However, it was found that the large weight increase was actually due to the formation of alkali hydroxide from H₂. Experiments with pure and dry hydrogen showed that adsorption on the same system was about 2 wt% (83). Hydrogen adsorption on SWNT, activated carbon and graphites was also measured. It was observed that hydrogen capacity of all samples at 295K and 8 MPa was less than 1wt%, while at 77K and 5 MPa, the highest capacity (2.9 wt%) was observed in SWNT which had been produced by laser ablation (84). Yang et al used the same method for preparing their samples as that used by Chen et al. The BET surface
area of samples was 148 m²/g, which was slightly higher than that obtained by Chen et al (130 m²/g). They performed hydrogen adsorption-desorption using ultra high purity hydrogen 99.999%. The results obtained were different from those obtained by Chen et al. Hydrogen uptake by K-doped MWNT was 1.8% and for Li-doped was 2.5%. Züttel et al measured hydrogen adsorption on carboneous material at 293K by an electrochemical techniques in which the sorption process involves a charge transfer (85). The range of reversibly stored hydrogen in graphite was from 0.04 to 0.46 wt%, for MWNT between 0.09 and 0.36 wt% and for SWNT between 0.18 and 0.36 wt%. Hydrogen adsorption capacities of SWNT, MWNT and aligned MWNT were measured by Gundiah et al. Measurements were performed on SWNT which were obtained by the electric arc method at 300K and pressures of up to 12.5 MPa. The hydrogen capacity obtained was 0.2 wt% which after treatment with nitric acid and washed with HCl and H₂O₂ increased to reach 1.2 wt%. The maximum hydrogen storage capacity observed was in aligned MWNT (3.7 wt%) (86). The above results are summarized in Table 4.1. Theoretical calculations on the adsorption of H₂ in carbon nanotubes have been performed using Monte Carlo and Molecular Dynamic calculations (87).
Table 4.1: summary of hydrogen uptake in carbon nanotube materials at different pressure and temperature

<table>
<thead>
<tr>
<th>References</th>
<th>Adsorbent</th>
<th>Hydrogen Storage wt %</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
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<td>10</td>
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</tr>
<tr>
<td>Gundiah et al</td>
<td>SWNT</td>
<td>1.2</td>
<td>300</td>
<td>12</td>
</tr>
</tbody>
</table>

4.8.2 Heat of adsorption

When a gas molecule adsorbs on a surface, generally heat is released and therefore the process of adsorption is exothermic. Heat of adsorption is a measure of the binding energy between the molecule and the adsorbent surface. The amount of heat released in the adsorption process is determined by various types of heat of adsorption.

Integral heat of adsorption $q_{int}$ is defined as the difference between the specific internal energies of the sorptive in gas state $U_g$ and in adsorbed state $U_a$ for n moles.
\[ q_{\text{int}} = \frac{Q_{\text{int}}}{n} = u_g - u_a \]  \hspace{1cm} (4.37)

Here \( Q_{\text{int}} \) is the total or integral heat released from the system during the adsorption process. Since the integral heat of adsorption depends on the amount of gas adsorbed the differential heat of adsorption is defined as

\[ q_{\text{diff}} = \frac{\partial Q_{\text{int}}}{\partial n} \]  \hspace{1cm} (4.38)

Isosteric heat of adsorption \( q_{\text{st}} \) is defined

\[ \frac{q_{\text{st}}}{R} = -\frac{\partial \ln p}{\partial \left(\frac{1}{T}\right)} \]  \hspace{1cm} (4.39)

This equation can be obtained from the Clausius-Clapeyron equation at constant coverage

\[ \frac{\partial \ln p}{\partial T} = \frac{q_{\text{st}}}{RT^2} \]  \hspace{1cm} (4.40)

differential and isosteric heat of adsorption are related by the following equation

\[ q_{\text{st}} = q_{\text{diff}} + RT \]  \hspace{1cm} (4.41)
4.8.3 The BET method

The BET (Brunauer, Emmett, and Teller) isotherm, developed in 1938, is based on the Langmuir assumptions, but considers also multilayer adsorption. The BET theory assumes that the upper layer is in equilibrium with the vapour phase. The BET isotherm is used for the determination of the surface area of powder samples. When adsorption is extended to the multilayer, it is assumed that the first layer has a heat of adsorption depending on the surface and the other layers are bound with energy given by the latent heat of liquid N\textsubscript{2}. The total number of molecules adsorbed is

\[ N = N_m (\theta_1 + 2\theta_2 + \ldots + n\theta_n) \]

Where \( N_m \) is the number of molecules in the complete monolayer sites per unit area and \( \theta_1, \theta_2, \ldots, \theta_n \) are fractions of surface coverage with 1,2,...,n molecules. By substituting for \( \theta_1, \theta_2, \ldots, \theta_n \) in equation The BET equation is obtained.

\[ \frac{n}{n_m} = \frac{c \frac{P}{P_0}}{1 - \frac{P}{P_0} \left( 1 + \left( c - 1 \right) \frac{P}{P_0} \right)} \]

The parameter \( c \), which involves several parameters, determines the shape of the isotherm i.e. as the value of \( c \) become greater the knee of the isotherm plot becomes sharper. For higher value of \( c \) the isotherm goes towards type II, and for lower values the isotherm goes towards type III. However only type II isotherms yield reliable values for \( n_m \). The reason is that in isotherms of type III, there is a strong tendency for the second and succeeding layers to begin to form well before the first layer is complete. For many
practical purposes, the BET equation is generally fitted to data in a range \( p/p_0 = 0.05-0.3 \).

By rearranging of equation 6.8 the convenient form of the BET equation is obtained (88).

\[
\frac{P}{P_0} = \frac{1}{n(1-P/P_0)} + \frac{c-1}{n_m c} \times \frac{P}{P_0}
\]

4.44

The plot of \( \frac{p/p_0}{n(1-p/p_0)} \) against \( \frac{p}{p_0} \) should be a straight line with slope

\[ s = c - \frac{1}{n_m c} \]

and intercept \( i = \frac{1}{n_m c} \). Solution of these two simultaneous equations gives \( n_m \) and \( c \). By substituting \( n_m \) in to the

\[ A = n_m a_m L \]

4.45

The surface area of sample can be identified. \( n_m \) is the monolayer capacity, \( a_m \) is the average area occupied by a molecule of adsorbate in the complete monolayer and \( L \) is the Avogadro constant.

4.9 Experimental method for measuring hydrogen on the sample

Adsorbed mass as a function of pressure can be obtained by either volumetric or gravimetric methods. The volumetric method is based on calibrated volumes and pressure measurements involving the use of the general gas equation. The adsorbed amount is
calculated by determining the difference in the total amount of gas admitted to a sample cell with adsorbent and the amount of gas in the free space in the cell. The correction is therefore needed to allow for the volume that is occupied by the sample. The gravimetric method is based on a sensitive microbalance and a pressure gauge. The adsorbed mass can be measured directly but a buoyancy correction is necessary due to the density of gas displaced by the sample. In this method, the adsorbent is not in contact with the thermometer so it is difficult to measure the exact temperature of the adsorbent.

4.9.1 Intelligent Gravimetric Analyser (IGA)*

The Intelligent Gravimetric Analyser (IGA) used in the present work is an instrument that is able to measure the mass of gas adsorbed by using microbalance system Fig 4.6. This technique relies upon the mass change that occurs at the sample due to the adsorbate as a result of a change of system parameters such as pressure or temperature. Measurements are usually performed in constant temperature (isothermal mode) to determine the pressure-concentration graph. This system was used throughout the studies of the nitrogen and hydrogen sorption in/on the ropes of single-walled carbon nanotubes presented in this thesis. The core of IGA is an electronic beam balance. Whenever the equilibrium is disturbed by increasing a mass, some extra current is passed through the electromagnetic coil to compensate for the change. The value of current required is proportional to the applied weight. There is a feed-back system to bring the beam back to the neutral position. System parameters such as pressure and temperatures are routinely

* Manufactured by Hiden Analytical
controlled. Pressure is controlled by two stepper motor-driven needle valves—admittance, connected to a gas source and exhaust connected to a vacuum unit consisting of a turbo-molecular and a rotary pump. Pressure can be varied in IGA from $10^{-6}$ mbar to 20 bar. The pressure is controlled by two valves, a high pressure valve and a low pressure valve. Each of the valves controls the pressure by admitting gas to or releasing it from the system chamber. IGA has temperature controllers for both internal and external thermal regulation. The internal system keeps the balance system and electronics at a constant temperature so that the accuracy of instrument is not varied by external thermal fluctuation. The external systems determine the sample environment temperatures such as a furnace or cryostat. In principle, the temperature is measured by two thermocouples: internal, near the sample position and external, outside the IGA reactor.

**Fig 4.6 The intelligent gravimetric analyzer (IGA) (89)**
4.9.2 The buoyancy correction

An essential part of the measurement of sorption isotherms by microgravimetry is the buoyancy correction. Buoyancy in IGA is always partly compensated since it acts in opposite directions on the counterweight and on the sample side components. A mode of operation in which the effect is fully compensated by choosing a counterweight with a relevant density is called symmetric. If the material of the counterweight is arbitrarily chosen then the balance and its operation mode are asymmetric. In this case the correction is calculated in the following way

\[
\delta m(P, T, T') = \rho_{gas}^{SS}(P, T) \sum_i \left( \frac{m_i}{\rho_i} \right)^{SS} - \rho_{gas}^{CWS}(P, T') \sum_i \left( \frac{m_i}{\rho_i} \right)^{CWS}
\]

Where \( T, \rho_{gas}^{SS} \) and \( T', \rho_{gas}^{CWS} \) are the temperature and the gas mass density at the sample side (SS) and at the counter-weight side (CWS). The temperature is generally different at the two sides. Then the mass as a function of pressure and temperature is obtained as

\[
M(p, T) = M_{exp}(p, T) + \delta m(p, T, T')
\]

If the gas is assumed ideal, its molar density is obtained by the ideal gas equation of state

\[
\rho_{gas}^{mol} = \frac{1}{V} \rho \frac{p}{RT}
\]
So the mass density is given by

\[ \rho_{gas} = M_{gas} \times \rho_{gas}^{mol} \]  

At higher gas densities, molar gas density can be obtained by the virial expansion of the equation of state

\[ PV = RT \left[ 1 + \frac{B_1}{V} + \frac{B_2}{V^2} + \ldots + \frac{B_i}{V^{i-1}} + \ldots \right] \]

Where \( B_i \) is the \( i \)-th virial coefficient which is also a function of temperature. Values of \( B_i \) are tabulated for all common gases.
Chapter 5. Raman Spectra of Samples

5.1 General concepts

When molecules are placed in electromagnetic radiation, the quanta of energy in the radiation may be transmitted, absorbed or scattered. In Rayleigh scattering, molecules scatter the light without changing the wavelength of the incident photon. Rayleigh scattering is an elastic collision between the incident photon and the molecule. Therefore the energy of the molecule, which contains vibrational, rotational and electronic energy, is unchanged (90). The Raman Effect is an inelastic collision between the incident photon and the molecules, which relates to a change in the vibrational, rotational or electronic quantum state of a molecule. The difference in energy between an incident photon and the Raman scattered photon is equal to the quanta of energy absorbed in the vibrational or rotational energy of the scattering molecule, $\Delta E_m$ (91).

$$h\nu_i - h\nu_s = \Delta E_m$$  \hspace{1cm} 5.1

where the energy of incident and scattered photon are $h\nu_i$ and $h\nu_s$ respectively. If $\Delta E_m$ is positive, in the Raman spectrum, it is called the Stokes line. Otherwise, if the molecule loses energy, it is called, the Anti-Stokes line. Fig 5.1 shows the vibrational energy levels of a molecule. The differences in energy between these levels are $\Delta E_m$. Absorption of a photon, the frequency of which is the same as the molecular frequency, $\nu_m$, gives rise to direct transition between these levels. The frequency of the incident photon in Rayleigh and Raman scattering is usually greater than the molecular frequency. In Raman scattering, if the molecule is in the ground vibrational
state, \( v = 0 \), it absorbs the energy of the photon and is excited to a high level of energy which is not a stable energy level. Then the molecule loses energy and falls to the \( v = 1 \) energy level. By emitting a scattered photon with energy less than the exciting photon, this scattered photon gives rise to a Stokes line in the Raman spectrum. According to quantum mechanics, for a harmonic vibration for Raman scattering the allowed change in the vibrational quantum number is \( \Delta v = \pm 1 \).

![Fig 5.1 Schematic of Raman and Rayleigh scattering and infrared absorption. (a) absorption, (b) Rayleigh scattering, (c) Raman stoke and (d) Raman antistoke](image)

### 5.2 The polarizability theory

If a molecule is placed in an electric field then electrons are displaced relative to atom cores and therefore the molecule becomes polarised. The electric dipole moment induced in a scattering molecule is proportional to the electric field, \( E \), of the incident radiation by the equation

\[
\mu = \alpha E
\]  

5.2
where \( \alpha \) is a polarizability of the molecule. The time dependence of the electric field of the radiation is given by

\[
E = E_0 \cos 2 \pi vt \tag{5.3}
\]

Where \( v \) is a radiation frequency. By substituting equation (5.3) in (5.2)

\[
\mu = \alpha E_0 \cos 2 \pi vt \tag{5.4}
\]

From classical theory, the dipole moment emits radiation, the intensity of which is proportional to the square of \( \mu \) which is \( \alpha^2 E_0^2 \). Vibrations and rotations of molecule can change the polarizability so in a molecule \( \alpha \) is not constant and its variation is given by

\[
\alpha = \alpha_0 + \frac{\partial \alpha}{\partial Q} Q + ... \tag{5.5}
\]

where \( \alpha_0 \) is equilibrium polarizability at low fields and \( Q \) is a normal coordinate.

\[
Q = Q_0 \cos 2\pi \nu_v t \tag{5.6}
\]

\( \nu_v \) is the frequency of the normal coordinate vibration. By substituting (5.5) and (5.6) into (5.4)

\[
\mu = \alpha_0 E_0 \cos 2\pi vt + \frac{\partial \alpha}{\partial Q} Q_0 \frac{E_0}{2} \left[ \cos 2\pi (\nu - \nu_v) t + \cos 2\pi (\nu + \nu_v) t \right] \tag{5.7}
\]

This equation shows that the induced dipole moment varies with three frequencies \( \nu \), \( \nu - \nu_v \) and \( \nu + \nu_v \). Therefore the intensity of the Raman scattered radiation is proportional to \( \left( \frac{\partial \alpha}{\partial Q} \right)^2 \).
5.3 Normal and Resonance Raman

The quantum mechanical approach to Raman scattering theory relates scattering frequencies and intensities to vibrational and electronic energy states of the molecule. The standard perturbation theory assumes that the frequency of incident light is below the frequency of the first electronic excited state. Raman spectroscopy is performed with green, red or near infrared lasers for which the frequencies are below the first electronic transitions of most molecules. If the wavelength of the laser is within the electronic spectrum of a molecule, the intensity of Raman-active vibrations increases by a factor $10^2-10^4$.

In quantum mechanics, the transition electric dipole related to transition of molecule from initial state $I$ to a final state $f$ can be written as (92)

$$P_{fi} = P^1_{fi} + P^2_{fi} + ...$$  \hspace{1cm} 5.8

Where $P^1$ is linear in $E$ and $P^2$ is quadratic in $E$ and so on. Therefore the total transition electric dipole is given by

$$P_{fi} = \langle \psi'_f | \hat{P} | \psi'_I \rangle$$  \hspace{1cm} 5.9

$\psi'_I$ and $\psi'_f$ are the time dependent perturbed wave function of the initial and final states. As a result of perturbation, the unperturbed state is modified by expanding the perturbed wave function in respect of the unperturbed state and its modification and thus if this modifications is expressed as a linear combination of the unperturbed wave functions, the electric dipole for this transition is given by
\[ P_{fi} = \langle \psi^0_i | \hat{P} | \psi^1_i \rangle + \langle \psi^1_i | \hat{P} | \psi^0_i \rangle \]  \hspace{1cm} (5.10)

Where \( \psi^1_i \) and \( \psi^0_i \) are the first order perturbed wave functions. The P component of (5.10), which only contains terms that describe the generation of Rayleigh and Raman scattering is given by

\[
\left( P^1_{P} \right)_{fi} = \frac{1}{2\hbar} \sum_{r \neq i, f} \left( \frac{\langle f | p_\sigma | r \rangle \langle r | p_\sigma | i \rangle}{w_{ri} - w_i} + \frac{\langle f | p_\sigma | r \rangle \langle r | p_\sigma | i \rangle}{w_{rf} + w_i} \right) E_{\sigma \sigma} e^{-iw_st} 
+ \text{complex conjugate} \hspace{1cm} (5.11)
\]

and

\[
\left( \alpha_{\rho \sigma} \right)_{fi} = \frac{1}{\hbar} \sum_{r \neq i, f} \left( \frac{\langle f | p_\rho | r \rangle \langle r | p_\sigma | i \rangle}{w_{ri} - w_i} + \frac{\langle f | p_\sigma | r \rangle \langle r | p_\rho | i \rangle}{w_{rf} + w_i} \right) \hspace{1cm} (5.12)
\]

Where \( W_s \) is frequency of the scattered radiation. \( W_s = W_1 - W_{fi} \)

When \( w_1 \ll w_{ri} \) the Raman process is termed normal, and if \( w_1 \approx w_{ri} \), it is termed resonance Raman scattering. The intensity of resonance Raman scattering is several times greater than normal scattering, because the denominator of the first term in the equation becomes very small in a resonance process.

By using the Born-Oppenheimer approximation, which separates the electronic and nuclear motions, we can get more information about normal and resonance raman scattering. Expansion of the \( J \)th electronic nuclear state to their components: electronic, vibrational and rotational are given by
and also energy of the jth state can be given

$$|j\rangle = |e^j\rangle |\nu^j\rangle |R^j\rangle$$

Under experimental conditions in Raman scattering, the rotational structure is not resolved. Therefore, the scattering may be described by the transition of the type $e^g \nu^i \rightarrow e^g \nu^f$ this is termed pure vibrational Raman scattering. Now we can write conditions for normal and resonance Raman scattering in detail.

If the frequency of the exciting radiation $\omega_i$ is much less than the vibronic absorption frequencies $\omega_{\nu^i}$ scattering is termed normal Raman scattering.

There are two cases in this situation. When $e^f = e^g$, only vibrational transitions in the ground electronic state occur, and when $e^f \neq e^g$ both electronic and vibronic transitions from the ground electronic state occur. The other situation occurs when the frequency of the exciting radiation approaches the vibronic absorption frequencies. In that case, scattering is called resonance raman scattering.

5.4 Raman Bands of SWNTs

The single wall carbon nanotube is a one-dimensional system (large length to diameter ratio) so their density of states is characterized by the Van Hove singularities (the one dimensional density of electronic states of nanotubes will show sharp
singularities below and above the Fermi level where known VHS). The electronic transitions between these singularities depend on the diameter and the electronic properties of SWNTs (93). Therefore, the electronic properties of SWNT can be probed by different incident laser energies. Raman scattering is one the most powerful techniques for characterising carbon nanotube samples. Radial breathing modes (RBM) of the tubes are found around 150-250 cm\(^{-1}\), the tangential modes (TM) or the G band between 1500-1600 cm\(^{-1}\) and a peak around 1340 cm\(^{-1}\) due to carbon nanoparticles, are the three important components of the Raman spectra of SWNT (94). The G band (TM mode) of SWNTs consists of two main components G\(^+\) and G\(^-\). G\(^+\) is related to the vibration of carbon atoms along the nanotube axis, while G\(^-\) is related to the vibration of carbon atoms along the circumferential direction of the nanotube and its line shape is sensitive to whether the SWNT is metallic or semiconducting (95). Raman spectroscopy, due to the resonance phenomena can be used to probe both the structural and electronic properties of the nanotubes. (96). Each part of the raman spectrum, RBM and TM, can show different properties of SWNT.

5.4.1 RBM mode

The intense bands in the low frequency range 150-250 cm\(^{-1}\) of SWNT relating to diameters between 0.7 to 2 nm, are assigned to the radial breathing modes. These bands are due to the coherent vibration of the carbon atoms in the radial direction. Since the frequency of the RBM mode is inversely proportional to the tube diameter, \(\omega_{\text{RBM}} = \frac{A}{d_t} + B\). The RBM bands positions can be used to calculate the nanotube diameter. For bundles of nanotube, A and B have been found to be 232 and 6.5 cm\(^{-1}\).
Respectively (96). B is an upword shift in the frequency related to tube-tube interactions. The RBM spectra for SWNT bundles contain RBM bands for different SWNT diameters which are in resonance with the particular incident laser line so the RBM peaks at each laser energy, do not reflect the entire diameter distribution in the sample. Therefore, in order to get information about the diameter distribution of the SWNT in the sample it is necessary to probe the SWNT with several excitation laser lines. For a diameter characterisation of the SWNT sample, it is useful to use the Kataura ($E_{ii}$ vs.$d_t$) plot which shows energy excitation against diameter of SWNT (97).

Fig 5.2 Allowed optical transitions for SWNT with various diameters. Black areas due to semi conducting tubes, dashed areas are due to metallic tubes and black dots to armchair tubes (97).
The measurements of RBM frequency with several laser energies can be used to characterise the ratio of metallic to semiconducting SWNT in a sample, because semiconducting and metallic tubes of similar diameters do not occur at similar $E_{\text{ij}}$. By using $d_i$ obtained from measurements of RBM frequency and resonance condition, the RBM can be used for making (n,m) assignments for individual SWNTs.

5.4.2 Tangential mode (TM)

The intense bands in the high frequency range 1500-1600 cm$^{-1}$ are assigned to the tangential c-c stretching modes. The TM mode can be used to distinguish between metallic and semiconducting tubes. The G band (from graphite) is broadened and asymmetric for metallic tubes in comparison with the lorentzian line shape for semiconducting tubes. This broadening is related to the resonance of the incident or scattered laser photon with the lowest transition $E_{11}$ between the singularities of the density of state of metallic SWNTs (95). In contrast to the graphite G band, which shows one single lorentzian peak at 1582 cm$^{-1}$ related to the tangential vibrations of the carbon atoms, the G band of SWNT is composed of several peaks (98).

5.5 Raman bands of SWNT sample

The Raman spectra of SWNT samples reported here were measured by A.Giannasi. Fig (5.3) shows the Raman spectra of SWNT sample measured in the radial breathing mode (RBM) range using three different laser lines. It is clear that the band shape is quite different from one line to another. This is because the sample contains carbon
nanotubes with a large diameter distribution. The shape of the RBM bands depends on
the relative population of each nanotube type that is in resonance with the laser
excitation frequency. In Fig 5.3a which shows measurement with the 2.55 eV
incidence energy a large number of peaks, corresponding to a diameter distribution
ranging from 1.1 to 1.31 nm are observed. From the diameter dependence of the
allowed optical transitions (97) only semiconducting tubes of such diameters can be
resonantly excited. This is in good agreement with the profile of the spectrum in the
TM mode which shows a lorentzian lineshape. The spectrum measured at 2.41 eV Fig
5.3b shows a similar profile. The peaks are shifted to lower frequencies and the range
of diameters is from 1.13 to 1.35 nm. The excited tubes are again semiconducting in
agreement with the TM mode. The spectra measured at 2 eV Fig 5.3c shows tubes
with sizes between 1.11 to 1.45 nm. Therefore, at this excitation energy, with such
diameters, both metallic and semiconducting tubes can be resonantly excited. It is
found that for higher wavelength laser lines, the peaks shift to lower frequencies. Fig
5.4 shows the fitting of these three RBM spectra by lorentzian lines. The fitted peak
frequencies are given in Table 5.1 together with their relative diameter sizes
determined according to \( w = \frac{232}{d} + 6.5 \). And also peak frequencies of the RBM and
corresponding chiral indices are described in Table 5.2. Fig 5.5 shows that the
diameter range of SWNT sample at three laser lines (2.55, 2.41, 2 eV). It shows that
the range in diameter lies between 0.97 and 1.35 nm, the most frequently occurring
diameter of tube at 1.1 nm. From observation of the Raman spectra we can conclude
for several reasons that SWNTs sample does not include tubes with armchair
symmetry. If armchair tubes are indeed present, their concentration must be very low
for the following reasons. First, a calculation of diameter dependence of the allowed
optical transitions (97) shows that the majority of the tubes in the sample are
semiconducting. Second, the diameter of the remaining tubes (metallic) are not the same as for armchair tubes calculated in the range n=7 to 15 (99). And, finally, armchair tubes exhibit several Raman active modes in the region 400 to 1500 cm\(^{-1}\) (100) which are not observed here.

The G band Raman spectra of graphite show a single lorentzian peak at 1582 cm\(^{-1}\) which results from the tangential stretching of the C atoms. In contrast to graphite, the G band of SWNT shows several peaks (98). In addition to this band, the so called D line appears at a slightly lower frequency which is characteristic of graphite nanocrystals (101). The G band of SWNTs sample was probed using three laser incident energies and the results are shown in Fig 5.6. Fig 5.6a shows that the G band consists of two main component, one peak at 1590 cm\(^{-1}\) (G\(^{+}\)) and the other at 1564 cm\(^{-1}\) (G\(^{-}\)). The G\(^{-}\) band is due to vibrations of carbon atoms along the circumferential direction of the SWNT, and show whether the SWNT is metallic or semiconducting (lorentzian lineshape) (95). This spectra, also shows a third peak at 1349 cm\(^{-1}\) which indicates the presence of carbon nanoparticles and amorphous carbon. It is found that on going from on incident beam energy of 2.55 eV to 2 eV, (i.e. decreasing the energy of the excitation photons) the weak peak changes to a shoulder in the left of the profile and also a slight asymmetry is observed, which is assigned to the contribution of metallic tubes. Moreover, using this excitation wavelength (\(\lambda=632.8\,\text{nm}\)), the peak due to carbon nanoparticles (D-line) is found at 1328 cm\(^{-1}\). Fig 5.7 shows the fitting of these three TM spectra from SWNT by a lorentzian lines. The frequencies of the peaks used for the fit are shown in Table 5.3.
Table 5.1: Frequencies (in cm$^{-1}$) of the lorentzian curves used to fit the bands associated with the radial breathing mode (RBM) of SWNT (CVD) sample, obtained with these laser excitation wavelengths. The corresponding diameters have been obtained using the expression reported in (97).

<table>
<thead>
<tr>
<th>Laser excitation</th>
<th>2.55 eV</th>
<th>2.41 eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v$(cm$^{-1}$)</td>
<td>$d$(nm)</td>
<td>$v$(cm$^{-1}$)</td>
</tr>
<tr>
<td>Line 1</td>
<td>...</td>
<td>268</td>
<td>0.89</td>
</tr>
<tr>
<td>Line 2</td>
<td>...</td>
<td>...</td>
<td>254</td>
</tr>
<tr>
<td>Line 3</td>
<td>245</td>
<td>0.97</td>
<td>245</td>
</tr>
<tr>
<td>Line 4</td>
<td>231</td>
<td>1.03</td>
<td>...</td>
</tr>
<tr>
<td>Line 5</td>
<td>226</td>
<td>1.06</td>
<td>227</td>
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<tr>
<td>Line 6</td>
<td>221</td>
<td>1.08</td>
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</tr>
<tr>
<td>Line 7</td>
<td>...</td>
<td>219</td>
<td>1.09</td>
</tr>
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<td>Line 8</td>
<td>216</td>
<td>1.11</td>
<td>215</td>
</tr>
<tr>
<td>Line 9</td>
<td>...</td>
<td>...</td>
<td>211</td>
</tr>
<tr>
<td>Line 10</td>
<td>202</td>
<td>1.19</td>
<td>203</td>
</tr>
<tr>
<td>Line 11</td>
<td>...</td>
<td>...</td>
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</tr>
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<td>...</td>
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<tr>
<td>Line 17</td>
<td>135</td>
<td>1.81</td>
<td>...</td>
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</tbody>
</table>
Table 5.2 : Peak frequencies (in cm\(^{-1}\)) of the Radial Breathing Mode (RBM) and corresponding chiral indices evaluated for armchair (n,n), zigzag (n,0) and chiral (n,m) tubes.

<table>
<thead>
<tr>
<th>Line</th>
<th>(\nu) (cm(^{-1}))</th>
<th>(n,m)</th>
</tr>
</thead>
<tbody>
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<td>Line 1</td>
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<td>(8,5)</td>
</tr>
<tr>
<td>Line 2</td>
<td>254</td>
<td>(10,3),(8,6)</td>
</tr>
<tr>
<td>Line 3</td>
<td>245</td>
<td>(7,7),(12,0)</td>
</tr>
<tr>
<td>Line 4</td>
<td>231</td>
<td>(13,0),(8,7)</td>
</tr>
<tr>
<td>Line 5</td>
<td>226</td>
<td>(13,1),(10,5)</td>
</tr>
<tr>
<td>Line 6</td>
<td>221</td>
<td>(12,3),(13,1),(14,0)</td>
</tr>
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<td>Line 7</td>
<td>219</td>
<td>(10,6),(9,7)</td>
</tr>
<tr>
<td>Line 8</td>
<td>216</td>
<td>(11,5),(13,2),(10,6)</td>
</tr>
<tr>
<td>Line 9</td>
<td>211</td>
<td>(14,1),(13,2)</td>
</tr>
<tr>
<td>Line 10</td>
<td>202</td>
<td>(11,6),(10,7),(14,2)</td>
</tr>
<tr>
<td>Line 11</td>
<td>198</td>
<td>(13,4)</td>
</tr>
<tr>
<td>Line 12</td>
<td>193</td>
<td>(9,9)</td>
</tr>
<tr>
<td>Line 13</td>
<td>186</td>
<td>(10,9),(14,4)</td>
</tr>
<tr>
<td>Line 14</td>
<td>183</td>
<td>(12,7),(13,6)</td>
</tr>
<tr>
<td>Line 15</td>
<td>178</td>
<td>(14,7),(15,4),(11,9)</td>
</tr>
<tr>
<td>Line 16</td>
<td>163</td>
<td>(13,8),(10,11),(14,7)</td>
</tr>
</tbody>
</table>

Table 5.3 : Frequencies (in cm\(^{-1}\)) of the lorentzian curves used to fit the bands associated with the tangential mode (TM) of SWNT (CVD) sample, obtained with three laser excitation energies.

<table>
<thead>
<tr>
<th>Laser excitation</th>
<th>2.55 eV</th>
<th>2.41 eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1</td>
<td>1614</td>
<td>1616</td>
<td>....</td>
</tr>
<tr>
<td>Line 2</td>
<td>....</td>
<td>....</td>
<td>1612</td>
</tr>
<tr>
<td>Line 3</td>
<td>1601</td>
<td>....</td>
<td>....</td>
</tr>
<tr>
<td>Line 4</td>
<td>....</td>
<td>1598</td>
<td>....</td>
</tr>
<tr>
<td>Line 5</td>
<td>....</td>
<td>....</td>
<td>1594</td>
</tr>
<tr>
<td>Line 6</td>
<td>1590</td>
<td>....</td>
<td>....</td>
</tr>
<tr>
<td>Line 7</td>
<td>....</td>
<td>....</td>
<td>1584</td>
</tr>
<tr>
<td>Line 8</td>
<td>....</td>
<td>1569</td>
<td>....</td>
</tr>
<tr>
<td>Line 9</td>
<td>1564.</td>
<td>....</td>
<td>1566</td>
</tr>
<tr>
<td>Line 10</td>
<td>1542</td>
<td>....</td>
<td>....</td>
</tr>
<tr>
<td>Line 11</td>
<td>....</td>
<td>1538</td>
<td>1537</td>
</tr>
</tbody>
</table>
Fig 5.3 Raman spectra of the Radial Breathing Mode (RBM) of single wall carbon nanotubes with three laser lines.
Fig 5.4 Fitting of the RBM mode of SWNT with laser lines 2.55, 2.41 and 2 eV by a sum of lorentzian lines.
Fig 5.5 Diameter distribution (nm) of SWNT sample with three laser line (a) 488 nm, (b) 514.5 nm and (c) 632.8 nm. The range of diameters is between 0.97-1.35 nm with the most frequently occurring tube diameter being 1.1 nm.
Fig 5.6 Raman spectra of the tangential mode (TM) of SWNT sample with three laser line.
Fig 5.7 Fitting of the (TM) mode of SWNT with three laser lines 2.55, 2.41 and 2eV by a sum of lorentzian lines.
5.6 Comparison of Sample with Hipco sample

Hipco describes one of the methods for making nanotubes (102). This method involves the application of high pressure gas phase decomposition of CO to produce nanotubes. In the Hipco process, the diameter of the nanotubes and the chiral angles depend on the high pressure reaction conditions used. The Raman spectra (RBM, TM mode) measurement reported here were performed on purified Hipco SWNT material. Fig 5.8 shows the Raman spectra of Hipco SWNT measured in the radial breathing mode range using two different laser lines (2.41, 2 eV). Fig 5.8a shows RBM measurements with a laser energy of 2.41 eV. A large number of peaks are observed which corresponds to a diameter distribution ranging from 0.9 to 1.47 nm. Figure 5.8b shows the spectrum measured at a laser energy of 2 eV. For this Laser energy, the peaks are shifted to higher frequencies and the range of diameters is from 0.82 to 1.32 nm. This is in contrast with SWNT sample produced by the CVD method, because when laser line goes to higher wavelengths, the peaks are shifted to lower frequencies. This different behaviour may be related to the electronic nature of the nanotubes in the two samples. In the Hipco sample, the majority of nanotubes which are excited by the two laser energies (2.41, 2 eV), from the diameter dependence of the allowed optical transitions, are metallic which is in contrast to the CVD sample where the majority of excited nanotubes are semiconducting. The range of diameters in the Hipco sample at the two laser lines is shown in Fig 5.9. This range is between 0.82-1.34 nm with the most frequently occurring tube at 1.14 nm. Peak frequencies together with their relative diameter sizes are given in Table 5.4. The G band of Hipco sample also was probed by two (2.41 and 2 eV) laser energies which is shown in Fig 5.10.

*Sample purchased from Carbon Nanotechnology Incorporated

*Measurements made at CNR Florence
It is clear that on going from incident beam energy 2 eV to 2.41 eV the weak
peak changes to a shoulder in the left of the profile. Fitting of these TM spectra by
Lorentzian lines are shown in Fig 5.11. The frequencies of the peaks used for these
fitting are shown in Table 5.5.

RBM and TM modes of Hipco with the same laser lines were investigated in
(102,103). These data are from SWNTs prepared by high pressure CO decomposition
over Fe catalyst by Carbon Nanotechnology Inc. and purified by HCl and thermal
treatment. Fitting of the RBM bands with Lorentzian functions shows five intense
bands at frequencies of 272, 265, 249, 209, 186 cm\(^{-1}\) for 2.41 eV energy and four
sharp bands at frequencies of 286, 259, 222.5 and 200 cm\(^{-1}\) for the 2 eV laser energy.

From the equation \(\omega_{RBM} = \frac{232}{d} + 6.5\) and with these frequencies it is found that the
Hipco SWNTs have diameters in the range of 0.8-1.3 nm. For comparison, the
position of the breathing Raman modes of samples (CVD sample, Hipco and Hipco
raw) are given in Table 5.6. From this table it is clear that the tube diameter
distribution is wider for the Hipco nanotube sample than for the SWNT sample at
these two lasers energies (2.41, 2 eV). It also shows that the bands for the SWNT
sample are shifted to lower frequencies (higher tube diameter) with respect to Hipco
on going from Laser excitation energy 2.41 eV to 2 eV. This table also shows that the
Hipco frequencies are the same as in Ref (102).

The diameters of the nanotubes in different samples for two laser energies (2.41 and 2
eV) are listed in Table 5.7, together with the diameters of the Hipco sample from
(102). It is clear that the diameters of nanotubes in our SWNT sample are higher than
for the Hipco SWNT material. The positions of the TM Raman modes for the two
samples (CVD sample and Hipco) are given in Table 5.8.
Table 5.4: Frequencies (in cm$^{-1}$) of RBM bands of Hipco SWNT together with corresponding diameters.

<table>
<thead>
<tr>
<th>Laser excitation</th>
<th>2.41 eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v$ (cm$^{-1}$)</td>
<td>$d$ (nm)</td>
</tr>
<tr>
<td></td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>214</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>195</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>184</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>176</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>169</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Table 5.5: Frequencies (in cm$^{-1}$) of the lorentzian curves used to fit the bands associated with the tangential mode (TM) of Hipco nanotube, obtained with two laser excitation line.

<table>
<thead>
<tr>
<th>Laser excitation</th>
<th>2.41 eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1</td>
<td>1583</td>
<td>1591</td>
</tr>
<tr>
<td>Line 2</td>
<td>1558</td>
<td></td>
</tr>
<tr>
<td>Line 3</td>
<td></td>
<td>1553</td>
</tr>
<tr>
<td>Line 4</td>
<td></td>
<td>1540</td>
</tr>
<tr>
<td>Line 5</td>
<td>1534</td>
<td></td>
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<tr>
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<td>1519</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Line 8</td>
<td>1509</td>
<td></td>
</tr>
</tbody>
</table>

93
Table 5.6: Frequencies (in cm$^{-1}$) of RBM bands of nanotube samples accompanied by frequency of Hipco from Ref (101).

<table>
<thead>
<tr>
<th>Laser excitation</th>
<th>2.41eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample CVD</td>
<td>Hipco (raw)</td>
</tr>
<tr>
<td>268</td>
<td>272</td>
<td>270</td>
</tr>
<tr>
<td>245</td>
<td>265</td>
<td>254</td>
</tr>
<tr>
<td>227</td>
<td>249</td>
<td>235</td>
</tr>
<tr>
<td>219</td>
<td>209</td>
<td>214</td>
</tr>
<tr>
<td>215</td>
<td>186</td>
<td>195</td>
</tr>
<tr>
<td>203</td>
<td>...</td>
<td>184</td>
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<tr>
<td>186</td>
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<td>176</td>
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<tr>
<td>182</td>
<td>...</td>
<td>169</td>
</tr>
<tr>
<td>178</td>
<td>...</td>
<td>166</td>
</tr>
</tbody>
</table>

Table 5.7: Diameter distributions (in nm) of nanotube samples at two different laser energies (2.41 eV, 2 eV).

<table>
<thead>
<tr>
<th>CVD Sample</th>
<th>Hipco (raw)</th>
<th>Hipco</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (nm)</td>
<td>d (nm)</td>
<td>d (nm)</td>
</tr>
<tr>
<td>0.9</td>
<td>0.83</td>
<td>0.82</td>
</tr>
<tr>
<td>0.93</td>
<td>0.87</td>
<td>0.86</td>
</tr>
<tr>
<td>0.97</td>
<td>0.89</td>
<td>0.9</td>
</tr>
<tr>
<td>1.05</td>
<td>0.91</td>
<td>0.95</td>
</tr>
<tr>
<td>1.08</td>
<td>0.95</td>
<td>1.04</td>
</tr>
<tr>
<td>1.09</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>1.1</td>
<td>1.14</td>
<td>1.13</td>
</tr>
<tr>
<td>1.13</td>
<td>1.19</td>
<td>1.14</td>
</tr>
<tr>
<td>1.18</td>
<td>1.29</td>
<td>1.26</td>
</tr>
<tr>
<td>1.21</td>
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<td>1.27</td>
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<tr>
<td>1.24</td>
<td></td>
<td>1.32</td>
</tr>
<tr>
<td>1.31</td>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td>1.35</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>1.45</td>
<td></td>
<td>1.47</td>
</tr>
</tbody>
</table>
Table 5.8: Frequencies (in cm$^{-1}$) of TM mode of nanotube samples obtained with two laser lines accompanied by TM bands of Hipco in Ref (101).

<table>
<thead>
<tr>
<th>Laser excitation</th>
<th>2.41 eV</th>
<th>2 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample</td>
<td>Hipco</td>
</tr>
<tr>
<td></td>
<td>CVD</td>
<td></td>
</tr>
<tr>
<td>1616</td>
<td>1583</td>
<td>1612</td>
</tr>
<tr>
<td>1598</td>
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<td>1594</td>
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<tr>
<td>1569</td>
<td>1534</td>
<td>1584</td>
</tr>
<tr>
<td>1538</td>
<td>1509</td>
<td>1566</td>
</tr>
<tr>
<td>......</td>
<td>......</td>
<td>1537</td>
</tr>
</tbody>
</table>
Fig 5.8 Raman spectra of the Radial Breathing mode (RBM) of Hipco nanotube
With two laser lines (a) 2.41eV and (b) 2eV
Fig 5.9 Diameter distribution (nm) of Hipco nanotube with two laser lines (a) 514.5 nm and (b) 632.8 nm. The range of diameters is between 0.82-1.47 nm.
Fig 5.10 Raman spectra of the tangential mode (TM) of Hipco nanotube with two laser line (a) 2.41 eV and (b) 2 eV
Fig 5.11 Fitting of the (TM) mode of Hipco nanotube with two laser line (a) 2.41 eV and (b) 2 eV
Chapter 6. Gravimetric measurements of gas adsorption

6.1 Nitrogen adsorption measurements

The material produced in all the CVD runs was amalgamated into two samples with different Fe content (Sample 1: 1.5% Fe by weight; Sample 2: 2% Fe by weight). Microgravimetric measurements of nitrogen and hydrogen adsorption were then applied to these two samples to evaluate the specific surface areas (BET) and H₂ storage capacities of the samples. These measurements were performed on 148mg of Sample 1 and 162mg of Sample 2. Prior to the adsorption measurements, both samples were degassed in the IGA chamber for a period of 16 hours in a vacuum < 10⁻⁶ Torr and at a different temperatures up to 450°C. It has previously been shown that this careful outgassing process is essential to measuring the full surface area. Following the adsorption measurement, a desorption measurement was made to ensure that the mass returned to the degassed value, indicating that the sample had not adsorbed impurity gases from the apparatus.

Nitrogen adsorption and desorption isotherms and BET plots of sample 1 at 77K and different degas temperatures are shown in Fig 6.1–6.4. These figures show the quantity of nitrogen taken up by 1g of sample. It is found that by increasing the degassing temperature the surface area of the sample increased but not by very much. Therefore measurement of nitrogen adsorption and desorption of sample 2 were only performed at 77K and 450°C degassing temperature. These isotherms and the BET plot are shown in Fig 6.5 It is clear that nitrogen isotherms show a type II isotherm for both samples. The resulting surface area for Sample 1 (350 m²/g) is higher than for Sample 2 (227 m²/g).
This difference could result from the different concentrations of iron in the two samples. Larger concentrations of Fe might be expected to produce fewer nanotubes if the Fe particles are so close that the resulting nanotube ropes would interfere with each other. Analysis of the hysteresis loop in the N\textsubscript{2} isotherms should allow us to derive information about the diameter of pores in the sample [73]. This shows that the mean pore diameters lie in the range from 3nm to 8nm in each sample. The lower values could be attributed to some large open-ended nanotubes or to defect structures in the bundles, whereas the larger pore diameters might be due to bundles interlacing with each other.

Nitrogen adsorption and desorption measurements were also performed on Hipco single-walled nanotube purchased from Carbon Nanotechnology Incorporated. The measurement was performed on 25 mg of Hipco sample. Before the adsorption measurement, the sample was degassed in IGA for a period of 16 hours in a vacuum < 10\textsuperscript{-6} torr and at 450\textdegree C temperature. The isotherm and BET plot is shown in Fig.6.6 as the figure shows the isotherm is a type II isotherm and the resulting surface area is 646 m\textsuperscript{2}/g. It is also shown that there is no porosity in this sample.
Fig 6.1 Nitrogen adsorption at 77K on CVD carbon containing 1.5 wt % Fe (sample 1) degassed at room temperature (a) sorption isotherms and (b) BET plot
Fig 6.2 Nitrogen adsorption at 77K on CVD carbon containing 1.5 wt % Fe (sample 1) degassed at 155°C.
Fig 6.3 Nitrogen adsorption at 77 K on CVD carbon containing 1.5 wt % Fe (sample 1) degassed at 250°C temperature.
Fig 6.4 Nitrogen adsorption AT 77k on CVD carbon containing 1.5 wt % Fe (sample 1) degassed at 450°C.
Fig 6.5 Nitrogen adsorption at 77K on CVD carbon containing 2 wt % Fe (sample 2) degassed at 450°C. (a) sorption isotherm and (b) BET plot.
Fig 6.6 Nitrogen adsorption at 77K in Hipco single-walled nanotube, degassed at 450°C. (a) sorption isotherms and (b) BET plot.
6.2 Hydrogen adsorption measurements

Hydrogen gas adsorption isotherms measured at 77K for the same samples are shown in Fig 6.7. It is clear that the hydrogen adsorption of both samples show type I isotherms. Because there is a direct relationship between the hydrogen storage capacity and the specific surface area, Sample 1 with the higher BET surface area takes up more hydrogen per gram [74]. The hydrogen adsorption shown in Fig 6.8 has been normalized to the surface area, measured from the nitrogen adsorption isotherm using the BET method [75]. Figure 6.8 shows the fractional surface coverage of hydrogen in mg per unit area, and demonstrates that the adsorption at low pressure is similar for both samples but that sample 1 shows an increasing adsorption/unit area at high pressures. Fig 6.10 shows the hydrogen adsorption of samples as a function of the chemical potential. As can be seen, higher adsorbate density is observed for Sample 2 at low chemical potentials. The reason for the enhanced hydrogen uptake at low chemical potential in sample 2, could be due to the presence of sites on its surface with higher heat of adsorption than sample 1.

Hydrogen adsorption at 77K as a function of pressure and chemical potential is plotted in Fig.6.11 and 6.12 for sample 1 and 2 respectively. Data in 6.11b and 6.12b is fitted with an isotherm in a Fermi-Dirac form.

\[
\theta = \frac{1}{\exp^{\frac{\mu}{kT}} + 1}
\] 6.1
Here \( \theta \) is the fractional coverage, \( \varepsilon \) is the adsorption energy of site and \( \mu \) is the chemical potential. The best fit was obtained for a site energy 51.7 meV and 57.0 meV for sample 1 and 2 and temperature 100 K. This higher temperature could be due to experimental error since in the IGA the sample is not in contact with the temperature sensor. A better fit is obtained if different sites are allowed at 80K. Fig 6.11c and 6.12c show fitting of data using Langmuir isotherm with two different sites of energy.

\[
\theta = a_1 \frac{1}{\exp \frac{\varepsilon_1 - \mu}{kT} + 1} + a_2 \frac{1}{\exp \frac{\varepsilon_2 - \mu}{kT} + 1}
\]

6.2

\( a_1 \) and \( a_2 \) are the fractions of the available sites with \( \varepsilon_1 \) and \( \varepsilon_2 \) adsorption energy respectively. The energy of sites for sample 1 are given -39.1 meV with concentration of 60% and -53.3 meV with concentration of 40% and for sample two are -47.7 meV with 70% concentration and -60.8 meV with 30% concentration. It is found that the site energies for Sample 2 is higher than for Sample 1.

The isotherms of hydrogen adsorption on Hipco sample are shown in Fig 6.13. these measurements were performed on 60 mg of sample with surface area 646 m²/g. Fig.6.14 shows hydrogen storage capacity of Hipco sample. As can be seen there is a hysteresis loop between adsorption and desorption. Plot of fractional coverage of Hipco sample against chemical potential is shown in Fig 6.14b. The data is fitted with a Langmuir Isotherm with two sites of energy and 77K temperature. The energy of the sites are given as -43.35 meV and -72.6 meV. Fig.6.15 shows the comparison between hydrogen adsorption of samples. As can be seen from Fig.6.15a because the surface area of Hipco...
nanotube is higher the uptake of hydrogen is also higher. The storage capacity wt % of samples at 10 bar pressure are given as 1.12, 0.5 and 0.25 for Hipco, sample 1 and sample 2 respectively.

Surface areas, storage capacities and the parameters obtained from the Fermi-Dirac fits of the samples are summarized in Table 6.1.

Table 6.1 : BET Surface Areas and Hydrogen Adsorption (weight/unit area) for the nanotube samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area, m²/g at 77 K</th>
<th>Storage capacity wt% at 10 bar</th>
<th>Isosteric heat of adsorption meV/H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CarboLex SE</td>
<td>374</td>
<td>1.05</td>
<td>-74.5, -32.1</td>
</tr>
<tr>
<td>Sample 1</td>
<td>350</td>
<td>0.5</td>
<td>-39.1, -53.3</td>
</tr>
<tr>
<td>Sample 2</td>
<td>227</td>
<td>0.25</td>
<td>-47.7, -60.8</td>
</tr>
<tr>
<td>Hipco nanotube</td>
<td>646</td>
<td>1.12</td>
<td>-43.3, -72.6</td>
</tr>
</tbody>
</table>
Fig 6.7 Hydrogen adsorption in samples at 77 K (a) sample 1, (b) sample2 and (c) sample 1&2
Fig 6.8 Hydrogen storage densities as a function of pressure (a) sample 1 (b) sample 2 and (c) sample 1 & 2
Fig 6.9 Comparison of hydrogen storage densities of samples 1&2 with Carbolex and Darco materials. Data of taken from P.A Georgiev Ph.D. Thesis, University of Salford 2003.
Fig 6.10 Hydrogen storage densities as a chemical potential (a) sample 1, (b) sample 2 and (c) sample 1&2
Fig 6.11 (a) Hydrogen adsorption on a sample 1 at 77K, (b) adsorption is fitted by single Fermi-Dirac distribution at 100K and (c) fitted by double Fermi-Dirac distribution at 77K.
Fig 6.12 Hydrogen adsorption on a sample 2 at 77K, (b) adsorption is fitted by single Fermi-Dirac distribution at 100K and (c) fitted by double Fermi-Dirac distribution at 77K.
Fig 6.13 (a) Hydrogen adsorption in Hipco nanotube at 77K, (b) hydrogen storage density as a function of pressure and (c) as a function of chemical potential.
Fig 6.14 (a) Hydrogen adsorption/desorption on Hipco sample at 77K and (b) fitting of hydrogen adsorption with double Fermi-Dirac distribution at 77K.

### H$_2$ ads on Hipco

- $E_1 = -49.9693 \pm 0.75309$
- $a_1 = 0.8618 \pm 0.02244$
- $E_2 = -79.2156 \pm 3.17437$
- $a_2 = 0.2267 \pm 0.0274$
- $\chi^2 = 0.0004$
Fig 6.15 (a) Hydrogen adsorption at 77K on sample 1, 2 and Hipco single-walled nanotube. As the surface area of Hipco is higher than the other two samples, the hydrogen uptake is also higher. (b) Hydrogen capacity of three sample against chemical potential.
Conclusions

A large number of Single-walled carbon nanotube (SWNT) bundles were observed by SEM and TEM in carbon samples prepared using a CVD technique. SEM images show the presence of SWNT bundles with diameters between 10 and 70 nm. Images also show many dark dots and shaded zones, which are due to metal particles encapsulated within the nanorubes and to amorphous carbon, respectively. The TEM images show that the size of bundles is between 5.3 and 16 nm and the lengths are up to tens of micrometers. The average diameter of SWNTs within these bundles are estimated to be about 1.05 nm. The difference between bundle size in the SEM and TEM images may be related to the sonication process used for samples prepared for the TEM. Besides the bundles of SWNTs, the individual SWNTs with average diameters of 1.5 nm are observed. The TEM image also shows that the average size of the carboneous deposits is about 7 nm.

Nitrogen adsorption and desorption were performed on samples at 77K, after different degas temperatures. It was found that by increasing the degas temperature the surface area of sample slightly increased. The resulting surface area for sample 1 (1.5%) is 350 m²/g and for sample 2 (2%) 227 m²/g. This difference could result from the different concentrations of iron in the two samples: larger concentrations of Fe might be expected to produce fewer nanotubes due to interference of nanotube ropes with each other. Also it is shown that the mean pore diameters in each sample are in the range of 3nm to 8nm where the lower size could be related to some large open-ended large nanotubes or to defect structures and the larger diameters might be due to bundles interlacing with each other. Nitrogen adsorption and desorption measurements were also performed on Hipco (SWNT) samples from Carbon
Nanotechnology Incorporated, under the same conditions. The measured N2 isotherm is a type II isotherm as for the other samples and the resulting surface area is 646 m$^2$/g.

Hydrogen gas adsorption isotherms measured at 77K for the same samples show type I isotherms. It is shown that the sample 1 with the higher BET surface area takes up more hydrogen per gram. Higher adsorbate density is observed for sample 2 at low chemical potentials. The reason could be presence of sites on its surface with higher heat of adsorption than sample 1. Fitting the data of hydrogen adsorption as a function of chemical potential by using Langmuir isotherm in a Fermi-Dirac form with two different energy sites, shows that the site energies for sample 2 are indeed higher than for sample 1. Hydrogen adsorption isotherms have also been measured on a Hipco sample and it is seen that there is a hysteresis loop between adsorption and desorption. Because the surface area of Hipco is higher than the two other samples the uptake of hydrogen for this sample is also higher. The storage capacity of samples at 10 bar pressure was 1.12, 0.5 and 0.25 wt % for Hipco, sample 1 and sample 2, respectively. Because the sample contains carbon nanotubes with a large diameter distribution the shape of the RBM bands are quiet different from one line to another. Therefore we used three different laser lines (2.55, 2.41 and 2eV) were used to cover all nanotubes diameter. Measurement with 2.55eV incident energy shows that the range of diameter distribution is between 1.1 to 1.35nm. Therefore, only semiconducting tubes of such diameters can be resonantly excited. This is in agreement with the profile of the spectrum in the TM mode, which shows a lorentzian lineshape. The spectrum measured at 2.41eV shows the peaks are shifted to lower frequencies and the range of diameters here is from 1.15 to 1.39nm. The excited tubes are semiconducting. Measurement with 2eV incident energy shows that the size of tubes is between 1.11 to
1.5nm. Therefore, both metallic and semiconducting tubes can be resonantly excited at this excitation energy. It is found that for higher wavelength laser lines, the peaks shift to lower frequencies. From observation of Raman spectra we can conclude for several reasons that the concentration of armchair tubes in sample must be very low. Raman spectra of Hipco SWNT were measured in RBM and TM modes using two different laser lines (2.41 and 2eV). Measurement with 2.41ev incident energy shows that the diameter distribution is 0.9 to 1.47nm. For 2ev incident energy, the peaks are shifted to higher frequencies and the range of diameters are from 0.82 to 1.32nm. The different behaviour exhibited by Hipco and CVD samples maybe related to the electronic nature of the nanotubes in the two samples.
Future work

From results of research to date, it is possible to identify future research that would contribute significantly to our understanding of the subject. These possible activities are described below:

1. In addition to the acid treatment that has been used for removing the support catalyst it would be interesting to use controlled oxidation for removing the carboneous materials.

2. It is of interest to use other materials as a catalyst and catalyst support materials to produce carbon nanotubes to establish how the production of nanotubes depend on the nature of these materials.

3. As mentioned above hydrogen adsorption in carbon nanotubes depends on forming optimal micropore sizes, high surface area and attractive surface potential. Further work in this area might involve improving the interaction potential between nanotubes and hydrogen molecules. For example, finding a material to decorate the nanotubes which will improve hydrogen uptake.
Appendices

A. Phonon modes of carbon nanotube

Phonons denote the quantized vibrations that affect many processes in condensed matter including thermal, transport and mechanical properties. The two dimensional graphite has two atoms per unit cell, so have a six phonon branches (104) as shown in Fig A1.

Fig.A1 Phonon dispersion curves for a two dimensional graphite.

The three phonon dispersion branches which originate from Γ point of the Brillouin zone relate to acoustic modes. Out of plane transverse acoustic (oTA), in plane transverse acoustic (iTA) and longitudinal acoustic (LA). The remaining three branches relates to optical modes. One out of plane mode, and two in plane modes.

Before any relaxation of lattice one, two, …phonon can be emitted which respectively is called one phonon, two phonon and multi phonon Raman processes. In two dimensional graphite the G band is the first order Raman peak ( Raman spectra
involving one phonon emission). In SWNTs the G band spectra and the Radial breathing mode both are first order Raman modes.

The phonon dispersion relations for a single walled carbon nanotube are determined by folding the phonon dispersion relations of a two dimensional graphite into the first brillouin zone of carbon nanotubes. Since there are 2N carbon atoms in the unit cell of a carbon nanotube, 6N phonon dispersion relations are folded into the one dimensional Brillouin zone of a carbon nanotube along the $K_2$ direction. Phonon dispersion relations of a nanotube also depend on the chirality and diameter of the nanotube. Energy dispersion relation of one dimensional phonon for the nanotube is given by

$$\omega_{1D}^{m\mu}(k) = \omega_{2D}^m(k \frac{K_2}{|K_2|} + \mu K_1)$$

Where $\omega_{2D}^m(k)$ belongs to the two dimensional dispersion relations of graphene sheet.

Electron and phonon eigenfunctions of a SWNT are characterized by their one dimensional wave vectors and also by their symmetries. Symmetries, which show by index $\mu$, are related to the number of nodes for their wave functions in the $k_1$ direction. $\mu = 0$ is related to the, $A$, totally symmetric with no nodes and $\mu = 1,2$ belongs to symmetries with 2,4 nodes respectively (105). In SWNT only $A$, $E_1$ and $E_2$ symmetry modes, which corresponds to phonon wave functions with $\mu = 0,1,2$, are Raman active in a first order process.

The G band in graphite involves an optical phonon mode. The G band frequency can be used for diameter characterization to distinguish between metallic and semiconducting SWNT and to probe the charge transfer (106).
The G band for SWNTs consists of two main components, G\(^+\) at 1590 cm\(^{-1}\) and G\(^-\) at about 1570 cm\(^{-1}\). The G\(^+\) band is associated with LO phonon mode and its frequency is sensitive to charge transfer and independent of diameter or chiral angle (107). The G\(^-\) band is associated with TO phonon mode and its frequency is dependent on diameter and whether the SWNT is metallic or semiconducting (108) Fig A2.

![Graph showing the frequency against 1/dt for the two G band features from isolated SWNTs.](image)

**Fig A2 Frequency against 1/dt for the two G band features from isolated SWNTs**
B. Processes during collisions

The processes, which can be occurred during the collision of a gas molecule with a surface, are:

Elastic collision there is no change in gas or surface from elastic collision observed

Inelastic collisions and trapping in this process the energy transfer from the gas to the surface. Loss of energy by gas may leave it with enough energy to escape from the surface but if more than some critical energy is lost the molecule will be trapped. Therefore the molecule is envisaged as occupying an excited physisorbed state.

Because attach of molecule to the surface is weak so a variety of surface processes is possible.

1. Loss of further energy to the surface at the same site
2. Migration over the surface with loss of energy at other sites.
3. Return to the gas phase by gaining additional energy from the solid
4. Transfer to the chemisorbed state, either at the initial site (1) or after migration (2)

When chemisorption has occurred further processes happen

5. Migration of the adsorbed molecule or surface reconstruction
6. Loss of vibrational energy of the new chemisorbed species to the lattice with resulting temperature rise
7. Migration of equilibrated chemisorbed species
8. Evaporation either directly from the chemisorbed state or via the physisorbed state. In general, return to the gas phase, involves recombination of the atoms of a diatomic molecule.

The above processes are shown in Fig B1. This figure shows that the activation energy for migration in physisorbed or chemisorbed states (\(E_{pm}\) or \(E_{cm}\)) is less than the
relevant heat of adsorption. Depending on where the curves for physisorption and chemisorption cross, \( E_a \) may be large enough for the reaction to be activated as shown by the broken line 4 in Fig or the reaction may be non activated as shown by the broken line 4 and barrier \( E_a \).

The effect of the migration is increase the chances of the chemisorb process by allowing more than one opportunity for chemisorption during lifetime of the molecule on the surface.

In order to make an estimate of the number of sites a molecule expect to visit during its lifetime in the physisorbed state, the movement of the molecule over the surface is described by the Einstein formula

\[
\bar{x}^2 = D \tau
\]

\( B.1 \)
Where $\bar{x}$ is the root mean square distance traversed, $D$ is the diffusion coefficient and $\tau$ is the lifetime on the surface. The diffusion coefficient can be written in a form

$$D = a^2 \nu_{pm} \exp\left(\frac{-E_{pm}}{RT}\right)$$ \hspace{1cm} B.2

$a$ is the distance between sites on the surface. Thus

$$\bar{x}^3 = \tau a^2 \nu_{pm} \exp\left(\frac{-E_{pm}}{RT}\right)$$ \hspace{1cm} B.3

Here the mean lifetime on the surface can be taken as the time for the first order desorption process so

$$\bar{x}^3 \approx a^2 \nu_{pm} \exp\left(\frac{\Delta H_{ad} - E_{pm}}{v_d RT}\right)$$ \hspace{1cm} B.4

The exponential factor relate to the vibrational motion in the physisorbed state. The two term has a similar order of magnitude so that

$$\bar{x} \sim a \exp\left(\frac{\Delta H_{ad} - E_{pm}}{2RT}\right)$$ \hspace{1cm} B.5

For sites of separation $a$ the average number visited, $m$ is

$$m = \frac{\bar{x}}{a}$$ \hspace{1cm} B.6

It is now possible to make an estimate of the value of $m$. 

C. Dependent of gas adsorption on the number of shells

The maximum specific surface area of graphite with density $\rho = 2267 \text{ Kg} / \text{ m}^3$ and assuming that all atoms are in one single plane is $S_1 = 1315 \text{ m}^2/\text{g}$ or if both sides of the plane are considered $S_2 = 2630 \text{ m}^2/\text{g}$. For nanotubes, the specific surface area depends on the number of shells. Table C1 shows the specific surface area, outer and total, of the nanotubes as a function of the number of shells.

Table C1 Properties of nanotubes as a function of the number of shells: total number of atoms $N_{\text{total}}$, the corresponding number of surface atoms $N_{\text{surf}}$, the surface atom in %, the outer $S_1$ and the total $S_2$ specific surface area.

<table>
<thead>
<tr>
<th>Number of shells</th>
<th>$N_{\text{tot}}$</th>
<th>$N_{\text{surf}}$</th>
<th>Surf (%)</th>
<th>$S_1$ (m²/g)</th>
<th>$S_2$ (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>20</td>
<td>100.0</td>
<td>1315</td>
<td>2630</td>
</tr>
<tr>
<td>2</td>
<td>59</td>
<td>40</td>
<td>66.7</td>
<td>877</td>
<td>1315</td>
</tr>
<tr>
<td>3</td>
<td>119</td>
<td>59</td>
<td>50.0</td>
<td>658</td>
<td>877</td>
</tr>
<tr>
<td>4</td>
<td>198</td>
<td>79</td>
<td>40.0</td>
<td>526</td>
<td>658</td>
</tr>
<tr>
<td>5</td>
<td>297</td>
<td>99</td>
<td>33.3</td>
<td>438</td>
<td>526</td>
</tr>
<tr>
<td>6</td>
<td>415</td>
<td>119</td>
<td>28.6</td>
<td>376</td>
<td>438</td>
</tr>
<tr>
<td>7</td>
<td>554</td>
<td>138</td>
<td>25.0</td>
<td>329</td>
<td>376</td>
</tr>
<tr>
<td>8</td>
<td>712</td>
<td>158</td>
<td>22.2</td>
<td>292</td>
<td>329</td>
</tr>
<tr>
<td>9</td>
<td>890</td>
<td>178</td>
<td>20.0</td>
<td>263</td>
<td>292</td>
</tr>
<tr>
<td>10</td>
<td>1088</td>
<td>198</td>
<td>18.2</td>
<td>239</td>
<td>263</td>
</tr>
</tbody>
</table>

Two type of gas adsorbing on carbon materials are nitrogen, which used for determination of the surface area of the samples and hydrogen gas. Once a monolayer of adsorbate molecules is formed on the surface of the sample, the molecules of gas
interact with a surface of the liquid or solid adsorbate. Therefore the binding energy of the second layer of adsorbate molecules is similar to the latent heat of sublimation or vaporisation of the adsorbate.

The properties of hydrogen and nitrogen such as: $M$ the molecular mass, $\rho$ the density of the liquid at the boiling point, $V_m$ the volume of the molecule, $d$ the diameter of the molecule and $S_m$ the surface area occupied by the molecule are summarized in Table C2.

### Table C2 Properties of hydrogen and nitrogen as adsorbate

<table>
<thead>
<tr>
<th>Property</th>
<th>$N_2$</th>
<th>$H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$ (g/mole)</td>
<td>28.0140</td>
<td>2.0159</td>
</tr>
<tr>
<td>$P$ (g/cm$^3$)</td>
<td>0.8070</td>
<td>0.0708</td>
</tr>
<tr>
<td>$V_m$ (nm$^3$)</td>
<td>0.0427</td>
<td>0.0350</td>
</tr>
<tr>
<td>$d$ (nm)</td>
<td>0.4336</td>
<td>0.4059</td>
</tr>
<tr>
<td>$S_m$ (nm$^2$)</td>
<td>0.1477</td>
<td>0.1294</td>
</tr>
</tbody>
</table>

The amount of hydrogen absorbed at the surface and in the cavity of the carbon nanotubes is calculated by Zuttel et al (109) Fig C1. as can be seen the SWNT has the highest surface absorption. And also it is clear that the bulk absorption in the cavity is proportional to the diameter of the tubes and is highest for SWNT. It is clear that the adsorbed hydrogen in the cavity of a tube increases with the tube diameter. This is based on the assumption that hydrogen would condense inside the nanotube. Because the critical temperature for nitrogen is 126.2K, nitrogen may condense in pores when the surface area is measured at 78K.
Fig. C1 calculated amount of adsorbed hydrogen on carbon nanotubes. (a) monolayer adsorbed at the surface of nanotubes as a function of the number of shells (markers and line), (b) hydrogen condensed in the cavity of nanotubes as a function of diameter (dash lines).

Fig C2 (a,b) shows the adsorption of nitrogen at 78K on SWNT and MWNT respectively. As shown the isotherm of SWNT can be divided to three parts. In the first part (low pressure), the pores with small size filled. The Second part is related to adsorption on the surface and the third part (high pressure) which shows a hysteresis loop is assigned to the capillary condensation.

For MWNT, the isotherm can be divided in to four parts. The first and second parts are the same as SWNT. A hysteresis loop, seen in parts III and IV, is related to capillary condensation. In part IV (high pressure range), the amount of adsorbed nitrogen sharply increases this resulting from enhanced capillary condensation in larger pores which is probably contributed by aggregated pores.
Fig. C2 Nitrogen adsorption isotherm of (a) SWNT (b) MWNT at low temperature

Recently reported experimental and calculated hydrogen storage capacities of CNT are summarized in Tables C3 and C4 respectively, accompanied by temperature, pressure and technique of synthesising.(110).
### Table C3 summary of experimental results for hydrogen storage

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis technique</th>
<th>Diameter nm</th>
<th>purity</th>
<th>Surface area m²/g</th>
<th>Pressure and temperature</th>
<th>wt%</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>Hipco</td>
<td>-</td>
<td>purified</td>
<td></td>
<td>8MPa, RT</td>
<td>0.43</td>
<td>(111)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>20-30</td>
<td>purified</td>
<td>33.7</td>
<td>100bar, 298K</td>
<td>3.3</td>
<td>(112)</td>
</tr>
<tr>
<td>SWNT</td>
<td>Hipco</td>
<td></td>
<td>unpurified</td>
<td>-</td>
<td>48bar, RT</td>
<td>1.2</td>
<td>(113)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td></td>
<td></td>
<td></td>
<td>145bar, 300K</td>
<td>3.7</td>
<td>(114)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>10-60</td>
<td></td>
<td></td>
<td>10MPa, RT</td>
<td>3.98</td>
<td>(115)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>53</td>
<td></td>
<td>25</td>
<td>13.59MPa, RT</td>
<td>4.6</td>
<td>(116)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>30</td>
<td></td>
<td>137</td>
<td>10MPa, 77K</td>
<td>0.45</td>
<td>(117)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>40</td>
<td></td>
<td>840</td>
<td>10MPa, 77K</td>
<td>6.46</td>
<td>(118)</td>
</tr>
<tr>
<td>SWNT</td>
<td>Arc discharge</td>
<td>1.2-1.5</td>
<td></td>
<td>1433</td>
<td>1bar, RT</td>
<td>0.02</td>
<td>(119)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1bar, 77K</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>SWNT</td>
<td>laser ablation</td>
<td>1.4</td>
<td>purified</td>
<td></td>
<td>9MPa, RT</td>
<td>0.3</td>
<td>(120)</td>
</tr>
<tr>
<td>SWNT</td>
<td>Hipco</td>
<td></td>
<td>purified</td>
<td>797</td>
<td>1bar, 295K</td>
<td>0.2</td>
<td>(121)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1bar, 77K</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>SWNT</td>
<td>Arc discharge</td>
<td>1.2-1.5</td>
<td>unpurified</td>
<td>728</td>
<td>300Torr, 77K</td>
<td>3.0</td>
<td>(122)</td>
</tr>
<tr>
<td>SWNT</td>
<td>Hipco</td>
<td></td>
<td>purified</td>
<td>710</td>
<td>3.5MPa, 303K</td>
<td>0.25</td>
<td>(123)</td>
</tr>
<tr>
<td>SWNT</td>
<td>Hipco</td>
<td></td>
<td>90wt%</td>
<td>800</td>
<td>300atm, 294K</td>
<td>0.91</td>
<td>(124)</td>
</tr>
<tr>
<td>SWNT</td>
<td>Arc discharge</td>
<td>1.2</td>
<td>75wt%</td>
<td></td>
<td>25bar, 77K</td>
<td>2.4</td>
<td>(125)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>25-30</td>
<td>purified</td>
<td></td>
<td>9MPa, RT</td>
<td>0.69</td>
<td>(126)</td>
</tr>
<tr>
<td>MWNT</td>
<td>CVD</td>
<td>60-100</td>
<td></td>
<td></td>
<td>10MPa, RT</td>
<td>5.0</td>
<td>(127)</td>
</tr>
</tbody>
</table>

### Table C4 summary of theoretical results for hydrogen storage

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter nm</th>
<th>Intertube distance nm</th>
<th>Method</th>
<th>Temperature and pressure</th>
<th>wt%</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>-</td>
<td>-</td>
<td>GCMC</td>
<td>293K, 10MPa</td>
<td>0.6</td>
<td>(128)</td>
</tr>
<tr>
<td>SWNT</td>
<td>2.719</td>
<td>Isolated</td>
<td>Classical potential and DFT</td>
<td>77K, 4Mpa</td>
<td>9.5</td>
<td>(129)</td>
</tr>
<tr>
<td>SWNT</td>
<td>2.719</td>
<td>Isolated</td>
<td>Classical potential and DFT</td>
<td>300K, 20Mpa</td>
<td>1.0</td>
<td>(129)</td>
</tr>
<tr>
<td>SWNT</td>
<td>1.17</td>
<td>0.7</td>
<td>Tight-binding</td>
<td>MD and GCMC</td>
<td>293K, 10Mpa</td>
<td>3.4</td>
</tr>
</tbody>
</table>
References

(5) Nijkamp M. G  2002;Hydrogen storage using physisorption Tekst Proefschrift Universiteit Utrecht
(9) Carpetis C  Int. J. Hydrogen 1980;5:539
(17) Reynolds W. N 1968 Physical properties of graphite
(18) Pierson H. O 1993 Handbook of carbon, Graphite, Diamond and Fullerenes-properties, processing and applications
(19) Dresselhaus M. S  Physics Reports 2004
(21) https://.../bugayon/structure.htm
(22) Bhabendra K  Physica B 2002;323:115-121
(26) Popov V. N  Material science and Engineering 2004;R43:61-102
(34) Thess A. Science 1996;273:483
(35) Ivanov V. Carbon 1995;33:1727-1738
(37) Mauron Ph. Carbon 2002;40:1339-1344
(41) The electrochemical society Inc. proceedings volume 97-14, 884-906
(44) J. chem. Soc., chem. commun 1343-1344
(48) Thess A. Science 1996;273:483
(51) Maiti A. Phy, rev, b 1997;55:R6097
(53) Kataura H. Carbon 2000;38:1691
(54) Kokai F. J. Phys. Chem. b 1999;103:4346
(56) Kanzow H. Phys. Rev. b 1999;60:11180
(57) J. appl. phys. 33,526,1994;carbon. 33,979,1995
(58) Trans. A IME 1965;233:1053
(63) wells, oliver c. scanning electron microscopy; p.R. Thornton, scanning electron microscopy
(64) Colomer J. F  Chem. Phys. Lett 2001;345: 11-17
(65) Lowel S. 2004; Characterisation of porous solids and powders: surface area, pore size and density, Springer
(67) Lowel S  Characterization of porous solids and powders: surface area, pore size and Density 2004; springer
(69) De.Boer J.H 1958; The structure and properties of porous materials, Butterworths London
(70) Anderson J. R 1975; Structure of Metallic Catalyst, Academic press
(71) Gregg S. J 1982; Adsorption, Surface area and Porosity
(72) Characterization of porous solids and powders: Surface area, pore size and density 2004
(77) Dillon A. C  Nature 1997;386:377-379
(81) Rzepka M  Journal of physical chemistry B 1998;102:10894-10898
(82) Liu C  Science 1999;286:1127
(83) Chen P  Science 1999;285:91
(84) Anson A  Nano technology 2004;1503-1508
(87) Wang Q  Journal of physical chemistry B 1999;103:277
(88) Adsorption, surface area and porosity, Academic London 1982
(89) Hiden Analytical IGA systems user manual
(90) Raman Spectroscopy theory and practice Edited by Herman A. Szymanski 1967
(91) Introduction to Infrared and Raman Spectroscopy, N.B.Colthup, L.H.Daly.
S.E.Wiberley
(92) The Raman Effect, Derek A. Long
(94) Colomer J.F Chem. Phys. Letts 2001;345:11-17
(100) Rao A. M Science 1997;275:185
(102) Karachevtsev V.A Carbon 2003;41:1567-1574
(103) Gregan E Carbon 2004;42:1031-1035
(116) Hou P X Carbon 2003;41:2471
(120) Shiraishi M Chem. Phys. Lett 2002;358:213

138
(124) Lawrence J Appl. Phys. Lett 2004;84:918
(126) Liu F Carbon 2003;41:2527
(127) Zhang H Y J. Appl. Phys 2003;94:6417
(128) Guay P Carbon 2004;42:2187