Fabrication and Characterization of 0.42 nm-sized single-walled carbon nanotubes array in one-dimensional channels of AlPO₄-5 single crystal

by

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Authorization

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Abstract

The 0.42 nm-sized single-walled carbon nanotubes (SWNTs) are synthesized by pyrolysis of large quantities of tripropylamine (TPA) in the one-dimensional channels of zeolite single crystal (AlPO₄-5). These singular diameter SWNTs are mono-dispersed inside the channels of AFI. First of all, the effects of fabrication conditions on the formation of the SWNTs are studied by the Degree of Polarization of samples, so that an effective growth temperature of tubes is determined at 530-580°C. Besides, a fingerprint of SWNTs Raman peak is observed in the high frequency region at about 1600 cm⁻¹. In low frequency region, a diameter dependent of SWNT Raman peak, radial breathing mode, is also found at about 530 cm⁻¹, which indicates the diameter of these SWNTs is 0.42 nm. Furthermore, a direct evidence of existence of SWNTs is confirmed by High resolution Transmission Electron Microcopy (HRTEM) image. This HRTEM image shows that there are many SWNTs with 0.42 nm diameter inside the AFI channels after chemical etching. This HRTEM image result is consistent with the Raman scattering result. Finally, possible structure of these 0.42 nm-sized SWNTs is suggested to be a (5,0) zig-zag tube after considering three approaches: tubule energetic stability, capping properties of the tube and the period matching between AFI crystal and this tube. The production of mono-dispersed and single diameter-sized SWNTs in 3D array represents an essential role in the development and application of carbon nanotubes.
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CHAPTER 1

INTRODUCTION

1.1 Review of Studies on Carbon Nanotubes

1.1.1 Background history of carbon science research

The ability of carbon to bond with itself and with other atoms in endlessly varied combinations of chains and rings forms the basis for the sprawling scientific discipline, that is modern organic chemistry. Yet until recently we knew for certain of just two types of all-carbon crystalline structure, the naturally occurring allotropes diamond and graphite. Despite the best efforts of some of the world’s leading synthetic chemists, all attempts to prepare novel forms of molecular or polymeric carbon came to nothing: the elegant all-carbon structures proposed by Roald Hoffmann, Orville Chapman and others remained firmly in realm of pure speculation. Ultimately, the breakthrough, which revolutionized carbon science, came not from synthetic organic chemistry but from experiments on clusters formed by the laser-vaporization of graphite.

Harry Kroto and Richard Smalley had different reasons for being interested in the synthesis of carbon clusters. Kroto had been fascinated since the early 1960s in the processes occurring on the surfaces of stars, and believed that experiments on the
vaporization of graphite might provide key insights into these processes. Smalley, on the other hand, had been working for several years on the synthesis of clusters using laser-vaporization, concentrating chiefly on semiconductors such as silicon and gallium arsenide. But he was also interested in what might happen when one vaporizes carbon. In August 1985, the two scientists came together and, with a group of colleagues and students, began the now famous series of experiments on the vaporization of graphite. They were immediately struck by a surprising result. In the distribution of gas-phase carbon clusters, detected by mass spectrometry, \( C_{60} \) was by far the dominant species. This dominance became even more marked under conditions which maximized the amount of time the clusters were annealed in the helium. There was no immediately obvious explanation for this since there appeared to be nothing special about open structure containing 60 atoms. The eureka moment came when they realized that a closed cluster containing precisely 60 carbon atoms would have a structure of unique stability and symmetry. Although they had no direct evidence to support this structure, subsequent work had proved them correct. The discovery of \( C_{60} \), published in *Nature* in November 1985 [1], had an impact that extended way beyond the confines of academic chemical physics, and marked the beginning of new era in carbon science and stimulated a deluge of research [2-5].
Carbon nanotubes (CNs) are perhaps the most important fruits of this research. Discovered by the electron microscopist Sumio Iijima, of the NEC laboratories in Japan, in 1991 [6], these molecular carbon fibers consist of tiny cylinders of graphite, closed at each end with caps which contain precisely six pentagonal rings. We can illustrate their structure by considering the two archetypal CNs which can be formed by cutting a C_{60} molecule by half and placing a graphene cylinder between the two halves. Nanotubes described by Iijima in 1991 invariably contain at least two graphite layers, and generally have inner diameters of around 4 nm. In 1993, Iijima and Toshinari Ichihashi of NEC, and Donald Bethune and colleagues of the IBM Almaden Research Centre in California independently reported the synthesis of single-walled nanotubes (SWCNs). This proved to be an extremely important development, since the single-walled tubes appears to have structures which approximate to those of the ideal nanotubes. Moreover, the single-walled tubes are completely novel.

Nowadays, carbon nanotubes have captured the imagination of physicists, chemists and materials scientists alike. Physicists have been attracted to their extraordinary electronic properties, chemists to their potential as nanotest-tubes and material scientists to their amazing stiffness, strength and resilience. On more speculative level, nanotechnologists have discussed possible nanotubes-based gears
and bearings. Therefore, synthesis of carbon nanotubes in high yield, mono-dispersed and single dimension is an essential criterion to be discussed.

1.1.2 Shortcomings of the conventional synthesis method

The experimental discovery of single-walled carbon nanotubes in 1993 [7,8] further stimulated the researches in the field, though, at first, only small quantities of SWCNs were available experimentally for systematic studies. These SWCNs were generally found along with very much larger concentrations of amorphous carbon, carbon nanoparticles and other carbon based materials. The single-walled constituents contained a distribution of diameters and chiral angles. For these reasons most of the experimental studies continued to be done on multi-walled nanotubes.

The recent discovery in 1996 a much more efficient synthesis route, involving laser vaporization of graphite [9] to prepare arrays or ropes of ordered single-walled nanotubes, offered major new opportunities for quantitative experimental studies of carbon nanotubes. By making the SWCNs available to many research groups worldwide, progress was made for the first time in quantitative measurements of the physical properties of single-walled carbon nanotubes.

Soon after the publication of the laser vaporization method for the synthesis of
single-walled carbon nanotubes ropes, another synthesis route was found for the
synthesis of gram quantities of SWCNs, using the carbon arc method [10]. Because
of the potential interest of carbon nanotubes for practical applications, there is also
an interest in developing continuous synthesis methods, which are more appropriate
for the scale-up and low cost, and this may be accomplished by vapor growth
methods [11-13]. However, no matter how many improvements had been done,
previous problems still remain: there are many possible range of diameters up to 17
in laser vaporization method [14]; surrounding the nanotubes is a hard gray shell
consisting of nanoparticles, fullerenes and amorphous carbon in carbon arc method
[15-17]; frequently-observed bending of growth axis of the nanotubes is related to
the introduction of a heptagonal defect at the bend location in vapor growth method
[18], etc. Further research is needed to optimize and control the synthesis process,
increase the yield of single-walled nanotubes ropes, minimize the concentration of
carbon nanoparticles and amorphous carbon produced, and to characterize the CNs
that are produced. Recently, many new methods are reported to synthesis single
walled carbon nanotubes [19-25]. Some articles state that they can synthesis a bundle
of aligned SWCNs [26] while other reports announce that they have a technique to
produce SWCNs in high yield [27]. However, their produced single walled
nanotubes at least have a 1 nm diameter range. Inside this 1 nm diameter range, there
are over 10 kinds of possible tubes so that we have difficulties to characterize the carbon nanotubes, although the alignment and high yield of CNs make an important step toward the commercial application of CNs.

1.2 Fundamental Parameters and Physical Properties of Carbon Nanotubes

A free carbon atom has the electronic structure \((1s)^2(2s)^2(2p)^2\). In order to form covalent bonds, one of the \(2s\) electrons is promoted to \(2p\), and the orbital are then hybridized in one of the three possible ways. In graphite, one of the \(2s\) electrons hybridizes with two of the \(2p\) to give three \(sp^2\) orbital at 120° to each other in a plane, with the remaining orbital having a \(p_z\) configuration, at 90° to this plane. The \(sp^2\) orbital form the strong \(\sigma\) bonds between carbon atoms in the graphite plane, while the \(p_z\), or \(\pi\), orbital provide the weak van der Waals bonds between the planes. The overlap of \(\pi\) orbital on adjacent atoms in a given plane provides the electron bond network which gives graphite a relatively high electrical conductivity. In naturally occurring or high-quality synthetic graphite, the stacking sequence of the layers is generally ABAB, with an interlayer \(\{0002\}\) spacing of approximately 0.334 nm, as shown in Fig. 1.1. This structure is often known as Bernal graphite after John D. Bernal who first proposed it in 1924. The unit cell contains four atoms, and the space group is \(P6_3/mmc\). In less perfect graphite, the
interplanar spacing is found to be significantly larger than the value for the single

interplanar spacing is found to be significantly larger than the value for the single
crystal graphite (typically ~ 0.344 nm), and the layer planes are randomly rotated
with respect to each other about the c axis. Such graphite is termed turbostratic.

In diamond, each carbon atom is joined to four neighbors in a tetrahedral
structure. The bonding here is $sp^3$ and results from the mixing of one 2s and three 2p
orbital. Diamond is less stable than graphite, and is converted to graphite at a
temperature of 1700 °C at normal pressure. Disordered carbons containing
$sp^3$-bonded atoms are also rapidly transformed into graphite carbon at high

Fig. 1.1 The structure of hexagonal (Bernal) graphite, showing the unit cell.
In the C\textsubscript{60} molecule, the carbon atoms are bonded in an icosahedral structure made up of 20 hexagons and 12 pentagons. Each of the carbon atoms in C\textsubscript{60} is joined to three neighbors, so the bonding is essentially \( sp^2 \), although there may be a small amount of \( sp^3 \) character due to the curvature. Note that all 60 carbons atoms are identical, so that the strain is evenly distributed over the molecule. The bonding in carbon nanoparticles and nanotubes is also primarily \( sp^2 \), although once again there may be some \( sp^3 \) character in regions of high curvature.

1.2.1 **Fundamental parameters of carbon nanotubes**

There are two possible high symmetry structures for nanotubes, known as zig-zag and armchair. Dividing C\textsubscript{60} parallel to one of the three-fold axes results in the zig-zag nanotube shown in Fig. 1.2(a), while bisecting C\textsubscript{60} along one of the five-fold axes produces the armchair nanotube shown in Fig. 1.2(b). The terms zig-zag and armchair refer to the arrangement of hexagons around the circumference. In practice, it is believed that most nanotubes do not have these highly symmetric forms but have structure in which the hexagons are arranged helically around the tube axis, as in Fig. 1.2(c). These structures are generally known as chiral, since they can exist in two mirror-related forms.
Fig. 1.2 Drawings of the three nanotubes which can be capped by one half of a $C_{60}$ molecule. (a) Zig-zag (9,0), (b) armchair (5,5) and (c) a chiral nanotube.
The simplest way of specifying the structure of an individual tube is in terms of a vector, which we label $C$, joining two equivalent points on the original graphene lattice. The cylinder is produced by rolling up the sheet such that two end-points of the vector are superimposed. Because of the symmetry of the honeycomb lattice, many of the cylinders produced in this way will be equivalent, but there is an irreducible wedge comprising one twelfth of the graphene lattice, within which unique tube structures are defined. Fig. 1.3 shows small part of this irreducible wedge, with points on the lattice labeled according to the notation of Dresselhaus et al. [28,29]. Each pair of integers $(n,m)$ represents a possible tube structure. Thus the Vector $C$ can be expressed as

$$C = na + mb,$$

(1.1)

where $a$ and $b$ are the unit cell base vectors of the graphene sheet, and $n \geq m$. It can be seen from Fig. 1.3 that $m = 0$ for all zig-zag tubes, while $n = m$ for all armchair tubes. All other tubes are chiral. In the cases of two ‘archetypal’ nanotubes which can be capped by one half of a $C_{60}$ molecule, the zig-zag tube is represented by the integers $(9,0)$ while the armchair tube is denoted by $(5,5)$. Table 1.1 lists out all the parameters including their definitions and values to a chiral nanotube [28].
Table 1.1 Parameters of carbon nanotubes

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Formula</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Length of unit vector</td>
<td></td>
<td>2.46Å</td>
</tr>
<tr>
<td>a, b</td>
<td>Unit vectors</td>
<td>$(\sqrt{3}/2, 1/2) \ a, (\sqrt{3}/2, 1/2) \ a$</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Chiral vector</td>
<td>$C = na + mb = (n, m)$</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>Circumference of nanotube</td>
<td>$L =</td>
<td>C</td>
</tr>
<tr>
<td>D</td>
<td>Diameter of nanotube</td>
<td>$D = L/\pi = a\sqrt{(m^2 + n^2 + nm)}/\pi$</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>Chiral angle</td>
<td>$\tan \ \theta = \sqrt{3m} / (2n + m)$</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>The highest common divisor of $(n, m)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_R$</td>
<td>The highest common divisor of $(2n + m, 2m + n)$</td>
<td>$d_R = d$ if $n - m$ not a multiple of $3d$ or $3d$ if $n - m$ a multiple of $3d$</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Translational vector of 1D unit cell</td>
<td>$T = t_1a + t_2b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$t_1 = (2m + n) / d_R$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$t_2 = -(2n + m) / d_R$</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Length of $T$</td>
<td>$T = \sqrt{3} L / d_R$</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Number of hexagons per 1D unit cell</td>
<td>$N = 2(n^2 + m^2 + nm) / d_R$</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Symmetry vector</td>
<td>$R = pa + qb = (p, q)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d = mp - nq$</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1.3 Coordinates of lattice points of a graphite sheet. Vectors $a$ and $b$ are unit vectors of two dimensional lattice. There is one to one correspondence between the tubule structure and the lattice points shown here.
1.2.2 Formation energy of carbon nanotubes

The earliest work on the stability of carbon nanotubes as a function of diameter was carried out by Gary Tibbetts in 1984 [30]. Using a continuum model, Tibbetts found that the strain energy of a thin graphite tube varies with $1/(\text{diameter})$. This implies that the strain energy per atom varies with $1/(\text{diameter})^2$. Following the discovery of fullerenes-related nanotubes, a number of groups have carried out more detailed theoretical studies of nanotube stability [31-33]. An interesting result was found by John Mintmire and colleagues from the Naval Research Laboratory in Washington that for tubes with diameters larger than about 1.6 nm, the strain energy becomes very close to that in planar graphite [31]. This diameter is approximately the same as the smallest observed experimentally in multiwalled nanotubes. However, Mintmire and colleagues found that strain energy was independent of tube structure.

Later, Sawada and Hamada suggested cohesive energy $E_c$ [32] of carbon nanotube from Tersoff’s empirical potential [34,35]. The cohesive energy $E_c$ of each tubule is constructed from the corresponding sized of graphite ribbon sheet. Bond-bending increases the cohesive energy when the sheet is rolled up. On the other hand, the cohesive energy is decreased by combining dangling bonds of edge atoms on both sides of the sheet. The result of competition between these two energies, the
bond-bending and bond-binding energies, determines which structure is energetically more favorable, the sheet or the tubule. The bond-bending energy per atom $E_{bend}$ is governed by the following equation,

$$E_{bend} = C_1(1/D)^2 + C_2(1/D)^4,$$  \hspace{1cm} (1.2)

where $C_1 = 5.46$ eV Å$^2$, $C_2 = 25.1$ eV Å$^4$ and $D$ is a diameter of the tube. On the other hand, the bond-binding energy per atom $E_{bind}$ is written as,

$$E_{bind} = -b \left(1/n\right),$$  \hspace{1cm} (1.3)

where $b = 2.31$ eV/atom and $n$ corresponds to the tubule donation $A(n,m)$. All coefficients $C_1$, $C_2$ and $b$ are calculated from Tersoff’s potential [34,35]. The difference of the cohesive energy between the sheet and the tubule is given by,

$$E_c = E_{bend} + E_{bind}.$$  \hspace{1cm} (1.4)

For a large value of $n$, $E_{bind}$ is dominant and the tubule has a lower energy than the sheet. For a value of $n$ smaller than a certain threshold value $n_{th}$, the tubule has a higher energy than the sheet. When $n$ is close to that threshold value $n_{th}$, $E_{bend}$ should be considered both the first and second part of Eq. 1.2. We can ignore the second part of Eq. 1.2 when diameter $D$ is larger than 10Å, as shown in Fig. 1.4.
**Fig. 1.4** The bond-bending energy as functions of $1/D^2$ (where $D$ is a diameter of the tubule) for various types of the tubules: ◦, $A(n,0)$; ▽, $A(n,1)$; □, $A(n,2)$ and △, $A(n,3)$. The solid line and the blue broken curve represent the first part and the whole of the Eq. 1.2, respectively.

From above discussion, it is shown that not only thick tubules but also very thin tubules, having several carbon atom hexagons in circumference, are energetically more favorable than graphite sheets of width equal to the circumference. Therefore, very thin tubules, say having 5 hexagons and 4Å in diameter, can be expected to be grown. There are three possible structures for 4Å diameter nanotubes, (5,0), (4,2) and (3,3). However, only (5,0) zig-zag is energetically stable while there is no any experimental observation for such small tubes.
1.2.3 Vibrating modes of carbon nanotubes

The symmetry assignments and spectroscopic activities of the vibrational modes for nanotubes have been discussed by Dresselhaus, Jishi, and co-workers [29, 36-39]. Since there are $2N$ atoms in the unit cell of a nanotube, the total number of vibrational modes will be $6N$. Group theory can be used to determine which of these modes are infra-red and Raman active. The modes can be decomposed into the irreducible representations of the point group appropriate to the tube. If we consider armchair tubes with $D_{nh}$ symmetry (i.e. those for which $n$ is an even integer), and assume that $n/2$ is odd, the vibrational modes will be decomposed into following irreducible representations,

$$
\Gamma^{\text{vib}} = 4A_{1g} + 2A_{1u} + 4A_{2g} + 2A_{2u} + 2B_{1g} + 4B_{1u} + 2B_{2g} + 4B_{2u} + 4E_{1g} + 8E_{1u} + 8E_{2g} + 4E_{2u} + \cdots + 8E_{(n/2-1)g} + 4E_{(n/2-1)u}.
$$

(1.5)

If $n/2$ is even, then the 8 and 4 in the last two terms will be interchanged. Consider the (6,6) armchair tube, for which $N = 12$, this will have 72 phonon branches, and the above equation gives a total of 48 distinct mode frequencies (since the final two terms disappear). At the zone center, one $A_{2u}$ mode, one $E_{1u}$ mode and one $A_{2g}$ mode have zero frequencies since they correspond to translation along the tube axis or perpendicular to the axis, or to rotations about the axis.
Appropriate character tables can be used to determine which modes are IR active and which are Raman active. For the $D_{nh}$ group, the $A_{2u}$ and $E_{1u}$ modes are IR active, while the $A_{1g}$, $E_{1g}$ and $E_{2g}$ are Raman active. Thus there are 8 IR mode frequencies ($A_{2u} + 7E_{1u}$) and 16 Raman active frequencies ($4A_{1g} + 4E_{1g} + 8E_{2g}$) at zone center. It is important to note that the number of IR and Raman active modes is independent of nanotube diameter; this is also true for all other classes of tube. However, the frequencies of these modes do vary with diameters, as discussed below.

In the case of armchair tubes with $D_{nd}$ symmetry ($n$ is odd), similar arguments show that there will be 7 IR active frequencies and 15 Raman active frequencies. Zig-zag tubes, whether $D_{nh}$ or $D_{nd}$, will also have 7 IR active frequencies and 15 Raman active frequencies.

Consider now the chiral tube, that belong to $C_n$-type symmetry groups, for which the vibrational modes contain the following symmetries,

$$\Gamma^{\text{vib}} = 6A + 6B + 6E_1 + 6E_2 + \cdots + 6E_{N/2-1}. \quad (1.6)$$

In this case the A and $E_1$ modes are IR active and the A, $E_1$ and $E_2$ modes are Raman active. It should be noted that there is an important difference between armchair and zig-zag nanotubes on one hand and chiral tubes on the other. In the case of both
armchair and zig-zag tubes, zone-folding results in the M point being superimposed on the center of the Brillouin zone, while for chiral tubes the M point does not map onto the $\Gamma$ point. This suggests that there should be a larger spread of IR and Raman frequencies for armchair and zig-zag tubes than for chiral tubes.

The vibrational mode frequencies of nanotubes can be calculated from those of a two dimensional graphene sheet using the equation

$$\omega_{1D}(k) = \omega_{2D}(kK_2 + \mu K_1), \quad \mu = 0, 1, 2, \ldots, N - 1,$$

where $\omega_{1D}$ is the vibrational mode frequency for one-dimensional tube, $\omega_{2D}$ is the frequency for a two-dimensional graphene sheet, $k$ is a wavevector in the direction $K_2$ in reciprocal space (i.e. along the tube axis) and $\mu$ is an integer used to label the wavevectors along the $K_1$ direction in reciprocal space, perpendicular to the tube axis. Jishi, Dresselhaus and others have used this expression to calculate the variation of IR and Raman active modes with nanotube radius for a variety of different tube structures. The frequencies are calculated at Brillouin zone center, since only modes close to this point are Raman and IR active. As an example, zig-zag tubes show the diameter dependence of IR and Raman active mode frequencies [39]. The higher frequencies modes can be seen as less diameter dependence becomes less marked for
tubes which indices larger than about (20,0), corresponding to a diameter of 1.57 nm.

For larger diameters the spectra tend towards those of graphite. The frequencies predicted for armchair and chiral nanotubes differ from those predicted for zig-zag tubes, suggesting that Raman and IR spectroscopy should provide a method of determining the chirality of nanotubes.

The Raman studies of single-walled nanotubes have tended to produce significantly different spectra from that of graphite. One of the first such studies was reported by J.M. Holden and colleagues [40]. Their samples were prepared using cobalt-containing electrodes, in the way described by Bethune et al. [41]. A Raman spectrum recorded from the SWNT-containing material is shown in Fig. 1.5(e), where it is compared with spectra from various other carbon materials. The spectrum contains two sharp first order lines at 1566 and 1592 cm\(^{-1}\). Sharp lines at these positions are not observed in the spectrum from arc-evaporated soot produced without cobalt, shown in Fig. 1.5(d), or in any of the other spectra from other carbons shown in Fig. 1.5. Fig. 1.5(e) shows the Raman spectrum of high oriented pyrolytic graphite (HOPG) which is always used as one of the benchmarks for the characterization of carbon fibers. The authors showed that the lines at 1566 and 1592 cm\(^{-1}\) were revealed clearly in a ‘different spectrum’ calcula...
spectrum of normal arc-evaporated soot from that of the cobalt-catalysed soot. The observation of sharp features in this region is consistent with the theoretical predictions for zig-zag tubes at \( \sim 1590 \text{ cm}^{-1} \), which splits into a doublet in the low-diameter region relevant to single-walled nanotubes. In low frequency zone, dramatic changes in the distribution of the line frequencies can be seen, which is attributed to a radial breathing mode (RBM), in which all of the atoms in the tube are displaced inward or outward by an equal amount. These observations apparently show that the electronic density of states is dependant on nanotube diameter, and therefore provide further evidence for quantum behavior in single-walled carbon nanotubes. The relationship between the radial frequency and tubule diameter is estimated from the formula [42],

\[
\omega = \frac{223.75}{D}
\]  

where \( D \) is the diameter of the tube in nanometers and \( \omega \) is the mode frequency of RBM in cm\(^{-1}\). The smaller the SWNT diameter, the higher the Raman frequency.
Fig. 1.5  Raman temperature Raman spectra for a variety of carbon samples, from the work of Holden et al [40]. (a) Glassy carbon, (b) ‘nanosoot’ produced by laser pyrolysis, (c) nanosoot after heat treatment at 2820 °C, (d) soot produced by arc-evaporation, (e) soot produced by arc-evaporation with Co added to anode, (f) HOPG, (g) single-crystal diamond.
1.3 Motivation for This Thesis

After discussing the development of carbon nanotubes studies and its physical properties, we learnt that it is important to develop a synthesis method for fabricating mono-sized single-walled carbon nanotubes so that they can be examined on applications. The usual approaches so far are difficult to fabricate SWNTs with well-defined structure. Very recently, Z. K. Tang et al. reports a synthesis method to fabricate aligned and mono-sized SWNTs in the channels of a kind of zeolite single crystals called AFI. That production of mono-dispersed and mono-sized SWNTs in 3D array represents an essential role in development and application of CNs. In this thesis, I study the effects of the fabrication conditions on the formation of the mono-sized SWNTs. The structure of the single-walled carbon nanotubes is observed by High Resolution Transmission Electron Microcopy (HRTEM) and is characterized by Raman scattering. An effective growth temperature of tubes is determined by studying the degree-of-polarization of samples. Base on the Raman spectra and the argument of the energetic stability of nanotubes, a possible structure is proposed for our SWNTs.
CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 Fabrication of Carbon Nanotubes

2.1.1 Zeolites

Traditional zeolites are alumino-silicate crystals with pores of molecular size (called channels or cavities), and have been used widely as catalysts, molecular sieves, and absorbents, etc. In particular, they become the most important catalyst in the petrochemical industry. Recently, much attention has been paid to zeolites as containers as metal- and/or semiconductor- clusters [43,44]. The pores of zeolite are periodically arrayed in three-dimension, they make it possible to design a cluster crystal, which consists of regular arrangements of uniform size clusters by containing in the channels or cavities of the zeolites.

In recent years, the zeolite family was extended to aluminophosphate, galliumphosphate, etc. There is a total of over 400 different types of zeolite crystals which are natural and synthetics. One of the aluminophosphate zeolite AIPO_4-5 molecular sieve (IUPAC code AFI [45]) has one-dimensional channels with 7.3Å in diameters. These channels are arrayed parallel to the length direction of the crystals in a hexagonal structure. The distance between neighboring channels is 13.7Å, as
shown in Fig. 2.1. The crystals used in our experiment are prepared by hydrothermal growth method [46]. Fig. 2.2 shows the optical microscope image of as-growth crystal. The typical dimension of the crystal is 100 to 400 $\mu$m long and 50 to 300 $\mu$m in diameter. They are clear and transparent, and look like a hexagonal prism.

The molecular equation of the as-grown crystal is $[\text{Al}_{12}\text{P}_{12}\text{O}_{48}] \cdot R \cdot q\text{H}_2\text{O}$, $R = (\text{C}_3\text{H}_7)_3\text{N}$. Large quantities of tripropylamine (TPA) molecules $((\text{CH}_3\text{CH}_2\text{CH}_2)\text{N})$ stay in the channels as template during the growth process. Hereafter, we term this as-growth zeolite crystal as AFI-TPA.

### 2.1.2 Fabrication process of carbon nanotubes

To obtain carbon nanotubes formed in the channels of zeolite, TPA molecules provide carbon atoms to us. We should first remove the hydrogen $\text{H}$ and nitrogen $\text{N}$ atoms from TPA and leave only carbon atoms $\text{C}$ in the channels of AFI. TPA will decompose when they are heated up to some temperature so that $\text{H}$ and $\text{N}$ will get out from the channels. If the crystals are processed under suitable growth temperature, carbon nanotubes will be arrayed in the channels of AFI crystals, named AFI-nanotube. Therefore, the pyrolysis process is an essential procedure for obtaining nanotubes.
Fig. 2.1  (a) The framework structure of an AFI crystal viewed along [001] direction and (b) overall view of the crystal.

Fig. 2.2  Optical microscopic image of as-grown AFI crystals. They show very high transparency and have regular structures.
Some AFI-TPA crystals were put into a bottom of a one end-sealed glass tube. This sealed end of glass tube was then put in a temperature programmable oven while the open end of the tube was connected to vacuum system. Fig. 2.3 shows the experimental setup for the above pyrolysis process. The pumping rate and temperature increasing rate were carefully controlled, in order to protect the crystals from crack due to rapid change of pressure and temperature. Fig. 2.4 shows the change of pressure and temperature for fabricating carbon nanotubes. After the pyrolysis process, the temperature programmable oven would turn off automatically and the system temperature should be cooled down in the closed oven gradually. It should be noted that we should use different pressure and temperature rate changes for fabricating different groups of samples.
Fig. 2.3  Experimental setup diagram for the preparation of carbon nanotubes in channels of AFI crystals by pyrolysis.

Fig. 2.4  Change in temperature and pressure rate in SWNT fabrication pyrolysis process.
2.2 Observation of the Samples Using Polarized Optical Microscopy

Observations of the samples using polarized optical microscope is a simple and direct way to check the quality of the prepared samples. The optical absorption in one-dimension materials is sensitively dependent on the polarization direction. Thus, this anisotropy of absorption is often used to test whether the material is ordered one-dimensional. An AFI-nanotube crystal acts as an analyzer for the light polarized parallel to the tube direction. When we rotate the polarizer, the sample would show strong anisotropy of absorption. Conversely, if the molecules inside the channels of AFI are amorphous, we would expect to see no change in light intensity when the polarizer is rotated.

In Fig. 2.5, schematically shows the generation of the polarized light using a linear polarizer, the polarizer lies on the plane of the page and the light is propagating into the page. The arrow $\mathbf{E}$ shows the plane of vibration of a randomly selected wavetrain falling on the sheet. Two vector components, $E_y$ (of magnitude of $E \cos \delta$) and $E_x$ (of magnitude of $E \sin \delta$) can replace $E$, one parallel to the polarizing direction and one at right angle to it. The latter will be absorbed within the sheet; only the former is transmitted.
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Fig. 2.5  A wave train $E$ is equivalent to two component $E_y$ and $E_x$. Only $E_y$ is transmitted by the polarizer. Dotted lines represent the polarizing direction of the polarizer.

An AFI-nanotubes crystal was vertically placed behind of the polarizer. The polarizer was rotated about the propagation direction, there are two positions, 180 apart, at which the transmitted light intensity is almost zero; these are the positions in which the polarization direction of the polarizer and the axis of the crystal is in parallel, or the polarized light intensity is parallel to $c$, $I_//$. If the amplitude of the linear-polarized light falling on the crystal is $E_m$, the amplitude of the light that emerges is $E_m \sin \theta$, where $\theta$ is the angle between the polarizing direction of the polarizer and the crystal axis $c$. We know that the intensity of the light beam is
proportional to the square of the amplitude. Thus, the transmitted light intensity $I$ varies with $\theta$ according to,

$$I = I_m \sin^2 \theta,$$

in which $I_m$ is the maximum value of the transmitted intensity.

### 2.3 Experimental Procedures of Degree of Polarization Measurement

As mentioned in the above section, we know that different kinds of materials inside the channels of AFI will show different absorption behavior. For example, if we examine different carbon-contained crystals, which grow in different temperatures, should show different optical polarization properties because of the difference of yield quantities and the arrangement qualities of nanotubes in different temperatures. Therefore, we expect to find an effective growth temperature $T_{cr}$ that the yield of nanotubes is the highest and the arrangement of the nanotubes is the best. Here, I suggest a term called Degree of Polarization (DOP) that is defined as follows,

$$\text{DOP} = \frac{|I_{\perp} - I_{\|}|}{|I_{\perp} + I_{\|}|}$$  \hspace{1cm} (2.2)

where $I_{\perp(\|)}$ represents the intensity of the light parallel (perpendicularly) polarized to the axis $c$ of the crystal AFI. The DOP value ranges from 0 to 1; the higher the DOP value, the higher the absorption rate of the sample, which means the more regular
array of carbon atoms along the channel direction. When DOP value is 0, i.e. $I_\| = I_\perp$, that implies random packing of carbon atoms (amorphous carbon) in the AFI channel. On the contrary, when DOP value is equal to 1, i.e. $I_\perp \gg I_\|$, that means the prefect array of carbon atoms in AFI channels.

A single AFI-nanotubes crystal was horizontally held by a piece of 5 mm-sized fluid ceramic. After solidification of the fluid ceramic, the two sides of this ceramic were polished until two surfaces of a AFI-nanotubes crystal appeared. In general, the thickness of this crystal ceramic is less than 100-micron meters. Fig. 2.6 shows the installation mechanism of a crystal into a ceramic holder.

DOP experiment is conducted at room temperature. First of all, tungsten lamp was used as a light source that firstly passed through the rotated polarizer and a chopper. The light was then focused by a curved focusing mirror to 50 $\mu$m light spot that was shone on the surface of an installed AFI-nanotubes sample. The 632 nm of light signal was collected by using an optical fiber which is connected to a monochromometer, and was detected by using a PMT. This light signal from the PMT was then amplifier by using a lock-in amplifier. Finally, we recorded the maximum and minimum light intensity, which represent $I_\perp$ and $I_\|$ respectively, by rotating the
polarizer.

Fig. 2.6 (a) Upper: Front view for the procedure of ceramic installation of AFI single crystal; Lower: Top view of the graph. (b) The AFI crystal is held by the ceramic. (c) Both surfaces of AFI crystal can be observed after polishing work. (d) Installed sample.
Fig. 2.7 DOP experimental apparatus and setup.
2.4 Experimental Procedures of Unpolarized Mirco-Raman Scattering Experiment

Raman spectroscopy is often used to identify the structures of materials. Due to the many structures of carbon materials, different Raman characterization will show different carbon structures [47-51]. Therefore, Raman spectroscopy is a powerful and efficient tool to characterize what structure of carbon is formed in the channels. Unpolarized micro-Raman scattering experiment is also measured at room temperature and its setup is shown in Fig. 2.8. Reneshaw 3000 micro-Raman system equipped with a single monochromator connected to electrical-cooled charge-coupled-device camera (CCD) was used in our experiment. A single crystal was excited using the 632.8 nm wavelength line of a He-Ne laser. The laser beam was focused to a typical spot size of about 2 μm. The measurement resolution and signal to noise S/N ratio are about 1 cm\(^{-1}\) and \(\sqrt{n}\), where \(n\) is the number of sampling, respectively. After the experimental alignment was ready, data can be collected to the computer automatically.
Fig. 2.8  Experimental setup of Raman scattering experiment.
2.5 High Resolution Transmission Electron Microscopy Observations

Physical and chemical properties of substances depend on the arrangement of the constituent atoms. This is especially the case for many advanced materials like metals and alloys, semiconductors, ceramic, etc. Therefore, the analysis of the atomic arrangement, which is called structure analysis, is a starting point to clarify the origin of their functions. High resolution transmission electron microscopy (HRTEM) is widely used as a powerful mean for analyzing microstructures in many advanced materials. HRTEM observation is viewed as the direct evidence of the existence of carbon nanotubes. A JEOL 2010 TEM system, which has 0.0204 nm measurement tolerances, was used in our experiment.

In our experiment, we needed to remove the framework of AFI crystal, since electron scattering from the AFI framework is much stronger than the nanotubes due to the weight differences between Al, P and C. For that reason, we etched the AFI-nanotubes crystals in HCl aqueous solution at about 80°C for 15 minutes. Subsequently, we added some 2-dichlorethene to the solution and shaked them. After a few minutes, the solution could separate into two individual layers. A light brown color of the upper layer was a HCl solution with dissolved AFI framework while a light black color of the lower layer was mainly composed of 2-dichlorethene
and carbon nanotubes. At last, we took the lower layer solution on a Cu grid with Holey carbon film and waited for an evaporation of 2-dichlorethane. We expected that some nanotubes would stay on the grid which would be ready for TEM experiment.
CHAPTER 3

EXPERIMENTAL RESULTS

and

DISCUSSIONS

3.1 Polarized Optical Microscopy Observations and Degree of Polarization Experiment

We expect that the transmitted light intensity vary with the polarization angle $\theta$ and would like to see the maximum and minimum transmitted light intensity while the polarization angle is changed with axis $c$. Schematic figure (Fig. 3.1) shows two extreme intensities of transmitted light.

![Diagram](image)

Fig. 3.1 Transmitted light intensity is maximum when $I_\perp$ and is minimum when $I_\parallel$. 

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Fig. 3.2 shows the transmitted intensity $I$ varies with polarization angle $\theta$ of a AFI-nanotubes crystal that was grown at 580°C following the pyrolysis process in Fig. 2.3.

$$I = I_0 \sin^2 \theta$$

Fig. 3.2 Transmitted intensity $I$ varies with $\theta$ of a AFI-nanotubes crystal that was grown at 580°C.

It is already seen that the transmitted light intensity of a AFI-nanotubes sample vary with the polarization angle and there are two clear periodical extreme values, which indicate the maximum and minimum of the light intensity. The minimum of light intensity is due to absorption of the parallel polarized light by the carbon nanotubes. In this sample, the DOP value is unit, implying the carbon atoms are well arranged in the channels of AFI.
After the AFI-TPA crystals grew at different temperatures, we can observe that their transmitted polarized light intensities are different, as shown in Fig. 3.3. This phenomenon implies that some one-dimensional materials with different order of arrangement are formed in the channels of AFI. At a certain temperature, called an effective growth temperature $T_{eg}$, in which DOP value is close to 1, these one-dimensional materials are well developed. DOP result is shown in Fig. 3.4.

It is seen that DOP value is close to 0 when the growth temperature is between 350°C and 430°C though the crystal was turned its color from transparent to dark. Moreover, there is a rapid increase in DOP value when the temperature is ranged between 440°C and 490°C which implies that a 1-D material is started to develop with high arrangement structure rapidly from disordered structure. Furthermore, DOP value trends to 1 starting from 490°C onwards and remains at this high value while the temperature is as high as 650°C. This means that carbon atoms are re-arranged in the channel from disorder to order in the temperature region between 440°C and 460°C and its structure is well developed starting from 470°C onwards. The nanotubes structure can be destroyed when the temperature is raised to higher than 800°C. The structure-destroyed crystal is black in color, but without polarizer effect. Polarized optical microscopy image of an AFI-TPA crystal grown at 900°C,
Fig. 3.3  Polarized optical microscopy images of different temperatures grown AFI crystals. Right (left) column crystals are observed under perpendicularly (parallel) transmitted light intensity to zeolite axis c.

Fig. 3.4  DOP experiment result.
called AFI-900°C crystal, is shown in Fig 3.3(d). The non-polarization black of the sample was due to the wholly decomposition of the 1-D nanotubes and it became an amorphous graphite again. Thus, we conclude from this section that an effective growth temperature $T_{cg}$ of a one-dimensional material formed inside the channels of AFI is started at 490°C and ended approximately at 650°C. It is interesting to note that the DOP experiment shows the consistency of the carbonization temperature ($\sim$ 650-750 °C) of carbon material [52]. The carbonization temperature is the temperature which volatile species are driven off from precursors, leaving behind the basic structural units in the order of 1 nm in thickness. Below the carbonization temperature, carbon cannot change its $sp^2$ covalent bonding configuration. In the next section, we further confirm the carbon nanotube structure using Raman scattering.

3.3 Unpolarized Micro-Raman Scattering Experiment

Five kinds of the samples were examined in Raman scattering experiment. They were AFI-TPA which is a as-growth zeolite single crystal discussed in section 2.1.1, AFI-carbon which was grown under the nanotubes pyrolysis process but stopped at temperature 380°C, AFI-nanotubes which was grown under exactly the same process in Fig. 2.4, AFI-900°C which was grown under the above process but the temperature was raised to 900°C, and AFI-hollow crystal which was grown under the process and oxygen was filled into the system when temperature reached at or above
380°C.

Fig. 3.5(a) shows Raman result of a AFI-TPA crystal with many observable characteristic peaks. Firstly, CH₃, CH₂ and CH symmetric and anti-symmetric stretching modes create peaks at a region between 2850 and 3010 cm⁻¹. Then, a peak near 1460 cm⁻¹ appears due to CH₃ anti-symmetric deformation mode. Next, a peak with a wide shoulder between 1040 and 1150 cm⁻¹ also appears mainly because of CN stretching mode and partly because of CH₃ rock vibration and CCC stretching mode. Last of all, a sharp peak near 570 cm⁻¹ is assigned to CCN bending mode. This rich Raman spectrum with many sharp and easily observable peaks indicates gaseous TPA is full in the channels of zeolite.

After a 380°C pyrolysis for two hours, this plenty of Raman spectrum became featureless, see Fig. 3.5(b). We could not observe the peaks that come from the TPA molecules again. It is because TPA molecules were decomposed when the temperature raised at about 380°C while N and H molecules were pumped out by vacuum system and only carbon atoms stayed in the channels, so-called AFI-carbon crystal. At that time, a transparent AFI-TPA crystal did change to dark gray because of disordered arrangement of carbon atoms in the channels of AFI. That is a reason
why we see no different in Fig. 3.3 and observe nearly zero DOP value of this sample, as shown in Fig. 3.3.

Fig. 3.5(c) shows the Raman spectra for the AFI-nanotubes samples. We can see three characteristic Raman peaks in the spectrum. The first one is located at 1614 cm$^{-1}$, so-called tangential modes, that correspond to the graphite $E_{2g}$ optic mode at 1582 cm$^{-1}$, splits due to the curvature of the rolled up graphite, which has been extensively studied in HOPG (highly oriented pyrolytic graphite) [11,53]. The existence of such a group is a fingerprint for SWNT since MWNTs and graphite exhibit only a single peak at 1580 cm$^{-1}$ [40]. These Raman frequencies can be understood by zone-folding of the graphite phonon dispersion relations [54]. The second group, in low frequency range near 530 cm$^{-1}$, consists of a significant $A_{1g}$ radial breathing modes (RBM) whose frequencies depend on the tube diameter (see Eq. 1.8). This Raman mode is specific to SWNTs since all other carbon specimens do not show any features in this frequency region. From the relation between diameter and frequency given in Eq. 1.8, the diameter of SWNT is 4.198Å which makes sense with the predicted diameter value from the structure of AFI. Inside each channel of a zeolite crystal, the distance between two neighboring $O^{2-}$ ions from two walls is 10.04Å. There is about 7.3Å free space for carbon materials formed in the channel.
Fabrication and Characterization of 0.4 nm-sized single-walled carbon nanotubes array in one-dimensional channels of AlPO₄-5 single crystals

By Wong Ka Ho, Gavin

Only SWNTs with 4-5Å will be formed in these 7.3Å channels after subtraction of twice the carbon van der Waals radius (∼1.7Å). It is important to note that the Raman intensity for graphite in 1300 – 1600 cm⁻¹ region is sensitive to sample quality. Generally, the intensity of E₂g mode of graphitic materials is sharp and strong when the sample is highly crystalline and defect free, while disordered graphites and carbons show a broad feature around 1350 cm⁻¹ [11,53,55,56]. A wide shoulder signal between 1150 – 1450 cm⁻¹ seen in Fig. 3.5(c) may come from a symmetry-lowering effect but with a weak contribution from SWNTs, due to defects or nanotube caps and the presence of carbon nanoparticles and amorphous carbon. The peak is usually used to estimate the purity of the sample. In our as-grown AFI-nanotubes samples, the intensity of this peak varies sample to sample.

To sum up the above discussion and this section, we confirm that 4.198 ± 0.204Å diameter SWNTs are formed inside the channels of a AFI single crystal under the effective growth temperature from 470 to 650°C. The diameter of this 0.4 nm-sized single-walled nanotubes is close to the diameter estimated confinement by the AFI channel. In the coming section, a HRTEM image of these SWNTs will be shown which is consistent with the experimental result of their diameter obtained from the Raman scattering experiment.
Fig. 3.5  Raman spectra of different temperatures grown AFI-TPA crystal. (a) Unprocessed. (b) 380°C. (c) 580°C. (d) 900°C and (e) 580°C with oxygen.
3.4 High Resolution Transmission Electron Microscopy Observations

Recording electron diffraction patterns from single-walled nanotubes is exceptionally difficult owing to their very small diameters and beam-sensitivity. Iijima has reported obtaining patterns from individual tubes [7,57] and in each case found the tubes to be helical. Samples of single-walled nanotubes tend to be much more homogeneous than samples of multiwalled nanotubes due to containing fewer obvious defects. High resolution electron micrographs of single-walled nanotubes generally show featureless narrow tubes, and are therefore relatively uninformative compared with images of multiwalled nanotubes. Both the single-walled nanotubes bundles and individual tubes are frequently curled and looped.

Our experimental HRTEM micrograph is shown in Fig. 3.6. There are three areas worth discussing. Let us begin with the G marked on the graph. The interplanar spacing is found to be 0.34 nm that is consistent with the typical value of interplanar spacing of turbostratic graphite, as discussed in section 1.2. The second part in the image is marked by T. We can see numerous 0.42 nm separations isolated layers in the middle of the same graph. There is no energetic stable graphite system with interplanar spacing 0.42 nm, except single-walled carbon nanotubes. This HRTEM observation provides us a direct evidence for the presence of SWNTs. Moreover, experimental result of RBM frequency also indicates the existence of 4.198 Å
diameter SWNTs. As a result, we can make sure that there are about 4.2 ±0.204Å diameter SWNTs formed in the channels of zeolite.

It is noted that there exist a lot of graphite scripts in the image. Where did the graphite scripts come form? We observed that the nanotubes are very unstable under electron beam. The tube structure can be destroyed by the electron beam in a few seconds. Thus, we think that the graphite scripts were formed due to the corruption of nanotubes. Another reason for the existence of these turbostratic graphite is that some single-walled carbon nanotubes were destroyed by HCl acid in the etching process. The rolling-up graphite sheet structures of the tubes were spread out to planer graphite sheets and then these sheets grouped together to form randomly rotated layer planes. Besides, a wide shoulder Raman signal between 1150 – 1450 cm⁻¹ in Fig. 3.5(c) indicates there exist defects and/or imperfects in our nanotubes. These defects enhance the corruption process of nanotubes into ribbons when the AFI framework is etched out. Hence, it is reasonable to observe the turbostratic in the image.
Fig. 3.6 HRTEM micrograph of our AFI-nanotubes crystal after etching.
3.5 Possible Structure of 0.4 nm-sized SWNTs

In the previous two sections, we concluded that the nanotubes formed in the AFI channels have diameter of 0.42nm $\pm 0.02$nm. The diameter of a $(n,m)$ tube is calculated by $D = L \cdot \pi = a \sqrt{(n^2 + m^2 + nm)} / \pi$, where $L$ is the length of circumference. Accordingly, there are four possible structures of nanotubes with diameter of 4Å. They are zig-zag tube $(5,0)$ with $D = 3.917$ Å, armchair tube $(3,3)$ with $D = 4.071$ Å, chiral tube $(4,2)$ with $D = 4.146$ Å and $(5,1)$ with $D = 4.362$ Å. As mentioned in section 1.2.2, each tube has cohesive energy which is governed by Eq. 1.4. In Fig. 3.7, we plotted the cohesive energy for tubes of $(n,0)$, $(n,1)$, $(n,2)$ and $(n,3)$, respectively. From the computed energetic models, we can see that among these four possible structures, $(5,0)$ is the only one which is energetically stable. In fact, there are also other two reasons to form $(5,0)$ zig-zag tubes in the AFI channels. The first reason is that the axial period of $(5,0)$ zig-zag tube is 4.3 Å which is almost the same of the period size of AFI channels along the crystal axial, AFI $c^* = 4.24$ Å. The consistence of their period is a very important factor for proving the existence of this tube. It is because atoms position of a material is dependent on its period. For example, if the period of the AFI channel is not equal to the period size of tube, then some carbon atoms from the tube may occupy a very close position of the atoms of AFI. However, it is absolutely an impossible case because there is a 1.7 Å carbon van
der Waals radius exists in every carbon structure material. For 0.42 nm-sized
diameter zig-zag tube, including addition twice of carbon van der Waals radius, there
is no extra space for filling any atom in the 7.3 Å diameter channels of AFI.
Therefore, only suitable period-sized nanotubes will exist in the AFI channels due to
a huge atomic force between the tubes and AFI.

Furthermore, we know that nanotubes are almost invariably closed at both ends
experimentally. Like fullerenes, all capped nanotubes must obey Eulers law. This
states that a hexagonal lattice of any size and shape can form a closed structure by
inclusion of precisely 12 pentagons. Therefore, any nanotube cap must contain 6
pentagons. Meanwhile, only (5,0) tube can be exactly capped by half of a C_{20}
fullerence because C_{20} has about 4.2Å diameter and has five carbon atoms in
z-direction which is the same with (5,0) zig-zag tubes. All above geometric structural
conditions also indicate that only (5,0) can exist in the channels of zeolite. As a result,
based on the structural and energetic consideration, we confirm that (5,0)
single-walled carbon nanotubes array in the channel of a zeolite single crystal.
Fig. 3.7 The bond-bending energies $E_{bend}$, the bond-binding energies $E_{bind}$ and the sum of them $E_C$ as functions of $1/n$ for the various types of tubule: (a) $(n,0)$, (b) $(n,1)$, (c) $(n,2)$, (d) $(n,3)$. 
CHAPTER 4

CONCLUSION and FUTURE WORKS

In this chapter, I would like to summarize and conclude the experimental results and some further studies on nanotubes will be suggested at last.

AlPO$_4$-5 AFI single crystal is used as a template for synthesizing single-walled nanotubes by pyrolyzing tripropylamine TPA in its 0.73 nm sized channels. Because of the space restriction of the channels and chemical structure of AFI, unique structure of single-walled nanotubes are one-dimensionally fabricated inside the zeolite. The SWNTs fabricated using this method are mono-sized (4.2 ± 0.2 Å), with single chirality of (5,0), and are well arrayed. This synthesis technique would play an essential role for experimental investigation of physical properties of carbon nanotubes.

By studying degree of polarization (DOP) of the samples as a function of pyrolysis, we observed that TPA molecules started to decompose into carbons at about 400°C, and the carbon atoms in the AFI channels re-arranged from random to orderly structure in the temperature region 400-650°C. When the temperature was over 650°C, nanotubes became amorphous graphite again due to carbonization. The
best temperature of the tube synthesis is about 530-580°C because this temperature range is far away from two critical temperature limits. One is the carbonization temperature at about 650°C and another is the starting point temperature, 490°C, of well-structured nanotubes.

Two important Raman peaks characterize the single-walled nanotubes structure. They are a single-walled nanotube Raman peak observed at about 1600cm\(^{-1}\) and a radial breathing mode (RBM) located at about 530cm\(^{-1}\), which is a fingerprint for the existence of the SWNTs. Furthermore, tube diameter dependence of RBM frequency indicates that these SWNTs have 0.42 nm diameter.

Meanwhile, single-walled nanotubes with 0.42 nm diameter are also observed in High Resolution Transmission Electron Microscopy (HRTEM) image. This result agrees with the Raman scattering experiment. We also find many graphite structure materials in the HRTEM image because tubes are unstable under electron beam.

Possible structure of this 0.42 nm-sized tube is recognized by three approaches: tubule energetic stability, periodic structure of AFI and the tube itself, and the capping property of the carbon nanotubes. We find that only (5,0) zig-zag tube can be
fabricated in the channels of AFI single crystals.

The discovery of buckminsterfullerenes itself was a wonderful accident, and nanotubes were an unanticipated by-product of the bulk synthesis of C_{60}. Other fruits of serendipity include single-walled nanotubes, inorganic fullerenes and carbon onions. Each of these developments has opened up a new area of enquiry, and frequently lead to further unexpected discoveries. Ultimately, the attempt to predict future directions in nanotube science is probably futile. We are still in the early days of the field, and many surprises undoubtedly lie ahead.
References


