Synthesis and Characterization of Ultra-small Single-walled Carbon Nanotubes Produced via Template Technique

by

ZHAI Jian Pang

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The Hong Kong University of Science and Technology
in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy
in the Department of Chemical Engineering

June 2007, Hong Kong
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This is to certify that I have examined the above PhD thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

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Synthesis and Characterization of Ultra-small Single-walled Carbon Nanotubes Produced via Template Technique

by
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ABSTRACT

Synthesis of ultra-small SWNTs using AlPO_4-5 (AFI) single as a template is a relatively new approach for carbon nanotubes synthesis (Tang, 1998). This method potentially has several advantages over the traditional synthesis and can be used to prepare SWNTs with pre-designed tube structures. The task of this thesis is to improve the density and study the formation mechanism of 0.4 nm SWNTs in AFI crystal channels, as well as produce and characterize even smaller SWNTs and iodine molecule arrays using AlPO_4-11 (AEL) single crystal as template.

I) To increase the density of 0.4 nm SWNTs in the AFI channels, two approaches are employed. The first approach is in-situ synthesis of AFI crystals with organic template that have a richer carbon content. Indirect evidence by micro-Raman spectra indicates that a higher filling factor of nanotubes can be reached by using carbon precursor of tetrapropylammonium hydroxide which contains 12 carbon atoms per molecule, in contrast to 9 carbon atoms of tripropylamine (TPA) precursor. The second approach is to generate negatively charged framework and Brønsted acid sites, by replacing P^{5+} using Si^{4+}, or replacing Al^{3+} using divalent metallic cations (Me^{2+}) such as Mn^{2+}, Mg^{2+}, and Co^{2+} in the AFI crystal lattices. The introduced metallic cation sites not only enhance the adsorption force of the channel walls to the guest molecules, but also play an important catalytic role in pyrolyzing the carbon precursor molecules.

II) We directly monitored the decomposition process of TPA in AlPO_4-5, and SAPO-5 crystals. It has been found that the TPA precursors exist in the as-synthesized crystals in three different forms: tripropylammonium fluoride, hydroxide and...
tripropylammonium cation compensating the negative charge of the framework. The latter is bonded to the framework by strong chemical interaction and its decomposition undergoes by a series of β-elimination reactions to give propylene and ammonia, with the stepwise formation of dipropylammonium and n-propylammonium cations. The 0.4 nm SWNTs filling density was found to be higher than that resulting from the carbon precursor of tripropylammonium fluoride and hydroxide, because of the strong adsorption force of the channel walls to pyrolyzate.

III) Mono-sized SWNTs with diameter only 0.3 nm are synthesized inside the channels of SAPO-11 crystals. The structure of this nanotube is confirmed by various techniques including Polarized optical microscopy, single crystal X-ray diffraction etc.. Micro-Raman spectra shows that two possible structure (2,2) and (3,0) nanotubes co-exist inside the channels of SAPO-11 crystals. Strong curvature effects induce instability of freestanding nanotubes. The electronic structure of the (2,2) and (3,0) nanotube are studied by polarized adsorption spectra and resonant Raman spectra.

IV) The iodine species are introduced into the channels of AEL single crystals by physical diffusion method. Due to size confinement of the AEL channels, iodine molecules can only be oriented in two directions, either along the long-axis of the elliptical channel or along the channel direction. Polarized absorption spectra and polarized Raman spectra have been investigated. They show that both Iodine molecular ribbon sheets and molecular chains exist inside the channels of AEL crystals. And the predominant structure will be altered by changing the iodine loading density.
Chapter 1

Introduction to Carbon Nanotubes

Until the late twentieth century, graphite and diamond were still the only known allotropes of carbon. Graphite appears as layered sheets of $sp^2$ bonded carbon atoms arranged in a hexagonal network, and is highly anisotropic. In contrast, diamond is composed of $sp^3$ bonded carbon atoms arranged in tetrahedrons, which is nearly isotropic. A new and unprecedented form of elemental carbon was discovered in 1985 and was termed Buckminsterfullerene or buckyball. A fullerene is a hollow sphere made up of sixty carbon atoms arranged in pentagons and hexagons, giving sufficient positive curvature for it to close into a sphere and showing an exceptional symmetry [1]. The discovery of the $C_{60}$ structure showed an intense renewal of interest for carbon science. As of the early twenty-first century, the chemical and physical properties of fullerenes are still under heavy study, in both pure and applied research labs [1-5]. As a consequence of fullerene research, carbon nanotubes emerged in 1991 [6]. These systems consist of graphitic sheets seamlessly wrapped to cylinders. Since then, a great deal of attention has been focused on these one-dimensional materials.

1.1 Discovery of Carbon Nanotubes

It appears that the first carbon filaments of nanometer dimensions were prepared in the 1970s by Morinobu Endo, as part of his PhD studies at the University of Orleans in France. He grew carbon fibers about 7 nm in dimension using a vapour-growth technique. Though these filaments were recognized as
nanotubes, they were not studied systematically [7]. It was not until 1991, Multiple-shell graphitic nanotubes with diameters in nanometer scale dimensions were first discovered by Iijima of the NEC laboratory in Tsukuba, Japan using High-Resolution Transmission Electron Microscopy (HRTEM) [6], who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes, of a type, which had never previously been observed. These nanotubes are typically composed of 2 to 50 concentric cylindrical shells, with diameters typically a few tens of nm and lengths in the order of several μm. Each shell has the structure of a rolled up graphene sheet with the $sp^2$ carbons forming a hexagonal lattice (see Fig. 1.1). A year later, Thomas Ebbesen and Pulickel Ajayan, [8, 9] also working for NEC in Tsukuba, developed a highly efficient way of making large quantities of these multi-walled nanotubes (MWNTs). This discovery opened the door for doing experiments on carbon nanotubes.

The discovery of MWNTs [6] has propelled a tremendous wave in the study of their novel properties and potential applications. Subsequently, Single-Walled Carbon Nanotubes (SWNTs) were fabricated using transition-metal such as Fe, Co, and Ni as catalysts by Iijima and his group at the NEC Laboratory and by Bethune and coworkers at the IBM Almaden laboratory [10, 11]. These findings were especially important because the SWNTs are more fundamental, and had been the basis for the large number of theoretical studies and predictions that preceded the experimental observation of SWNTs. The most striking of these theoretical developments was the prediction that the carbon nanotubes could be either semiconducting or metallic as a function of diameter and chirality [12-14].
1.2 Structure of carbon nanotubes

The structure of carbon nanotubes has been studied early by HRTEM and Scanning Tunneling Microscopy (STM) techniques [15, 16], yielding direct confirmation that the SWNTs is formed from a single atomic layer of crystalline graphite, called a graphene sheet. A multi walled carbon nanotube is basically a single walled tube with 1-50 more tubes around it, with an interlayer spacing of
0.34-0.36 nm that is close to the typical spacing of turbostratic graphite. Like graphite, nanotubes are comprised of interconnected six-member rings, or hexagons, of carbon atoms. These hexagons of carbon span the entire surface of a nanotube and are the source of many of the impressive qualities of nanotubes.

**Fig. 1.2:** The unrolled honeycomb lattice of nanotube. When we connect sites O and A, and B and C, a nanotube can be constructed. OA and OB define the chiral vector $C_h$ and the translation vector $T$ of the nanotube, respectively. The rectangle OACB defines the unit cell for the tube. The vector $R$ denotes a symmetry vector. The figure corresponds to $C_h = (4, 2)$, $d=d_R=2$, $T= (4, -5)$, $N= 28$, $R = (1,-1)$. 
The structure of a single-walled carbon nanotube can be described by so-called chiral vector, which is defined on the hexagonal lattice as \( C = n \mathbf{a}_1 + m \mathbf{a}_2 \), where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are unit vectors in the two dimensional hexagonal lattice, and \( n \) and \( m \) are integers. The chiral angle \( \theta \) between \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) is measured relative to the direction defined by \( \mathbf{a}_1 \). In Fig. 1.2 [17-19], a structure diagram has been constructed for \( (n, m) = (4, 2) \), and the unit cell of this nanotube is bounded by OACB. To form the nanotube, imagine that this cell is rolled up so that O meets A and B meets C, and the two ends are capped with half of a fullerene molecule. Different types of carbon nanotubes have different values of \( n \) and \( m \). The physical properties of nanotubes are strongly related to their structure. In other words, the properties of nanotubes are determined by their diameter and chiral angle, both of which depend on \( n \) and \( m \).

Fig. 1.3: Classification of carbon nanotubes: (a) Armchair tube (5,5), (b) Zigzag tube (9,0) and (c) Chiral tube (10,5). It can be seen that the orientation of the six-membered ring in the honeycomb lattice relative to the axis of the tube can be taken almost arbitrarily.
SWNTs chiralities can be divided into three categories. The spatial orientation of the hexagon with respect to the nanotube’s length is not fixed, resulting in three chiralities classifications of nanotubes – armchair, zigzag, and chiral. Armchair is formed when n=m and the chiral angle is 30°. Zigzag nanotubes have chiral vectors of the form (n, 0). All other nanotubes with chiral angle intermediate between 0° and 30° are known as chiral nanotubes. The names of armchair and zigzag arise from the shape of the cross-sectional ring. Fig. 1.3 schematically shows typical examples of these three kinds of nanotubes [19].

1.3 Synthesis

Since the first report of carbon nanotubes, this new class of carbon nanostructures has stimulated an intense research effort due to their high mechanical strength, unique electronic properties, and the possibility of building nanoscale molecular devices. Understanding these properties and exploring their potential applications have been a main driving force for this area. The full potential of nanotubes for applications will be realized until the growth of nanotubes can be optimized and well controlled. There are many methods to fabricate carbon nanotubes such as Arc discharge, Laser ablation and Chemical Vapor Deposition (CVD).

Arc discharge, or Arc-evaporation Synthesis, was the first method discovered and is still widely used for producing both MWNTs and SWNTs, but the growth product is not as pure as laser ablation. Initially, the carbon arc method was developed to produce C_{60} fullerenes. This method fabricates nanotubes through the arc-vaporization of two carbon rods placed end to end separated by approximately about 1mm. The chamber was first pumped and then filled with inert gas. Once the
DC voltage about 20 V is applied to the electrodes, plasma with temperature about 3700°C occurred. The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod. Carbon nanotubes can be obtained by controlling the growth conditions such as the pressure of inert gas in the discharge chamber and the arcing current. In the laser ablation process, a laser used to vaporize a graphite target held in a controlled atmosphere oven at temperatures near 1200°C. The target was placed in a tube-furnace heated to 1200°C. During laser ablation, a flow of inert gas was passed through the growth chamber to carry the grown nanotubes downstream to be collected on a cold finger.

The catalytic CVD involves heating a catalyst material to 773K to 1473K in a tube furnace, after that, a feed gas goes through the tube reactor for a period of time. Materials grown over the catalyst are collected upon cooling the system to ambient temperature. CVD is one of the slower methods of nanotubes growth. Carbon comes from the decomposition of a feed gas such as methane or ethylene. Decomposition of the feed gas occurs only at the catalyst sites, reducing amorphous carbon generated in the process. Decomposed carbon molecules then assemble into nanotubes at the catalyst nano-particle sites.

1.4 Micro-Raman spectra of SWNTs

Raman spectroscopy is a particular promising technique to obtain structural information including quality and diameter, as well as distinguishing between metallic and semiconducting SWNTs. This is because the Raman spectroscopy of carbon nanotubes has unique properties. Theoretically, it is anticipated that a SWNT exhibits more Raman-active modes than graphite does. The symmetry analysis for carbon nanotubes predicted that there are 15 or 16 Raman-active modes at \( k = 0 \) for a SWNT; the exact number depends on the chirality of the tube but is independent of
its diameter [19-21]. In general, the Raman spectra of SWNTs exhibit three main features: the radial breathing mode (RBM) frequency in the lowest energy is due to tubular vibrations along the radial direction; the defect lines (D line) in the middle energy range are due to disorder carbon, and graphite derived modes (G-bands) in the highest frequency region are due to the bond stretching vibrations.

RBM frequencies are observed in low frequency, in which all the carbon atoms on the tube surface vibrate in phase perpendicular to the tube axis, as if the tube is “breathing”. This mode is of \( A_{1g} \) symmetry for all nanotubes (see Fig. 1.4). They are in the silent region for graphite and other carbon materials except carbon nanotubes. The frequency of this mode has been used to assign \((n, m)\) indices to the nanotubes. This is because of the fact that the RBM frequencies and their scale are inversely proportional to the diameter. RBM frequencies are observed between 100 and 350 cm\(^{-1}\) for carbon nanotubes for diameter in the range \(0.7 \text{ nm} < d_t < 2 \text{ nm}\) [17].

**Fig. 1.4:** The calculated Raman mode atomic displacements, frequencies, and symmetries for those \((10, 10)\) nanotube modes which show strong Raman intensity. [Z. M. Li’s thesis].
D lines are at 1300 - 1350 cm\(^{-1}\). The behavior of the D-band Raman signals is complex, as the D-band originated from (1) double resonance, (2) one-phonon-emission, and (3) second-order Raman process in which one of the two scattering processes is an elastic scattering process due to a defect, and the other is a phonon emitting (or absorbing inelastic scattering process) [22].

The G-band in graphite involves an optical phonon mode between the two dissimilar carbon atoms A and B in the unit cell. The corresponding mode in SWNTs bears the same name. In contrast to the G-band in graphite, which exhibits one single Lorentzian peak at 1582 cm\(^{-1}\) related to tangential mode vibration of the C atoms. Several high frequency modes are roughly located near 1582 cm\(^{-1}\), due to the phonon wave vector confinement along the SWNT circumferential direction and due to symmetry-breaking effects associated with SWNT curvature. The G-band consists of modes of three symmetries: A\(_{1g}\), E\(_{1g}\) and E\(_{2g}\). Each of them is further split into two lines denoted by G\(^{+}\) and G\(^{-}\) because of curvature effect [23]. The G-band profile for a semiconducting SWNT is deconvolved into four intrinsic components with the following symmetry assignments: \(\omega_{G}^{+}[E_{2}(E_{2g})]\), \(\omega_{G}^{-}[A(A_{1g})+E_{1}(E_{1g})]\), \(\omega_{G}^{-}[A(A_{1g})+E_{1}(E_{1g})]\), and \(\omega_{G}^{+}[E_{2}(E_{2g})]\) [24].

1.5 Applications

Today, carbon nanotubes are driving scientific research. This field has several important directions in basic research, including electronic transport, field emission properties, electrochemistry, and mechanics. Furthermore, the perspectives for applications are very challenging and exciting. The main avenues of potential applications of carbon nanotubes are: conducting nanowires; field emitters (individual nanotube field emitters, large area flat panel displays); ultimate reinforcement fibers for composites (high strength, high aspect ratio, and high
thermal and chemical stability); nanotools (tips for Scanning Tunneling, Atomic Force) [25].

Field emission results from the tunneling of electrons from a metal tip into vacuum under application of a strong electric field. The electronic properties of carbon nanotubes are the most challenging to determine, because carbon nanotubes have the right combination of properties, such as nanometer size diameter, structural integrity, high electrical conductivity, and chemical stability, which make good electron emitters. Electron field emission from carbon nanotubes was first demonstrated in 1995 [26], and has since been studied intensively on various carbon nanotube materials. Compared to conventional emitters, carbon nanotubes exhibit a lower threshold electric field. The current-carrying capability and emission stability of the various carbon nanotubes, however, vary considerably depending on the fabrication process and synthesis conditions. Although carbon nanotube emitters show clear advantageous properties over conventional emitters in terms of threshold electrical field and current density, their emission site density (number of functioning emitters per unit area) is still too low for high resolution display applications.

The mechanical properties of nanotubes are nearly as extraordinary as their electronic properties. The carbon atoms of a single sheet of graphite form a planar honeycomb lattice in which each atom is connected via a strong chemical bond to three neighbour atoms. The basal-plane elastic modulus of graphite is one of the largest of any known material. For this reason, carbon nanotubes are expected to be the ultimate high-strength fibres. On the other hand, they have few or no defects, nanotubes especially SWNTs are stiff, tough, and strong. In measurements in which atomic-force microscopes were used to bend nanotubes, their elastic modulus, a
measure of stiffness, has turned out to be as high as 4 TPa, or about four times the value of larger carbon fibers now used as reinforcement in very lightweight and strong materials, and reported strengths 10 times higher than the strongest steel. Recent measurements of a nanotube’s tensile strength have shown that it, too, is high, about eight times that of carbon fibers. In addition, when the tubes are highly stressed, they buckle like drinking straws rather than break, a reversible process that allows them to bounce back into shape. These mechanical properties make nanotubes natural candidates for use as reinforcing elements in composite materials [25].

1.6 Ultra-small single-walled carbon nanotubes

1.6.1 Brief introduction to porous zeolite AlPO₄-n crystals

Zeolite is an inorganic porous material having a highly regular structure of pores and chambers that allows some molecules to pass through, and causes others to be either excluded, or broken down. It is in many ways, the inorganic equivalent of organic enzymes, many of which also have specific sized chambers that trap chemicals within their bodies, holding them where they either break down, or react with specific chemicals. The first zeolite, stilbite, was discovered by Cronstedt in 1756, who found that the mineral loses water rapidly on heating and thus seems to boil. The name "zeolite" comes from the Greek words zeo (to boil) and lithos (stone).

In the early 1980s, the aluminophosphate AlPO₄-n family of zeolites was first discovered and studied [27], where n is an integer indicating the structure type. Of the more than twenty AlPO₄ molecular sieves prepared so far, some have structures of known zeolites, but many have novel structures, even with such limited
variation in chemical composition. The overall composition of the AlPO₄-n molecular sieves is written as:

\[ xR \cdot Al_2O_3 \cdot 1.0(\pm 0.2)P_2O_5 \cdot yH_2O \]

where \( R \) is an organic amine or quaternary ammonium ion; the quantities \( x \) and \( y \) represent the amount of organic material and water that fills the pores of the crystal, respectively.

Zeolites have broad industrial applications as highly selective adsorbents, ion exchangers, and most importantly, catalysts of exceptionally high activity and selectivity in a wide range of reactions [28]. The possible fields of applications for zeolites have been extended greatly over the last years with the possibility of generating new supra-molecular structures by in situ inclusion of guest molecules into the pores of molecular sieves crystal. Since the AlPO₄-5 single crystal is optically transparent from ultraviolet to near infrared, electrically insulated and thermally stable up to 900°C, It has been the focus for the host-guest chemistry, especially with respect to optical applications [29-35].

1.6.2 Ultra-small SWNTs formed inside the channels of AlPO₄-5 single crystals

The carbon nanotubes can be synthesized by several standard processes, including arc-discharge, laser ablation, and chemical vapor deposition [6, 8, 36]. Using those methods, however, it is not easy to produce single-walled carbon nanotubes (SWNTs) with pre-designed tube structures. The lacks of purity and uniformity in diameter, chirality and their alignment have been a hindrance to explore intrinsic chemistry and physics as well as to develop nano-scaled device
applications of the novel electronic system. In 1996, a major breakthrough occurred when Smalley and coworkers at Rice University [36] successfully fabricated bundles of aligned SWNTs, with a small diameter distribution. In 1998, Tang’s group in Hong Kong University of Science and Technology synthesized ultra-thin, SWNTs with a diameter as small as 0.4 nm in the channels of AlPO₄-5 zeolite (structure code AFI) crystals [37-39]. These perfectly aligned 0.4 nm SWNTs provide a platform on which the experimental and theoretical studies can be carried out on the quasi-one-dimensional (1D) material system [40-43].

**Fig. 1.5:** (a) The framework structure of the AFI crystal viewed along the [001] direction. (b) Microscope view of typical SWNTs@SAPO-5 crystals: SAPO-5 single crystals without nanotubes (left), and with nanotubes imaged under the light polarized perpendicular to the tube direction (middle), and parallel to the tube direction (right). (c) Three possible nanotubes with diameter of 0.4 nm: (5,0), (4,2), and (3,3).
AlPO$_4$-5 framework is composed of alternating tetrahedral (AlO$_4$)$^-$ and (PO$_4$)$^+$, which form parallel open channels and packed in the hexagonal structure with space group P6cc. The inner diameter of the 12-ring channel is 0.73 nm. Organic template molecules in the channels were oriented in a head-tail manner along the c-axis [44]. Its framework structure viewed along the [001] (c-axis) direction is shown in Fig. 1.5(a). The ultra-small SWNTs were generated by pyrolyzing the carbon precursor in the channels of AFI crystals using a temperature programmable oven [37, 39]. The carbon-precursor contained AFI crystal is transparent in color (see Fig. 1.5(b), left). When it was gradually heated in a vacuum of $10^{-3}$ mbar at temperature up to 723 K, the carbon precursors were decomposed, and carbon nanotubes were formed.

**Fig. 1.6:** High-resolution transmission electron microscope image showing single-walled carbon nanotubes (indicated by T and large arrowheads) coexisting with graphite in raft-like stripes (G).
in the channels gradually, and the crystal turned its color to homogeneous black. The SWNTs-contained AFI crystals are highly optically anisotropic with strong optical absorption when the electric field of the incident beam is polarized parallel to the \(c\)-axis of the crystal. And it is almost transparent when the electric field \((E)\) of the incident light is perpendicular to the \(c\)-axis (see Fig. 1.5(b), middle and right) [42, 43]. There are only three possible structures for the 0.4 nm SWNTs: the zigzag \((5,0)\), the armchair \((3,3)\), and the chiral \((4,2)\), as schematically shown in Fig. 1.5(c) [45-48].

In order to provide direct evidence of the existence SWNTs using high-resolution TEM, the SWNT-containing AFI crystals were grounded into powder and then the SWNTs were extracted by dissolving the SWNTs@AFI crystals in HCl (30\%) acid. The SWNTs-contained solution was subsequently enriched and dispersed on a carbon lacy film for TEM investigation. Fig. 1.6 shows a typical TEM image of the specimens. The small pieces of highly curved, raft-like graphite strips marked by ‘G’ are products of collapse of 0.4 nm SWNTs. The spacing between neighboring parallel fringes of graphite is about 0.34 nm, which matches well with the \(\{002\}\) lattice plane spacing of graphite. By using the \(\{002\}\) spacing of graphite as an internal reference, the diameter of SWNTs paired dark fringes and marked by ‘T’ is about \(0.42 \pm 0.02\) nm [38, 49, 50].
References:


Chapter 2

Experimental Methods

In this chapter, the synthesis process of AlPO₄-5 (AFI) and AlPO₄-11 (AEL) single crystals, characterization methods used in this thesis will be described briefly. The description is helpful to the discussion on the experimental results.

2.1 Synthesis process of AlPO₄-5 and MeAPO-5 crystals

In the synthesis of AlPO₄-5, aluminum tri-isopropoxide [(iPrO)₃Al 99wt%] and phosphoric acid (H₃PO₄ 85wt.%) were used as aluminum and phosphorus sources, respectively. A solution of hydrogen fluoride was added, triethylamine ((CH₃CH₂)₃N, TEA 99wt %), tripropylamine ((CH₃CH₂CH₂)₃N, TPA 98wt %), tetrapropylammonium-hydroxide ((CH₃CH₂CH₂)₄NOH, TPAOH 20% in H₂O), and tetrabutylammonium hydroxide [(CH₃CH₂CH₂CH₂)₄NOH, TBAOH] were employed as an organic template, respectively. The gel mixture consisted of the following composition Al₂O₃: P₂O₅: (1.0~1.2) R: 1.2HF: 400H₂O, where R is the organic templates. The typical procedures were as follows: (1) the calculated amounts of aluminum source was first dissolved in distilled water, stirring for 14 hours; (2) followed by the dropwise addition phosphoric acid to the solution, stirring for 2 hours; (3) afterwards the organic amine was slowly added to the viscous aluminophosphate gel at room temperature, stirring for 2 hours; (4) subsequently, the aqueous HF solution was slowly dropped into the homogenous slurry, until the final PH was at 5~6, continuously stirring for 4~5 hours; (5) the gel was aged at
room temperature for 24 hours; (6) the slurry was then sealed in Teflon-lined stainless steel autoclaves and heated at 433K~ 473K under autogenous pressure for 24 ~ 48 hours; (7) after the reaction the autoclave were quench cooled in water. The solid products were filtered and washed with distilled water, and dried at 333K temperature. Fig. 2.1 shows the SEM image and optical micrograph of the AlPO₄-5 crystals.

![Fig. 2.1: (a) The SEM image of the AlPO₄-5 crystals; (b) The optical microscopic image of the AlPO₄-5 crystals.](image)
MeAPO-5 single crystals are synthesized using the same procedure as that of AlPO₄-5, with the exception of gel mixture composition \( x \text{Me}: 1.0\text{Al}_2\text{O}_3: 1.0\text{P}_2\text{O}_5: 1.2 \text{TPA}: 0.8\text{HF}: 800\text{H}_2\text{O} \), where \( x \) is the molar ratio of metal Me (Me = Si, Co, Mg, Mn, V, and Ti) to phosphorus.

2.2 Preparation of AlPO₄-11 crystals

2.2.1 Structure of the AlPO₄-11 crystals

AlPO₄-11 is one of the crystalline microporous aluminophosphates that first reported in 1982. It is built of alternating AlO₄ and PO₄ tetrahedral linking together via oxygen atoms to form a three-dimensional framework with a 1-D channel system of \( 4.4 \times 6.7\text{Å} \) [1-3]. Fig. 2.2(a) shows the framework viewed along [001] direction. As-grown crystals are transparent in color. Fig. 2.2(b) shows the optical microscopic image of the AEL single crystals.

The framework structures of AlPO₄-5 and AlPO₄-11 are closely related (see Fig. 2.3). The sheets of AlPO₄-5 are composed of 4-, 6- and 12-rings. Removal of a pair opposing 4-ring converts the 12-ring to 10-ring and generates the sheet found in AlPO₄-11. Whereas 4- and 6-rings alternate around the 12-ring channel of AlPO₄-5, two pair of 6-rings is adjacent around the 10-ring elliptical channel of AlPO₄-11 [4, 5].
Fig. 2.2: (a) The framework of an AEL crystal viewed along (001) direction; (b) The optical microscopic image of the AEL single crystal.
2.2.2 Synthesis of large optically clear AlPO₄-11 single crystals

A pure AlPO₄-11 crystal is optically transparent from ultraviolet to near infrared, is a good insulator, and thermally stable up to 1173 K. Hence nanomaterials accommodated in its channels can be probed both optically and electrically. Both for fundamental research and practical applications arising from the novel properties of these AlPO₄-11@guest nanostructures, synthesis of large-sized AlPO₄-11 crystals with high optical quality is essential. Several groups have reported growth methods of AlPO₄-11 [6], NiAPO-11[7], MnAPO-11 [8], MgAPO-11 [9] and CoAPO-11 [10] crystals. However, most of the AlPO₄-11 products synthesized previously were powders or nanocrystals of AlPO₄-11 have also been reported [11]. Chen et al., [12] reported that large MAPO-11 single crystals were obtained by introducing MgO into the reaction system of AlPO₄-11. The crystal size of MAPO-11 is about eight times that of AlPO₄-11. Compared with that of AlPO₄-11, the
The crystallization time of MAPO-11 is shortened greatly while the crystallinity is increased. As mentioned in chapter 2, SWNTs can be formed in a higher density in the SAPO-5 framework than that in AlPO4-5 framework. Thus, our work is focused on the synthesis of SAPO-11 crystals.

In our experiment, dipropylamine ((CH3CH2CH2)2NH, DPA 98wt %) is employed as an organic template. The gel mixture consisted of the following composition 0.03SiO2: Al2O3: P2O5: (2.0~2.2) DPA: 1.8HF: 400H2O. The typical procedures are similar with that of SAPO-5 crystals, with the exception of crystallization duration 48 h. The as-grown SAPO-11 crystals have a typical size of 150 μm × 60 μm × 40 μm.

2.3 Characterization methods

2.3.1 XRF spectra

When a primary X-ray excitation source from an X-ray tube or a radioactive source strikes a sample, the X-ray can either be absorbed by the atom or scattered through the material. The process in which an X-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "photoelectric effect." During this process, if the primary X-ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic X-ray whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The
process of emissions of characteristic x-rays is called "X-ray Fluorescence," or XRF. Analysis using X-ray fluorescence is called "X-ray Fluorescence Spectroscopy." In most cases the innermost K and L shells are involved in XRF detection. A typical X-ray spectrum from an irradiated sample will display multiple peaks of different intensities.

### 2.3.2 Mass spectrometry

Mass spectrometry is an analytical technique to measure the mass-to charge ratio (m/Z) of ions, it is most generally used to identify unknown compounds by the mass of the compound and /or fragments thereof. Different molecules have different masses, and this fact is used in a mass spectrometer to determine what molecules are present in a sample. As shown in figure 2.4, the gas species are broken down (ionized) into electrically charged particles, called ions, in ionization chamber the first part of the mass spectrometer. The volatile ions have specific molecular weights. They also have a charge, which means that they will be moved under the influence of an electric field. These ions are then sent into an ion acceleration chamber and passed through a slit in a metal sheet. A magnetic field is applied to the chamber, which pulls on each ion equally and deflects them (makes them curve instead of travelling straight) onto a detector. The lighter ions deflect further than the heavy ions because the force on each ion is equal but their masses are not (this is derived from the equation \( F = ma \) which states that if the force remains the same, the mass and acceleration are inversely proportional). The detector measures exactly how far each ion has been deflected, and from this measurement, the ion's 'mass to charge ratio' can be worked out. From this information it is possible to determine with a high level of certainty what the chemical composition of the original sample was.
2.3.3 Thermal analysis

Thermal analysis includes differential scanning calorimetry (DSC) and thermogravimetry (TG). DSC is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. TG is one of the oldest thermal analytical procedures and has been used extensively in the study of mass change of a substance (and/or its reaction product(s)) as a function of temperature whilst the substance is subjected to a controlled temperature program. The principle of the thermal analyzer (STA 449 C Jupiter) is shown in figure 2.5.
In the most popular DSC design, two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path. One pan is for holding the sample, the other one is empty serving as the reference. The computer controls the furnace after heating rate and temperature range are set. The computer makes absolutely sure that the heating rate stays exactly the same throughout the experiment. When the samples melt, they must absorb heat. Remember melting is a first order transition. This means that the furnace is going to have to put additional heat into the sample in order to melt both the crystals and keep the temperature rising at the same rate as that of the reference pan. These are techniques by which the difference in heat flow to or from a sample and to or from a reference is monitored as a function of temperature or time, while the sample is subjected to a controlled temperature program. The DSC curves can provide us the information on specific heat, melting temperatures, transition enthalpies, phase

**Fig. 2.5:** The configuration of a thermal analysis.
transformations, phase diagrams, crystallization temperatures, degree of crystallinity, glass transition temperatures, decomposition effects, reaction kinetics, purity determination, while TG curves provide information on mass changes, decomposition temperatures, dehydroxilation, corrosion/oxidation, thermal stability, reduction studies, composition, reaction kinetics, purity determination.

2.3.4 FTIR spectra

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of various infrared light wavelengths by the material of interest. In a molecule, the atoms are not held rigidly apart. Instead they can move, as if they are attached by a spring of equilibrium separation $R_e$. This bond can either bend or stretch. If the bond is subjected to infrared radiation of a specific frequency ($300 - 4000\text{cm}^{-1}$), it will absorb the energy, and the bond will move from the lowest vibrational state, to the next highest. Chemical bonds absorb infrared energy at specific frequencies (or wavelengths). Thus, the basic structure of compounds can be determined by the spectral locations of their IR absorptions. The plot of a compound's IR transmission vs. frequency is its "fingerprint", which when compared to reference spectra identifies the material.

2.3.5 Micro-Raman spectra

Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules. The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations. Typically, in Raman spectroscopy high intensity laser radiation with
wavelengths in either the visible or near-infrared regions of the spectrum is passed through a sample. Photons from the laser beam are absorbed by the molecules, exciting them to a virtual energy state. If the molecules relax back to the vibrational state that they started in, the reemitted photon has the same energy as the original photon. This leads to scattering of the laser light, but with no change in energy between the incoming photons and the reemitted/scattered photons. This type of scattering is known as Rayleigh scattering. However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is the termed the Stoke scattering. It arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule’s electric field. In quantum mechanics, the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10^{-14} seconds or less. According to the Boltzmann population of states, a small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy, which is anti-Stoke scattering. The virtual state description of scattering is shown in Fig. 2.6(a).

Raman spectroscopy is conventionally performed with green, red, or near-infrared lasers. The wavelengths are below the first electronic transitions of most molecules, as summed by scattering theory. In resonance Raman spectroscopy, the energy of the incoming laser energy is adjusted such that it or the scattered light
coincide with an electronic transition of the molecule or crystal (see Fig. 2.6(b)). When the frequency of the laser beam is tuned to be near an electronic transition (resonance), the vibrational modes associated with that particular transition exhibit a greatly increased Raman scattering intensity. This resonance enhancement or resonance Raman effect can be quite useful [13].

Fig. 2.6: (a) Energy level diagram for non-resonant Raman scattering. (b) Energy level diagram for resonant Raman scattering.

2.3.6 Polarized adsorption

Absorption occurs when a photon interacts with the atom/molecule and causes a transition from a state of lower energy to a state of higher energy. In order
to easily handle the small crystal for optical measurements, the guest@AEL crystal was horizontally fixed using epoxy resin inside a copper ring (500 μm in diameter). After the resin became hardened, the sample was polished mechanically and then using Ar-ion milling to a thickness of about 10 μm. Transmission spectra were measured at room temperature, using a xenon incandescent lamp as a light source. The incident polarized light was focused onto the sample by a reflecting microscope objective, and the transmitted light was collected by another reflecting objective coupled with an optical fiber. The signals were dispersed by an Acton 275-mm single grating monochromator before it was sent to the detector. Fig. 2.7 schematically shows the experimental setup.

![Experimental setup for polarized optical adsorption.](image)

**Fig. 2.7:** Experimental setup for polarized optical adsorption.
References:


Chapter 3

Quality Improvement of 0.4 nm Single-walled Carbon Nanotubes inside the Channels of AFI Crystals

In this chapter, we report our recent studies on improvement in filling density of the 0.4 nm single-walled carbon nanotubes (SWNTs) in the channels of AlPO₄-5 (AFI) crystals, and consequently, decreasing the density of the vacancy defects of the nanotubes. In what follows, we present the effect of various organic templates / carbon precursors on the filling density of the SWNTs in the AFI channels in section 3.1. Indirect evidences by micro-Raman spectra and TG curves indicated that a higher filling density of nanotubes can be reached by using carbon precursor of tetrapropylammonium hydroxide which contains 12 carbon atoms per unit cell, in contrast to 9 carbon atoms of tripropylamine precursor \[1\]. The effect of channel-wall decoration using different metal cations on the filling density of nanotubes is discussed in section 3.2. The incorporations of metal cations (Mn, Mg, Co, and Si) into AFI framework give rise to formation of negatively charged frameworks and Brønsted acid sites, which play an important catalytic role in the carbonization of hydrocarbon molecules as well as in formation of SWNTs \[2, 3\]. In section 3.3, we report the effect of substituted silicon concentration in AlPO₄-5 crystal lattices on the filling density of SWNTs.
3.1 Effects of carbon precursors on the filling density of SWNTs in the AFI channels

In our previous work, the 0.4 nm SWNTs were synthesized inside the channels of AlPO₄-5 single crystals by pyrolyzing hydrocarbon molecules of TPA which were incorporated in the channels during the synthesis of the AFI crystals. There exists one TPA molecule (9 carbon atoms) per unit cell of the AFI framework. The 9 carbon atoms in a unit cell are not sufficient to form a SWNT with perfect structure. In other words, the nanotubes generated using TPA as precursor might be rich in structural defects and discontinuity in the channels with a low filling factor. From a fundamental point of view, the interest in such quasi-one-dimensional (1D) material system lies on its structural perfection and high filling density in the pores. The quality of nanotube samples is crucial in exploring their novel electronic properties. One approach to improve the sample quality is the in-situ synthesis of AlPO₄-5 crystals with organic templates that have richer carbon content. An organic precursor with higher carbon content should be more facile to the formation of carbon nanotubes, and should thereby improve SWNTs’ filling density.

This work aims to study the effect of carbon precursors on filling density of the SWNTs inside the channels of AlPO₄-5 crystals. To see how the carbon sources affect the filling density of carbon nanotubes, four carbon precursors, which have different number of carbon atoms per molecule, were used in the synthesis of SWNTs. They are triethylamine ((CH₃CH₂)₃N, TEA), tripropylamine ((CH₃CH₂CH₂)₃N, TPA), tetrapropylammonium-hydroxide ((CH₃CH₂CH₂)₄NOH, TPAOH), and tetrabutylammonium hydroxide [(CH₃CH₂CH₂CH₂)₄NOH, TBAOH], which contains 6, 9, 12 and 16 carbon atoms per molecule as shown in Fig. 3.1, respectively.
The as-grown AlPO₄-5 crystals have a typical size of 500µm×50µm×50µm.

The crystallinity of as-synthesized samples has been checked using powder X-ray diffraction (Philips PW1830 diffractometer). The AlPO₄-5 crystals with various organic templates showed the same X-ray diffraction pattern as that of pure AFI crystals (see Fig. 3.2). SWNTs are produced by pyrolyzing the carbon precursor templates in rising temperature steps. The detailed synthesis process of ultra-small SWNTs inside the channels of the AlPO₄-5 crystals was carried out using the method reported previously [1, 2].

**Fig. 3.1:** Molecular structure of the various carbon precursors: TEA, TPA, TPAOH and TBAOH.
Fig. 3.2: X-ray diffraction patterns of the AlPO₄-5 crystals containing various carbon precursors.

The AlPO₄-5 crystals containing carbon precursors are transparent in color (see Fig. 3.3 left). All crystals are of regular hexagonal crystal shape and have a good morphology, indicating high crystalline quality. We put AlPO₄-5 crystals containing various carbon precursors into a programmable oven. When gradually heated in a vacuum of 10⁻³ mbar up to a temperature of 853 K, the crystals turned into homogeneous black with strong optical anisotropy [4-6]. From the optical anisotropy and the black color, we can qualitatively estimate the quality of the SWNTs formed in the channels. In the two panels on the right side of Fig. 3.3 (middle, and right), we show optical microscope images of the SWNT@AlPO₄-5
single crystals. These images were taken by inserting a polarizer (vertically polarized) in the optical path. For the $E//c$ configuration, we see that for those samples produced using carbon precursors which contained more carbon atoms (from TEA to TPAOH), the color is darker and more uniform. This indicates that the filling density of the SWNTs is improved. However, for the sample with TBAOH as the carbon precursor, though the number of carbon atoms per molecule is larger than all the other precursors, the produced SWNT@AlPO$_4$-5 crystals show less anisotropy with a relative diluted black color, implying lower density of SWNTs.

**Fig. 3.3:** AlPO$_4$-5 single crystal without SWNTs (left), images taken under the light polarized perpendicular to the tube direction (middle), and under the light polarized parallel to the tube direction (right).
Fig. 3.4: Raman spectra of the SWNTs produced using various carbon precursors.

A significant difference of the SWNTs formed inside the channels of AlPO₄-5 crystals can be evidenced by the Raman spectra. Fig. 3.4 shows typical Raman spectra of the 0.4 nm SWNTs formed in AlPO₄-5 crystals using different carbon precursors. In general, the Raman spectra exhibit three main features: the radial breathing mode (RBM) in the low frequency region (400-600 cm⁻¹) due to tubular vibrations along the radial direction. In particular, the Raman lines at 510 and 550 cm⁻¹ are attributed to the $A_{1g}$ RBM of the chiral (4, 2) nanotubes and the zigzag (5, 0)
nanotubes, respectively [7-9]; the $D$ bands in the intermediate frequency region (1200-1500 cm$^{-1}$) due to disordered carbons; and tangential $G$ bands in the high frequency region (1500-1620 cm$^{-1}$) due to the bond stretching vibrations. As the RBM vibrations are specific to the tubular structure, and the $G$-band is common structure for graphitic carbon materials. Not only nanotubes, but also other type of graphites structure present in AlPO$_4$-5 crystals, which contribute to the $G$-band and $D$-band. It is qualitatively to say more carbon nanotubes are generated when RBM mode is higher for a carbon material assembly. Thus, we use the relative ratio of the RBM to the $G$-band ($I_{RBM}/I_G$) as a measure of tubular carbon structure contained in the AFI channels. Larger value of $I_{RBM}/I_G$ implies higher filling density of carbon nanotubes. As can be seen in Fig. 3.4, the relative intensity of the RBM bands at 510 cm$^{-1}$ and 550 cm$^{-1}$ are obviously enhanced with increase of the carbon numbers per precursor molecule (from TEA to TPAOH). On the other hand, the line width of the $G$-band near 1600 cm$^{-1}$ became narrow upon the increase of carbon atoms per molecule (from TPA to TPAOH), indicating that hydrocarbon molecules are well graphitized in the channels. However, further increase of the carbon content leads to a decrease in the relative RBM intensity, when TBAOH was adopted as carbon precursor. The RBMs of the SWNTs generated from TEA and TBAOH are almost undetectable from the background noise. We thus conclude that TPAOH is superior to either TEA or TPA as the carbon precursor for the growth of the 0.4 nm SWNTs.

Fig. 3.5(a) shows the TG curves of the SWNT@AlPO$_4$-5 crystals grown using different carbon precursors. The weight loss in the temperature region from 320 K to 400 K is due to the moisture desorption. Assuming that all the AlPO$_4$-5 crystals channels are saturated with SWNTs and water, then a larger weight loss of water implies a lower filling density of SWNTs inside the channels. In comparison
with TEA, TPA, and TBAOH, the weight loss of water in the sample prepared using TPAOH as carbon precursor (see the inset) is relatively low, indicating a higher filling fraction of the SWNTs in this sample. To study the effect of carbon precursors on the filling density of the SWNTs in the channels of AlPO_4-5 crystals under the same synthesis condition, it is important to know the initial loading density of respective carbon precursors inside the channels. We have traced the gravimetric change of AlPO_4-5 crystals containing various carbon precursors during heating.

As shown in Fig. 3.5(b). The common TG curve features of AlPO_4-5 crystals with different carbon precursors are similar to each other. They exhibit two main features: the weight loss in the regime from 320 to 400 K is due to the moisture desorption, and the loss in the region from 483 to 800 K is due to the decomposition of carbon precursors. The signal becomes flattened when the sample is heated to above 800 K, indicating complete decomposition of hydrocarbon precursors. The channels of an as-grown AlPO_4-5 crystal are fully occupied by crystal water as well as hydrocarbon molecules. Thus the weight loss of water is an indicator of the carbon precursors loading density; more weight loss of water indicates less loading density of carbon precursors. Not surprisingly, the weight loss of AlPO_4-5 crystals due to the moisture desorption decreased with increasing initial carbon content in carbon precursors (from TEA to TPAOH). The exception is again TBAOH. This can be due to the fact that the molecular size of TBAOH is so big that the lattice matching between TBAOH and AlPO_4-5 unit cell is not perfect, leading to increased inter-molecular space. The mismatch results in even lower loading density, in comparison with the well-fitted molecules of TAP and TPAOH. The inset to Fig. 3.5(b) shows the TG curve of TPA. As a reference, we show the corresponding
curves of TEA and TPAOH inside the channels of AlPO$_4$-5 crystals. It is seen that the mass loss of carbon precursors increased with increasing internal carbon content (in carbon precursors), due to the higher loading density.

**Fig. 3.5:** TG curves measured at temperatures ranging from 273 K to 873K for: (a) SWNTs@ AlPO$_4$-5 crystals using various organic templates as carbon precursors; (b) AlPO$_4$-5 crystals with various organic templates inside the channels.
After carefully taking the balance between the content of carbons in the precursor and the molecular size and channel size, we found the best-matching carbon precursor for the fabrication of 0.4 nm SWNTs is Tetrapropylammonium-hydroxide. The filling density as well as the structural quality of SWNTs can indeed be improved by using proper precursors.

3.2 Effects of metal cations on the formation of SWNTs

3.2.1 Effects of metal cations on the filling density of SWNTs

As the AlPO$_4$-5 framework is relatively inert chemically, the adsorption of the guest molecules (to the channel wall) is weak. As a result, a significant amount of hydrocarbon guest molecules can escape from the channels during pyrolysis process. The remaining carbon atoms are insufficient in number to form continuous carbon nanotubes. The density of the SWNTs in the AlPO$_4$-5 matrix is thus low. Also, the SWNTs formed inside the channels usually have a large density of atomic defects, as evidenced by the hopping electrical conduction along the c-axis. The flexibility of AlPO$_4$-5 crystal in its ability leads to substitute other elements into its framework. Incorporation of metal cations (Mn, Mg, Co) and Si gives rise to formation of negatively charged frameworks and Brønsted acid sites [10, 11]. These frameworks thus play an important catalytic role in the pyrolysis and conversion of the organic molecules to SWNTs within the crystal channels. It is shown that the MeAPO-5 single crystals have a higher density of SWNTs than those crystals without the metal cations. In this section, we study the effect of metal cations on the formation of SWNTs.
To see how the metal cations affect the filling density of carbon nanotubes, six metal cations were incorporated into the frameworks of AlPO_4-5 crystals during the crystals growth process using hydrothermal method. They are Si^{4+}, Mg^{2+}, Mn^{2+}, Co^{2+}, V^{6+}, and Ti^{4+}. MeAPO-5 single crystals are synthesized using the same procedure as that of AlPO_4-5, with the exception of gel mixture composition 1.0Al_2O_3: 1.0P_2O_5: 1.2 TPA: 0.8HF: 800H_2O, where x is the molar ratio of metal Me (Me = Si, Co, Mg, Mn, V, and Ti) to phosphorus. The left panel of Fig. 3.7 shows optical microscopic image of as-grown MeAPO-5 single crystals substituted with carbon precursor TPA.

**Fig. 3.6:** X-ray diffraction patterns of the MeAPO-5 crystals containing carbon precursor TPA.
various metal elements. All crystals are of regular hexagonal crystal shape and have a good morphology, indicating high crystalline quality. Confirmed by X-ray diffraction analysis, these MeAPO-5 crystals are of the same structure as the AFI (see Fig. 3.6). Thus structural imperfections, potentially caused by the incorporation of metal ions into the AFI framework, can be excluded. The composition of the crystals was determined by X-ray fluorescence (XRF) using element analyzer JSX-3201Z. Table 3.1 shows the composition of Me/P ratio in the crystal. Typical Me/P ratio ranges from 0.005 to 0.014, less than one half of that in the gel composition, indicating that not all metal ions in the gel were incorporated in the framework.

**Table 3.1:** Composition of the samples as measured by XRF

<table>
<thead>
<tr>
<th>Sample</th>
<th>Me/P Ratio (gel)</th>
<th>Chemical analysis (crystal) Me/P ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAPO-5</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>VAPO-5</td>
<td>0.03</td>
<td>0.011</td>
</tr>
<tr>
<td>AlPO4-5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MnAPO-5</td>
<td>0.03</td>
<td>0.011</td>
</tr>
<tr>
<td>MgAPO-5</td>
<td>0.07</td>
<td>0.014</td>
</tr>
<tr>
<td>CoAPO-5</td>
<td>0.07</td>
<td>0.009</td>
</tr>
<tr>
<td>SAPO-5</td>
<td>0.03</td>
<td>0.008</td>
</tr>
</tbody>
</table>

The TPA-contained MeAPO-5 crystals are transparent. When gradually heated in a vacuum of $10^{-3}$ mbar at temperature up to 853 K, the crystal color turned to black. In the right panel of Fig. 3.7, we show the optical microscope images of SWNTs@MeAPO-5 crystals. These images were taken by inserting a polarizer (vertically polarized) in the optical path, thus vertically aligned crystals become
opaque. As mentioned above, the color of crystals is an indicator of the nanotubes loading density; darker color indicates higher filling density of the SWNTs inside the channels of AFI crystals. Comparing with VAPO-5, TiAPO-5, and AlPO₄-5 crystals, the color of MnAPO-5, MgAPO-5, CoAPO-5, and SAPO-5 single crystals are darker and more uniform. It indicates that the filling density of SWNTs has been noticeably increased.

**Fig. 3.7:** MeAPO-5 crystals viewed under the microscope. On the left are the crystals with the organic precursor. In the middle and on the right are the crystals with SWNTs inside the channels. Electric field (E) polarization of the viewing light is as indicated.
A significant difference of the SWNTs formed in the MeAPO-5 crystals can also be evidenced by the Raman spectra. Fig. 3.8 shows the Raman spectra of the SWNTs fabricated in the channels of MeAPO-5 single crystals. We use the relative ratio of the RBM to the G-band \( \frac{I_{RBM}}{I_G} \) as a measure of tubular carbon structure contained in the AFI channels. Compared to VAPO-5, TiAPO-5, and AlPO4-5 crystals, the \( \frac{I_{RBM}}{I_G} \) ratios in MnAPO-5, MgAPO-5, CoAPO-5 and SAPO-5 crystals exhibit sharp increases, indicating a higher density of SWNTs in these crystals.

**Fig. 3.8:** Raman spectra of the SWNTs fabricated in the channels of MeAPO-5 single crystals: (a) SWNTs@SAPO-5, (b) SWNTs@CoAPO-5, (c) SWNTs@MgAPO-5, (d) SWNTs@MnAPO-5, (e) SWNTs@AlPO4-5, (f) SWNTs@TiAPO-5, (g) SWNTs@VAPO-5.
In order to study the catalytic effect of various metal cations on the TPA decomposition process, we measured Fourier Transform Infrared Spectroscopy (FTIR) spectra of the TPA@AFI crystals during pyrolysis process, in the temperature range of 300 K ~ 873 K. Fig. 3.9 shows the FTIR spectra of the TPA-containing CoAPO-5 crystals (right) as a function of pyrolysis temperature. As a reference, we also show the corresponding spectra of the TPA-contained AlPO$_4$-5 crystals in the left panel. At room temperature (300 K), the two spectra are generally similar: overtones and their combinations of Al-O-P vibrations of the AFI framework in the frequency region of 2000-2600 cm$^{-1}$, vibrations of the TPA molecules in the frequency region of 2600-3400 cm$^{-1}$, and the O-H stretching.

**Fig. 3.9:** Results of FTIR measurements from room temperature to 873 K for AlPO$_4$-5 and CoAPO-5.

In order to study the catalytic effect of various metal cations on the TPA decomposition process, we measured Fourier Transform Infrared Spectroscopy (FTIR) spectra of the TPA@AFI crystals during pyrolysis process, in the temperature range of 300 K ~ 873 K. Fig. 3.9 shows the FTIR spectra of the TPA-containing CoAPO-5 crystals (right) as a function of pyrolysis temperature. As a reference, we also show the corresponding spectra of the TPA-contained AlPO$_4$-5 crystals in the left panel. At room temperature (300 K), the two spectra are generally similar: overtones and their combinations of Al-O-P vibrations of the AFI framework in the frequency region of 2000-2600 cm$^{-1}$, vibrations of the TPA molecules in the frequency region of 2600-3400 cm$^{-1}$, and the O-H stretching.
vibration of the physisorbed water in the frequency region of 3400-3700 cm\(^{-1}\) [12, 13].

Fig. 3.10: Results of FTIR measurements from room temperature to 873 K for VAPO-5 and MgAPO-5.

With increasing temperature, the relative intensity of the O-H band weakens, and becomes undetectable at 573 K. We thus conclude that all water is desorbed at this temperature. The sharp lines at 3180 and 3243 cm\(^{-1}\) are due to the vibrations of N-H. With still increasing temperature, the signals of the N-H vibrations become weaker and finally undetectable when the sample is heated above 673 K, indicating that the propylene (C\(_6\)H\(_6\)) or its smaller oligomers have been released from the TPA molecules. The carbonization process is evidenced by the continuous weakening of
the C-H vibration signals at 2886 and 2945 cm\(^{-1}\). It is worth pointing out that, in the AlPO\(_4\)-5 crystals, the C-H absorption peaks are still significant even at 873 K, indicating that the hydrocarbon molecules have not completely carbonized even at this temperature. In contrast, the C-H absorption peaks disappeared at 823 K in the CoAPO-5 crystals. This fact indicates that the Co-site in the CoAPO-5 framework plays a catalytic role in pyrolyzing the TPA molecules.

Fig. 3.11: Results of FTIR measurements from room temperature to 873 K for TiAPO-5 and MnAPO-5.

To further clarify the nature of the different metal substitutions responsible for the catalytic effect, the decomposition processes of the TPA molecules in TiAPO-5, VAPO-5, MnAPO-5, MgAPO-5 crystals have been analyzed using the FTIR spectra. The results are shown in Figs. 3.10 and 3.11. It is seen from the
figures that the C-H absorption peaks are still seen at 873 K in VAPO-5 and TiAPO-5 crystals. In contrast, the same peaks vanished completely at a lower temperature of 823 K in MnAPO-5, MgAPO-5, and SAPO-5 crystals. The data of SAPO-5 can be found in reference [2]. These results are fully consistent with the thesis discussed previously, i.e., the Brønsted acid sites are generated when a $P^{5+}$ is replaced by a $Si^{4+}$, or when $Al^{3+}$ is replaced by divalent cations $Mn^{2+}$, $Mg^{2+}$, and $Co^{2+}$; thus catalytically accelerating the decomposition of TPA. These effects are not obvious when the substitution is positive charged, e.g., substitution of $Al^{3+}$ by $V^{5+}$.

**Fig. 3.12**: The DSC curves in the range of 273 ~873 K for: (a) SAPO-5, (b) CoAPO-5, (c) MgAPO-5, (d) MnAPO-5, (e) AlPO4-5, (f) TiAPO-5, (g) VAPO-5 single crystals with TPA organic template inside the channels.
An alternative tool of probing the carbonization process of organic molecules TPA in the channels of AlPO₄-5 and MeAPO-5 crystals is DSC, which measures the amount of energy absorbed or released by a sample when it is heated and thus provides quantitative and qualitative data on endothermic (heat of absorption) and exothermic (heat of evolution) processes. To study the decomposition process of TPA and the formation process of SWNTs inside the channels of AlPO₄-5 and MeAPO-5 crystals, we have monitored the pyrolysis of TPA in the temperature range of 273 K – 873 K by the DSC. The results were shown in Fig. 3.12. Three endothermic peaks and one exothermic peak are seen in the DSC spectra: the endothermic peak at 330 K is assigned to desorption of water from the AFI matrix, and the peaks near 532 K (marked by solid square) and 608 K (marked by solid circle) are due to the breaking of C-N bonds of TPA. Subsequently, the endothermic peak at 673 K (marked by open square) is attributed to the breaking of C-H bonds, and the exothermic peak at 697 K (marked by open circle) is due to the formation of ordered structures with low energy – ultra-small SWNTs. Compared to the AlPO₄-5, TiAPO-5, and VAPO-5 crystals, the C-H endothermic peaks in MnAPO-5, MgAPO-5, CoAPO-5, and SAPO-5 crystals are slightly shifted to lower-temperature side, owing to the catalyst role of negative charged framework and the Brønsted sites on the channel walls. While the exothermic peaks are significantly shifted to lower temperatures, indicating the nanotubes formation energy in these crystal matrix to be notably decreased. It should be pointed out that the ultra-small SWNTs can not be formed until enough C-H bonds in carbon dimers and trimers (C₃H₆ or its smaller oligomers) are broken. The formation of SWNTs gives rise to the observed exothermic peaks in MnAPO-5, MgAPO-5, CoAPO-5, and SAPO-5 at above 725 K. In contrast, no exothermic
peaks can be observed for VAPO-5, VAPO-5, and AlPO₄-5 crystals, presumably due to the low adsorption potential of the channel walls so that most of C₆H₆ and its smaller oligomers were desorbed from the channels at temperatures up 725 K.

![Graph showing TG curves for AlPO₄-5 and MeAPO-5 crystals](image)

**Fig. 3.13:** The TG curves in the range of 273 K~873K for MeAPO-5 single crystals with TPA organic template inside the channels.

To study the adsorption effect of AlPO₄-5 and MeAPO-5 crystals, we have traced the gravimetric change of AlPO₄-5 and MeAPO-5 crystals during heating by the thermogravimetry (TG). Fig. 3.13 shows the measured TG curves. The general features of the TG curve of AlPO₄-5 are similar to that of the MeAPO-5 crystals. The TG curve exhibits two main features: the weight loss of AlPO₄-5 crystals in the temperature region from 320 K to 400 K due to the moisture desorption, and the loss
in the region from 483 K to 873 K due to the decomposition of TPA. The signal becomes flattened when the sample is heated at above 800 K. Compared with MeAPO-5 crystal, the weight loss of AlPO$_4$-5 crystal due to the moisture desorption is relatively low (see inset (a)). This can be explained as follows. Various metal cations are incorporated into the AFI framework by substituting Al$^{3+}$ or P$^{5+}$ to yield MeAPO-5 crystals, which leads to a locally charged framework. In order to keep the framework neutral, H$^+$ (if P$^{5+}$ replaced by Si$^{4+}$, or Al$^{3+}$ replaced by Co$^{2+}$, Mn$^{2+}$ or Mg$^{2+}$) or F$^-$ (if Al$^{3+}$ replaced by V$^{5+}$ or Ti$^{4+}$) have to accompany the metal ions, forming an electric dipole. The adsorption force on the channel walls of the MeAPO-5 crystals is hence significantly increased, leading to more water being adsorbed inside the framework in the pores of MeAPO-5 crystals. As a result, the weight loss of MeAPO-5 crystals is higher than that of the AlPO$_4$-5 crystals. With increasing temperature, the weight of TPA-containing AlPO$_4$-5 and MeAPO-5 crystals begins to decrease notably above 483 K. The decomposition of TPA molecules results in the successive release of propylene or its smaller oligomers molecules. These C$_6$H$_6$ and its smaller oligomers can either be carbonized in the channels or desorbed from the channels. The number of carbon atoms which can be kept inside the channels is determined by the competition between these two processes of carbonization and desorption. Stronger the channel adsorption force, less the desorption during the pyrolysis process. Inset (b) shows the TG curve of the TPA inside the channels of AlPO$_4$-5 crystal. As a reference, we show the corresponding curves of the TPA inside the channels of SAPO-5 and TiAPO-5 crystals. It is seen that the mass loss for SAPO-5 crystal is less than that of TiAPO-5 and AlPO$_4$-5, indicating the density of SWNTs in SAPO-5 crystal to be higher. Also,
the mass losses for MnAPO-5, MgAPO-5, and CoAPO-5 crystals are much smaller compared to that of VAPO-5 and AlPO4-5 crystals.

Table 3.2: Calculated heat of formation for tube in MeAPO-5 (unit: eV)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Formation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlPO4-5</td>
<td>0.650</td>
</tr>
<tr>
<td>SAPO-5</td>
<td>−1.050</td>
</tr>
<tr>
<td>CoAPO-5</td>
<td>0.024</td>
</tr>
<tr>
<td>MgAPO-5</td>
<td>−1.320</td>
</tr>
<tr>
<td>MnAPO-5</td>
<td>0.340</td>
</tr>
<tr>
<td>VAPO-5</td>
<td>0.480</td>
</tr>
</tbody>
</table>

More important, the incorporations of Si4+, Co2+, Mg2+, and Mg2+ into the framework are also favorable to the formation of nanotubes inside the channels. The formation energies of SWNTs inside the AlPO4-5 and MeAPO-5 crystals channels have been calculated using a first-principles pseudo potential approach. As done previously [14], a supercell geometry is adopted in which the (5,0) tubes are confined inside the channels, arranged in a hexagonal array. There are 112 atoms in the supercell in which 72 atoms are from the AlPO4-5 unit cell (Al12P12O48) and others from the double unit cell of the tube. In the MeAPO-5 unit cell, a P5+ is replaced by a Si4+, or an Al3+ is replaced by Mn2+, Mg2+, Co2+, Ti4+, and V5+, which corresponds a stoichiometric ratio Me/P (Si/Al) = 8.3%. The formation energy $H$ is defined as:
\[ H = E_{\text{SWCN@MeAPO-5}} - E_{\text{SWCN}} - E_{\text{MeAPO-5}}, \]

where \( E_{\text{SWCN@MeAPO-5}} \) is the total energy of nanotube-contained MeAPO-5 crystal, \( E_{\text{SWCN}} \) is the total energy of the (5,0) tube, and \( E_{\text{MeAPO-5}} \) is the total energy of the MeAPO-5 crystal. All energies are calculated with the same supercell parameters. The results are summarized in Table 3.2. We see that the formation energies of SWNTs in MnAPO-5, MgAPO-5, CoAPO-5, and SAPO-5 crystals are lower than those of the other crystals, indicating that the formation of SWNTs are more favorable in these crystals. It agrees well with the DSC results.

### 3.2.2 Effects of substituted Si\(^{4+}\) concentration on the filling density of SWNTs

The XRF was used to analyze chemical composition of as-grown SAPO-5 crystals using the starting gel mixture that consisted the composition \( 2x\text{Si}: 1.0\text{Al}_2\text{O}_3: (1-x)\text{P}_2\text{O}_5: 1.2 \text{TPA}: 0.8\text{HF}: 800\text{H}_2\text{O} \). The results are shown in Fig. 3.14(a). The value of horizontal axis is the molar ratio of silicon in the starting gel, which has the same meaning as \( x \), and the vertical axes are the stoichiometric ratio Al, P (left) and Si (right) in the SAPO-5 crystals. The analytical data indicate an increase in the silicon content and a corresponding decrease in phosphor content in the as-synthesized SAPO-5 crystals with increasing \([\text{Si}]:([\text{Si}]+[\text{P}])\) ratio \( x \) in the synthesis gel. This strongly suggests the substitution of P by Si, which leads to the generation of negatively charged framework and Brønsted acid sites.

The relative integrated RBM intensity of SWNTs inside the channels of SAPO-5 crystals is plotted by the solid dots in Fig. 3.14(b) as a function of the Si ratio (in the starting gel). It is seen that the relative intensity of the RBM signals increased sharply when the Si ratio increased from 0 to 1%, reaching a plateau that extends to 6%. At higher Si ratios, the relative intensity of the RBM signals is seen
to decrease, owing to the difficulty of growing good quality SAPO-5 crystals with substitution of Si higher than 6%. The SAPO-5 crystals with a high Si ratio are usually small in size and rich in defects, thus are not favorable to generate nanotubes inside the channels. So the optimized Si ratio for nanotube growth ranges from 1% to 6%.

Fig. 3.14: (a) The molar ratios of silicon, aluminum, and phosphorus measured by the X-ray fluorescence element analyzer. (b) The integrated intensity of RBMs plotted as a function of Si ratio in the starting gel.
3.3 Summary

This chapter describes the synthesis of high density 0.4 nm SWNTs in the AFI crystals channels. A higher density SWNTs can be formed by replacing the initial carbon precursor TPA with TPAOH which contains more carbon atoms. The incorporation of metal cations (Mn, Mg, Co) and Si into AlPO₄-5 framework gives rise to the formation of negatively charged matrix and Brønsted acid sites. It is observed that the negatively charged framework and Brønsted acid sites on the walls can play an important catalytic role in the carbonization of TPA molecules as well as in the formation of SWNTs. The experimental results agree well with the predictions of first-principles calculations, which show the metal-incorporated frameworks to be favorable for the SWNTs formation.
References:


Chapter 4

Formation Mechanism and Air Stability of 0.4 nm Single-walled Carbon nanotubes inside the Channels of AFI Crystals

Although 0.4 nm single-walled carbon nanotubes (SWNTs) have been systematically studied, some of their basic physical and chemical properties are not yet well understood. For instance, the formation mechanism and the air stability of SWNTs are not precisely known. Since the SWNTs produced inside the channels of AlPO₄-5 (AFI) crystal have three possible structures: the zigzag (5, 0), the armchair (3, 3), and the chiral (4, 2). These three structures co-exist inside the channels, which are not favorable for studying the intrinsic properties of each chirality tube. Although it is challenging to precisely control the tube chirality, we can use the difference in air stability of these tubes to selectively destroy undesired type of tubes, leaving behind a single chirality.

4.1 The initial predominating forms of tripropylamine (TPA) inside the channels of AFI crystals

As many other zeolite crystals, an AlPO₄-5 single crystal is usually rich in structural defects and its crystal size is usually limited to a few ten micrometers in diameter and a hundred micrometers in length. Hence, the growth of large sized AFI single crystals with high structural perfection is crucial in producing high quality SWNTs in the channels. It has been reported that addition of F⁻ ions into the starting
gel of AlPO$_4$-5 synthesis is favorable to the formation of large-sized optical grade single crystals [1, 2]. The function of F$^-$ ions in the growth gel is to restrain nucleation in the gel. Meanwhile, the existence of F$^-$ ions can also affect the form of the TPA (CH$_3$CH$_2$CH$_2$)$_3$N) precursor molecules. The TPA molecules exist in the channels of AlPO$_4$-5 crystals in form of tripropylammonium hydroxide ((CH$_3$CH$_2$CH$_2$)$_3$NH$^+$OH$^-$), if the starting gel is F$^-$ free, and tripropylammonium fluoride ((CH$_3$CH$_2$CH$_2$)$_3$NH$^+$F$^-$) if the crystals are grown from a gel with F$^-$ ions. Different forms of the TPA molecules might lead to different carbonization processes, and thus affect the formation of carbon nanotubes inside the channels. The adsorption force between the channel walls and guest molecules is relatively weak for pure AlPO$_4$-5 crystals because of their chemical inert character. The weak adsorption force leads to escape of the hydrocarbon guest molecules from the channels. As a result, the remaining carbon atoms are insufficient in amount to form continuous carbon nanotubes, leading to very poor electric conductivity of the resulting nanotubes [3]. Catalytic Bronsted acid sites on the channels walls can be generated by replacing framework elements, P$^{5+}$ or Al$^{3+}$ using inequi-covalent elements, such as P$^{5+}$ replaced by Si$^{4+}$, or Al$^{3+}$ replaced by divalent metallic (Me) cations. High quality and high filling density SWNTs have been synthesized in catalytic MeAPO-5 crystals [4-6]. The TPA may exist in these decorated crystals in three predominant forms: a lone tripropylammonium (CH$_3$CH$_2$CH$_2$)$_3$NH$^+$) counteracting the negative charge lattice, tripropylammonium fluoride or tripropylammonium hydroxide, depending on the synthesis medium. The latter two were occluded as physisorbed amine, which is readily lost at a low temperature. The number of tripropylammonium ions associated with lattice per unit cell varies with the content of Me ions in the crystal lattice or F$^-$ content in the starting gel. Thus the
F⁻ in the carbon precursor molecules is a crucial factor in forming high filling density and high quality nanotubes.

To study the decomposition process of carbon precursor TPA, it is important to know the initial predominating forms of TPA inside the channels of AFI crystals (AlPO₄-5 crystals prepared either in the presence or absence of F⁻ ions and negatively charged MeAPO-5 crystals prepared either in the presence or absence of F⁻ ions). Herein, we studied the initial predominating forms of TPA inside the channels of CoAPO-5 crystals prepared either in the presence or absence of F⁻ ions.

The as-grown CoAPO-5 crystals have typical size of ~50 µm in diameter and ~400 µm in length. As confirmed by X-ray diffraction and FTIR, the CoAPO-5 crystals have the same crystal structure as that of AlPO₄-5 crystals (see chapter 3).

**Fig. 4.1:** The molar ratios of cobalt, aluminum, and phosphorus measured by the X-ray fluorescence element analyzer.
The composition of crystal is tested by X-ray fluorescence (XRF). Fig. 4.1 shows the composition of the CoAPO-5 crystals plotted as function of the cobalt molar ratio in the starting gel. The vertical axes are the stoichiometric ratio of Al, P (left) and Co (right) in the CoAPO-5 crystals. The analytical data indicate an increase in the cobalt content in the as-synthesized CoAPO-5 crystals with increasing the cobalt molar ratio $x = [\text{Co}]/([\text{Co}]+[\text{Al}])$ in the starting gel. The Co stoichiometric ratio in crystals is, however, smaller than the Co ratio in the starting gel, implying only a fraction of Co ions in the starting gel is incorporated in crystal lattice sites. With increasing Co molar ratio in crystals, the aluminum content in the crystals is correspondingly decreased. In contrast, the phosphorus content in crystals is unchanged. These results strongly suggest that $\text{Al}^{3+}$ was substituted by $\text{Co}^{2+}$, which leads to the generation of negatively charged framework and Bronsted acid sites.

The vibration spectra provide useful information about the organic template molecules inside the channels of as-synthesized CoAPO-5 crystals. Micro-Raman spectra in the C-H bond-stretching region (2600–3200 cm$^{-1}$) measured for the TPA inside the channels of CoAPO-5 crystals prepared with or without $\text{F}^-$ ion are shown in Fig. 4.2. The spectra of liquid TPA and the aqueous solution of tripropylammonium fluoride are shown in the same figure as well. From this figure, we can observe that the C-H bond-stretching modes of the TPA inside the channels of CoAPO-5 single crystal at 2890, 2948, and 2975 cm$^{-1}$ obviously shift to the high-frequency side compared with that of liquid TPA. The corresponding shift in the CH$_3$ anti-symmetrical deformation mode at 1455 cm$^{-1}$ (not shown) has also been observed. The Raman-active vibrational frequencies of the TPA in CoAPO-5 crystals channels are close to those of the tripropylammonium fluoride. Schnable and Popescu et al. reported that the organic template triethylamine (TEA) is
protonated in the channels of AlPO$_4$-5 single crystal [7, 8]. Mali also reported that the organic template dipropylamine (DPA) is in the form of dipropylammonium hydroxide ionic pairs in the channels of AlPO$_4$-31 single crystal [9]. Thus, it can be expected that the organic TPA is also protonated inside the channels of AFI single crystal.

![Raman spectra](image)

**Fig. 4.2:** Raman spectra of: (a) TPA incorporated in the channels of CoAPO-5 single crystal prepared in the presence of F$^-$ ion, (b) TPA incorporated in the channels of CoAPO-5 single crystal prepared in the absence of F$^-$ ion, (c) tripropylammonium fluoride, aqueous solution, and (d) liquid TPA.
4.2. Thermal decomposition of the TPA precursors in the channels of AlPO₄-5 crystals prepared either in the presence or absence of F⁻ ions

We used mass spectrometer to *in-situ* monitor the pyrolysis process of the carbon precursor molecules accommodated in the AlPO₄-5 crystals that were prepared either with or without presence of F⁻ ions. The mass spectra recorded at temperatures range from 373 to 648 K are shown in Fig. 4.3. The general feature in the spectra of the TPA@AlPO₄-5 crystals prepared with or without F⁻ ions are similar to each other in this temperature range. By elevating temperature up to 473K, the signal of water molecules (m/z = 18 and 17) converted from the tripropylammonium hydroxide is increased gradually. Then the signals at m/z = 114, 86, 72, 41 and 30 resulted from the neutral (CH₃CH₂CH₂)₃N molecules are observed. The intensity of these signals increased when the sample was heated to 648 K, implying the conversion of (CH₃CH₂CH₂)₃NH⁺OH⁻ to (CH₃CH₂CH₂)₃N occurred in the temperature region of 473 ~648 K:

$$(CH₃CH₂CH₂)₃NH^+OH^- \rightarrow (CH₃CH₂CH₂)₃N + H₂O(473K)$$

The mass spectra of the pyrolyzate of the (CH₃CH₂CH₂)₃N molecules in the AlPO₄-5 crystals recorded at temperatures of 673 K – 923 K are shown in Fig. 4.4(a). These spectra indicate the decomposition of the (CH₃CH₂CH₂)₃N molecules to lower amines and propylene, via sequential β-elimination reactions, as evidenced by the signals at m/z = 101, 72 and 30 from dipropylamine ((CH₃CH₂CH₂)₂NH) and n-propylamine ((CH₃CH₂CH₂)NH₂) molecules, the signals at 42, 41, 39 and 27 from propylene (C₃H₆) molecules, and the signals at 17 and 16 from ammonia (NH₃) molecules. The characteristic signal of methane molecules was seen when the sample was heated up to 873 K, meanwhile the intensity of H₂ (m/z = 2) signal
increased. After dissociation, these propylene molecules were carbonized and finally formed into carbon nanotubes inside the channels. At higher temperature, the intensities of all these signals mentioned above decreased, and finally became undetectable. These observations agree well with the earlier report by Schnabel et al. [7] who investigated the decomposition of triethylamine (TEA) in the channels of AlPO₄-5 crystals by means of Fourier transform infrared (FTIR) techniques. The decomposition process mentioned above can be summarized as below using the dissociation equations:

\[
\begin{align*}
(CH_3CH_2CH_2)_3N & \rightarrow (CH_3CH_2CH_2)_2NH + C_3H_6 (673 – 723 K) \\
(CH_3CH_2CH_2)_2NH & \rightarrow (CH_3CH_2CH_2)NH_2 + C_3H_6 \\
(CH_3CH_2CH_2)NH_2 & \rightarrow NH_3 + C_3H_6
\end{align*}
\]

Fig. 4.4(b) shows the mass spectra of the \((CH_3CH_2CH_2)_3N^+F^-\) molecules decomposition in the channels in the temperature region of 673 – 973 K. It is interesting to note that, in comparison with the F⁻-free AlPO₄-5 crystals, the signals of the neutral \((CH_3CH_2CH_2)_3N\) at \(m/z = 114\) and 86 due to the conversion of \((CH_3CH_2CH_2)_3NH^+OH^-\) to \((CH_3CH_2CH_2)_3N\) vanished at a lower temperature of 723 K, as shown in Fig. 4.4(a). In contrast, in Fig. 4.4(b), the signals of \((CH_3CH_2CH_2)_3N\) are still seen in the spectrum at 923 K, implying that \((CH_3CH_2CH_2)_3N^+F^-\) molecules are more stable than \((CH_3CH_2CH_2)_3N^+OH^-\) molecules. As a result, a significant amount of \((CH_3CH_2CH_2)_3N\) molecules were escaped out from the channels without carbonization in a wide range of temperature. Thus the signals of the small hydrocarbon molecules generated from the decomposition of \((CH_3CH_2CH_2)_3N\) are almost undetectable.

\[
(CH_3CH_2CH_2)_3NH^+F^- \rightarrow (CH_3CH_2CH_2)_3N + HF (673 – 923 K)
\]
Fig. 4.3: Mass spectra obtained at various points during the thermal pyrolysis of template occluded within AlPO₄-5 crystals in the temperature range 373 ~ 648 K: (a) AlPO₄-5 crystals prepared in the absence of F⁻ ion; (b) AlPO₄-5 crystals prepared in the presence of F⁻ ion.
Fig. 4.4: Mass spectra obtained at various points during the thermal pyrolysis of template occluded within AlPO₄-5 crystals in the temperature range 673 ~ 973 K: (a) AlPO₄-5 crystals prepared in the absence of F⁻ ion; (b) AlPO₄-5 crystals prepared in the presence of F⁻ ion.
The pyrolysis process of the carbon precursors that exist inside the channels in the form of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-\) was further monitored by a thermogravimetry (TG) analyzer. In the experiment, we kept the sample under a continuous flowing of helium gas, and carefully dehydrated the samples at 383 K to eliminate the influence of physisorbed water in the crystals. Fig. 4.5 shows the measured TG curves. The weight loss appeared in the temperature region of 320 – 387 K is due to the desorption of physisorbed moisture (see the inset in Fig. 4.5). At temperatures above 390 K, the TG curve of the \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-\) contained AlPO_4-5 samples can be cataloged into four distinct regions denoted by I to IV. In region I (390 – 490 K), the weight loss is due to the water molecules resulted from the conversion of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-\) to \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}\). In region II (490 – 640 K), the weight loss can be attributed to the vaporization of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}\) molecules, which is in agreement with the mass spectra measured in the same temperature region. The main dissociation of the carbon precursor molecules degradation occurred in temperature region III (640 – 760 K). The weight loss in this region is due to the decomposition of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}\) molecules which leads to the successive release of propylene molecules, with the intermediate formation of \((\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}\) and \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{NH}_2\). Pyrolysis of the propylene molecules occurs in the final temperature region IV (760 – 873 K). Some small molecules, such as H_2, CH_4 and C_2H_2 are pumped out from the crystal channels during the pyrolysis process. As a reference, the corresponding TG curves of the \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{F}^-\) inside the channels are also shown in Fig. 4.5. The TG curve exhibits three main features: the weight loss in the region from 400 to 490 K due to the moisture desorption, the weight loss in the region from 490 to 640 K due to the release of neutral \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}\) formed from \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-\) molecules, and the weight
loss in the region 640 -700K due to the release of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}\) generated from \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{F}^-\) molecules. It is seen that the mass loss of the carbon precursors \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{F}^-\) is higher than that of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-\) molecules. Thus, we can conclude that the number of carbon atoms dissociated from the carbon precursor \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-\) for SWNTs growth in the channels is much more than that of \((\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{F}^-\).

**Fig. 4.5:** TG curves measured at temperatures ranging from 390 K to 873 K for AlPO_4-5 crystals prepared in the presence and absence of F^- ion. The inset shows the dehydrated sample (upper) and undehydrated sample (lower).
A significant difference of the SWNTs formed inside the channels of these two kinds of crystals can also be evidenced by the Raman spectra. Fig. 4.6 shows the typical Raman spectra of the 0.4 nm SWNTs formed in AFI crystals [10-11]. As mentioned in chapter 2, we use the relative intensity ratio of the RBM to the $G$-band ($I_{RBM}/I_G$) as a measure of the tubular carbon structure. Large value of the $I_{RBM}/I_G$ indicates high filling density of the carbon nanotubes in the channels [6]. The relative integrated RBM intensity is plotted by the column in the inset. It is seen that the relative integrated RBM intensity increased when $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-$ was adopted as the carbon precursor. Thus, it is concluded that $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{OH}^-$ is superior to $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{F}^-$ as the carbon precursor for the growth of 0.4 nm SWNTs inside the channels of AlPO$_4$-5 crystals.

![Raman spectra](image)

**Fig. 4.6:** Raman spectra of the 0.4 nm SWNTs formed inside the channels of AlPO$_4$-5 crystals prepared in the presence or absence of $\text{F}^-$ ion.
4.3 Thermal decomposition of TPA molecules in the pores of SAPO-5 crystals prepared with or without F⁻ ions

As aluminum and phosphor exist in the AlPO₄-5 framework in forms of Al³⁺ and P⁵⁺, the framework becomes locally charged when a P⁵⁺ is replaced by a Si⁴⁺. The charged lattice is neutralized by an accompanying proton or a tripropylammonium ion. In this case, the carbon precursor molecules exist in the channels in three different forms: \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{NH}^+\text{OH}^-, (\text{CH}_3\text{CH}_2\text{CH}_2)\text{NH}^+\text{F}^-\) and \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{NH}^+\) by interacting with the negatively charged lattice. In order to understand the effect of F⁻ as well as the negatively charged framework on the decomposition of the carbon precursors and the formation of carbon nanotubes, we monitored the pyrolysis process of the precursor molecules in the SAPO-5 crystals prepared either with or without F⁻ ions in vacuum using a mass spectrometer.

Fig. 4.7 shows the mass spectra of the carbon precursor molecules in-situ measured during the pyrolysis process in the temperature region of 373 - 623 K. The general feature of the mass spectra from 373 K to 598 K is similar to that in AlPO₄-5 crystals. With increasing temperature, the signals of water \((m/z = 18 \text{ and } 17)\) are detected, and then the signals of \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{N}(m/z = 114, 86, 72, 41 \text{ and } 30)\) are observed and their intensity increase with temperature significantly, implying the conversion of \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{NH}^+\text{OH}^-\) to TPA molecules of \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{N}\) occurred in this temperature region:

\[
(\text{CH}_3\text{CH}_2\text{CH}_2)\text{N}^+\text{OH}^- \rightarrow (\text{CH}_3\text{CH}_2\text{CH}_2)\text{N} + H_2O(473K)
\]

The signal intensity of the TPA molecules starts to decrease when the temperature is increased to 623 K, meanwhile, the signals of propylene at \(m/z = 42, 41, 39 \text{ and } 27\) and ammonia (NH₃) at \(m/z = 17 \text{ and } 16\) are observed. The carbon
precursor molecules were decomposed stepwisely into lighter molecules through sequential abstraction of propylene. It is interesting to note that, no signals of (CH₃CH₂CH₂)₂NH and (CH₃CH₂CH₂)NH₂ are observed in these mass spectra, although the signals of propylene and ammonia molecules are clearly seen. This may be due to the fact that the (CH₃CH₂CH₂)₃NH⁺ cations are strongly attracted by the negative charged lattice (Z⁻). The subsequent pyrolysis reaction of the (CH₃CH₂CH₂)₃NH⁺Z⁻ can be described by the following reaction equations:

\[
(CH₃CH₂CH₂)₃NH⁺Z⁻ \rightarrow (CH₃CH₂CH₂)₂NH₂⁺Z⁻ + C₃H₆, \quad (623 - 673K)
\]
\[
(CH₃CH₂CH₂)₂NH₂⁺Z⁻ \rightarrow (CH₃CH₂CH₂)NH⁺Z⁻ + C₃H₆
\]
\[
(CH₃CH₂CH₂)NH⁺Z⁻ \rightarrow NH₃ + C₃H₆ + H⁺Z⁻
\]

These observations agree well with the earlier report by Soulard, Nowotny and Park et al. [12 - 14], who investigated the decomposition of tetrapropylammonium cations in MFI-type zeolites. A similar mechanism has been reported by Fajula et al. [15] for the decomposition of tetraethylammonium in zeolite β. The decomposition of the carbon precursors in the SAPO-5 crystals prepared with F⁻ ions is more difficult than that in those crystals prepared without F⁻ ions. As seen in Fig. 4.7(b), the signals of (CH₃CH₂CH₂)₃N can still be seen even at temperature as high as 623 K in SAPO-5 crystals prepared with F⁻ ions, because of stronger binding between (CH₃CH₂CH₂)₃NH⁺ and F⁻ in comparison with the relatively weak binding between (CH₃CH₂CH₂)₃NH⁺ and OH⁻. The decomposition of (CH₃CH₂CH₂)₃NH⁺F⁻ into (CH₃CH₂CH₂)₃N at temperature above 623 K is described by the following equation:

\[
(CH₃CH₂CH₂)₃NH⁺F⁻ \rightarrow (CH₃CH₂CH₂)₃N + HF, \quad (623 - 648K)
\]

Fig. 4.8 shows the mass spectra of the carbon precursors measured in a higher temperature region (648 – 823 K) in SAPO-5 crystals prepared without F⁻
ions (a) and with F⁻ ions (b). The general features of these two samples are similar to each other, but with a notable difference at 648K: in SAPO-5 crystals prepared with F⁻, the neutral (CH₃CH₂CH₂)₃N signals (m/z = 114, 72 and 30) are weakened, and became undetectable at 673 K (not shown). These neutral (CH₃CH₂CH₂)₃N molecules can escape from the channels in this temperature range, which leads to decreasing of the remaining carbon atoms. The decomposition of the (CH₃CH₂CH₂)₃NH⁺Z⁻ composites leads to a successive release of C₃H₆ molecules. These C₃H₆ molecules can either be pyrolyzed into smaller molecules (such as CH₄ and C₂H₄) and subsequently carbonized in the channels, or converted into bigger molecules such as 2-methylbutane and xylene. These carbonization or conversion processes are evidenced by the signals of C₂H₄ at m/z = 28, 27, 26, the signals of CH₄ at m/z = 16, 15, or the signals of the converted larger molecules of C₃H₈ at m/z = 43, 42, 41, 39, 29 and 27, and even the signals of xylene at m/z = 91, 92, 105 and 106. The number of carbon atoms kept inside the channels is determined by the competition between the carbonization and conversion processes. However, precise control of the carbonization is still a challenge. All signals became weaker and finally undetectable when the sample was heated to 823 K, indicating a complete carbonization of hydrocarbon precursor.

In comparison with that of AlPO₄-5 single crystals prepared with F⁻ ions, the temperature of carbon precursor decomposition inside the channels of SAPO-5 crystals prepared with F⁻ ions is notably decreased, owing to the catalytic effect of Brønsted acid sites and the strong adsorption force of the channel walls. The resulting 0.4 nm SWNTs have better quality and higher filling density than those fabricated without Si doping, evidenced by deeper crystal color and stronger RBM in the Raman spectra (see chapter 3) [4-6].
Fig. 4.7: Mass spectra obtained at various points during the thermal pyrolysis of template occluded within SAPO-5 crystals in the temperature range 373 – 623 K: (a) SAPO-5 crystals prepared in the absence of F⁻ ion; (b) SAPO-5 crystals prepared in the presence of F⁻ ion.
Fig. 4.8: Mass spectra obtained at various points during the thermal pyrolysis of template occluded within SAPO-5 crystals in the temperature range 648 ~ 873 K: (a) SAPO-5 crystals prepared in the absence of F⁻ ion; (b) SAPO-5 crystals prepared in the presence of F⁻ ion.
Furthermore, we monitored the weight loss of the TPA@SAPO-5 crystals using TG to see the pyrolysis behavior of the carbon precursors at different temperatures. The TG curves are shown in Fig. 4.9. Similar to that of AlPO₄-5 crystals, the TG curve of the TPA@SAPO-5 crystals prepared without F⁻ ions can also be divided into four distinct regions: the weight loss due to the moisture desorption from the conversion of (CH₃CH₂CH₂)₃N⁺OH⁻ to (CH₃CH₂CH₂)₃N in the temperature region I (400 ~ 480 K), the weight loss due to the vaporization of (CH₃CH₂CH₂)₃N molecules in the temperature region II (490 ~ 610 K), the mass loss in region III (610K ≤ T ≤ 690K) due to the decomposition of (CH₃CH₂CH₂)₃NH⁺Z⁻ molecules, which leads to the successive release of propylene.
and ammonia molecules, the degradation of the precursor molecules occurred in the final region IV (690 – 873 K) where pyrolysis of the propylene molecules occurs inside the channels and the small molecules such as H₂, CH₄ and C₂H₂ are generated. The TG curve of the TPA@SAPO-5 crystals prepared with F⁻ ions is split into three distinct regions. The weight loss in the initial region, I, from 400K to around 627K is mainly due to the release of (CH₃CH₂CH₂)₃N generated from (CH₃CH₂CH₂)₃N⁺OH⁻ and (CH₃CH₂CH₂)₃N⁺F⁻. The loss in region II: 627K ≤ T ≤ 690K is attributed to the decomposition of (CH₃CH₂CH₂)₃NH⁺Z⁻ molecules, which leads to the successive release of propylene and ammonia molecules. The mass loss in the final region, III, is attributed to the degradation of propylene. It is seen that the mass loss of TPA@SAPO-5 crystals prepared with F⁻ ion is higher than that of TPA@SAPO-5 crystals prepared without F⁻ ion. It is interesting to note that this discrepancy is mainly due to the release of (CH₃CH₂CH₂)₃N molecules generated from the (CH₃CH₂CH₂)₃N⁺F⁻ molecules in the temperature region of 400 ~ 627 K, that is, most of (CH₃CH₂CH₂)₃N molecules escape from the channels before being pyrolyzed. However, in SAPO-5 crystals without F⁻ ions, the (CH₃CH₂CH₂)₃NH⁺ ions are bonded to the framework by a strong energetic interaction and decomposed successively into lighter ammonium ions with the abstraction of propylene at higher temperature. Thus, the number of carbon atoms which can be kept inside the channels is more than that of other precursors. The number of the (CH₃CH₂CH₂)₃NH⁺ ions per unit cell can be increased by increasing the Si content in the crystal lattice or decreasing the F⁻ content in the starting gel. A higher (CH₃CH₂CH₂)₃NH⁺ ions content inside the channels of crystals will be facile to keep more carbon atoms.
Fig. 4.10 shows the Raman spectra of the 0.4 nm SWNTs formed inside the channels of SAPO-5 crystals prepared with or without F⁻ ions. The relative integrated RBM intensity is plotted by the column in the inset. Not surprisingly, the relative integrated RBM intensity of nanotubes formed inside the channels of the SAPO-5 crystals prepared without F⁻ ions is notably increased, owing to the strong adsorption force between (CH₃CH₂CH₂)₃NH⁺ and negatively charged crystal lattice. The F⁻ ions are favorable to grow large size optical grade AFI crystals, but not facile to the growth of the 0.4 nm SWNTs in the SAPO-5 matrix.
4.4 Thermal decomposition of TPA molecules in the pores of CoAPO-5 crystals prepared with or without F⁻ ions

The decomposition of TPA molecules inside the channels of AlPO₄-5 and SAPO-5 crystals results in the successive release of propylene molecules. These C₆H₆ can either be pyrolysed into smaller molecules (such as CH₄ and C₂H₄) and subsequently carbonized in the channels, or converted into bigger molecules such as 2-methyl-butane and xylene. The number of carbon atoms which can be formed SWNTs is determined by the competition between these two processes, i.e., carbonization and conversion. The AlPO₄-5 crystals can substitute other metal cations into its frame structure, giving rise to the formation of surface acidity. The dependence of the catalytic effect and selectivity on surface acidity, in the transformation process of the carbon precursor into 0.4 nm SWNTs inside the crystals channels, can be very different for different metal cation substitutions. We also studied the decomposition process of TPA carbon precursor inside the channels of CoAPO-5 crystals.

Fig. 4.11 and Fig. 4.12 show the mass spectra of the carbon precursor molecules in-situ measured during the pyrolysis process in the temperature region of 373 - 823 K. The general feature of the mass spectra from 373 to 823 K is similar to that of TPA confined inside the channels of SAPO-5 crystals, but with a notable difference at 723K: in SAPO-5 crystals (see figure 4.8), the signals of the larger molecules of C₅H₈ at m/z = 43, 42, 41, 39, 29 and 27, and the signals of xylene at m/z = 91, 92, 105 and 106 are observed, implying C₆H₆ molecules can converted into bigger molecules. In contrast, in CoAPO-5 crystals (see figure 4.12), no signals of 2-methyl-butane and xylene are detected. This minor discrepancy may be due to the transition-metal Co²⁺ also contributed to the decomposition of TPA.
Fig. 4.11: Mass spectra obtained at various points during the thermal pyrolysis of template occluded within CoAPO-5 crystals prepared in the absence and presence of F⁻ ion in the temperature range 373 ~ 623 K.
Fig. 4.12: Mass spectra obtained at various points during the thermal pyrolysis of template occluded within CoAPO-5 crystals prepared in the absence and presence of $F^-$ ion in the temperature range 648 ~ 873 K.
The carbonization process of the TPA molecules contained inside the channels of CoAPO-5 crystals was analyzed by micro-Raman spectroscopy. Raman spectra of the TPA@CoAPO-5 crystals measured at various temperatures from 373 K to 773 K in a vacuum of $10^{-3}$ mbar are shown in Fig. 4.13. When the CoAPO-5 crystals were treated at a temperature below 573 K, the spectrum remained essentially the same as that at 373 K, except that the intensities decreased. It shows typical characteristic Raman-active modes for TPA molecules: The peaks near 2850-3050 cm\(^{-1}\) are assigned to the CH\(_3\) and CH\(_2\) symmetric and anti-symmetric stretching modes, the peak at about 1460 cm\(^{-1}\) is due to the CH\(_3\) anti-symmetrical deformation mode and that near 967~1150 cm\(^{-1}\) is attributed to C-N stretching mode [16]. When the sample is pyrolyzed at temperature 623 K for 3 h, all signals related to TPA molecules disappeared from the spectrum. This implies that the carbon precursor TPA molecules start to decompose at this temperature. When the temperature was increased further, the G-band at 1600 cm\(^{-1}\) appeared when the sample was heated at temperature above 648 K, implying that carbon precursor TPA molecules was carbonized inside the channels of CoAPO-5 single crystal. With still increasing temperature, the relative intensity of G-band gradually strengthens. The sharpness of the peaks is an indicator that carbon atoms are highly ordered in the channels. While the radial breathing mode (RBM) frequencies at 510 and 550 cm\(^{-1}\) and the disorder-induced D line appeared at temperature up to 673 K, indicative of the 4-Angstrom carbon nanotubes appeared. As a result, the crystals turned homogeneous black with strong optical anisotropy. The relative intensity of RBM is increased with the increasing of temperature. All these results indicate that the 0.4 nm SWNTs inside the channels of CoAPO-5 crystal start to be formed from small graphite sheet. Compared with that of AlPO\(_4\)-5 single crystal, the temperature of TPA carbonization
inside the channels of CoAPO-5 single crystal is notably decreased [17, 18]. It should be pointed out that there also exist Raman signals for the CoAPO-5 lattice at frequencies of 450 cm\(^{-1}\), due to the P-O-Al vibration [19]. However, the Raman intensity of SWNTs is at least 20 times stronger than that of CoAPO-5, owing to the resonant behavior. Thus the contribution of the vibrations from the CoAPO-5 framework to the Raman spectra is negligible [20]. We also observed the RBM of freestanding SWNTs after removing the zeolite framework [21].

**Fig. 4.13**: Raman spectra of the TPA contained inside the channels of CoAPO-5 crystal were measured at various temperatures in a vacuum of 10\(^{-3}\) mbar.
4.5 Air stability of 0.4 nm SWNTs inside the channels of SAPO-5 crystals

There is recently a strong interest on the gas adsorption by carbon nanotubes [22-24]. Among them, the interactions of oxygen with SWNTs are widely studied [25-27]. The sensitivity of their electronic properties to oxygen exposure can be used as the basis for chemical sensor. However, such property could also affect the stability of the device built from carbon nanotubes when exposed in ambient conditions. It was theoretically shown that SWNT with diameter of 0.4 nm are energetically stable. Due to large curvature, these tubes are expected to be more reactive than larger-diameter tubes when exposed in ambient conditions, and thus whether they are air stable is an issue that needs to be addressed. In addition, the zigzag (5,0), the armchair (3,3), and the chiral (4,2) tubes co-exist inside the channels of SAPO-5 crystals, which are not favorable for studying the intrinsic properties of each chirality tube. We can use the difference in air stability of these tubes to selectively destroy undesired type of tubes and leave behind a single chirality.

In order to explore the air stability of (4,2) and (5,0) tubes, the 4 Å nanotubes confined in SAPO-5 crystals channels are treated under the vacuum of 10⁻⁵ mbar and 10⁻³ mbar at various temperatures for 5 h, respectively. Raman spectra of the SWNTs treated under the vacuum of 10⁻⁵ mbar are shown in Fig. 4.14(a). After treated at 1223 K, the general feature of the Raman spectrum is similar to that of nanotubes treated at 1073 K, indicating that SWNTs are not damaged. In contrast, the intensity of RBM at 510 cm⁻¹ weakens and the relative intensity of D bands is increased, when the samples were heated at 1123 K for 5 h under the vacuum of 10⁻³ mbar (see Fig. 4.14(b)). This is because that at a low vacuum condition, these 0.4 nm nanotubes are oxidized at 1123 K. With further increasing temperature to 1273
K, the RBM Raman signal at 510 cm\(^{-1}\) finally became undetectable. In contrast, the RBM at 550 cm\(^{-1}\) survived up to 1273 K, which indicates that among the two types of the 0.4 nm SWNTs, the (5,0) tube with zigzag structure is more air stable than the (4,2) tubes with chiral structure. In the intermediate Raman spectra, with increasing temperature, the relative intensity of D bands is increased. This can be due to the fact that the concentration of oxygen is so low that the reaction rate between nanotubes and oxygen is slow, which leads to nanotubes structure collapse and turn into amorphous carbon due to the strong curvature effect of nanotubes induced by their ultra-small diameter.

Isothermal Raman spectra in Fig. 4.14(c) are measured by keeping the temperature at 1123 K for different heating time. With increasing heating duration, the relative intensity of D bands is increased slightly, while the intensity of RBM at 510 cm\(^{-1}\) weakens, indicating the (4,2) tubes are damaged. Under isothermal condition for 50 h, the (4,2) tubes are completely oxidized, and the specified chirality (5,0) tubes are obtained, which indicates that (5,0) tube is more stable than (4,2) tube in the sense of oxidation. These observations agree well with the earlier report by Ye et al. [21], who investigated the stability of freestanding 0.4 nm SWNTs.
Fig. 4.14: Measured Raman spectra of 0.4 nm SWNT treated (a) at various temperatures under the vacuum of $10^{-5}$ mbar; (b) at various temperatures under the vacuum of $10^{-3}$ mbar; (c) at various duration times under the vacuum of $10^{-3}$ mbar. The inset shows the magnified spectra around RBM.
The physisorption and chemisorption of $O_2$ on the outer wall of a (4, 2) carbon nanotube have been studied by density functional calculations. The minimum-energy paths from physisorbed products to chemisorbed products are calculated by the nudged elastic band technique. In our calculations we use the plane-wave pseudopotential method within the framework of density functional theory (DFT) [28-30]. The exchange-correlation energy is in the form of Perdew-Wang 91 functional and the cutoff energy is set to 396 eV. The hexagonal supercell contains 56 carbon atoms and two adsorbed oxygen atoms, with dimensions of 16 Å.

**Fig. 4.15:** Three different adsorption sites on the outer surface of (4, 2) tube, marked as A, B and C.
The Brillouin zone is sampled with $1 \times 1 \times 8$ Monkhorst meshes, and the atomic positions are fully relaxed. To calculate the minimum-energy path during the adsorption process, we use the so-called nudged elastic band (NEB) technique [31, 32], and eight image points are chosen between a chemisorbed product and a physisorbed product. As before, we only consider the singlet $\text{O}_2 (^1\Delta_g)$ since it is much more reactive than the triplet state ($^3\Sigma_g^-$) and is mainly responsible for the oxidation of carbon nanotubes [23].

The chiral (4, 2) tube has three different C–C bonds and thus offers three distinct adsorption sites marked as A, B and C in Fig. 4.15. Among the three distinct adsorption sites, site C has the largest angle with the tube axis. As before, the physisorbed product has a small adsorption energy of 0.15 eV. However, the chemisorbed state is much lower in energy and the adsorption is no longer cycloaddition-like. We find that $\text{O}_2$ is dissociated and the underlying C–C bond is broken, very similar to those previously found for (3,3) tube [34, 35]. The calculated adsorption energy is 3.17 eV, and the tube’s geometry is significantly changed. All these indicate that there is a very strong interaction between the tube and oxygen. We have also calculated the minimum-energy path from physisorbed product to chemisorbed state for site C and find that the energy barrier is even smaller (0.42 eV). The energy barrier of site A and B are 0.52 eV and 0.45 eV, respectively. It is interesting to note that due to curvature effect, site C is more reactive than site A, with site B in between. According to our NEB calculation, site C has the lowest energy barrier for reaction with $\text{O}_2$, while site A the highest and site B is also in between. Both of these findings suggest that upon oxygen exposure, (4, 2) tube will be oxidized firstly from site C. Once such oxidization occurs and the chemisorbed product is formed, the (4,2) tube’s structure will be destroyed according to the above
discussions. This is however not the case for (5,0) tube as reported previously [34, 35]. The geometry of (5,0) tube is still kept when exposed to oxygen, which indicates that (5,0) tube is more stable than (4,2) tube in ambient conditions [36].

Our theoretical calculations and experimentally measured Raman spectra both indicate that (4,2) tube is not more air stable than (5,0) tube. As we known, the as-grown product of 4 Å SWNT usually contains a mixture of (5,0), (4,2) and (3,3). The different adsorption behaviors of O₂ could be used to select a single chirality from these three kinds of tubes.

4.6 Summary

In this chapter, we directly monitored the decomposition process of TPA in AlPO₄-5, SAPO-5 and CoAPO-5 crystals. It has been found that the TPA precursors exist in the as-synthesized crystals in three different forms: tripropylammonium fluoride, hydroxide and tripropylammonium cation compensating the negative charge of the framework. The latter is bonded to the framework by strong chemical interaction and its decomposition undergoes by a series of β-elimination reactions to give propylene and ammonia, with the stepwise formation of dipropylammonium and n-propylammonium cations. The 0.4 nm SWNTs filling density was found to be higher than that resulting from the carbon precursor of tripropylammonium fluoride and hydroxide, because of the strong adsorption force of the channel walls to pyrolyzate, as evidenced by the clear and strong radial breathing modes in Raman spectra. Our theoretical calculations and experimentally measured Raman spectra both indicate that (5,0) tube is more air stable than (4,2) tube.
References:


Chapter 5

Synthesis and Optical Characterization of 0.3 nm SWNTs formed inside the Channels of AEL Crystals

Synthesis of ultra-small single-walled carbon nanotubes (SWNTs) using AlPO$_4$-5 (AFI) single crystals as a template is a relatively new approach for carbon nanotubes synthesis. This method potentially has several advantages over the traditional synthesis and can be used to prepare SWNTs with certain unique properties. Besides AlPO$_4$-5 single crystals, there are many other types of Aluminophosphate zeolites. It is interesting to see what kinds of carbon structure can be formed in a pore system of channels with smaller diameter than that of AFI crystals. Smaller channels provide us a possibility of producing even smaller SWNTs, e.g., fabrication of zigzag (3,0) and armchair (2,2) tubes (their diameter is about 0.3 nm) is potentially possible. Since the 0.3 nm is probably below the stability limit for free-standing SWNTs, template confinement may be the only way to promote their formation. Due to the strong curvature effect induced by their ultra-small diameter, these SWNTs would exhibit very peculiar properties. In this chapter, we report the synthesis and characterization of 0.3 nm SWNTs formed inside the channels of SAPO-11 (AEL) single crystals, as well as their optical properties.

5.1 Synthesis of 0.3 nm SWNTs in the channels of SAPO-11 crystal

Organic temperate molecules dipropylamine (DPA) are oriented in a head-tail manner in the 10-ring channels of AEL crystals. Mali and Han et al., reported
that the organic template DPA is protonated in the channels of AlPO₄-11 single crystals [1, 2]. Thus, it can be expected that the organic DPA is also protonated inside the channels of SAPO-11 single crystals. The DPA molecules exist in the channels of SAPO-11 crystals in the form of dipropylammonium hydroxide \(((\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2^+\text{OH})\), if the starting gel is F⁻ free, dipropylammonium fluoride \(((\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2^+\text{F}^-)\) if the crystals are grown from a gel with F⁻ ions, and \((\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2^+\) ion by interacting with the negatively charged SAPO-11 crystal lattice when a P⁵⁺ is replaced by a Si⁴⁺. These predominating forms are similar to that of tripropylamine in AFI crystals [3-5]. In this chapter, we studied the carbonization process of DPA occluded within SAPO-11 crystals prepared without F⁻ by a combined technique of Fourier Transform Infrared Spectroscopy (FTIR), mass spectrometry, thermogravimetric (TG) and micro-Raman spectroscopy within the temperature range from 300 to 873 K.

To study the carbonization process of DPA molecules in the SAPO-11 crystals channels, 0.5 mg crystals powder was pressed into a tablet and put on a temperature-controlled holder for \textit{in-situ} FTIR spectral measurement with continuously flowing nitrogen gas. The temperatures were varied from 300 K to 823 K. Fig. 5.1 shows the FTIR spectra in the frequency regime 2000-4000 cm⁻¹. At room temperature, the spectrum exhibits three main features: the peaks in the regime 2000-2600 cm⁻¹ are due to the overtones plus their combinations of the Al-O-P vibrations (from crystal framework), the peaks in the regime 2600-3400 cm⁻¹ are due to the DPA molecules, and the peaks in the regime 3400-3700 cm⁻¹ are due to the O-H vibration. With increasing temperature, the relative intensity of the O-H band weakens, becoming undetectable above 573 K, implying desorption of water. We can thus assume that dipropylammonium hydroxide \((\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2^+\text{OH}\) has
been partially converted to $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$ at this temperature. With further increasing temperature to 723 K, the relative intensity of the N-H peaks (3095 – 3263 cm$^{-1}$) and the C-H peak at 2985 cm$^{-1}$ decrease and vanish, implying that the thermal treatment leads to the decomposition of $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2^+$ ion by sequential abstraction of propylene (C$_6$H$_6$) and ammonia molecules (NH$_3$), with stepwise formation of n-propylammonium ion (CH$_3$CH$_2$CH$_2$)NH$_3^+$. At even higher temperatures, the C-H vibration signal at 2892 and 2944 cm$^{-1}$ became weaker, and finally became completely undetectable above 823 K, indicating that at this temperature, the C-H bonds of C$_3$H$_6$, or its smaller oligomers, start to break.

**Fig. 5.1:** FTIR spectra of SPO-11 crystals containing DPA, recorded at various temperatures under a nitrogen atmosphere.

FTIR spectra can only monitor the decomposition process that happens inside the crystal channels, but can not identify the gas species that escape from the
channels. The use of mass spectrometer remedied this situation. We used mass spectrometer to monitor the pyrolysis process of DPA molecules in vacuum. In order to eliminate the influence of the physisorbed water inside the channels, the as-synthesized sample was firstly treated under the vacuum of $10^{-3}$ mbar at 373 K for 3 h. After the water was desorbed, these crystals were treated in a range of temperatures between 373 and 873 K, with a 3 K/min ramping rate. Adequate sensitivity was obtained with 5 grams of sample. The total mass spectra recorded at different temperatures are shown in Fig. 5.2. Upon elevating temperatures up to 548 K, the intensity of water signals ($m/z = 18$ and 17) was increased significantly owing to the desorption of H$_2$O. The presence of new $m/z$ signals at 101, 72 and 30 is attributed to the formation of neutral DPA, and these signals increased when the sample was heated to 623 K.

\[(CH_3CH_2CH_2)_2NH_2^+ + OH^- \rightarrow (CH_3CH_2CH_2)_2NH + H_2O(473K)\]

The spectra recorded between 648 and 698 K indicate the decomposition of the $(CH_3CH_2CH_2)_2NH_2^+$ ion to lower ammonium ion and propylene, via sequential Hofmann elimination reactions. This is evidenced by the signals at 42, 41, 39 and 27 due to propylene and the signals at 17 and 16 due to ammonia (NH$_3$). Upon heating to 723 K, the signals at $m/z$ 91, 92, 105 and 106 were observed. These are characteristics of xylene. The mass spectral data ($m/z = 72, 57, 56, 55, 43, 42, 41, 39, 29$ and 27) confirmed that 2-methyl-butane (C$_5$H$_{12}$) were also produced, and suggested that propane and butane may also have been produced. It is possible that a small amount of catalytic activity was responsible for this. The signals of 2-methyl-butane became weaker and finally undetectable when the sample was heated to 773 K, while the intensities of H$_2$ ($m/z = 2$), C$_2$H$_4$ ($m/z = 28, 27$ and 26) were still observed. With further increase of temperature, the intensities of all the above-mentioned signals deceased, and finally became negligible, when the heating temperature reached 873 K or above.
**Fig. 5.2:** Mass spectra obtained at various points during the thermal pyrolysis of template occluded within SAPO-11 crystals in the temperature range 373 ~ 823 K.
The pyrolysis process of DPA that exist inside the channels of SAPO-11 single crystals was further monitored by a TG analyzer. In the experiment, we kept the sample under a continuous flowing of helium gas, and carefully dehydrated the samples at 383 K to eliminate the influence of physisorbed water in the crystals. Fig. 5.3 shows the measured TG curve. The TG curve can be cataloged into four distinct regions denoted by I to IV. In region I (390 - 490K), the weight loss is due to the water molecules resulted from the conversion of (CH$_3$CH$_2$CH$_2$)$_2$NH$_2^+$OH$^-$ to (CH$_3$CH$_2$CH$_2$)$_2$NH. In region II (490 - 590K), the weight loss can be attributed to

$$(CH_3CH_2CH_2)_2NH_2^+Z^- \rightarrow (CH_3CH_2CH_2)NH_3^+Z^- + C_3H_6 \ (648 - 698K)$$

$$(CH_3CH_2CH_2)NH_3^+Z^- \rightarrow NH_3 + C_3H_6 + H^+Z^-$$

$$C_3H_6 \rightarrow 3C + 3H_2 \uparrow \ (698K)$$

Fig. 5.3: TG curves measured at temperatures ranging from 390 K to 873K
the vaporization of \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{N}\) molecules, which is in agreement with the mass spectra measured in the same temperature region (see Fig. 5.2). The weight loss in region III (640 – 760 K) is due to the decomposition of \((\text{CH}_3\text{CH}_2\text{CH}_2)\text{NH}_2^+Z^-\) molecules, which leads to the successive release of propylene and ammonia molecules, the degradation of the precursor molecules occurred in the final region IV (690 – 873 K) where pyrolysis of the propylene molecules occurs inside the channels and the small molecules such as \(\text{H}_2\), \(\text{CH}_4\) and \(\text{C}_2\text{H}_2\) are generated.

**Fig. 5.4:** Raman spectra of the DPA contained inside the channels of SAPO-5 crystal were measured at various temperatures in a vacuum of \(10^{-3}\) mbar.
We study the carbonization process of the DPA molecules contained inside the channels of SAPO-5 crystals by using micro-Raman spectroscopy. Raman spectra of the DPA@SAPO-5 crystals measured at various temperatures from 373 K to 773 K in a vacuum of $10^{-3}$ mbar are shown in Fig. 5.4. At room temperature, it shows typical characteristic Raman-active modes for DPA molecules: The peak at about 1462 cm$^{-1}$ is due to the CH$_3$ anti-symmetrical deformation mode and that near 967~1150 cm$^{-1}$ is attributed to C-N stretching mode, the peaks near 2850-3050 cm$^{-1}$ are assigned to the CH$_3$ and CH$_2$ symmetric and anti-symmetric stretching modes (not shown). All signals related to DPA molecules disappeared from the spectrum when the sample is pyrolyzed at temperature 673 K for 3 h. This implies that the carbon precursor DPA molecules start to decompose at this temperature. With temperature increasing further, the G-band at 1600 cm$^{-1}$ and RBM at 760 cm$^{-1}$ appeared when the sample was heated at temperature above 673K, implying that the carbon precursor DPA molecules were carbonized. With still increasing temperature, the relative intensity of G-band gradually strengthened. The sharpness of the peaks is an indicator that carbon atoms are highly ordered in the channels. However, the relative intensity of $I_{\text{RBM}}/I_G$ is decreased with the increasing of temperature. This is due to the fact that more hydrocarbon molecules escape from the channels with increasing temperature, leading to the decrease of nanotube density inside the channels. It indicates that 773K is the optimization carbonization temperature for fabrication nanotubes.

5.2 DPA@SAPO-11 and SWNTs@SAPO-11 Crystal structures

AlPO$_4$-11 is one of a series of crystalline microporous aluminophosphates first described by Wilson et al in 1982 [6]. The AlPO$_4$-11 crystal structure was solved by Bennett and Richardson Jr using a pulsed neutron source [7, 8]. They also determined the crystal structure of the as-synthesized precursor to molecular sieve MnAPO-11 by single-crystal X-ray diffraction [9]. It is notable that in the initial
patent [10] two different powder patterns were listed for AlPO$_4$-11, but no explanation for this was provided. Richardson et al. [7, 8] carried out their refinement using dehydrated AlPO$_4$-11 under vacuum conditions and appear to have ignored the existence of a second set of data. Verdine et al. [11] in their investigation of sorption properties of SAPO-11 noted a difference between the XRD powder patterns of the precursor and a calcined, air equilibrated materials.

![X-ray diffraction patterns of AlPO$_4$-11 crystals: (a) as synthesized; (b) calcined, dehydrated; (c) calcined, rehydrated.](https://example.com/xray-patterns.png)

**Fig. 5.5:** X-ray diffraction patterns of AlPO$_4$-11 crystals: (a) as synthesized; (b) calcined, dehydrated; (c) calcined, rehydrated.

The X-ray powder diffraction spectra of the crystallization product and the calcined products (dehydrated and rehydrated) are given in Fig. 5.5. The X-ray diffraction spectra demonstrate the pure and highly crystalline nature of the products. The dehydrated and as synthesized AlPO$_4$-11 crystals traces are similar, whereas that of the rehydrated sample exhibits substantial peak shifts and the appearance of
new reflections. This may be an indication of the interaction of water molecules with framework T sites [12, 13]. Tapp et al. [14] reported that upon water adsorption the crystal symmetry changes from body-centered orthorhombic (space group Icmm, a = 13.54, b = 18.51, c = 8.37 Å) to primitive orthorhombic (space group Pbn21, a = 13.85, b = 18.02, c = 8.12 Å). Due to the lowering of the symmetry, the pores become more elliptical [15].

**Fig. 5.6:** X-ray diffraction patterns obtained at various points during the thermal pyrolysis of DPA organic template occluded within SAPO-11 crystals in the temperature range 373 ~ 623 K.

As mentioned in chapter 2, Owing to AlPO₄-5 framework is relatively inert chemically, the adsorption of the guest molecules (to the channel wall) is weak. As a
result, a significant amount of hydrocarbon guest molecules can escape from the channels during pyrolysis. The remaining carbon atoms are insufficient in number to form continuous carbon nanotubes. We have incorporated Si$^{4+}$ into the AlPO$_4$-5 framework to partially replace the P$^{5+}$ sites, forming SAPO-5. To maintain electrical neutrality, a cation automatically accompanies the substituted Si$^{4+}$, forming a local electric dipole on the channels wall. Thus, the adsorption potential of the channel walls is enhanced owing to the localized dipoles. As a result, more carbon atoms can be kept inside the channel during the pyrolysis process. Based on these experimental results, we fabricate ultra-small SWNTs using SAPO-11 crystals as template.

What we concern about is the structure of carbon nanotubes in the channels of SAPO-11 crystals. In view of change of the AEL crystal symmetry between as synthesized product and the calcined products (dehydrated and rehydrated), it is necessary to explore the structure of SWNTs@SAPO-11. Fig. 5.6 shows the X-ray diffraction patterns obtained at various points during the thermal pyrolysis of DPA organic molecule occluded within SAPO-11 crystals in the temperature range 373 ~ 873 K. With increasing temperature, the relative intensity of peaks at $2\theta = 16^\circ$ and $19^\circ$ decrease and vanish when the sample was heated to 573 K. At this point the pattern resembles to that of calcined product (dehydrated) (see Fig.5.5) [14, 15]. We can thus assume that SWNTs@SAPO-11 (dehydrated) and calcined AlPO$_4$-11 crystals (dehydrated) have the same structure.

Single crystal X-ray diffraction technique is often used to determine the crystal structure. We can use the single crystal X-ray diffractometry to measure the crystal structures of DPA@SAPO-11 and SWNTs@SAPO-11 (rehydrated). The instrument used in our experiment is $P4RA$ X-ray single crystal diffraction system (Siemens). The X-ray source is from Mo target with voltage of 50 kV and current of 200 mA. The results can clearly give the size of channels containing nanotubes, and
determine the diameter of the nanotubes. A SWNTs@SAPO-11 single crystal (rehydrated) with a good morphology and smooth surface was selected. As a reference, a DPA@SAPO-11 optical-clear single crystal was also selected. They have a typical dimension of 150 x 60 x 50 μm³. As shown in Table 5.1, the unit cell parameters of DPA@SAPO-11 agree well with those obtained by Pluth who studied the crystal structure of the as-synthesized precursor to molecular sieve MnAPO-11 using single-crystal X-ray diffraction [9]. The unit cell parameters of SWNTs@SAPO-11 (rehydrated) are comparable to the results of Bennett et al. [7] who investigated the structure of calcined AlPO₄-11 single crystal (dehydrated) by means of pulsed neutron source. It indicates that SWNTs@SAPO-11 (rehydrated), SWNTs@SAPO-11 (dehydrated) and calcined AlPO₄-11 crystal (dehydrated) have the same structure. This can be due to the fact that the SAPO-11 channels are fully occupied by carbon nanotube, leading to decreased space for physisorption water. As a result, the structure of SWNTs@SAPO-11 is unchanged after water adsorption has reached equilibrium at ambient temperature.

Table 5.1: Unit cell parameters of DPA@SAPO-11 and SWNTs@SAPO-11

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Vol (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPA@SAPO-11</td>
<td>Ima2</td>
<td>18.60</td>
<td>13.384</td>
<td>8.414</td>
<td>2094</td>
</tr>
<tr>
<td>SWNTs@SAPO-11</td>
<td>Ima2</td>
<td>18.451</td>
<td>13.542</td>
<td>8.3763</td>
<td>2092.9</td>
</tr>
</tbody>
</table>

The SWNTs@SAPO-11 crystal structure derived from single crystal X-ray diffraction data is displayed in Fig. 5.7. The structure of SWNTs@SAPO-11 crystal is composed of AlO₄ and PO₄ tetrahedra. Three vertices of each tetrahedron are linked to form sheets containing 4-, 6-, and 10-rings. Columns of 4-, 6-, and 10-
rings are formed running parallel to c axis. Isolated parallel channels spanned by 10-rings have an elliptical cross section and have a surface bounded by 6-rings. The diameters of the major and minor axes are 9.1 and 6.9 Å, which result in a channel opening of 6.5 and 4.3 Å. Assuming a free diameter of 2.6 Å for O (see Fig. 5.8). In principle, single-crystal X-ray diffraction can determine the exact position of each atom in a unit cell of a crystal. The structure of SAPO-11 crystal containing nanotubes was determined. However the position of each carbon atom on the nanotubes in a channel could not be determined, this is due to that there exists small difference of period between the tubes and crystal. Nevertheless, considering of 0.4 nm SWNTs formed in 7.3 Å AFI crystal channels, the diameter of nanotubes can be predicted from the size of SAPO-11 crystals channels, and is estimated to be about 0.3 nm.

![Framework structure of SWNTs@SAPO-11 single crystal](image)

**Fig. 5.7:** Framework structure of SWNTs@SAPO-11 single crystal derived from single crystal X-ray diffraction data. The edges of the unit cell are shown, and the view is along the c axis.
5.3 Micro-Raman spectra of SWNTs formed in SAPO-11 crystals

Fig. 5.9 shows the Raman spectra of the ultra-small SWNTs formed inside the channels of SAPO-11 crystals and after the SAPO-11 framework was removed using HCl acid. The Raman spectrum of SWNTs@SAPO-11 crystal exhibits three main zones at low (400–850 cm\(^{-1}\)), intermediate (1100–1500 cm\(^{-1}\)), and high (1500–1650 cm\(^{-1}\)) frequency regions. Among the low frequency modes, there exist three Raman modes at 504 cm\(^{-1}\), 548 cm\(^{-1}\) and 760 cm\(^{-1}\). It is believed that there is carbon tube with diameter of 0.3 nm in AEL zeolite. Theoretical simulation is necessary to verify whether it is possible. A series of density functional calculations have been done on the carbon tubes (2,2), (3,1), (4,0), (3,0) and (4,1), etc. The theoretical results show that a characteristic Raman breathing mode (RBM) at 760 cm\(^{-1}\) can be found in the carbon tube (2,2) phonon spectrum. The breathing modes of the other carbon tubes are quite different from this value. If there is carbon tube in AEL zeolite and its experimental RBM is 760 cm\(^{-1}\), the tube is most likely the carbon tube (2,2). In the intermediate frequency, there exist few peaks. In the high frequency,
there are a main Raman band at 1596 cm$^{-1}$ and some shoulders at higher frequency. These bands can be assigned to the tangential vibrations of carbon nanotubes with $A_{1g}$, $E_{1g}$, and $E_{2g}$ symmetry, which originate from the splits of the graphite $E_{2g2}$ mode. The geometry structure of carbon tube (2,2) is shown in Fig 5.10.

![Raman spectrum](image)

**Fig. 5.9:** Raman spectrum of the 0.3 nm SWNTs: (a) formed inside the channels of SAPO-11 crystals; (b) after the SAPO-11 framework was removed using HCl acid.

However, only the signals of amorphous carbon are detected when nanotubes are exposed in free space after removing the AEL framework using HCl acid, indicating that the freestanding 0.3 nm SWNTs are below the stability limit due to the strong curvature effect induced by their ultra-small diameter. This result is
consistent with the calculation of cohesive energy for nanotubes [18]. Therefore, it is very difficult to determine the true structure directly by High Resolution Transmission Electron Microscopy (HRTEM) or Scanning Tunneling Microscopy (STM).

Because the (2,2) SWNTs are perfectly aligned inside the channels of SAPO-11 crystals, we can measure the polarized Raman spectra when the polarization of incident laser is parallel or perpendicular to the nanotubes axis. This is because the polarization analyses are related to the symmetry selection rules for different phonon/electron symmetries [16]. Jorio et al., studied the polarized Raman spectra of aligned semiconducting SWNTs and reported that the G-band profile was deconvolved into four intrinsic components with the following symmetry assignments: 1549 cm\(^{-1}\) \([E_2(E_{2g})]\), 1567 cm\(^{-1}\) \([A(A_{1g})+E_1(E_{1g})]\), 1590 cm\(^{-1}\) \([A(A_{1g})+E_1(E_{1g})]\) and 1607 cm\(^{-1}\) \([E_2(E_{2g})]\) [17]. Thus, it is possible to observe the

**Fig. 5.10:** The geometry structure of carbon tube (2,2). The left figure shows the side-view of the tube and the right figure shows the top-view of the tube.
predictions from group theory and distinguish the Raman vibration modes of (2,2) nanotubes.

**Fig. 5.11:** Raman spectra of SWNTs@SAPO-11 crystal when the polarization of incident laser is parallel (upper) and perpendicular (bottom) to the nanotubes axis. Both the G-bands are well fitted by four Lorentzian lines: (a) the polarization of incident laser is parallel to the nanotubes axis; (b) the polarization of incident laser perpendicular to the nanotubes axis.

Fig. 5.11 shows the unpolarized Raman spectra of SWNTs@SAPO-11 crystal when the polarization of incident laser is parallel to the nanotubes axis and propagation of incident laser is perpendicular to the nanotubes axis. As a reference, we also show the unpolarized Raman spectra of SWNTs@SAPO-11 crystal when the polarization of incident laser is perpendicular to the nanotubes axis and
propagation of incident laser is parallel to the nanotubes axis. Carbon nanotubes behave as antennas, with adsorption/emission of light being highly suppressed for light polarized perpendicular to the nanotubes axis [18]. We can see that all modes show maximum intensity when the polarization of incident radiation is parallel to the nanotubes axis, while the signals become very weak when the polarization of incident radiation is perpendicular to the nanotubes axis. In the low frequency, the Raman modes at 504 cm$^{-1}$, 548 cm$^{-1}$ are nearly unobserved, in contrast, the RBM mode at 760 cm$^{-1}$ is still seen. This fact is in good agreement with A$_{1g}$ mode [16]. In the middle frequency, The D bands also exhibits strong polarization dependence, as previously observed in multi-walled carbon nanotubes (MWNTs) [19]. It is worth noting that the G band when the polarization of incident radiation is parallel to the nanotubes axis is broader than that of the polarization of incident radiation is perpendicular to the nanotubes axis, which indicates that it contains more components. The former one needs at least four Lorentzians to fit, with frequencies (widths): 1615 (30), 1591 (40), 1564 (37), 1528 (30) cm$^{-1}$, while the latter needs only two, with frequencies (widths): 1615 (30), 1591 (40) cm$^{-1}$ (see inset (a) and (b)). This fact indicates that the Raman modes at 1564 cm$^{-1}$, 1528 cm$^{-1}$ are polarization dependence. This result is in agreement with group theory predictions for the E$_{1g}$ mode. The relative intensity of Raman mode at 1615 cm$^{-1}$ in inset (b) is higher than that of in inset (a), we assign this Raman vibration to E$_{2g}$ symmetry. However, the Raman vibration mode at 1615 cm$^{-1}$ appears with the highest intensity in inset (a), implying this mode originates from the A$_{1g}$ symmetry.
Fig. 5.12: Polarized Raman spectra of aligned (2,2) nanotube formed inside the channels of SAPO-11 crystal in the four configurations ZZ, XX, ZX and XZ, where Z and X denote that the polarization direction of the laser is along Z or X axis. The first (second) axis is the polarization direction of incident laser (scattering light). The major axis of elliptical channel is along Z axis.
In order to confirm the one-dimensional property of carbon nanotubes, it is very interesting to measure the polarized Raman spectra of nanotubes formed inside the channels of SAPO-11 crystals when the polarization of incident laser is perpendicular to the nanotubes axis with propagation along nanotubes axis. We used (ZZ), (XX), (ZX), and (XZ) polarization geometries, where the letters indicate the polarization directions of the (incident, scattered) light. Suppose that the major (minor) axis of elliptical channel is in the Z (X) direction (see Fig. 5.8), the incident laser light and the Raman scattering light are along the nanotubes axis. Fig. 5.12 shows polarized Raman spectra of the aligned (2,2) nanotubes. The intensity of the modes is not sensitive to the experimental scattering geometry, which indicates that the Raman vibration of the cross section of nanotubes is polarization independence. To our best knowledge, this is first time to study the polarized Raman spectra of the cross section of carbon nanotubes.

5.4 Optical properties of 0.3 nm SWNTs in SAPO-11 crystal channels

A SWNT is a quite unusual object which has no analog in the solid state. It has a nanometer-sized length along the nanotube diameter and a several microns length in the nanotube-axis direction. Since the wavelength of light lies in between these two characteristic lengths, the optical behavior of SWNTs is unique in the sense that the behavior exhibits both molecular nature and solid state nature. For the molecular nature of SWNTs, the optical absorption spectra are rich and sharp because of the quantization of wave vectors $k$ along the circumferential direction of the one-dimensional system to form 1D electronic energy bands, which give sharp van Hove singularities in the joint density of states (JDOS), just like a molecular level. For the solid state nature of SWNTs, the wave vector $k$ is continuous in the
direction of the nanotube axis and scattering or relaxation behavior occurs by phonons or conduction electrons. The co-existence of the two concepts in a SWNT gives rise to a unique behavior in the optical properties of SWNTs [20].

Optical absorption spectra have been measured for bundles of SWNTs and nanotube thin films [21–23]. The absorption bands can be attributed to optical transitions between the van Hove singularities. More controlled experimental studies on the optical properties for SWNTs are, however, not easy to carry out because of the technical difficulty in fabricating mono-sized and well-aligned nanotubes. In our previous work, Li et al., reported the polarized optical adsorption spectra of 4 Å SWNTs arrayed in the channels of AlPO₄-5 single crystals. Three adsorption bands are assigned to the transitions between the Van Hove singularities, and they are agreed well with the \textit{ab initio} calculation of band structure based on the local density function approximation [24, 25]. At this point, the system of mono-sized 3Å SWNTs embedded in the AEL matrix is superior and can bring the experimental results much closer to theoretical predications. The perfectly aligned and monodispersed 0.3 nm SWNTs in the SAPO-5 matrix provide another platform on which the optical experimental and theoretical studies can be carried out.

A series of optical absorption spectra (plotted in optical density, OD) of the SWNTs@SAPO-11 single crystal for light polarized along different directions are shown in Fig. 5.13. The top curve labeled 0° corresponds to the absorption of light polarized parallel to the nanotubes axis (E \parallel c). In this spectrum, a very broad adsorption band from 1.8 eV to 3.2 eV is observed, which is mainly due to the large thickness of sample. However, two peaks A and B centered at 1.9 eV and 2.7 eV, respectively, are seen when the polarization angle is 30°. The intensities of absorption bands A and B decrease monotonically with increasing polarization angle.
(the increment is $15^\circ$), and finally become negligible in the perpendicular configuration ($E \perp c$), as indicated by the rather flat curve labeled $90^\circ$. Thus, the SWNTs@SAPO-11 single crystal is nearly transparent in the whole measured energy region. All these results indicate that two one-dimensional structures co-exist inside the channels of SAPO-11 crystals. Because of the improper resonant conditions, only one structure is responsible in Raman spectrum for laser wavelength around 514.5 nm (2.4 eV).

![Graph showing polarized adsorption spectra of SWNTs@SAPO-11 single crystal.](image)

**Fig. 5.13:** The polarized adsorption spectra of the SWNTs@SAPO-11 single crystal. The topmost and bottommost curves are for the $E \parallel c$ and the $E \perp c$ polarization configurations, respectively, where $E$ is the electronic field and $c$ is the channels axis.
To study the other carbon structure formed in SAPO-11, we measure the Raman spectra of SWNTs@SAPO-11 using incident laser around 514.5 nm and 632.8 nm (1.95 eV). As shown in Fig 5.14, a strong Raman mode at 760 cm\(^{-1}\) is observed and assigned to the radial breathing mode (RBM) for (2,2) nanotubes. However, an extra vibration frequency at 831 cm\(^{-1}\) is observed when the wavelength of incident laser is 632.8 nm. The frequency of the RBM, as stated before, varies as 1/d\(_i\) (\(\omega = \alpha/d_i\)). Furthermore, there are only one possible nanotubes (3,0) with diameter smaller than that of (2,2) tube. As a result, we assign the adsorption band at 1.8 eV in Fig. 5.13 to (3,0) nanotubes, while the adsorption band at 2.7 eV can be attributed to the (2,2) nanotubes.

![Raman spectra](image)

**Fig. 5.14:** The Raman spectra for SWNTs formed inside the channels of SAPO-11 crystals using 514.5 nm and 632.8 nm as incident laser, respectively.
5.5 Resonant Raman spectra of 0.3 nm SWNTs

The Raman scattering technique has been shown to be a powerful tool for obtaining information about material lattice vibration frequencies. In addition, it also can also provide information on electron-phonon interaction in materials. The intensity of the Raman line associated with a transition from an initial vibrational state $|i\rangle$ to a final vibrational state $|f\rangle$ can be expressed as:

$$I_{i\rightarrow f} \propto \frac{16\pi^4 v_i^3 v_s}{c^4} \sum_{\rho,\sigma} (\rho \cdot e_s)(\sigma \cdot e_i)a_{\rho\sigma}^2 \quad (5.1)$$

where $v_i$ is the frequency of the incident photon, $v_s$ is the frequency of the scattered photon $v_s = v_i - v_{ff}$, $v_{fi}$ is the frequency of the created phonon, $a_{\rho\sigma}$ is the transition polarizability tensor and is given by the Kramers-Heisenberg dispersion formula:

$$a_{\rho\sigma} = \sum_e \left\{ f_D|e\rangle\langle e|D_\sigma|i\rangle + \frac{f_D|D_\sigma|e\rangle\langle e|D_\rho|i\rangle}{h(v_e - v_i - v_i) + i\Gamma_e} \right\} \quad (5.2)$$

in which $\langle e|D_\sigma|i\rangle$ is the transition dipole moment for the transition from initial state $|i\rangle$ to intermediate state $|e\rangle$ and $i\Gamma_e$ is a damping factor that is inversely proportional to the lifetime of the state $|e\rangle$. It is evident that the denominator in the first term of equation (2) can become very small as the frequency of the incident laser radiation is close to that of a transition $|i\rangle \rightarrow |e\rangle$. This can result in an enormous increase in one or more components of the transition polarizability and enhancement of the normally weak Raman signal, leading to the Resonant Raman Effect. A study of resonant Raman intensities provides us unique information regarding the excited electronic states in the substance.
Raman scattering is excited with laser lines from 457.9 nm to 647.1 nm of an Ar/Kr-ion laser and a He-Ne laser. The wavelength of the monochromators is calibrated using a standard mercury lamp, and the detection sensitivities of the systems at different wavelengths are calibrated using a quartz-tungsten-halogen irradiation source. Fig. 5.15 shows the representative spectra of a SWNTs@SAPO-11 single crystal for thirteen different laser energies in the range 400 - 900 cm\(^{-1}\). The weak PL from the sample was baseline corrected from the spectra. And the spectra intensity is normalized to the laser power. The Raman bands of nanotubes demonstrate the resonance enhancement of the spectra at particular laser wavelengths. The spectra recorded in the red are very weak except that an extra

**Fig. 5.15:** Normalized resonant Raman spectra of SWNTs@SAPO-11 with excitation wavelength from 457.9 to 647.1 nm.
vibration frequency at 831 cm\(^{-1}\) is observed. With decreases of the laser wavelength, the signals decreased significantly, implying the resonant maximum for (3,0) nanotubes is achieved when laser wavelength is around 632.8 nm (1.79 eV). While the Raman vibration modes at 504 cm\(^{-1}\), 548 cm\(^{-1}\) and 760 cm\(^{-1}\) increased significantly, the resonant maximum is observed when the spectra are excited with the laser excitation for wavelength around 472.2 nm (2.64 eV). Then they are weak again as demonstrated by the spectrum at 465.8 nm laser line.

![Graph showing integrated intensity as a function of photon energy](image)

**Fig. 5.16:** The integrated intensity of peaks at 504 cm\(^{-1}\), 548 cm\(^{-1}\) and 760 cm\(^{-1}\) are plotted as a function of excitation laser energy.

The intensity profile can be visualized by evaluating the integrated intensity of each peak as demonstrated in Fig. 5.16. The solid square, stars and circle correspond to the peaks at 504 cm\(^{-1}\), 508 cm\(^{-1}\) and 761 cm\(^{-1}\), respectively. Two dominating peaks are clearly seen at ~ 2.4 eV and ~ 2.6 eV. The Raman signal is
obviously resonance enhanced for the two particular energies. This means that the energies match an electronic transition. As agree well with the absorption bands observed for (2,2) SWNTs. Note that the spectra were corrected for the sensitivity of the system in addition to the laser power normalization. The spectra clearly demonstrate resonance behaviour of the RBM.

5.6 Perfect alignment of 0.3 nm SWNTs

As-grown crystals are clear and transparent (see Fig. 5.17 (left)). When gradually heated in a vacuum of $10^{-3}$ mbar at temperature up to 773 K, the DPA molecules will decompose so that N and H will be pumped out of the channels and carbon nanotubes can be formed. Thus, the crystal color turned to black. The crystal is highly optically anisotropic with strong optical absorption when the electric field of the incident light is polarized parallel to the $c$-axis of the crystal, and is almost transparent when the electric field ($E$) of the incident light is perpendicular to the $c$-axis (see Fig. 5.17). This phenomenon is in agreement with previous work for 0.4 nm SWNTs formed inside the channels of AlPO$_4$-5 crystal [31].

Fig. 5.17: AEL crystals viewed under the microscope. On the left are the crystals with the organic precursor. In the middle and on the right are the crystals with SWNTs inside the channels. Electric field (E) polarization of the viewing light is as indicated.
Polarization of the incident and scattered light is not an important issue for sample of misaligned carbon nanotubes, but polarization effects are very important for Raman resonance of sample of aligned nanotubes. Carbon nanotubes behave as antennas, with the adsorption/emission of light being highly suppressed for light polarized perpendicular to the nanotubes axis. As a result, the sample is anisotropic, as shown in Fig. 5.17. Thus the study on the polarization dependent Raman spectra will give us useful information to understand how the 0.3 nm SWNTs are aligned in the AEL crystal channels. Raman spectra were excited with a Ar/Kr ion laser (514.5 nm) and recorded using a micro-Raman setup. A 100× microscope objective was used to focus the laser beam and collect of the scattered light. All Raman spectra

Fig. 5.18: Sketch show of the Raman scattering configuration. The incident excitation laser is polarized along the axis (z), and propagates along axis (-x). The back scattered signals are along axis (x). c represents nanotubes axis; θ is the polarization angle from the z axis to the nanotubes axis.
were taken in backscattering configuration, with the incident and scattered light propagating perpendicular to the nanotubes axis.

**Fig. 5.18** shows the polarized Raman scattering configuration. The incident laser is polarized along the z axis, and propagates along -x axis. The back-scattered Raman signals are along x axis. \( c \) represents crystal channels axis (nanotubes axis);

**Fig. 5.19**: shows the polarized Raman spectra in the RBM region (a) and in the G-band region (b) from 0° to 90° after suppressing the broad luminescent background.

Fig. 5.18 shows the polarized Raman scattering configuration. The incident laser is polarized along the z axis, and propagates along -x axis. The back-scattered Raman signals are along x axis. \( c \) represents crystal channels axis (nanotubes axis);
θ is the polarization angle from the z axis to the channels axis. In the experiment, the polarization angle was turned by rotating the sample stage. A linear polarizer was put in the collection path. Thus, we could measure the signals both in VV (polarizations of laser light and the Raman scattering light are parallel) and VH (polarizations of laser light and Raman scattering light are perpendicular) geometries.

Fig. 5.19 (a) and (b) display, respectively, the polarized Raman spectra in the RBM region and in the G-band region taken from one spot on the sample. It was measured under variant polarization angles ranging from 0° to 90° after suppressing the broad luminescent background. Both VV (upper curves) and VH (lower curves) configurations are shown in each figure. In the VV configuration, the incident and the scattered polarization are parallel to each other, while they are perpendicular to each other in VH configuration. It is obviously seen in the figures that the intensities of all Raman modes decrease dramatically with increase of the polarization angle from \( \theta = 0^\circ \) to \( \theta = 90^\circ \) with a maximum at \( \theta = 0^\circ \) in VV configuration. In the VH configuration, the intensities of these Raman modes increase with increase of the polarization angle until \( \theta = 45^\circ \), then decrease symmetrically to 90° with a maximum at \( \theta = 45^\circ \). This polarization dependence arises from the anisotropic geometry of the SWNTs@AEL crystal, and the resonant transitions between van Hove singularities. As the length-to-diameter ratio of a SWNT is very large, the polarization effect of its dielectric function is obvious. Considering that only the light polarized along the tube axis could be absorbed by the nanotubes, i.e. the polarizability factor in the tube direction is \( \alpha_{zz} = 1 \), and all other elements of the polarizability factor are zero [26], then for perfectly aligned SWNTs the intensity of resonant Raman signals in the VV and VH configurations are given by:

\[
I_{R-VV} \propto \cos^4 \theta; \quad I_{R-VH} \propto \cos^2 \theta \sin^2 \theta \quad (5.3)
\]
The $\theta$ dependence of the RBM and G-band Raman intensities is plotted in Fig. 5.20. The open symbols correspond to VV configuration, while the solid symbols correspond to VH configuration (The intensity is normalized by the intensity at 0° in the VV geometry for each peak). They are well fitted by two lines with the functions of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$.

**Fig. 5.20:** The $\theta$ dependence of the RBM and G-band Raman intensities. The solid symbols correspond to VV configuration, while the open ones correspond to VH configuration (The intensity is normalized by the intensity at 0° in the VV geometry for each peak). They are well fitted by two lines with the function of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$.

The $\theta$ dependence of the RBM and G-band Raman intensities is plotted in the Fig. 5.20. The open symbols correspond to VV configuration, while the solid symbols correspond to VH configuration (The intensity is normalized by the intensity at 0° in the VV geometry for each peak.). They are well fitted by two lines with the functions of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$. Resonant Raman investigations on carbon nanotube bundles showed a similar dependence with the polarization angle...
[26-29]. The misalignment of the nanotubes in those bundles with an orientation distribution varying from $10^\circ$ to $75^\circ$ made the Raman intensity dispersed in their fitting curves. In contrast, the data for the 0.3 nm SWNTs were well fitted using equation (5.3) (see Fig. 5.20), which showed again that the carbon nanotubes were perfectly aligned.

![Figure 5.21](image-url)

**Fig. 5.21:** shows the polarized Raman spectra in the RBM region (a) and in the $G$-band region (b) from $0^\circ$ to $90^\circ$ after suppressing the broad luminescent background.
We also measured the polarized Raman spectra of SW NTs@SAPO-11 with the laser excitation for wavelength around 632.8 nm. Fig. 5.21 shows the polarized Raman spectra in the RBM region (a) and in the G-band region (b) measured under variant polarization angles ranging from 0° to 90° after suppressing the broad luminescent background. Both VV (upper curves) and VH (lower curves) configurations are shown in each figure. It is obviously seen in the figures that the intensities of all Raman modes are polarization dependence. The θ-dependence of

![Graph showing polarization angle vs. intensity ratio]
the Raman intensities is plotted in the Fig. 5.22. The open symbols correspond to the VV configuration, while the solid ones correspond to the VH configuration. (The intensity is also normalized by the intensity at 0° in the VV geometry for each peak). They are well fitted by using equation (5.3). The good agreement also indicates that the (3,0) tubes are perfectly aligned along the channels of AEL crystals

5.7 Summary

In summary, mono-sized SWNTs with diameter only 0.3 nm are synthesized inside the channels of SAPO-11 crystals. The SWNTs@SAPO-11 crystal structure derived from single crystal X-ray diffraction data shows that the major and minor axes of elliptical channels are 0.65 and 0.43 nm. Considering of 0.4 nm SWNTs formed in 0.73 nm AFI crystal channels, the diameter of nanotubes can be predicted from the size of SAPO-11 crystal channels, and is estimated to be about 0.3 nm. The structure of this nanotube is investigated by micro-Raman spectroscopy, Two strong Raman modes at 760 cm⁻¹ and 831 cm⁻¹ are observed and assigned to the radial breathing A₁g mode for (2,2) and (3,0) nanotubes, respectively. Strong curvature effects induce instability of freestanding nanotubes. The electronic structures of the (2,2) and (3,0) nanotubes are studied by polarized adsorption spectra and resonant Raman spectra.
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Chapter 6

Iodine nanostructures

Incorporated inside the Channels of AEL Crystals

In this chapter, we report the fabrication method of nanostructured iodine species incorporated inside the channels of AlPO_4-11 (IUPAC code AEL) single crystals, and investigation of the structural and optical properties of these nanostructured iodine species.

6.1 Introduction

During the last two decades, microporous single crystals, such as molecular sieves proved to be pertinent in ion-exchange, separation, and catalysis in a variety of hydrocarbon reactions, such as cracking, hydrocracking, alkylation and isomerisation [1]. Recent years, the applications of porous crystalline materials have been extended to the generation of new supra-molecular structures by intercalating guest molecules into the pores of the molecular sieve templates [2-9]. These novel guest-host composites are of many potential applications, such as for optical data storage [2], laser-frequency conversion [3-6], and microcavity lasers [7-9]. These applications could greatly benefit from nano-structured guest materials in which molecular sieve crystals are aligned. In the previous chapters, we showed two examples of the formation ultra-small single-walled carbon nanotubes (SWNTs) created inside the channels of AlPO_4-5 (AFI) and AEL single crystals. These perfectly aligned SWNTs provide a platform on which the experimental and
theoretical studies can be carried out on the quasi-one-dimensional (1D) material system. This discovery suggests that zeolite crystals are ideal host for the preparation mono-sized nanomaterials as promising system to realize novel optoelectronic functional devices.

Iodine (atomic number=53, atomic mass=127) is a dark-gray/purple-black solid that sublimes at standard temperatures into a purple-pink vapor that has an irritating odor. This halogen forms compounds with many elements, but is less active than the other members of its Group VII (halogens) and has some metallic-like properties. The iodine vapor consists of a weakly bound diatomic molecule, I₂, which facilitates assembly molecular-sized functional units in zeolite crystal channels. AEL framework consists of parallel open one-dimensional channels with inner diameter around $4.3 \times 6.7$ Å [10-12]. A pure AEL crystal is optically transparent from ultraviolet to near-infrared, a good insulator, and thermally stable up to 1273 K. The highly ordered pore structure is ideal special template for the fabrication iodine molecule arrays.

### 6.2 Iodine@AEL sample preparation

As shown in Fig. 6.1, Iodine species were incorporated into the AEL channels by a physical diffusion method. The AEL crystals were firstly calcined at 580°C in O₂ atmosphere for about 48 hours to remove the organic templates of dipropylamine (DPA) molecules in the channels. Thus the channels are emptied. The calcined zeolite crystals were then sealed together with pure iodine source (BDH 99%) in a Pyrex tube at a vacuum of $10^{-3}$ mba. With rising temperature, iodine was introduced to the channels by physical adsorption. The samples turned colourful
after being exposed to iodine vapour. The excess of iodine on the zeolite surface was removed by sublimation at room temperature for 3 days.

Fig. 6.1: schematically shows the experimental setup for synthesis Iodine@AEL composite.

Fig. 6.2: The diffusion process of occluding iodine molecules into the channels of AEL single crystal. (a) calcined AEL crystal. (b) Low loading iodine@AEL. (c) Moderate loading iodine@AEL. (d) High loading iodine@AEL.
The saturated iodine-loaded AEL (iodine@AEL) crystals were red in color, while the calcined AEL crystals are clear and transparent. As shown in Fig. 6.2, the iodine loading density increases gradually with increasing exposure duration and treating temperature as well. The iodine@AEL crystal is optically isotropic at a low loading level, and optical anisotropic at high loading density.

![X-ray fluorescence (XRF) pattern of iodine@AEL crystals. The signals in (a) are taken from the calcined AEL crystals, and signals in (b) are taken from the iodine@AEL composite.](image)

**Fig. 6.3:** The X-ray fluorescence (XRF) pattern of iodine@AEL crystals. The signals in (a) are taken from the calcined AEL crystals, and signals in (b) are taken from the iodine@AEL composite.
Fig. 6.3 shows the X-ray fluorescence (XRF) pattern of the iodine@AEL single crystals. The signals in (a) are taken from the calcined AEL crystals, distinguished the elements of Al, P, and O that contained in the AEL framework. And signals in (b) are taken from the iodine@AEL composite. Because of low sublimation point, it confirms that the iodine species are adsorbed inside the channels of AEL crystals. No iodine species have been distinguished in the AEL external surface and the channels nearby AEL surface.

6.3 Iodine molecular ribbon sheets formed in AEL crystals

6.3.1 Structural characterization of low loading iodine@AEL samples

AEL single crystals were synthesized using hydrothermal method. The as-grown AEL crystals have a good morphology and a typical dimension of 30 µm×20µm×90µm, as shown by the Scanning electron microscopy (SEM) image in the Fig. 6.4 (a). The crystallinity of the as-synthesized samples was checked by powder X-ray diffraction (Philips PW1830 diffractmeter). Our samples have the same crystal structure as that of AEL reported [13-14]. Fig. 6.4 (b) and (c) show schematic configuration and model of AEL crystal plane (001), respectively. The structure of AEL crystal is composed of AlO$_4$ and PO$_4$ tetrahedra. Three vertices of each tetrahedron are linked to form sheets containing 4-, 6-, and 10-rings. Columns of 4-, 6-, and 10-rings are formed running parallel to y axis. Isolated parallel channels spanned by 10-rings have an elliptical cross section and a surface bounded by 4- and 6-rings. The diameters of the major and minor axes of the AEL crystal are 6.7 and 4.3 Å. Thus, it can be expected that the iodine molecules can only be oriented in yz plane.
Since the iodine molecules are confined in yz plane, the study on the polarization dependent Raman spectra will give us more useful information to understand the structure and intrinsic properties of iodine species inside the elliptical channels of AEL crystals. Fig. 6.5 shows the polarized Raman scattering configuration. The incident laser is polarized along the y axis, and propagates along -x axis. The back-scattered Raman signals are along x axis. \( c \) represents the channels axis; \( \theta \) is the polarization angle from the y axis to the channels axis. In the experiment, the polarization angle was turned by rotating the sample stage. A linear polarizer was put in the collection path. Thus, we could measure the signals both in VV (polarizations of laser light and the Raman scattering light are parallel) and VH (polarizations of laser light and Raman scattering light are perpendicular) geometries.

**Fig. 6.4:** (a) Scanning electron microscopy images of pristine AEL single crystals. (b) Geometric configuration of (001) plane. (c) Model of the AEL crystal viewed along (001) direction.
As shown in Fig. 6.6, in both VV and VH configurations, there are two highly polarized modes at 207 cm\(^{-1}\) and 213 cm\(^{-1}\). These vibration modes can be attributed to vapor like molecule. In iodine vapor, these modes are usually observed at 214 cm\(^{-1}\). The slight downshift 7 cm\(^{-1}\) can be explained by the increased interaction between iodine species and zeolite frameworks [15-18]. The intensity of Raman signal at 207 cm\(^{-1}\) decreases dramatically with increase of the polarization angles from \(\theta = 0^\circ\) to \(\theta = 90^\circ\) in VV configuration. In the VH configuration, the intensities of these Raman modes increase with increase of the polarization angle.

**Fig. 6.5:** Sketch show of the Raman scattering configuration. The incident excitation laser is polarized along the axis (y), and propagates along axis (-x). The back scattered signals are along axis (x). \(\textbf{c}\) represents channels axis; \(\theta\) is the polarization angle from the y axis to the channels axis.
until $\theta = 45^\circ$, then decrease symmetrically to $90^\circ$. Thus the vibration mode can be attributed to the iodine molecules which are oriented along the AEL crystal channels. In contrast, the intensity of Raman signal at 214 cm$^{-1}$ increases significantly with increase of the polarization angles from $\theta = 0^\circ$ to $\theta = 90^\circ$ in VV configuration. In the VH configuration, the intensities of these Raman modes increase with increase of the polarization angle until $\theta = 45^\circ$, then decrease symmetrically to $90^\circ$. Therefore the vibration mode at 214 cm$^{-1}$ can originate from the molecular iodine which is orientated perpendicular to channels. Due to size confinement of the AEL channels, this vibration mode is slightly shift 7 cm$^{-1}$ to high frequency. As shown in Fig. 6.7(a).
Fig. 6.6: Polarization Raman spectra of iodine@AEL at VV and VH configurations are shown in (a) and (b), respectively. The measurement method has been described in Fig. 5.5.
As mentioned in the above section, the iodine molecules are confined in the yz plane, there are no adsorption when the light polarized along x axis (see Fig. 6.7 (b) and (c)). Considering that the light polarized along the channels (y axis) could be adsorbed by iodine molecules B (along the channels), and the light polarized along z axis could be adsorbed by iodine molecules A (perpendicular the channels), it is interesting to study polarization dependent Raman spectra when the incident excitation laser is polarized along the y axis with propagation along –z axis, as well as polarized along z axis with propagation along –y axis, respectively. Hence, by comparing these polarized Raman spectra, we can get more detailed information about the geometrical structure for iodine species; Fig. 6.8 shows the polarized Raman scattering configuration. The incident excitation laser is polarized along the axis (y), and propagates along axis (-z). The back scattered signals are along axis (z).

Fig. 6.7: Schematic diagram illustrating structure of iodine encapsulated in the channels of AEL crystal: (a) viewed along x axis; (b) viewed along z axis; (c) viewed along y axis. A represents iodine molecule oriented perpendicular to channels; B represents iodine molecule oriented along channels (y axis).
\( c \) represents channels axis; \( \theta \) is the polarization angle from the \( y \) axis to the channels axis.

Fig. 6.9 shows polarized Raman spectra at VV and VH configuration. Not surprisingly, only one highly polarized mode at 207 cm\(^{-1}\) is observed. This vibration mode is due to the iodine molecules oriented along crystal channels. For the VV configuration, the intensity of Raman signal at 207 cm\(^{-1}\) decreases dramatically with increase of the polarization angles from \( \theta = 0^\circ \) to \( \theta = 90^\circ \) with a maximum at \( \theta = 0^\circ \). For the VH configuration, the intensities of this Raman mode increase with increase of the polarization angle until \( \theta = 45^\circ \), then decrease symmetrically from \( \theta = 45^\circ \) to \( \theta = 90^\circ \) with a maximum at \( \theta = 45^\circ \). Obvious anisotropy of Raman vibration mode at 207 cm\(^{-1}\) in polarized Raman scattering indicate that these iodine molecules are oriented along the AEL crystal channels.

Fig. 6.8: Sketch show of the Raman scattering configuration. The incident excitation laser is polarized along the axis (y), and propagates along axis (-z). The back scattered signals are along axis (z). \( c \) represents channels axis; \( \theta \) is the polarization angle from the \( y \) axis to the channels axis.
Fig. 6.9: Polarization Raman spectra of iodine@AEL at VV and VH configurations are shown in (a) and (b), respectively. The measurement method has been described in Fig. 6.8.
Fig. 6.10: Sketch show of the Raman scattering configuration. The incident excitation laser is polarized along the axis (z), and propagates along axis (-y). The back scattered signals are along axis (y). \( m \) represents major axis of elliptical channel; \( \theta \) is the polarization angle from the z axis to the channels axis.

Fig. 6.10 shows the polarized Raman scattering configuration. The incident excitation laser is polarized along the axis (z), and propagates along axis (-y). The back scattered signals are along axis (y). \( m \) represents major axis of elliptical channel; \( \theta \) is the polarization angle from the y axis to the channels axis. As shown in Fig. 6.11, for both VV and VH configuration. Only one highly polarized mode at 214 cm\(^{-1}\) is observed. For the VV configuration, the intensity of Raman signal decreases dramatically with increase of the polarization angles from \( \theta = 0^\circ \) to \( \theta = 90^\circ \). For the VH configuration, the intensities of this Raman mode increase with increase of the polarization angle until \( \theta = 45^\circ \), then decrease from \( \theta = 45^\circ \) to \( \theta = 90^\circ \), which indicate that these iodine molecules are perpendicular to the AEL crystal channels. Based on the experimental data in Fig. 6.6, Fig. 6.9 and Fig. 6.11, we can reasonably assign the Raman bands 207 cm\(^{-1}\) and 214 cm\(^{-1}\) to iodine molecules along and perpendicular crystal channels, respectively.
**Fig. 6.11:** Polarization Raman spectra of iodine@AEL at VV and VH configurations are shown in (a) and (b), respectively. The measurement method has been described in Fig. 6.10.
6.3.2 Optical properties of low loading iodine@AEL samples

To study the electronic properties of the iodine molecular ribbon sheets confined inside the channels of AEL single crystal, we have measured the polarized absorption spectra. The spectra are recorded for polarization angles from $0^\circ$ to $90^\circ$ by a step of $15^\circ$. In order to carry out the transmission spectrum measurements, we mounted the low loading iodine@AEL sample in a hole drilled on a ceramic plate with epoxy resin and polished the sample to a thickness as thin as about 10 µm. Fig. 6.12 shows the absorption spectra of low loading iodine@AEL single crystal measured at room temperature for the light polarized along different directions. The top curve labeled $0^\circ$ corresponds to the absorption spectrum for the light polarized parallel to the crystal axis ($\theta = 0^\circ, E//c$). One absorption band with peak energy at 2.5 eV is observed. However, this absorption band gradually decreases as increasing the polarization angle, and finally becomes negligible at $\theta = 90^\circ$ ($E\perp c$). In contrast, a new absorption band at 2.4 eV is detected, and intensity of this absorption band increases with increasing the polarization angle. The very different polarization behavior of these two absorption bands indicates that they might originate from two different structures of iodine specimens, consistent with the double structures observed in polarized Raman spectra (Fig. 6.6(a)). Thus, we attribute the band at 2.5 eV to the adsorption of molecular iodine oriented along crystal channels. The band at 2.4 eV is attributed to molecular iodine oriented perpendicular to crystal channels (see Fig. 6.7). The slight red shift is due to the interaction between crystal framework and iodine molecules.
The iodine molecules are introduced inside the channels of AEL crystals by physical diffusion method, the loading density increases gradually with increasing temperature. The high loading iodine@AEL crystals are obtained after heating crystals at around 473 K for several hours, which exhibit a strong anisotropic absorption of light when viewed under an optical microscope with white linearly polarized light. The crystal becomes dark when the light polarized parallel to the \( c \)-axis of the crystal, whereas they show only a red colour when the electronic field of incident light is turned by 90°, as shown in Fig. 6.13. This anisotropic optical property implies that an ordered iodine species with a large aspect ratio was formed.

**Fig. 6.12:** The polarized adsorption spectra of the high loading iodine@AEL single crystal. The topmost and bottommost curves are for the \( E \parallel c \) and the \( E \perp c \) polarization configurations, respectively, where \( E \) is the electronic field and \( c \) is the channels axis.

### 6.4 Iodine molecular chains formed in AEL crystals

The iodine molecules are introduced inside the channels of AEL crystals by physical diffusion method, the loading density increases gradually with increasing temperature. The high loading iodine@AEL crystals are obtained after heating crystals at around 473 K for several hours, which exhibit a strong anisotropic absorption of light when viewed under an optical microscope with white linearly polarized light. The crystal becomes dark when the light polarized parallel to the \( c \)-axis of the crystal, whereas they show only a red colour when the electronic field of incident light is turned by 90°, as shown in Fig. 6.13. This anisotropic optical property implies that an ordered iodine species with a large aspect ratio was formed.
along the channels.

![Image](image.jpg)

**Fig. 6.13:** The optical microscopic view of an iodine@AEL crystal with polarized transmitted electric field. They behaved as a good polarizer.

### 6.4.1 Structural characterization of high loading iodine@AEL samples

The different loadings of iodine molecules inside the channels of AEL crystals are characterized by Raman spectra. The incident laser is polarized along the crystal channels, and propagates along the minor axis of elliptical channels. As shown in Fig. 6.14, in the lower diffusion stage, Raman spectra of the iodine species inside the channels of AEL crystals exhibit the typical spectra of molecular iodine in vapor phase, which give rise to the vibrational frequency at 207.6 cm\(^{-1}\); we assign this Raman mode to iodine molecules oriented along the AEL crystal channels. Two new Raman features at 198 cm\(^{-1}\) and 211.6 cm\(^{-1}\) are observed when the iodine density inside AEL crystal becomes higher, respectively. With regard to above-mentioned iodine molecules oriented perpendicular to channels in the low loading sample, which give rise to the Raman mode at 214 cm\(^{-1}\). The vibration mode at 211.6 cm\(^{-1}\) can originate from iodine molecules oriented partially perpendicular to the AEL crystal channels. The vibration mode at 198 cm\(^{-1}\) can be attributed to iodine molecule chain (I\(_2\))\(_n\). The downshift of Raman scattering is possibly caused by the increased interaction between iodine molecules under the higher density of iodine diffusion. The same phenomena can also be observed in the other energy part of the
second-order spectra from 375 cm\(^{-1}\) to 450 cm\(^{-1}\). More recently, Ye et al., investigated iodine insertion compounds of AlPO\(_4\)-5 zeolite using polarization dependence Raman spectra and polarized optical adsorption spectra [19]. They found two one-dimensional iodine wire species (I\(_n^+\) and (I\(_2\))\(_n\)) formed inside the channels of AlPO\(_4\)-5 crystal, which give rise to the vibration mode at 110 cm\(^{-1}\) and 168 cm\(^{-1}\) in Raman spectra, respectively. The vibration mode of (I\(_2\))\(_n\) also have been observed at 175 to 190 cm\(^{-1}\) in liquid iodine as well as amorphous iodine [20, 21]. Due to the confinement of AEL crystal channels, the vibration frequency of (I\(_2\))\(_n\) in AEL crystal is higher than that observed in liquid iodine.

![Raman spectra of iodine@AEL](image)

**Fig. 6.14:** Raman spectra of iodine@AEL: (a) high loading density; (b) low loading density. The incident excitation laser is polarized along the channels axis.

Since the high loading iodine@AEL crystal exhibits a strong anisotropic absorption, in contrast, the low loading iodine@AEL crystal is almost isotropic.
Hence, by study on the polarized Raman spectra, we can get more detailed information about the geometrical structure of high loading iodine species in the channels of AEL crystals. Polarized Raman scattering of the iodine@AEL single crystal is measured using the 514.5 nm line from an Ar/Kr ion laser as the excitation source. The photon energy of this laser line corresponds to a transition form the lowest vibrational level of the singlet electronic ground state to high vibrational level of a triplet excited state. The Raman scattering configuration has been shown in Fig. 6.5. The incident excitation laser is polarized along the axis (y), and propagates along axis (-x). The back scattered signals are along axis (x). Then we consider the effect of rotating the crystal c axis from y axis to z axis.

As shown in Fig. 6.15, in both VV and VH configurations, all of these three Raman vibration modes at 198 cm\(^{-1}\), 207.6 cm\(^{-1}\) and 211.6 cm\(^{-1}\) are highly polarized. In VV configuration, we see that the intensity of Raman modes at 198 cm\(^{-1}\) and 207.6 cm\(^{-1}\) decreases dramatically with increase of the polarization angles from \(\theta = 0^\circ\) to \(\theta = 90^\circ\) with a maximum at \(\theta = 0^\circ\). In the VH configuration, the intensities of these two Raman modes increase with increase of the polarization angle until \(\theta = 45^\circ\), then decrease symmetrically to 90\(^\circ\) with a maximum at \(\theta = 45^\circ\). The obvious anisotropy of the iodine@AEL system in polarized Raman scattering indicates that these anisotropic modes are associated with one-dimensional iodine molecular chains and vapor-like molecules species oriented along the crystal channels. In contrast, the Raman signal at 211.6 cm\(^{-1}\) slightly shifts to 212.8 cm\(^{-1}\), while the intensity increases dramatically with increase of the polarization angles from \(\theta = 0^\circ\) to \(\theta = 90^\circ\) in VV configuration. In the VH configuration, the intensities of this Raman mode increase with increase of the polarization angle until \(\theta = 45^\circ\), then decrease symmetrically to 90\(^\circ\). It is worth noticing that the weak signal of this Raman mode can be observed in VV configuration at \(\theta = 0^\circ\), as well as in VH configuration at \(\theta = 0^\circ\) and at \(\theta = 90^\circ\). Thus, we assign this Raman mode to the
vapor-like iodine molecules which are partially perpendicular the AEL crystal channels (see Fig.6.17 (a)).

Fig. 6.15: The polarized Raman spectra of I species in the channels of AEL crystals (a) VV configuration and (b) VH configuration. The measurement method has been described in Fig. 6.5.
The $\theta$-dependence of the Raman intensities is plotted in the Fig. 6.16. The solid square symbols correspond to the VH configuration, while the open squares correspond to the VV configuration. (The intensity is normalized by the intensity at $0^\circ$ in the VV geometry for each peak). They are well fitted by two lines with the functions of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$.

The $\theta$-dependence of the Raman intensities is plotted in the Fig. 6.16. The solid square symbols correspond to the VH configuration, while the open squares correspond to the VV configuration. (The intensity is normalized by the intensity at $0^\circ$ in the VV geometry for each peak). They are well fitted by two lines with the functions of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$. The good agreement between our experiment data and these curves indicates that the iodine molecular chains are perfectly aligned along the channels of AEL crystal.
In view of the elliptical space limitation, the vibration of iodine molecules B (along the channels), iodine molecules C (partially perpendicular the channels), and iodine molecular chains along z axis are allowed when the incident laser is polarized along the channels (y axis) (see Fig. 6.17(b)). However, these vibrations are prohibited when the incident laser is polarized along the x axis. Thus, it could be very interesting to study the polarization dependent Raman spectra by rotating the crystals from y axis to x axis. In Fig. 6.17 (c), in the case of the incident laser is polarized along the major axis of elliptical channel (z axis), only the vibration of iodine molecules C is allowed. However, this vibration is prohibited when the incident laser is polarized along the minor axis of elliptical channel (x axis). While the vibrations of iodine molecules B and iodine molecular chains D are always prohibited. We can distinguish them by their polarization dependence Raman spectra.

**Fig. 6.17:** Schematic diagram illustrating structure of iodine encapsulated in the channels of AEL crystal: (a) viewed along x axis; (b) viewed along z axis; (c) viewed along y axis. B represents iodine molecule oriented along channels (y axis); C represents iodine molecule oriented partially perpendicular to channels; D represents iodine nano-chain oriented along channels.
Fig. 6.18: The polarized Raman spectra of I species in the channels of AEL crystals (a) VV configuration and (b) VH configuration. The measurement method has been described in Fig. 6.8.
Fig. 6.18 shows polarized Raman spectra at VV and VH configuration. The measurement method has been described in Fig. 6.8. The incident excitation laser is polarized along the axis (y), and propagates along axis (-z). The back scattered signals are along axis (z). We rotate the crystal form x axis to y axis. $\theta$ is the polarization angle from the y axis to the channels axis. For the VV configuration, the intensity of Raman signals at 198 cm$^{-1}$, 207 cm$^{-1}$ and 211 cm$^{-1}$ decreases gradually with increase of the polarization angles from $\theta = 0^\circ$ to $\theta = 90^\circ$. For the VH configuration, the intensities of these Raman modes increase with increase of the polarization angle until $\theta = 45^\circ$, then decrease from $\theta = 45^\circ$ to $\theta = 90^\circ$. Obvious

Fig. 6.19: The $\theta$ dependence of the iodine nano-chain Raman intensities. The solid symbols correspond to VV configuration, while the open ones correspond to VH configuration (The intensity is normalized by the intensity at $0^\circ$ in the VV geometry for each peak). They are well fitted by two lines with the function of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$.

Fig. 6.18 shows polarized Raman spectra at VV and VH configuration. The measurement method has been described in Fig. 6.8. The incident excitation laser is polarized along the axis (y), and propagates along axis (-z). The back scattered signals are along axis (z). We rotate the crystal form x axis to y axis. $\theta$ is the polarization angle from the y axis to the channels axis. For the VV configuration, the intensity of Raman signals at 198 cm$^{-1}$, 207 cm$^{-1}$ and 211 cm$^{-1}$ decreases gradually with increase of the polarization angles from $\theta = 0^\circ$ to $\theta = 90^\circ$. For the VH configuration, the intensities of these Raman modes increase with increase of the polarization angle until $\theta = 45^\circ$, then decrease from $\theta = 45^\circ$ to $\theta = 90^\circ$. Obvious
The anisotropy of iodine@AEL system in polarized Raman scattering indicates that these iodine species are oriented in yz plane.

The $\theta$-dependence of the Raman intensity at 198 cm$^{-1}$ is plotted in the Fig. 5.19. The solid circle symbols correspond to the VH configuration, while the open squares correspond to the VV configuration. (The intensity is normalized by the intensity at $0^\circ$ in the VV geometry for each peak). They are well fitted by two lines with the functions of $\cos^4 \theta$ and $\cos^2 \theta \sin^2 \theta$. The good agreement between our experiment data and these curves indicates that the iodine molecular chains are perfectly aligned in the crystal channels.

We also measured polarized Raman spectra of iodine@AEL when the incident excitation laser is polarized along the major axis of elliptical channel (z axis), and propagates along axis (-y). In the experiment, the polarization angle was tuned by rotating sample stage from major axis to minor axis (x axis) of elliptical channel. The measurement method has been described in Fig. 6.10. The polarized Raman spectra at VV and VH configuration are shown in Fig. 6.20, where only the Raman mode of iodine molecules C at 212.5 cm$^{-1}$ is observed. For the VV configuration, the intensity of this Raman mode decreases gradually with increase of the polarization angles from $\theta = 0^\circ$ to $\theta = 90^\circ$. For the VH configuration, the intensities of this Raman mode increase with increase of the polarization angle until $\theta = 45^\circ$, then decrease from $\theta = 45^\circ$ to $\theta = 90^\circ$. These results are consistent with our assumption (see Fig. 6.17), which again indicate that all of the iodine species are oriented in yz plane.

Based on the information, we assign these Raman modes to different types of the iodine species confined inside the channels of AEL crystal. The exact structure of iodine molecular chains are, however, not clears.
Fig. 6.20: The polarized Raman spectra of iodine species in the channels of AEL crystals (a) VV configuration and (b) VH configuration. The measurement method has been described in Fig. 6.10.
6.4.2 Optical properties of high loading iodine@AEL samples

Polarization adsorption spectra are measured for a high loading iodine@AEL single crystal, which is mechanically polished into a thin foil with thickness of about 10 μm. Transmission spectra were measured at room temperature, using a xenon incandescent lamp as a light source. The incident polarized light was focused onto the sample by a reflecting microscope objective, and the transmitted light was collected by another reflecting objective coupled with an optical fiber and dispersed by an Acton 275-mm single grating monochromator.

Fig. 6.21 shows a series of optical absorption spectra (plotted in optical density, OD) of the iodine@AEL crystal for light polarized along different directions. The polarization geometry is the same as that of polarization Raman measurement (see Fig. 6.5). The top curve labeled 0° corresponds to the absorption of light polarized parallel to the crystal axis (E‖c). In this spectrum, three peaks A, B and C centered at 1.9 eV, 2.4 eV, and 3.3 eV, respectively, are seen. The intensities of absorption bands A and C decrease monotonically with increasing polarization angle (the increment is 15°C), and finally become negligible in the perpendicular configuration (E⊥c). In contrast, the B band is less polarization dependent. The very different polarization behavior of the three bands indicates that they might originate from two different structures of iodine, consistent with the two structures observed in the polarization Raman spectra (Fig. 6.15). Based on the result of polarized adsorption for low loading iodine@AEL, we assign the A and C bands to the adsorption of iodine chains. We attribute the peak at 2.4 eV to the adsorption of iodine molecules. We could not carry out the measurement in the energy region higher than 4.0 eV, because the epoxy (EPOTEK 301, spectrally
transparent epoxy) used to hold the sample has strong absorption in the ultraviolet region.

**Fig. 6.21:** The polarized adsorption spectra of the high loading iodine@AEL single crystal. The topmost and bottommost curves are for the $E \parallel c$ and the $E \perp c$ polarization configurations, respectively, where $E$ is the electronic field and $c$ is the channels axis.

### 6.4.3 Stability of iodine molecular chain in AEL crystals

Thermal adsorption/desorption process of the iodine@AEL samples have been investigated using a thermal analysis apparatus (STA 449C Jupiter). The mass resolution of the equipment is 0.1 µg. The Differential scanning calorimetry (DSC) and thermogravimetry (TG) curves were taken simultaneously. In the experiment,
we kept the sample under a continuous flowing of helium gas, and carefully dehydrated the sample at 383 K to eliminate the influence of physisorbed water in the crystals. Fig. 6.22 shows the TG and DSC curves measured in the temperature range of 293K - 973K. The sample mass loss during heating is shown in TG curves. When temperature is above 450 K, the weight of the sample begins to decrease significantly due to desorption of the iodine species from the AEL crystal channels. The mass loss is not saturated even at temperature higher as high as 900 K, indicating the slow desorption speed of iodine species. The total weight losses is 8.4 wt% in the TG analysis. In the DSC curve, only a very broad peak in higher temperature range (> 500 K) is mainly due to the endothermic process of desorption of iodine species from the channels of AEL crystals.

![Graph of TG and DSC curves](image)

**Fig. 6.22:** The TG and DSC curves for high loading iodine@AEL samples in the temperature range of 293 K~ 973 K.
With micro Raman scattering, the high loading iodine@AEL crystal before and after DSC experiment is measured. As shown in Fig. 6.23, the chain species are the main population before the DSC experiment, as evidenced by the strongest Raman mode at 198 cm\(^{-1}\). However, the relative intensity of iodine chain decreases significantly after treatment. In contrast, the intensity of iodine molecules becomes the predominant Raman mode. The different behaviors of the chain and molecular mode indicate that the chain species are converted into molecular iodine.

**Fig. 6.23:** Raman spectra of high loading density iodine@AEL: (a) after DSC experiment; (b) before DSC experiment.
6.5 Summary

The iodine species are introduced into the channels of AEL single crystal by physical diffusion method. Due to the space confinement of the AEL channels, iodine molecules can only be oriented in two directions, either along the long-axis of the elliptical channel or along the channel direction. The structures of iodine species are characterized by polarized absorption spectra and polarized Raman spectra. It shows that the iodine specimens accommodated inside the channels show typical single molecular behavior at a low loading density and gradually evolved into one dimensional chain structure with increasing the loading level.
References:


Chapter 7

Conclusions and Future Works

In this chapter, I will summarize the main works done the thesis research. Conclusions of the research will be presented first, and then some suggestions for future works will be proposed.

7.1 Conclusions

Based on template-technique, several kinds of nano-materials, including 0.4 nm single-walled carbon nanotubes (SWNTs), 0.3 nm SWNTs, iodine molecules arrays were fabricated and characterized. Because the species are mono-sized and well aligned, they show interesting optical and electronic properties. In addition, these perfectly aligned species provide a platform on which the experimental and theoretical studies can be carried out on the quasi-one-dimensional (1D) material system. Five sequential parts can be classified in my PhD thesis as following:

I) AlPO₄-5 (AFI) and MeAPO-5 (AlPO₄-5 with metal ions, such as Si⁴⁺, Co²⁺, Mg²⁺, Mn²⁺, V⁵⁺ and Ti⁴⁺ incorporated into the lattice) crystals were synthesized using hydrothermal method. Optical Microscopy, Scanning Electron Microscopy (SEM), X-ray Diffraction Analysis (XRD) and X-ray Fluorescence (XRF) have been used to characterize these crystals. The results showed that the crystal quality was very good. Large AlPO₄-11 (AEL) and SAPO-11 zeolite crystals with a typical dimension of 30×50×150 micron were also fabricated. The crystals are of perfect orthorhombic morphology and high optical quality. To our best knowledge, they are the largest AEL crystals reported so far.
II) The effect of the carbon precursors on the quality as well as the filling density of the 0.4 nm SWNTs in the channels of AlPO₄-5 single crystals, were studied by means of Raman spectroscopy and polarized optical spectroscopy. Higher filling density of the SWNTs can be achieved by replacing the carbon precursor tripropylamine (TPA) with tetrapropylammonium-hydroxide (TPAOH), which contains more carbon atoms in a unit cell. Thermogravimetry (TG) measurements indicated that the loading density of TPAOH carbon precursors inside the channels of AlPO₄-5 crystals is much higher than others. Incorporation of metal cations (Mn, Mg, Co) or Si into AlPO₄-5 crystals gives rise to the formation of negatively charged frameworks and Brønsted acid sites. These frameworks thus play an important catalytic role in the pyrolysis and conversion of the organic molecules to SWNTs within the crystal channels. It is shown that the MeAPO-5 single crystals have a higher filling density of SWNTs than in those channels without the metal cations. The experimental results agreed well with the predictions of first-principles calculations, which showed the metal-incorporated frameworks to be favorable for the SWNTs formation.

III) Mass spectrometry, micro-Raman spectroscopy and thermogravimetric analysis are used to explore the thermal decomposition of carbon precursors (primarily the tripropylammonium cations) occluded within AlPO₄-5 crystals prepared in various medias (in the presence or absence of F⁻ ions, Si⁴⁺ substations of P⁵⁺), with the aim to fabricate high density 0.4 nm SWNTs. It has been found that the tripropylammonium precursors exist in the as-synthesized crystals in three different forms: tripropylammonium fluoride, hydroxide and tripropylammonium cation compensating the negative charge of the framework. The latter is bonded to the framework by strong chemical interaction and its decomposition undergoes by a
series of β-elimination reactions to give propylene and ammonia, with the stepwise formation of dipropylammonium and n-propylammonium cations. The 0.4 nm SWNTs filling density was found to be higher than that resulting from the carbon precursor of tripropylammonium fluoride and hydroxide, because of the strong adsorption force of the channel walls to pyrolyzate, as evidenced by the clear and strong radial breathing modes in Raman spectra.

IV) Even smaller sized SWNTs of diameter only 0.3 nm are synthesized inside the channels of SAPO-11 (AEL) crystals by pyrolysing organic template dipropylamine (DPA) molecules. The SWNTs@SAPO-11 crystal structure derived from single crystal X-ray diffraction data shows that the major and minor axes of elliptical channels are 0.65 and 0.43 nm. Considering of 0.4 nm SWNTs formed in 0.73 nm AFI crystal channels, the diameter of nanotubes can be predicted from the size of SAPO-11 crystal channels, and is estimated to be about 0.3 nm. The structure of this nanotube is investigated by micro-Raman spectroscopy, the results indicate that two possible structure (2,2) and (3,0) coexist inside the channels of SAPO-11 crystals. Strong curvature effects induce instability of freestanding nanotubes. The electronic structure of the (2,2) and (3,0) nanotubes are studied by polarized adsorption spectra and resonant Raman spectra.

V) The iodine species are introduced into the channels of AEL single crystal by physical diffusion method. Polarized absorption spectra and polarized Raman spectra have been investigated. It shows that both Iodine molecular chains and molecules exist inside the channels of AEL crystals. And the predominant structure will be altered by changing the iodine loading density. When the loading density is low, some iodine molecules are oriented along the AEL crystal channels, while others are oriented perpendicular to the channels. Due to size confinement of the
AEL channels, this vibration mode is slightly shift 7 cm\(^{-1}\) to high frequency. When the loading density is high, iodine molecular chain are formed. As a result, the crystals behave as good polarizer with high absorption for the light polarized parallel to the \(c\)-axis of the crystal. The polarization angle dependence of the Raman intensity indicates that the enclosed iodine molecular chains are highly oriented in the channels with their dipole transition moment mostly along the channels.

7.2 Suggestions for future work

In this thesis, we fabricated several kinds of nanomaterials using template technique, and obtained some interesting and valuable results. However, because of the limitation of time and equipment, some works still remain to be done to further understand the physical property of these nanostructures and fabrication of other nano-species. Here I would like to present some thought and suggestions for the future works.

I) Since the SWNTS formed inside the channels of SAPO-11 crystals are mono-sized and parallel in alignment. They offer the opportunity to study the electronic properties by transport measurement. However there is still a difficulty. The nanotubes are not continuous enough, thus a detectable current can not be passed under reasonable bias. A qualified SWNTs@SAPO-5 single crystal is delicate and fragile. In order to understand the electronic properties of the (2,2) and (3,0) nanotubes, more theoretical calculations should be carried out.

III) Besides tube (2,2), there are may other types SWNTs with diameter of about 0.3 nm such as tube (4,1), tube (4,0), tube (3,2) and tube (3,1). They are possibly produced using other zeolite crystal as template. A potential candidate is zeolite AIPO\(_4\)-31 (ATO) crystal, which have one-dimensional 12-ring channels with an inner diameter of 0.54 nm. By using this channel lattice as the template, ultra-small SWNTs with diameter lager than that of tube (2,2) but less than of tube (5,0)
might be attempted. This goal will be possible as the progress of Large optically clear MeAPO-31 single crystal.

IV) We have shown that both iodine molecular ribbon sheets and molecular chains exist inside the channels of AEL crystals. And the predominant structure will be altered by changing the loading density. It is an interesting work to find an optimal condition to get only iodine chains in the matrix.