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Synthesis and characterization of carbon-based materials

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Summary

Carbon is a fascinating element which can be observed in a large variety of morphologies and atomic structures due to its chemical ability to form different hybridizations. The present PhD thesis proposes the synthesis of several carbon-based materials using a unique and quite simple technique: *the oxy-acetylene combustion flame method*. From crystalline sp^3 - diamond to planar sp^2 - graphite, from the unidirectional nanotubes, needles and rods to bidimensional petals, a large variety of carbon materials are synthesized under the atmospheric pressure.

These various carbon forms have been produced using a set of different experimental parameters. Both the input gas ratio and the substrate temperature are found to play a key role in the synthesis of these new carbon materials. The high quality of the graphitic phases can be correlated to the large acetylenic content in the gas and to the high temperature of the substrate. Some specific morphologies such as petal-like single graphite crystals have been synthesized. Their sizes reach up to 20 μm . These bidimensional carbon materials are of particular importance to investigate fundamental physics in ideal low-dimensional systems. Polyhedral graphite crystals, which exhibit a 1D morphology, have also been produced. Their crystal structure is found to be highly graphitic although they display a cylindrical/polyhedral shape. Preliminary measurements of their field emission properties reveal a huge emission current, which is higher than the emission current obtained for multi-wall carbon nanotubes. The latter have also been synthesized in large amount and high quality using our oxy-acetylene combustion flame technique.

At last, using again the same experimental setup, a crystalline carbon nitride phase has been synthesized for the first time using a specific molecule called "melamine" as an organic precursor. Several experimental techniques, such as Energy Dispersive X-ray (EDX), X-ray Photoelectron Spectroscopy (XPS), Electron Energy Loss Spectroscopy (EELS), X-ray diffraction and Raman and infra-red spectroscopies have been used to analyze both the chemical composition and the crystalline structure of this new material, revealing a graphitic- C_3N_4 phase.

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Introduction

Since more than a quarter century, many progresses in the development of carbon-based materials have been reported due to the importance of carbon in modern science, in high-technology, and in a large domain of human activities. Unquestionably, carbon is the most versatile element of the periodic table. The largest group of compounds, the organics, owe their existence to the ability of carbon to simultaneously bond to itself and a variety of heteroatoms. Moreover, the properties of pure carbon allotropes span an enormous range. From crystalline sp^3 -bonded diamond to planar sp^2 -bonded graphite, from the recently discovered ball-shaped fullerenes molecules and carbon nanotubes ($sp^{2+\epsilon}$ -hybridization) to the unidimensional sp -bonded chains or rings, carbon research offers a unique richness and diversity.

Diamond materials are widely studied for various high-tech applications such as machining tools, coatings, for the protection against corrosion and biomaterials. The carbon nanotubes are expected to have an important potential impact in a variety of application domains such as molecular electronics and high-strength composite, thanks to its specific morphology. The poly-aromatic materials, based on sp^2 -bonded carbon, are very important industrially and are produced with a wide range of structures. The various possibilities of the orientation of the fundamental structural unit, the layer consisting of a carbon hexagonal network, result in a large set of carbon-based materials such as carbon fibers, pyrolytic carbons, carbon blacks, which exhibit specific properties directly related to their corresponding morphologies.

Several production techniques have been proposed for the synthesis of all these carbon-based materials. However, each of these technique is mainly focusing on the growth of one specific material. The aim of the present thesis is to synthesize several carbon-based materials using a single and quite simple technique: the oxy-acetylene combustion flame method. Such a technique has originally been developed for the synthesis of diamond films in the early nineties. In this method, only a simple experimental apparatus is required as the synthesis can be carried out under atmospheric pressure. The precursor gas ratio and the substrate temperature are the two experimental parameters which are found to play the major key role in the carbon-based material synthesis. Different morphologies of diamond have already been produced by

varying these two parameters, and the diagram of the possible diamond-like products has been previously reported in the literature.

In the present thesis, several carbon-based materials including various diamond phases are synthesized with the oxy-acetylene combustion flame technique performed in an experimental apparatus specially designed in our laboratory. Our goal is to complete the diagram of the carbon materials which could be produced with such technique, and more specifically to explore the region of the high temperatures for the substrate. As graphite is more stable than diamond at high temperatures, a large variety of graphitic materials with different morphologies are synthesized and their structures are accurately characterized using a huge set of experimental techniques.

The properties of graphitic materials are strongly influenced by the large anisotropy of graphite and the high quality of the crystal produced. Several characterizations are carried out in order to investigate the samples synthesized in our experimental set up at different scales. Scanning Electron Microscopy (SEM) is used for the investigation of the morphology at microscopic scale. Transmission Electron Microscopy (TEM), accessible in several modes (high resolution mode, electron diffraction mode,) is an efficient technique to reveal the ordering and the orientation of the fundamental structural unit of graphite at the nanoscale. In addition, the Raman spectroscopy is also applied to determine the in-plane correlation length as an indication of the degree of the graphitization. Using these techniques, two unusual crystalline morphologies of highly-oriented graphite have been accurately characterized. These two specific phases are a 2-dimensional layered structure and a 1-directional polyhedral structures, respectively. These new graphitic structures can be interesting potential candidates for many applications owing to their high crystallinity and specific morphologies. These new phases have not reported in the literature previously, and are one of the main scientific result of the present thesis.

The synthesis of carbon nanotubes is also performed using the oxy-acetylene combustion flame technique by adding a metal catalyst during the process. The nanotubes produced display a highly-crystalline well-ordered hollow structure. Consequently, our technique is shown to be an efficient tool for the growth of graphite-based materials.

In a second step, the oxy-acetylene combustion flame technique is also used to synthesize carbon-nitride materials which are very difficult to produce

and are expected to possess remarkable physical properties such as hardness, wide band gap and high thermal conductivity, leading to a huge domain of possible applications.

In order to synthesize carbon nitride phases, our technique has been modified to incorporate an organic precursor containing nitrogen. A special graphite cell is used as a reaction chamber and heated by the oxy-acetylene torch. This experimental set up generates a high thermal gradient inside the reactor, inducing a fast polycondensation of the precursor organic material. Electron Dispersive X-ray (EDX), X-ray Photoelectron Spectroscopy (XPS) and Electron Energy Loss Spectroscopy (EELS) are carried out for the chemical analysis of the different samples produced. A new *graphitic*-C₃N₄ phase is suggested; this is the second major scientific result of the present thesis.

In the first chapter, after a brief description of the standard carbon allotropes based on their hybridization states, different graphitic materials are classified in order to clarify the effect of their crystal structures and morphologies on their specific properties. In the second chapter, the oxy-acetylene combustion flame method is described. A brief summary related to the previous works based on this technique for the synthesis of diamond films is proposed. The various carbon materials successfully synthesized using the oxy-acetylene technique are presented in the third chapter. In the fourth chapter, the carbon nitride synthesis is carried out using the oxy-acetylene combustion flame method. The experimental characterization of this new carbon nitride phase is also accurately described in the fourth chapter. In addition, the field emission properties of one of the carbon materials synthesized in this work, the polyhedral graphite crystal, are measured and is described in the appendix. The synthesis and characterization of a new type of carbon material, the *carbonnecklace*, using one another plasma technique are also presented in appendix.

Chapter 1

Carbon based Materials

1.1 Introduction

The extraordinary ability of the chemical element carbon to atomically combine in different ways gives rise to a rich diversity of structural forms of solid carbon. Since fullerenes and carbon nanotubes have recently been discovered in addition to graphite and diamond, carbons still attract the attention of many researchers. Despite the fascinating structure and properties of fullerene-based materials and carbon nanotubes (CNTs), graphite-based materials, such as carbon fibers, still occupy the central position of the industrial production and applications. The extreme anisotropy in their bond energies of their crystal lattice results in highly anisotropic physical properties.

This chapter begins by summarizing the structure and chemical bonding of the various phases of carbon, including the four allotropes; diamond, carbynes, fullerenes and graphite, and is specially focused on carbon materials based on a graphitic structure in the following parts. The graphitic based structure can organize a variety of carbon materials because of their structural ordering and capacity of morphologies. A generic description of microstructures, including whole state of crystallinities, and a classification of graphitic materials are attempted to understand the rich polymorphism of carbon [1].

1.2 Carbon allotropes

The chemical element carbon can combine with itself and other elements in three types of hybridizations. This produces the rich diversity of structural forms of solid carbon. Carbon has the electronic ground state configuration $1s^2 2s^2 2p^2$ and can form sp^3 , sp^2 and sp hybrid bonds. Fig.1.1 shows the different hybridizations of carbon. In the sp^3 hybridization, four equivalent $2sp^3$ hybrid orbitals are tetrahedrally oriented around the atoms (Fig.1.1.c).

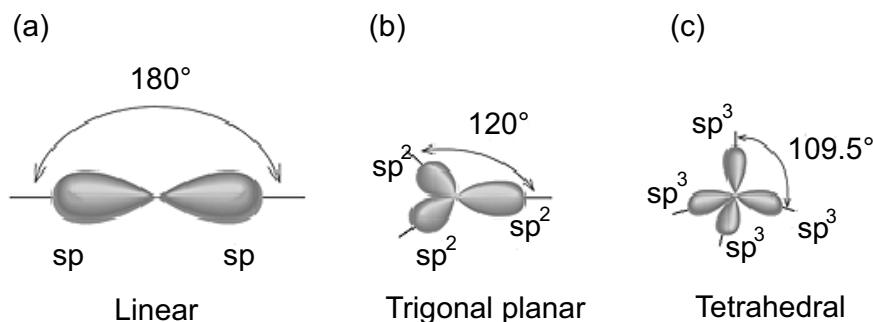


Figure 1.1: Different hybridization of carbon (a) sp , (b) sp^2 and (c) sp^3 .

In the sp^2 hybridization, three equivalent $2sp^2$ orbitals are formed and one unhybridized $2p$ orbital still remains (Fig.1.1.b). The sp^2 orbitals are coplanar, oriented at 120° to each other, and form σ bonds by overlap with orbitals of neighboring atoms. The remaining p orbitals on each carbon atom form a π bond by overlapping with the p orbitals from the neighboring C atoms. In the sp hybridization, two linear $2sp^1$ orbitals are formed and two $2p$ orbitals remain. Linear σ bonds are formed by the overlap of the $2sp^1$ hybrid orbitals of neighboring atoms (Fig.1.1.a). Two π bonds are formed with the overlapping unhybridized p orbitals of the two C atoms. Depending on these hybridization states, solid carbon shows different structures which possess different chemical and physical properties. In this section, all of the possible carbon allotropes are presented. We may classify pure carbon families into 4 classes, as diamond, carbyne, fullerenes/nanotubes and graphite. Fig.1.2 shows a carbon allotrope diagram based on carbon valence bond hybridization[2]. We can express all carbon materials by combinations of these different hybridizations.

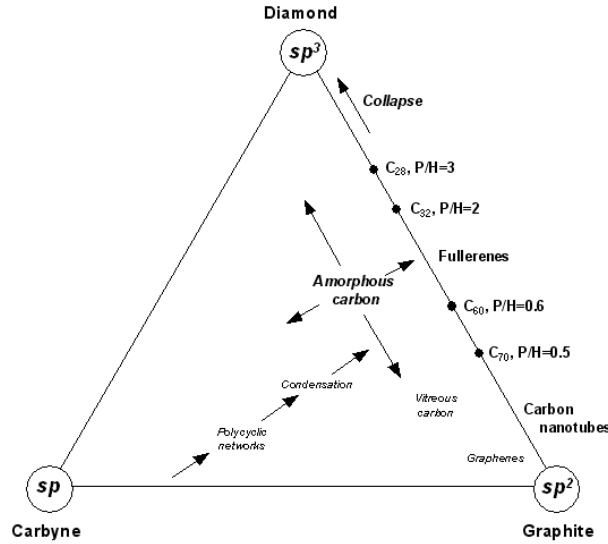


Figure 1.2: Different forms of carbon depending on the hybridization [2].

Fig.1.3 presents the thermodynamic phase diagram of the element carbon. The stable thermodynamic phase under ambient conditions is hexagonal graphite. Cubic diamond is the stable phase under high pressure. The carbyne should exist at high temperature, below the melting line of graphite [3]. A stable thermodynamic state is defined by the absolute minimum of Gibbs free energy expressed as a function of P and T ($G=H-TS$). A phase transition can occur between two states depending on the difference of Gibbs energy (ΔG). Two possible paths can be considered from one state to another. If the activation energy $E_A \cong 0$, only the stable state will exist after a phase transition. While with a large activation energy barrier, a metastable state can be obtained and stabilized.

1.2.1 sp^3 hybridization - Diamond

Diamond consists of sp^3 bonded carbon atoms where several types of structure have been observed. The classical form is a face centered cubic phase which is a thermodynamically metastable phase under atmospheric pressure at room temperature. Fig.1.4 shows the unit cell of cubic and hexagonal (Lonsdaleite) diamond crystals. The cubic unit cell (Fig.1.4.a) shows the smallest group of carbon atoms, arranged in three-dimensions, that can represent the essential features of the diamond crystal. The edges of this cube

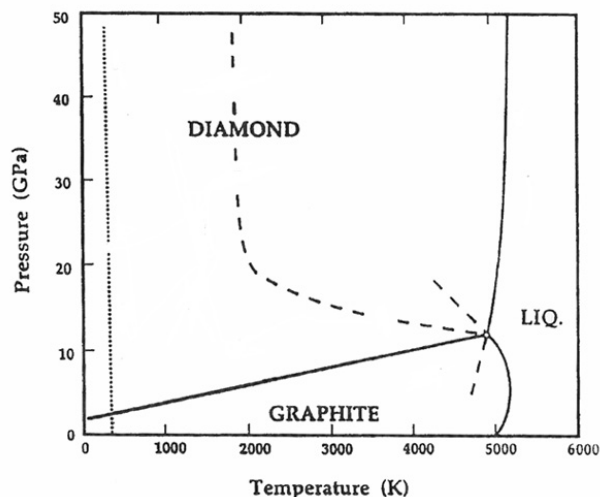


Figure 1.3: Phase diagram of carbon [3].

are 3.57 Å in length. Each carbon atom in diamond is surrounded by four nearest neighbors forming strong covalent sp^3 bonds. They are connected together by covalent sigma bonds that separate them by a distance of 1.54 Å. The angle between these bonds is 109° . As a result, the central atom and its neighbors form a tetrahedron. Because of the interlocking network of covalent bonds, cubic diamond shows remarkable properties. Since diamond is industrially quite an important material, many efforts have been made to realize its synthesis. The synthesis techniques are often based on pressure and temperature conditions and the presence of a catalyst. The best known transformation happens under temperatures $> 1700^\circ\text{C}$ and pressures $> 80000\text{Pa}$.

1.2.2 sp^1 hybridization - Carbyne

Carbyne is a linear carbon allotrope with pure sp -hybridization. Due to their unique geometrical structure, carbynes are expected to have many interesting properties as fullerenes and carbon nanotubes. Fig.1.5 demonstrates several structures of carbyne proposed with orientations of formation from graphene sheets, α carbyne (a) and β carbyne (b). α carbyne is a structure poly-yne $(-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-)_n$ with two types of bonds of length 1.20 and 1.38 Å respectively. β carbyne is a cumulene $(\text{C}=\text{C}=\text{C}=\text{C})_n$, resonant form of first type, with a bond length of 1.28 Å. These two structures form white powders when

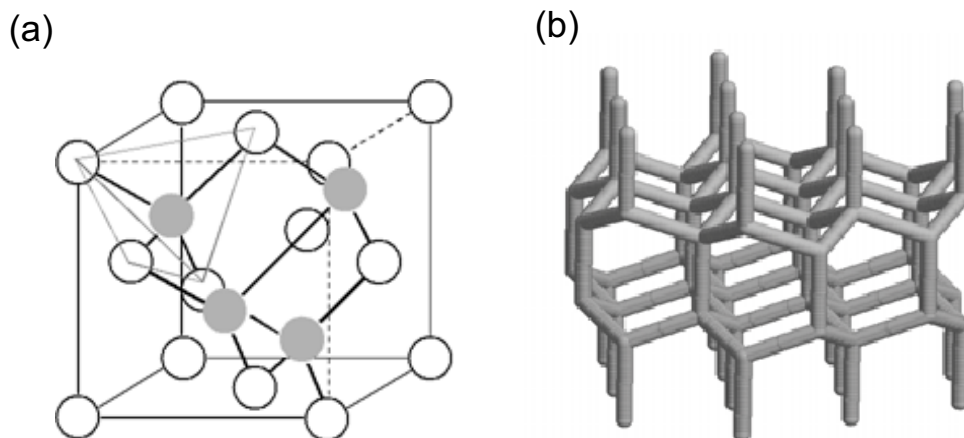


Figure 1.4: Schematic models of (a) cubic and (b) hexagonal (Lonsdaleite) diamond structures.

they are crystallized. However, the preparation of carbyne is quite difficult because this phase is metastable compared to hexagonal graphite. It has been reported by Whittaker that carbyne can be thermodynamically stable at about 2600 K under weak pressure. Several paths of chemical and physical synthesis have been reported and phases consisting of oligomers with 20 -30 atoms are observed [4].

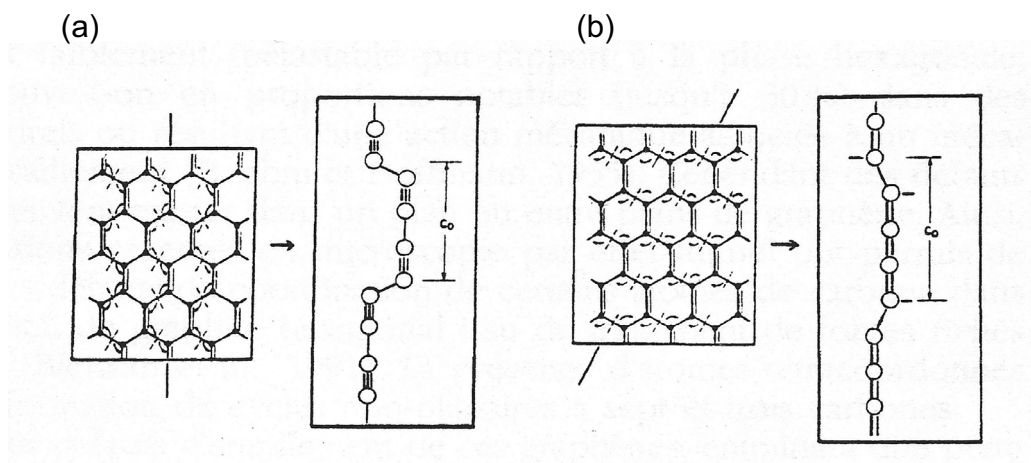


Figure 1.5: Schematic models of structures of carbyne type (a) α and (b) β .

1.2.3 $sp^{2+\epsilon}$ hybridization - Fullerenes

Fullerenes are relatively new molecular phases of carbon discovered in 1992 by Kroto *et al.* [5]. They can be formed during the condensation of carbon vapor obtained by a beam irradiation of graphite blocks [6, 7]. A large yield synthesis has been also reported using an arc-discharge by Kratschmer *et al.* [8]. An important point of the formation of this phase is the presence of isolated pentagons placed in closed structures. The structure of fullerenes is defined to be formed by 12 pentagons and n hexagons composed of carbon atoms bonded in a nearly spherical configuration by the hybridization $sp^{2+\epsilon}$. In addition to C_{60} which has a perfect spherical form with 20 hexagons, C_{70} , C_{76} , C_{80} , C_{82} , C_{84} , C_{90} are possible. Fig.1.6 shows C_{60} and C_{70} . Much simulation work has been carried out, exploiting their structural symmetry, to understand the properties of this type of molecule [9, 10]. One important point on their properties is the strong electronic density inside the spherical structure [10]. In particular alkali- C_{60} compounds are good conductors and superconductors [11].

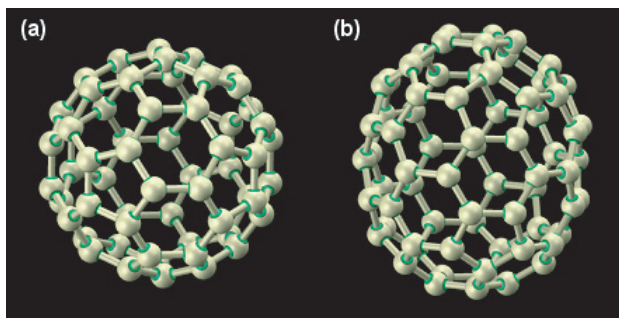


Figure 1.6: Schematic models of (a) C_{60} and (b) C_{70} .

Carbon nanotubes have a cylindrical structure formed from graphene sheets and closed by Fullerenoid end-caps, containing a half of the number of pentagons in C_{60} as illustrated in Fig.1.7.a. The structure of carbon nanotubes depends on the orientation of the hexagons in the cylinder with respect to the tubule axis. There are a number of chiral forms in which the carbon hexagons are oriented along a screw axis. Fig.1.7.b is schematic illustration of arm-chair, zig-zag and spiral forms. Typical dimensions of multiwall carbon nanotubes, consisting of several nested co-axial single wall tubules, are 2-20 nm in outer diameter and 1-3 nm in inner diameter. Carbon nanotubes have attracted a lot of interest because of their one-dimensional

periodic structures with electronic properties (metallic or semi-conducting) that depend on their diameter and chirality [12, 13].

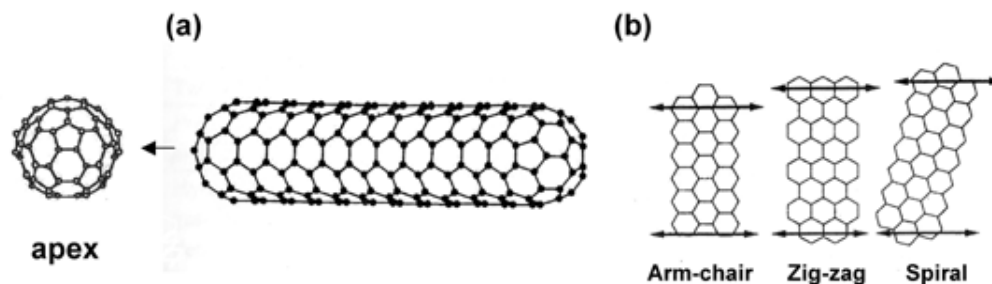


Figure 1.7: (a) Structure of a single wall nanotube and (b) schematic illustration of arm-chair, zig-zag and spiral forms of single wall nanotubes (arrows denote the tubule axis).

1.2.4 sp^2 hybridization - Graphite

The carbon material with sp^2 bonding is represented as graphite. In this structure, layers of hexagons of carbon atoms bonded by sp^2 orbitals are stacked in parallel using π electron clouds. Graphite crystallizes in the hexagonal system (space group $P6_3/mmc$) with $a = b = 2.461 \text{ \AA}$ and $c = 6.708 \text{ \AA}$. The layers can be regularly stacked in several systems. The basic phase is an ABAB stacking giving a hexagonal crystal (Fig.1.8). An ABCABC stacking giving a rhombohedral crystal is also possible but it occurs only locally, due to stacking faults. The random stacking of layers can often be observed in carbon materials prepared at low temperatures; this is called a turbostratic structure. In this case, the lateral size of continuous perfect hexagonal layers is also small. It is well known that the size and the regularity of stacking can be improved by High Temperature Treatment (HTT). The properties of graphitic materials strongly depend on the size and regularity of layers as explained in Chapter 1.4 and 1.5.

1.3 Graphitic materials - *polyaromatic solids*

As described above, carbon has a variety of allotropic forms thanks to its different hybridization states and none of the elements of the Mendeleiev Table

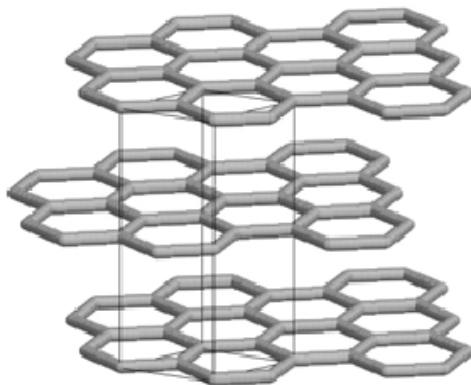


Figure 1.8: Hexagonal graphite (ABAB stacking) with unit cell

exhibits such large allotropy. In addition, the properties of the phases are often fascinating such as hardness, tensile resistance, stiffness, conductivity, etc. Since the discovery of fullerenes, many researchers have studied them experimentally and theoretically. However applications and even preparation processes of fullerenes are still currently under studying. For diamond too, despite widespread use of synthetic diamond and other diamond related materials in high-tech applications (such as machining tools, coatings for protection against corrosion and abrasion, biomaterials, etc.), there is little large scale production.

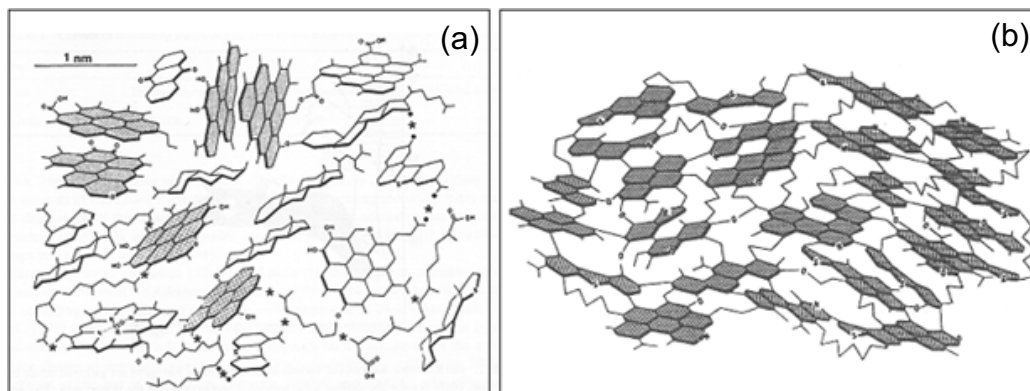


Figure 1.9: Schematic illustrations of the chemical structure of (a) kerogen macromolecule and (b) modified macromolecule by heat treatment [16].

On the contrary, the amount of industrially produced 'polyaromatic carbon materials' is huge, compared to that of fullerene and diamond-based materials. This kind of carbon falls in the category of 'pregraphitic types' involving more or less developed aromatic systems which are considered as Basic Structural Units (BSU)[14, 15]. In this section, the classification of polyaromatic materials and their evolution from non-crystalline structures to crystalline graphite, and more particularly the transformation processes for textures resulting in plastic or liquid phases, are discussed.

Most of the carbon existing on earth is contained in fossilized organic remains, such as anthracites and in particular kerogens (fossilized organic matter dispersed in sediments). All these natural carbonaceous materials contain polyaromatic molecules, and the aromaticity increases with increasing temperature. Fig.1.9 shows a schematic illustration of the chemical structure of kerogene macromolecules and the modification of their structure with temperature [16]. This process governs their thermal transformation, which can change their structure to pure carbon, sometimes graphite, by the steps called carbonization and graphitization.

1.3.1 Carbonization

During a heating process under an inert atmosphere, to prevent any oxidation or combustion, a natural or an artificial organic carbonaceous precursor such as kerogen undergoes drastic chemical modifications. Usually the following steps are applied: pyrolysis of the organic matter below 700°C, then the primary and secondary carbonizations between 700-1000°C and at 2000°C, respectively. This heat step eliminates all the other hetero-elements such as hydrogen, nitrogen and oxygen.

At first, during the primary carbonization between 700-1000°C, volume condensation occurs which favors molecular interactions, especially between aromatic molecules. When they reach a threshold diameter (a seven aromatic ring molecule about 0.7 nm wide which corresponds to the size of a coronene molecule (Fig.1.10.a)), they tend to associate each other, preferably face-to-face because of thermodynamical requirements [17]. This is a primary entity called Basic Structural Unit (BSU) first investigated by Oberlin *et al.* [18]. Fig.1.10.b shows a schematic illustration of a BSU. BSUs are single stacks of two or three polyaromatic layers which have been found in a large number of carbonaceous products such as pitches, coals [19], petroleum derivatives [20], anthracene based carbons and saccharose-based carbons [21] at random in

the bulk. As pyrolysis goes on, the aromatization and the subsequent BSU formation proceeds.

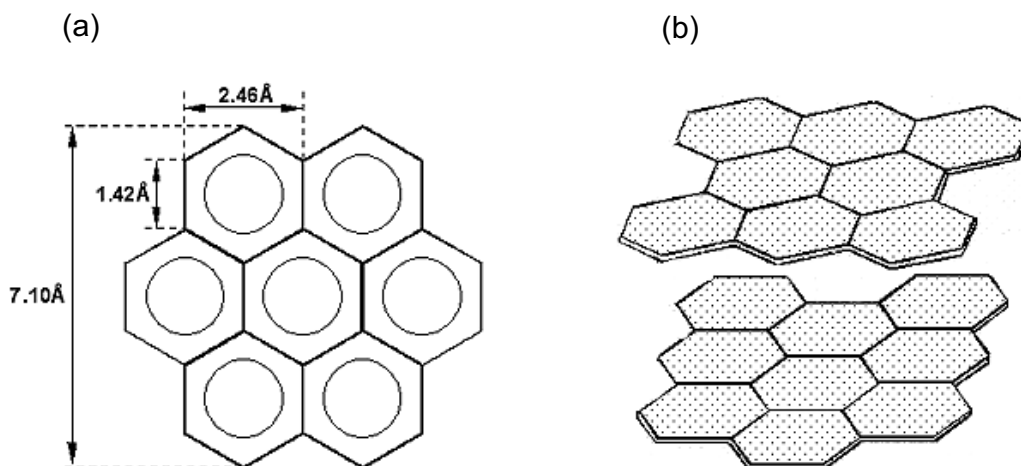


Figure 1.10: Schematic illustrations of (a) coronene molecule and (b) example of a Basic Structural Unit (BSU).

After the primary carbonization, a further physical and chemical evolution is needed to lead to pure carbon. The carbonaceous products obtained at the end of the primary carbonization still contain a non-negligible amount of heteroatoms. They are removed during the secondary carbonization steps at various temperatures depending on their chemical functions. The temperature for complete removal for oxygen, nitrogen and hydrogen is as high as 1500°C [22] and even higher for sulphur (2000°C). After this secondary carbonization, pure carbon is obtained.

During this last step, Local Molecular Orientation (LMO) appears. LMO is one of the most important phenomena which determines the ability of materials to graphitize. It is the consequence of the mutual orientation of BSUs forced to align locally. It is known that the formation of LMO is strongly related to the produced graphitic structure and texture, which will be discussed in following sections concerning structure and texture.

1.3.2 Graphitization

The materials purified after two steps of carbonization should reach the long range order of hexagonal graphite during a subsequent graphitization process

at up to 3000°C. By heating at high temperature, the three-dimensional crystalline state of graphite, which is the thermodynamically stable phase, is obtained.

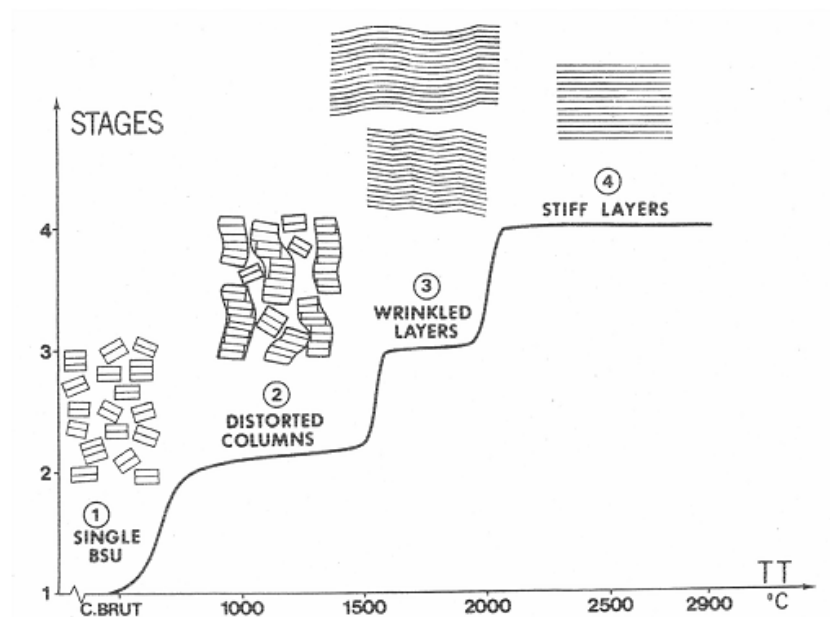


Figure 1.11: Stage of increasing organization versus high temperature treatment [21].

At the end of the secondary carbonization, which temperature boundary is thus more accurately defined by physical (temperature of final distortion removal) than chemical (temperature of heteroatom removal) criteria, graphene sheets appear to be already stiff, though they are still stacked with turbostratic disorder. In this manner, graphitization starts. Graphitization occurs above 2100°C and up to 3000°C, which allows the carbon atoms within graphenes to rearrange so that they tend to acquire locally the three-dimensional order of graphite with nearly perfect domains within the grains. Fig.1.11 shows the steps of increasing order for graphitizing carbons as a function of treatment temperature. The order of graphitized domains increases progressively as the temperature increases. At the end of the graphitization step, all the graphene sheets of any polyaromatic carbon material should have locally and visually achieved the perfect crystallinity.

1.3.3 Structures and textures

1.3.3.1 Graphite and 'Turbostratic' carbon

In the case of graphitic materials, the basic structural unit is a layer of carbon hexagons. As shown in section 1.2.4, these layers can be stacked in several ways (ABAB or ABCABC....) in the case of quasi perfect graphite. A random parallel stacking of the layers can be found, mostly in carbon materials prepared at low temperature. This is called a 'turbostratic' structure. Fig.1.12.a and b show graphite and a turbostratic carbon, respectively.

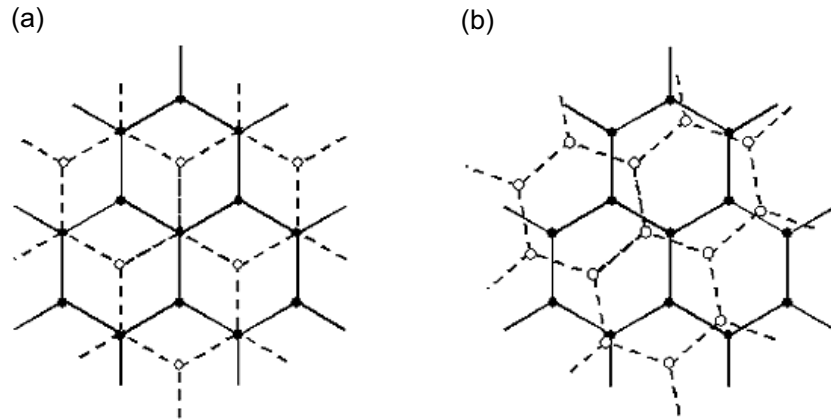


Figure 1.12: Schematic illustrations of (a) graphitic and (b) turbostratic stacking of carbon layers.

In the case of the turbostratic structure, there is no crystallographical relation between the graphene layers even if each graphene layer is perfectly ordered. All the intermediate situations between pure turbostratic and perfect graphite (all the graphene pairs in the AB or ABC stacking) can be identified by X-ray or electron diffraction. The turbostratic phase is characterized by the absence of hkl reflections (three indices) which are replaced by asymmetric hk bands. However, the $00l$ reflections which are due to the graphene stacking are still present [23]. The minimum possible distance of the intergraphene spacing d_{002} is 0.344 nm [24], which is defined between the two average superimposed graphenes in turbostratic order. However this spacing can depend on the thermal conditions and most turbostratic materials show a distance of 0.4 nm or more. On the contrary, in the case of graphite, half of the atoms are exactly facing an atom of the graphene underneath and the other half are facing a potential well. This configuration can

lower the intergraphene distance to the value d_{002} 0.335 nm. Of course, the X-ray and electron diffraction patterns exhibit all the gaussian hkl reflections in the graphite stacking.

1.3.3.2 Isotropic and anisotropic carbons

Although graphitic materials can be graphitized by high temperature thermal treatment (HTT) (see the section 1.3.2), the final level of graphitization depends not only on the treatment temperature but also on the formation of LMO, defined at the early stage of carbonization. Fig.1.13 shows the evolution of anisotropically (a) and isotropically (b) oriented LMO. The material made of oriented anisotropic domains, where aromatic layers (BSUs) are oriented in parallel over large domains limited by randomly distributed small disclinations, is called graphitizing material and provides HOPG, after high temperature thermal treatment [25].

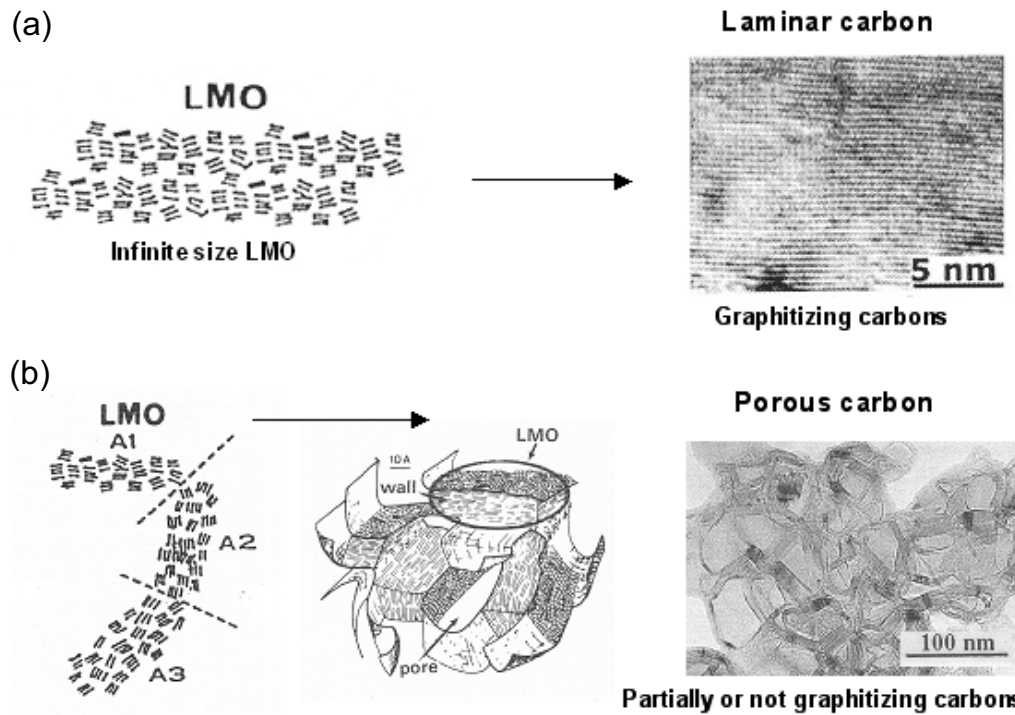


Figure 1.13: Schematic models of oriented textures with different symmetries for examples of (a) graphitizing and (b) non-graphitizing carbons [25].

On the contrary, the material made of domains of LMO with different orientations is called partially or non-graphitizing material and is graphitized only partially even after long duration thermal treatment. It provides porous carbons, such as vitreous carbon. Vitreous carbon has no long-range crystalline order and the increase of the interatomic distance between carbon atoms from that in the perfect graphite crystal, is greater than 5 % in both the basal plane (a-b directions) and between planes (c direction), as determined by X-ray diffraction.

1.3.3.3 Crystallites

All graphitic materials can be defined as aggregates of graphitic crystallites, with structurally perfect graphite crystal domains. These crystallites may vary considerably in size, defined by the mean in-plane correlation length (L_a), and out of plane correlation length (L_c), characterized by the mean interlayer distance d_{002} which is normally larger than in graphite. These two scales L_a and L_c can be determined by TEM observation and X-ray diffraction [26, 27].

1.3.3.4 Defects and Dislocations in graphite

Within each crystallite, a varying number of imperfections can be found, such as point defects and dislocations. The basic types of point defects found in graphite are interstitials and vacancies (Fig.1.14.a and b). The formation energies have been estimated at 7.0 eV for both types of defects, which is large enough to ensure that only small equilibrium concentrations should exist at room temperature in highly crystalline samples. However, since many synthetic graphitic materials are not highly crystalline, large concentrations of metastable defects can be expected [28].

Both basal and non-basal dislocations have been observed in graphite, screw and edge dislocations (Fig.1.14.c and d). Basal plane dislocations split into part which bound a region of stacking faults in which there is rhombohedral stacking. Vacancy and interstitial loops are common non-basal dislocations. Twinning is common in crystalline graphite and can be readily induced by stress [29].

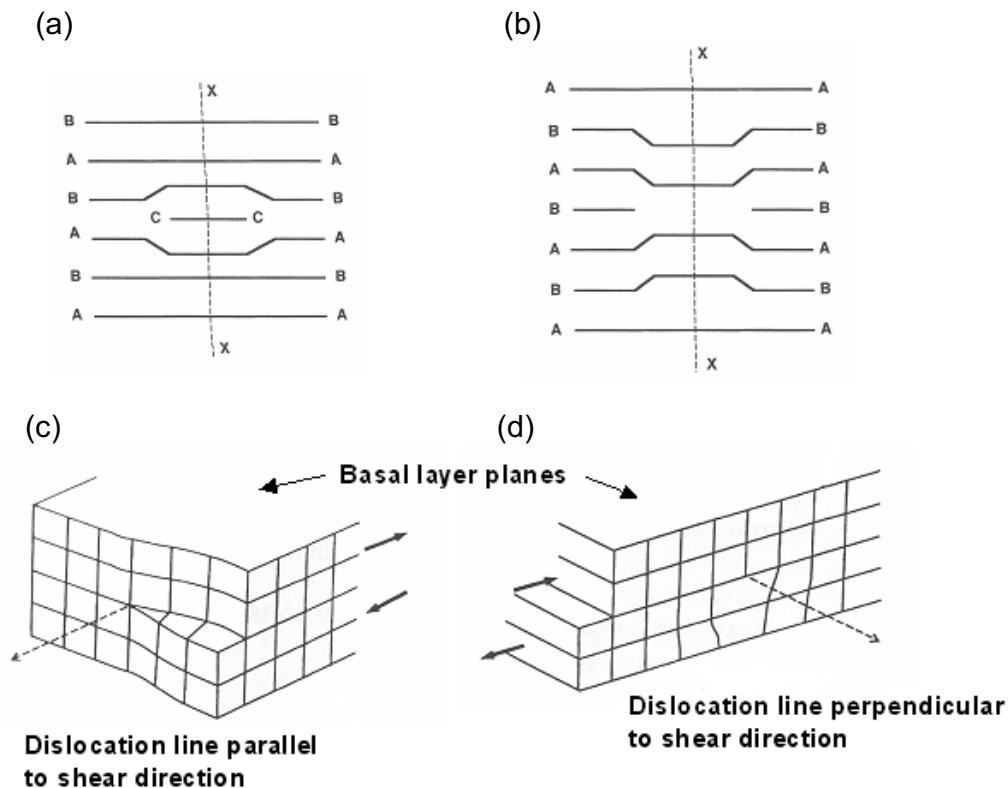


Figure 1.14: Schematic illustrations of (a) interstitial and (b) vacancy defects and (c) screw and (d) edge shear dislocations [30].

1.3.3.5 Morphologies of materials

A large variety of morphologies is obtained by varying the synthesis conditions, methods and precursors. Recently Inagaki and Delhaès *et al.* have proposed the classification of typical carbon materials based on the degree of preferred orientation of anisotropic layers [25, 31]. Fig.1.15 illustrates the texture of typical carbon materials based on the preferred orientation anisotropic hexagonal layers [31]. The nanoentities (BSUs) oriented locally (LMO) at the early step of synthesis tend to evolve their structure microscopically along reference planes, axis or points, during the heat treatment for the plastic phase carbons, and during the growth for the gaseous phase carbons.

The type of orientation causes different morphologies of final carbon ma-

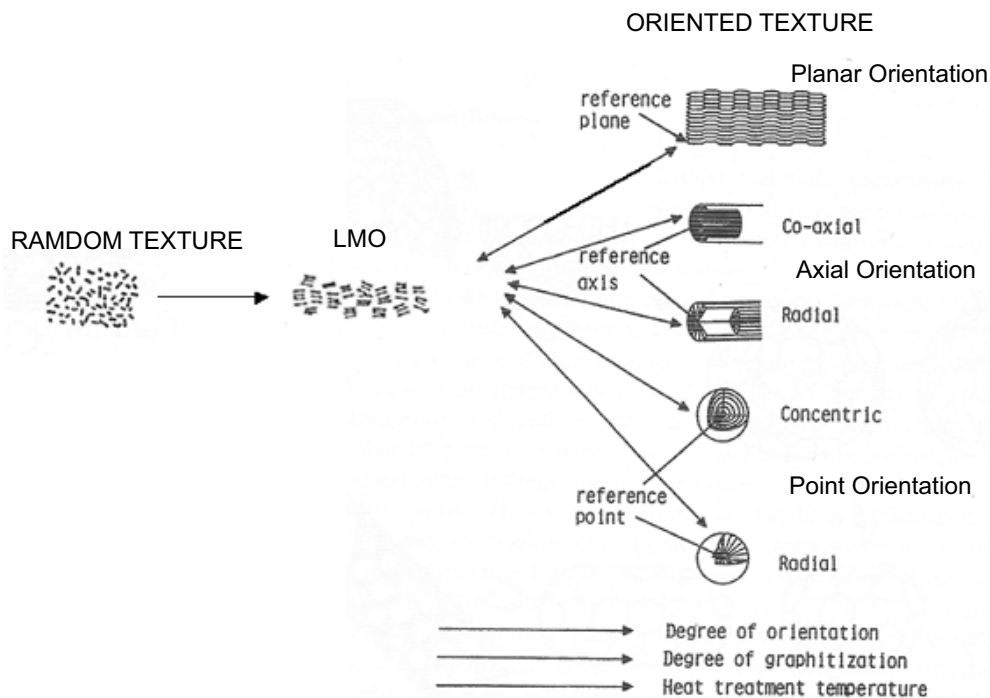


Figure 1.15: Texture of the typical carbon materials based on the preferred orientation of anisotropic hexagonal layers [25, 31].

terials. The materials oriented along the reference plane show planar symmetry and form laminar carbons. Single crystals of graphite and HOPG (High Oriented Pyrolytic Graphite) are examples of the products in the case of planar orientation. The cylindrical symmetry, as in carbon fibers, results from orientation along a reference axis. We can classify them into two types of morphologies: radial and random orientations, especially for the plastic phase carbons [32], and concentric orientation for the typical gaseous phase carbons [33]. Carbon nanotubes correspond to the concentric morphology. Point orientation results in spherical symmetry and a concentric alignment is often observed in materials such as carbon blacks and onion-like carbon [34]. In this manner, almost all morphologies of graphitic based materials can be classified by the orientations of self-associated basic structural units (BSUs). Since the resulting materials can consist of different degrees of orientation and graphitization, it is important to examine the products at different length scales in order to determine correctly their structures and properties.

1.4 Synthesis of graphitic materials

Nowadays, many different graphitic (sp^2 based) carbon materials can be synthesized by various techniques. These techniques can be classified according to the types of precursors. In this section, synthesis techniques using liquid or plastic carbon precursors and using gaseous or vapor carbon precursors are presented in the different materials production.

The synthesis of graphitic materials in liquid or plastic phase proceeds normally following the carbonization and graphitization steps described in the section 1.3. In this case, the formation of LMO from the precursors may be a key parameter to determine the obtained carbon materials.

1.4.1 Industrial synthetic graphite

Synthetic graphite is molded by heating filler particles composed of a mixture of petroleum coke or coal with a binder (usually coal tar pitch) and a petroleum-based oil to facilitate extrusion, and in some cases, anthracite coal. The characteristics of the synthetic graphite depend on many factors, including the quality of the coke and binder, the degree of orientation of the filler particles, and the temperature and time of processing. The graphite synthesized by this extrusion method exhibits an anisotropy in the block since the filler particles are oriented during the extrusion. In addition, Cold Isostatic Pressing (CIP) is also applied for molding the filler particles. It is a method of compacting powders into green bodies and near-net shaped in a pressure vessel. The filler particles are sealed in a flexible mold shaped like the end product. High pressure is used up to 600 MPa (6,000 bar/87,000 psi) having water as pressure medium. A high and uniform density is achieved, resulting in easier handling, easier machining and even predictable shrinking during sintering. The products exhibit a perfect isotropic structure. After the extrusion or the cold pressing, the materials are annealed to be carbonized and then treated at high temperature to be graphitized.

1.4.2 Planar carbons

1.4.2.1 Laminar carbon

Laminar carbons can be synthesized from different precursors, and the resulting products exhibit variations of structure and crystallinity, depending

on the preferred orientation of LMO and the heat treatment conditions.

Inagaki *etal.* have reported the formation of laminar carbons by a heat treatment of thermoresistant polymers, such as polyimide films [35]. The polyimide film obtained by a chemical reaction is treated through the carbonization and surface graphitization processes.

1.4.2.2 Highly oriented pyrolytic graphite (HOPG)

Hydrocarbon gases deposit carbon at high temperatures on a substrate, called pyrolytic carbon. The reaction has been widely studied to control the structure and texture of pyrolytic carbons formed by varying the deposition conditions [36]. By hot pressing the pyrolytic carbon formed from the gaseous phase, HOPG can be produced [37]. The first step of preparation is hot-pressing in the temperature range of 2800 to 3000°C, where the cone texture of the grown pyrolytic carbon, deposited at 2100 - 2500°C, is destroyed and the preferred orientation (LMO) is improved. After this hot-pressing the samples are easily cleaved and their surfaces give mirror reflections. However, their physical properties are still far from those of a single crystal of graphite. In a second step, an annealing under pressure at high temperature, up to 3400°C, should be carried out to improve the physical properties.

1.4.3 Cylindrical carbons

1.4.3.1 Carbon whiskers

A graphite whisker can be imagined as a graphitic material formed by rolling a graphene sheet, oriented parallel to the axis of the texture, into a scroll [38]. Graphite whiskers are synthesized in a DC discharge between carbon electrodes. In the arc apparatus, the diameter of the positive electrode is smaller than that of the negative one and the discharge is carried out in an inert gas using a high gas pressure. The whiskers exhibit a high crystalline perfection with high electrical conductivity and high elastic modulus along their axis.

1.4.3.2 Carbon fibers

There are two processes used in carbon fiber production. The first process is carried out in the vapor phase and progresses by decomposition of hydrocarbon precursors. The resulting fiber structure, especially the cross-sectional

structure, varies depending on the details of the process. The second process is carried out in the plastic phase and mainly PAN (polyacrylonitrile) and pitch are used as precursors. The process consists of the spinning of the precursor, stabilization of the spun fibers and a heat treatment of stabilized fibers under high temperatures.

Vapor-grown carbon fibers (VGCF) grow from the decomposition of hydrocarbons at such as benzene, methane or acetylene, at temperatures around 1100°C in the presence of a metallic catalyst, such as Fe, Ni or Co. In all cases, growth is favored in a hydrogen atmosphere [39]. The production of VGCF can be performed by two methods: the seeding catalyst and floating catalyst processes [40]. In both cases, the growth of VGCF occurs in the following steps; the activation of the catalysts, on the substrate or floating, the initial growth and elongation of a hollow core fiber, and a subsequent thickening process, in which rough laminar pyrocarbon layers are deposited around the VGCF core [41, 42]. Characteristics of the structure of VGCF are the concentric alignment of carbon hexagonal layers along the fiber axis, the presence of a catalyst particle at the top of the fibers, and the formation of a hollow tube at the center of fibers. Consequently the graphitization behavior of VGCF is similar to that of graphitizable carbons and they are polygonized after high temperature treatment (HTT) above 2500°C [43, 44].

PAN-based fibers are heated in an oxygen containing atmosphere at temperatures between 200 and 300°C to stabilize them for the subsequent carbonization steps. Two of the important transformations which occur during this stabilization step are 1) the nitrile groups react to form closed ring structures and 2) the oxygen helps to crosslink the chains. If this process is done under tension, called hot stretching, the LMO and pores are oriented parallel to the fiber axis, axial orientation (see section 1.3.3.5). After this stabilization, carbonization is carried out normally at temperatures between 1000 and 1500°C and then subsequently graphitization at 2000 to 3000°C.

Pitch-based fibers are generally produced from petroleum asphaltene or coal tar that consist partially of fused aromatic molecules. The important point is the formation of a highly oriented, optically anisotropic liquid crystal, called the mesophase, during the heat treatment of pitch materials for a period of time at around 350°C. Although isotropic pitch-based fibers have also been produced to lower a cost/performance ratio [45], this mesophase pitch material is widely used because of a highly preferred orientation (LMO) [46]. In the synthesis of mesophase pitch carbon fibers, the mesophase is prepared

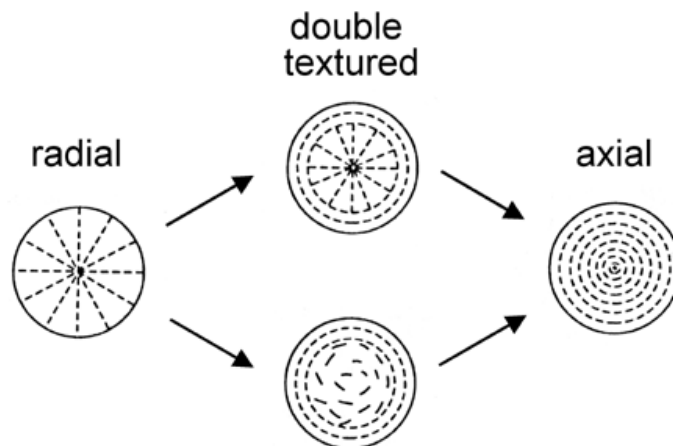


Figure 1.16: Schematic illustrations of various textures in cross-section of mesophase pitch-based carbon fibers [48].

by first hydrogenating a coal tar precursor and then heat treating the precursor above the softening point (308°C) to evaporate volatile components. The resulting mesophase pitch is spun to form carbon fibers by extrusion through a capillary tube [32]. If the extrusion occurs without stirring, the final product exhibits a radial cross-sectional structure [47], but with stirring, a random and onion-type cross-sectional structure is formed [32]. After extrusion, the fibers are stabilized at temperatures ranging from 200 to 300°C and then cooled down in an argon atmosphere. The fibers are subsequently heat treated in the temperature range of 800 to 1200°C for carbonization and of 2500 to 2700°C for graphitization.

The structure of PAN-based carbon fibers is essentially turbostratic and is composed of small two dimensional ribbons. An advantage of mesophase pitch-based carbon fibers is the ability to realize various textures in their cross-sections (Fig.1.16) [48]. The VGCF consists in an axial structure and can represent a high graphitizability owing to the development of a graphitic structure with heat treatment.

1.4.3.3 Carbon nanotubes

As research on VGCF at the microscopic scale proceeded, the growth of very small diameter (less than 10nm) fibers were occasionally observed and reported [41, 49]. This is, in fact, the first observation of carbon nanotubes.

After works by several researchers, including the discovery of fullerenes [5], Iijima's report established unequivocally the existence of carbon nanotubes [50]. Since his pioneering work, the study of carbon nanotubes has progressed rapidly.

For the production of carbon nanotubes, two kinds of methods have been developed; high temperature processes such as arc-discharge and laser ablation, and relatively low temperature processes such as Chemical Vapor Deposition (CVD) methods.

Arc-discharge and laser ablation methods involve the condensation of carbon atoms generated from the evaporation of solid carbon sources. The temperatures involved in these methods are from 3000 to 4000°C, close to the melting point of graphite. In arc-discharge, carbon atoms are evaporated by a plasma of helium gas ignited by high currents passed through opposing carbon electrodes. This is an excellent method for producing both high quality multi-walled nanotubes (MWNT) [51] and single-walled nanotubes (SWNT) [52, 53]. For the growth of SWNT, a metal catalyst is needed in the arc-discharge system. In the laser ablation technique, intense laser pulses are used to ablate a carbon target placed in a tube-furnace heated to around 1200°C. During laser ablation, a flow of inert gas is passed through the growth chamber, to carry the grown nanotubes to be collected on a cold finger. This method has been reported especially to synthesize high quality SWNTs [54].

The CVD process involves heating a catalyst material in a tube furnace and flowing a hydrocarbon gas through the tube reactor for a period of time. Catalytically grown materials are cooled down to room temperature and collected. The CVD process involves the dissociation of hydrocarbon molecules catalyzed by the metal, and the dissolution and saturation of carbon atoms in the metal particle leads to the formation of tubular carbon. For MWNT growth, ethylene and acetylene are often used as the carbon feedstock, and the growth temperatures are typically in the range of 550 to 750°C [55, 56]. Although arc-discharge and laser ablation have been the principal methods for obtaining SWNT with high perfection for long time, it is reported that high quality SWNT can also be produced by a simple CVD process with methane as carbon feed stock, suitable metal catalyst and at reaction temperatures in the range of 850 to 1000°C [57, 58].

1.4.4 Spherical Carbons

1.4.4.1 Carbon black

Carbon black is formed by the incomplete combustion of many organic substances. Carbon blacks can be classified as furnace blacks, channel blacks, thermal blacks and lamp blacks, and are composed of elemental units (BSUs) associated into a statistically spherical symmetry, similar to non-graphitizing pyrocarbons generated from plastic phase carbons.

Furnace blacks are made in a furnace by partial combustion of hydrocarbons. Channel blacks are manufactured by impingement of natural gas flames on channel irons. Thermal blacks are produced by thermal decomposition of natural gas. Acetylene black, a special type of thermal black, is made by exothermic decomposition of acetylene. Lamp blacks are made by burning hydrocarbons in open, shallow pans [34].

1.4.4.2 Fullerenes

Fullerenes have been found to possess a quite important potential for the applications. Although fullerenes are not really graphitic materials, their synthesis technique is briefly described in this section. The existence of soccer-ball structured C_{60} , fullerenes, has been firstly demonstrated by Kroto and Smally through their time-of-flight mass spectra of carbon clusters generated by the laser-vaporization supersonic nozzle technique [5]. Later, a simple technique for macroscopic generation using an arc discharge was proposed by Kratschmer and Huffman [8]. A large yield of carbon soots are fabricated by a direct-current arc discharge between carbon electrodes immersed in a noble gas. Fullerenes are isolated from the soots by solvents and separated using a liquid chromatography. The proportion of fullerene contained in the soots depends on the applied gas, the pressure and synthesis apparatus. the maximal yield of 10-15 w% is reported to be gained with He gas under 100 Torr [59].

1.5 Structure and Physical properties

Carbon in its various forms is a fascinating material for solid state physics. In this section, some physical properties of graphitic materials are briefly overviewed, and related to their structure and morphologies. Indeed, phys-

ical properties are strongly influenced by the structural anisotropy of the material.

1.5.1 Mechanical properties

Graphitic materials take many different forms and exhibit a wide range of mechanical properties. This is the unavoidable result of the extreme anisotropy in bonding, characteristic of graphite crystal with extreme two Young's moduli in the (001) plane $E_a = 1020$ GPa and E perpendicular to them $E_c = 36.4$ GPa [60]. The value of E_a , 1020 GPa, reflects the magnitude of the in-plane, covalent sp^2 C-C bonds, which are the strongest one of any known materials. The very weak interlayer, van der Waals type, bonding results in low values of E_c . Young's modulus of most of the graphitic materials lies between these two extreme values, depending on their structure (combination of these two orientations). Microstructural and crystallographic characteristics collectively control the response of the materials to an imposed stress. The key features are the degree of perfection of the crystals and their orientation with respect to the applied stresses.

In the case of planar carbons, mechanical properties depend on the size and orientation of crystallites. They decrease from HOPG to the non graphitizing carbons. However, in this case a boundary strains between crystallites, involving C-C bonds, should be taken into account. It is important specially for materials with very small crystallite dimensions in which the crystallites are highly defective [61]. Therefore the measured elastic modulus can be sometimes lower than the E_c value in certain materials, such as isotropic carbons. Anisotropic textures, such as pyrolytic graphite and fibers, demonstrate a similar set of elastic moduli and compliances, which can be defined relative to the axis of symmetry. High performance structures arise from vapor grown filaments after high temperature graphitization. Graphitized catalytically grown VGCFs have exhibited values of 760 GPa. The range of mesophase fibers gives rise to materials of varying crystallinity and orientation when they are progressively graphitized. The most highly oriented can show Young's moduli of 900 GPa [62]. The alignment of layer planes along the fiber axis is high in the high performance fibers from PAN and from mesophase pitch. In these materials, the elastic modulus increases with heat treatment temperature as L_a increases and the average degree of orientation of plane with respect to the fiber axis increases. Moreover, the most perfect filamentary type of graphitic structure is probably a single wall nanotube,

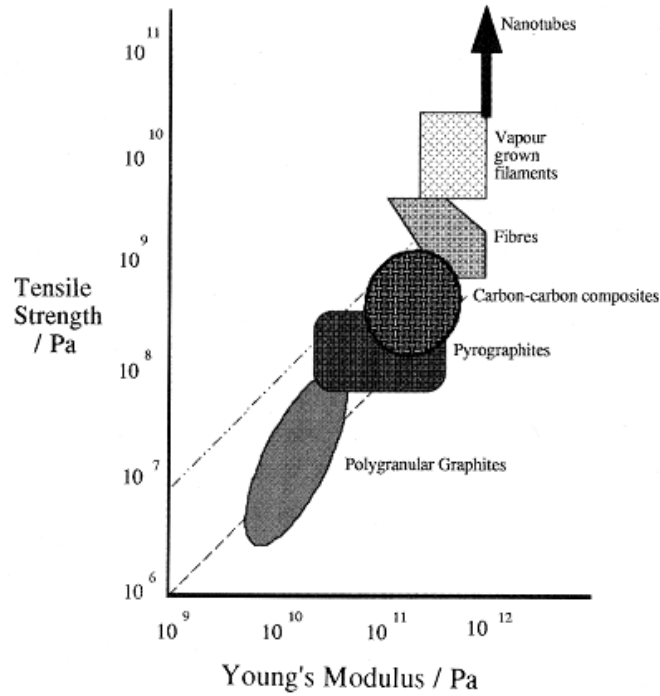


Figure 1.17: Variation of tensile strength and Young's modulus for the range of graphitic materials [62].

which Young's modulus should be close to the theoretical maximum. Fig.1.17 shows the variation of tensile strength with Young's modulus to compare the different types of graphitic materials.

A similar trend is found for electrical resistivities and thermal conductivities because all the physical properties are dependent on the size and orientation of the BSU building blocks.

1.5.2 Transport properties

The σ bonding and antibonding orbitals of carbon create a full valence band and an empty conduction band separated by a large energy gap, which allows us to obtain an insulator as diamond. However, the presence of π electrons fills the band gap between the σ bands, with the two π electronic bands in contact. Following this electronic model and the resulting lamellar structure, the graphitic family can generate highly anisotropic electrical conductors.

Carbons and graphites have generally more than one type of charge carriers. HOPG is, for example, a semimetal with an equal density of electrons and holes, which semimetallic behavior is due to their small Fermi surfaces. In the absence of interplanar interactions, such as for a graphene layer, it would be a zero gap semiconductor. Intercalation usually increases the carrier density leading to metallic behavior.

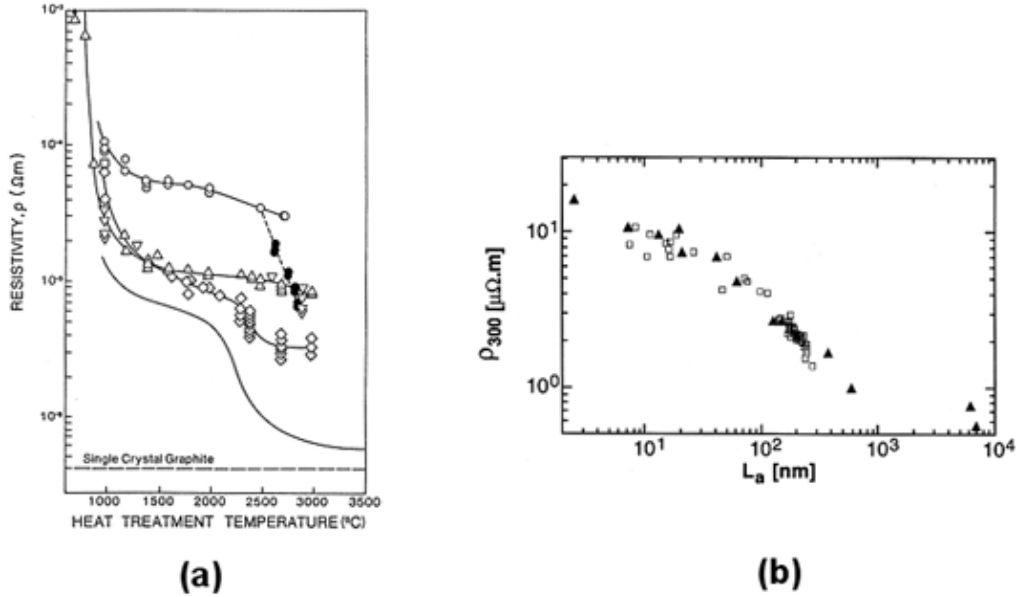


Figure 1.18: Room temperature electrical resistivity of selected carbon fibers as a function of (a) heat treatment temperature (T_{HT}) [39] and (b) in-plane coherence length (L_a) [63].

Electrical resistivities and thermal conductivity are very sensitive to crystal perfection. The heat treatment temperature (HTT) is thus the key parameter to obtain the graphitic materials with different resistivities. The difference in resistivity is more pronounced for two samples of the same precursor heat treated at different temperatures than for two different precursors heat treated at the same temperatures. Fig.1.18.a and b shows a room temperature resistivity of various experimental carbon fibers as a function of heat treatment temperature HTT [39] and crystallite size L_a [63], respectively. Consequently the measurements of electrical resistivity and thermal conductivity can also be applied to determine structural parameters such as the crystallite size L_a and to obtain information about point defects, giv-

ing an overall view of the entire sample, contrary to microscopic techniques which only probe a tiny position of the sample.

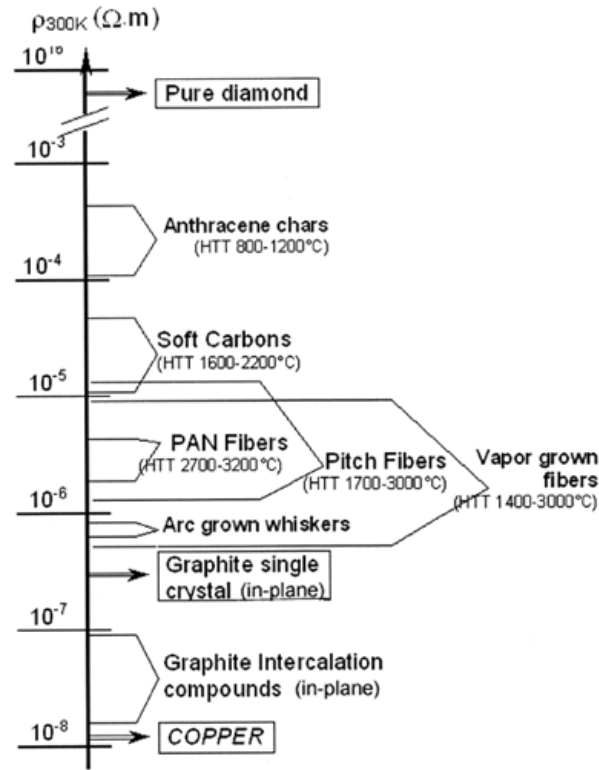


Figure 1.19: Orders of magnitude of the room temperature electrical resistivities of various forms of carbons compared to that of copper [64].

Fig.1.19 shows room temperature electrical resistivities of various forms of carbons [64]. Samples with high structural perfection exhibit resistivities below $10^{-6} \Omega \cdot m$ [39], which can be described using the semimetallic graphite band model. For partially carbonized carbons with low heat treatment temperature, such as anthracene chars, resistivity values are above $10^{-4} \Omega \cdot m$, since an excitation gap between bonding and anti-bonding states produces the decrease of charge carriers. For the same value of the heat treatment temperature, the resistivity is lower for VGCF than for ex-pitch fibers, and ex-PAN fibers. This is due to the relative difficulty to graphitize these carbons materials. In addition, for the cylindric materials, as VGCF, the resistivity also depends on the diameter of the samples. The lower the diameter

the higher the resistivity [65]. The value of the in-plane mobility or mean free path is found to decrease with decreasing fiber diameter.

Of all materials, diamond and graphite (in-plane) exhibit the highest known room temperature thermal conductivity, exceeding $2000\text{Wm}^{-1}\text{K}^{-1}$. Contrary to metallic solids where heat is generally carried by the charge carriers, in graphite heat is almost exclusively carried by phonons (except at very low temperatures), as for diamond, owing to the small density of the charge carriers and the large in-plane lattice thermal conductivity due to the strong covalent bonds. The thermal conductivity is less anisotropic than the electrical conductivity because phonon processes dominate both the in-plane and c-axis thermal conductivities around room temperature [60]. However, the very high anisotropy of the room temperature thermal conductivity still exists in graphite. A strong correlation is also found between thermal conductivity and crystal perfection. The values of thermal conductivity at room temperature for graphitic materials, such as carbon fibers, strongly depend on the heat treatment temperature. The higher the HTT the larger the thermal conductivity [66, 67].

Since the mechanical, electrical and thermal properties are structure-sensitive, a relation between these properties is expected. Electrical and thermal properties are related to the elastic modulus and there is also a relation between electrical and thermal properties [39]. For example, the electrical resistivity experimentally determined can be used to calculate the thermal conductivity. The structural informations about in-plane coherence length L_a and point defects can also be obtained with these measured properties.

1.6 Conclusion

A carbon atom can exhibit several coordination numbers, giving a variety of allotropes. Diamond, graphite, carbyne and fullerenes are considered allotropes of inorganic carbon family. Each allotrope possesses interesting characteristics. In addition to the brief description about these carbon allotropes with different hybridizations, carbon materials based on sp^2 -hybrid orbital, graphitic structure, are summarized in this chapter. Basic structural units composing these materials are hexagonal carbon layers, which causes a strong anisotropy. Graphitic materials should be analyzed at different scales;

at atomic scale to understand the electronic structure, at the nanoscopic scale to estimate the quality as crystallite size and at the microscopic scale to define their morphologies. The combination of these diagnostics helps us to correctly understand the obtained materials. The degree of stacking order of hexagonal carbon layers in each basic structural unit varies from random (turbostratic) to regular (graphite) stacking. The degree of graphitic order expressed by means of crystallite size, L_a , varies from very low, such as for glassy carbon, to quite high such as for HOPG. These structural orders strongly depend on the precursor and heat treatment temperature. The preferred orientation, expressed with plan, point or axis symmetry, of anisotropic structural units makes various morphologies, which results from various synthesis method. This variety in structure and texture widens the range of properties of graphitic carbon materials. All the forms of graphite based materials give rise to many industrial applications, depending on their various morphological forms and microstructures. For the synthesis it is quite important to control the structure and morphology for each applications.

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Chapter 2

Oxy-acetylene combustion flame method

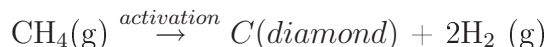
2.1 Introduction

The synthesis of diamond crystals and films at low pressures had been interested in 1980s. By activating a mixture of gases consisting of a supersaturation of hydrogen and a hydrocarbon, such as methane, it is possible to synthesize diamond. During this period, Hirose and co-workers have demonstrated that diamond crystals can be synthesized by the use of a combustion flame, named 'combustion flame method' [1, 2]. Specifically, it has been shown that diamond can be synthesized by the impingement of an oxy-acetylene flame, emanating from a torch, onto a suitably prepared substrate. This technique can be easily carried out under atmospheric pressure with a simple apparatus and has been widely studied as a significant method. Our purpose is to apply this simple method for the synthesis of various carbon materials. In this chapter, in order to understand the principle of the technique, previous works on this technique performed by many workers are summarized.

2.2 Low-pressure processes for diamond synthesis

The low-pressure process is based on chemical vapor deposition (CVD) and utilizes temperature and pressure conditions under which graphite is clearly

the stable form of carbon. However, kinetic factors allow crystalline diamond to be produced by the net chemical reaction:



In addition to methane, a wide variety of carbon-containing reactant gases can be used. In reality, the deposition mechanism is a complex interaction of many factors and is not fully understood. Two essential conditions have been identified: (a) activation of the carbon species and (b) the action of atomic hydrogen. Diamond has been deposited from a large variety of precursors such as methane, aliphatic, alcohols, aromatic hydrocarbons, etc... These substances generally decompose into two stable primary species, the methyl radical (CH_3) and acetylene (C_2H_2) [3].

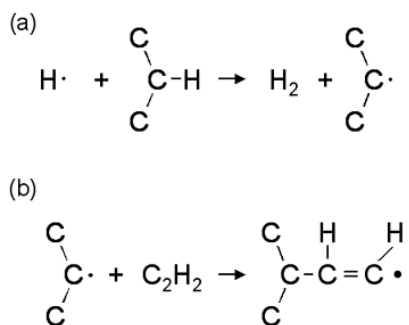


Figure 2.1: Two step deposition model by Frenklash and Spear [4]: (a) activation of diamond surface and (b) reaction of the surface carbon radical with the carbon-hydrogen species.

A two-step deposition model has been presented by Frenklash and Spear [4]. In the first step, the diamond surface is activated by the removal of a surface-bonded hydrogen ion by atomic hydrogen as shown in Fig.2.1.a. In the second step, the activated surface-carbon radical reacts with the carbon-hydrogen species in the gas phase to become the site for carbon addition (as demonstrated in Fig.2.1.b). A similar model has been proposed that is based on the addition of a methyl group to one of the carbons followed by atomic hydrogen abstraction from the methyl group [5]. Since graphite is thermodynamically stable at low pressure and only graphite would be formed without activation of carbon species, the carbon species must be activated. Activation is promoted by two basic method: high temperature and plasma,

both of which requiring a great deal of energy. Several CVD processes based on these two methods have been proposed. The four most important are high-frequency plasma, plasma arc, thermal CVD and oxy-acetylene combustion flame. Their major characteristics are summarized in Table 2.1 [3].

Activation method	Process	Deposition rate	Temperature control	Main product
HF plasma	Microwave	Low (0.1 – 10 $\mu\text{m/h}$)	Good	Coating
Arc plasma	DC Arc RF Arc	High (50 – 1000 $\mu\text{m/h}$)	Poor	Coating
Thermal CVD	Hot-filament	Low (0.1 – 10 $\mu\text{m/h}$)	Good	Coating
Combustion	Torch	High (10 – 100 $\mu\text{m/h}$)	Poor	Coating Powder

Table 2.1: Characteristics of diamond deposition processes [3].

2.3 Principle of the oxy-acetylene combustion flame method

Concerning the oxy-acetylene combustion flame method, a great deal of efforts have been concentrated especially (1) to determine the range of deposition parameters that control diamond growth, (2) to observe the crystal morphology, and (3) to determine the main precursors and their concentrations in the mixed gases. In this section, previous reports focused on these subjects are briefly summarized.

2.3.1 General

In order to obtain carbon materials grown in the gas phase, it is necessary to obtain carbon active species formed by the decomposition of a carbon source. In general, the carbon sources are decomposed using high temperature or "plasma" introduced by arc discharge, micro wave, and so on as described in section 2.1. Hirose *et al.* have pointed out that we can also find a kind of plasma in the combustion flame. The oxy-acetylene combustion flame has

been applied for the following reason; 1) the flame temperature is quite high (3300K), 2) there is a reductive part in the flame. As a consequence, the flame acts as the reaction chamber and supplies the heat necessary to create the radical species of the diamond growth plasma.

2.3.2 Flame structure

The flame nature changes depending on the gas mixture ratio as shown in Fig.2.2.a. To obtain a reductive flame which is essential for carbon deposits, the gas ratio, $R_f = O_2/C_2H_2$, should be less than 1. Fig.2.2.b schematically illustrates the three distinct regions characteristic of an oxy-acetylene combustion flame with the ratio of input gases (R_f) < 1. The first region (region (I) in Fig.2.2.b) called inner cone is where the gases mix and combust to form CO and H_2 . This sharp region is quite luminescent and the hottest region of the combustion flame with temperature around 3160°C. The second region (II) is called 'acetylene feather' and results from non-stoichiometry of input gases (excess acetylene). The feather is primarily composed of CO and H_2 with the remainder C_x and C_xH_y hydrocarbon radicals. Carbon deposition is possible in this reduction part of the flame. The third region (III) is known as the diffusion or secondary flame. This region is formed as the acetylene feather reacts with the atmosphere to oxidize CO and H_2 to CO_2 and H_2O respectively.

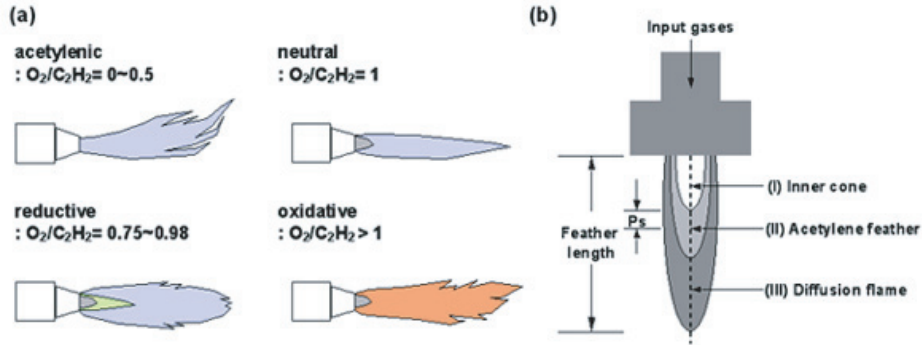


Figure 2.2: (a) Structure of an oxy-acetylene combustion flame operating at $R_f < 1$ and (b) schematic illustration of the flame with different R_f .

2.3.3 Experimental parameters

The fundamental process parameters of oxy-acetylene combustion flame technique can be identified in Fig.2.2. The ratio of input gases ($R_f = O_2/H_2$) governs the carbon concentration in the combustion flame. A direct measurement of carbon content is provided by the acetylene feather length, which increases approximately linearly with decreasing R_f values ranging up to 1, which tends to yield high quality diamond with low percentages of non-diamond phases.

The substrate temperature T_s is the most crucial process parameter of the oxy-acetylene combustion flame technique to determine morphology, growth rate and quality of diamond [6, 7]. The substrate temperature T_s is often measured by an infra-red pyrometer. The best temperature range for the diamond synthesis has been reported to be between 700 and 900°C [8] (see in section 2.4.1).

The position of the substrate in the flame can be defined as the distance from the top of the inner cone, P_s . Throughout the entire region of the acetylene feather, diamond synthesis is possible and almost the same morphology can be observed. Since the details of consequences, such as variation of uniformity, diamond quality, growth rate etc., can change a little depending on P_s , it is necessary to determine the best P_s .

The morphologies of the deposition generally change from the center to the outer boundary of the growth region on the substrate [9]. The effects of variations in temperature and concentration of oxidizing species, as a function of radial and vertical positions in the flame, are important in determining deposited morphology. The temperature variation within the diameter of growth has been observed to be up to 250°C [10]. The concentration of active species such as CO, H_2 , N_2 and CO_2 has also been determined as a function of position on the substrate surface.

2.3.4 Carbon active species

Though the growth mechanism from the vapor phase is not clear, it is generally considered that methyl radicals (CH_3) deposit on the substrate and atomic hydrogen (H) etches graphite component. This mechanism is supported by the quantum chemical calculation for the surface reaction of CH_3 and by the chemical kinetic calculation on the deposition for the mixture of methanol (CH_3OH) and hydrogen (H_2) [11]. On the other hand, the quite

high growth rate, which is not so different from that obtained by hot thermal plasma, can be realized by the use of oxy-acetylene flame at atmospheric pressure. To explain the high growth rates, which are ten times higher than that of low pressure CVD, it may be necessary to consider other candidates such as C, C₂, CH and C₂H₂, which have much larger equilibrium concentrations than CH₃ in high temperature gases T more than 3000°C.

To give an insight into the diamond growth mechanism in the acetylene feather, precise gas analyses have been carried out by Matsui *et al.* [12] using mainly laser induced fluorescence and mass spectrometry. The concentration of C₂H₂ and other carbon containing radicals in the feather are approximately in equilibrium near the burner exit and decrease almost linearly toward the feather tip via inter-diffusion and reactions with O-radicals in the intermediate zone. The feather boundary is characterized by emissions of C₂^{*} (swan band) and CH^{*} (Fig.2.3).

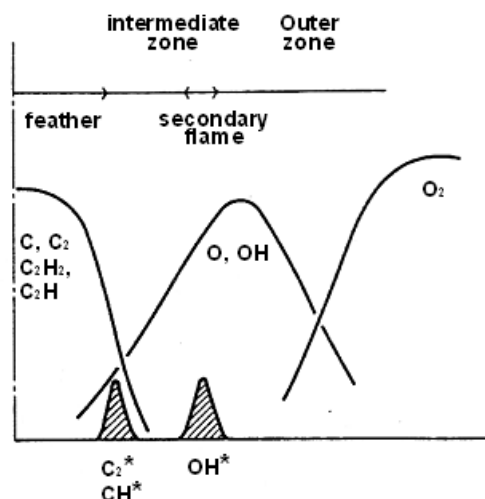


Figure 2.3: Schematic presentation of radical and emission profiles [12].

The thermodynamic quasi-equilibrium model [13] successfully applied to the CVD of diamond from C_xH_y/H₂ mixtures can also be applied to the diamond growth via the oxy-acetylene torch by including oxygen as an additional reactant. At the basis of the quasi-equilibrium model remains the assumption that thermodynamical equilibrium exists between the solid carbon C(s) surface and the vapor species desorbed and/or evaporated from it. In addition to the hydrocarbon species C_xH_y present in the C-H system, the

reactions between C(s), hydrogen and oxygen yield products such as CO, CO₂, CHO, H₂O etc. A total of 23 different gaseous species (H, H₂, CH, CH₂, CH₃, CH₄, C₂H₂, C₂H₄, C₂H, O, O₂, CO, CO₂, C₃O₂, OH, H₂O, HO₂, C₂HO, HCO, C₂H₄O, C, C₂, and C₃) have been considered to be produced in the flame [9].

The adiabatic calculation for the equilibrium concentrations has shown that C₂H_x(x = 1, 2), C_x(x = 1–3) and CH_x(x = 1–3) are dominant C-radicals in the feather which is realized only in the high temperature O₂/C₂H₂ flames for the ratio of R_f=0.83-1.0, diamond growth region [12]. Finally, among several candidates, CH and C₂ radicals are verified to be important because their R_f-dependences are in good agreement with that of the growth rate.

In addition, hydrogen and oxygen are also important active species for the low-pressure CVD growth of diamond. They are responsible for etching the surface rather than for the carbon growth. Since molecular hydrogen would thermally etch graphite at a rate much faster than it would etch diamond, a super equilibrium concentration of atomic hydrogen at the growth surface is responsible for the major reduction in graphite co-deposition [14, 15]. The addition of oxygen also decreases the quantity of non-diamond carbon [3]. While oxygen containing radicals (O, OH) are found in the intermediate and outer zones of the flame as shown in Fig.2.3 [12]. The carbon etching dominates the carbon growth, which limits the deposition zone on the substrate.

2.4 Diagram of the produced phases using the oxy-acetylene technique

2.4.1 Diamond synthesis region in the diagram

The mixed gas ratio and the substrate temperature are the most important parameters to determine the obtained material. Fig.2.4 demonstrates the domain of the diamond production as a function of the input gas ratio and substrate temperature. Concerning the diamond deposition region, various workers have obtained slightly different results. Hirose *et al.* found diamond deposition under acetylene-rich conditions, R_f=0.7-1.0 [2, 16]. Wang *et al.*, however, have reported that the diamond film growth region is located in the range R_f=0.89-0.99 [9]. Since combustion systems are strongly convective by an atmospheric air, the experimental conditions sensitively depend on design of system, total gas flow rates etc. Moreover, to measure real substrate

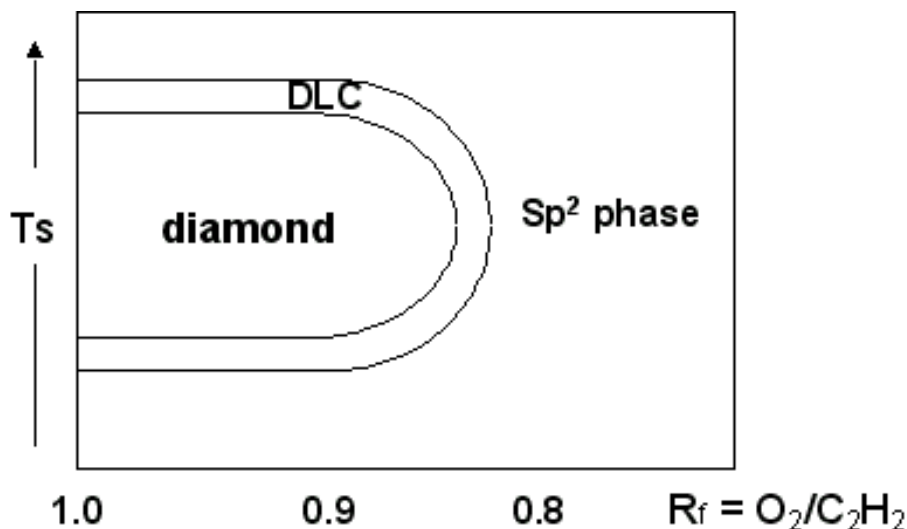


Figure 2.4: A domain of diamond production as a function of the input gas ratio R_f and substrate temperature T_s .

temperatures is quite difficult because of a lack of uniformity in the flame and of the measurement method with infra-red pyrometer. Anyway, we can summarize the diamond growth region to be in the range $R_f=0.80-1.0$ with a substrate temperature $T_s=700-1200^\circ\text{C}$ (as shown in Fig.2.4). Although the exact values can vary a little depending on the apparatus, sp^2 bonded carbons are produced outside the diamond deposition region and DLC, sp^2-sp^3 mixed phase, is found between 2 zones in any case.

2.4.2 Morphology of diamond

The most commonly observed shape taken by diamond crystals, synthesized by low pressure CVD techniques, is a cubo-octahedron, which is a shape bound by cubic (100) faces and octahedral (111) faces [17, 18]. During the crystal growth, the cubic and octahedral faces can grow at different rates. Kim *et al.* have proposed a model for the development of diamond crystal morphology [19]. The ratio of total surface energy to volume is the most important factor in determining the morphology at a nucleation stage. The lowest one is octahedron, composed of (111) crystallographic plane. Therefore, the initially formed diamond crystal might be theoretically octahedron, the thermodynamic equilibrium shape. However, the growth shape is dif-

ferent from equilibrium shape. At growth stage, many factors and surface energy contribute to the growth in each direction such as active species.



Figure 2.5: The variation of the crystal morphology with the ratio of the growth rates along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions [19].

The relative growth rates in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions might determine the crystal habit. Fig.2.5 represents the variation in the crystal shape from octahedron via cubo-octahedron to cubic by the growth ratio of (111) faces to (100) faces in their normal directions, $\langle 100 \rangle$ and $\langle 111 \rangle$ respectively [19]. The exact cubo-octahedron shape is determined by V_{100}/V_{111} value of 0.8660 and the ratios for modified cubo-octahedrons range from 0.577 to 1.732.

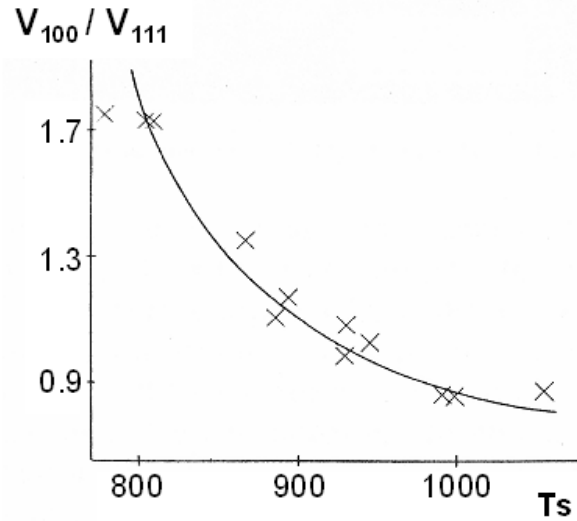


Figure 2.6: The variation of the ratio of the growth rates along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions as a function of substrate temperature [22].

The surface morphologies of synthetic diamond are changed as a function of substrate temperature. It has been experimentally reported that the (111) faces dominated the crystal morphology in lower temperature range (up to 900°C) and the (100) faces are dominant in higher temperature range (more than 1000°C) [20, 21]. Fig.2.6 shows that the ratio of $\langle 100 \rangle$ to $\langle 111 \rangle$ growth rate changes with the substrate temperature. To understand such growth habit, the contributed active species should be discussed [22].

For the surface chemistry, the type of hydrogen adsorption is very important. A 1×1 surface structure of (111) has been observed by LEED (low energy electron diffraction) to be covered with CH_3 radicals (fig.2.7.a). On the contrary, a 2×1 surface structure of (100) is monohydrogenated with CH radical (Fig.2.7.b) [23]. This results show that the intermediate reaction states on the surface between (111) and (100) are completely different. Which radicals contribute to each growth orientation? Spitsyn *et al.* have reported the contribution of C_2H_2 and CH_4 radicals on the surface to these two different surface constructions [21]. According to their reports, both C_2H_2 and CH_4 contribute to the growth of the diamond $\langle 111 \rangle$ direction, whereas only CH_4 to the growth of the $\langle 100 \rangle$ direction.

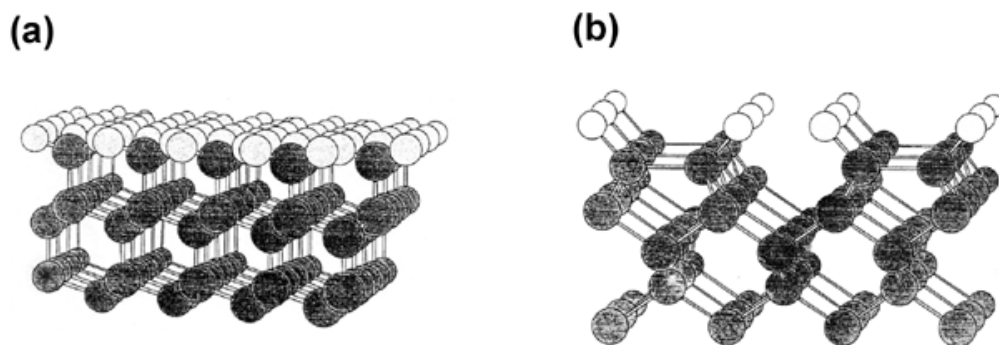


Figure 2.7: (a) Model of CH_3 adsorption on the surface of diamond (111)- 1×1 and (b) model of mono-hydride (CH) on the surface of diamond (100)- 2×1 [23].

The ratio of the concentration of C_2H_2 to that of CH_4/CH_3 control the dominant morphology. If only CH_4/CH_3 are primary precursors, the growth rate of the $\langle 111 \rangle$ direction is lower than that of the $\langle 100 \rangle$. If the mixture of C_2H_2 and CH_4/CH_3 are primary precursors, the growth rate of $\langle 111 \rangle$ direction rises relative to that of the $\langle 100 \rangle$ and thus (100) surface appears. Because the growth rate of $\langle 111 \rangle$ is controlled by the concentration of C_2H_2

at the reaction surface and CH_4/CH_3 contributes to the growth of $\langle 100 \rangle$ [24]. The higher the ratio of CH_4/CH_3 , the higher the growth rate of $\langle 100 \rangle$, whereas the higher the concentration of C_2H_2 , the higher the growth rate of $\langle 111 \rangle$. Hay *et al.* have been reported that the concentration of C_2H_2 increases with substrate temperature and that of CH_4/CH_3 decreases with the substrate temperature [22]. This fact just matches the result of Ravi and Spitsyn [20, 21].

In addition, the growth of (100) faces at high temperatures is related to the presence of oxidizing species in the flame atmosphere. Oxygen and its variants, such as CO and OH radicals, perform the dual function of etching non diamond bonded phase formed during synthesis, creating growth site on the diamond surface. Since diamond formation can compete with graphitization of the diamond at high temperature, the etching of non-diamond (graphitized) phases by the oxidizing species propagates the lateral diamond growth (formation of (100) faces). The temperature dependence of diamond morphology is explained on the basis that at low temperatures the low partial pressure of oxidizing species in the flame ambient may not be effective in creating growth edges on the diamond surface, leading to (111) oriented surfaces.

2.5 Advantages and disadvantages of the technique

As shown in the sections above, the oxy-acetylene combustion flame technique consists in a quite simple apparatus at atmospheric pressure. It offers a low-cost alternative to conventional techniques of diamond synthesis such as microwave plasma, hot filament, DC arc-discharge, etc., which require expensive vacuum chambers capable of withstanding high temperatures associated with diamond CVD. In addition, this technique offers advantages not found in other methods of diamond CVD. Firstly, at atmospheric pressure, the growth rates are still among the highest reported, over $100 \mu\text{mh}^{-1}$ [25]. Secondly, the combustion method can produce high quality diamond for use in optics and electronics because the presence of oxygen species improves the diamond quality by etching graphitic impurities up to 100 times more efficiently than atomic hydrogen [26]. On the contrary, the strong thermal gradient generated in the flame and the substrate temperature are difficult

to control. A large deposition area is also still a problem in spite of much effort by many researchers [27]. The reductive part of the flame where carbon deposition occurs is surrounded by the oxidative flame. The oxidative flame etches all kinds of carbon deposit, which limits the size of diamond deposition area.

2.6 Conclusion

The oxy-acetylene combustion flame technique with a simple apparatus developed for diamond synthesis has been summarized in this chapter. The combustion of oxy-acetylene mixed gas generates several kinds of active species inside the flame. The deposition is defined by the competition between the carbon deposition by carbon containing species, such as C_2 and C_2H_2 radicals, and the etching by oxygen and hydrogen containing species, such as H and OH. To obtain a diamond deposit, input gas ratio R_f and substrate temperature T_s are the most important experimental parameters. The crystal morphology can be determined by the combination of experimental parameters, which displays cubo-octahedral crystal orientation with a variation of the ratio between cubic and octahedral forms. The principles of thermodynamics and kinetics of CVD are appreciable to both the diamond and graphite formation. In addition, graphite is clearly the more stable form than diamond at low pressure. Since this technique has several advantages compared to other CVD methods, such as simplicity of process and high growth rate, etc..., we will apply it for the synthesis of graphite-based materials.

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Chapter 3

Synthesis and characterization of carbon materials produced using the oxy-acetylene technique

3.1 Introduction

An oxy-acetylene combustion flame method has been widely studied for diamond synthesis (summarized in Chapter 2) since its development by Hirose *et al.* in 1988 [1]. This technique can be easily carried out under atmospheric pressure with a simple apparatus. Although other carbonaceous species can also be produced by oxy-acetylenic flame combustion by varying the preparation conditions and the source gases composition, almost no work has been reported on the subject. In this chapter, the oxy-acetylene combustion flame technique is applied in wide range of experimental conditions to explore the possibilities of graphite based materials synthesis. We demonstrate the synthesis of various morphologies of graphitic materials by this technique in addition to diamond.

3.2 Experimental set up

Fig. 3.1 illustrates a schematic experimental set up. All the experiments are carried out using an oxy-acetylene torch. The oxygen and acetylene source gases are controlled by a standard mass flow meter system. Substrate plates are mounted on a temperature controlled water-cooled copper sample holder.

The O_2/C_2H_2 volume gas ratio is maintained typically at 0.9, with a C_2H_2 gas flow of 2.0 lit./min. No catalyst is used. During the deposition time, the substrate is maintained in the acetylene vertical inner flame zone (acetylene feather), 2 mm below the center cone. The deposition time is fixed to mainly 3 minutes. The substrate temperature ranges from 800 to 1500°C as determined by an infrared pyrometer. The substrate should be resistant and stable during the experiments at high temperatures. Preliminary experiments are carried out with Tungsten, Molybdenum and graphite substrates. The deposition of carbon materials, except diamonds, is not dependent on the substrate materials. Since the same results are obtained with graphite substrate, metal substrates are considered not to introduce catalytic effects. Molybdenum plates are chosen as deposition substrates for an economical reason. Normally the size of substrates used for the carbon deposition is $10 \times 10 \text{ mm}^2$ because the diameter of the flame is around 10-12 mm.

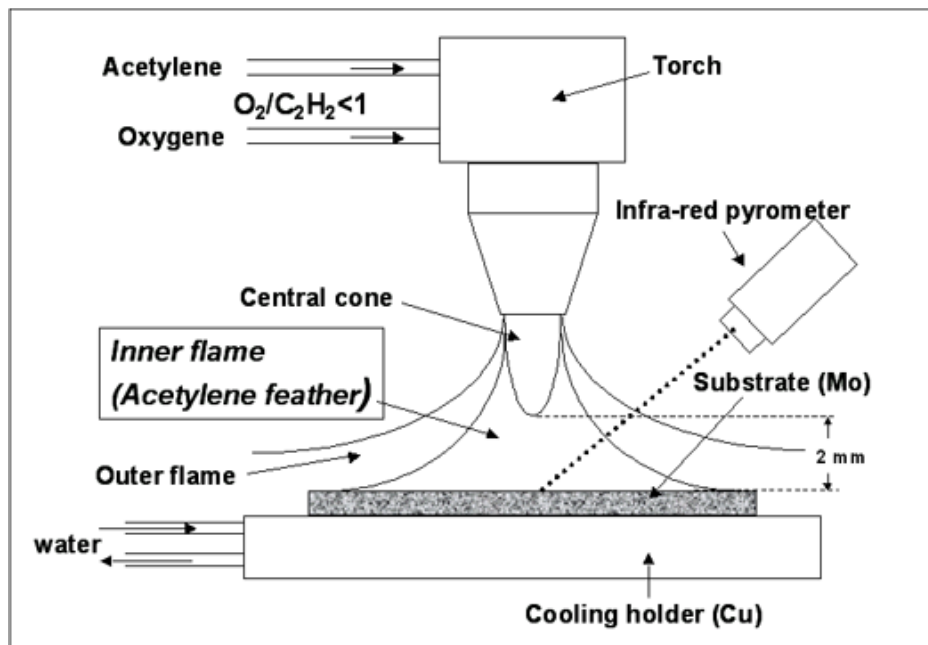


Figure 3.1: Schematic illustration of the experimental set up of an oxy-acetylene combustion flame technique for carbon deposition in the PCPM laboratory.

3.3 Characterization techniques

Field-emission scanning microscopy (LEO982, SEM-FEG), transmission electron microscopy (LEO922, TEM-200KeV) at high resolution (HR-TEM) and Raman spectroscopy (Jovan-Yvon microspectrometer with an excitation wavelength of 632 nm) are used to characterize the samples. The morphologies of all samples obtained in this work are firstly characterized by Scanning Electron Microscopy (SEM). Since we can place the substrate directly in the SEM chamber, the deposited surface condition and morphology can be analyzed without any modification. To characterize their nanometer scale structures, Transmission Electron Microscopy (TEM) is used in several modes (high resolution, bright field, dark field and diffraction). For all TEM analyses, the deposited surface is scratched with a sharp cutter and dispersed in a solvent (often iso-propyl alcohol) to put small particles of sample on the operation grid. Selected Area Diffraction (SAD) is used to further probe the graphitic structure and crystalline order. Bright and dark field (BF and DF) modes are used to determine the microstructure and the anisotropy. High resolution mode (HR-TEM) is used to analyze the nanotextures. Micro Raman spectroscopy is an efficient method to determine the in-plane correlation length L_a , an indication of the degree of graphitization using a relation between the intensities of G and D bands [2, 3].

3.4 Diagram of the produced materials

In this work, experiments are carried out at substrate temperatures in the range of 800 to 1500°C with a combustion gas ratio O_2/C_2H_2 ranging from 0.50 to 1.00. This temperature range is much higher than that used in previous studies on diamond formation by other authors (see Chapter 2). Graphitic-based materials are known to be often synthesized under high reaction temperature conditions. To reveal all possibilities of carbon materials formation, especially graphite-based materials, by this technique, a wide range of experimental conditions is applied. Fig.3.2 demonstrates produced materials using the oxy-acetylene technique under the different experimental conditions.

First, we observed a difference of nucleation mode between the gas ratio $R = O_2/C_2H_2$ exceeding 0.65 and less than 0.55. With the gas ratio $R \geq 0.65$, carbon materials deposit on the substrate surface. The nucleation starts in a

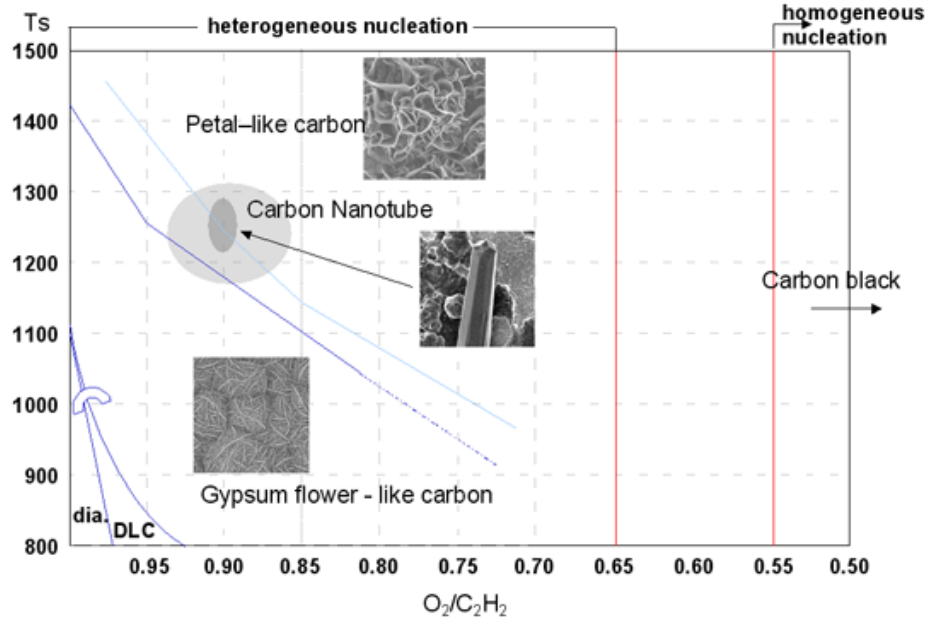


Figure 3.2: Carbon materials synthesized by the oxy-acetylene combustion flame technique.

heterogeneous way because of the thermal gradient, in which substrate temperature plays a quite important role to determine obtained phases. While the gas ratio $R \leq 0.55$ yields carbon black deposits directly in the flame. Since the homogeneous nucleation starts in the gas phase, controllable temperature parameter does not exist because temperature is determined only by the flame. This chapter is focused on the carbon materials produced on the substrate surface with $R \geq 0.65$. In addition to diamond, a variety of sp^2 -bonded graphitic materials are synthesized. The graphite-based materials are obtained at higher substrate temperatures and with less O_2 composition than those necessary for diamond formation. In any case, these materials are found with unusual morphologies. In large zone of sp^2 carbon formation, carbon aggregates with peculiar form are synthesized. The basic form is called 'Gypsum Flower'-like carbon (GF) [4]. In higher temperature ranges, the walls composing GF become larger and thinner and the texture is called 'Petal'-like carbon. Uni-directional carbon structure, called polyhedral graphite crystal, is also found in a small zone of the diagram (indicated in Fig.3.2). Although all these structures are generated without any catalyst,

the addition of catalytic metals allows us to obtain carbon nanotubes. In this chapter, structural characterizations for each material obtained are realized to understand their structures.

3.5 Diamond

3.5.1 Experimental conditions

Diamond, the sp^3 carbon phase, is synthesized with an input gas ratio ranging between 0.95 and 0.98 for substrate temperatures ranging from 700 to 1100°C, depending on the input gas ratio (see Fig.3.2). The Mo substrates are scratched with diamond powder of 1 μ m in diameter since defects of substrate surface enhance the diamond nucleation [5]. The deposition time is mainly kept to 5 min for each deposition.

3.5.2 Diamond morphology

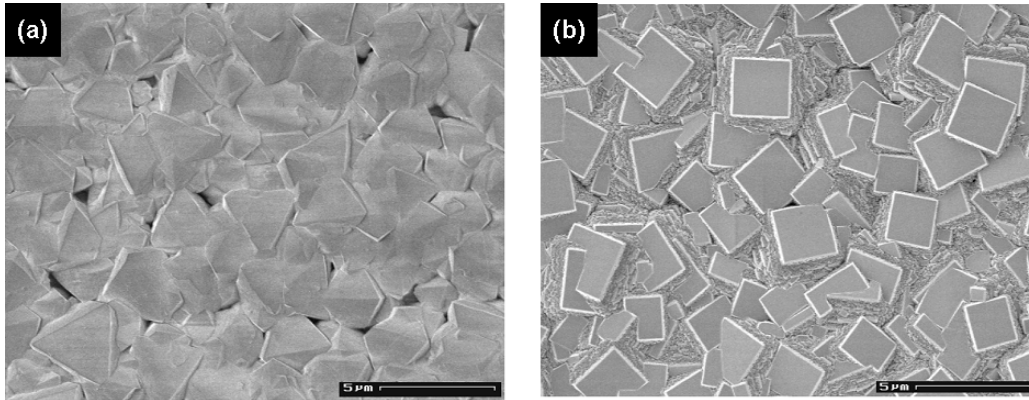


Figure 3.3: Scanning Electron Micrograph (SEM) of thin layers of (a) (111) oriented diamond obtained at 800°C and (b) (100) oriented diamond produced at 950°C.

Thin layers of diamond oriented (111) and (100) appear on the scratched substrate after 5 min. of deposition time. Fig. 3.3 (a) and (b) demonstrate the thin layers composed of (111) and (100) oriented diamond crystals obtained at 800 and 950°C, respectively. As reported by other authors, (100) diamond film is smoother with less defects than (111) one [6].

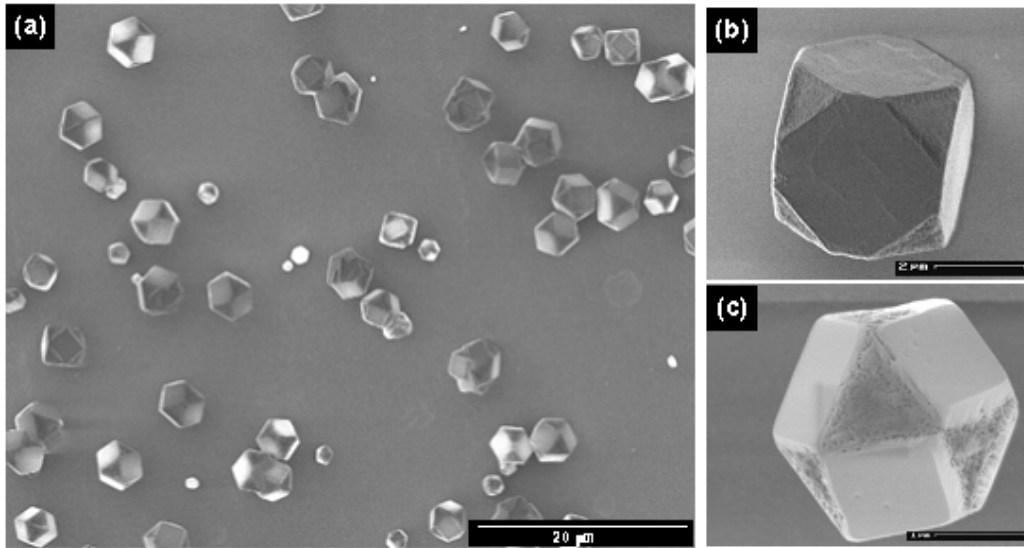


Figure 3.4: SEM images of (a) diamond crystals deposited on the non (few)-scratched substrate surface (b-c) diamond crystals with different proportions of growth rate between $\langle 100 \rangle$ and $\langle 111 \rangle$.

The nucleation of diamond is strongly dependent on the substrate surface conditions. Fig. 3.4 displays the diamond crystals deposited on a lightly scratched Mo substrate with only a few scratched sites on the surface. The nucleation of crystals can be observed only on the scratched sites with a low density. In this case, the diamond crystals do not connect to each other during their growth, they do not form thin layers but isolated large single crystals. The size can reach a few tens of microns after long time deposition. The isolated crystals are always grown in a cubo-octahedral shape. The dominating face on cubo-octahedral (always (111) or (100)) is determined by the proportion of growth rate between $\langle 100 \rangle$ and $\langle 111 \rangle$ and it depends on the experimental conditions. Fig.3.4(b) and (c) are crystals grown with different proportions of growth rate.

This chapter is focused on the production of graphitic based materials. This section is just to confirm the results obtained for diamond formation in our apparatus. The observed results are well matched with previous results summarized in Chapter 2. In addition, we observed at higher substrate temperatures unusual formation of diamond in this work. It is discussed in section 3.8 as the phase transition from graphite to diamond.

3.6 Two-dimensional graphitic materials

Much research has been carried out on one-dimensional structures such as nanotubes and nanowires. In this section, the formation of two-dimensional graphitic structures is presented. The 2D graphitic materials would be very useful not only for fundamental physics studies, but also for practical applications, due to their high anisotropy for electrical conduction and their large surface to volume ratio. The materials obtained are classified into several categories, depending on their crystallinity and synthesis conditions then characterized their structures and compared to each other.

3.6.1 'Gypsum Flower'-like carbon

3.6.1.1 Experimental conditions

At temperatures higher than 1000°C, sp^2 bonded carbon phases begin to appear. After the formation of an sp^2 - sp^3 intermediate phase (Diamond like carbon), a peculiar carbon entity, called 'gypsum-flower'-like carbon (GF), is produced at substrate temperatures ranging from 1050 to 1300°C with the O_2/C_2H_2 gas ratio between 0.80 and 0.98. The formation (nucleation) of GF on the substrate surface starts to be observed after 15 seconds of deposition time. Although their fast deposition is quite stable, compared to diamond formation, it is still dependent on the substrate surface condition (scratched or non-scratched). To analyze this structure, the deposition time is kept to 3 min for each sample in this section.

3.6.1.2 Morphology and structure

This sp^2 phase coating appears mat brown-black on the substrate surface. Fig. 3.5 demonstrates a SEM photograph of a typical coating of GF. This structure has been already reported in the literature [4]. At beginning of the deposition, isolated spherical 'Gypsum flower'like structures are formed. After a few minutes of deposition time, the isolated GF spherical structures grow uniformly on the substrate surface and connect to each other, forming a thin layer which covers entirely the substrate surface. The nucleation, which occurs generally at a quite early deposition stage, tends to start on the scratched areas of the surface. The surface condition determines the nucleation density of the GF deposition. When the nucleation density is not too high, isolated GF hemispherical balls of 10 μm in diameter are sometimes

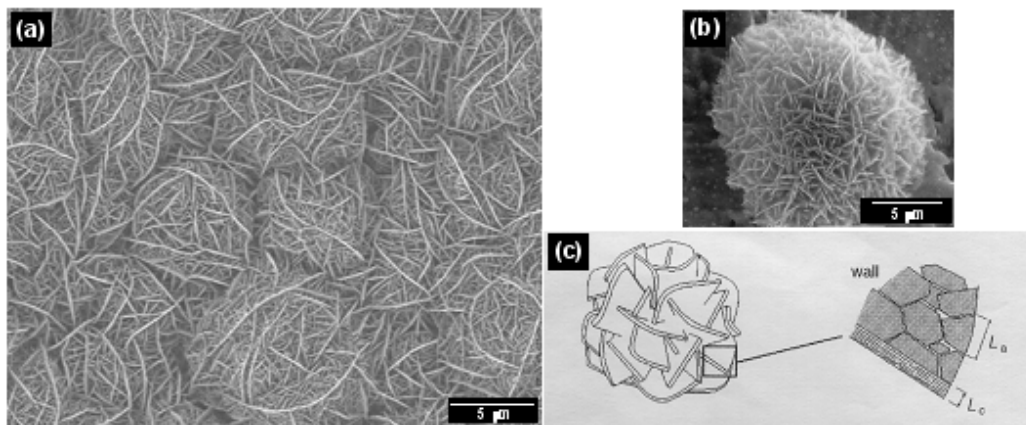


Figure 3.5: SEM images of (a) Gypsum flower-like carbon (GF) with a typical morphology, (b) isolated spherical GF and (c) schematic illustration of the GF structure [4].

observed even after 3 min. of deposition time (Fig.3.5.b). The surface of deposited GF coating is quite uniform and flat up to 5min. of deposition time. After 5 min. of deposition, each GF become too large and the coating forms rough surfaces. Fig.3.5.c illustrates a model of the GF structure composed of sp^2 carbon [4]. A GF particle is grown in radial orientation from a nucleus. The walls observed on the GF surface are formed of only sp^2 based carbon and are oriented randomly on the GF surface, strictly perpendicular to the spherical surface.

Although the GF is synthesized in a large zone of the diagram of produced materials (Fig.3.2), its structure, especially the wall structure, may vary depending on the experimental conditions such as the substrate temperature (T_s) and the input gas ratio ($R_f = O_2/C_2H_2$). Fig.3.6 displays four types of GF depositions obtained at a substrate temperature of $1000^\circ C$ with different input gas ratios R_f , (a) 0.95, (b) 0.90, (c) 0.85 and (d) 0.80. When the proportion of oxygen to acetylene decreases, the thickness of the walls forming the GF increases. We assume that the growth direction of graphitic walls changes when the input gas ratio changes. This could be due to the different active species generated in each gas condition. The degree of graphitization for each sample will be discussed in section 3.6.3.

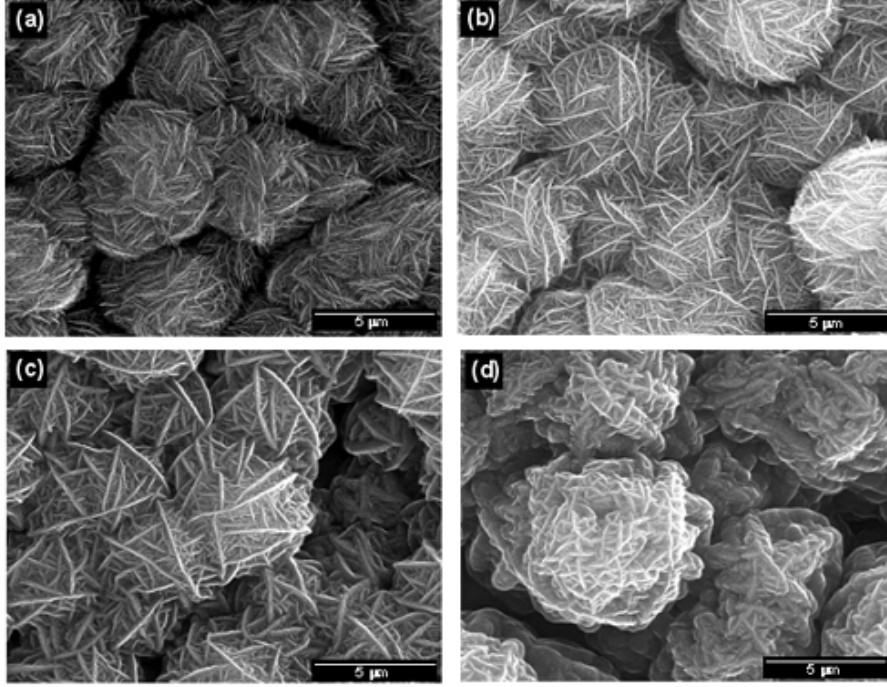


Figure 3.6: SEM images of GF obtained at 1000°C with the input gas ratio $R_f =$ (a) 0.95, (b) 0.90, (c) 0.85 and (d) 0.80.

3.6.2 Petal-like carbon

3.6.2.1 Experimental condition

A different carbon form based on the same morphology as that for the GF is produced for higher temperature range. We call it petal-like carbon because of the shape of the thin graphitic sheets composing the aggregates. Petal-like carbon is produced at substrate temperatures above 1300°C with O_2/C_2H_2 gas ratio between 0.80 and 0.98. The formation of the petal-like carbon also occurs quite rapidly and the nucleation is more stable than that of GF. The petal-like carbon can be formed even on non-scratched substrate surface. To analyze this structure, the deposition time is kept to 3 min for each experiment.

3.6.2.2 Morphology and structure

Fig.3.7 shows the petal-like coating produced at a substrate temperature of 1350°C. At early deposition times, the aggregate forms round features with diameters in the range of 1 to 5 μm , whose surface consists of thin entangled layers (demonstrated in Fig.3.7.b). Since the growth of the petal-like carbon is uniform on the substrate and the growth rate is very high, the round-shaped aggregates connect after a few minutes, covering entirely the deposit zone of the substrate surface (Fig.3.7.a). The petal-like sheets are quite thin compared to the walls of GF, approximately 20 nanometer in thickness, are not always flat, and may sometimes roll up like paper. The nucleation and growth of graphitic structures is known to be promoted by the presence of metal catalysts. In this work, the synthesis of petal-like structures was also possible on graphite surfaces. This evidence suggests that there is no catalytic effect for the formation of these crystals.

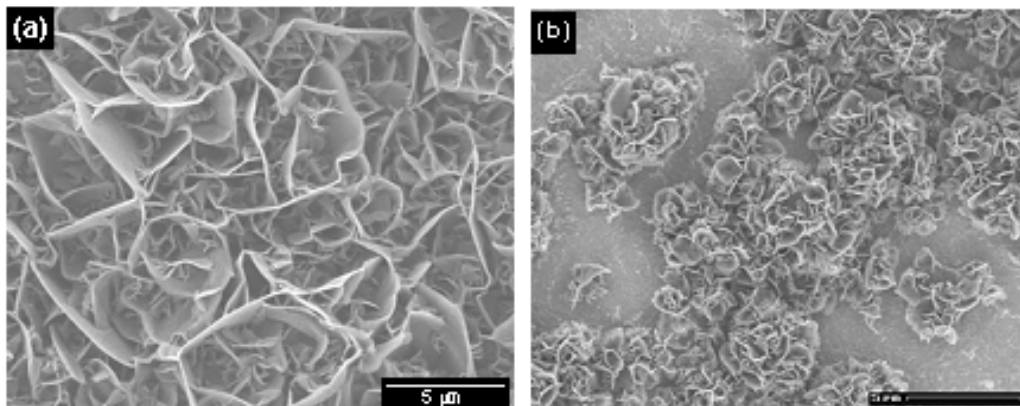


Figure 3.7: SEM images of petal-like carbon obtained at 1350°C (a) after 3 min of deposition time and (b) at an earlier deposition time.

TEM studies allow us to estimate the degree of graphitization. Fig.3.8 displays TEM images of dispersed thin layers forming the petal-like carbon, in BF mode. Bragg fringes appearing on the edges of the petal sheets (indicated by an arrow in Fig.3.8.a) show quite thin rolling graphitic sheets. By the continuous lines because of Moiré (in Fig.3.8.b), the estimated minimum size of coherent domain ranges (crystallite size L_a) is at least 100 nm. This value indicates a quite high quality of graphitic structure.

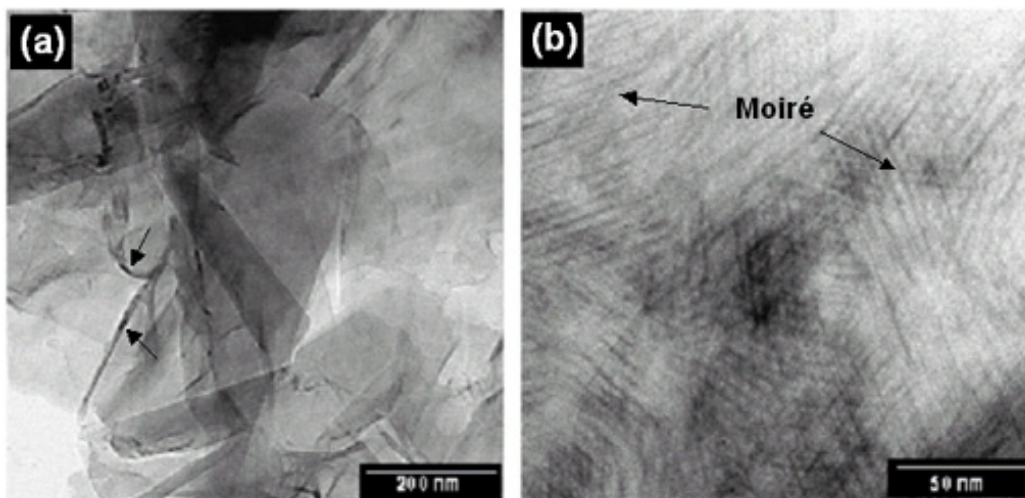


Figure 3.8: (a-b) TEM images of petal-like carbon produced at 1350°C in Bright Field (BF) mode.

3.6.3 2-dimensional graphitic structures studied by Raman spectroscopy

3.6.3.1 Raman spectra of graphitic materials

It is known that only two modes, the E_{2g} mode (Fig.3.9.a) at 42 and the mode at 1580 cm^{-1} called the G band, are active in hexagonal single crystal of graphite, together with a second-order feature, an intense band around 2700 cm^{-1} .

One of the most unusual properties of graphite is that the spectrum of micro-crystalline material shows additional lines, that are not observed in large single crystals. The first-order spectrum of micro-crystalline graphite shows additional bands at $\cong 1350\text{ cm}^{-1}$ and 1620 cm^{-1} called D and D' bands respectively, which are due to the presence of lattice defects and to the loss of the long range in-plane symmetry which relax the usual selection rules. The D peak around 1360 cm^{-1} is a breathing mode of A_{1g} symmetry (Fig.3.9.b). This mode is forbidden in perfect graphite, and only becomes active in the presence of structural disorder. This band shows a laser energy dependence and exhibits a strong dispersive nature as a function of excitation wave length (λ_L).

In the first report of the D mode Tuinstra *et al.* showed that its inten-

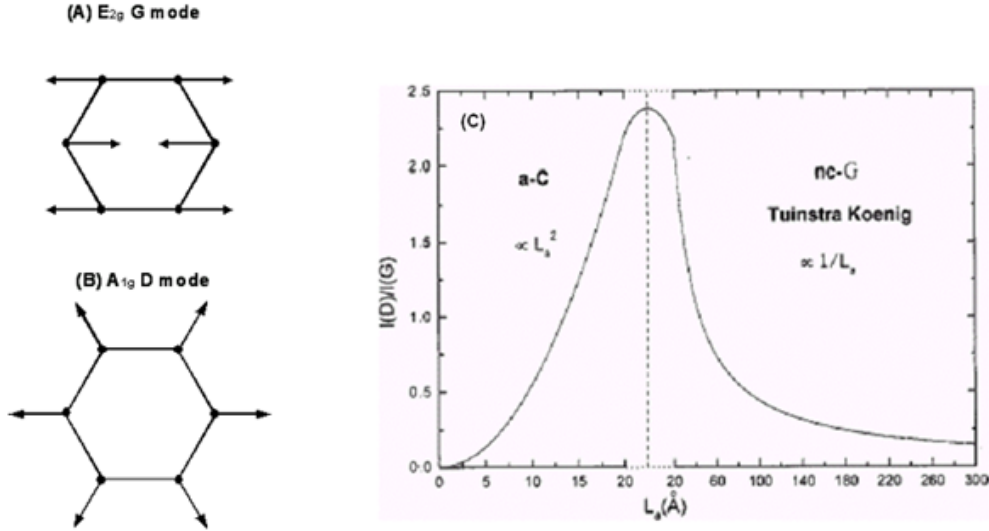


Figure 3.9: Carbon motions in the (a) G and (b) D modes and (c) variation of the $I(D)/I(G)$ ration with L_a [2].

sity increases linearly with decreasing size of the scattering graphite crystals [2]. They proposed the mode to be associated with a high phonon density of states around the K point of the Brillouin zone, i.e., a classical example of a density of states feature seen in Raman scattering because of relaxed k conservation. This obvious interpretation was only questioned ten years later when Vidano *et al.* published Raman spectra on graphite excited with different lines of an Ar/Kr laser [7]. Their spectra showed the D mode frequency to increase with increasing excitation energy. They reported a shift of 56 cm^{-1} for 1 eV change in laser energy, similar values were published by many groups for a wide range of excitation energy [8, 9, 10]. No explanation was found for this frequency shift. An empirical $k = q$ selection rule that the wave vector of the resonantly excited electron is somehow transferred to the phonon gave agreement with the experimentally found shift, but lacked any physical grounding. Moreover, it failed to explain the last peculiarity in the disorder induced Raman spectrum, the difference in Stokes and anti-Stokes frequency. Tan *et al.* found that the Stokes and anti-Stokes spectra of the D mode excited with the same laser wave length differed by 7 cm^{-1} whereas the G mode frequencies agreed to within 1 cm^{-1} , as expected in Raman scattering [11]. The double resonances is suggested to be the origin of the D peak in the graphite Raman spectrum [12]. They found that the electronic

dispersion in graphite gives rise to double resonant Raman scattering where, the calculation for D-mode frequency shift agreed well with the experimental value. In the recent studies the dispersion effect of the D mode is explained in terms of the coupling between electrons and phonons with the same wave vector near the K point of the Brillouin zone [9]. Two Kohn anomalies have been observed in the graphite phonon dispersions with two sharp kinks. The slope of these kinks was proportional to the square of the electron-phonon coupling [13].

3.6.3.2 Estimation of the degree of graphitization

The intensity of the D band is commonly used for practical applications to evaluate the amount of disorder in carbon materials [14]. The degree of graphitization in carbon materials can be estimated by the relative intensity of the D band to G band. The relative intensity varies as the inverse of the crystal planar domain size, L_a [2]:

$$R(\lambda) = \frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a} \quad (1)$$

where $C(\lambda)$ is dependent on the laser excitation wavelength (λ_L), $C(515.5 \text{ nm}) \simeq 4.4 \text{ nm}$ and $C(632.8 \text{ nm}) \simeq 8.28 \text{ nm}$. Here, an important second parameter is the line width of the Raman bands. It has been observed that with increasing HTT of carbon materials, an increase in the Raman intensity and a decrease in the line width of the G-band, and a decrease of the intensity and line width of the D-band occur[15]. The line width thus should be taken into account to determine the relative intensity of the bands. The relative intensity is obtained from integrated areas of the G and D bands.

The variation of the relative intensity $I(D)/I(G)$ is separated into two parts, as a function of the crystallite size of graphitic materials (Fig.3.9.c) [3]. In the first part (region I), the crystallite size is very small and the material is almost an amorphous carbon. Too many defects introduced into the graphitic layers cause its vibrational modes to soften, particularly the G peak. The equation (1) is no longer valid. In the second part (region II), which is important for our investigations, the D peak appears and $I(D)/I(G)$ decreases following the equation (1). To examine graphitic materials by this equation, the required crystallite size is superior to 20 Å.

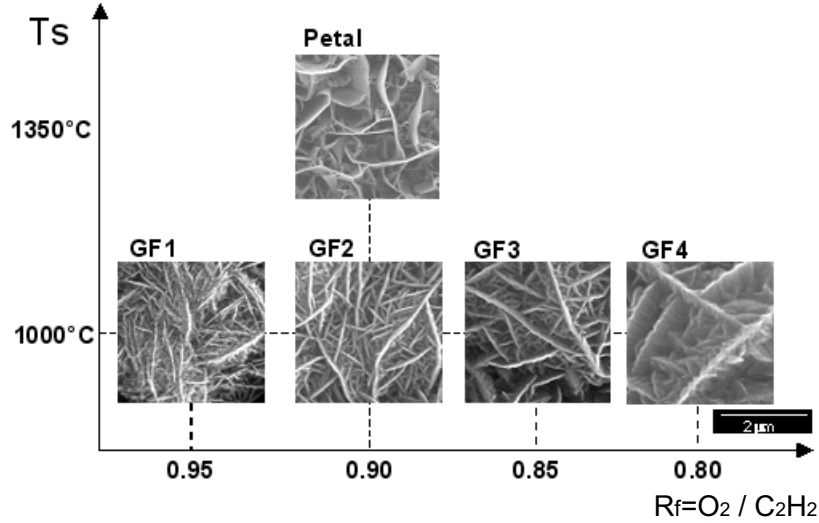


Figure 3.10: Experimental parameters for the examined samples.

3.6.3.3 Raman spectroscopy of several graphitic structures

Since our samples are considered to consist in the graphitic structures with crystallite sizes greater than 20 Å, the estimation of the degree of graphitization is calculated by the equation (1). In this series of experiments, a Jobin-Yvon microspectrometer with a laser emitting at $\lambda=632.8$ nm is used. The $C(\lambda)$ is applied as 8.28 nm. Five different samples are examined by Raman scattering. The experimental conditions for each sample are illustrated in Fig.3.10. To investigate effects of the substrate temperature T_s and the input gas ratio $R_f = O_2/C_2H_2$ on the graphitization process, four different GFs synthesized with $R_f=0.95, 0.90, 0.85$ and 0.80 at $T_s=1000^\circ\text{C}$ and a petal-like structure produced with $R_f=0.90$ at $T_s=1350^\circ\text{C}$ are examined.

Typical spectra observed for these samples are presented in Fig.3.11. The intensity of D peak associated with defects inside the aromatic rings, progressively decreases for lower R_f values, and becomes quite small under higher temperature condition. Table 3.1 represents the respective line width and the relative intensity $R=I_D/I_G$ obtained from integrated areas of the G and D bands, observed for our samples. An increase of the L_a with increasing the acetylene content in the input gas is obviously observed.

In addition, a temperature effect on the graphitization is also confirmed by the estimation of L_a . The Raman spectrum of the petal-like structure

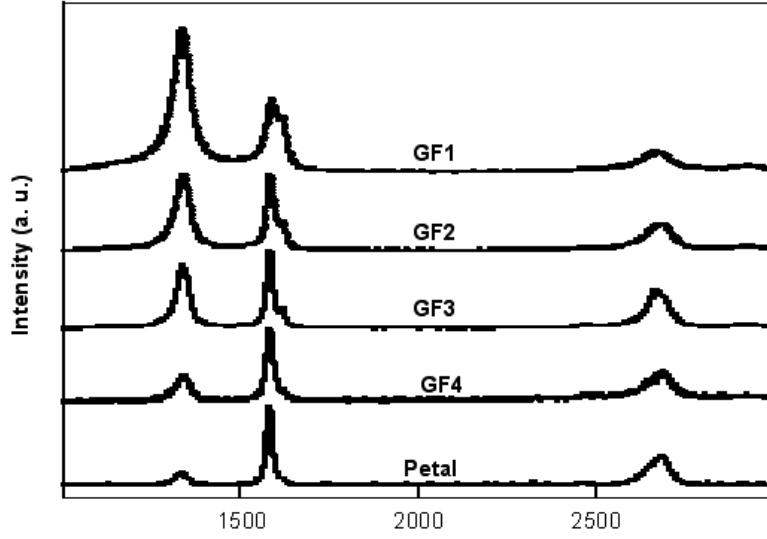


Figure 3.11: Raman spectra of each samples of Fig.3.10.

produced at 1350°C demonstrates a quite small D peak, giving the relative intensity of 0.31. Although this value corresponds to an L_a value of 26.70 nm from the equation (1), the value of the relative intensity is already small enough to exhibit a linear regime (Fig.3.9.c).

Examined sample	$\Delta\nu_{12}$ (cm ⁻¹)		$R = I(D)/I(G)$	L_a (nm)
	D line	G line		
GF1	55	46	2.20	3.76
GF2	50	24	2.02	4.10
GF3	43	19	1.71	4.84
GF4	49	22	0.76	10.89
Petal	38	18	0.31	26.70

Table 3.1: Raman data on different samples of Fig.3.10.

The obtained L_a value is a minimum estimated one. Compared with the sample so-called GF2 produce with the same gas condition but at lower temperature, the L_a is estimated more than six times larger. It suggests that the substrate temperature is very important parameter for the degree of the

graphitization of produced sample.

3.6.4 Large Petals - graphite single crystal

3.6.4.1 Experimental conditions

For substrate temperatures around 1400°C, the surface of petal-like deposits becomes rough and some petal-like sheets can selectively grow as displayed in Fig.3.12. The size of these large petals grown reaches up to 20 μm . At substrate temperatures above 1500°C, the deposit surface becomes smooth again.

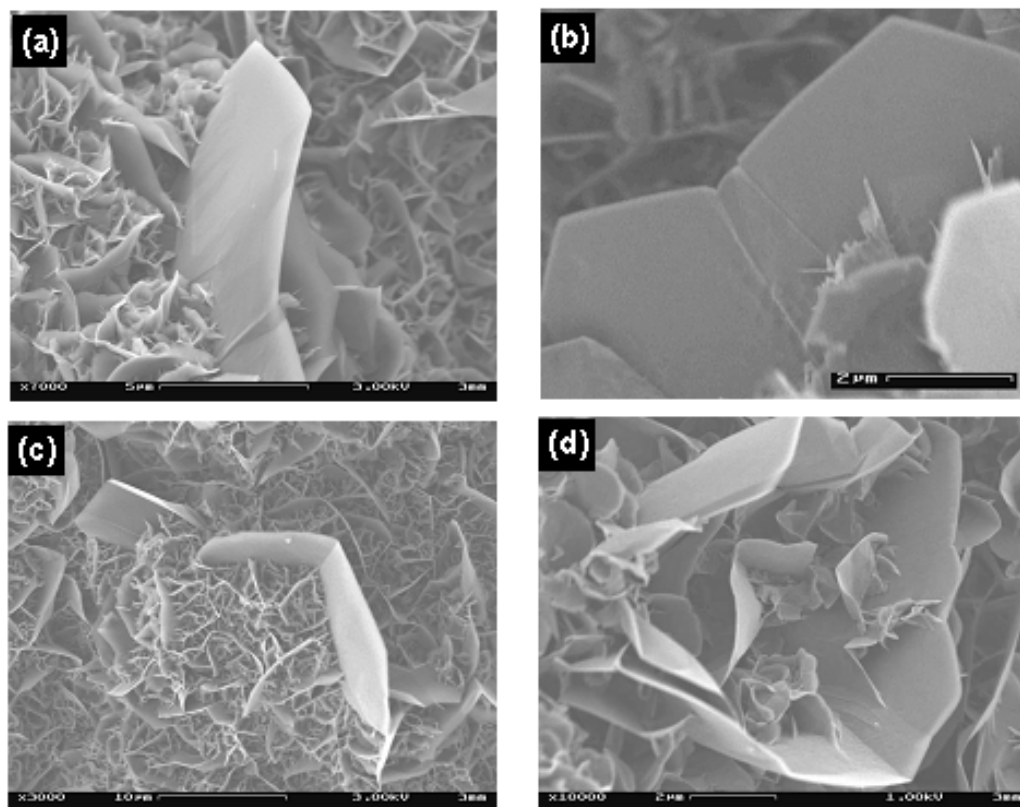


Figure 3.12: SEM images of large petal-like sheets obtained at 1400°C.

3.6.4.2 Morphology and structure

Fig.3.12 shows the large crystals grown in petal sheet aggregates. Their size varies between 5 and 20 μm . These large sheets often exhibit hexagonal shapes (Fig.3.12.a and b).

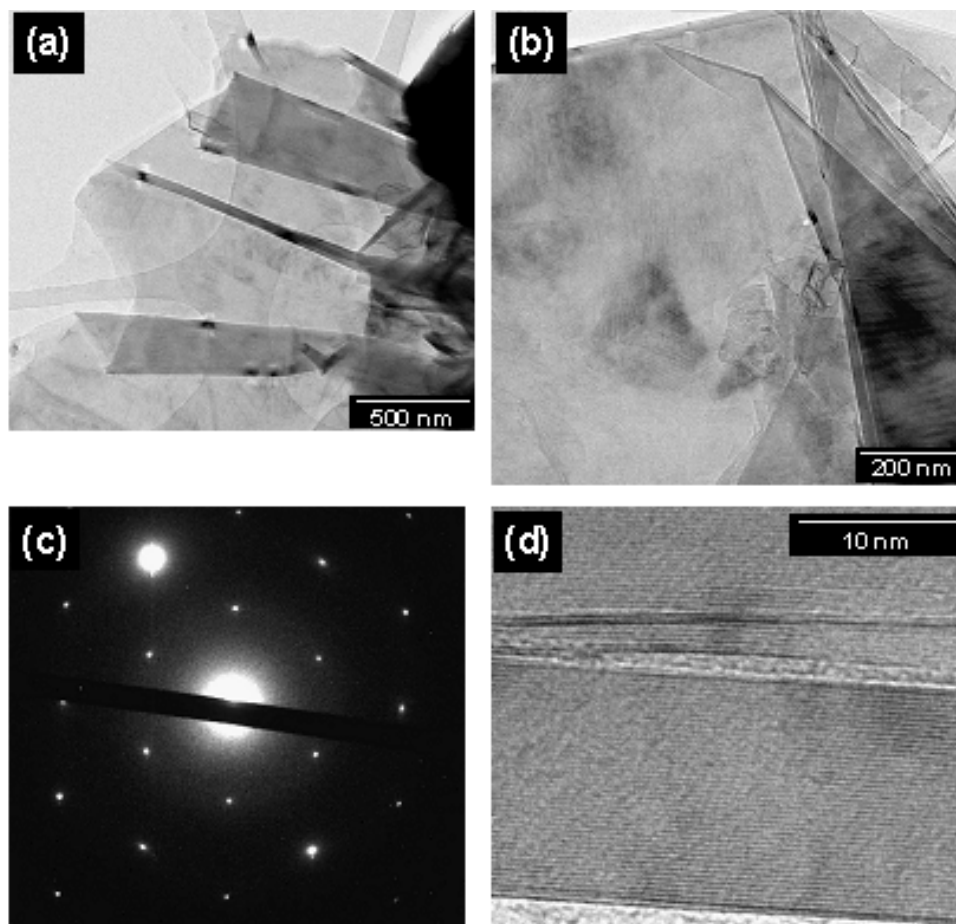


Figure 3.13: (a-b)TEM images of petal-like carbon obtained at 1350°C in Bright Field mode, (c) diffraction pattern (zone axis [001]) on a large petal and (d) HR-TEM image of a cross section.

TEM observations of the large petal-like sheets are carried out. Fig.3.13.a and b illustrate petal-like sheets observed in bright field (BF). By the continuous lines because of Moiré (indicated by an arrow), the estimated minimum size of coherent domain ranges (crystallite size) is at least 500 nm.

Fig.3.13.d demonstrates a HR-TEM image of the cross-section of a petal sheet. It demonstrates perfectly oriented graphitic layers, $\simeq 20$ nm in thickness. In addition, a diffraction pattern, obtained with a selection aperture of 800 nm, exhibits the perfectly defined hexagonal symmetry of graphite (see Fig.3.13.b). The domain consists of a single crystal being at least 800 nm in size.

3.6.4.3 Raman spectroscopy

Micro Raman studies are performed on petal-like textures grown to large sizes. These structures are large enough to allow selective micro Raman analysis of their surface. Fig.3.14 demonstrates the Raman spectrum of a large grown petal. The spectrum corresponds to almost perfect graphite, with a narrow G band (1580 cm^{-1}) which full width at half maximum is approximately 10 cm^{-1} , nearly no D band (1350 cm^{-1}) and the G' band being the second order peak (2700 cm^{-1}). It is remarkable that the spectra are very close to that of the single crystal of graphite despite the large size of the petals, of the order of a few tens of microns. This demonstrates the formation of two-dimensional high-quality graphite crystal.

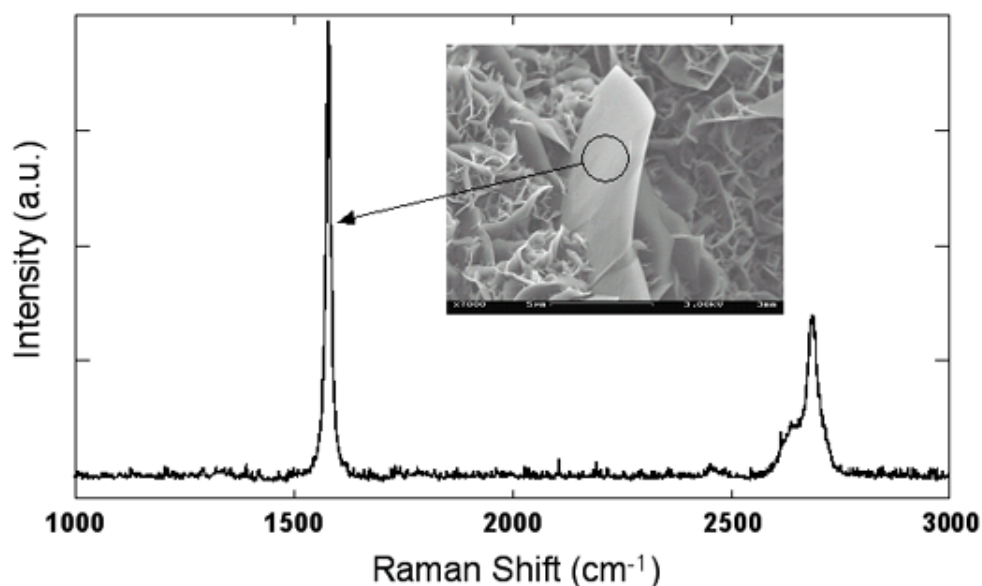


Figure 3.14: Raman spectrum of petal like graphite crystal.

3.6.4.4 Synthesis of single crystals and interests for physics

Although many kinds of graphitic materials such as carbon fibers [16], carbon nanotubes [17] and fullerenes [18] have been successfully produced in various laboratories using several types of techniques, artificial single crystals of graphite are not so frequently obtained. Natural graphite can be found only in limited regions of the world. Synthetic graphite, also called 'Kish Graphite', is produced by precipitating super saturated carbon from iron [19]. This artificial structure possesses very high crystallinity, but again the synthesis technique suffers from the difficulty to produce large size graphite single-crystals. Highly Oriented Pyrolytic Graphite (HOPG) can be synthesized in large amounts. However, HOPG is composed of crystalline domains, called crystallites, which display a high degree of orientational order along the c-axis, but the a-axes have varying orientations [20]. Consequently, HOPG is not really a candidate material for single-crystals of graphite. In this chapter, bidimensional graphite single-crystals of large size with quite high crystallinity are synthesized after a few minutes of deposition time using the oxy-acetylene flame method. The thickness of these crystals does not change after their early growth stage. The crystal growth proceeds mainly along the direction parallel to the graphitic layer (a-axis), which could be attributed to the presence of a high thermal gradient in the process. Since the crystal growth occurs in the direction toward the flame source, growth mechanisms are certainly different from that of polycrystalline graphite, such as HOPG, where crystallization starts in many places simultaneously to finally form highly-oriented structures.

These two-dimensional petal-like single crystals can be very useful to study fundamental physics in ideal low-dimensional systems on account of its structural perfection. This material should be also interesting for practical applications due to their high anisotropy in the electrical conduction and their large surface to volume ratio.

3.6.4.5 Growth mechanism of 2-dimensional graphitic structures

In this section, a possible growth mechanism for the 2-dimensional graphitic materials is proposed. After a quite short time deposition (a few tens of seconds), the aggregates are composed of only a few directions of graphitic walls. Each graphitic wall can be assumed to nucleate identically and homogeneously in the gas phase. Then they are associated with an heterogeneous

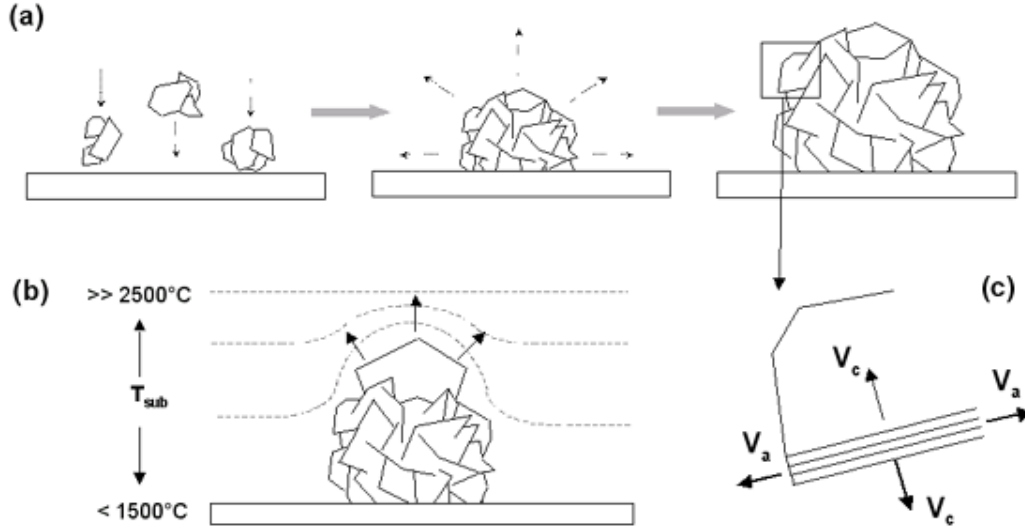


Figure 3.15: Schematic models of (a) nucleation and growth of the carbon aggregate, (b) growth of large petal crystal, related to the thermal gradient and (c) graphitic wall growth directions along a-axis and c-axis.

process on the substrate, leading to a first formation of aggregates, such as the GF and Petal-like carbon (Fig.3.15.a). Since the edge of basal plane in graphite is quite active due to the presence of free bonded atoms, the growth rate of the graphitic walls in a-axis (parallel to the basal plane) should be higher than that in c-axis direction. It results in the hemispherical shape composed of the graphitic walls oriented perpendicular to the surface. The ratio of the growth rates along c-axis and a-axis, $R_v = V_c/V_a$, determines the thickness of the graphitic wall organizing the aggregates. Fig.3.15.c illustrates the growth direction along these two axes. The R_v value is much lower than 1 in any cases. The thicker walls are formed with the higher R_v . The R_v increases when decreasing the input gas ratio R_f since the thickness of graphitic walls composing the GF increases (see in the section 3.6.1.2). However, parameters contributing to the growth in each direction have not yet been revealed. Both V_c and V_a are assumed to be multiplied with increasing the substrate temperature, but lowering the R_v value. It is the reason why the graphitic walls become very thin in the case of Petal-like carbon synthesized at high temperature. With the input gas pressure toward the substrate, there should be a strong convection process in the flame. When the distribution of active species in the gas phase is relatively uniform, the

deposit surface of GF and Petal-like carbon may be homogeneous. On the contrary, the formation of large scale petal sheets is supposed to be due to a non-uniform concentration of species introduced by the strong convection in the gas phase. Once a petal sheet is grown to larger size than the others, a high thermal gradient is introduced at its top as illustrated in Fig.3.15.b. The active carbon species are deposited on this sheet with a more important growth rate. Consequently, the individual crystal size reaches sometimes a few tens of microns.

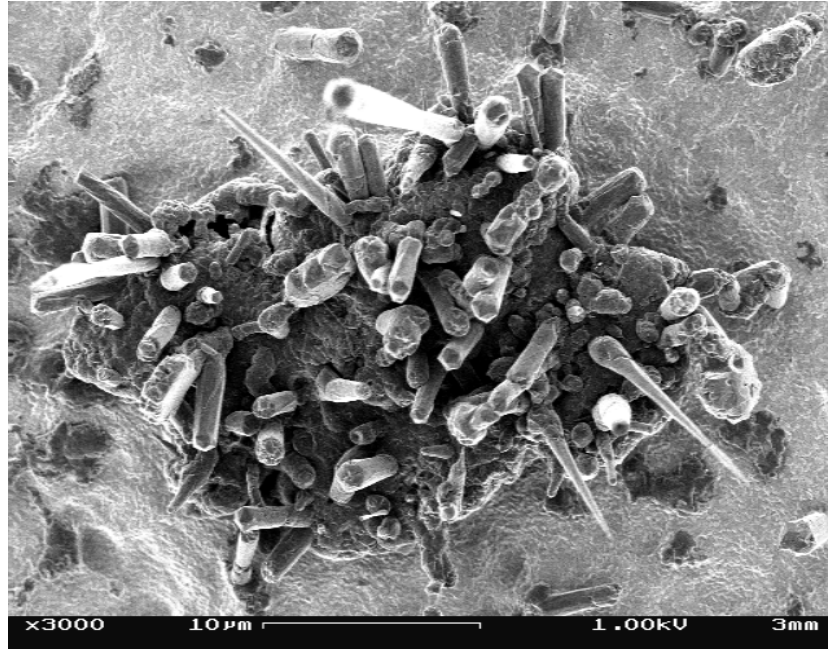


Figure 3.16: Scanning Electron Micrograph (SEM) of polyhedral crystals as synthesized by the oxy-acetylenic flame combustion technique.

3.7 Uni-directional graphitic materials

3.7.1 Graphite polyhedral crystals

3.7.1.1 Experimental conditions

Carbon micron-sized crystalline structures are produced in large amounts on the substrate (Fig.3.16). These crystals are synthesized within peculiar and

limited experimental conditions: the O_2/C_2H_2 gas ratio being around 0.90 and the substrate temperature ranging from 1230 to 1280°C.

3.7.1.2 SEM observations

The crystal size can reach up to 3 μm in diameter and 15 μm in length. We call the carbon micro-crystals polyhedral crystals [21] because of their complex polyhedral shapes with facets along their sides; the number of facets is frequently eight (Fig.3.17). Such polygonization of the crystal sides is assumed to be due to higher surface energy minimization when compared with the cylindrical shape. This phenomena has already been observed and reported in the literature for thermally annealed material at 2000°C [22, 23, 24]. At the end of the graphitic micro-crystals, various tips have been observed (Fig.3.17). For example, a hexagonal symmetry is observed at the apex of the tip of a rod-like structure, illustrated in Fig.3.17.a. Fig.3.17.c shows a crystal exhibiting a pin-like apex at the end. In this case, the polyhedral shape is twisted along the rod axis and the diameter of the crystal becomes smaller toward the tip, leading to a quite sharp apex (Fig.3.17.d). Carbon nanotubes are also frequently observed protruding at the tip of these crystals, especially for the rod-like structure (Fig.3.17.b).

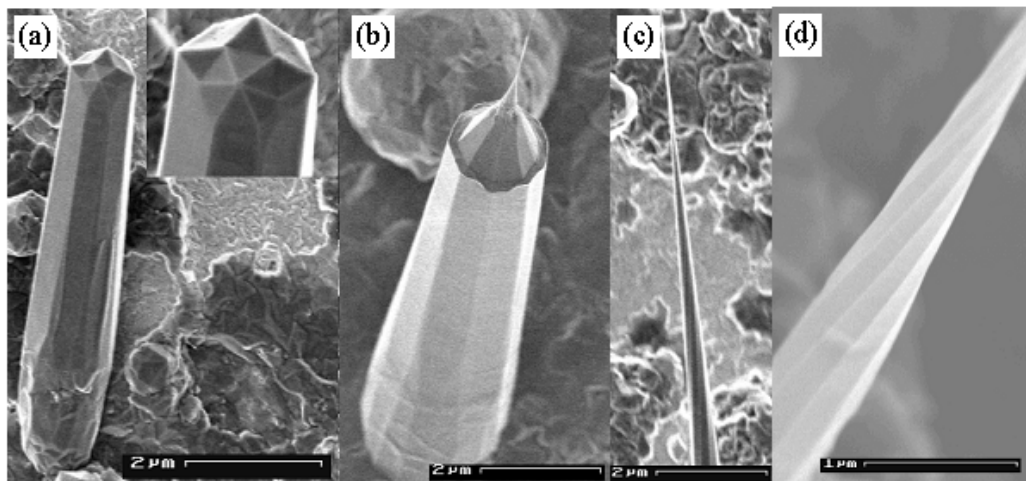


Figure 3.17: SEM images of (a,b) representative polyhedral crystals with rod-like and (c,d) pin-like morphologies, illustrating their polygonal shapes. The tip of these carbon microstructures is also highly symmetrical, exhibiting a crystalline apex as shown in the inset of (a).

3.7.1.3 TEM observations

A High-Resolution TEM image of the side face of a rod-like crystal is presented in Fig.3.18.a. The (002) lattice fringes demonstrate the very good ordering of the graphitic layers which are oriented parallel to the surface sides of the crystal. However, these planes need to reorganize at the rod end in order to form a faceted apex (see Fig.3.17.a).

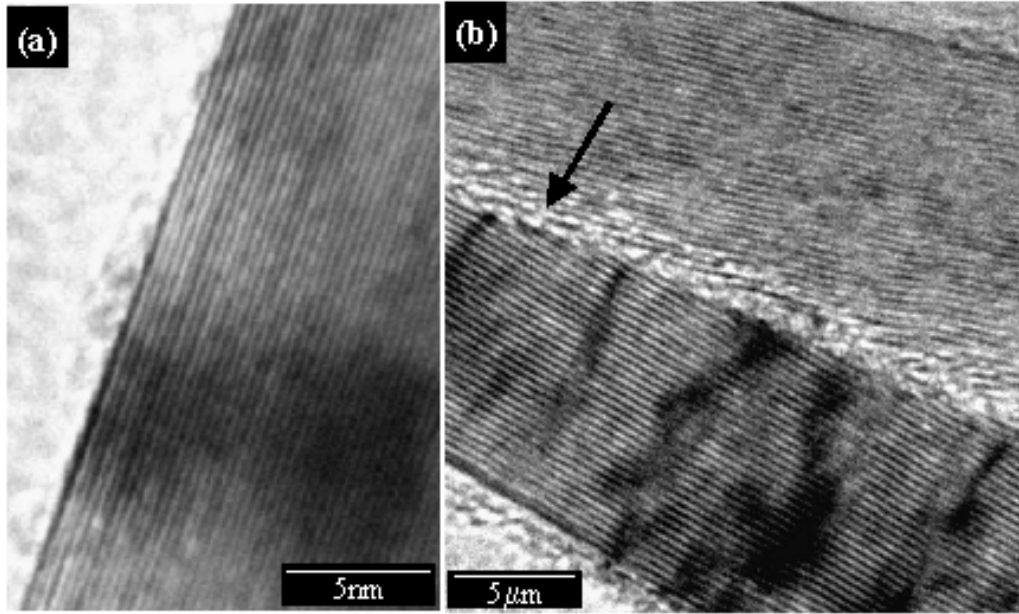


Figure 3.18: HR-TEM images of (a) the graphitic layers of a rod-like and (b) a pin-like micro-crystal. Both observations demonstrate the high crystallinity of these carbon structures and the orientation of the graphitic layers with the crystal axis.

For the pin-like morphology, the graphitic layers are also parallel to the surface side but not to the crystal axis, where a reorganization of graphitic layers is observed at the crystal core (Fig.3.18.b). These two micrometer-sized graphite structures have already been reported in the literature [25, 26]. However, to the best of our knowledge, it is the first time that both of them, the rod-like (Fig.3.17.a and b) and the pin-like (Fig.3.17.c and d) crystals, are observed within the same experiment. The main difference in their morphologies is the orientation of the graphitic layers versus the core axis of the crystal. When the graphitic layers form a cylinder around the core axis, the diameter of the rod does not decrease significantly, leading to

a rod-like structure. On the contrary, when the orientation of the graphitic planes is tilted, leading to a conical shape for the layers. The layers intersect at the crystal core and stop growing successively by reorganizing their free edges (indicated by an arrow in Fig.3.18.b). Consequently, the corresponding structure displays a decrease of its diameter depending on the tilt angle of its graphitic layers with respect to its axis.

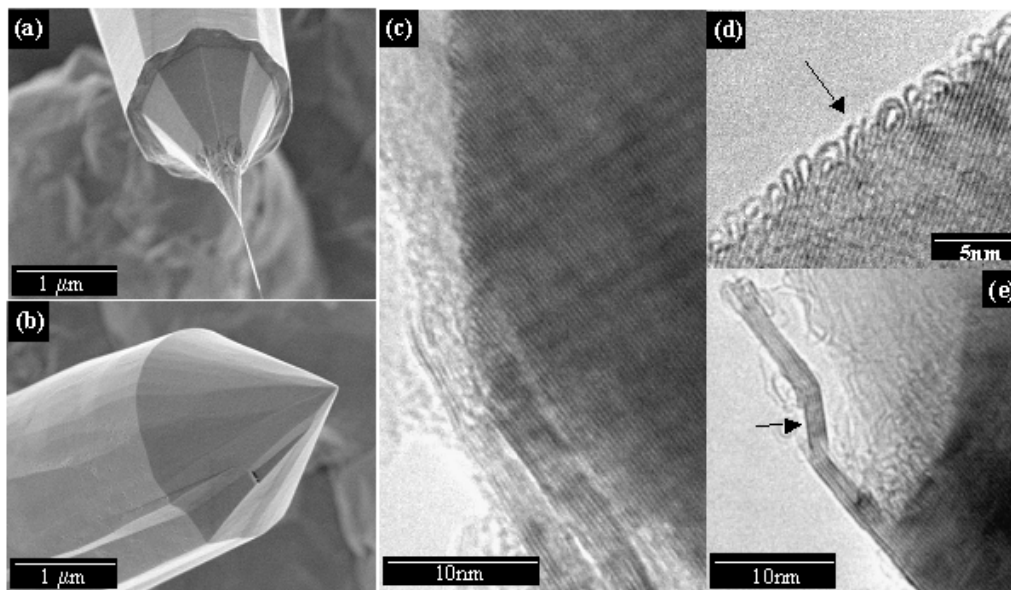


Figure 3.19: SEM images of (a-b) various tips of rod-like graphitic crystals. HR-TEM images characterizing the top of (c) the crystal, (d) folded carbon layers and (e) curved carbon layers. The arrows indicate the edge reconstruction in (d) and some declination due to topological defects in (e).

These crystals also display various tips as previously illustrated in Fig.3.17. The growth of the pin-like structure is supposed to stop when its diameter is inferior to a threshold value. On the other hand, the growth of rod-like crystals leads to the formation of various terminations as illustrated in Fig.3.19. HR-TEM reveals the orientations of the graphitic layers on these two terminations. The graphitic layers are frequently oriented parallel to the core axis up to the end of the crystal (Fig.3.19.a-b). However, when the crystal ends, the graphitic layers do not stop abruptly. Nano-arches are observed at the edges of the graphitic planes (Fig.3.19.d). These nano-arches result in a swelling of the edge planes, producing a peculiar surface reconstruction in

graphite [27]. Typical nano-arches are built by folding two graphene layers, but sometimes, the number of layers could increase to three or four. Less frequently, a single non-terminated graphene sheet is also observed enclosed between folded layers. Such a reconstruction stabilizes the structure by satisfying a large number of dangling bonds at the graphitic edge, and has also been reported for carbon filaments after thermal treatment at 2800°C [28]. Other observations illustrate the presence of declinations within the graphitic layers (Fig.3.19.e.). This could be due to the presence of topological defects such as pentagons ($+60^\circ$ declination) or heptagons (-60° declination). Both the edge reconstruction (nano-arches) and the presence of topological defects located at the tip of these crystals could explain the D band in the corresponding Raman spectrum (Fig.3.20).

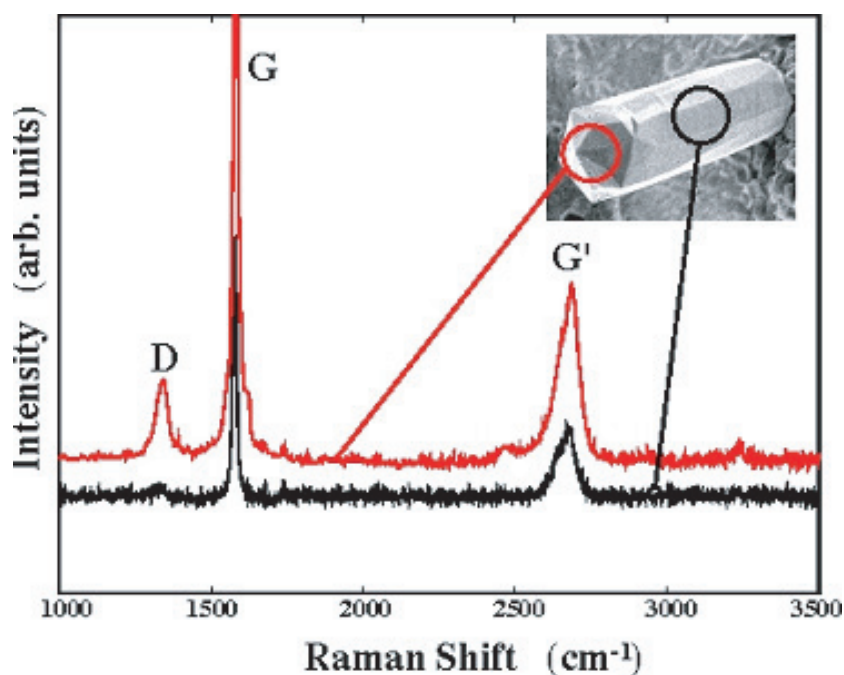


Figure 3.20: First- and second order Raman spectra obtained from the faceted part and the tip of a graphitic rod as illustrated in the inset using a SEM micrograph.

3.7.1.4 Raman spectroscopy

The sizes of these carbon microstructures are large enough to allow selective micro Raman analysis from the side face to the tip (Fig.3.20). The Raman

spectra are taken by focusing the laser beam with excitation wavelength of 632.8 nm on an area of about $1 \mu\text{m}^2$. The Raman spectrum associated with the crystal faces is quite analogous to pure graphite, with a narrow G band (1580 cm^{-1}), nearly no D band (1350 cm^{-1}) and the G' band being the second order peak (2700 cm^{-1}). The full width at half maximum of G peak is approximately 13 cm^{-1} , corresponding to the value for the HOPG crystal with $L_a > 100 \text{ nm}$. The Raman spectrum obtained at the tip displays a D peak and an unusually strong second order G' band peak that exceeds in intensity half of the G band of graphite. Such differences in the spectra could be attributed to the presence of topological defects, dangling bonds, and edge reconstruction at the end of the graphite rods.

3.7.2 Carbon nanotubes

3.7.2.1 Sample preparation

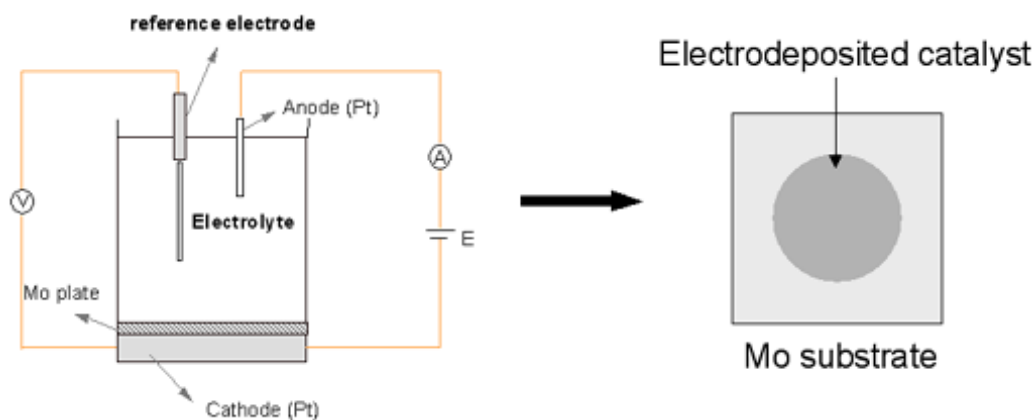


Figure 3.21: Electrodeposition system applied to pre-deposit transition metals as a catalyst.

In this section, samples are prepared in the presence of catalysts. Transition metals such as Fe, Co and Ni are introduced as catalysts to the carbon synthesis process. To introduce these metals, metal powders are first tried to be compressed directly on the substrate surface. However, the expected catalytic effects are not obtained because of pressure due to the flame source. Moreover, the catalysts could not be uniformly introduced to the system. To intimately fix them uniformly on the substrate surface, an electrodeposition

technique is applied. This system allows to pre-deposit the transition metal thin layer directly on the Mo surface. Fig.3.21 shows a system of electrodeposition.

CNTs are produced on a Co/Ni catalyzed substrate surface after 5 seconds of deposition time using the oxy-acetylene combustion flame.

3.7.2.2 Experimental condition-Morphologies

Fig.3.22 displays two typical sets of nanotubes, illustrating curved (Fig.3.22.a) and straight (Fig.3.22.b) morphologies, respectively [29]. The morphologies are found to be strongly related to the volume ratio of the source gases and to the substrate temperature. The set of curved nanotubes can be formed under a large domain of experimental conditions, while the straight nanotubes can only grow under limited conditions, and the respective yield is also lower. With a O_2/C_2H_2 gas ratio between 0.85 and 0.98 at the substrate temperature between 900 and 1100°C, a large amount of the curved nanotube are produced. When the O_2/C_2H_2 gas ratio is fixed to 0.95, the synthesis of the curved structure is maintained at low substrate temperature (up to 1100°C), while the straight morphology is observed at higher substrate temperature (above 1200°C).

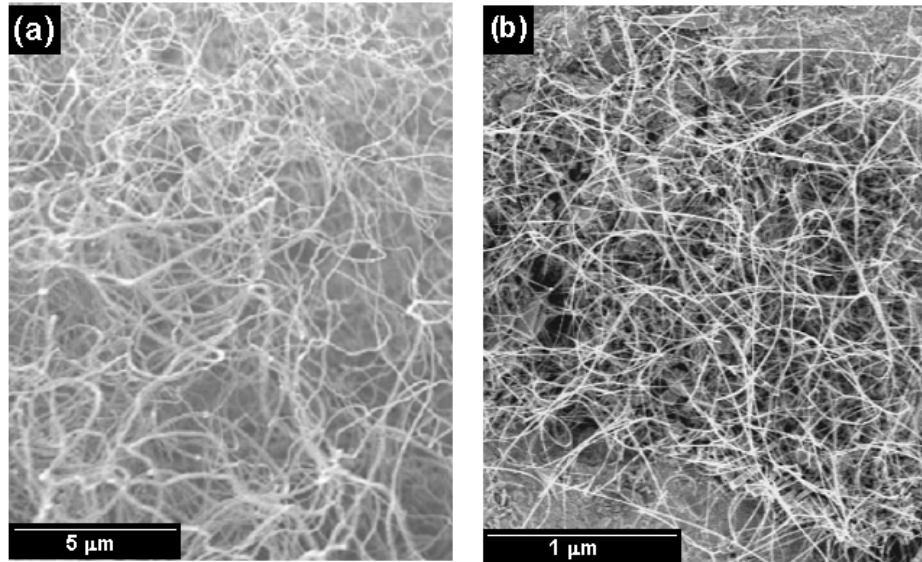


Figure 3.22: SEM images of (a) curved and (b) straight CNTs, synthesized by the oxy-acetylene combustion flame technique.

The curved CNTs are produced with a dense entanglement covering uniformly the substrate surface. They are frequently observed together with other carbon forms, especially soot-like structures. Their outer diameter is in the range of 50 to 100 nm. On the contrary, the straight structure grows at the surface of the metal carbide particles deposited on the substrate, and no other carbon forms are observed. They are characterized by lengths up to 20 μm long and an outer diameter varying between 5 and 20 nm.

3.7.2.3 TEM observations

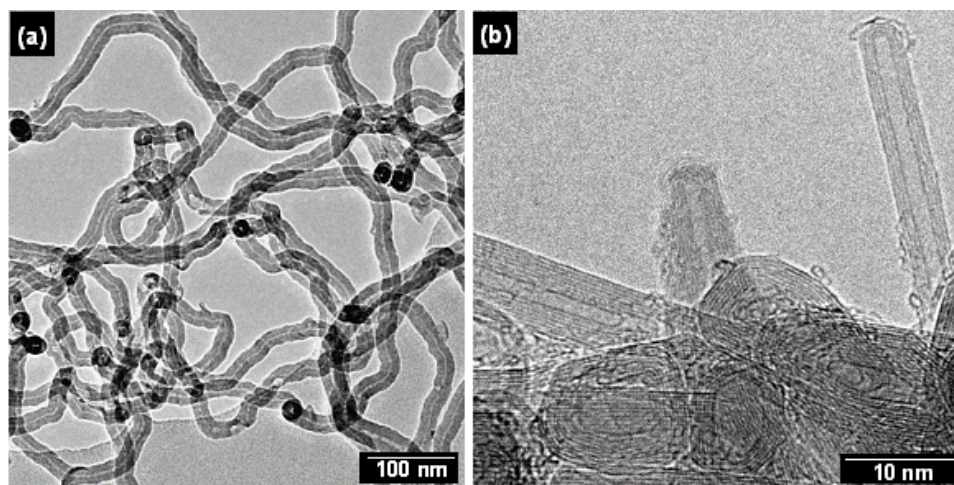


Figure 3.23: TEM images of (a) curved and (b) straight CNTs.

Fig.3.23 displays TEM images for the curved (a) and the straight (b) CNTs produced using the oxy-acetylene flame technique. Fig.3.24 shows HR-TEM observations of the curved CNTs. The inside of the nanostructure is regularly closed with compartment caps as indicated by an arrow in Fig.3.24.a. Their corresponding lattice fringes are curved and not well-oriented (Fig.3.24.b). These nanostructures are analogous to the CNTs usually obtained by the diffusion flame method [30, 31]. On the contrary, the straight morphology possesses a perfect hollow structure (Fig.3.25) within the well-known concentric shell model. The graphene layers are perfectly oriented along the nanotube axis. The number of graphene layers varies from 2 to 20. Fig.3.25 illustrates straight CNTs with 4 and 6 graphene layers, respectively. Sometimes small metal catalysts residues are observed in the core of CNTs (Fig.3.25.b).

The difference in the morphology of the CNT structures can be explained by the unusual temperature conditions in the flame. Temperature is known to play a decisive role in the level of graphitization and also in the growth mechanism of CNTs. The temperature maintained at the substrate surface varies from 900 to 1500°C, which is higher than what is frequently used in conventional CVD methods (800 - 900°C), but is much lower than that in the arc-discharge techniques (>3000°C). However, in the flame technique, the temperature can reach around 3000°C at a few tens of μm above the substrate surface [32].

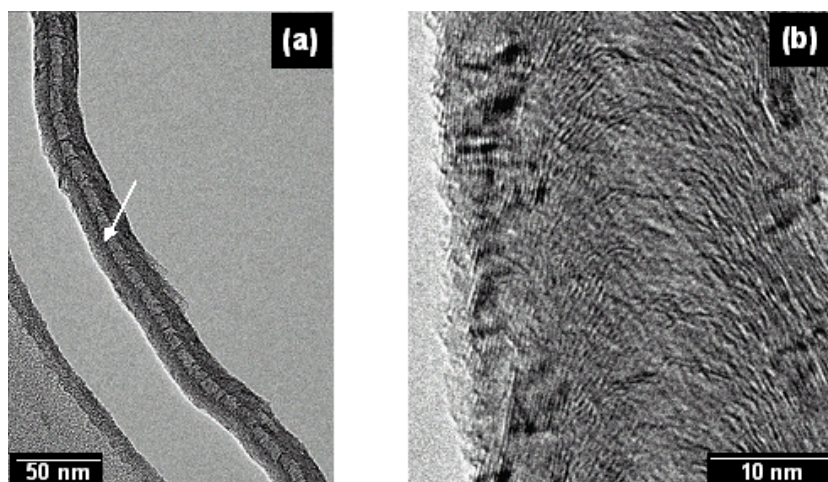


Figure 3.24: HR-TEM images of curved CNTs.

The highly oriented graphitic crystals (graphite polyhedral crystals and petal-like carbon) synthesized using this technique have already demonstrated that its products of synthesis can reach high levels of graphitization. At lower temperatures, the nanotubes grow following a sequence of dissolution of carbon inside the catalyst particles, super-saturation of carbon in the particles, and precipitation of carbon at the surface of the particle, thus forming conventional CVD nanotubes. At higher temperatures, when the melting point of Co and Ni is reached, the metal particles are evaporated in the flame, leading to catalytic growth mechanism. Although the latter is still a debated issue, the high temperature in the flame should be an important parameter to produce straight and well-oriented CNTs.

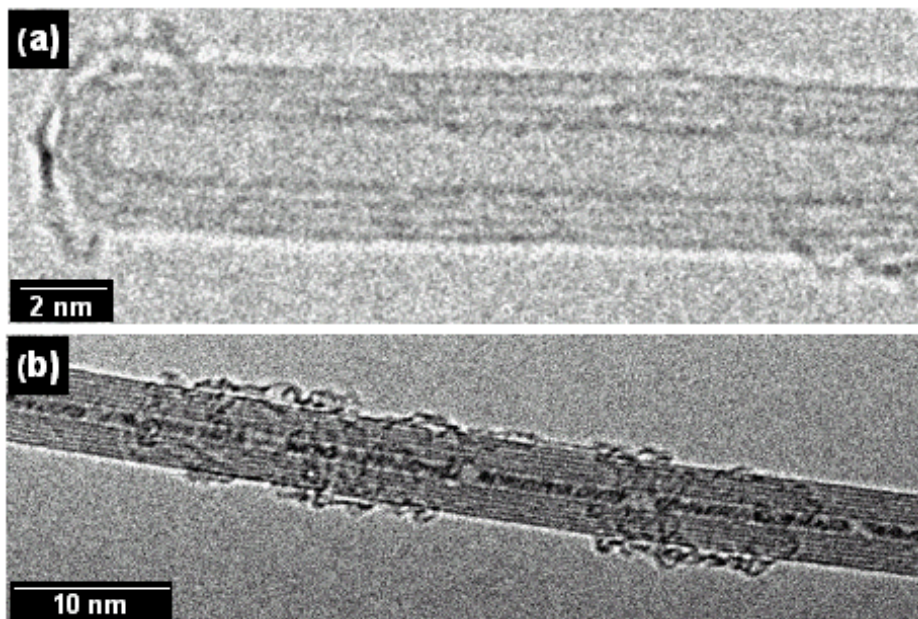


Figure 3.25: HR-TEM images of straight CNTs with (a) 4 and (b) 6 graphene layers.

3.7.2.4 Long time deposition

As described above, introduction of the electro-deposited Ni-Co catalytic layer in the combustion flame technique results in the formation of multi-wall carbon nanotubes (MWNTs) in the early stages of the deposition (5-10 sec.). After a deposition time of 1 minute, the polyhedral crystals are synthesized around these MWNTs (Fig.3.26.a). Several segments of crystal are grown simultaneously along the nanotube axis. Their selected-area diffraction pattern can be indexed by the graphite spacing as shown in Fig.3.26.b. This sharp symmetry profile exhibits isolated 100 and 101 spots, suggesting a highly-oriented graphitic structure. All these micro-crystals possess an empty core (Fig.3.26.c), which can be evidenced as the MWNT which plays the role of support for the deposition. HR-TEM image (Fig.3.26.d) displays the 002 fringes of a MWNT pre-deposited and the polyhedral crystal. No discontinuity is observed in the stacking of the graphitic layers of the two structures which is probably due to the good graphitization imposed by the heat treatment.

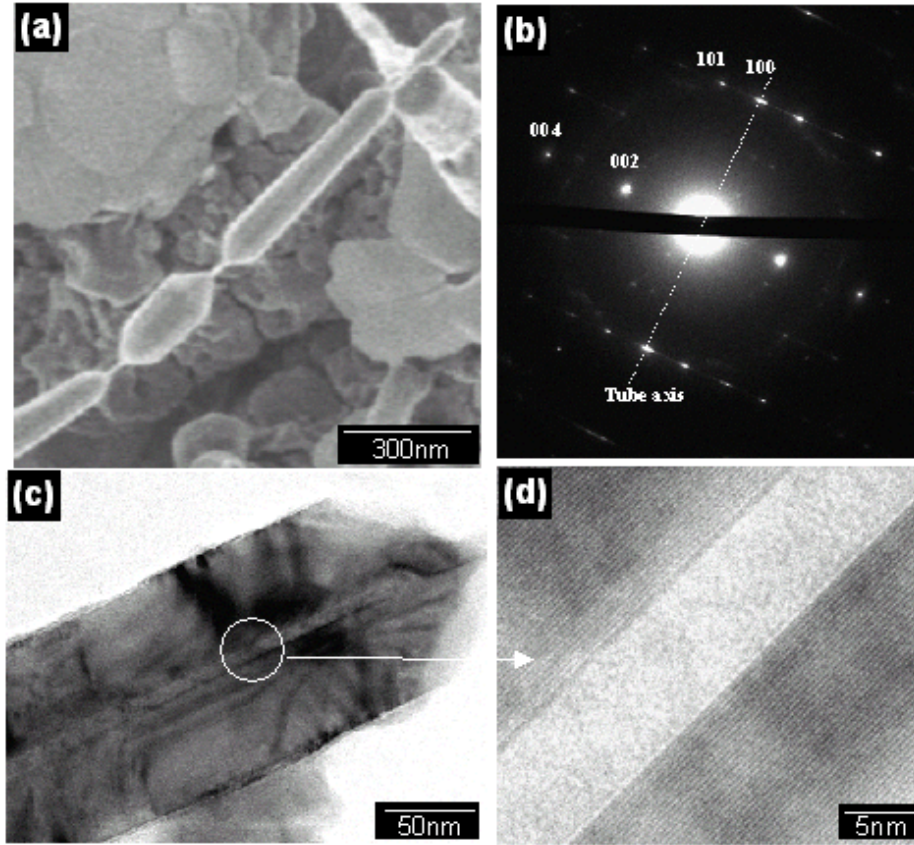


Figure 3.26: (a) SEM , (b) electron diffraction pattern, (c) TEM, and (d) HR-TEM images of a polyhedral crystal grown around a multi-wall nanotube.

3.7.3 Growth mechanisms of 1-directional graphite crystal

Two different mechanisms of the polyhedral crystal growth are observed with / without metal catalyst. Without catalyst, the polyhedral crystal growth starts directly from the substrate surface toward the flame source (Fig.3.27.a). When MWNTs are preformed using catalysts, the crystal growth does not start on the substrate surface, but directly around the MWNTs (Fig.3.27.b).

Fig.3.28.a illustrates a possible growth model for the rod-like structure without catalyst. At the early stages of the deposition, graphitic layers are formed on the substrate. The crystal growth may start from thermal fluc-

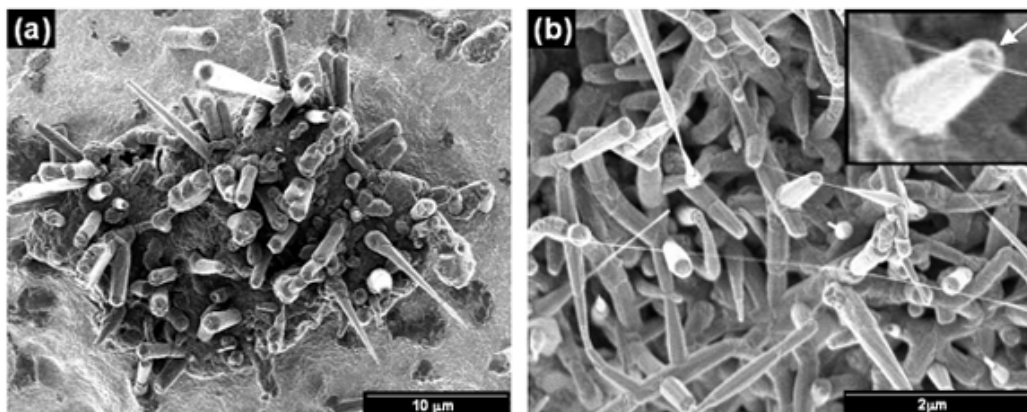


Figure 3.27: SEM image of the polyhedral crystal deposition around carbon nanotubes.

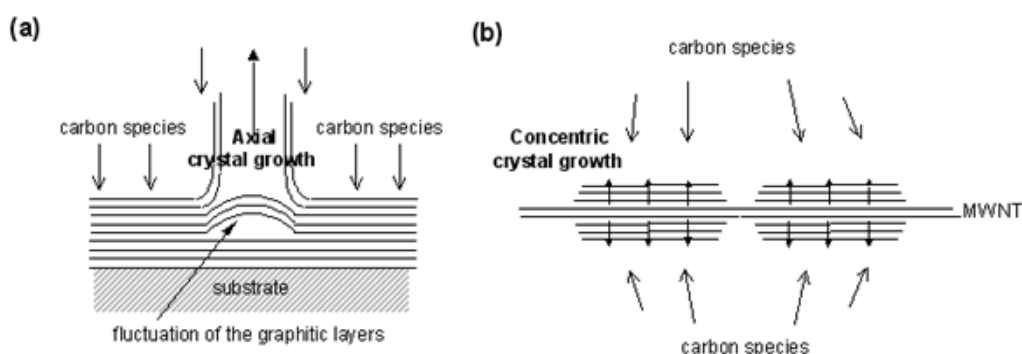


Figure 3.28: Growth models for a polyhedral crystal grown (a) on a substrate, and (b) on the surface of a multi-wall nanotube.

tuations that would appear on these graphitic layers, leading to topological anomalies (Fig.3.28.a). The presence of a high thermal gradient in the process could promote the crystal growth in the perpendicular direction toward the flame source. The difference of temperature between the substrate and the flame source reaches about 1500°C [33]. Although the substrate temperature is maintained around 1200°C , the growth temperature is assumed to be higher. No obvious differences in crystal diameters are observed for different deposition times, suggesting that this diameter is determined by the fluctuations in the graphitic layers. Only the length of the crystal varies with the deposition time, leading to an axial growth. In the solid state graphitization of pyrolytic carbon, crystallization starts in many places simultaneously to form randomly shaped and faceted particles consisting of inter-grown poly-

crystals [34]. As polyhedral crystals are progressively grown toward the flame at higher temperature, this technique might allow the synthesis of graphitic structures with crystalline perfection close to that of a single crystal. In the presence of catalyst, carbon nanotubes are formed at the early deposition stage. The nucleation appears simultaneously in several places due to the diffusion of the carbon species on the nanotube surface, and gives rise to several crystal segments (see Fig.3.28.b). In this case, the MWNT plays the role of the deposition substrate, and is thus the core of the graphitic crystal. Crystal cores, pre-deposited as carbon nanotubes, are often observed (see in-set of Fig.(Fig.3.27.b). For longer deposition times, the crystal diameter is found to increase, leading to a possible control of the concentric growth for potential applications. Although the growth mechanism could be either concentric or axial, the same crystalline perfection is observed in both cases, suggesting that the high temperature conditions of the present technique play a key role in the graphitization process.

3.7.4 Interests of 1-directional materials for applications

Both rod-like and pin-like micro-structures represent a novel group of low-dimensional graphite crystals with an interesting variety of shapes. These novel structures are expected to have at least the mechanical properties of graphite whiskers (Young modules of $\simeq 800$ Gpa, and strength of $\simeq 20$ Gpa²), and electronic properties similar to those of graphite. The polyhedral structure of the micro rods could also provide a higher rigidity compared with cylindrical micro fibers. When a MWNT is getting out of the structure, the micro-crystals could be used as probes for field emission sources. As their sizes are controlled by experimental conditions, growing larger and longer crystals could be challenging. Thus, this technique may provide a way to grow graphite single crystals to the size of a pencil, although preserving their crystalline perfection. If this can be carried out in practice, tailored microscopic carbon shapes can be produced with a degree of perfection never obtained before. In addition, this technique is quite efficient for local deposition, such as on the tip of STM probe. This might be an important application for these uni-directional carbon deposits.

3.8 Phase transition from graphite to diamond

Many authors have shown that diamond formation can occur directly from other carbon species by various techniques [35, 36, 37]. Computer calculations of transition between diamond and graphite have also been carried out [38, 39]. In this section, we present results where the diamond formation occurred directly on the surface of Gypsum flower-like carbon (GF) following a 'pre-orientation' of the graphitic walls composing the GF. This phenomenon has been firstly reported by J.F. Despres, H. Okuno *etal* [40]. In this work, a correlation between the phase transition and the morphology is argued. This phenomenon suddenly appears in the domain of GF formation on the diagram (Fig.3.2). Although mixed phases of diamond like carbon (DLC) and diamond and graphitic sp^2 species can easily be synthesized, it is rare to observe the co-existence of diamond and sp^2 bonded carbon during a continuous experiment. The understanding of this diamond formation directly from the sp^2 bonded carbon under non-equilibrium conditions can reveal new possibilities of phase transitions between sp^2 and sp^3 bonded carbons.

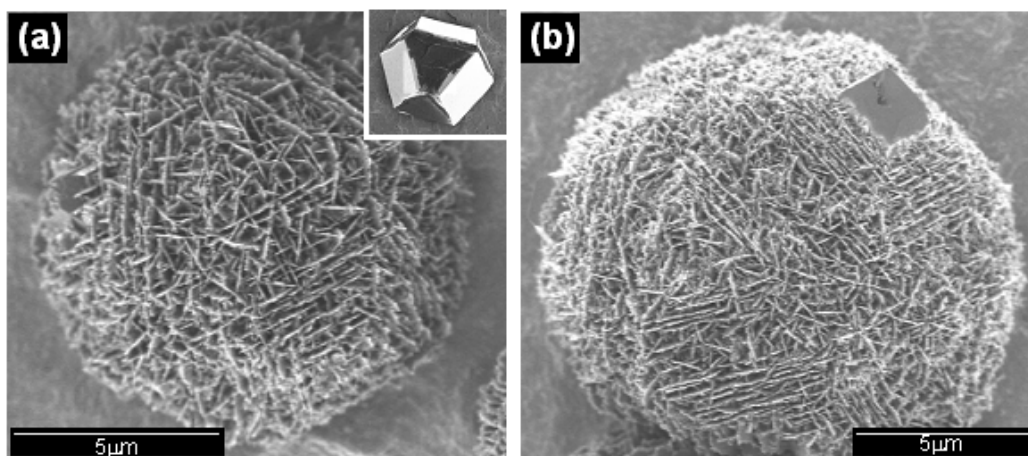


Figure 3.29: SEM photographs of (a) pre-orientation of graphitic walls and (b) appearance of diamond (100) crystals.

3.8.1 Diamond formation on the GF surface

Several types of GF have been obtained, depending on the experimental conditions as described in section 3.6.1. In the GF formation zone of diagram

(Fig.3.2), diamond crystals suddenly appear on the surface of the GF aggregates under specific conditions ($R=0.95$ to 0.98 and T_s is around 1200°C). The diamond crystals are normally synthesized at much lower temperatures (see Fig.3.2 and Chapter 2) and have been never observed directly on a substrate under this condition. Fig.3.29 shows the formation of diamond (100) crystals on the GF observed at a substrate temperature around 1200°C . When the diamond appears on the GF, a pre-orientation of the graphitic walls of the GF is also observed. At the conditions for this diamond formation, the graphitic walls have an anisotropic organization on the surface of GF. Fig.3.29.a shows a pre-orientation of the graphitic walls in which it is possible to recognize some preferred orientation creating square shapes on the surface. Fig.3.29.b demonstrates the diamond (100) crystals deposited on these squares. A GF aggregate organizes this self-orientation as if it is cubo-octahedral single crystal. The square and triangle shaped orientation appear on the position corresponding to (100) and (111) of cubo-octahedral crystal respectively (an inset in Fig.3.29 shows a diamond crystal oriented in cubo-octahedral by the flame method). In the products, mostly (100) diamond faces are produced, and rarely (111) faces. This preference is related to the high reaction temperature (explained in chapter 2). Diamond crystals are known to be sometimes etched by active species such as oxygen containing radicals during the deposition [41].

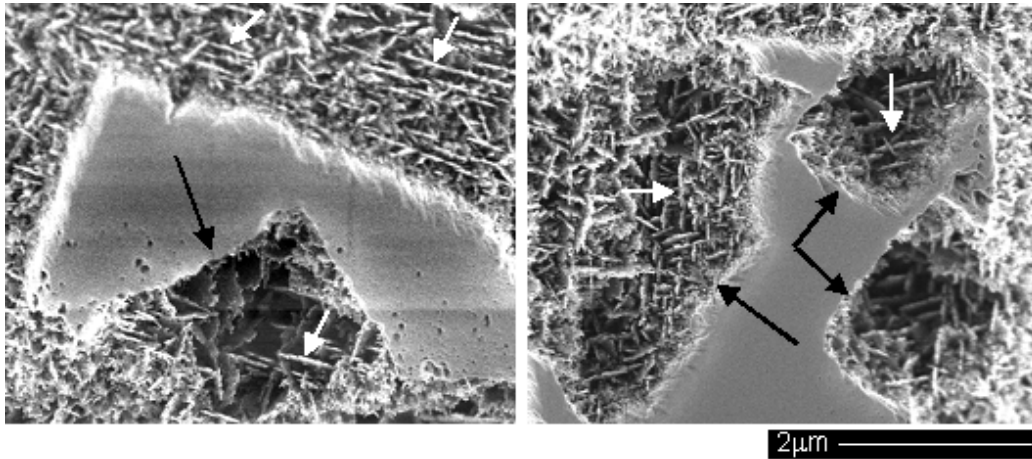


Figure 3.30: SEM photographs of the etched diamond (100) crystals.

Fig.3.30 shows etched diamond crystals (indicated by black arrows). The graphitic walls under diamond crystals are also oriented parallel to the square

shape of pre-orientation as indicated by white arrows.

3.8.2 TEM observations

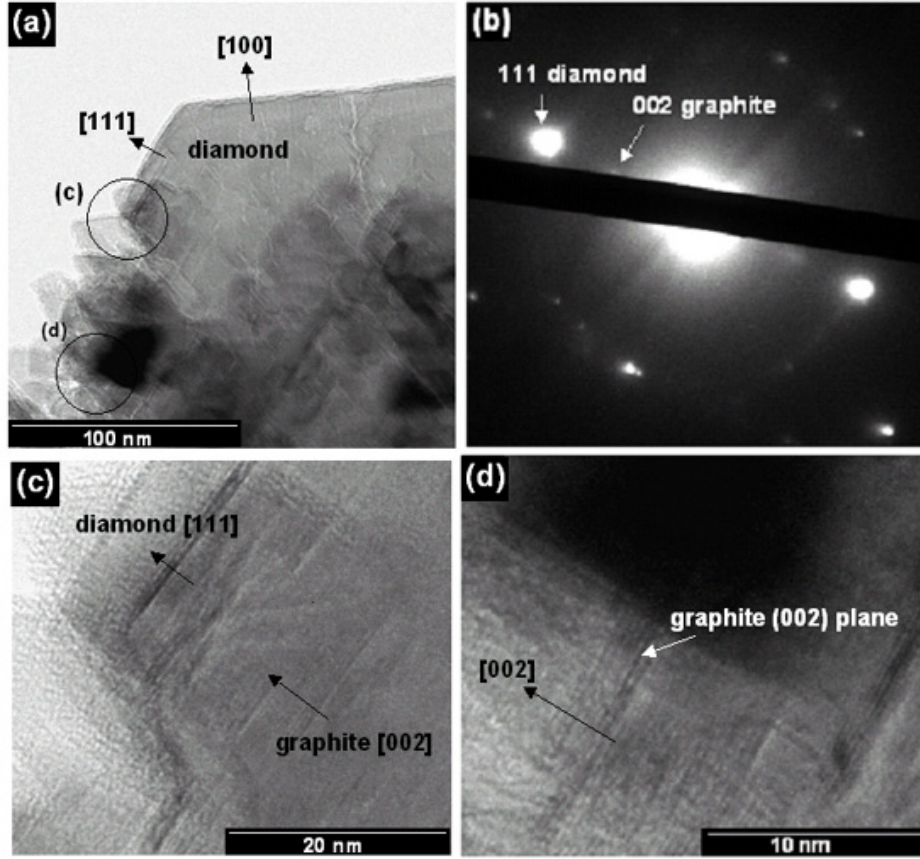


Figure 3.31: TEM images of (a) the diamond crystal deposited on GF, (b) nano-diffraction pattern and (c-d) high magnification images.

To understand the crystallographic correlation between diamond and graphite, TEM observations are carried out. The best way to observe the boundary between graphite and the diamond crystal deposited on it is to cut using the classical sample preparation techniques such as an ion beam. However, it is impossible to cut the samples keeping the boundary condition because of a large difference of hardness between the diamond and the graphite. To resolve this problem, the samples are deposited directly on a

tungsten tip which can be introduced directly in the microscope, which allows us to investigate the diamond formed on GF without scratching. Fig.3.31 shows TEM photographs of diamond, in which (100) and (111) faces can be recognized as indicated by arrows. Fig.3.31.c and d are high magnification images of two parts in Fig.3.31.a. In both images, graphitic sheets are observed with the orientation parallel to 111 diamond as shown in Fig.3.31.b. The diffraction pattern shows diamond 111 spots and graphite 002 spots on the same line, which also indicate that 111 diamond is formed parallel to 002 graphite of GF. These results confirm the observation of scratched small samples, previously reported by J.F. Despres and H. Okuno *etal.* [42].

3.8.3 Hypothesis for transition mechanisms

In this work, the possibility of obtaining some diamond crystals on the surface of GF is demonstrated. This diamond formation on GF can be considered as the direct phase transition from graphite to diamond during the growth under non-equilibrium conditions because of the epitaxial relationship between the diamond 111 and the graphite 002. These two planes are quite similar in structure and the 111 projection of the diamond bond length ($1.45\text{\AA}$) is only 2% larger than the corresponding distance of $1.42\text{\AA}$ in graphite. When graphite transforms into diamond, the a-axis of graphite (parallel to the basal plane) should expand by 31% (from 2.461 to $3.567\text{\AA}$) to become the lattice constant of an fcc diamond. The bending or corrugation of the hexagonal graphitic sheets should also take place to give the necessary carbon atoms forming an sp^3 hybridized bonding. Fig.3.32 demonstrates one of the transition models from graphite to diamond structure. In the literature, diamond nucleation has been reported to start epitaxially on the edge of graphite substrate [43, 44, 45], in which the transformation of structure takes place by hydrogenation of the graphite edge atoms [46, 47]. The presence of hydrogen can be supposed to contribute to the growing phase transition in our case too. As described above, the diamond obtained on GF is often etched on its surface, compared to the diamond synthesized directly on the substrate at lower temperature. It assumes that the hydrogen containing species are rich in the necessary conditions. Nevertheless, it is not enough to explain the sudden transition of growing phase.

The most commonly observed shape assumed by diamond crystals, synthesized by CVD techniques, is a cubo-octahedron, which is a shape bound by cubic (100) faces and octahedral (111) faces [46, 48], as described in the previ-

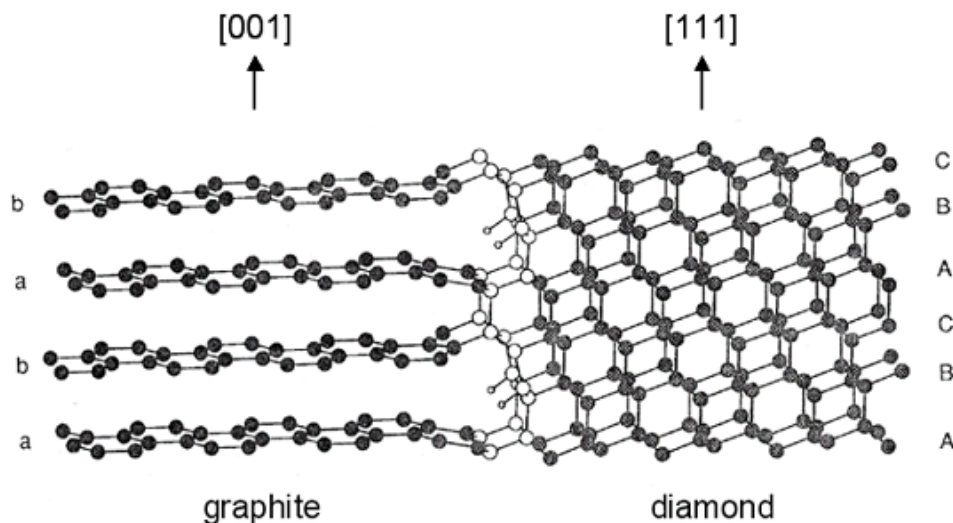


Figure 3.32: Schematic diagram showing the crystal structures of graphite and diamond [47].

ous chapter. Around the necessary conditions, the pre-orientation occurs on the GF surface following the cubo-octahedral orientation. The reason of the arrangement of graphitic walls from isotropic to anisotropic texture is not yet understood. However, this arrangement which organizes a cubo-octahedral morphology is certainly the most essential phenomenon for the transition to diamond. We can conclude that this phase transition follows the steps; 1) the anisotropic arrangement of graphitic walls allows the GF to orient with a cubo-octahedral shape, in which (002) graphite planes are already oriented in the direction of (111) of cubo-octahedral diamond crystal, 2) subsequently, the growing plane transforms from (002) graphite to (111) diamond during the growth by their epitaxial relationship and 3) (111) diamond continues to grow on the GF forming 'pseudo-cubo-octahedral crystal'.

3.9 Correlation between the produced materials

We demonstrated the synthesis of a large variety of carbon materials using oxy-acetylene combustion flame method. Although many research works have proposed various processes for the carbon materials synthesis, each tech-

nique is often specific only for a few materials. However, the oxy-acetylene flame technique is successfully applied to produce several kinds of carbon materials. In this work, the diamond and the graphitic based materials are mainly obtained and the carbon nanotubes are also synthesized in a catalytic way. As described in chapter 1, the graphitic based carbons are multiscale materials. The correlations between the carbon materials produced using this technique is summarized in this section. Structures of carbon at atomic scale corresponds to the hybridization of carbon atoms, resulting in different allotropes such as diamond and graphite. The two routes to obtain the diamond are investigated.

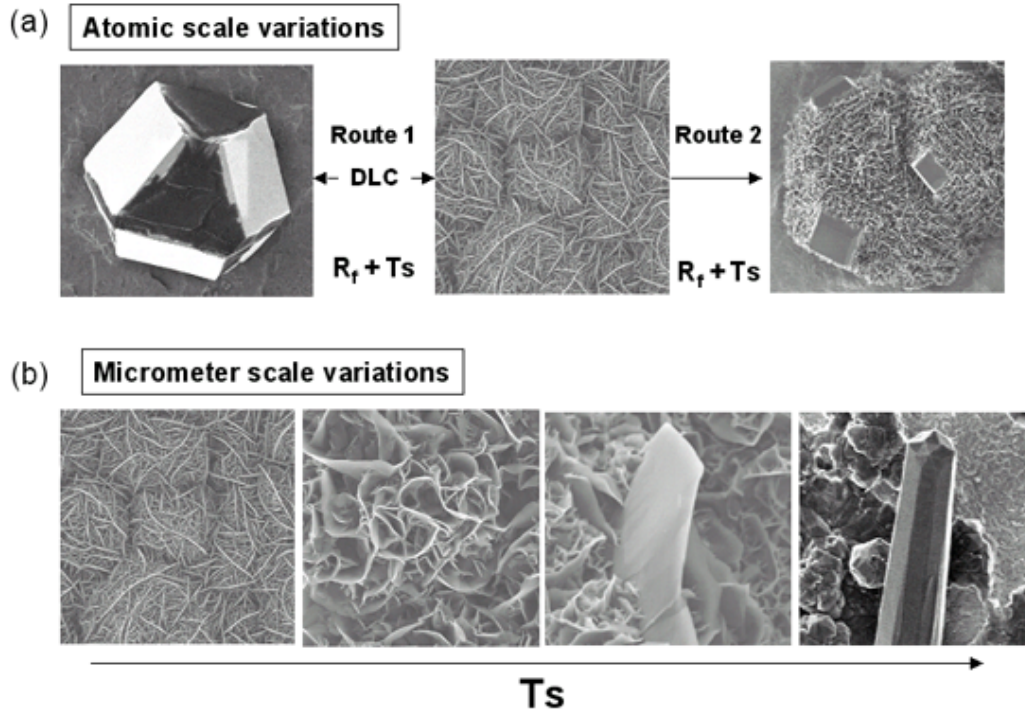


Figure 3.33: Schematic illustration of the structure modification of carbon materials synthesized by the oxy-acetylene technique, at (a) atomic scale and (b) micrometer scale.

Fig.3.33.a displays the variation of the carbon forms at atomic scale, where arrows indicate the position in the diagram established in section 3.4. Normally, the domains of experimental condition for the diamond and graphite synthesis in the diagram are clearly divided by the presence of diamond-like carbon (DLC), a mixed phase of sp^2 and sp^3 (see in chap-

ter 2). When we vary the experimental condition, the proportion of sp^2 and sp^3 in the DLC changes, resulting in the diamond or graphite under each extreme condition (indicated as Route 1). In this work, an appearance of diamond directly on the sp^2 carbon without any intermediate phase is also observed (indicated as Route 2). The former is attributed to the chemistry evolved in the flame with generated active radicals. On the contrary, in order to understand the latter process, the hydrodynamic in the flame should be studied since the diamond formation suddenly appears by way of an unusual arrangement of graphitic walls of the Gypsum flower-like carbon. A nanometer scale ordering of carbon materials determines the molecular forms of carbon resulted from an assembly of fundamental structural units (USBs) and graphene sheets, which results in the different carbons such as fullerene, nanotubes, graphitite, etc. For the graphite-based materials, the crystal quality indicated as the degree of the ordering of USBs are differed one from others at nanometer scale. Although the Gypsum flower-like carbon and petal-like carbon represent aggregates with the same morphology, they display a structural difference at nanometer scale with different orders of crystallinity, as demonstrated with Raman spectroscopy in section 3.6.3. Experimentally, this difference arises from the substrate temperature and the proportion of carbon in the input gas.

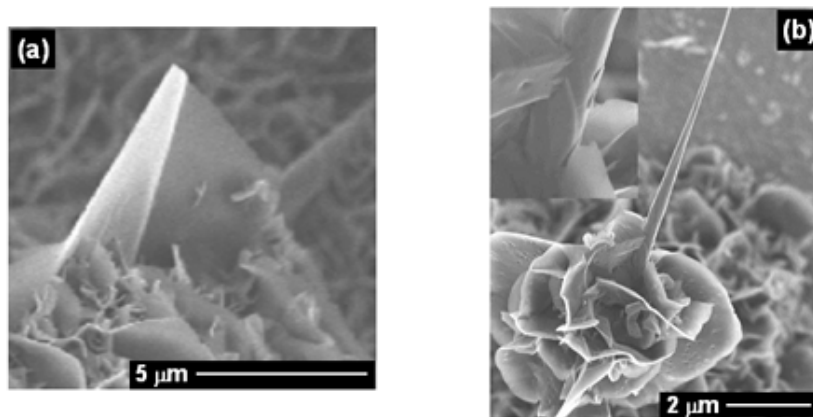


Figure 3.34: SEM photographs of (a) an individual petal-like crystal starting to roll up and (b) a polyhedral crystal grown from petal-like sheets.

A difference at micrometer scale is emerged as the morphology of graphitic materials. For example, the both petal-like crystal and the polyhedral crystal consist in an almost perfect graphite structure. They exhibit the same

structure by nanoscopic analysis such as Raman spectroscopy. However, their morphologies are completely different. Fig.3.33.b illustrates the variation of carbon forms at micrometer scale, where the substrate temperature is strongly responsible for this transformation. We observed several forms of carbon and those are classified with their preferred orientation (see in Chapter 1). The round shapes of the Gypsum flower-like carbon and the petal-like carbon are explained to be due to point orientation. The grown large petal-like crystal is formed with planar orientation. The polyhedral crystal is due to axial orientation with radial arrangement. With increasing the substrate temperature, the variation of carbon morphology is observed with following steps: 1) the growth of the round shaped aggregates passes into that of individual planar graphite crystals and then 2) the preferred orientation of the graphite crystal growth changes from planar one to axial one, where the intermediate structure is also investigated. Fig.3.34 demonstrates the carbon forms synthesized under the experimental condition boundary between for two structures. The individually grown petal-like crystal starts to roll up (Fig.3.34.a and an inset of Fig.3.34.b) and the growth of petal-like crystal transform its preferred orientation to axial one, resulting in the formation of polyhedral crystal (Fig.3.34.b). These transformations of preferred orientation during the growth occur by a slight change of the substrate temperature. Though the mechanism to determine the preferred orientation during the growth, it will be important to accurately analyze the process in order to understand the hydrodynamic contributing to it.

3.10 Conclusion

In this chapter, the formation of several kinds of carbon materials is demonstrated using the oxy-acetylene combustion flame method. In addition to diamond, as reported by many authors, a variety of graphite-based materials are successfully synthesized. Gypsum-flower like carbon (GF) and petal-like carbon are aggregates composed of graphitic walls. The structural ordering of the walls increases from GF to petal-like carbon. This ordering is maximum for large petal wall grown up to a few tens of microns, which crystalline quality corresponds to that of single crystal graphite. A new type of uni-directional graphite crystal, polyhedral crystal, is demonstrated to grow without any catalyst. It has a perfect cylindric morphology and its quality sometimes reaches almost that of defect-free high quality graphite. Carbon

nanotubes (CNTs) could be obtained by introducing metal catalysts. The formation of CNT can be applied to control the synthesis of the polyhedral graphite crystals since polyhedral crystals are grown selectively around the pre-deposited CNTs.

The oxy-acetylene combustion flame method is thus a promising technique to obtain almost all kinds of carbon-based materials. Although the combustion flame technique varies from conventional CVD processes, where carbon structures grow with the help of a catalytic particle [49], the deposition of carbon under the extreme conditions of the oxy-acetylene torch is found to generate interesting structures with unusual morphologies. It is probably not surprising that carbon, with its ability to exist in so many allotropic forms, produces a large set of crystalline structures not observed for other materials.

This technique is not yet applicable to large yield synthesis but is quite efficient for local deposition, such as on the tip of STM probe. This might be an important application especially for the uni-directional carbon deposits such as the polyhedral crystal and the CNTs. Preliminary exploration of this field is described in Appendix A.

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Chapter 4

Synthesis and characterization of a carbon nitride phase

4.1 Introduction

Carbon nitride is a new material expected to exhibit remarkable physical properties such as high hardness, wide band gap and high thermal conductivity. As a consequence, intensive experimental and theoretical works have been carried out in order to synthesize and characterize new carbon nitride phases. In 1985, Cohen *et al.* [1] developed a theory based on the calculation of bulk moduli in tetrahedral solids, and investigated for the first time a hypothetical β -C₃N₄ compound. As a result, in 1989 Liu and Cohen suggested that its bulk modulus and hardness may be comparable to that of diamond, due to the expected short bond length and low ionicity [2]. In 1990, they presented a pseudo-potential study of the structural and electronic properties of the β -C₃N₄, compared to β -Si₃N₄ whose properties are well-known [3]. The good agreement between the calculations and the experimental data for the β -Si₃N₄ compound validates the calculations for β -C₃N₄. Contrary to the successful theoretical works, a great difficulty is still lying in the experimental synthesis of super hard materials, β -C₃N₄. Despite much effort, only a great deal of amorphous carbon nitride phase formations have been reported. This difficulty may be because of its structure involving two chemical components: sp³-bonded carbon and sp²-bonded nitrogen. With further theoretical work, the other C₃N₄ phases were proposed [4, 5]. As one of C₃N₄ forms, graphitic form of C₃N₄ (*g*-C₃N₄) also attracted the attention of many groups for an

application to organic semiconductors and its possibility to be an effective precursor of hypothetical super hard β -C₃N₄. Consequently, syntheses and related experimental data have been reported on g-C₃N₄ [6, 7, 8, 9]. However, the synthesized phases often contain a large portion of oxygen and the experimentally observed data exhibit frequently some mismatches with the calculated ones from the hypothetical structure.

In this work, a crystalline planar form of C₃N₄ samples is synthesized using the oxy-acetylene combustion technique and a synthetic precursor, 1,3,5-triazine-2,4,6-triamine (melamine). These samples of C₃N₄ are characterized using various experimental techniques.

4.2 Predicted structures of C₃N₄

4.2.1 β -C₃N₄

The hexagonal beta phase (β -C₃N₄) is similar to the β -Si₃N₄ structure, with C substituting Si as illustrated in Fig.4.1. This structure contains 14 atoms per unit cell and consists in four-fold coordinated carbon and three-fold coordinated nitrogen atoms. The structure proposed by Liu *et al.* has P6₃/m symmetry and appears as a three dimensional chicken wire with six-, eight- and 12-fold rings of alternating C and N sites [5]. The structural parameters of the β -C₃N₄ phase estimated by different authors are listed in Table 4.1.

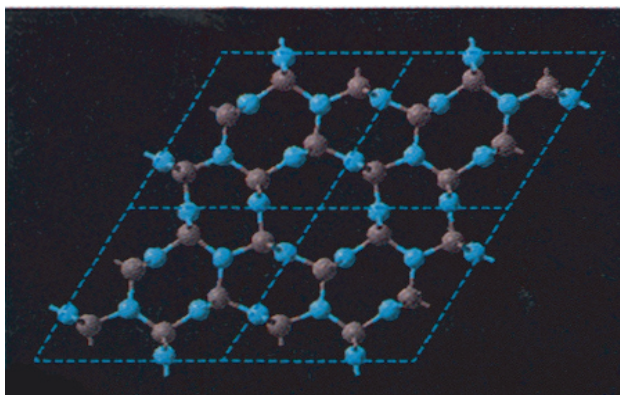


Figure 4.1: Representation of β -C₃N₄ structure down the [001] axis. The carbon and nitrogen atoms are depicted as gray and blue spheres, respectively [4].

Space group	Lattice constant a (Å)	Lattice constant c (Å)	c/a
P63/m (Hexagonal)	^a 6.44	2.46	0.382
	^b 6.41	2.40	0.375
	^c 6.47	2.45	0.379
	^d 6.37	2.40	0.377
	^e 6.38	2.47	0.387
	^f 6.44	2.89	0.370
P3 (Trigonal)	^g 6.40	2.40	0.376
	^h 6.35	2.46	0.387

Table 4.1: Crystallographic data for the β - C_3N_4 phase. These structural parameters have been extracted from the following references: ^a [3], ^b [5], ^c [10], ^d [11], ^e [12], ^f [13], ^g [4], ^h [12].

4.2.2 α - C_3N_4

The alpha phase (α - C_3N_4) possesses a hexagonal symmetry and contains 28 atoms per unit cell ($P3_1c$ space group) as illustrated in Fig.4.2. Such structure can be viewed as a sequence of A and B layers in an ABAB stacking in which A is the α - C_3N_4 unit cell and B is the mirror image of A. The structural parameters of the α - C_3N_4 phase estimated by different authors are listed in Table.4.2.

Space group	Lattice constant a (Å)	Lattice constant c (Å)	c/a
P3 ₁ c (Trigonal)	^a 6.47	4.71	0.728
	^b 6.35	4.64	0.731
	^b 6.59	4.71	0.715

Table 4.2: Crystallographic data for the α - C_3N_4 phase extracted from the references.

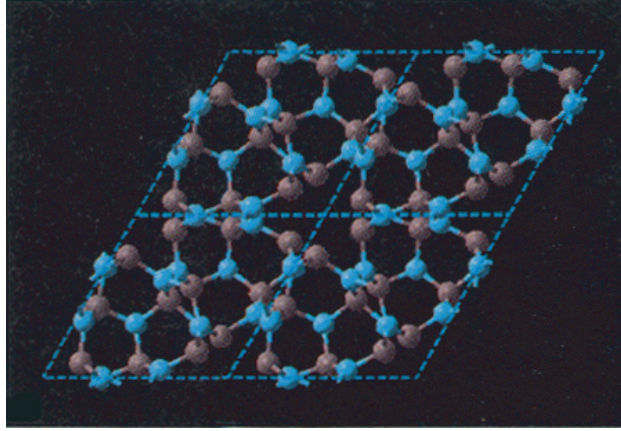


Figure 4.2: Crystal structure of α - C_3N_4 down the $[001]$ axis.

4.2.3 Cubic- C_3N_4 and Pseudo-cubic- C_3N_4

The cubic structure (*cubic*- C_3N_4) is based on the high-pressure willemite-II structure of Zn_2SiO_2 , where C substitutes Zn and Si, and N substitutes O. This phase contains 28-atoms per unit cell and belongs to the $\bar{1}\bar{4}3m$ space group. The pseudo-cubic structure, usually called defect-zinc blend structure (*bl*- C_3N_4), exhibits $P\bar{4}2m$ symmetry and contains 7-atoms per unit cell. The crystal structures of the *cubic*- C_3N_4 and *bl*- C_3N_4 are illustrated in Fig.4.3. The estimated structural parameters are listed in Table 4.3.

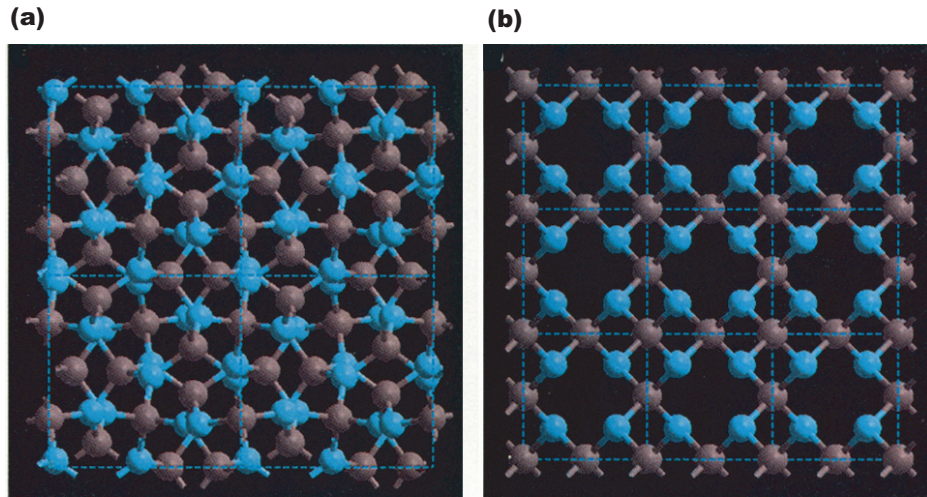


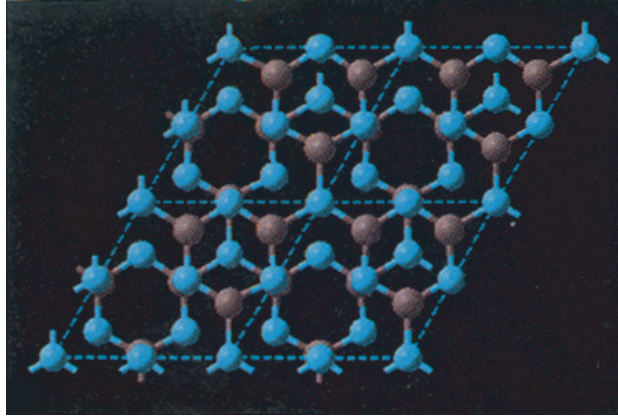
Figure 4.3: Crystal structures of (a) *bl*- C_3N_4 and (b) *cubic*- C_3N_4 .

	Space group	Lattice constant a (Å)
<i>Cubic</i> - C_3N_4 (Cubic)	$I\bar{4}3m$	^a 5.40
	$I\bar{4}3d$	^b 5.40
<i>BI</i> - C_3N_4 (Cubic)	$P\bar{4}2m$	^a 3.42
	$P\bar{4}3m$	^c 3.43 ^b 3.44

Table 4.3: Crystallographic data for the *cubic*- C_3N_4 phase extracted from the references.

4.2.4 Graphitic- C_3N_4

The graphitic form of C_3N_4 (*g*- C_3N_4) is represented by a planar structure mainly within an ABAB stacking. Several possible forms have been proposed in the literature. Teter *et al.* proposed a unit cell containing 14 atoms and consisting in graphite-like sheets with the symmetry $P\bar{6}m2$ (Fig.4.4) [4]. Each C atom is three-fold coordinated, as is one of the four N atoms per cell. The other three N atoms are two-fold coordinated. Another model has recently been suggested by Alves *et al.* [14]. They present a crystal structure ($P2mm$ space group) with an orthorhombic unit cell.

Figure 4.4: Representation of *graphite*- C_3N_4 structure (Teter's model) [4].

For this model, a different vacancy ordering has been displayed inside each of the graphitic planes with respect to the hexagonal system introduced by Teter et al (Fig.4.20) [4]. A structure with ABC stacking mode, containing 7 atoms per unit cell with rhombohedral stacking order (R3m space group) is also proposed [5]. The structural parameters of the g -C₃N₄ phase estimated by different authors are listed in Table 4.4.

Layer stacking	Space group	Lattice constant a (Å)	Lattice constant c (Å)	c/a
ABAB	P $\bar{6}$ m2 (Hexagonal)	^a 4.74	6.72	1.417
ABCABC	R3m (Trigonal)	^b 4.74	9.19	1.940
ABAB	P2mm (Orthorhombic)	^c 4.1	6.40	1.561

Table 4.4: Crystallographic data for the g -C₃N₄ phase extracted from the references.

4.3 Predicted properties for the C₃N₄ phases

In this section, we will review the relative stability, electronics and mechanical properties of the various C₃N₄ phases.

4.3.1 Relative stability of various C₃N₄ phases

According to pseudo-potential plane-wave calculations, Teter *et al.* [4] suggested, the g -C₃N₄ with ABAB stacking phase to be the most stable form; the α -C₃N₄ lying only marginally higher in energy by 0.041 eV. The energy of the β -C₃N₄ has been found to be 0.266 eV above the α phase. The cubic and pseudo-cubic phases are estimated to have much higher total energies. The simple cubic phases and the β phases lie at 1.015 eV and 1.178 eV, respectively. In summary, these abinitio results indicate that both the α and β phases are more stable than the cubic phases. In addition, the graphitic phase is the most stable of all with the smallest energy density. The influence of the pressure on the relative stability of the various phases has also been studied. The zero-pressure *cubic*-C₃N₄ structure is higher in energy

than both α and β phases, but becomes energetically more favorable as the volume decreases. Teter *et al.* [4] predicted that the transition pressure from α to cubic phase is approximately 68 GPa. The predicted transition pressure from graphitic to cubic structure is approximately 12 GPa, which can be easily obtained using large volume presses.

4.3.2 Electronic properties

Within the framework of the local density approximation (LDA) of the density-functional theory (DFT), theoretical values of the band-gap for β - C_3N_4 were proposed by many authors. These estimated values are ranging from 3.0 to 4.0 eV (direct and indirect) [3, 4, 10, 15]. However, the DFT is known to suffer from the band gap problem as such a theory always underestimates its value. Using a more rigorous calculation based on the GW approximation, Corkill and Cohen [16] suggested for the β - C_3N_4 phase a direct band gap of 6.75 eV.

4.3.3 Mechanical properties

Using both a semi-empirical scaling relationship and pseudo-potential total energy calculations, it has been predicted that the metastable tetrahedral phase of carbon nitride, β - C_3N_4 , have bulk moduli close to that of diamond [2]. The semi-empirical model expresses the bulk modulus (B in GPa) as $B = N_c / 4 \{ (1971 - 220I) / d^{3.5} \}$, where N_c is coordination number, d is the bond length (in Å), and I is a measure of the ionicity of the compound. The form of the equation exhibits a strong dependence on the bond length and a weak dependence on the degree of ionicity. Consequently, for diamond, assuming $I=0$, $N_c=4$ and $d=1.54\text{Å}$, the expression gives $B=435$ GPa, which is in good agreement with the experimental value: 443 GPa. Similarly, predictions for *cubic*-BN reveal a bulk modulus exactly the same as the experimental value of 369 GPa. For β - Si_3N_4 , a predicted value of 230 GPa compares well with the experimental value of 250 GPa. Based on a crystal structure of β - C_3N_4 , with a coordination number $N_c=3.43$ and a bond length $d=1.43\text{Å}$, the bulk modulus of this compound is calculated to be 414 GPa, while pseudo-potential total energy calculations predict a bulk modulus of 427 GPa [3]. It should be noted that most of the values of bulk modulus proposed in the literature are found between 421 and 451 GPa. Only the value proposed by Guo *et al.* [12] (250 GPa) is inferior to this range probably due to their structural

prediction. They explain that the N in β -C₃N₄ strongly prefers to be non planar whereas the N in β -Si₃N₄ strongly prefers to be planar. This remark is also applicable to α -C₃N₄ (B=189 GPa). Guo *et al.* reported also interesting results about the property of α -C₃N₄. According to their prediction, this structure has negative Poisson ratio because of the non-planarity of the nitrogens incorporated as spheroidal cavities into a tetrahedral lattice. The value of the bulk modulus, proposed by Teter *et al.* for cubic-C₃N₄, is the largest of all the other systems: 496 GPa [4] (10 % superior to that of diamond). This calculation has been confirmed by Martin-Gil *et al.*, where the proposed value is 480 GPa [17]. For g-C₃N₄, the bulk modulus is estimated at 51 GPa [5]. Because of its layer structure, g-C₃N₄ is not in the hard material group and its compressibility is quite high.

4.4 Previous experimental results

Previous attempts to synthesize C₃N₄ have used various techniques such as ion implantation [18], RF sputtering of carbon targets in a nitrogen atmosphere [19], bias-assisted hot filament chemical vapor deposition of various hydrocarbons [20], DC magnetron sputtering of a graphite target in a nitrogen ambient [21], shock wave compression of carbon nitride precursors [22], plasma-enhanced chemical vapor deposition [23], ion-assisted dynamic mixing [24] and laser abrasion of a carbon target in a stream of atomic nitrogen [25]. Although several attempts have tried to synthesize β -C₃N₄ for its predicted super hard properties, the experimental results point out the formation of amorphous carbon films containing various amounts of nitrogen. However, Niu *et al.* obtained microcrystalline β -C₃N₄ [25]. This phase was identified by comparing the electron diffraction powder patterns with the Bragg angles predicted by Liu and Cohen [2]. On the other hand, graphitic-C₃N₄ (g-C₃N₄) has recently attracted much attention for their potential use as organic semiconductors and the precursors of β -C₃N₄ [4, 7]. The graphitic carbon nitride phases prepared experimentally from various molecular precursors have been reported. Komatsu *et al.* reported melamine-based quasi-carbon nitride by de-ammonation of melamine [7] and by polycondensation and pyrolysis of tri-s-triazine [8]. Montigaud *et al.* prepared graphite-like carbon nitride with C/N ratio higher than that of C₃N₄ by pyrolysis of melamine under pressure [6].

4.5 Synthesis of a carbon nitride phase

The aim of this section is to report on the synthesis of a carbon nitride phase by means of polycondensation of an organic molecule using an oxy-acetylene torch to attain a g - C_3N_4 phase.

4.5.1 Choice of the starting material

Over the past few years, 1,3,5-triazine ring motif (C_3N_3) (Fig.4.5.a) has played a key role in molecular routes to carbon nitride. The hypothetical g - C_3N_4 structures are derived from an assembly of triazines linked by nitrogen atoms with creation of carbon vacancies (Fig.4.5.c and d). In this work, the 1,3,5-triazine-2,4,6-triamine (melamine) (Fig.4.5.b) is chosen as the synthetic precursor for the carbon nitride synthesis.

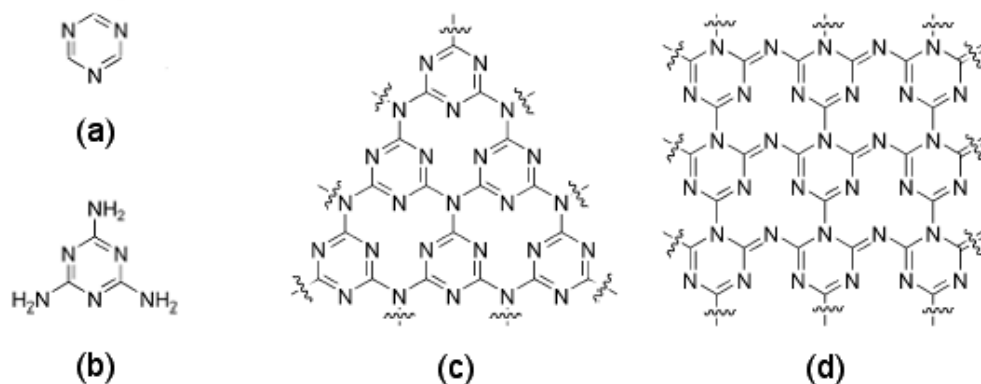


Figure 4.5: Structure models of (a) 1,3,5-triazine, (b) 1,3,5-triazine-2,4,6-triamine (melamine), (c) g - C_3N_4 Teter's model [4] and (d) Alves's model [14].

4.5.2 Experimental set up

Fig.4.6 displays the experimental set up for the carbon nitride synthesis. Melamine is used as a synthetic precursor, compressed inside the graphite cell. The reaction cell is fabricated within a graphite rod of 3 cm in diameter to prevent the sample from chemical contaminations. The cell can be closed by a graphite cap by a screw system. The graphite cell is placed

on a water-cooled copper sample holder and heated on the top of the cell using an oxy-acetylene torch. Since the oxy-acetylene flame is used to heat the graphite cell, results are independent on the mixed gas composition but clearly depend on the flame temperature. The deposition time is varied from 30 seconds to 1 min. After the reaction, the samples are removed from the cell and characterized.

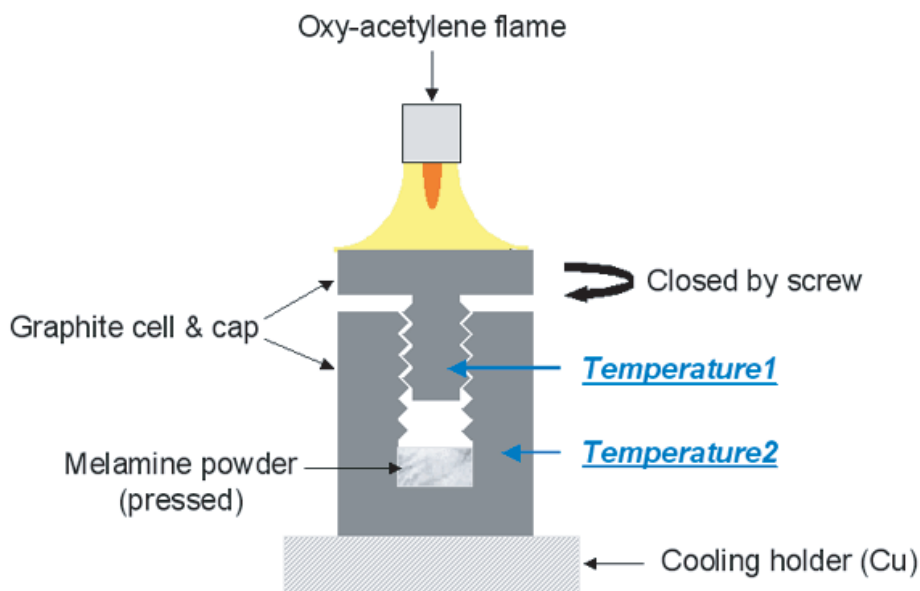


Figure 4.6: Schematic experimental set up for the carbon nitride synthesis.

Field-mission scanning electron microscopy (SEM) is used to observe their morphology. X-ray photoelectron spectroscopy (XPS), Electron dispersive X-ray (EDX) and Electron energy loss spectroscopy (EELS) are applied for chemical analysis. Transmission electron microscopy (TEM) at high resolution (HR-TEM), electron diffraction and X-ray diffraction are used for structural analysis. The samples are also characterized using Raman spectroscopy and infra-red spectroscopy.

4.6 Experimental results

The temperature of the graphite cell has been measured with thermo-couples and infra-red pyrometer. A large difference of the temperature is observed

between the cap and the cell. The temperature of cap (indicated as 'Temperature 1' in Fig.4.6) and the temperature of the cell (indicated as 'Temperature 2' in Fig.4.6) are estimated to be around 1500°C and 800°C, respectively. From these two temperatures, a strong thermal gradient is generated inside the empty space of the cell where the precursor (melamine powder) has been placed. Since the graphite cell is not completely sealed, white smoke goes out of the cell at the beginning of the experiment. This smoke probably consists in sublimated melamine. Although the sublimation point of melamine is around 500°C, a residue is observed after the experiments. A Yellow deposit remains on the bottom of the graphite cell, assuming that a phase transition occurred during this thermal treatment. To accurately characterize the synthesized phase, elemental and structural analyses are carried out.

4.6.1 SEM observations

The morphologies of the produced samples are investigated using a LEO982 Scanning Electron Microscope. The yellow deposit is found at the bottom of graphite cell and is scratched to be collected for the analyses. The deposit consists of several hard blocks. Crystalline parts are recognisable on the surface of the collected block by the electron microscopy. Although a variety of crystallinities is observed, it can be classified into two kinds of crystal morphologies; finger-like and hexagonal structures. Fig.4.7.a and b show finger-like crystals. The finger-like crystals are 2 to 3 μm wide and about 10 μm in length. All these crystals are oriented in the same direction, which should be due to their crystal growth direction. Since a strong thermal gradient is generated in the graphite cell, the crystal growth can be assumed to occur in the direction of thermal gradient. Fig.4.7.c shows hexagonal-based crystals. These crystals are found to organize into some aggregates and there is no relation between the crystals orientation. As illustrated in Fig.4.7.d, the core of these crystals are often amorphized.

The crystalline deposits are often mixed with amorphous phases, consequently it is difficult to determine the crystalline composition.

4.6.2 Chemical analysis

Although many groups reported in the literature carbon/nitrogen-based materials synthesized by a large variety of processes, the products frequently contain other chemical elements such as silicon and oxygen. In this section,

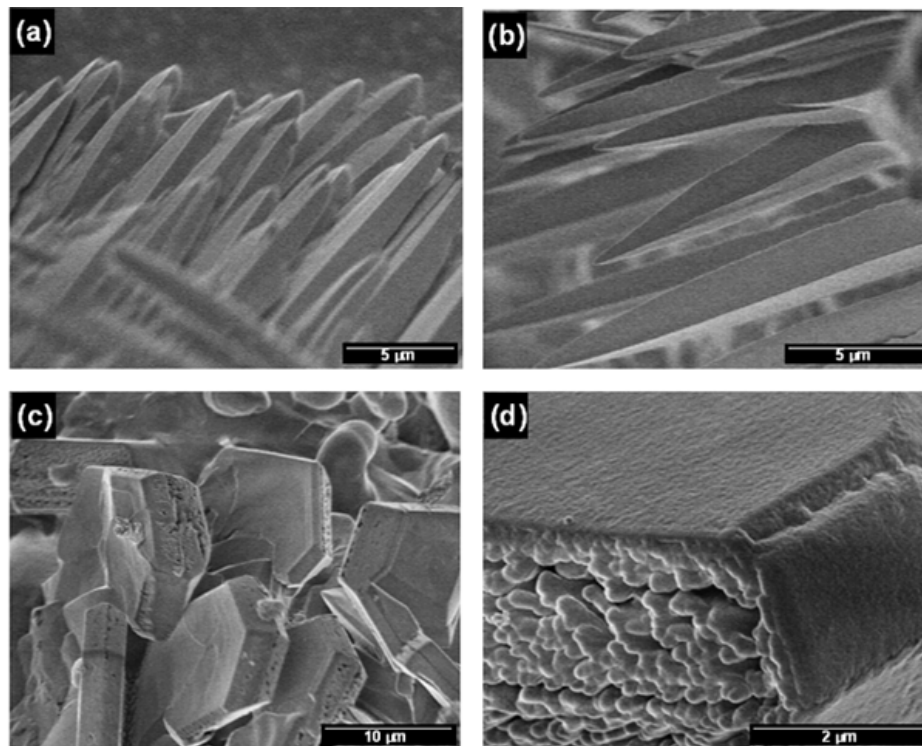


Figure 4.7: SEM images of (a-b) finger-like crystals, (c) hexagonal-based crystals and (d) amorphized hexagonal crystal.

elemental analyses using Electron dispersive x-ray (EDX), X-ray photoelectron (XPS) and Electron energy loss spectroscopies (EELS) are accurately carried out to be sure that our material consists of carbon and nitrogen only. At the same time, elemental quantifications are also performed.

4.6.2.1 Electron dispersive X-ray analysis (EDX)

Electron dispersive X-ray (EDX) analysis is performed using a Scanning electron microscope (LEO982). The samples are focused in different magnifications to choose the analyzing areas ($1 \times 1 \mu\text{m}^2$, $100 \times 100 \text{nm}^2$ etc.). The analysis is carried out for a wide energy range to check the existence of all possible elements. Only carbon and nitrogen peaks and a quite small oxygen peak are observed. Fig.4.8 is a typical EDX spectrum of the carbon nitride produced using our technique. Since the oxygen content is estimated to be only a few percent by the quantification, we assume that it has been detected on the

sample surface. The quantification takes into account the sensitivity of each element and indicates the average atomic concentrations of C and N to be 42 and 58 % respectively. The N/C ratio is found to be 1.38 which is close to the stoichiometry of C_3N_4 (1.33). Other measurements on different samples indicate analogous values for the N/C ratio in the range of 1.30 to 1.65.

The stoichiometry of the pure melamine demonstrates the N/C ratio to be 2 from its chemical structure. The EDX analysis of the pure melamine is also performed to compare the experimentally measured value to its real stoichiometry. The melamine powder is not quite stable under the electron beam. The N/C ratio decreases during the acquisition, being due to the degradation by the electron beam. However, the pure melamine always exhibits a N/C ratio larger than that of our samples. This presents a change of stoichiometry of sample from before to after the experiments.

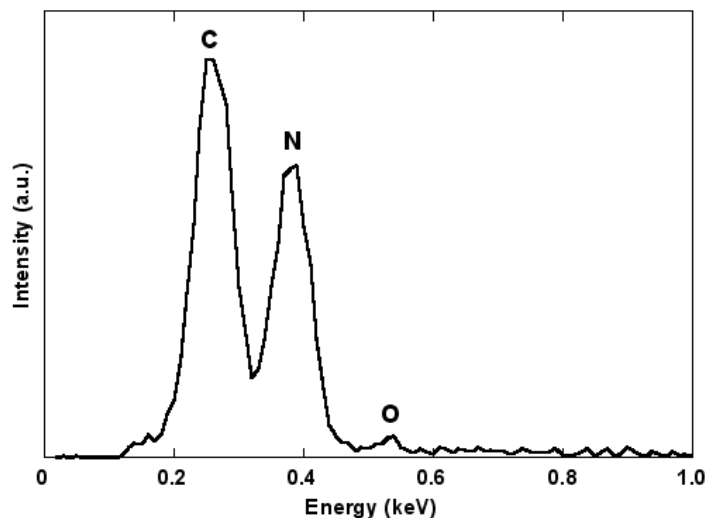


Figure 4.8: Electron dispersive X-ray analysis of our sample.

4.6.2.2 X-ray photoelectron spectroscopy (XPS)

The wide scan XPS is performed on a zone of $100 \mu m^2$ of the bulk sample. The XPS spectrum indicates the presence of carbon, nitrogen and small amounts of oxygen in the sample, in agreement with the results of EDX analysis described above. Fig.4.9 presents a typical XPS spectrum for our sample and for pure melamine. The concentration of oxygen is about 4 %,

probably due to surface contamination so that almost the same quantity of oxygen is detected also in melamine. The quantification of carbon and nitrogen indicates the atomic concentrations of C and N to be 46 and 49 % respectively, so the N/C ratio is 1.05. Since carbon is detected by XPS not only from samples but also from environment of the chamber, the obtained value should be corrected. The chemical equation of melamine is $C_3N_6H_6$ and the N/C ratio is 2.00. The N/C ratio obtained by the XPS quantification is about 1.40 instead of 2.00. About 30 to 40 % excess of carbon is detected from the environment. Such a value indicates the real N/C ratio of the products to be about 1.30 to 1.40, in agreement with the EDX results. Accurate quantification will be described in following section by peak separation for each bonding. By these analyses, an important point is that the products consists only of carbon and nitrogen.

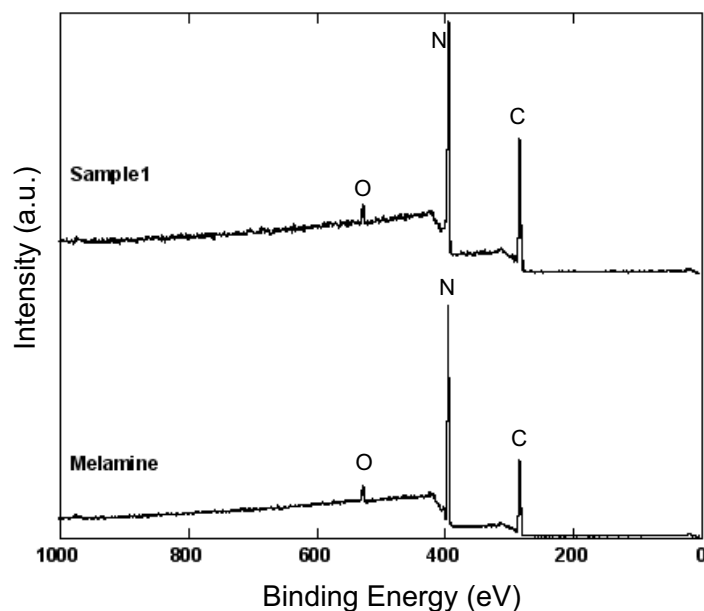


Figure 4.9: X-ray photoelectron spectrum of our C_3N_4 sample.

4.6.2.3 Electron energy loss spectroscopy (EELS) - chemical mapping

In order to analyze the elemental distribution of the products, chemical mappings using electron energy loss spectroscopy (EELS) are performed using a

transmission electron microscope (LEO922). The samples are powdered and prepared on a TEM grid. The crystallinity of the particles is confirmed by electron diffraction pattern and analyzed by parallel EELS (PEELS). The sample is frequently observed as a mixture of crystalline and amorphous particles. The proportion of crystalline to amorphous part varies from samples to samples. Fig.4.10 displays a typical PEELS spectrum, which presents carbon and nitrogen peaks. Although a small oxygen peak is also detected, its quite small intensity agrees with both EDX and XPS results. From this spectrum, a chemical mapping is carried out using slits to chose the corresponding energy band.

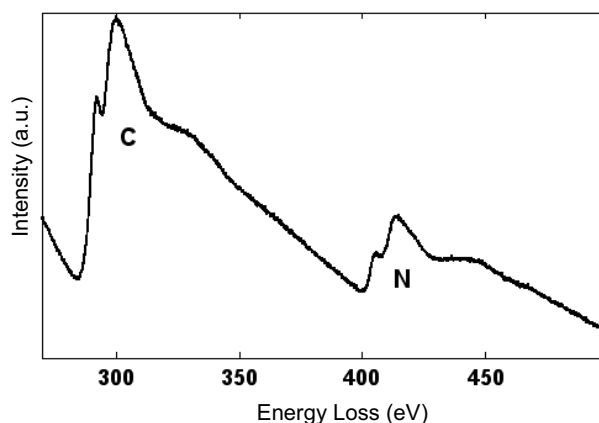


Figure 4.10: EELS spectrum at the carbon and nitrogen K edges.

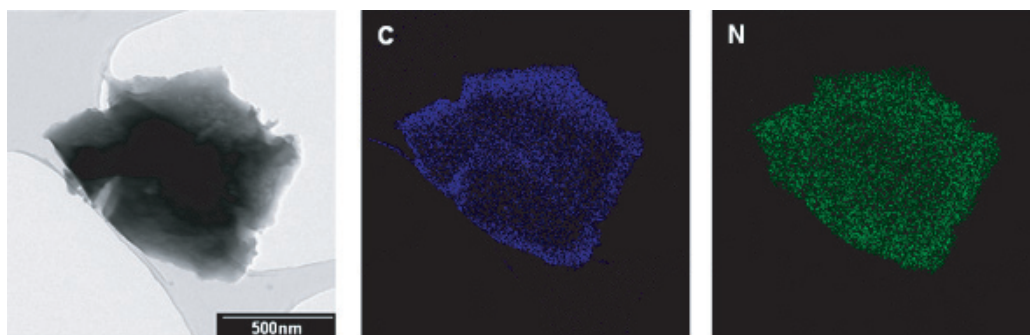


Figure 4.11: EELS chemical mappings for carbon and nitrogen.

Fig.4.11 presents a TEM image and the corresponding chemical elementary mapping for carbon and nitrogen. Both carbon and nitrogen are de-

tected on the particle. Nitrogen is homogeneously mixed in a particle, which is an evidence that they have some structural relation. Even the particles which do not exhibit any electron diffraction (amorphized phase) display a homogeneous nitrogen content.

4.6.3 Structural analysis

From chemical analysis, the product is demonstrated to consist only in carbon and nitrogen. In the following, structural analyses will be carried out to identify the exact phase structure. In this section, XPS, HR-TEM, PEELS, electron diffraction and X-ray diffraction are used to characterize the C_3N_4 sample.

4.6.3.1 X-ray photoelectron spectroscopy (XPS)

Fig.4.12.a and b display typical N and C 1s XPS spectra of our sample as well as that of the pure melamine, respectively. The data are presented after inelastic background subtraction and using Gaussian fits. From a comparison of binding energies of the pure melamine, an obvious phase transition is observed after the experiments.

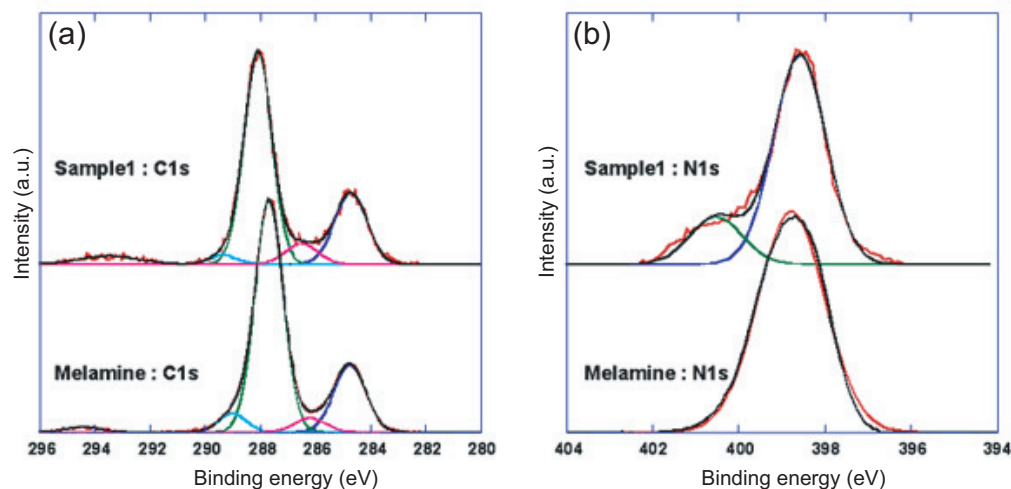


Figure 4.12: A comparison of X-ray photoelectron spectra between our sample and melamine: (a) C(1s) peaks and (b) N(1s) peaks.

The C 1s peak can be accordingly deconvoluted into four peaks, at 284.7,

286.3, 287.9 and 289.5 eV. The N 1s spectrum appears to consist of two main peaks at 398.8 and 400.2 eV. The C peak at $E_b=284.7$ eV is identified to the C-C bond and originates not from the sample but from adventitious carbon. It is confirmed by the melamine peak, displaying the same peak, despite the absence of C-C bonds in the structure. The peak at 289.5 eV is identified as originating from CO type bonds, in good agreement with the presence of oxygen at the surface of the sample (see the section 1.6.2.2.). These two peaks are incidental and are excluded from further consideration [26]. The remaining two peaks at 285.9 and 287.9 reflect two different C-N bonding states. These correspond to two C-N bonds in N 1s spectrum at 400.2 and 398.8 eV, respectively [26]. In agreement with most authors, the peak at 400.2 eV should be assigned to N in substitutional graphite site as shown in Fig.4.13.b, while the other peak at 298.8 eV corresponds either N in C-N=C pyridine-like bonding [27, 28] as illustrated in Fig.4.13.a.

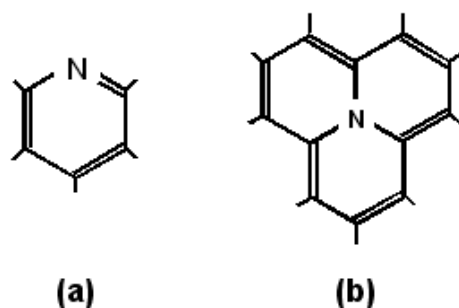


Figure 4.13: Schematics of the different nitrogen bonding environment (a) pyridine-like N and (b) nitrogen in substitution in a graphitic network.

By comparison with XPS spectrum of melamine, the peak at 400.2 eV in our sample clearly indicates the presence of substitutional nitrogen atoms. New quantification demonstrates that the proportions of pyridine-like and substitutional nitrogen atoms are 20-25 % and 75-80 % respectively.

4.6.3.2 High Resolution-Transmission electron microscopy (HR-TEM)

HR-TEM bright field imaging revealed that the material possesses a layered structure with some fraction of nanocrystallites, as shown in Fig.4.14. Although these particles are confirmed to be crystalline by electron diffraction, they are degraded toward amorphous by the electron beam during the

analysis. After about 10 min of imaging, only a series of diffraction of layer structure remains (see an inset of Fig.4.14). The distance between the lattice planes measured by the image and the diffraction pattern is $\simeq 3.40$ nm.

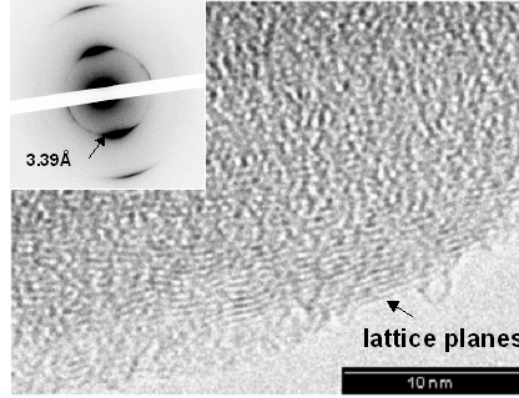


Figure 4.14: High resolution-TEM image of our sample.

4.6.3.3 Parallel EELS

EELS spectra collected from one of the particle areas is presented in Fig.4.15, showing energy loss regions corresponding to carbon and nitrogen K-edges.

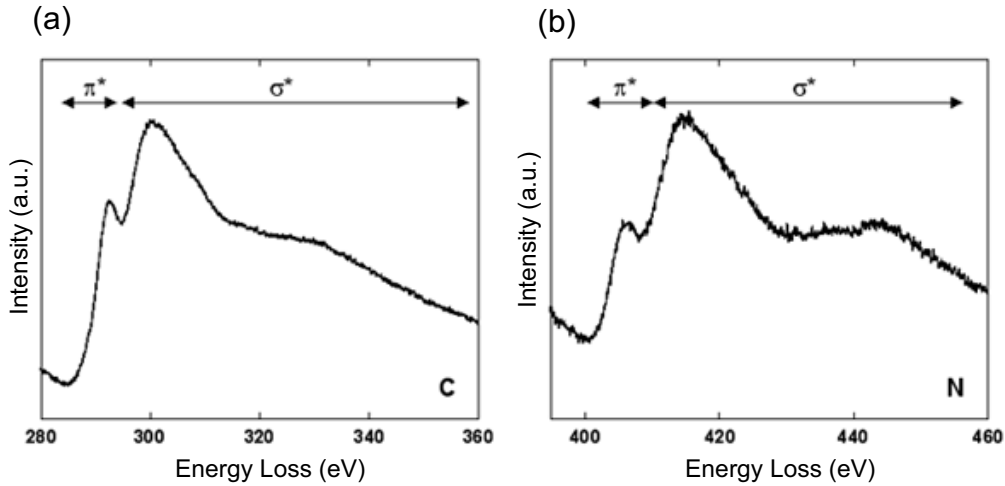


Figure 4.15: EELS spectra of our C_3N_4 sample at the (a)carbon K edge and the (b)nitrogen K edge.

Note that a little oxygen peak is sometimes observed at around 530 eV but quite small in intensity compared to carbon and nitrogen peaks. The main features observed in the Carbon K-edge are one peak at 287 eV due to transitions from the orbital 1s to π^* states and a broad band centered at 302 eV due to the transitions from 1s to σ^* states (Fig.4.15.a). Nitrogen K-edge also presents the same aspect, composed of one peak at 408 eV due to the transition of 1s to π^* and a broad band centered at 418 eV due to the transition of 1s to σ^* (Fig.4.15.b). The participation of nitrogen in the π bonds is accompanied by the shift of the π^* resonance toward higher energy loss (287 eV instead of 285 eV) [29]. Therefore, the π^* peak in the carbon K-edge is assumed to be ascribed to trigonal sp^2 -hybridized C bonded to N.

4.6.3.4 Infra-red spectroscopy

Fig.4.16 presents the IR spectrum of our C_3N_4 sample. For comparison, the spectrum of melamine is also shown in Fig.4.16. The spectrum of melamine exhibits several strong bands near 3000 cm^{-1} , a series of strong bands in the $1400\text{-}1660\text{ cm}^{-1}$ and another peak centered 810 cm^{-1} . The bands near 3000 cm^{-1} are consistent with modes involving N-H stretching vibrations. The bands observed in the $1400\text{-}1650\text{ cm}^{-1}$ region are typical for molecules that contain CN heterocycles and are generally associated with the skeletal stretching vibrations of these aromatic rings [30, 31]. The absorption at 810 cm^{-1} is characteristic of out-of-plane bending modes of the rings [6, 30]. By comparison with the IR spectrum of melamine, the peak at 810 cm^{-1} in our sample can be attributed to an out-of-plane bending modes of CN heterocycles, the peak observed at 1630 cm^{-1} corresponds to the C=N in aromatic ring. In addition to the peaks concerning to the melamine, a band in the $1250\text{-}1330\text{ cm}^{-1}$ appears in our sample. This band corresponds to the C-N bond. The results of IR indicate the existence of CN aromatic ring and the presence of the C-N peak can be attributed to the appearance of substitutional nitrogen in the graphitic hexagonal network (N-3C). This result supports the hypothetic structure of the melamine-based carbon nitride introduced by Teter *et al.* [4], formed by a perfect deammonation polycondensate of melamine. The lack of absorption band at 2200 cm^{-1} indicates that our sample does not contain the nitrile groups with a CN triple bonding, which is the characteristic feature of amorphous carbon nitride films. The broad absorption band at 3100 cm^{-1} is mainly due to the O-H stretching mode of adsorbed H_2O while only a marginal contribution originates from

N-H bonds compared to melamine.

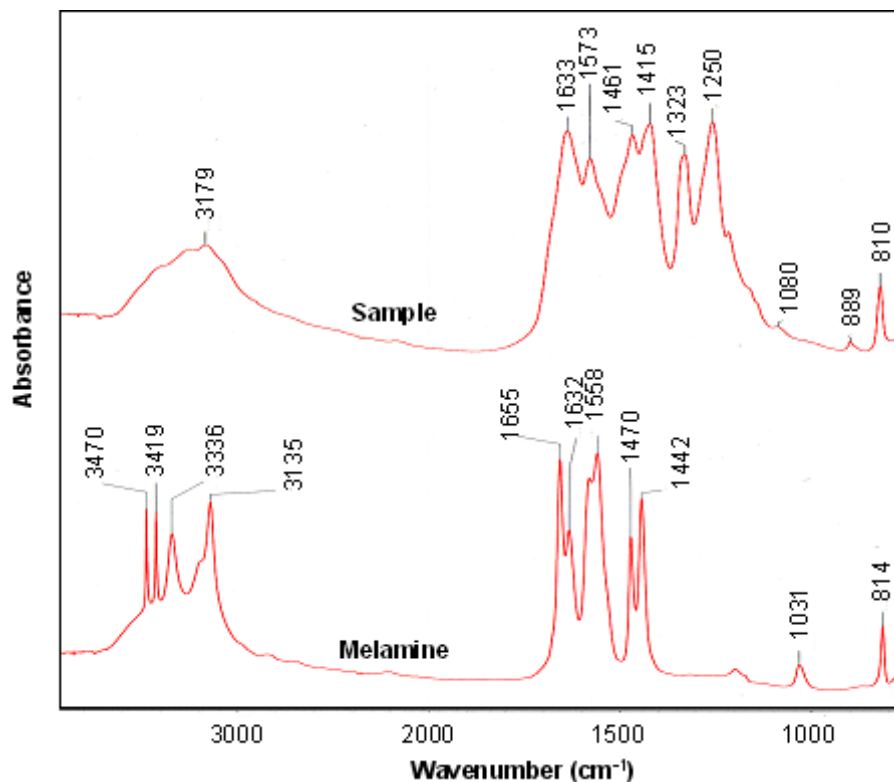


Figure 4.16: IR spectrum of our C_3N_4 sample, compared to that of melamine.

4.6.3.5 X-ray diffraction

Fig. 4.17 demonstrates the powder XRD pattern of our sample. The scattering data is acquired on a Siemens D5000 diffractometer in Bragg-Brentano geometry. In addition to a strong peak corresponding to a lattice distance $d = 3.2$ Å, peaks are observed for 8.04, 7.28, 6.75, 4.87, 4.08, 2.02 and 1.61 Å. By comparison with the peaks of melamine, several peaks are characteristic of the sample. From HR-TEM observation, the products can be assumed to form a layered structure. The strong peak, indicating $d = 3.2$ Å, can probably be indexed for the distance of these inter-layers. Although the inter-layer distance is estimated to be 3.4 Å by HR-TEM image, it is probably due to an expanding of inter-layer distance because of the amorphization of the sample produced by the electron beam irradiation during TEM observation. The

indexation of this XRD pattern will be analyzed and described compared to structure models in the following section.

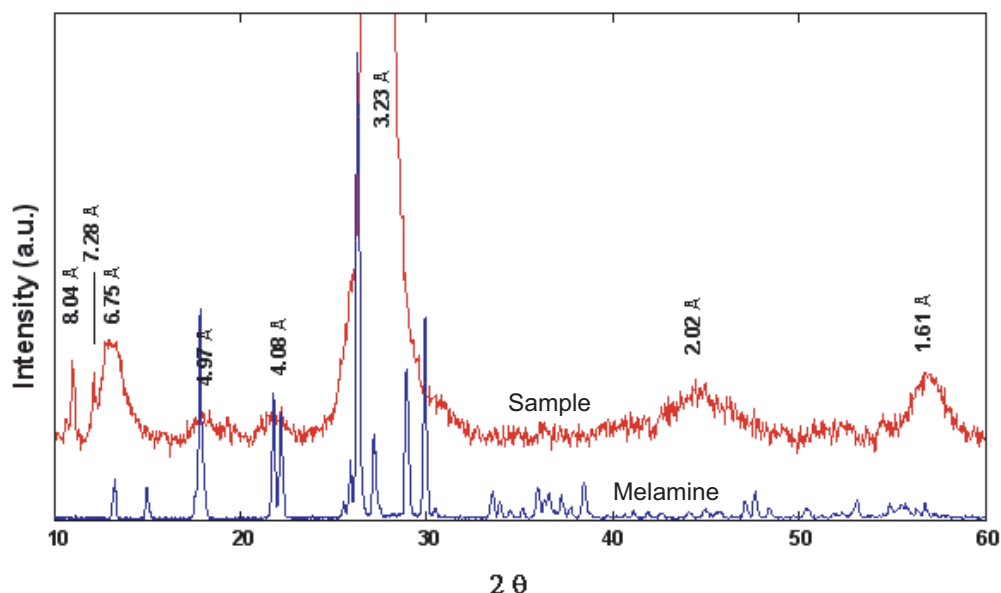


Figure 4.17: X-ray diffraction of our C₃N₄ sample, compared to that of melamine.

4.6.3.6 Electron diffraction

During TEM experiments, the sample easily amorphized under the electronic beam. Such instability does not allow a complete analysis of the crystal structure by electron diffraction. However, some typical diffraction patterns have been frequently observed for various samples (as illustrated in Fig.4.18). The electron diffraction pattern exhibits a hexagonal symmetry, and reveals relatively large values for lattice distances. Unfortunately, the corresponding zone axis orientation has not been determined because the diffraction pattern disappeared during the tilting process, again due to the instability of the sample under the beam.

4.6.3.7 Raman spectroscopy

Raman spectroscopy analysis is also carried out on our sample. The spectrum was taken by the laser beam with the excitation wavelength of 1064 nm. For

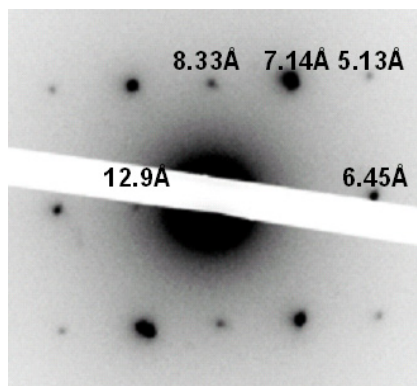


Figure 4.18: Typical electron diffraction pattern of our sample.

all kind of morphology and crystallinity of the samples, the same frequencies are observed.

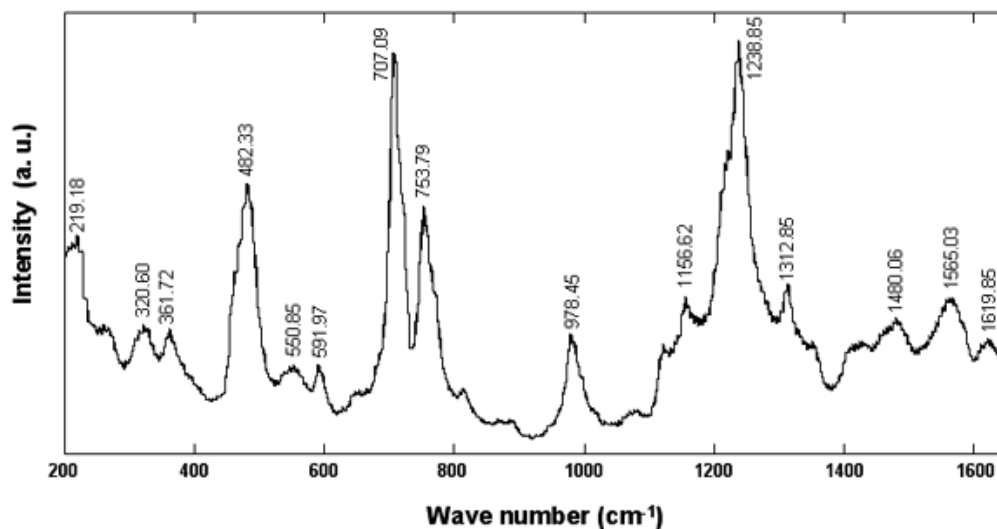


Figure 4.19: Raman spectrum of produced sample.

Fig.4.19 displays the typical Raman spectrum of our C_3N_4 samples. Many sharp lines are observed, characteristic of crystals. It consists of five prominent bands at 219, 482, 700-750, 978 and 1100-1320 cm^{-1} and some other small peaks. The pure melamine is also examined by Raman spectroscopy to compare with the spectrum of our sample. However, it was impossible to obtain the Raman spectrum of melamine because the melamine fluoresces

strongly under the laser beam and it completely saturates the signal. Previously, the Raman frequencies of *g*-C₃N₄ calculated from the hypothetical structure have been reported [32]. No peak is found to correspond to this result.

4.7 Discussion

In previous works reported on the carbon nitride synthesis, the products frequently contain other elements such as silicon and oxygen. Elemental analysis is quite important to confirm the production of a pure carbon/nitrogen compound. EDX, XPS and EELS results demonstrate that our sample is a pure carbon/nitrogen compound without any other elements. Although a few percent of oxygen is detected, it can be considered as a surface contaminant because the same amount of oxygen is also detected from melamine which does not contain oxygen. This result is quite important because in the other previous works carbon nitride phases have been frequently synthesized with a large amount of oxygen. The elemental chemical mapping displays homogeneous distribution of carbon and nitrogen, which is a necessary condition to confirm the formation of carbon nitride. The quantification by EDX and XPS suggests approximate proportion of nitrogen to carbon; N/C is in the range of 1.3 to 1.4. This value corresponds to that of C₃N₄ where N/C = 1.33.

A nitrogen atom incorporated into an amorphous carbon network could have different bonding environments up to three neighbors. Especially single neighbored nitrogen atom with triple bond should be observed only in amorphous phase, not in crystalline C₃N₄ phase. Both IR and XPS spectra of our sample do not exhibit obvious CN triple bond, which indicates a quite low level of amorphous content. Melamine is expected to be the most suitable precursor for manufacturing graphitic-C₃N₄ by its deammonation/polycondensation. Since HR-TEM images indicate the formation of layered structures, the sample obtained in this work is suggested to be a kind of graphitic C₃N₄. The basic graphitic-C₃N₄ structure can be considered as graphene sheets with the substitution of one of two carbon neighboring atoms by a nitrogen atom and the creation of carbon vacancy. The XPS results of our sample indicate the presence of the substitutional nitrogen atoms. The quantification by XPS suggests 25 % of substitutional nitrogen atoms and 75 % of nitrogen in pyridine-like bondings. This result is

in good agreement with the stoichiometry of typical graphite like C_3N_4 layer (see Fig. 4.20).

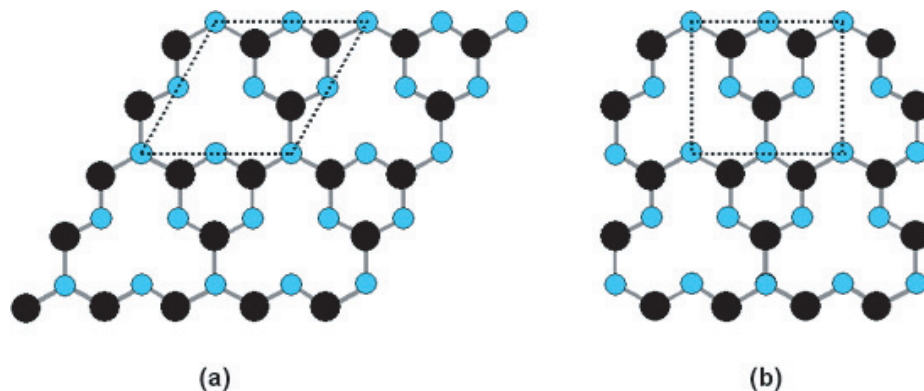


Figure 4.20: Structural models of graphitic C_3N_4 (a) Teter's model [4] and (b) Alves's model [14].

Different models for ordering the carbon vacancy inside the graphitic plane have been previously proposed. Fig.4.20.a and b illustrate Teter's model the $P\bar{6}m2$ space group and Alves's model $P2mm$ space group, respectively. Since both structures have the same stoichiometry, X-ray diffractions are needed to understand the crystallographic structure.

Table 4.5 lists the observed d -spacing of the X-ray diffraction peaks in our sample, compared to the calculated values of Teter's [4] and Alves's [14] models. The d -values of several reflections are in good agreement with those calculated for g - C_3N_4 . However, some of our peaks are not indexed for these structures, especially for higher d values such as 8.04 and 7.28 Å. The width of these two peaks is found to be relatively smaller than other peaks, suggesting the presence of another crystal structure. The electron diffraction pattern also exhibits a crystal structure with large lattice parameter. This fact may be caused by a formation of another network organized with a sequence of the classical models at larger scale. The appearance of (001) reflection in XRD data indicates a distinction between two planes in the stacking.

Another convincing analysis for the material structure is Raman spectroscopy, which is sensitive to slight variation in the lattice symmetry. Raman spectra of our products is totally different from calculated ones by means of Teter's model [32]. These results suggest a formation of new g - C_3N_4 structure. In order to determine the accurate structural parameters of our C_3N_4 phase, additional analyses should be performed for the vacancy ordering and

d_{exp}	Teter model d_{cal}	hkl	Alves model d_{cal}	hkl
8.04	-	-	-	-
7.28	-	-	-	-
6.75	6.72	(001)	6.40	(001)
4.87	-	-	4.70	(010)
4.08	4.10	(100)	4.10	(100)
3.23	3.36	(002)	3.20	(002)
2.02	2.05	(200)	2.04	(120)
1.61	1.62	(004)	1.60	(004)

Table 4.5: Indexation of the X-ray diffraction pattern, compared to Teter's model ($a = 4.74$, $b = 6.72$ Å) and Alves's model ($a = 4.1$, $b = 4.7$, $c = 6.4$ Å).

the stacking way of hexagonal sheets. In addition, a correlation between the symmetry in the diffraction pattern (Fig.4.18) and one of the crystal forms observed by SEM (Fig.4.7) is remarked. Both of them exhibit an hexagonal form with a slight distortion (angles are not exactly 120°). Theoretical calculations of cohesive energy and crystal structure stability should also be performed to propose new bidimensional models.

The difficulty of the carbon nitride synthesis in organic molecular route is a limitation of the reaction temperature. The sublimation temperature of melamine is around 500°C . The technique using the oxy-acetylene torch allows to heat one side of the graphite cell rapidly up to 1500°C , keeping the temperature of the other side at around 800°C . A strong thermal gradient generated inside the cell is suggested to cause a decomposition of melamine and a re-crystallization of the decomposed elements in the small chamber consisting in the interior part of the graphite cell.

4.8 Conclusion

In this work, a new technique to synthesize a g -C₃N₄ phase based on the polycondensation of melamine using a strong thermal gradient in a quite simple apparatus. The heat treatment of melamine is performed using oxy-acetylene torch. Chemical analyses confirm a pure carbon-nitrogen compound without any obvious impurities. The synthesized phase is found to be layered structure by HR-TEM observation and has two kinds of C-N bonds, pyridine like and substitutional, with a stoichiometry of C₃N₄, as revealed by XPS analysis. Despite the good correlations of XRD results between our sample and classical g -C₃N₄ structures proposed by Teter and Alves, some conflicts still remain. In addition, more analysis of the process, such as the temperature condition at each part of the reactor, is still required. It will allow us to understand the mechanism of the phase transition from the melamine to the C₃N₄ and to control the C₃N₄ synthesis. The success of the C₃N₄ synthesis is an important result, leading to the possible synthesis of other light compounds such as B-C-N using this technique.

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Perspectives

1. Analysis of the technique

The combustion flame method is a simple technique that can be performed in ambient atmosphere. The main advantage of the method is the ability of thick diamond film formation with high growth rates [1]. Synthesis of large single crystal diamond is also realized using this technique [2]. On the contrary, the control of process is quite difficult, due to the instability of the gas phase. In the present thesis, this synthesis method is demonstrated to be a promising technique for the formation of a large variety of carbon materials, especially graphitic structures. The different combinations of chemistry and hydrodynamic varying with the experimental conditions determine the obtained product. Large scale novel forms of highly oriented graphite crystal are synthesized. It might be caused by the strong convection and thermal gradient introduced in the flame. In order to understand the growth mechanism of each structure, a plasma analysis should be carried out to reveals the involved active species and the hydrodynamics of the flame. In addition, since a strong thermal gradient exists between the substrate and the gas phase, the local temperature distribution around the growing site should be accurately analyzed. A comparative study of laminar and turbulent oxyacetylene flames for carbon deposition will be also an unavoidable subject. The summary of all these parameters will give us the key factors for the formation of each structure.

2. Possible applications of the new carbon forms

2.1 Uni-directional structures

Polyhedral crystal is a novel size of highly oriented graphite crystal. Due to its morphology, it can be also classified in a low-dimensional graphite group which is now attracting great interest with researchers in physics and chemistry as well as materials science. Carbon nanotube is a quasi-one-dimensional material which exhibits unique physical properties and are under investigation toward several applications. Among the proposed applications,

field emission electron sources would be industrially the most promising and are nearly within reach of practical use. Although many research works on the field emission properties of the carbon nanotubes have reported remarkable experimental results, some subjects still remain to be improved, such as high emission current, destruction phenomena related to thermal heating, isolation of an individual nanotube, etc.

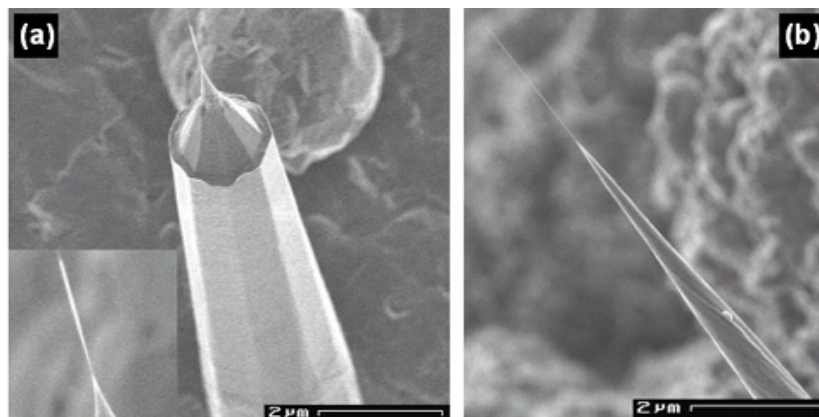


Figure 4.21: Scanning electron micrographs of (a) a rod-like and (b) pin-like polyhedral crystals with carbon nanotube at their apex. They can be good candidates as electron source for field emission applications.

The polyhedral crystal consists of the same basic structure as that of the carbon nanotube, composed of cylindrically rolled graphene sheets. Using the combustion flame method, a local deposition is possible. It allows us to make deposits directly on the metal tip. In the preliminary experimental results with a polyhedral crystal synthesized on the Mo tip reported in Appendix A, they demonstrate a remarkable emission current with high stability, being better than that previously reported for carbon nanotubes. This structure has been confirmed in this first attempt to be a good possible emitter. A series of complete measurements should be carried out to acquire more informations about this new candidate for electron sources.

We can also synthesize the polyhedral crystals with a carbon nanotube at the growth end (Fig.4.21). It can be expected to exhibit remarkable properties, such as a high field amplification factor due to its geometry, a low threshold voltage, a high brightness. This structure should possess good thermal properties (thermal conductivity of graphite) and the polyhedral crystal can help to release the heat during from the emitter. This will limit

the destruction mechanism at high emission current. The polyhedral crystal at bottom of the carbon nanotube should reduce the electrical contact resistance to the cathode.

2.2 Two-dimensional structures

When electrons are confined in two-dimensional materials, quantum mechanically enhanced transport phenomena such as the quantum Hall effect can be observed. Graphene, consisting of an isolated single atomic layer of graphite, is an ideal realization of such a two-dimensional system. Since its behaviour is expected to differ from the well-studied case of quantum wells in conventional semiconductor interfaces due to the unique electronic properties of graphene [3, 4], many researchers are trying to experimentally observe it. Conduction processes in 2D electron or hole systems have recently been investigated in semimetallic graphite-based materials at the quantum limit, illustrating the importance of synthesizing pure single-crystals of graphite in order to study fundamental physics in ideal low-dimensional systems [5]. The two-dimensional petal-like single crystals would be very useful for precise measurements in this domain. This materials should be also interesting for practical applications due to their high anisotropy in the electrical conduction and high surface to volume ratio.

Hydrogen storage in carbon solids reaches the performance required for vehicles. The aggregates of 2-dimensional graphitic structures (GF and petal-like carbon) are expected to have a high performance in this domain, due to their large surface to volume ratio. In addition, their cristallinity can be easily controlled for different requirements. The chemical and physical absorption capacities should be measured. Interesting field emission properties can be also expected from these aggregates since all graphitic walls are oriented in perpendicular to the deposit surface.

3. Development of carbon nitride synthesis technique

Despite a great effort during long time, most of the experimental investigations have failed to produce stoichiometric crystalline C_3N_4 compound. In this thesis, a new structure of graphitic- C_3N_4 is successfully synthesized

by the polycondensation of melamine using a novel technique. The strong thermal gradient is a key parameter for this transition. The optimal experimental condition, such as the local temperatures in the reaction cell and experiment time should be determined in order to obtain the g-C₃N₄ with maximal efficiency. Since this experimental set up is quite simple, it should be scaled up for a large yield formation. It will be useful to test the theoretical model of β -C₃N₄ synthesis from g-C₃N₄ phase. The obtained new structure of g-C₃N₄ is not yet accurately determined. The possible crystal structures should be tested by theoretical calculations. It is also interesting to apply this technique to synthesize other light elements compounds, such as boron nitride (BN) and Boron-carbon nitride (BCN) expected to possess interesting properties.

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Conclusions

Carbon is a fascinating element which forms a huge variety of morphologies and crystal structures due to its ability to be connected to two, three or four neighbors as explained by its possible hybridizations. As summarized in the first chapter, carbon can exist in several allotropic forms, such as diamond, graphite, fullerenes, nanotubes and carbyne. The graphitic materials can be observed in so many different forms classified using both the fundamental structural unit and the referenced orientation which determines the morphology.

The oxy-acetylene combustion flame method is an experimental technique developed in the past for the diamond synthesis. However, taking into accounts the simplicity of the experimental set up and the ability to easily introduce a high temperature in the process, such technique is worth to be applied for the production of a wide variety of carbon materials.

In the present thesis, we demonstrate the possible synthesis of various carbon-based materials using the oxy-acetylene combustion flame method. The diagram of the produced carbon materials as a function of the input gas ratio and the substrate temperature, which are the key parameters of the technique, is established for a wide range of experimental conditions. In addition to the diamond phase, a large variety of highly-crystalline graphitic materials are synthesized.

Gypsum flower-like carbon and petal-like carbon are aggregates constituted by graphitic layers within a peculiar morphology. The degree of graphitization of these graphitic walls can be increased by varying the experimental conditions. The petal-like carbon is an almost perfect graphite single crystal. As reported in the literature, those single crystals of microscopic scale only rarely appear in nature and despite great research efforts, their synthesis is still under trial. The petal-like single crystal whose size reaches up to 20 μm , is a very important bi-dimensional object to study fundamental physics in ideal low-dimensional systems. For example, our sample should be quite helpful to investigate the electronic transport both parallel and perpendicular to the graphitic planes.

A new type of uni-directional graphite crystal, called polyhedral graphite crystal, is also synthesized using the oxy-acetylene combustion flame method.

Such a crystal possesses a high quality graphite structure and exhibits a perfect cylindrical morphology. The crystal size reaches up to 3 μm in diameter and 15 μm in length. All these new carbon products are synthesized with relatively high growth rate, where the 3 min. of deposition are found enough to obtain crystals of a few microns in size. The strong thermal gradient generated in the experimental set up is one of the characteristics of this technique.

Carbon nanotubes are also synthesized using the oxy-acetylene combustion flame method when a metal catalyst is added in the process. The produced nanotubes display a well ordered hollow structure. During this synthesis, polyhedral crystals are found to grow around the carbon nanotubes, leading to a possible control of the production of the polyhedral structure. Such technique has been applied for the local deposition of polyhedral crystal on the apex of tungsten tip in order to measure its field emission properties. A 120 μA stable emission current was observed during 20 min. which is higher than what has been previously reported in the literature for carbon nanotubes.

The synthesis of a carbon nitride phase is also suggested using our experimental set up. Melamine is introduced as an organic precursor containing both carbon and nitrogen. For this synthesis, the oxy-acetylene torch is used to heat the reaction chamber which consists in a small graphite cell. A phase transition is unambiguously observed during the experiment. The chemical analyses using several techniques such as Energy Dispersive X-ray (EDX), X-ray Photoelectron Spectroscopy (XPS) and Electron Energy Loss Spectroscopy (EELS) reveal the formation of a C_3N_4 phase. Structural characterizations using X-ray diffraction and infra-red spectroscopy suggest this new C_3N_4 phase to be close to the *graphitic*- C_3N_4 predicted in the literature. The details of the accurate atomic arrangement still remain to be elucidated.

In the present thesis, the oxy-acetylene flame method is shown to be a unique technique to produce a large variety of crystalline carbon structures. Our results reveal the necessary experimental conditions to obtain each of these carbon structures. Plasma chemistry and hydrodynamics inside the flame should be analysed to give some valuable insight and to increase our understanding related to the CVD growth mechanisms. This would also help to control the production of a required materials in any other CVD processes and to access the fundamental aspects of growth mechanisms. The success

of the C_3N_4 synthesis is also an important aspect, leading to the possible synthesis of other light compounds such as B-C-N.

Appendix A

Measurement of field emission properties of polyhedral crystal

A.1 Introduction

The field emission properties of carbon nanotubes and related materials have recently attracted intense research activities due to their possible applications in field emission devices such as flat panel displays and nanoelectronic sources for imaging, lithography and Xrays sources [1, 2]. The most important characteristics are the voltage threshold and the maximum current density which are the key parameters for the applications. For such a purpose both basic research and technological innovation are required. Experiments were carried out in the Laboratoire de Physique de la Matière Condensée et Nanostructures (LPMCN, University Claude Bernard in Lyon) in collaboration with Dr. Steve Purcell and Monica Rodriguez. The experimental set-up allows the study of field emission and mechanical properties of nanostructured material. Consequently, we investigated some physical properties of the polyhedral carbon crystal synthesized by the oxy-acetylene flame. From these experiments, a good current emission stability ($120\ \mu\text{A}$ during 20 minutes) was observed and Young's modulus of 34.5 GPa was estimated. A high current is extracted from the emitter with the elastic property as good as for carbon nanotubes.

A.2 Field emission mechanism

The field emission mechanism is based on the possible tunneling of electrons from a material to vacuum in the presence of strong external applied field. Fig.A.1 displays a schematic on the physics of field emission. The difference of the Fermi level between the conduction band (CB) in the material and the vacuum corresponds to Φ , the work function. In vacuum, the expression of the potential at a given position z for the electrons is given in figure A.1.I. This is the sum of energy at the Fermi level and the work function altogether with the potential given by the so-called "charge image". The "charge image" reflects the fact that electrons in vacuum are absorbed by a metallic surface. At this point no electrons are emitted from the surface because they are reflected at the interface between the metal and vacuum. When applying a voltage between the metal and the vacuum, the field (F) decreased the potential at given z point by a factor eFz , resulting in a linear decrease of the potential away from the surface (see Fig.A.1.II). At the threshold voltage, the electrons start to cross the remaining potential barrier by tunneling (Fig.A.1.III), leading to the field emission regime.

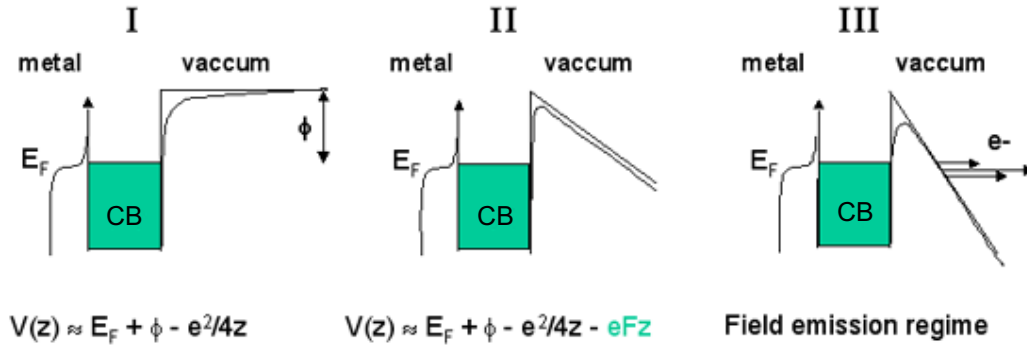


Figure A.1: Schematic illustrations of field emission physics.

After the threshold voltage, the current evolution is described by the Fowler-Nordheim equation [3]. In the case of the sharp crystal, this equation at the apex of the tip can be expressed as follows :

$$I(E) = A(\beta F)^2 \exp\left(-\frac{B\Phi^{\frac{3}{2}}}{\beta F}\right) \quad (\text{A.1})$$

where A and B are two constants, F is the applied field : $F = V/d$ where

V is the applied voltage and d is the cathode-grid distance, β is the field enhancement factor due to the sharp emitter. Note that the emitted current is very sensible to a small change in the applied voltage. Nevertheless, there is some deviation to the Fowler-Nordheim predictions. The resistance in series with the emitter and the emitter itself lead to a voltage drop when a current is emitted. This results in a decrease of the effective field at the apex of the emitter. Also the presence of nanometric adsorbate structures at the apex of the emitter lead to some fluctuations of the emission current. The emission current is unstable when there are some random displacements of these adsorbates. The phenomena of the emission is thus quite complex. There is a sequential tunneling of the electrons from the emitter to the adsorbate and from the adsorbate to the vacuum [4]. Consequently, it is quite important to remove the adsorbates by cleaning the emitter using heating treatment [5].

An important parameter of the field emission is the so-called β factor. This factor reflects the field amplification at the apex of the emitter compared to the case of two infinite plates where, the field is simply equal to V/d . An important value of the field amplification factor leads to a lower threshold voltage and an increase in the emission current. In wire-like structures, the β factor is close to r/L , where r is the radius at the apex of the emitter and L , its length.

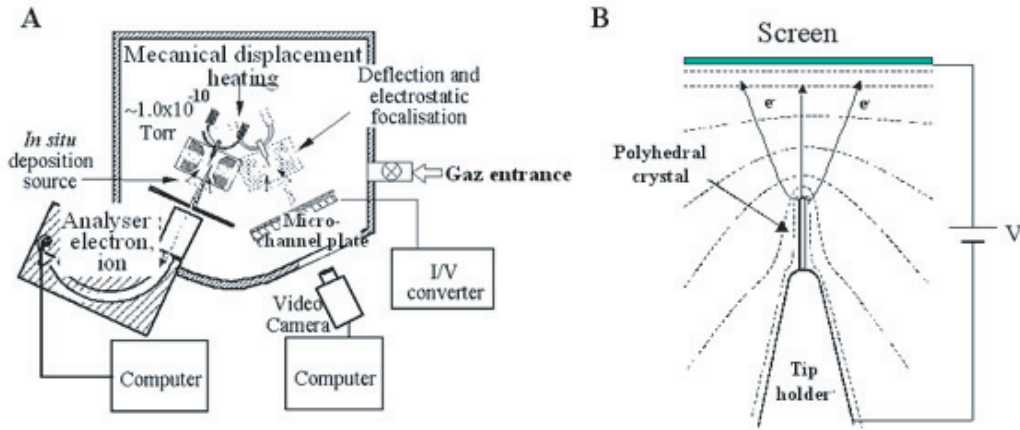


Figure A.2: Schematic analysis system used to obtain emission diagram: (A) experimental set up of whole system and (B) schematic illustration of the field enhancement at the apex of the emitter.

A.2.1 Experimental set up

The field emission experiments are carried out in an ultrahigh vacuum system with a base pressure around 2×10^{-11} Torr. Fig.A.2 displays a schematic system for field emission measurements. The W tip is held in a Ni spiral to allow cleaning by standard Joule heating. A circular cathode loop placed in front of the tip is used to heat the tip by electron bombardment. The emission patterns are measured on a multichannel plate placed at ~ 30 mm from the tip. The emission current (I_{FE}) is considered as the total current leaving the tip. The emission strikes a polarized metal plate connected to a picoamperemeter.

A.3 Sample preparation

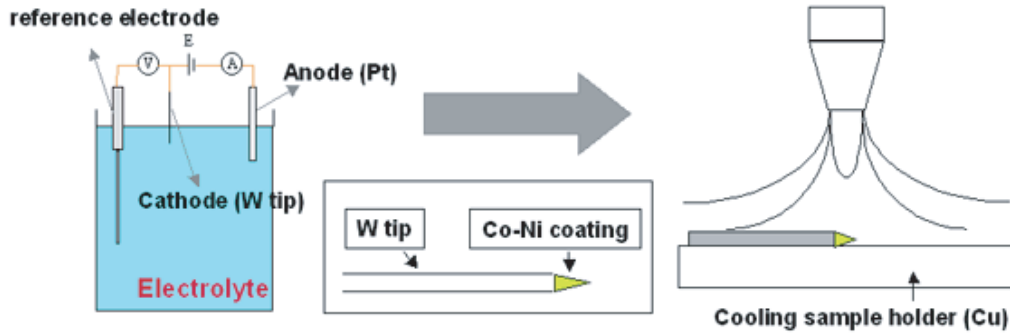


Figure A.3: Schematic overview of the preparation of the sample dedicated to field emission measurements.

The purpose of this chapter is to measure the field emission properties of a polyhedral graphite crystal synthesized using the oxy-acetylene combustion flame method, as presented in chapter 3. In order to understand its intrinsic properties, we need to isolate one of these crystals on the top of tungsten tip.

The introduction of transition metal catalyst has been found to be quite efficient to control the geometry of graphite polyhedral crystal, in chapter 3. In order to obtain an isolated crystal on the apex of W tip, the catalyst metal is coated on the apex of W tips which are previously electrochemically etched in an HCl solution. Fig.A.3 illustrates the various steps of the preparation of the samples.

A mixture of Co-Ni is coated on only 1mm of the apex of W tip. The W tip is positioned on the cooling sample holder before being introduced inside the oxy-acetylene flame. Compared to planar substrates as used in chapter 3, the W tip is not easily kept at the constant temperature because of its 1D geometry. The O_2/C_2H_2 volume ratio is maintained at 0.9 with a C_2H_2 gas flow of 1.0 lit./min. After 30 seconds, graphite crystals are observed at the apex of W tip, as demonstrated in Fig.A.4.

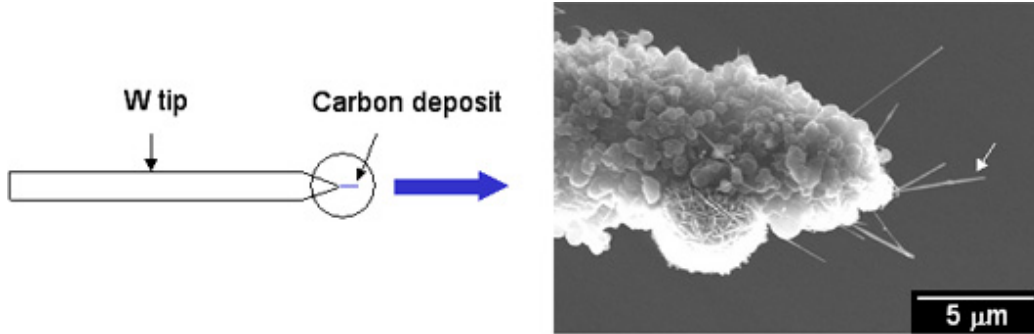


Figure A.4: (a) Schematic illustration and (b) SEM photograph of our sample used for the field emission measurement: the emission was obtained from the crystal indicated with an arrow.

Although several graphitic crystals are deposited on the apex of the W tip (Fig.A.4), their emissions are in general projected at different angles. In our experiment, the crystal indicated by an arrow in Fig.A.4 is placed perfectly perpendicular to the detector plate and is considered to be the only observed emitter. This is also confirmed by a vibration mode (the detail of the vibration of crystal will be explained in following section 4.4.2). If several crystals emit, each crystal should oscillate at different frequencies when the frequency is varied. As only one resonance mode is observed, only one crystal is detected on the screen.

A.4 Experimental results

Cleaning the surface of emitters is quite important because the amorphous layers and adsorbed molecules covering the carbon emitters perturb the electron emission [6]. The surface perfection is thus crucial especially for I-V characteristics of the emitter. Since the modification of the surface could

appear during the measurement due to these impurities covering the emitters, the graphite crystal should be heated up to 1600 K in order to perfectly remove all impurities from its surface. However, we succeeded to increase the temperature only up to 1400 K due to contact problems. The field emission current exhibits a diffused pattern that form is not stable, being due to remaining impurities which causes the modification of the surface condition during the measurement. The measurement of both current stabilities and mechanical properties are mainly performed on our sample, which are not strongly influenced by the surface conditions.

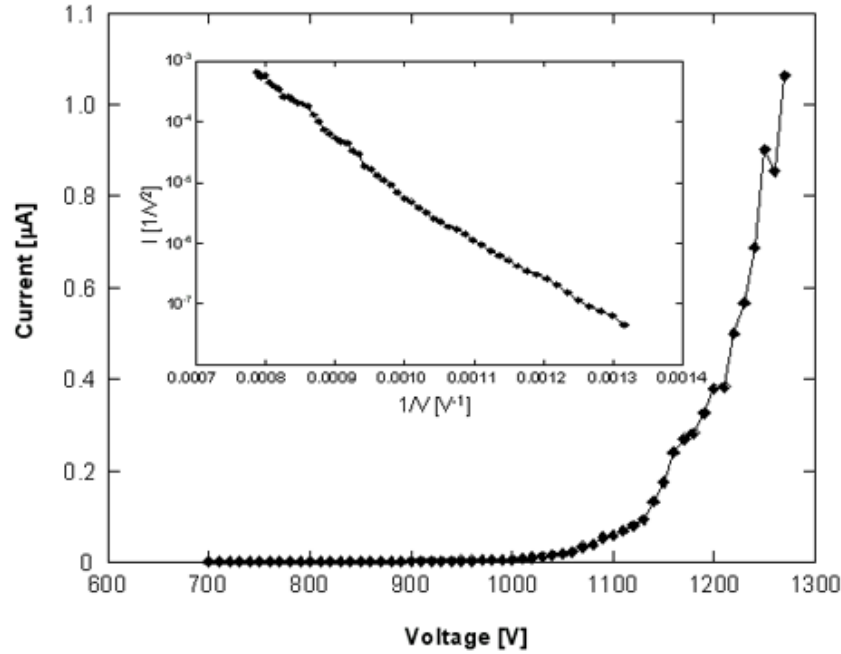


Figure A.5: I-V characteristics for a polyhedral crystal, with in inset the corresponding Fowler-Nordheim plot.

A.4.1 I-V characteristics

Fig.A.5 illustrates the I-V characteristic of our sample for current ranging from pA to μ A. The threshold voltage is around 800 V. The inset of the Fig.A.5 represents the corresponding Fowler-Nordheim plot. The evolution is almost linear. Some little jumps and instabilities are observed, they can

correspond to adsorbate displacements at the apex of the emitter. At higher currents, a small increase of the emitting current compare to the linear evolution appeared. This can be due to heating effect. Nevertheless, no obvious saturation is observed at this current range.

A.4.2 Current stability

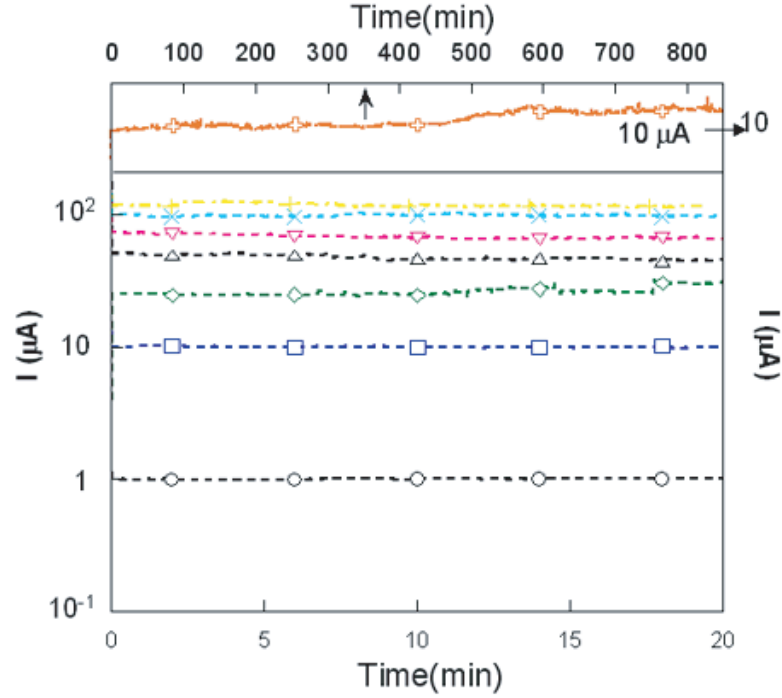


Figure A.6: Emission currents versus time for a graphite polyhedral crystal deposited on the top of W tip.

For the applications of field emission from uni-dimensional carbon materials, as possible electron source, the most important requirements are emission stability and long-lifetime. In Fig.A.6, we report the current stability of the graphite crystal over the current ranges varying from 1 μA to 120 μA . The emission currents over whole explored current ranges are found to be quite stable. The stability of a 10 μA current has also been observed during 15 hours. These values are not the maximal performance of our sample because the measurements do not limitate the lifetime of our sample. In addition, as

the cleaning of the emitter by heating is not completed, the current stability can still increase.

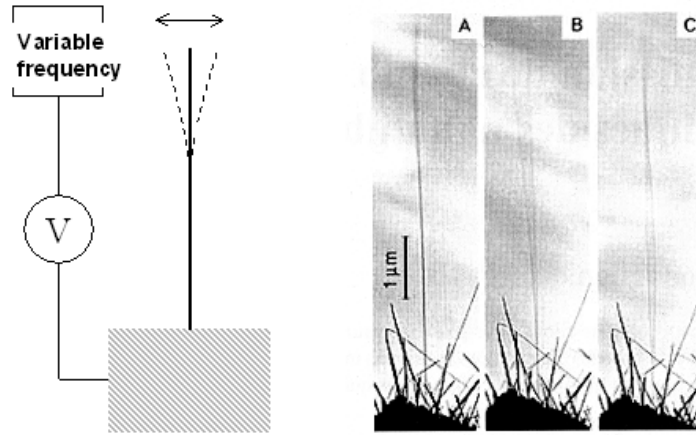


Figure A.7: (left) Principle of resonance of the emitter (right) Observation of the resonance of a carbon nanotube by transmission electron microscope A) non excited nanotube, B) first resonance and C) second resonance [7].

A.4.3 Mechanical property

The excitation of the natural resonances ν_R of carbon nanotubes by alternating electric field is one of the important effects in nanomechanics. Such a vibration of carbon nanotube has been firstly observed in 1999 [7], where the mode form and resonance response were directly observed by transmission electron microscopy as shown in Fig.A.7(right). When the excitation frequency corresponds to the one of the nanostructures, the latter goes into resonance. Determining the frequency of the vibrations gives access to the mechanical properties of the emitter. The inherent values of resonance can be determined as a function of the Young's modulus and some geometrical parameters.

A.4.3.1 Vibration in a 1D nano-system

Our goal is to investigate the mechanical properties of the polyhedral crystal using this resonant technique. In our work, the field emission system is used for the observation of the resonance, instead of the microscope.

The W tip is mounted on a heating loop, inserted into the field emission chamber in ultra high vacuum (10^{-10} Torr). An emission pattern of an isolated graphite crystal appears on the observation screen when the corresponding voltage V_A is applied to the tip.

A variable digital function generator is connected to the excitation anodes in order to excite the natural resonance of the emitter. When a resonant frequency is found, the emission pattern is suddenly enlarged and the field emission current $I(\nu)$, detected by the observation screen connected to a picoamperemeter, abruptly decreases. It is due to a changing of physical position of the apex of the emitter. The $I(\nu)$ is varied due to the amplification factor which depends on the distance between the apex of the emitter and the current detector. The response as a function of frequency thus can be measured by the variation of $I(\nu)$. Fig.A.8 illustrates a variation of a total emission current (I_{FE}) caused by the excitation frequency where, I_{FE} is expressed with a conversion of data: $I_{FE} = -(I(\nu) - I(\nu)_{\max}) / I(\nu)_{\max}$. The maximum of I_{FE} thus corresponds to the maximal amplitude of vibration, giving the resonant frequency. In addition, when we vary the applied voltage V_A from -700 to -900 Volts, a variation of the resonant frequency (ν_R) is observed to be quite small, $\cong 0.05$ kHz/Volt.

A.4.3.2 Estimation of Young's modules

In Fig.A.8, the position of the maximum appears at the inherent excitation frequency of the graphite crystal. The resonant frequency of our sample is 6.1 MHz.

The resonance frequency of a emitter depends on the crystal diameter (r), the length (L), the density (ρ_1) and Young's modulus (E). For a polyhedral crystal with uniform structural and mass distribution, the classical elasticity theory [8] gives the following resonance frequency:

$$\nu_n = \frac{B_n^2}{2\pi} \frac{1}{L^2} \sqrt{\frac{EI}{\rho}}$$

where B is a proportional constant for the n^{th} harmonic. However, in our case, we should take into account the dependence of ν_R on the applied voltage (V_A) in the field emission system [9]. The previous equation can be modified to;

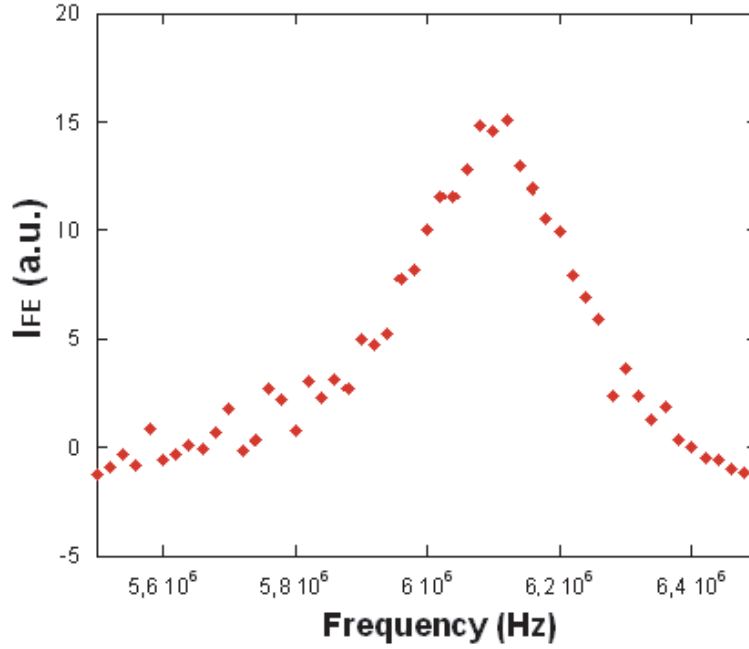


Figure A.8: Field emission current (I_{FE}) as a function of the frequency for the graphite polyhedral crystal.

$$\nu_R(V_A) = \nu_{R0} + pV_A; \nu_{R0} = \frac{n}{L^2} \sqrt{\frac{EI}{\rho_L}}$$

where $I = \pi r^4/4$ is the geometrical moment of inertia and $\rho_l = \rho \pi r^2$ (ρ is the density of graphite) is a mass per unit length.

From the ν_R plot as a function of V_A , p is found to be $\cong 0.05$ KHz/Volt, being quite small and the second term pV_A can be considered to be negligible. The length and diameter of the oscillating crystal are measured by electron microscopy imaging, and estimated to $4 \mu\text{m}$ in length and 50 nm , respectively. The natural frequency ν_{R0} observed for our sample is 6.1 MHz . The estimated Young's modulus is 34.5 GPa .

A.4.3.3 Linear and non-linear regimes

The field emission current ($I(\nu)$) change reflects the amplitude of vibration of the apex of the polyhedral crystal. Our sample exhibits a Lorentzienne

like response (Fig.A.8), which is typical of a linear regime [10]. Such a linear regime is normally observed when the amplitude is weak enough to keep the voltage and the form of emitter during the resonance. On the contrary, a strong amplitude causes a variation of voltage and the form of emitter during the oscillation, which modify suddenly the natural resonance frequency of emitter. This fact results in non-linear regime. Non-linear vibration mode, obtained for a multi-wall carbon nanotube is displayed in Fig.A.9.b as an example [11].

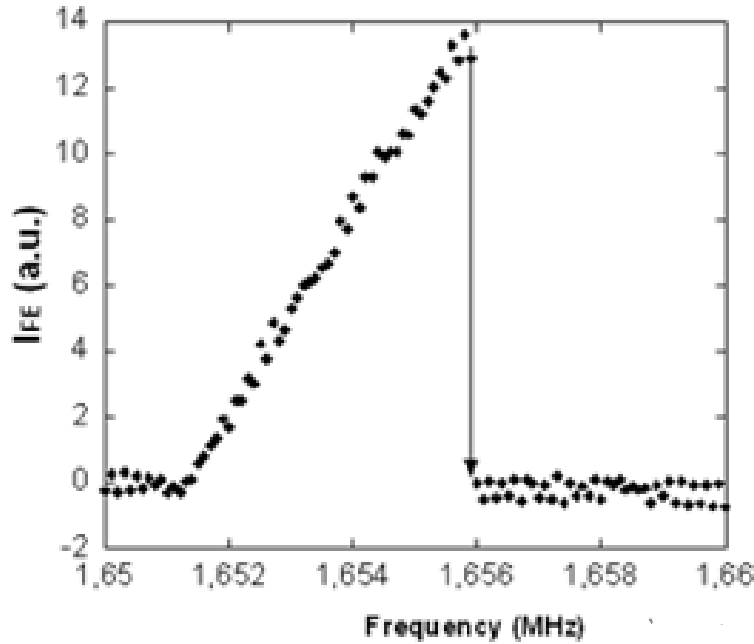


Figure A.9: Comparison of vibration mode; field emission current as a function of the excitation frequency for carbon nanotube [11].

A.5 Discussion

As previously reported in the literature [9, 12], the current stabilities for carbon nanotubes are in the range of a few nA to 10 μ A during more than 10 hours even after complete cleaning. However, the current could sometimes reach 100 μ A but during only a few seconds [13, 14]. It is thus remarkable

that the emission current for polyhedral crystal reaches $120\ \mu\text{A}$ during 20 min. Despite the crystal surface covered with amorphous layers and adsorbed molecules, a quite high and stable emission current is observed. It is probably due to the crystal structure. Concerning the limitation of the lifetime, one of the main problems consists in some heat effect of the emitter due to the high intensity of the current. The structure of polyhedral crystal consists of a multi-wall nanotube for its core and high oriented graphitic layers around this inner multi-wall tube. Since the oriented graphite has quite high thermal conductivity, these layers can certainly play a role to release the heat of the emitter, allowing such a high stable current. In order to increase the current stability, the perfectly cleaned sample should be prepared. This will help to improve the reproducibility of all measurement data. Though the Young's modulus (E) for MWNTs is very large ($\leq 1\ \text{TPa}$) for a diameter around 10 nm, E drops dramatically to lower values for tubes of larger diameter ($E \sim 100\ \text{GPa}$ for 40 nm in diameter) [7]. The value of the Young's modulus for MWNTs of 50 nm has been reported to be $\sim 30\ \text{GPa}$ [15]. Young's modulus of polyhedral crystal is thus analogous to that of MWNT of the same diameter. However, the linear regime suggests a vibration mode for the polyhedral crystal which differs from the carbon nanotube. It can be an effect of emitter diameter. The polyhedral crystal used during the present experiment possesses a large diameter $\sim 50\ \text{nm}$ and a relatively short length $\sim 4\ \mu\text{m}$. The amplitude should be small enough to keep its natural resonance frequency, which causes the linear regime. A preliminary I-V characteristic measurement of our sample demonstrated in this work (Fig.A.5) is devoid of information. This study should be continued up to the current limit. Their destruction phenomenon is also important to be understood.

A.6 Conclusion

In the present chapter, the potential application of polyhedral crystal as a field emitter is revealed. Especially, the current stability of polyhedral crystal is found to be quite important, compared to that of carbon nanotube. Because of the high oriented graphite layers composing the polyhedral crystal, the heat caused by the high intensity of the current inside the emitter is released. This protects the emitter during the measurement. Since the estimated Young's modulus of the polyhedral crystal is close to that of carbon nanotube with the same diameter, the polyhedral crystal can be an alter-

native material of carbon nanotube as a field emitter with higher current stability. In addition, the local deposition of isolated individual crystal is possible using the combustion flame method. To reach the maximum possible current, it should be important to succeed heating enough to clean the surface of the emitter.

Appendix B

Formation of carbon nano-necklace by thermal plasma process

During my PhD thesis, I have been involved in the characterization of samples synthesized using a plasma arc discharge within the PLASMACARB European contract. The samples were characterized by Scanning electron microscopy, Transmission electron microscopy, Electron energy loss spectroscopy and Energy dispersive X-ray spectroscopy. New carbon structures were revealed during this scientific collaboration.

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B.1 Introduction

Carbon nanomaterials reveal a rich polymorphism including multi- and single wall carbon nanotubes (CNTs) [16], fullerene molecules [17], graphitic onions [18], toroids [19], boxes [20], cones [21], etc. Each step in the discovery of a new carbon material morphology leads to new potential application

fields. In particular, it is expected that the original nanometric morphologies of CNTs could have an important potential impact in applicative domains such as molecular electronics or high-strength composite materials [22]. Carbon nanotubes are mainly produced by three conventional techniques: arc discharge [23, 24] or laser ablation methods [25], which are two high temperature processes ($T \approx 4000\text{K}$), and chemical-vapour-deposition (CVD) methods [26], which operate at medium temperature ($T \approx 1500\text{K}$). In the arc-discharge and laser ablation techniques, the carbon and the catalyst are vaporized simultaneously. In the CVD methods, the carbon source is obtained from the decomposition of a gas phase (CO, methane, ethylene, etc.) in the presence of small metallic particles covering a substrate. In the present letter, a new method, based on a 3-phase alternative current (AC) plasma technology, is used to synthesize carbon nanostructures.

B.2 Synthesis technique

Our plasma technology, initially designed for the production of carbon black by cracking of liquid or gaseous hydrocarbons [27], was adapted in order to treat solid powders at high temperature (carbonaceous and catalytic products) [28, 29]. In this process, a carbon aerosol mixed with metal catalysts is injected into the plasma at a predetermined position along the reactor axis, corresponding to precise injection temperature and reactive flow patterns. After a chosen residence time in the plasma zone allowing the total vaporization of the solid powders, the plasma gas, carbon and metal mixture is quenched and extracted from the reactive zone at a so-called extraction position. The main difference with the classical arc and laser processes is the solid carbon flow rate, which is not limited to the electrodes erosion but can be totally controlled independently of plasma gas and metal catalysts flow rates. In addition, a system was specially designed for the sampling of the species inside the reactor, their quenching and their transport up to a filter. This system is mainly composed of a water cooled suction pipe, a set of modular cooling pipes and a filter / exhauster system. The thermal plasma is produced by an electric arc between three graphite electrodes connected to each phase of a three-phase AC power supply, which allows a maximum power input of 260 kW. In opposition to direct current (DC) torches, which are characterized by a high velocity of the plasma gas, this technology allows low velocities, large high temperature volumes and long

residence times. Carbon black (Ensaco 250G from Erachem), coated with 3% of Ni and 3% of Co as submicronic catalyst, is used as precursor. Among the wide set of parameters that can be evolved in the present technique, the temperature field in the plasma reactor, the carbon concentration, the plasma gas/carbon ratio, the residence time, the quenching rate, the extraction position and the nature of the gas flow are identified to play a key role in the production and the quality of the final product. In the synthesis of the carbon nanostructures presented in the present paper, helium and nitrogen were used as plasma gas. Plasma gas and precursor were injected at atmospheric pressure with flow rates of $2.8 \cdot 10^{-4} \text{kg.s}^{-1}$ and $13.9 \cdot 10^{-4} \text{kg.s}^{-1}$ for helium and nitrogen, respectively, whereas the solid carbon flow rate was fixed to $2.8 \cdot 10^{-5} \text{kg.s}^{-1}$. The extraction point was at 0.88 m from the injection position. Once the experiment finished, different samples related to specific process components were collected and analysed. The carbon nanostructures characterised in this paper correspond to samples collected after scraping of the internal wall of the reactor and in the bag filter. In a second step, these carbon nanostructures were characterized using a high-resolution scanning electron microscope (LEO982, SEM-FEG), and a high-resolution transmission electron microscope (LEO922, TEM-200KeV) equipped with electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDXS).

B.3 SEM observations of produced materials

Scanning electron micrographs (Fig.B.1.a) reveal large quantities of carbon nanotubes embedded in the carbon black used as the carbon source in the plasma technique. Conical terminations are clearly visible in Fig.B.1.a, as well as opened nanotubes, displaying their cylindrical shape. Although this SEM image shows no visible difference from the conventional CNTs, TEM images reveal a 'stacked-cup' structure consisting of a series of long hollow conical compartments instead of the conventional long cylinders (Fig.B.1.b). The graphene layers are not oriented parallel to the cylindrical axis (Fig.B.1.c), but parallel to the surfaces of the catalyst particle. Electron diffraction analyses reveal a conical angle frequently close to 30° , as also observed in Fig.B.1.c. Such a peculiar structure has already been reported in the literature [30, 31], although previously referred to as a 'herring-bone' structure where the graphene sheets do not connect but surround a hollow core. The

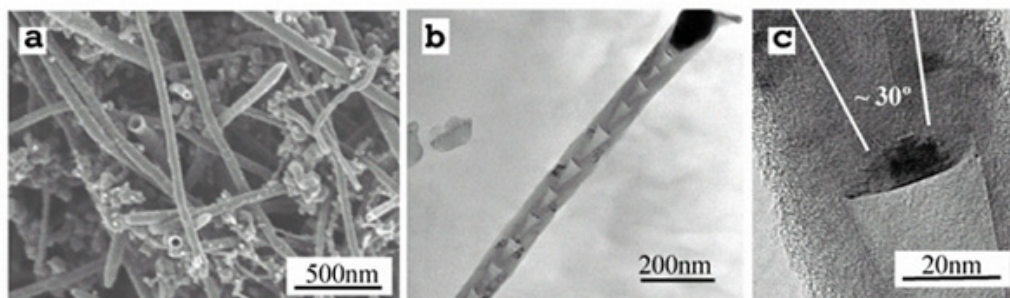


Figure B.1: (a) Scanning electron micrograph of carbon nanotubes embedded into carbon black materials, (b) Transmission electron micrograph of the 'stacked-cup'-like structure of the carbon nanotubes, (c) High resolution TEM images illustrating the graphene layers in the stacked-cups (white lines are guide for the eyes) and the average conical angle ($\approx 30^\circ$).

diameter of the nanotubes ranges from 50-100 nm and the length in the order of a few micrometers. As the end of the tubes is often capped by a cone-shaped catalytic particle, a 'tip'-like growth model could be suggested in analogy with carbon fibers and filaments [32, 33].

Large scale synthesis of 'necklace'-like carbon nanostructures is also revealed by SEM micrographs (Fig.B.2.a). These nano-necklaces are up to several mm long with outer diameters in the range 50-100 nm. Carbon spheres are found to be regularly spaced along the filament. Unlike the straight nanotubes (Fig.B.1), carbon nano-necklaces usually curve smoothly and entangle together (Fig.B.2.a). The necklace can include more than 50 bell-like units linked from the end of the bell to its head. In order to analyse their nanostructure, these carbon necklaces are also characterized by TEM, illustrating the repetition of an elementary unit looking like a nano-bell, sometimes filled by catalytic particles. The segments, which are completely filled with the Ni-Co catalyst used during the synthesis, are observed as segments with dark core in Fig.B.2.b. The joined segments in the carbon nano-necklaces are actually short variable-diameter compartments with one end sealed and the other one open. The number of graphene layers can vary between the top of the nano-bell and its end (see Fig.B.2.b inset).

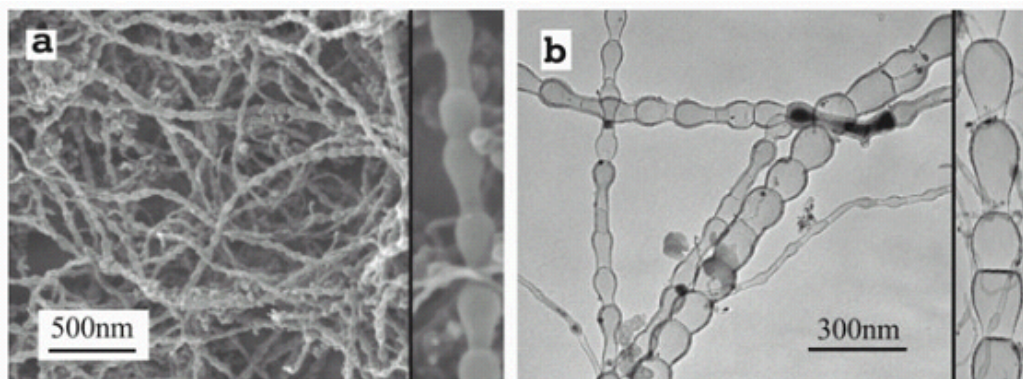


Figure B.2: (a) Scanning electron micrographs of carbon necklaces embedded into carbon black materials, used as carbon source in the plasma technique. These nano-necklaces are made of carbon spheres regularly spaced along the filament. (b) Transmission electron micrographs of carbon necklaces presenting the repetition of an elementary unit looking like a nano-bell, sometimes empty or filled with a metal particle. Both insets (on the right) are magnification of an isolated nano-necklace in SEM (a) and TEM (b), respectively.

B.4 Characterizations of carbon necklace

B.4.1 TEM observation

Understanding the connection between the successive nano-bells is not an easy task. Fig.B.3.a shows this connection for a nano-necklace, constituted by joined spherical segments, nearly parallel to the electron beam of the microscope. The connections seem to be performed by the open part of the nano-bell. High-resolution TEM characterization (HRTEM) shows that these segments of the carbon necklaces are composed of graphitic shells (Fig.B.3.b). The separation between these planes is estimated around $3.4\text{\AA}$, and is clearly visible in Fig.B.3.c-d. The connection between the nano-bells is illustrated in Fig.B.3.d, where all the graphitic sheets of the previous unit (6 graphitic sheets remaining at the open region) are surrounding the graphene-based shells of the next one. The interaction between the two segments is thus probably strong. Similar structures have been previously reported for CN_x [34, 35] and BN [36] systems. In ref. [37], highly deformed carbon structures looking like 'necklaces' have been reported in a very low yield and at very high pressure.

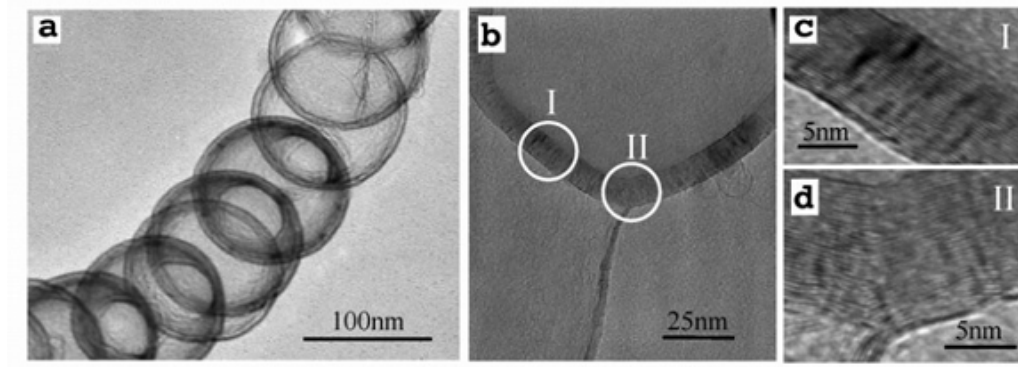


Figure B.3: High-resolution transmission electron microscopy (HRTEM) of carbon necklaces. The images present the connection between the successive elementary units (a), called nano-bells. The nano-necklace is nearly parallel to the electron beam of the microscope. This nano-bell consists of graphene-based shells (b). HRTEM images (c-d) respectively detail region I and region II of the necklace illustrated in (b).

B.4.2 Raman spectroscopy

A confocal laser Raman spectrometer (Labram) has also been used to characterize the carbon necklaces. The measurements were performed using a 10 mW power beam (632.8 nm excitation wavelength) with a spot of about one micrometer in diameter. The Raman spectrum of the necklaces (Fig.B.4) shows the typical signature of a well-graphitised material. The spectrum displays the typical peak at 1580 cm^{-1} associated to the G-band mode of graphite compounds. As the necklace structure is spherical, it certainly contains several topological defects such as pentagons in the hexagonal network in order to curve the graphite sheets (spherical shape, connection between segments, etc). The peak around 1330 cm^{-1} is attributed to disorder, inducing Raman scattering (D-band mode). In the region of higher-order Raman spectrum, the three peaks at 2465 cm^{-1} , 2660 cm^{-1} (2D), et 3230 cm^{-1} (2D') are also observed in pristine highly-oriented pyrolytic graphite [38]. However, the peak at 179 cm^{-1} cannot be easily explained for graphitic systems, although for single-wall carbon nanotubes, it is attributed to the radial breathing mode of the tube in the region (180 cm^{-1} , 200 cm^{-1}) [39]. In our case, such a peak could be attributed to the presence of metallic particles, enhancing inelastic Raman scattering at the interface between metal and graphite due to electronic effects such as charge transfer.

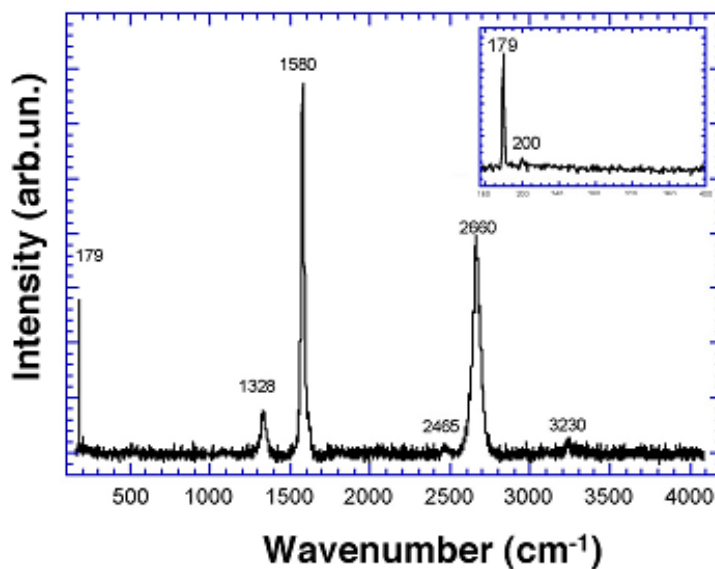


Figure B.4: First and second-order Raman spectrum of carbon necklaces obtained using a laser excitation wavelength of 632.8 nm.

B.4.3 Chemical mapping using electron energy loss spectroscopy (EELS)

In order to accurately check the chemical composition of the carbon necklaces, the EDX technique has been used for their chemical characterisation. Fig.B.5.a shows two compartments containing metal catalysts, connected by several graphene-based shells. The metal is found not to fill completely the empty space. The interface between the graphene-based shells and the catalyst is illustrated in Fig.B.5.b which also shows the crystalline nature of the catalyst after solidification. Empty and filled nano-bells can be easily distinguished using the EDXS technique. When the nano-bell is empty, the spectrum presents only the carbon peak. On the other hand, in the presence of a catalytic particle, a small peak, compared to the dominant carbon peak, is detected and attributed to Ni and Co. These EDXS results are corroborated by electron energy loss spectroscopy (EELS) measurements which have also been performed in order to investigate the chemical composition of the nano-necklaces.

From the elemental chemical mapping (Fig.B.5.c-f), it is clear that the

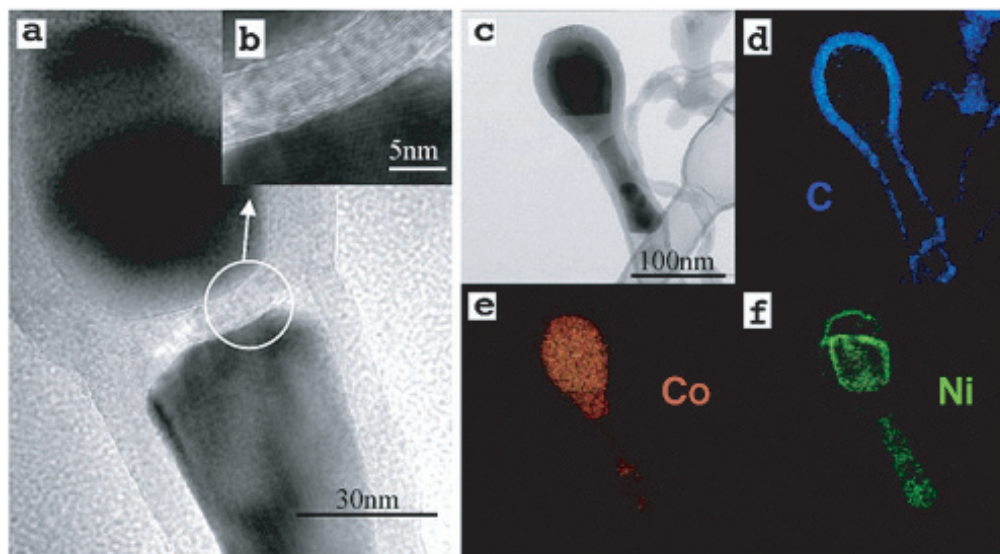


Figure B.5: HRTEM images of necklaces filled with metal (a). The crystalline nature of the catalyst is observed in (b). Low resolution TEM image of the end of a nano-necklace (c). Electron energy loss spectroscopy (d) carbon mapping (blue), (e) cobalt mapping (red), and (f) nickel mapping (green) of the image shown in (c). The nano-necklace contains non-uniform concentration of catalyst (Co and Ni) inside the nano-bell only constituted of carbon.

nano-bell is only constituted of carbon (Fig.B.5.d). However, the metal composition of the catalytic particles encapsulated in these carbon structures is not always homogeneous. In the present example, the cobalt is homogeneously distributed in the empty space (Fig.B.5.e), while the nickel is more localized at the surface of the metal particle (Fig.B.5.f). Such situation cannot be generalized, and is found to be varying from case to case. As only a threshold value of carbon can be detected by the EELS technique, the absence of the carbon which forms the top and the bottom of the cavity in Fig.B.5.d is an artefact. Consequently, the chemical mappings of Fig.B.5.e-f does not allow us to state the absence of a small quantity of carbon inside the catalytic particle.

B.5 Growth mechanisms

Within this original thermal plasma technique, the synthesis of these two nano-structures can be easily triggered by modifying the nature of the plasma gas in the reactor. The nature of the plasma gas has a strong influence on the arc voltage of the plasma generator and hence strongly modifies the power input and therefore temperature prevailing in the system. When helium is used as plasma gas, the temperature of the reactor walls is medium (1000-1300°C) and mainly carbon nanotubes are produced. On the other hand, carbon necklaces are favoured when the temperature of the reactor walls is higher (1700-2400°C), and the plasma gas used is nitrogen. Consequently, the temperature distribution inside the plasma reactor is thus an important factor to explain the growth of these carbon nanostructures.

At medium temperature (1000-1300°C), the catalytic particles are still solid, although very close to the melting point (i.e. the melting temperature of the Ni-C eutectic is 1311°C). The carbon nanotubes are suggested to form through diffusion of carbon at the particle heated surface, which promotes its precipitation into graphene sheets (Fig.6.a). As the carbon nanotube grows further, the metal particle is pushed upward, forming a metal cap which stabilizes the dangling bond at the edge of the tube by saturating them. The growth of the nanotube is stopped when the catalytic particle is completely solidified and encapsulated by graphene layers (Fig.1.b). This growth mechanism, adapted from the process proposed previously for the CVD-grown carbon filaments [17,18], easily explains the stacking of graphene-based cones observed along one peculiar surface direction of the catalytic particle and the presence of the latter at the end of the structure.

At higher temperature (1700-2400°C), the catalytic particles are in a liquid state. The formation of carbon necklaces proceeds via solvation of carbon vapour into metal particles, diffusion through the bulk, followed by the precipitation of carbon in excess at the surface of the particles. This scenario is based on the Vapour-Liquid-Solid (VLS) model proposed long ago to explain the synthesis of silicon whiskers [40]. When the catalytic particle is formed by condensation of metal plasma/vapour in the reactor, carbonaceous structures are preferentially adsorbed at its surface and dissolved into the liquid metal phase, leading to a supersaturation of carbon. During the synthesis, the catalytic particle is able to incorporate a large amount of carbon (30-50 at.%) depending on the local temperature and on its size. Upon cooling, the solubility limit of carbon decreases and carbon starts to segregate. This

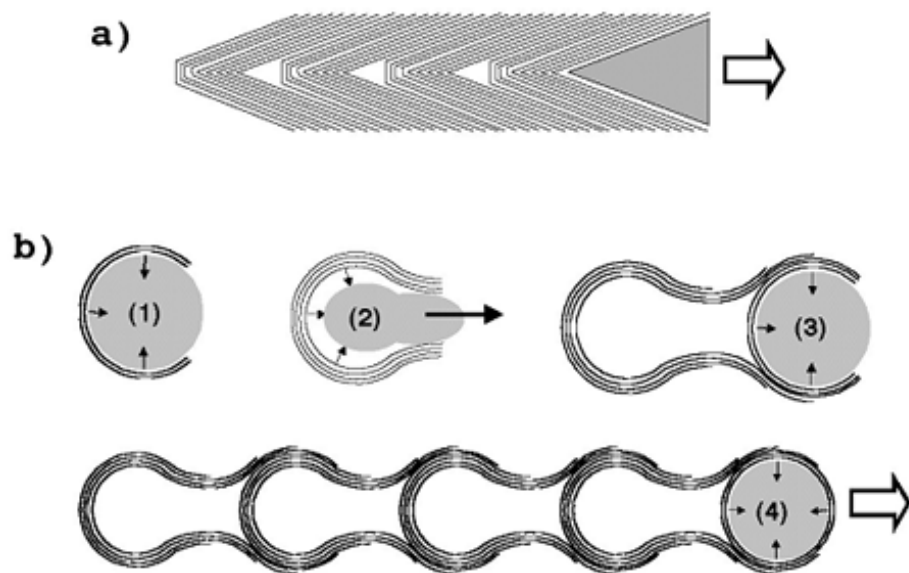


Figure B.6: Schematic representations of proposed growth mechanisms for carbon nanotubes (a) and nano-necklaces (b). The black lines and curves represent graphene layers. The catalytic particle is illustrated in light grey. The small black arrows represent the pressure on the catalytic particle, while the big arrows show the direction of the motion of the catalytic particle during the growth process.

effect increases as the temperature decreases and the segregation force is maximum close to the solidification point. Below the solidification temperature (which value depends on the composition of the particle), there is at equilibrium a complete segregation between metal and carbon. The occurrence of such a segregation process is supported by the absence of carbon inside the catalytic particles after complete solidification (Fig.B.5.d). Once expelled, carbon crystallizes at the surface of the particles and forms graphene sheets around the droplet. The formations of the first polyaromatic layer defines a volume for the particle. After the formation of several graphene-based layers, the catalytic particle is trapped inside a smaller volume. As the confinement increases, the particle elongates, allowing the formation of longer graphene-based layer. This explains the thinning down observed at the open part of the nano-bell (Fig.B.2.b inset and Fig.B.3.b). When the compression is too intense, the nano-particle is expelled from the bell-like

graphene-based structure and restarts the process. This growth scenario is illustrated in Fig.B.6.b. Sometimes, the catalytic particle is not entirely expelled, which explains the presence of catalyst trapped in several cavities of the necklaces. The structure observed in Fig.B.3.d. confirms the internal growth scenario. This figure shows that the internal graphene-based sheets of the previous nano-bell are linked by the end to the head of the next one and are surrounding the shells of the following bell, as schematically illustrated in Fig.B.6.b. A similar mechanism, based on a sequential growth has recently been proposed for nanofilaments made of repeated units of multi-wall carbon nanotubes with a metal particle encapsulated at one end. These morphologies were synthesized by thermal chemical vapor deposition (CVD) of methane on Ni-Fe catalysts [41].

B.6 Conclusion

We report on the characterization of carbon nanotubes and nano-necklaces synthesized by thermal plasma process. Both carbon nanostructures have been linked to specific operative conditions and more particularly to the nature of the plasma gas used and by consequence, to the temperature field in the reactor. To resume, the 'stacked-cup'-like structure is the result of the growth of carbon nanotubes at a temperature where the metal catalyst is at a solid state whereas the 'necklace'-like structure has grown at a temperature where the metal catalyst is liquid. This technique could be easily scaled up to obtain even large amount of these new compounds. Both nanostructures could be designed for many potential applications based on their respective morphologies. The stacked-cup carbon nanotubes exhibit a surface structure with a very high density of open ends of graphene-based layers, which could serve as emitting centres for field emission applications. This structure also exhibits a large amount of opened graphene-based layers which could be advantageous for gas storage. The nano-necklaces, which are composed of varying numbers of connected nano-bells may also have interesting electrical properties. Due to their morphology, they could certainly be used in composite materials with an intrinsically strong interaction with the host matrix. The presence of topological defects at the surface of these nanostructures can also be useful for functionalisation.

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