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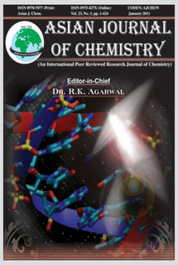

REVIEW

Carbon Nanotube Growth *via* Chemical Vapour Decomposition Method

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This paper illustrates a short review in the carbon nanotubes structure and other carbon forms and explains different forms of carbon nanotubes. The various attractive and unique properties of carbon nanotubes are also discussed. There are several methods for carbon nanotubes production but the best sufficient method for mass production with lower cost is the chemical vapour decomposition method, which is the main subject of present article. Furthermore, the various effective factors on the carbon nanotubes growth in the chemical vapour decomposition process like temperature, inert gas flow rate, carbon source, catalyst and the reaction time are discussed here.

Key Words: Carbon Nanotube, Chemical vapour decomposition, Synthesis, Catalytic.

INTRODUCTION

Three different kinds of carbon allotropes including diamond, graphite and amorphous structures were known until 1985. The structure of diamond is tetrahedrally bonded of each carbon atom to other carbon atoms in the form of sp^3 hybrid bonds. Because of the covalent [sigma (σ)] bonds among the carbon atoms in diamond, it has electrically insulating properties. The structure of the graphite is a layered structure in the form of hexagons that carbon atoms bonded together in the sp^2 hybrid bonds. Therefore, graphene layer form three in-plane σ bonds and one out-of-plane π bond (orbital) in the outer layer. Because of delocalizing and distributing the out-of-plane π orbital or electron over the entire graphene plane, it has thermally and electrically conductive properties.

Kroto *et al.*[1] discovered a novel structure of carbon that is called fullerene in 1985. The most renowned form of fullerene is the buckyball (C_{60}), which is composed of 12 pentagons and 20 hexagons of carbon atoms[2,3].

In 1991, Iijima[4] discovered a new form of fullerenes, called carbon nanotubes. Carbon nanotubes have a high aspect ratio and referred to as one-dimensional materials. They comprise coaxial cylinders of graphite sheets which range from 2 to 50 sheets[4,5].

Types of carbon nanotubes: Carbon nanotubes are produced in two types: Single-wall carbon nanotubes consisting of one graphite tube and multiwall carbon nanotubes, consisting of several concentric tubes and cylinders inside other cylinders[4-6].

Single-wall carbon nanotubes are stronger and more flexible than multiwall carbon nanotubes due to the sliding the individual cylinders inside one another in multiwall carbon nanotubes. In addition, electrical conductivity of single-wall carbon nanotubes are better than multiwall carbon nanotubes. In spite of their difficult production, purify challenging and so more expensive process of single-wall carbon nanotubes, it has attracted a lot of attention for production[7].

According to the orientation of the graphite sheet, three types of single-wall carbon nanotubes are obtained: armchair, chiral and zigzag configuration. In the armchair configuration, the carbon bonds are located on opposite sides of each hexagon in the honeycomb lattice. In fact, the chiral angle is 30º in armchair type[4-6].

If the chiral angles are in between 0º and 30°, this carbon nanotubes are known as chiral nanotubes. In the zigzag configurations, the chiral angle equals to zero[2,4-6].

In the zigzag configuration, the C-C bonds are located on opposite sides of the hexagons. The structure of single-wall carbon nanotubes with three different chiralities[2-6,8-10] are shown in Fig. 1.

Properties of carbon nanotubes: The properties of carbon nanotubes strongly depend on the degree of graphitization, chirality and their diameter. Actually, the electronic, electrical and mechanical properties of carbon nanotubes are made by their topology, structure and size. Carbon nanotubes

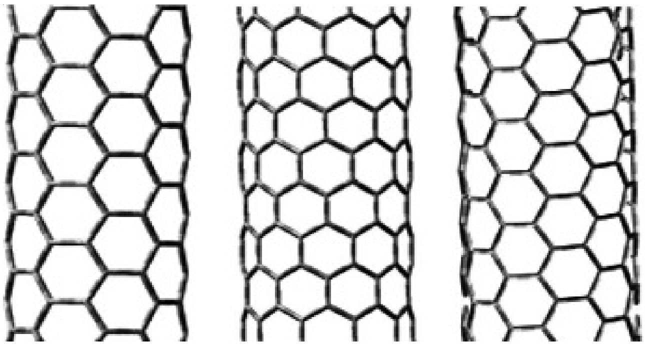
(a) Armchair (b) Zigzag (c) Chiral

Fig. 1. Structural models of single-wall carbon nanotubes presented at three different chiralities: (a) armchair, (b) zigzag, and (c) chiral configuration [Ref. 1-3, 6, 8, 9]

have a high aspect ratio, high heat conductivity, high tensile strength, large surface area, low mass density and versatile electronic behaviour. Carbon nanotubes behave as ideal one-dimensional "quantum wires" with either semiconducting or metallic properties[3].

Electronic properties of carbon nanotubes: Carbon nanotubes have very interesting electronic properties because of their small dimensions and high aspect ratio. Single-wall carbon nanotubes are either metallic or semiconducting depending to the carbon nanotubes' diameter and chirality. All "armchair" configuration carbon nanotubes are metallic, while "chiral" and "zigzag" configuration carbon nanotubes, may be either metallic or semiconducting[3,6,8].

Metallic conduction of carbon nanotubes can be attained without presenting the doping effects. For semiconducting nanotubes the band gaps are proportional to a fraction of the diameter, not depending to the tubule chirality[3-4,8].

There are both σ covalent bonds and π covalent bonds between the carbon atoms. The carbon atoms in graphite sheets possess an unhybridized π orbital, which causes to transport π electrons through the carbon nanotube. The π bonds are delocalized and are shared over the whole carbon nanotube. The π electrons move freely without constrictions throughout the axial direction of carbon nanotubes. Conversely, electrons are restricted by the monolayer thickness of the graphene sheet in the radial direction[11]. It is an important point that the electron wavelength have to be integer multiples of the carbon nanotube circumference. If the electron wavelength is not a multiple of the carbon nanotube circumference, it will interfere with itself destructively[8]. As a result, carbon nanotubes act as one-dimensional "quantum wires" because of the quantum limitation effects on the carbon nanotubes circumference[9]. By rolling the graphite sheet into a cylinder for carbon nanotubes production, the π orbitals become more delocalized outside the carbon nanotubes; therefore, the σ bonds of carbon will be partly out-of-plane[9]. The carbon nanotubes possess stronger mechanical properties and more electrical and thermal conductivity than graphite because of σ-π rehybridization. In addition, the σ-π rehybridization leads to exchange in the carbon nanotubes electronic properties[9]. The electronic states of the carbon nanotubes split into one-dimensional sub-bands, instead of a single wide electronic energy band. In the semiconductor carbon nanotubes, there are a gap between the conduction band and the valence band. The band gap is equal to 0 eV in the armchair configuration of the carbon nanotubes and it is equal to 0.4-0.7 eV in the semiconductor configuration of carbon nanotubes[11]. In the armchair configuration of carbon nanotubes, the conduction and valence bands cross each other in the Fermi level[3].

Electrical properties of carbon nanotubes: Carbon nanotubes possess high electrical conductivity more than copper because their resistances are very low and they have very few defects among their structures. The Fermi level of carbon nanotubes are very sensitive to the type of dopant which comes with contacting to the carbon nanotubes[9,10]. The main methods of doping carbon nanotubes are interstitial doping and substitutional doping. In interstitial doping, the carbon nanotube lattice remains the same (the dopant atoms do not substitute the carbon atoms) and the newly introduced dopants are adsorbed at the surface. Different gas molecules are adsorbed by the carbon nanotubes at the surface and between the tube bundles. Also, in many cases if the carbon nanotubes are open-ended the dopants reside inside the carbon nanotubes. In interstitial doping, dopants and carbon nanotubes come together through non-covalent bonding. On the other hand, in substitutional doping, the dopant atoms replace the carbon atoms and form sp^2 bonding in the carbon nanotube structure[3,12].

Mechanical properties of carbon nanotubes: The mechanical properties of a solid must ultimately depend on the strength of its interatomic bonds[4]. One of the strongest bonds is the C-C bonds present in the honeycomb lattice. Furthermore, with rolling the graphite sheet to produce carbon nanotubes, the axial component of the σ bonding between carbon atoms enhances significantly. Therefore, the mechanical properties of carbon nanotubes are considerable[3,8,9,12,13].

The strength of the carbon bonds determines the actual value of Young's modulus. In addition, reduction in diameters decrease the Young's modulus[3,13]. Therefore, The carbon nanotube chirality does not influence on Young's modulus, but the diameter of carbon nanotubes affect on this properties[3,9]. Vaccarini[6,14] investigated the influence of the chairality and structure of carbon nanotube on the elastic properties including bending, tension and torsion. The results exhibited that the chirality has a low effect on the carbon nanotube tensile modulus, while the chiral carbon nanotubes shows asymmetric torsional behaviour regarding the right and left twist, whereas the other structure carbon nanotubes do not exhibit this asymmetric torsional behaviour.

The Young's modulus of multiwall carbon nanotubes is generally higher than the young's modulus of singlewall carbon nanotubes because the multiwall carbon nanotubes have larger diameter than single wall, also there are vander Waals forces between the tubes in multiwall carbon nanotubes[3,9].

Moreover, the carbon nanotubes are very flexible. They can be twisted, elongated, flattened or bent into circles before breakage. In addition, they can be recovered to their original shapes. The 'kink-like' ridges of carbon nanotubes allow them to relax elastically under compression[3,8]. The tensile strength of multiwall carbon nanotubes is *ca.* 50GPa[15] which is *ca.* 20 times stronger than steel[2,3]. The carbon nanotubes have a very large fructure strain which is lowered by increasing the temperature[8,13,16].

Vibration properties of carbon nanotubes: There are two normal modes of vibration in carbon nanotubes which are shown in Fig. 2. The first mode includes in and out oscillation of the diameter of carbon nanotubes. The second mode includes a squashing of the carbon nanotubes that they squeeze down in one direction and extend in the perpendicular direction oscillating between an ellipse and a sphere. The frequency of both modes depends on the diameter of carbon nanotube[8].

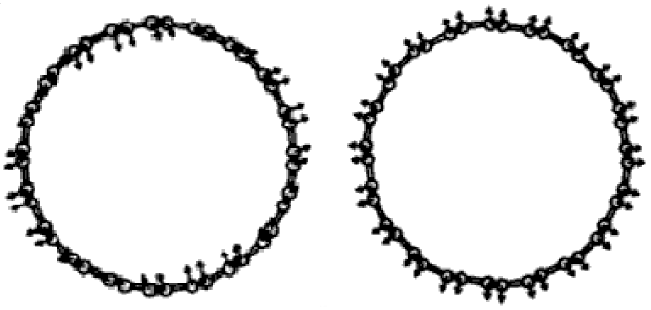

Fig. 2. Illustration of two normal modes of vibration in the carbon nanotubes [Ref. 8]

Thermal properties of carbon nanotubes: The carbon nanotubes possess considerable thermal properties including specific heat and thermal conductivity that are determined primarily by the phonons. The lattice vibrations result to production phonon which is observed by the Raman spectroscopy. At the temperature lower than 100 K, the phonon quantization occurs. Therefore, the thermal properties have to be considered above 100 K[9,12,13].

Optical properties of carbon nanotubes: The band gap and also well-defined band and sub band structure of carbon nanotubes make them a suitable choice for optical and optoelectronic applications. The optical transition happen by exciting the electrons or holes from one level of energy to another level[9].

Intermolecular forces: The carbon nanotubes have a little bit sticky property due to intermolecular forces. In fact, the electron clouds on the surface of carbon nanotube supply a moderate attractive force between the carbon nanotubes, which is termed as vander Waals' force. This includes forces between non-polar molecules. A carbon nanotube just take places to be a non-polar molecule.

Chemical vapour decomposition process: There are several methods for production of carbon nanotubes. Chemical vapour decomposition (CVD) offers controlled synthesis and continuous operation is catalytic decomposition of hydrocarbons[13,17,18].

The chemical vapour decomposition process is a comparatively slow process that produces long carbon nanotubes in the large quantities. During this process, the hydrocarbon source is heated at high temperatures, typically between 700 and 1000 ºC, inside a quartz tube in the presence of catalytic systems[3,10,13,17,18].

In the chemical vapour decomposition method, hydrocarbon molecules is dissociated in presence of a metal catalyst with nano size and carbon atoms saturate in the metal nanoparticle. Carbon precipitate from the metal particle and tubular carbon solids in a sp^2 structure will be formed. Controlling the growth of aligned carbon nanotubes with surface modification is very important for most of the application. According to the substrate in the chemical vapour decomposition process two-dimensional (2D) or three-dimensional (3D) micropatterns can be produced[3].

The metal substrate provides nucleation locations for the growing of carbon nanotubes. Hydrocarbons sources decompose into hydrogen and carbon atoms at high temperatures and then carbon atoms dissolve and diffuse into the metal surface and reorganize themselves into a hexagon of carbon atoms network and precipitate out. Sometimes, amorphous carbons cover the metal surface and metals surface is poisoned. Therefore, the carbon atoms cannot contact with the metal catalyst and the growth of carbon nanotube is stopped.

Generally, in a thermal chemical vapour decomposition setup, the quartz tube is first flushed with an inert gas such as He or Ar for 10 min and then usually the catalyst is reduced under hydrogen at around 400 ºC for *ca.* 0.5 h. It has been observed that hydrogen influences the particle size of the catalyst. Next, the hydrocarbon source is introduced and the carbon nanotubes start growing. The catalytic system is composed of metal catalysts such as Fe, Co, Ni, or Mo and metal supports such as MgO, $CaCO_3$, Al_2O_3 or Si. The schematic of the chemical vapour decomposition method[19] are illustrated in the Fig. 3.

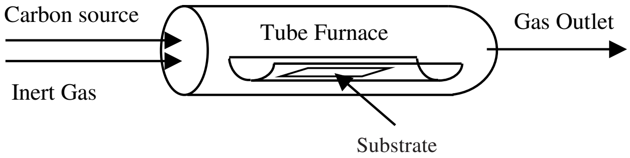

Fig. 3. Schematic diagram of chemical vapour decomposition method [Ref. 19]

It is approved that chemical vapour decomposition is a feasible method for single-wall carbon nanotubes growth directly on a substrate surface, allowing for integration of the nanotube growth into the fabrication of electronic devices based on the carbon nanotubes[20].

Chemical vapour decomposition categories: Chemical vapour decomposition synthesis is divided into two main categories called supported catalyst growth and floating or gas-phase growth[17,21].

In the supported catalyst growth process, the catalyst is prepared in advance and deposited in some way on a support medium. This is placed into a flow device such as an atmospheric pressure tube in a temperature-controlled furnace, where it can be exposed to flowing carbon-rich gas at elevated temperatures (typically 500-1100 ºC) for a sustained period of time[17]. This approach is based upon the *in situ* formation of floating catalyst particles by thermal decomposition of organometallics[21].

A high-temperature flow-furnace is used in the floating or gas-phase catalyst growth. Both of the catalyst and carbon sources are injected into the reactor simultaneously. Therefore, the subsequent decomposition and reaction can happen entirely suspended in the gas flow either following self-deposition on the reactor surface[17,21].

In fact, this method consists of the continual injection of a pre-prepared colloidal metal catalyst particles solution into the reactor[21].

There are two different chemical vapour decomposition configurations *i.e.*, horizontal furnace and vertical furnace[2,3]. The most popular configuration of carbon nanotubes production is horizontal furnace. The length of carbon nanotubes can be controlled by the length of the hydrocarbon deposition time.

Conversely, for continuous mass production of carbon nanotubes, the vertical furnace is typically used. In this approach, the hydrocarbon source is injected from the top of the furnace and the produced carbon nanotubes are collected at the bottom of the reactor[2].

During the synthesis of carbon nanotubes in a fixed bed reactor, the mass of carbon deposited is a function of the mass transport and diffusion to the active catalyst sites. Therefore, the carbon nanotube mass yield per unit weight of catalyst is a proportion of the reactor geometry instead of the catalyst quantity. In the large scales (industry), the reactor geometry of fixed bed plays a less significant role in product separation where the products are either a liquid or gas[22].

Thus, in the large scale process optimization is required to eliminate of heat and mass transfer limitations, *e.g.* by using small particles and/or porous materials, thin catalyst films, to increase the gas-solid interfacial area.

In contrast, in a fluidized bed reactor, stagnant film production at the solid surface, which slows down heat and mass transfer, can be remarkably decreased due to the tremendously improved gas-solid mixing which is intrinsic in well-designed systems. In fact, heat and mass transfer under ideal fluidization conditions has no limitation[9]. The sufficient mixing between gas and solid particles in the fluidized bed reactor provides access to the active catalyst sites even in 3D geometries. Further, fluidized beds provide suitable space for carbon nanotubes growth in compared with fixed bed reactors[22-24].

Mass production of carbon nanotube: The continues carbon nanotube mass production is a great challenge in industry due to the high molecular weight (106-1013) with having desirable structure and morphology that provides sufficient physical and chemical properties. In fact, the process for mass production of carbon nanotube includes length scale and large time[18] as shown in Fig. 4.

The carbon nanotubes mass production process is decoupled into four scale levels: (1) Atomic scale of carbon nanotube self-assembly includes the carbon nanotubes growth condition and mechanism, design of catalyst and controllable structure synthesis of individual carbon nanotubes. The important characteristics affected in this scale are the carbon nanotubes wall number, the carbon nanotubes diameter and length, the defects, the chirality and the crystallinity or graphitization of carbon nanotubes[18]. (2) With carbon nanotubes growth, the aspect ratio increase and thus, the various carbon nanotubes agglomerated structures are produced due to the interactions between the carbon nanotubes. Therefore, there are diffrent carbon nanotubes agglomerated structures such as carbon nanotube agglomerated particles, suspended single carbon nanotubes and carbon nanotube arrays. It is so crucial to control the morphology of carbon nanotubes in the mass production[18]. (3) The flow behaviour scale is significant to the transport properties of carbon nanotube agglomerates due to the unique properties of carbon nanotubes. Thus, the traditional facilities are necessity to modification of hydrodynamic behaviour and as a result the modification of the carbon nanotubes production[18]. (4) There are some macroscopic objectives that must also be optimized. These process engineering includes the process operation, the existence relationship between microscopic carbon nanotube structure and the macroscopic operation, environmental conditions, ecological considerations, the carbon nanotubes delivery and applications[18].

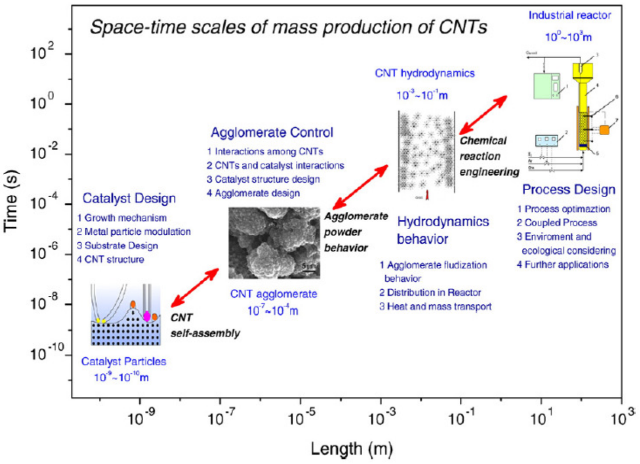

Fig. 4. Multiscale space-time analysis of the mass production of carbon nanotubes

Advantages of the chemical vapour decomposition method: (a) It can be scaled up for large scale and high-quality production of carbon nanotubes at a relatively low cost[2,3,18]. (b) Possibility to control the carbon nanotubes growth by optimizing the reaction parameters such as the temperature, catalyst system, hydrocarbon source and the flow rate of feed[2,3,18,25]. (c) Possibility of the deposition of carbon nanotubes on predesigned lithographic structures and so producing ordered arrays of carbon nanotubes. (d) Possibility to grow vertically aligned carbon nanotubes (Fig. 5), which can be used in applications such as flat panel displays[2,3,25,26].

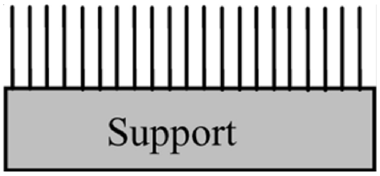

Fig. 5. Schematic vertically aligned carbon nanotubes grown by chemical vapour decomposition on a catalyst system

Scenarios of carbon nanotubes growth: Two different scenarios can be possible during carbon nanotube growth including the base growth and tip growth. In the root or base growth method [Fig. 6(a)], there is a strong interaction between the support and the nano particles. Therefore, the carbon atoms will precipitate from the metal nanoparticle (M) and the carbon nanotubes grow on top of the nanoparticles. These nano particles are attached to the support[2,3,18,26-28].

In an opposite manner, in the tip growth method [Fig. 6(b)], there is a week interaction between the support and the nano-particles. Therefore, the carbon atoms will precipitate from the bottom of the metal surface and the carbon nanotubes growth in between the support and the metal nanoparticles[2,3,10,18,26,29].

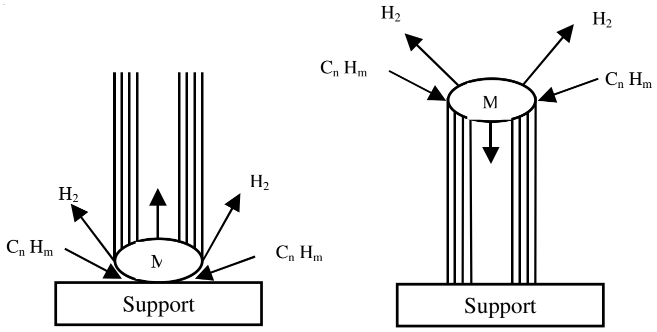

Fig. 6. Base growth (a) and tip growth (b) mechanisms

Affected factors on carbon nanotubes growth in the chemical vapour decomposition method: The carbon nanotubes characteristics produced by chemical vapour decomposition method is related to the operating conditions such as the operation temperature and the pressure, the carbon source volume and concentration, the size and the pretreatment of metallic catalyst and the time of reaction[4].

Operating temperature: Chemical vapour decomposition process is a thermal decomposition method. Therefore, the operating temperature is an important factor on carbon nanotubes growth. It is founded that single-wall carbon nanotubes produce at higher temperatures with the presence of well-dispersed and supported metal catalyst while multiwall carbon nanotubes are formed at lower temperatures and even with the absence of a metal catalyst[4].

Du and Pan[30] investigated growth of carbon nanotubes directly on nickel substrate. They studied nucleation and growth behaviour of nano-tubes with respect to growth sites and reaction temperature. At lower synthesis temperatures nickel nano-particles served as the nucleation sites, however at high temperatures grain boundaries and defective sites were the nucleation sites. It is reported that lower synthesis temperatures than optimum synthesis temperature results in lower carbon nanotube yield in the product. It is also reported that the reaction temperature plays an important role in the alignment properties and diameter of the synthesized nano-tubes[19].

Inert gas flow rate: The carbon source is pumped into the reactor in the gaseous phase under the suitable process conditions. The reactor must be kept free of oxygen atoms during all the operation process for avoiding of carbon oxidation. For this goal, inert gas such as nitrogen or argon flows continuously to the reaction chamber. The flow rate of both feed and inert gas must be optimized for having the sufficient production yield. It is not requested to change the carbon source or inert gas with variation of the support material[19].

With reduction of inert gas velocity, the feed source consumption starts to produce carbon nanotubes at the front end of the catalytic substrate. The feed source is rapidly transported to the tail end with increment in the inert gas velocity because the residence time is not adequate for starting the carbon nanotubes production at the front end of the substrate. Hence, the increment in the velocity of the inert gas, enhances the total production rate of carbon nanotubes[31].

Carbon source: The sufficient carbon source properties are the high conversion, the stable supply and the low cost[18].

The flow rate of carbon source is typically between 10 and 30 mL/min. The flow rate of inert gas and also exposure time has to be larger than the flow rate of carbon source gas. The reduction in the pressure of carbon source results in the carbon nanotubes production with higher quality and higher yield[19].

With increasing the gas flow rate in the fluidized-bed, the gas residence time reduces and larger bubbles produce. Thus, the interfacial contact area and the contact time between gas and solid particles are decreased, leading to a higher 'carry through' and therefore lower conversion[32].

The carbon source concentration is another significant factor. Very high or low carbon concentration will lead to produce in a high percentage of amorphous carbon although the mechanism of production is probably to be different[33].

Considering equal binding between the reactants with catalyst active site and their similar decomposition, we have followed the equations:

acetylene > ethylene > toluene > propylene >
methane > *n*-pentane > methanol > acetone

and

acetylene > acetone > ethylene > *n*-pentane >
propylene >> methanol = toluene >> methane[34,35]

Catalyst: The nano catalyst particles act as the initiating cores for carbon nanotubes growth *via* a vapour-liquid-solid (VLS) mechanism[36,37].

The metallic catalyst determines the type of produced carbon nanotube. In the chemical vapour decomposition process, the single-wall carbon nanotubes are produced at higher temperatures respect to multiwall carbon nanotubes with a well-dispersed and supported metal catalyst while multiwall carbon nanotubes are produced even with the absence of a metal catalyst. Furthermore, the diameter of carbon nanotubes are closely depend on the metal catalyst nono particles diameter[2,38].

It is crucial to use adequate diameter of catalyst, with enough narrow distribution that clusters can be formed and simultaneously control the process conditions for avoiding the agglomeration[21,39]. The catalyst particle size, the catalyst composition, the carrier and catalyst activity can affect on the carbon nanotubes structure. Fig. 7 shows the influence of the catalysts particle size on the carbon nanotube diameter[40].

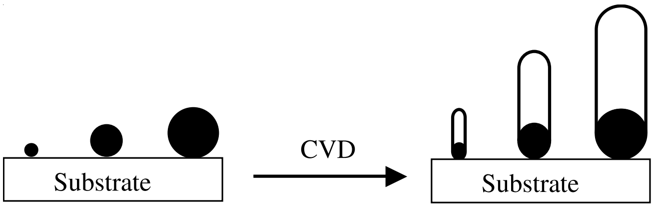

Fig. 7. Schematic depicting the use of different diameter iron nanocluster catalysts for the controlled diameter synthesis of carbon nanotubes

The commonly catalysts are Fe, Co and Ni. Recently, Cu catalyst is proved to be an efficient catalyst with very high catalytic activity for growing of both random networks and horizontally aligned single-wall carbon nanotube arrays. In addition, the other noble metals such as Au, Ag, Pt and Pd are effective catalysts for growth of single-wall carbon nanotubes. The results of some literature for production of carbon nanotubes according to the catalyst particles are summarized in Table-1.

TABLE-1
DIFFERENT STRUCTURES OF CARBON NANOTUBES (CNTs) PRODUCED IN CHEMICAL VAPOR DECOMPOSITION METHOD BY USING Fe, Ni AND Co CATALYSTS

Catalyst particles	Multiwall carbon nanotubes	Single-wall carbon nanotubes
Iron based catalyst	[Ref. 23, 25 35, 41-60]	[Ref. 26, 40, 61-68]
Nickel-based catalysts	[Ref. 46, 49, 69-82]	[Ref. 83-85]
Cobalt-based catalysts	[Ref. 46, 49, 52, 53, 86-94]	[Ref. 2, 67, 84, 95]

To sum up, the IVA group metal Pb are effective catalysts for growing both random networks and horizontally aligned single-wall carbon nanotube arrays on silicon wafers in the chemical vapour decomposition method. The melting point of lead is quite low (327 ºC); therefore, the lead catalyst can volatilize continually during the growth process and finally disappears at the end of the growth. This method produces the carbon nanotubes without metal catalyst and do not request to purity step of single-wall carbon nanotubes[96].

It is more effective to use a composition of two different metal catalyst systems for having higher yields of carbon nanotubes production. The ratio between two metals catalyst mixture powerfully controls the carbon nanotube production yield and morphology[2,3,38,79]. The results of some experiments have been summarized in Table-2.

TABLE-2
DIFFERENT STRUCTURES OF CARBON NANOTUBES PRODUCED IN CHEMICAL VAPOR DECOMPOSITION METHOD BY USING Fe, Ni, AND Co ALLOYS CATALYSTS

Catalyst particles	Multiwall carbon nanotubes	Single-wall carbon nanotubes
Nickel-cobalt alloy	–	[Ref. 64]
Iron-nickel alloys	[Ref. 97-99]	–
Iron-cobalt alloys	–	[Ref. 100-104]
Iron-molybdenum alloy	–	[Ref. 105-116]
Cobalt-molybdenum alloy	–	[Ref. 117-126]

For example by adding Ni to the Fe/Al_2O_3 catalyst and thus producing the Fe-Ni alloy, the catalyst stability increased due to the stable phase and high activity. However, the addition of Ni caused more defects in the carbon nanotubes products. By adding the Ni, the fish bone type carbon nanotubes produce more. Therefore, this method modulate the carbon nanotubes graphite arrangement[127].

The catalytic activities of transition metals in the carbon nanotubes production depends on the graphitization ability, low solubility in the carbon atoms and stable crystallographic orientation on graphite[38].

Some catalyst such as Fe/Al_2O_3 can be inhaled into the carbon nanotube and the coaxial carbon-metal nanowires is formed because the metal particles are agglomerated and lifted-up into the carbon nanotubes and deformed[128]. By using a copper microgrid catalyst without any catalyst carrier, the produced carbon nanotubes has completely hollow channels and/or completely filled copper nanowires[129]. Therefore, the multiwall carbon nanotube structures can be modulated by the proportion between the carrier and catalyst active phase.

One limitation to usage of supported-catalyst growth is that finally the catalyst is covered by pyrolyzed hydrocarbons and it becomes deactivated. Introducing the catalyst directly into the gas flow can circumvent the effects of catalyst deactivation, as well as permit the process to be operated in a more continuous fashion. There has been relatively limited success in using floating-catalyst techniques to produce nanotubes[17,130].

The usage of dispersed magnetic fluids is another novel effective method. Application of magnetic fluid of surfactant-coated magnetite nanoparticles by spin coating method on Si substrates results in successful growth of dense and aligned carbon nanotubes. Furthermore, if the magnetic fluid mixes in PVA, the solution provides uniform particles distribution. Thus, the agglomeration phenomenon do not occur and it is possible to control the nanoparticle catalyst density on the substrate[19].

For indicating the parametric conditions employed, the catalyst lifetime is a significant factor. The longer the synthesis time achievable at 'optimal' conversion rates by the longer the catalyst lifetime. The catalyst lifetime is directly as a function of the synthesis temperature, type of carbon feedstock and catalyst. All of these factors together govern the carbon concentration at the surface of the catalyst particles. Typically, the catalyst lifetime reduce by increasing in the feedstock concentration and synthesis temperature. In contrast, these parameters increase the growth rate of carbon nanotubes[32,131].

Catalyst preparation and distribution: There are several methods of catalyst preparation for carbon nanotube synthesis by chemical vapour decomposition method such as patterning of catalytic islands on the substrate material, ion-exchange, incipient wetness impregnation, organo-metallic grafting and sol-gel technique. The important factors related to the catalyst that affect on carbon nanotube production are larger surface area of the catalyst (smaller powder size) and well dispersed of the catalyst material[19].

Support material: A single metal and mixture of metals which are supported on clays, oxides, or zeolites have a very great catalytic activity for carbon nanotube synthesis. The number of oxides and mixed them are affected on dispersion and also stabilization of the metallic catalyst. The catalytic properties strongly related to the interaction between the catalyst and the support material.

Using mesoporous materials such as silica for supporting materials have an important role in leading the initial carbon nanotube growth. The strength and the type of the catalyst-support material determine the conditions of metallic catalyst free carbon nanotubes or carbon nanotubes filled with metal catalysts. Therefore, the sufficient choice of catalyst material as a support material is very effective on carbon nanotube synthesis. It is not requested to change the carbon source flow rate or inert gas flow rate by variation of support material[19]. Fig. 8 explains the carbon nanotube process on the porous material.

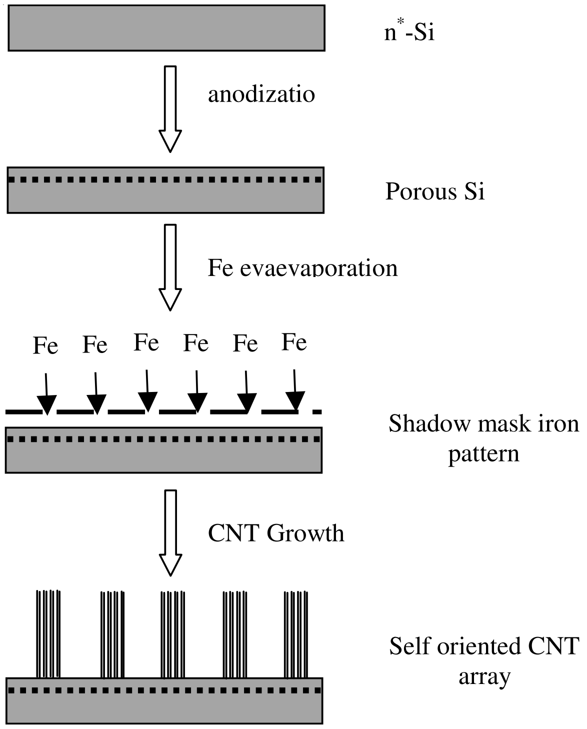

Fig. 8. Schematic process for the synthesis of regular arrays of oriented nanotubes on porous silicon by catalyst patterning and chemical vapour decomposition [Ref. 60]

Reaction time: Typically the reaction time is *ca.* 1 h for synthesis of the carbon nanotubes. In fact, the reaction time is related on the amount of desired carbon nanotube. Aberration of the optimum reaction time in the specific carbon nanotube synthesis reduces the quality of the product[19]. At the reaction time more than optimized time, the amorphous carbon is formed and deposits on both catalyst and outer surface of the carbon nanotubes due to the deactivation of catalyst as a function of the reaction time[52].

Rate of production: Recently, the single-wall carbon nanotubes are produced continuously at a rate of 1 g /h in the fluidized bed reactor. In addition, the single-wall carbon nanotubes are produced continuously with a high production yield up to 6 g/h (after purification) using an enhanced catalytic chemical vapour decomposition method, which the previously prepared catalyst has injected into the vertical furnace. The main advantage of this technique is the use of an especially designed injector which enables the introduction of a previously prepared catalyst. This catalyst consists of metal particles with sufficient diameter for the single-wall carbon nanotubes growth which are embedded in a support powder. Thus, they are protected from agglomeration during the carbon nanotube synthesis. Furthermore, this method solves the important problems related to the catalyst particle diameter and also catalyst concentration. Therefore it increases the synthesis efficiency. In addition, The usage of powder support catalysts avoid the production of undesired carbon forms because of the surfactant pyrolysis in the case of colloidal particles[21].

Purification: There are a considerable amount of impurities such as amorphous carbon, multishell carbon nanocapsules and metal particles. Therefore, the impurities removal is important for the characterization stages. There are several methods for carbon nanotubes purification[19]. In general, the purification methods are divided to two cases, wet methods and dry methods[13]. The purification can selectively remove in the dry methods but the carbon nanotubes are treated in solution in the wet methods[13]. The popular processes are described as follow:

(i) Oxidation method: One of the main processes for purification of single-wall carbon nanotube is oxidation. In purpose of amorphous carbon removal, oxidation is an effective method because the impurities tend to have more defects and open structures. Therefore, they are oxidized more easily than the carbon nanotubes. In addition to the metal, the impurities tend to attach themselves catalysts and the catalysts act as an oxidizing agent.

(ii) Acid refluxing method: Another main effective method for purification is acid refluxing. The metal catalyst removes from the product by usage of this technique, but other carbon impurities leave. As a result, a combination of these two methods included of oxidation and acid refluxing techniques are more effective. Amorphous carbon is removed in oxidation stage and the residual catalyst is removed in acid treatment stage[7]. It is an important point to control over the oxidation period to prevent burning off of the pure carbon nanotube.

(iii) Liquid-phase oxidation method: Another method for purification is using of liquid-phase oxidation such as $KMnO_4/H_2SO_4$ solution. This method is very effective to obtain the extremely pure carbon nanotubes, but during this process the final carbon nanotubes may be severely damaged.

(iv) Graphite intercalation: It is another purification method. It is investigated that the resistance to bromination of carbon nanotubes is smaller than the carbon nanoparticles.

(v) A new improved method is a multi-step purification process for removal of undesired impurities from carbon nanotubes with an improved yield. In the first step of the purification process, the ultrasonic and heat-treatment of the raw material is used for obtaining a well dispersed carbon nanotube structure[19].

The carbon yield after the purification step is determined as follows:

$$\text{Carbon yield (\%)} = 100 \times (m_{pure}/m_{crude})$$

where m_{pure} = The weight of sample after carbon nanotube production; m_{crude} = The weight of sample after purification[84].

Conclusion

Carbon nanotubes have attracted a lot of attention due to their specific properties such as mechanical, electrical, optical and thermal properties. Carbon nanotubes have been categorized to single wall carbon nanotubes and multiwall carbon nanotubes. There are several methods for carbon nanotubes synthesis, but the most suitable method for mass production is chemical vapour decomposition method. Chemical vapour decomposition syntheses are also categorized to supported catalyst growth and floating or gas-phase growth.

The operating conditions such as the operating temperature and pressure, the carbon source volume and concentration, the size and the pretreatment of metallic catalyst and the time of reaction will determine characteristics of carbon nanotubes.

Therefore, controlling the process parameters is very important for mass production. The synthesized carbon nanotubes may contain impurities such as multi-shell carbon nano capsules, amorphous carbon and metal catalysts particles. Thus, these impurities must be removed from the final products by means of a sufficient purification method.

REFERENCES

1. H.W. Kroto, J.R. Heath, S.C. O'Brein, R.F. Curl and R.E. Smalley, *Nature*, **318**, 162 (1985).
2. C.N.R. Rao and A.K. Cheetham, The Chemistry of Nanomaterials: Synthesis, Properties and Application, Wiley VCH Verlag GmbH & Co. KGaA, Vol. 2 (2004).
3. M.S. Dresselhaus, G. Dresselhaus and P.C. Eklund, Science of fullerenes and carbon nanotubes. New York: Academic Press (1996); M.S. Dresselhaus, G. Dresselhaus and P. Avouris, Carbon Nanotubes: Synthesis, Structure, Properties and Applications, Springer (2001).
4. S. Iijima, *Nature*, **354**, 56 (1991).
5. R.H. Baughman, A.A. Zakhidov and W.A. de Heer, *Science*, **297**, 787 (2002).
6. E.T. Thostenson, Z. Ren and T.-W. Chou, *Composit. Sci. Technol.*, **61**, 1899 (2001).
7. E. Pfautsch, Challenges in Commercializing Carbon Nanotube Composites, pp. 1-42 (2007).
8. C.P. Poole Jr. and F. J. Owens, Introduction to Nanotechnology, A Wiley Interscience Publication (2003).
9. M. Meyyappan, Carbon Nanotubes: Science and Applications, CRC Press LLC (2005).
10. H. Dai, *Acc. Chem. Res.*, **35**, 1035 (2002).
11. M. Terrones, *Ann. Rev. Mater. Res.*, **33**, 419 (2003).
12. Y.M. Wong, W.P.K., J.L. Davidson, B.K. Choi and J.H. Huang, *Diamond Rel. Mater.*, **15**, 1132 (2006).
13. G.D.A. Jorio, G. Dresselhaus and M.S. Dresselhaus, Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Application, Springer (2008).
14. L. Vaccarini, C. Goze, L. Henrard, E. Hernández, P. Bernier and A. Rubio, *Carbon*, **38**, 1681 (2000).
15. P.M. Ajayan, L.S. Schadler and P.V. Braun, Nanocomposite Science and Technology, Wiley VCH GmbH & Co., KGsA (2003).
16. P. Eklund, P. Ajayan, R. Blackmon, A.J. Hart, J. Kong, B. Pradhan, A. Rao and A. Rinzler, WTEC Panel Report on International Assessment of Carbon Nanotube Manufacturing and Applications (2007).
17. C.T. Kingston and B. Simard, *Anal. Lett.*, **36**, 3119 (2003).
18. F. Wei, Q. Zhang, W.-Z. Qian, H. Yu, Y. Wang, G.-H. Luo, G.-H. Xu and D.-Z. Wang, *Powder Technol.*, **183**, 10 (2008).
19. Ç. Öncel and Y. Yürüm, *Fullerenes, Nanotubes and Carbon Nanostructures*, **14**, 17 (2006).
20. P.R. Poulsen, J.B., J. Nygård, D.H. Cobden, M.M. Andreasen and P.E. Lindelof, Single-Wall Carbon Nanotube Devices Prepared By Chemical Vapor Deposition. AIP Conference Proceedings of Electron Properties of Novel Materials-Molecular Nanostructures, Vol. 21, p. 544 (2000).
21. E. Mora, T. Tokune and A.R. Harutyunyan, *Carbon*, **45**, 971 (2007).
22. C.H. See and A.T. Harris, *Chem. Eng. J.*, **144**, 267 (2008).
23. M. Pérez-Cabero, I. Rodríguez-Ramos and A. Guerrero-Ruíz, *J. Catal.*, **215**, 305 (2003).
24. Q. Weizhong, W. Fei, W. Zhanwen, L. Tang, Y. Hao, L. Guohua, X. Lan and D. Xiangyi, *AIChE J.*, **49**, 619 (2003).
25. Y.-S. Cho, G.-S. Choi, S.-Y. Hong and D. Kim, *J. Cryst. Growth*, **243**, 224 (2002).
26. S. Zhu, C.-H. Su, J.C. Cochrane, S. Lehoczky, Y. Cui and A. Burger, *J. Cryst. Growth*, **234**, 584 (2002).
27. R. Xiang, G. Luo, W. Qian, Q. Zhang, Y. Wang, F. Wei, Q. Li and A. Cao, *Adv. Mater.,* **19**, 2360 (2007).
28. Q. Zhang, W. Zhou, W. Qian, R. Xiang, J. Huang, D. Wang and F, Wei, *J. Phys. Chem. C*, **110**, 14638 (2007).
29. Y. Hao, Z. Qunfeng, W. Fei, Q. Weizhong and L. Guohua, *Carbon*, **41**, 2855 (2003).
30. C. Du and N. Pan, *Mater. Lett.*, **59**, 1678 (2005).
31. I. Kunadian, R. Andrews, M.P. Mengüç and D. Qian, *Chem. Eng. Sci.*, **64**, 1503 (2009).
32. C.H. See, K.J. MacKenzie, O.M. Dunens and A.T. Harris, *Chem. Eng. Sci.*, **64**, 3614 (2009).
33. F. Ding, K. Bolton and A. Rosén, *J. Phys. Chem. B*, **108**, 17369 (2004).
34. T.Y. Lee, J.-H. Han, S.H. Choi, J.-B. Yoo, C.-Y. Park, T. Jung, S. Yu, J. Lee, W. Yi and J.M. Kim, *Surf. Coat. Technol.*, **169-170**, 348 (2003).
35. K. Hernadi, A. Fonseca, J.B. Nagy, A. Siska and I. Kiricsi, *Appl. Catal. A: Gen.*, **199**, 245 (2000).
36. R.T.K. Baker, *Carbon*, **27**, 315 (1989).
37. S.B. Sinnott, R. Andrews, D. Qian, A.M. Rao, Z. Mao, E.C. Dickey and F. Derbyshire, *Chem. Phys. Lett.*, **315**, 25 (1999).
38. J.A. Elliott and Y. Shibuta, *Molecul. Simulat.*, **34**, 891 (2008).
39. A.G. Nasibulin, P.V. Pikhitsa, Hua Jiang and E.I. Kauppinen, *Carbon*, **43**, 2251 (2005).
40. C.L. Cheung, A. Kurtz, H. Park and C.M. Lieber, *J. Phys. Chem. B*, **106**, 2429 (2002).
41. Á. Kukovecz, Z. Kónya, N. Nagaraju, I. Willems, A. Tamási, A. Fonseca, J.B. Nagy and I. Kiricsi, *Phys. Chem. Chem. Phys.*, **2**, 3071 (2000).
42. M. Mayne, N. Grobert, M. Terrones, R. Kamalakaran, M. Rühle, H.W. Kroto and D.R.M. Walton, *Chem. Phys. Lett.*, **338**, 101 (2001).
43. R. Sen, A. Govindaraj and C.N.R. Rao, *Chem. Phys. Lett.*, **267**, 276 (1997).
44. Z.J. Zhang, B.Q. Wei, G. Ramanath and P.M. Ajayan, *Appl. Phys. Lett.*, **77**, 3764 (2000).
45. M.A. Ermakova, D. Yu. Ermakov, A.L. Chuvilin and G.G. Kuvshinov, *J. Catal.*, **201**, 183 (2001).
46. Z.W. Pan, S.S. Xie, B.H. Chang, L.F. Sun, W.Y. Zhou and G. Wang. *Chem. Phys. Lett.*, **299**, 97 (1999).
47. V. Ivanov, J.B. Nagy, Ph. Lambin, A. Lucas, X.B. Zhang, X.F. Zhang, D. Bernaerts, G. Van Tendeloo, S. Amelinckx and J. Van Landuyt, *Chem. Phys. Lett.*. **223**, 329 (1994).
48. C. Klinke, J.-M. Bonard and K. Kern, *Surface Sci.*, **492**, 195 (2001).
49. D. Venegoni, P. Serp, R. Feurer, Y. Kihn, C. Vahlas and P. Kalck, *Carbon*, **40**, 1799 (2002).
50. K. Hernadi, A. Fonseca, J.B. Nagy, D. Bemaerts, A. Fudala and A.A. Lucas, *Zeolites*, **17**, 416 (1996).
51. A. Fonseca, K. Hernadi, J.B. Nagy, D. Bernaerts and A.A. Lucas, *J. Mol Catal A: Chem*., **107**, 159 (1996).
52. H. Cui, O. Zhou and B. R. Stoner, *J. Appl. Phys.*, **88**, 6072 (2000).
53. A. Sacco Jr., P. Thacker, T.N. Chang and A.T.S. Chiang, *J. Catal.*, **85**, 224 (1984).
54. A.M. Valiente, P.N. López, I.R. Ramos, A.G. Ruiz, C. Li and Q. Xin. *Carbon*, **38**, 2003 (2000).
55. Y.H. Wang, J. Lin, C.H.A. Huan and G.S. Chen, *Appl. Phys. Lett.*, **79**, 680 (2001).
56. G.S. Duesberg, A.P. Graham, M. Liebau, R. Seidel, E. Unger, F. Kreupl and W. Hoenlein, *Nano Lett.*, **3**, 257 (2003).
57. S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell and H. Dai, *Science*, **283**, 512 (1999).
58. S. Fan, W. Liang, H. Dang, N. Franklin, T. Tombler, M. Chapline and H. Dai. *Physica E*, **8**, 179 (2000).
59. Z.W. Pan, S.S. Xie, B.H. Chang, C.Y. Wang, L. Lu, W. Liu, W.Y. Zhou, W.Z. Li and L.X. Qian, *Nature Material*, **394**, 631 (1998).
60. K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts and A.A. Lucas, *Carbon*, **34**, 1249 (1996).
61. P. Nikolaev, M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert, K.A. Smith and R.E. Smalley, *Chem. Phys. Lett.*, **313**, 91 (1999).
62. H. Hongo, M.Y., T. Ichihashi, F. Nihey and S. Iijima, *Chem. Phys. Lett.,* **361**, 349 (2002).
63. H.M. Cheng, F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun and M.S. Dresselhaus, *Appl. Phys. Lett.*, **72**, 3282 (1998).
64. W. Kim, H.C.C., M. Shim, Y. Li, D. Wang and H. Dai, *Nano Lett.*, **2**, 703 (2002).
65. T. Hayashi, Y.A. Kim, T. Matoba, M. Esaka, K. Nishimura, T. Tsukada, M. Endo and M.S. Dresselhaus, *Nano Lett.*, **3**, 887 (2003).
66. YY. Zhang, Y. Li, W. Kim, D. Wang and H. Dai, *Appl. Phys. A*, **74**, 325 (2002).
67. B.C. Satishkumar, A. Govindaraj, R. Sen and C.N.R. Rao, *Chem. Phys. Lett.*, **293**, 47 (1998).
68. Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang and H. Dai, *J. Phys. Chem. B*, **105**, 11424 (2001).
69. Y.C. Choi, Y.M.S., Y.H. Lee, B.S. Lee, G.-S. Park, W.B. Choi, N.S. Lee and J.M. Kim, *Appl. Phys. Lett.*, **76**, 2367 (2000).
70. L. Valentini, J.M.K., L. Lozzi and S. Santucci, *J. Appl. Phys.*, **92**, 6188 (2002).
71. J. Jiao and S. Seraphin, *J. Phys. Chem. Solids*, **61**, 1055 (2000).

72. K.B.K. Teo, M. Chhowalla, G.A.J. Amaratung, W.I. Milne, D.G. Hasko, G. Pirio, P. Legagneux, F. Wyczisk and D. Pribat, *Appl. Phys. Lett.*, **79**, 1534 (2001).
73. Z.P. Huang, J.W. Xu, Z.F. Ren, J.H. Wang, M.P. Siegal and P.N. Provencio, *Appl. Phys. Lett.*, **73**, 3845 (1998).
74. M. Yudasaka, R. Kikuchi, Y. Ohki, E. Ota and S. Yoshimura, *Appl. Phys. Lett.*, **70**, 1817 (1997).
75. Z.F. Ren, Z.P.H., J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal and P.N Provencio, *Science*, **282**, 1105 (1998).
76. W.D. Zhang, Y. Wen, W.C. Tjiu, G.Q. Xu and L.M. Gan, *Appl. Phys. A*, **74**, 419 (2001).
77. K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, G. Pirio, P. Legagneux, F. Wyczisk, J. Olivier and D. Pribat, *J. Vac. Sci. Technol. B*, **20**, 116 (2002).
78. P.E. Nolan, D.C. Lynch and A.H. Cutle, *J. Phys. Chem. B*, **102**, 4165 (1998).
79. A.C. Wright, Y. Xiong, N. Maung, S.J. Eichhorn and R.J. Young, *Mater. Sci. Eng. C*, **23**, 279 (2003).
80. M. Yudasaka, R. Kikuchi, T. Matsui, Y. Ohki, S. Yoshimura and E. Ota, *Appl. Phys. Lett.*, **67**, 2477 (1995).
81. M.P. Siegal, D.L. Overmyer and P.P. Provencio, *Appl. Phys. Lett.*, **80**, 2171 (2002).
82. E.F. Kukovitsky, S.G. Lvov, N.A. Sainov, V.A. Shustov and L.A. Chernozatonskii, *Chem. Phys. Lett.*, **355**, 497 (2002).
83. J.F. Colomer, G. Bister, I. Willems, Z. Konya, A. Fonseca, G. Van Tendeloo and J.B. Nagy, *Chem. Commun.*, **14**, 1343 (1999).
84. J.-F. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z. Kónya, A. Fonseca, Ch. Laurent and J.B. Nagy, *Chem. Phys. Lett.*, **317**, 83 (2000).
85. R. Seidel, G.S. Duesberg, E. Unger, A.P. Graham, M. Liebau and F. Kreupl, *J. Phys. Chem. B*, **108**, 1888 (2004).
86. M. Chhowalla, K.B.K. Teo, C. Ducati, N.L. Rupesinghe, G.A.J. Amaratunga, A.C. Ferrari, D. Roy, J. Robertson and W.I. Milne, *J. Appl. Phys.*, **90**, 5308 (2001).
87. H. Ago, K.Murata, M. Yumura, J. Yotani and S. Uemura, *Appl. Phys. Lett.*, **82**, 811 (2003).
88. C. Bower, W Zhu, S. Jin and O. Zhou, *Appl. Phys. Lett.*, **77**, 830 (2000).
89. S.-H. Jeong, H.-Y.H., K.-H. Lee and Y. Jeong, *Appl. Phys. Lett.*, **78**, 2052 (2001).
90. H. Ago, T. Komatsu, S. Ohshima, Y. Kuriki and M. Yumura, *Appl. Phys. Lett.*, **77**, 79 (2000).
91. C.M. Hsu, C.H. Lin, H.L. Chang and C.T. Kuo, *Thin solid films*, **420-421**, 225 (2002).
92. M. Terrones, N. Grobert, J. Olivares, J.P. Zhang, H. Terrones, K. Kordatos, W. K. Hsu, J.P. Hare, P.D. Townsend, K. Prassides, A.K. Cheetham, H.W. Kroto and D.R.M. Walton, *Nature Material*, **388**, 52 (1997).
93. S. Helveg, C. López-Cartes, J. Sehested, P.L. Hansen, B.S. Clausen, J.R. Rostrup-Nielsen, F. Abild-Pedersen and J.K. Nørskov, *Nature Material*, **427**, 426 (2004).
94. M. Terrones, N. Grobert, J.P. Zhang, H. Terrones, J. Olivares, W.K. Hsu, J.P. Hare, A.K. Cheetham, H.W. Kroto and D.R.M. Walton, *Chem. Phys. Lett.*, **285**, 299 (1998).
95. L. Marty, V. Bouchiat, A. M. Bonnot, M. Chaumont, T. Fournier, S. Decossas and S. Roche, *Microelectr. Eng.*, **61-62**, 485 (2002).
96. Y. Zhang, W. Zhou, Z. Jin, L. Ding, Z. Zhang, X. Liang and Y. Li. *Chem. Mater.*, **20**, 7521 (2008).
97. Y.-G. Baek, S.-i. Honda, T. Ikuno, S. Ohkura, M. Katayama, T. Hirao and K. Oura, *Japan. J. Appl. Phys.*, **42**, 579 (2003).
98. J.-G. Wang, C.-J. Liu, Y.-P. Zhang, X.-L. Zhu, K.-L. Yu and J. Zou, *Mol. Simult.*, **29**, 667 (2003).
99. Y Yang, Z Hu, Y.J. Tian, Y.N. Lu, X.Z. Wang and Y. Chen, *Nanotechnology*, **14**, 733 (2003).
100. I. Willems, Z. Kónya, J.-F. Colomer, G. Van Tendeloo, N. Nagaraju, A. Fonseca and J.B. Nagy, *Chem. Phys. Lett.*, **317**, 71 (2000).
101. S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi and M. Kohno, *Chem. Phys. Lett.*, **360**, 229 (2002).
102. B. Chen, G. Parker II, J. Han, M. Meyyappan and A.M. Cassell, *Chem. Mater.*, **14**, 1891 (2002).
103. Y. Murakami, Y. Miyauchi, S. Chiashi and S. Maruyama, *Chem. Phys. Lett.*, **374**, 53 (2003).
104. A.M. Cassell, G.C. McCool, H.T. Ng, J.E. Koehne, B. Chen, J. Li, J. Han and M. Meyyappan, *Appl. Phys. Lett.*, **82**, 817 (2003).
105. J. Kong, H.T. Soh, A.M. Cassell, C.F. Quate and H. Dai, *Nature*, **395**, 878 (1998).
106. G.L. Hornyak, L. Grigorian, A.C. Dillon, P.A. Parilla, K.M. Jones and M.J. Heben, *J. Phys. Chem. B*, **106**, 2821 (2002).
107. Y. Li, J. Liu, Y. Wang and Z.L. Wang, *Chem. Mater.*, **13**, 1008 (2001).
108. A.R. Harutyunyan, B.K. Pradhan, U.J. Kim, G. Chen and P.C. Eklund, *Nano Lett.*, **2**, 525 (2002).
109. B. Zheng, Y. Li and J. Liu, *Appl. Phys. A*, **74**, 345 (2002).
110. A.M. Cassell, J.A. Raymakers, J. Kong and H. Dai, *J. Phys. Chem. B*, **103**, 6484 (1999).
111. L. Delzeit, B. Chen, A. Cassel, R. Stevens, C. Nguyen and M. Meyyappan, *Chem. Phys. Lett.*, **348**, 368 (2001).
112. N.R. Franklin, Y. Li, R.J. Chen, A. Javey and H. Dai, *Appl. Phys. Lett.*, **79**, 4571 (2001).
113. M. Su, Y. Li, B. Maynor, A. Buldum, J.P. Lu and J. Liu, *J. Phys. Chem. B*, **104**, 6505 (2000).
114. M. Su, B. Zheng and J. Liu, *Chem. Phys. Lett.*, **322**, 321 (2000).
115. J.H. Hafner, M.J. Bronikowski, B.R. Azamian, P. Nikolaev, A.G. Rinzler, D.T. Colbert, K.A. Smith and R.E. Smalley, *Chem. Phys. Lett.*, **296**, 195 (1998).
116. H. Cui, G. Eres, J.Y. Howe, A. Puretkzy, M. Varela, D.B. Geohegan and D.H. Lowndes, *Chem. Phys. Lett.*, **374**, 222 (2003).
117. H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert and R.E. Smalley, *Chem. Phys. Lett.*, **260**, 471 (1996).
118. H. Ago, S. Ohshima, K. Uchida and M. Yumura, *J. Phys. Chem. B*, **105**, 10453 (2001).
119. J.E. Herrera and D,E, Resasco, *J. Catal.*, **221**, 354 (2004).
120. W.E. Alvarez, B. Kitiyanan, A. Borgna and D.E. Resasco, *Carbon*, **39**, 547 (2001).
121. Y. Murakami, Y. Miyauchi, S. Chiashi and S. Maruyama, *Chem. Phys. Lett.*, **374**, 49 (2003).
122. A. Lan, Z. Iqbal, A. Aitouchen, M. Libera and H. Grebel, *Appl. Phys. Lett.*, **81**, 433 (2002).
123. B. Kitiyanan, W.E. Alvarez, J.H. Harwell and D.E. Resasco, *Chem. Phys. Lett.*, **317**, 497 (2000).
124. J.E. Herrera, L. Balzano, A. Borgna, W.E. Alvarez and D.E. Resasco, *J. Catal.*, **204**, 129 (2001).
125. H. Ago, S. Ohshima, K. Uchida, T. Komatsu and M. Yumura, *Physica B*, **323**, 306 (2002).
126. S Tang, Z Zhong, Z Xiong, L Sun, L Liu, J Lin, Z.X Shen and K.L Tan. *Chem. Phys. Lett.*, **350**, 19 (2001).
127. W.Z. Qian, T.L., Z.W. Wang, H. Yu, Z.F. Li, F. Wei and G.H. Luo, *Carbon*, **41**, 2487 (2003).
128. W.Z. Qian, F. Wei, T. Liu and Z.W. Wang, *Solid State Commun.*, **126**, 365 (2003).
129. Q. Zhang, W.Z. Qian, H. Yu, F. Wei and Q. Wen, *Appl. Phys. A*, **86**, 265 (2007).
130. H. Endo, K. Kuwana, K. Saito, D. Qian, R. Andrews and E.A. Grulke, *Chem. Phys. Lett.*, **387**, 307 (2004).
131. E. Mora and A.R. Harutyunyan, *J. Phys. Chem. C*, **112**, 4805 (2008).