

Theoretical Descriptions of Carbon Nanotubes Synthesis in a Chemical Vapor Deposition Reactor: A Review

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Review

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The mechanisms by which carbon nanotubes nucleate and grow are still poorly understood. Understanding and mathematically describing the process is crucial for its optimization. This paper reviews different models which have been proposed to explain carbon nanotube growth in the chemical vapor deposition process. The review is divided into two sections, the first section describes some nucleation, growth and termination simulations based on molecular dynamics, and the second section describes some mathematical models based on transport and kinetics theories.

Key words:

Carbon nanotubes, CVD, growth simulations, kinetics

1. Introduction

Carbon nanotubes (CNTs) are one of the key materials in nanotechnology and are currently among the most intensively investigated materials. Since their first TEM observation by Iijima¹ in 1991 CNTs have been a subject of many researchers due to their unique mechanical,^{2–4} electrical^{5–7} and thermal^{8–10} properties. CNTs are a promising material for applications such as carbon nanotube-polymer composites,^{11,12} extra strong yarns of carbon nanotubes,^{13,14} nanoelectronics,^{15,16} hydrogen storage,¹⁷ etc. The CNTs mechanical, electric and thermal properties are strongly dependent on their structure; therefore many research groups investigate theoretical relations between structural characteristics and CNTs quality.^{18,19}

The simplest way to visualize the structure of a single-walled carbon nanotube (SWCNT) is to consider a graphene sheet rolled up to form a cylinder. SWCNTs have small diameters (around 1 nm), since multi-walled carbon nanotubes (MWCNTs) which are composed of multiple coaxial SWCNTs have diameters from 4 nm to 20 nm and more if the number of walls is very high.

At the beginning of research, carbon nanotubes were produced only by the arc-evaporation technique,¹ but many more advanced techniques have arisen in the course of investigation. One of the most promising is a catalytic method known as chemical vapor deposition (CVD). The key features of this method are pyrolysis of hydrocarbon over the catalyst particle and carbon deposition on the active site in the form of a nanotube.²⁰

Despite the importance of the chemical vapor deposition method of nanotube synthesis, the theoretical description of the process has not been fully developed, although many researches were carried out about this subject.^{21,22} Without such understanding, there is not much hope of developing techniques for preparing nanotubes with defined structures. This paper is a review of various mechanisms and mathematical models for the synthesis of carbon nanotubes by the CVD method. There are many features which directly influence the shape, length, number of walls, and chirality of CNTs. Growth begins with (i) nucleation, which is the crucial process that defines the CNT diameter and the number of walls. Generally, the nanotube does not change its diameter and wall number during (ii) growth, unless the synthesis parameters change dramatically or unexpected defects take place in CNT structure. The final process is (iii) termination, which is caused by catalyst deactivation, lack of reactants due to high transport resistances and other usually unwanted phenomena. The growth rate of CNTs is defined by growth kinetics, activation energy and transport resistances, which are topics of many research groups.

The first section of this review describes simulations of CNTs formation, growth and termination. These descriptions are mostly based on molecular dynamics (MD) simulation methods. MD simulation is a technique that allows us to generate the atomic trajectories of a system of N particles by numerical integration of Newton's equation of motion for a specific interatomic potential.²³

The second section of this review deals with the kinetics, transport phenomena, activation energies and other values that can be numerically de-

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fined and verified with experiments. The order of reaction and activation energy can be experimentally determined by changing reaction parameters such as concentration, temperature, and pressure.

2. Experimental details

The catalytic method of producing CNTs was discovered shortly after the first CNT observation by Iijima.¹ Some of the first experimental observations of catalytically produced CNTs were made by Ivanov *et al.*²⁴ and Hernadi *et al.*²⁵

Set up for chemical vapor deposition (CVD) synthesis of carbon nanotubes is shown in Fig. 1.

The carbon source is typically a hydrocarbon such as acetylene, ethylene, toluene, ethanol etc. If the source is a liquid at room temperature, then it is usually supplied by a bubbler. The carrier gases are a mixture of inert gas and hydrogen, used as reducing agent. The concentration of reactants in the mixture is determined by accurate flow meters. The mixture of gases is supplied into the quartz tube, which is inside a furnace operating at 500 °C to 1200 °C. Inside the tube, there is a porous substrate with a thin alloy of catalyst such as iron, nickel, cobalt or other metals. The substrate with the catalyst is an active site for carbon nanotubes growth. The gases exiting the quartz tube are directed through the cleaning bubbler and filters before they are re-

leased into the atmosphere. Some CVD systems include vacuum pumps for pressure control, which in addition to temperature and concentration is an important parameter that defines nanotubes properties.

3. CNTs formation mechanisms

CNTs formation mechanism is very complicated and not fully understood, which is why the proposed theories on nucleation and growth of CNTs differ. There are two widely recognized mechanisms of CNTs formation: root growth and tip growth. The difference between these mechanisms is in the catalyst nanoparticle position during the growth of CNTs. Root growth mechanism is involved when a catalyst particle remains on the substrate surface.²⁶ If the catalyst is lifted from the surface along with the CNT, then the proposed mechanism is tip growth.²⁷ Tip growth usually occurs when there is a weak catalyst – substrate interaction, while root growth occurs when the interaction is strong. Fig. 2 presents the difference between tip and root growth.

In general, the desirable mechanism in CVD synthesis is root growth, since CNTs produced in this way are longer, more symmetrical, and better aligned than those produced by tip growth mechanism.²⁵ The mechanism of SWCNTs production is usually root growth, but MWCNTs can be produced

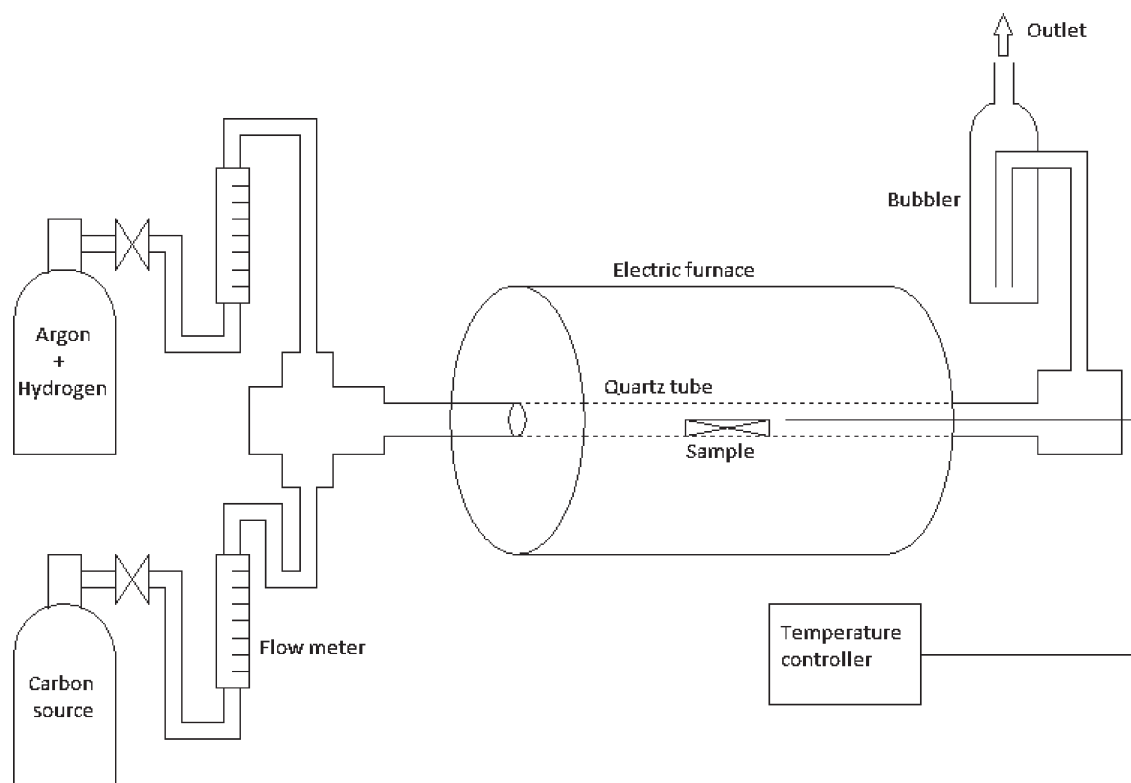


Fig. 1 – Scheme of a typical CVD apparatus for the production of carbon nanotubes

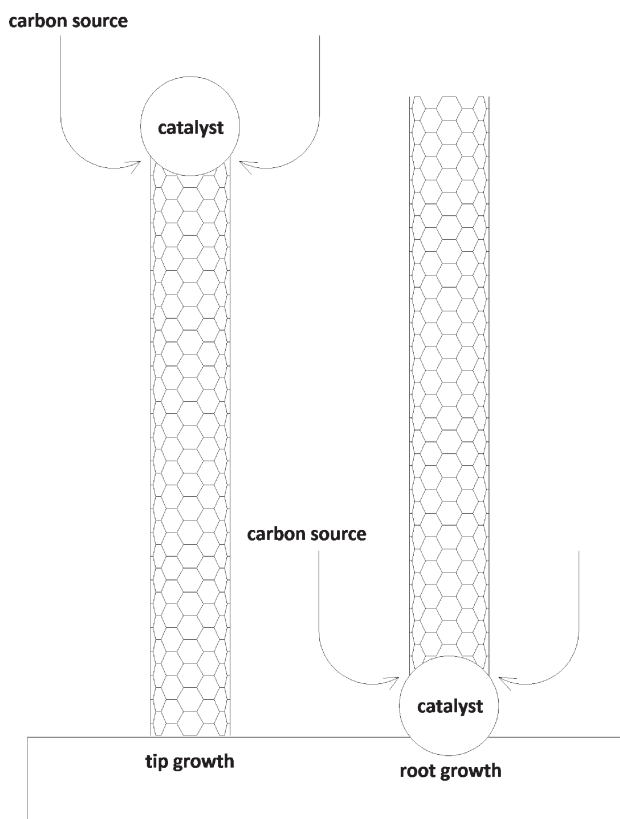


Fig. 2 – Tip growth and root growth mechanisms of CNT formation. The arrows show the carbon source flow towards the active site.

by both growth mechanisms. Methods of switching between growth mechanisms have been reported by Dijon *et al.*²⁸ They demonstrated that the oxidation state of the catalyst determines the growth mechanism. Their experiments have shown, that the catalyst in oxidized form remains on the substrate during the synthesis (root growth), while the catalyst in reduced form detaches from the substrate in the course of CNT growth (tip growth).

First MD investigation of CNT formation was performed by Shibuta and Maruyama²⁹ in 2002. They started from randomly distributed carbon and nickel atoms and obtained cage structures of carbon atoms after 6 ns. Their simulations showed that the collisions of random cage structures of carbon lead to the formation of tubular structures.

An important step in understanding the formation of CNTs was the proposition of Vapor-Liquid-Solid model in CVD synthesis.³⁰ The model assumes that the first stage of nanotube formation involves the co-condensation of carbon and metal atoms from the vapor phase to form a liquid metal carbide particle. When the particles are supersaturated, solid phase nanotubes begin to grow. The driving force for the diffusion of carbon through the particles is either a temperature gradient or a concentration gradient.

3.1. Nucleation mechanism

Nucleation is the most important step in CNTs production, since it defines the shape, wall number and geometry of the product. The diameter of CNTs is strongly dependent on the diameter of the catalyst particle – it is approximately the same size as the catalyst nanoparticle.³¹ Since the diameter also defines the number of walls of CNTs, there is a strong connection between the catalyst particle diameter and the number of walls. Many research groups have developed models of vapor-liquid-solid (VLS) mechanisms related to CVD synthesis.

Molecular dynamics simulations of the formation process of SWCNTs were performed by Bolton *et al.*³² They assume a VLS mechanism in which catalyst nanoparticles become saturated with carbon and then small graphitic islands nucleate on the catalyst particle surface. After that, if conditions are appropriate, the graphitic island can lift off the particle forming a cap, which later grows into a tube. The simulation techniques are based on the Brenner bond order potential in its simplified form. A basic assumption of VLS mechanism is that carbon diffuses through a liquid metal particle, driven by concentration and temperature gradient.

A different mechanism was proposed by Raty *et al.*³³ They modeled the CVD growth of SWCNTs on Fe nanoparticles using *ab initio* molecular dynamics. The molecular dynamics (MD) method determines trajectories of molecules by numerical solving of Newton's equation of motion for a system of interacting particles. While the classic MD simulation assumes a pre-specified connectivity among the atoms, *ab initio* combines finite temperature dynamics with forces obtained from electronic structure calculations performed "on the fly" as the molecular dynamics simulation proceeds. According to the results of their investigations, carbon does not dissolve in the Fe nanoparticles, but instead diffuses onto the surface of the catalyst, and then forms a graphene sheet with the form of a nanotube cap. Carbon atoms then diffuse to the root and are incorporated into the growing tube. A snapshot from *ab initio* simulation is shown in Fig. 3.

In 2010 Page *et al.*³⁴ investigated the mechanism and kinetics of SWCNTs nucleation from Fe- and Ni-carbide nanoparticles using quantum molecular dynamics methods. They employed a self-consistent charge density-functional tight-binding (SCC-DFTB/MD) method, in conjunction with model Fe_xC_y and Ni_xC_y nanoparticle precursors. Their simulations showed that SWCNTs nucleation occurred in three distinct stages. The first stage is precipitation of carbon from the carbide nanoparticle bulk, the second stage is the formation of a surface/subsurface carbide species and the third

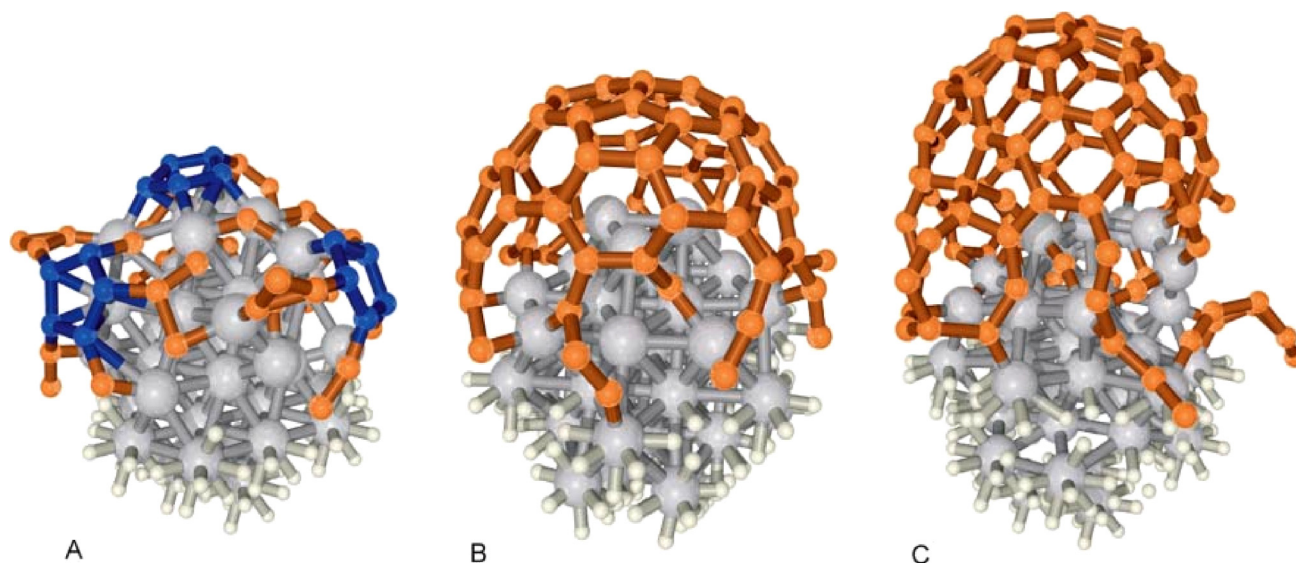


Fig. 3 – Early stage of SWCNT growth on a 1 nm Fe catalyst. Metal atoms are represented in gray, carbon atoms in brown. Reprinted with permission.³³

stage is the formation of a nascent sp^2 -hybridized carbon cap structure. Their simulation showed no difference in the carbon nanotube nucleation mechanism when changing the synthesis temperature and concentration, but there were distinct dependences of nucleation kinetics on the mentioned parameters. The simulation also suggested that nucleation from Ni_xC_y nanoparticles proceeded more favorably compared to nucleation from Fe_xC_y nanoparticles. The mechanism of SWNT nucleation from Ni_xC_y nanoparticle precursors observed in this work is shown in Fig. 4.

3.2. Growth mechanism

The growth of carbon nanotubes is the step that defines the length and shape of the CNTs. The growth mechanism does not usually change during the synthesis unless there are radical changes in synthesis parameters, such as rapid temperature or concentration changes. Changing the growth mechanism gives us the opportunity to make specially shaped CNTs for specific applications. One example is changing the mechanism from root to tip growth, which was discussed in Chapter 3 of this review. Growth mechanism models also describe the formation of various CNT shapes, such as helical CNTs or nanocoils.

Among the first models proposed for catalytic growth of CNTs was the research done by Amelinckx *et al.*³⁵ The model is based on the spatial-velocity hodograph shown in Fig. 5, which explains the extrusion of the carbon tubule from catalytic nanoparticles. The model can describe straight CNTs formation as well as the formation of helical and differently shaped CNTs. They suggested that

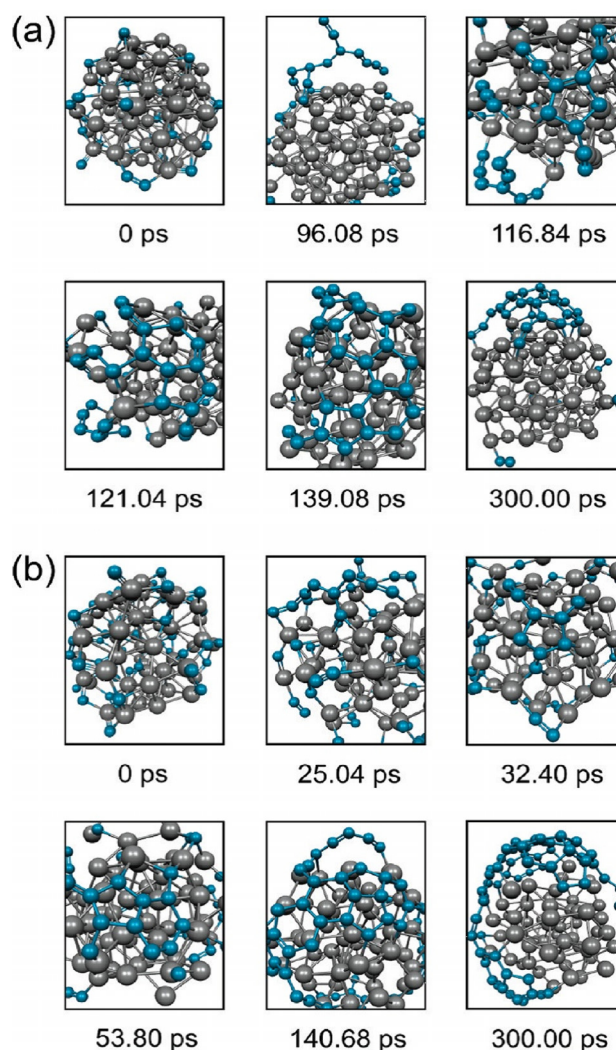


Fig. 4 – Evolution of SCC-DFTB/MD simulations of SWNT nucleation at 1400 K from Ni_xC_y nanoparticle precursors. (a) Trajectory $Ni_{77}C_{59}$ at 1400 K and (b) Trajectory $Ni_{58}C_{58}$ at 1400 K. Reprinted with permission.³⁴

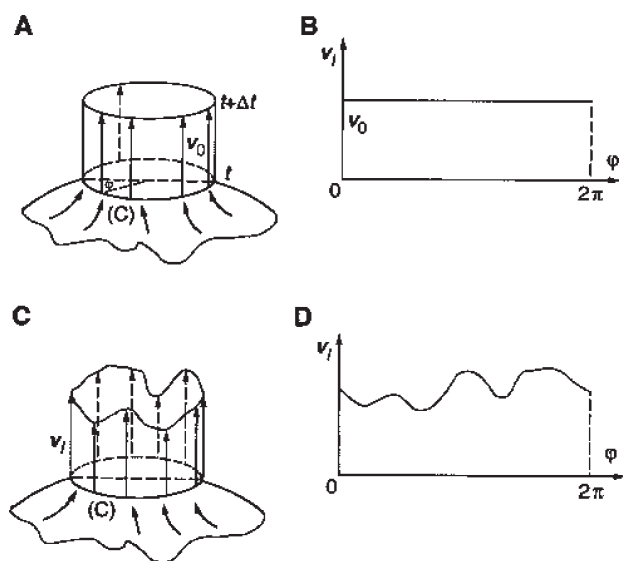


Fig. 5 – Hodograph of the extrusion velocities for the formation of straight tubules. The locus of active sites is a circle (C). A) Spatial hodograph with constant extrusion velocity, B) Planar hodograph corresponding to A), C) General spatial hodograph, D) Planar hodograph corresponding to C). Reprinted with permission.³⁵

catalyst particle is anisotropic and inhomogeneous, and that consecutively leads to different extrusion speeds of carbon and CNTs of various shapes. However, the model disregards the atomic structure of CNTs and considers the graphene sheet as a continuum. The model is valid for the prediction of CNT growth by the tip and root growth mechanism.

The growth model proposed by Gao *et al.*³⁶ includes the atomic structure of CNTs and describes details of helical CNTs formation. The model suggests that the creation rates of pentagon and heptagon carbon rings determine the geometrical shape of CNT. It is proposed, that pairing of pentagonal-heptagonal carbon rings is essential in forming the helical structure. Their statements are confirmed by observations on the high-resolution transmission electron microscope.

Grujicic *et al.*³⁷ analyzed the growth of CNTs during the transition-metal particles catalytically-assisted thermal decomposition of methane in hydrogen as the carrier gas at the atomic scale using the kinetic Monte Carlo method. With this method, one surface/edge reaction is allowed to take place at one nanotube surface/edge site during each step. At each time step, a list of all possible events is constructed and the probability for each event is set proportional to the rate of the associated surface reaction scaled by a sum of the rates of all possible events. The kinetic Monte Carlo method for chemical vapor deposition simulations was developed by Battaile *et al.*³⁸ The method has proven to be very successful for CNTs growth simulations and predic-

tion of the diameter and the number of walls for different synthesis conditions. Evolution of the CNT morphology during growth under the CVD processing conditions is presented in Fig. 6.

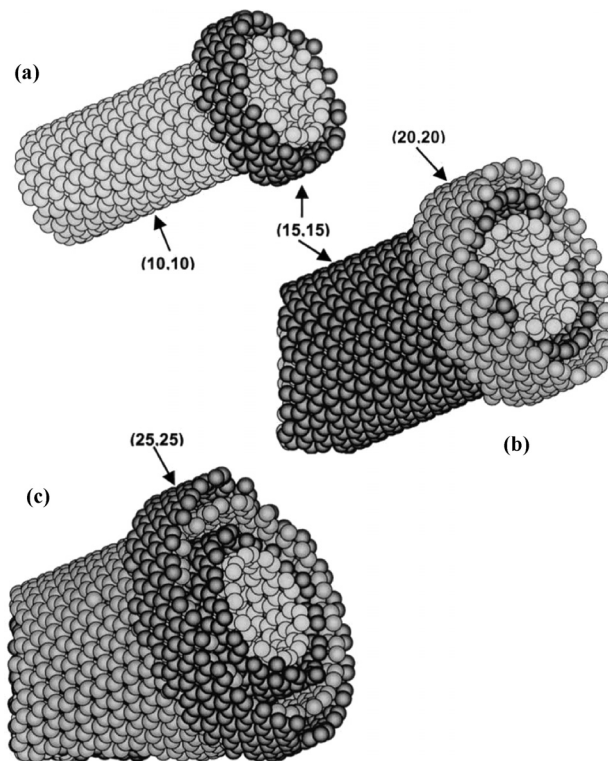


Fig. 6 – The nanotube morphology at three different simulation times: a) 1 s, b) 3.2 s and c) 6.5 s. Reprinted by permission.³⁷

Quantum molecular dynamics simulations based on the self-consistent charge density-functional tight-binding (SCC-DFTB) method was demonstrated by Ohta *et al.*³⁹ in 2008. They presented trajectories of 45 ps in length, where continuous supply of carbon atoms is directed toward the C-Fe boundary between SWNT fragment and an attached Fe cluster. Formations of five- six- and seven-membered carbon rings extend tube sidewall, resulting in overall continued growth of the SWCNT. They generated a continuous graphical presentation of the model with a plot of tube length versus time from 0 to 45 ps shown in Fig. 7.

Recent investigations on CNT chirality were performed by Neyts *et al.*⁴⁰ using hybrid reactive molecular dynamics/force-biased Monte Carlo simulations. The CNT growth was simulated on a Ni₄₀ cluster. Their simulations have shown that the chirality of CNT changes during the carbon network restructuring process. This is the first growth simulation of an armchair SWCNT with a definite chirality on a surface-bound catalyst.

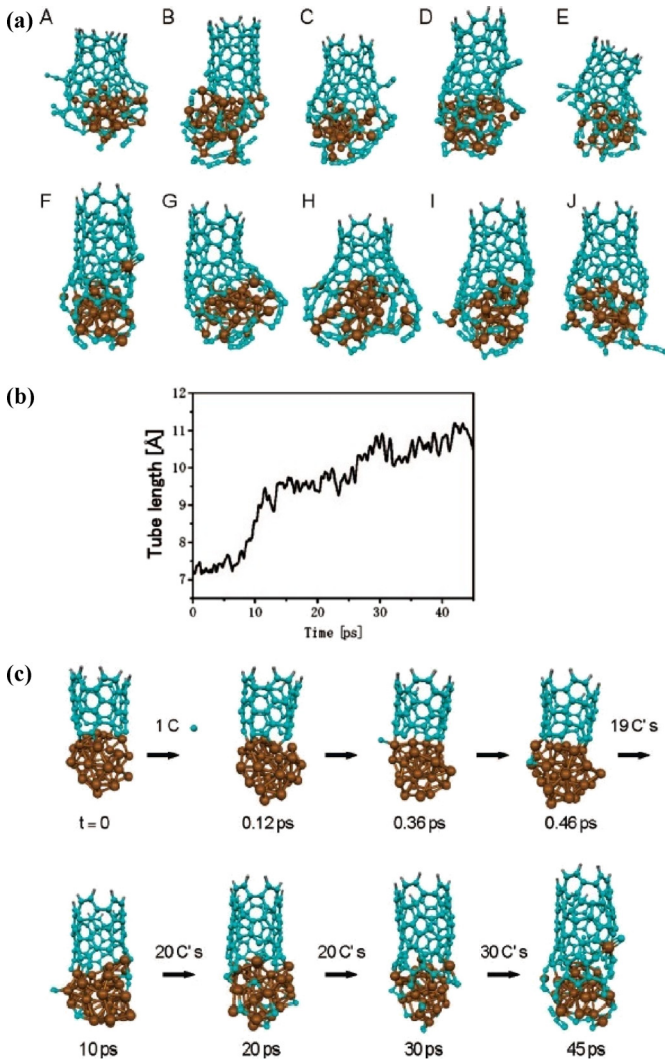


Fig. 7 – Growth process of a seed nanotube on an Fe_{38} cluster. a) Structures of 10 trajectories after 45 ps simulation. For trajectory F, b) length of the nanotube versus time and c) snapshots of trajectory F at relevant intervals. Reprinted by permission.³⁹

3.3. Termination mechanism

Termination of CNT growth is a process that defines when the nanotube stops growing and determines the maximum length of CNTs produced. Termination usually occurs due to catalyst deactivation or increase in diffusion resistance of reactants feed due to CNTs forest length. Termination of growth can be induced either by a decrease of reactants concentration or a decrease of synthesis temperature. Understanding the termination process is very important for the production of long CNTs, since it must be delayed for as long as possible in that case.

A model based on the catalyst phase transformation using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory^{41–43} was proposed by Wang *et al.*⁴⁴ The JMAK theory has been extensively applied to

solid-state phase transformations and surface growth kinetics since its introduction and is therefore suitable for CNT growth simulations. The results indicated that the mechanism for the sudden termination of CNT growth could be the phase transformation of iron carbide from cementite to Hägg carbide. The model-based assumptions were confirmed by experimental results.

Han *et al.*⁴⁵ proposed a model to explain growth termination caused by deflection of the top surface of CNTs by mechanical coupling between neighboring nanotubes. The model is based on Monte Carlo simulation of film growth, which can qualitatively reproduce the shape by assuming that the coupling is limited by the thermodynamics of the carbon forming reaction.

4. Transport and kinetics simulations

CNTs production rate is determined by numerous phenomena such as bulk diffusion, surface diffusion, interparticle diffusion, activation energies, etc. The overall goal of modeling the CNTs synthesis is to predict the yield of CNTs in a CVD reactor. A predictive model should consider the growth of CNTs at the catalyst surface including the effect of catalyst deactivation, formation of catalyst nanoparticles and detailed gas-phase reactions. Many research groups investigate the transport and kinetics phenomena of CNTs synthesis, including all steps from the transport of reactants from bulk fluid flow to surface reactions on active sites.

Optimization of the CNT synthesis reactor is very complex due to many different steps of this heterogeneous process. It is possible to simplify models with some experimental data, such as growth rates at different temperatures and partial pressures of reactants, from which we can calculate activation energies of individual steps and the order of the CNT synthesis reaction. Liu *et al.*⁴⁶ developed a simple growth mark method to make marks during the growth process of carbon nanotube arrays. Based on this method, the growth rates at different temperatures and under different reactant concentrations were measured, from which the activation energy and the order of reaction were determined.

A coupled boundary-layer laminar-flow hydrodynamic, heat-transfer, gas-phase chemistry and surface chemistry model was developed by Grujicic *et al.*⁴⁷ to analyze the deposition of carbon and CNTs growth in a CVD reactor. They developed a simulation method using a system of steady-state conservation equations including momentum conservation equation, K_g gas-phase species conservation equations, energy conservation equation and

equation of state for gas phase. The model predicts CNTs and amorphous carbon deposition rates and CNTs growth rates, which are in good agreement with experimental data. The model was developed to maximize the overall carbon deposition rate and to maximize the amount of carbon deposited as nanotubes.

An axisymmetric two-dimensional computational fluid dynamics (CFD) model to predict the production rate of CNTs from xylene in a CVD reactor was presented by Endo *et al.*⁴⁸ Two gas-phase reactions and four surface reactions were considered in this model. It was assumed that the diffusion rate in the iron/carbon system is at equilibrium and does not affect the concentrations in the gas-phase; therefore a global rate equation for surface reaction for each carbon source could be used. The considered reactions were based on the tail gas analysis from the experimental reactor. The CFD model predicted uniform velocity and temperature distributions in the CVD reactor, a favorable condition for producing uniform quality CNTs. The calculated total production rate of CNTs is in 90 % agreement with the experiments, indicating that the proposed reactions were reasonably accurate for the prediction of CNTs production rate.

The CFD model was also applied by Kuwana *et al.*⁴⁹ for the prediction of the formation process of iron nanoparticles used as catalyst. The model includes nucleation, surface growth and collision of nanoparticles. Because the detailed kinetic information on reactions between ferrocene and the radicals is not available, an overall ferrocene decomposition suggested by Linteris *et al.*⁵⁰ was adopted. The model predicted increased particle diameter with increased temperature, and this was confirmed with experimental data.

Recently, a growth model for CNTs in a horizontal tube reactor has been developed by Ma *et al.*⁵¹ The model includes detailed gas-phase reactions of acetylene pyrolysis and surface catalytic reactions for CNT growth. The model was employed for analyzing the change of CNTs growth rate at different conditions: the pressure, temperature, density of catalytic particles and their diameter. The model suggested that the optimal temperature for CNT synthesis is 700 °C, the growth rate increases with acetylene partial pressure and growth rate increases with decreasing the diameter of catalyst nanoparticles.

A reaction scale simulation was performed on a tube flow CVD reactor by Lombardo *et al.*⁵² using a software package COMSOL. The simulation was done to observe how different combinations of parameters affect the growth rate of CNTs in order to understand how to optimize the reactor. The model

revealed multiple limiting regimes of CNT growth at different reaction conditions. Figure 8a displays an Arrhenius plot of CNT mass deposition rate as a function of temperature for different inlet methane concentrations. Fig. 8b shows the activation energy calculated using data from the Arrhenius plot shown in Fig. 8a.

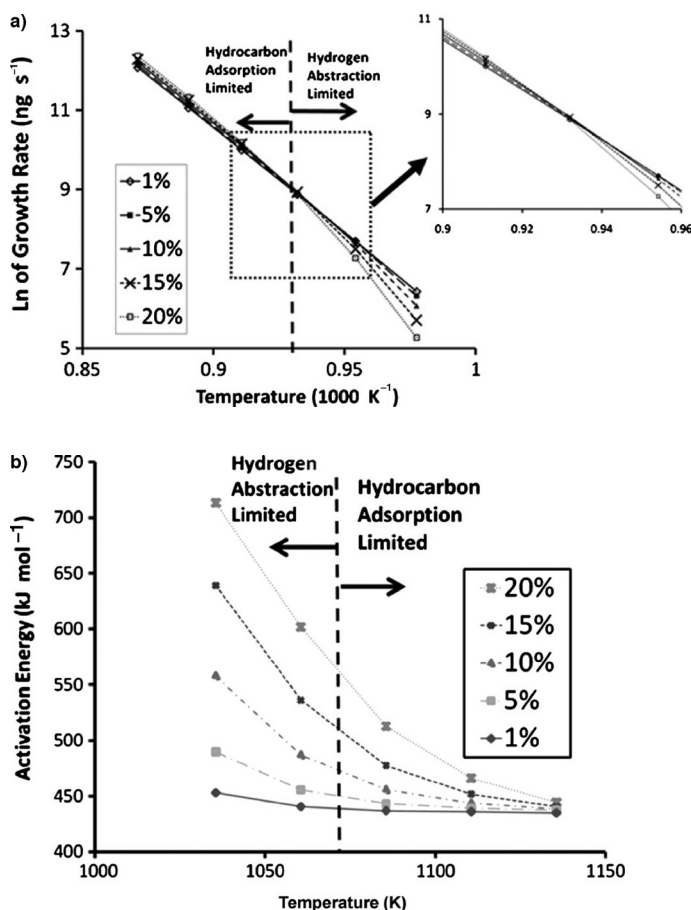


Fig. 8 – a) Arrhenius plot of CNT mass deposition rate as a function of temperature for different inlet methane concentrations. b) Activation energy plot for CNTs synthesis. Reprinted by permission.⁵²

5. Conclusion

This paper has discussed the chemical vapor deposition method for the synthesis of carbon nanotubes, and has reviewed some theories and simulations that have been put forward to model these processes. It seems that progress is being made in simulating the nucleation, growth and termination mechanisms involved. Although the simulations of carbon nanotube synthesis differ in several respects, it appears that the main elements applied in simulations are similar. For better and more accurate numerical simulations of carbon nanotubes synthesis based on the transport and kinetics in the chemical vapor deposition reactor, a simpler system

should be employed. Reactors with channels at micrometer scale are very convenient for such a task, due to laminar flows of reactant gases and low thermal and volume capacities.

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