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Flame Synthesis of Carbon Nanotubes

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1. Introduction

Carbon is one of the most abundant elements found in nature. It is also one of the elements that form the fundamental building blocks of life on earth. Carbon, in solid, liquid and gaseous forms, is a major contributor in many human activities. Solid forms of carbon have a diverse phase diagram ranging from very soft graphitic to very hard diamond structures. These forms are produced through various processes ranging from coking to crystalline condensation from gaseous precursors. These diverse processes and the variables that define them lead to many different forms of solid carbon including coke, carbon blacks, graphitized carbon, pyrocarbon, glossy carbon, active carbon, diamond, fullerenes, carbon fibers and the newest identified form- carbon nanotubes. Carbon nanotubes (CNTs) are one of the most elegant arrangements of solid carbon that are elongated structures of C60 molecules (also known as fullerenes (Kroto, 1987; Kroto et al., 1985)). CNTs were first observed by Baker et al. in the 1970s (Baker et al., 1972; , 1973; Oberlin et al., 1976). However, these findings did not spark as much interest in the scientific community as that sparked by the re-discovery of CNTs by Iijima(Iijima, 1991). For the last two decades carbon nanotubes and their remarkable properties have been extensively studied and different synthesis methods have been developed for their production.

Carbon nanotubes can be classified by the number of concentric walls. A single wall carbon nanotube (SWNT) can be visualized as a flat graphene sheet of fullerene (C60) molecules rolled up to make a seamless cylinder. C60 molecules are tiny spherical structures (diameter of ~ 7 Å) of 60 carbon atoms connected together forming 20 hexagons and 12 pentagons. Two halves of the fullerene molecule can be visualized to form the end caps of the nanotube. SWNTs exhibit extraordinary physical properties including very high thermal (1750-5800 W/m-k) and electrical conductivity (resistivity equals ~ 10^{-6} Ω-m) in the axial direction (Hone et al., 1999; Thess et al., 1996) and equally remarkable structural properties such as high Young's modulus (1054 GPa) (Yu et al., 2000). A multi wall carbon nanotube (MWNT) can be visualized as a structure with concentric cylinders of increasing diameters with correspondingly larger hemispherical end caps terminating them at each end. MWNTs are more commonly found in products of synthesis than the SWNTs. SWNTs are produced by carefully controlling the condensation process. Diameters of SWNTs are, typically a few nanometers, and those of MWNTs are generally of tens of nanometers. Another classification of CNTs is based on the orientation of the hexagonal (six-member carbon ring) in a honeycomb lattice with respect to the axis of the nanotube. Three possible structures include armchair, zigzag and chiral, as shown in figure 1. Armchair and zigzag structures are achiral, that is, their mirror image is identical to the original object. On the other hand,

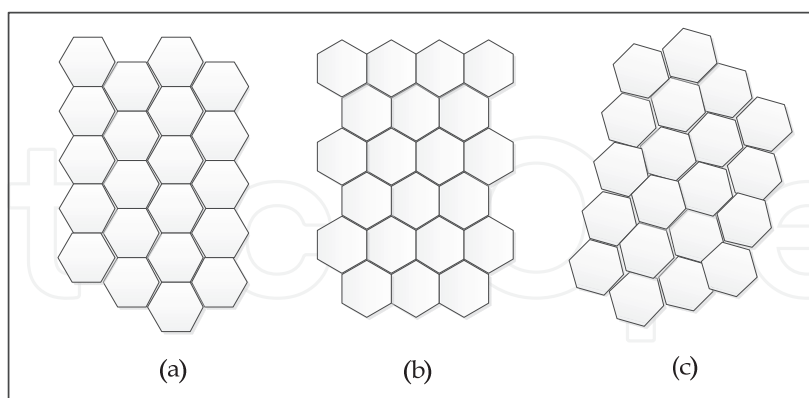chiral structures exhibit spiral symmetry, whose mirror images cannot be superimposed on the original one.

Fig. 1. Various configurations of carbon nanotubes (a) Armchair, (b) Zigzag and (c) Chiral

Catalytic synthesis of carbon nanotubes is typically a multiple length-scale multi-step process in which carbon is deposited in solid form. This conversion occurs at the nano scale via endothermic reactions occurring at surface of catalyst nano-particle. Therefore, a synthesis reactor generally consists of three essential components: (i) source of gaseous carbon (ii) source of heat and (iii) catalyst particles that provide the reaction sites. A mixture of carbon containing gaseous precursor species at appropriate temperature is maintained throughout the reactor. The size of the reactor defines the largest scale. The catalyst is added either in a form of nano-scale depositions on a substrate or freely floating nano-particle aerosol embedded in the bulk phase. In the past, carbon nanotubes have been produced using methods such as plasma arc discharge, pulsed laser vaporization (PLV), chemical vapor deposition (CVD), Plasma Enhanced (PECVD) and hydrocarbon flame synthesis. Schematic representation of these synthesis processes is shown in figure 2.

Iijima (Iijima, 1991) used the arc discharge method for production of CNTs. The process involved condensation of carbon atoms generated from evaporation of a solid carbon source. In this method, high electric current (~50 - 120 A) is passed through graphite electrodes placed at a distance of approximately 1 mm in the synthesis chamber that causes material from the cathode to sublimate and the nanotubes to form on the anode. The arc discharge process is difficult to control because of the very high temperature (~3200 K) in the electrode gap. The method is also cost and energy intensive and unwanted byproducts such as polyhedron graphite particles contaminate the relatively low yield of CNTs.

In the pulsed laser vaporization or laser ablation method, a high energy laser is directed to ablate a carbon target that contains some nickel and cobalt in a tube furnace, at the temperature of ~ 1400 K. A flow of inert gas is passed through the chamber to carry the CNTs downstream, to a collector surface. Single walled carbon nanotubes, mostly in the form of ropes, at a 1- 10g scale have been formed by this method. The CNTs formed by the laser ablation method are of a higher quality than those produced by the arc discharge method. However, the production rate is low, and the pulsed laser vaporization or laser ablation method is both capital and energy intensive.

The chemical deposition method (CVD) is an alternative method in which CNTs are grown using catalysis. This method involves decomposition of a hydrocarbon gas over a transition metal catalyst and initiation of CNT synthesis by some of the resulting carbon atoms. CVD

growth mechanism generally involves the dissociation of hydrocarbon molecules and saturation of carbon atoms in the catalyst metal nano-particles. The precipitation of carbon from the saturated metal particles leads to the formation of carbon nanotubes. Use of catalysis reduces the need for high temperatures. Hydrogen from the decomposition process, and supplemented by that carried with the bulk phase, contributes to the activation and reactivation of the catalytic surface. The CVD method has a better CNT yield and is potentially scalable to commercial manufacturing.
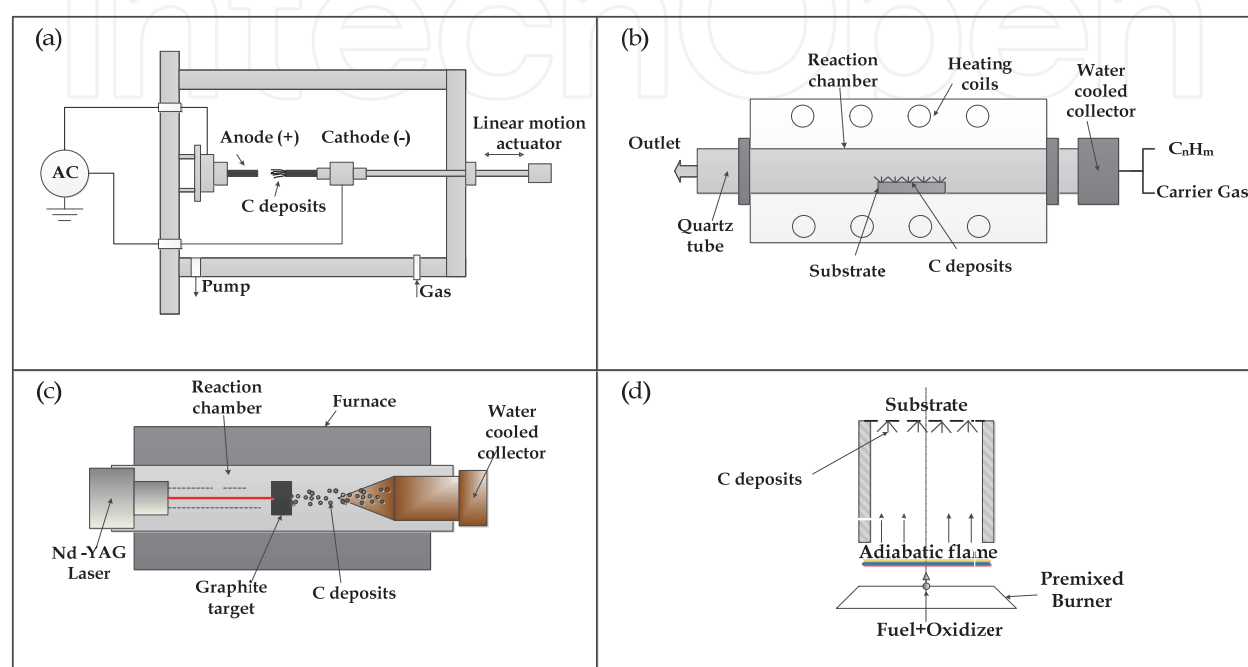
Fig. 2. Schematic representation of methods used for carbon nanotube synthesis (a) Arc discharge (b) Chemical vapor deposition (c) Laser ablation (d) hydrocarbon flames

Hydrocarbon flames provide a unique combination of the chemical and catalytic factors that are conducive to initiation and growth of carbon nanotubes. Gases (CO, CH_4, C_2H_2, C_2H_4 and C_2H_6) present in the post flame environment form a diverse source of gaseous carbon. The chemical energy released in the form of heat in the flame supports the endothermic carbon deposition reactions. Catalysts in appropriate form (substrate or aerosol) provide the reaction sites for deposition of solid carbon. Growth mechanisms similar to those observed in the CVD process govern the growth of nanotubes in flames. The geometry and characteristics of the catalysts play an important role in the structural properties of the carbon nanotubes. Flames are scalable and are commercially used for the production of solid carbon forms such carbon black and printing ink. Appropriately tailored flame conditions may provide an ideal environment for growth of CNTs on a large commercial scale.

The rest of this chapter summarizes the mechanisms of carbon nanotubes formation in flames followed by a summary of the types of flame configurations and chemistry that have been used in the synthesis process. The process parameters such as equivalence ratio, temperature, pressure are discussed next. Computational models for exploring the parameter space for optimization of the synthesis process are discussed next and the chapter ends with a few comments about future trends.

2. Mechanism of carbon nanotube formation in a catalytic synthesis process

The inception and growth mechanisms of CNTs have been studied extensively but a consensus on a single mechanism has not emerged. In fact, more than one mechanism may be involved in the inception and growth of CNTs depending on the specifics of the gaseous precursors, catalysts and operating parameters. One of the most popular descriptions involves the carbon dissolution-diffusion-precipitation mechanism proposed by (Baker et al., 1972). Catalytic nano-particles from transitional metal/metal alloys (e.g. Fe, Ni, and Co) are assumed to be spherical or pear-shaped and are either floating or supported on a substrate. The catalytic decomposition of the carbon precursor molecules (e.g. CO, CH_4, C_2H_2, C_2H_4 and C_2H_6) is conjectured to occur on one half of the nano-particle surfaces (the lower curvature side for the pear shaped particles). The released carbon atoms diffuse into the catalyst nano-particles along the concentration gradients until carbon super-saturation at the particle temperature occurs (Moisala et al., 2003). Post super saturation of the catalyst particle, carbon atoms precipitate in solid carbon form on the opposite half of the catalyst particle around and below the bisecting diameter. This description is similar to the Vapor-Liquid-Solid (VLS) process suggested by (Tibbetts, 1984). As per this process, the solid carbon fibers grow from a super-saturated molten liquid catalyst droplet. Decomposition of the gas phase hydrocarbon molecules provides the carbon necessary for saturation of the molten catalyst. The possibility of gas phase and surface decomposition of the hydrocarbon molecules exists. Melting of metal catalyst particles at the normal synthesis temperature (900 – 1200 K) is plausible only as a result of non-equilibrium processes within the thin surface layer of the particle. Reduction in size of the particles also leads to increased carbon solubility within available process time.

The specific physical form (e.g. MWNT, SWNT, amorphous carbon and particle-encapsulated graphite cell) of the precipitated solid carbon depends on several factors; including catalyst particle size and precipitation rate (Moisala et al., 2003). When the precipitation rate is in equilibrium with or less than the carbon diffusion rate, graphitic layers are formed surrounding the catalytic nano-particles resulting in the thermodynamically most stable carbon forms. When the precipitation rate is larger than the carbon diffusion rate can CNT growth occur. Generally only catalytic nano-particles that are sufficiently small (<20nm) are active for CNT nucleation and growth, with the tube diameter corresponding to that of the catalytic nano-particle. For particles smaller than 20 nm, solid carbon atoms do not precipitate from the apex of the hemisphere but from a circular ring close to one of the diameters of the spherical particle. This accounts for the hollow core characteristic of CNTs with diameter approximately corresponding to that of the catalyst particles. For supported catalysts, formation occurs either by "extrusion" (also known as base growth as shown in Figure 3 (a)), in which CNTs grow upward from the nano-particles that remain attached to the substrate, or by lifting of the catalyst nano-particles by the growing CNT (tip growth as shown in Figure 3 (b)).

As summarized in Figure 3 (c) below, catalyst particle diameter plays an important role in defining the synthesized carbon nano-structure. Particles of the order of 1 nm diameter predominantly form SWNTs (Rao et al., 2001). MWNTs are formed with catalyst particle diameters in the range of 10~50 nm with the number of layers increasing with the particle diameter. Particles with diameters larger than 50 nm are covered with amorphous graphitic sheets often given another visually descriptive name "nano-onion."
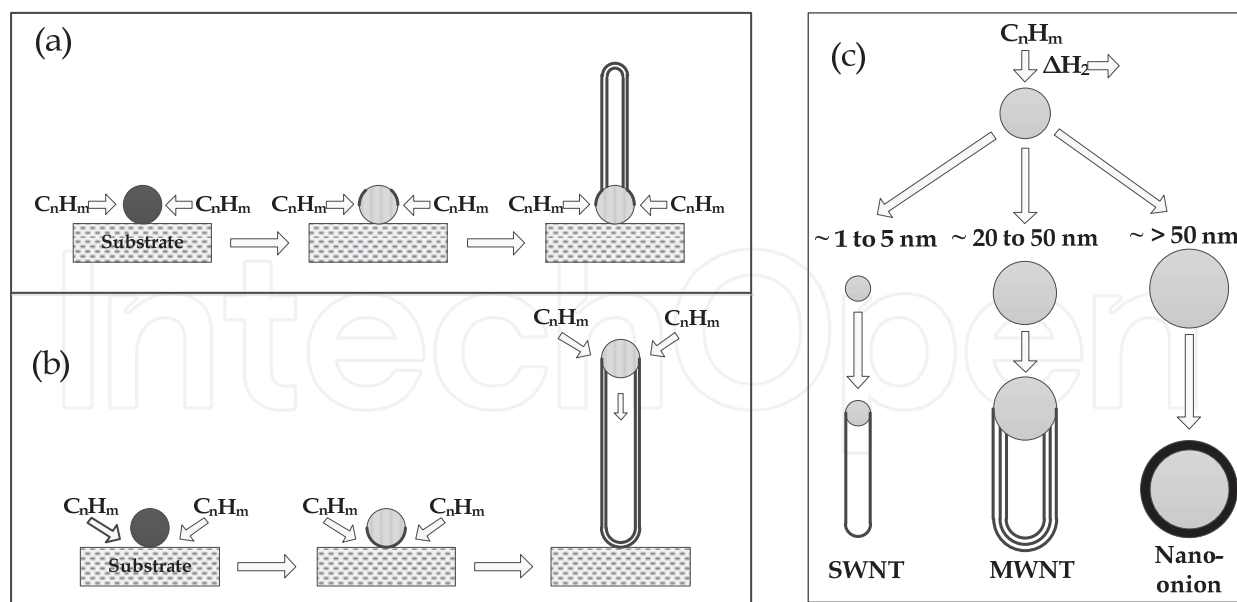
Fig. 3. Mechanisms for carbon nanotube growth (a) Base growth (b) tip growth (c) Structural dependence on catalyst particle size

Dai et al. provided a visually descriptive "yarmulke (Yiddish for skull cap) mechanism," name to the observed growth of MWNTs (Dai et al., 1996). A key characteristic of this mechanism involves nucleation on the catalyst material (e.g. Fe, Ni, and Co) surface by decomposition of gaseous hydrocarbon molecules followed by diffusion of the hydrogen away from the surface. Once the nano-particle is supersaturated with the carbon atoms, the linking of the carbon atoms together in the form of a hexagonal sheet that conforms to the curvature of the particle is energetically favored (Tibbetts, 1984). For experiments in which the nano-particles are supported on a substrate the carbon "yarmulke" grows approximately half the particle diameter towards the substrate and then starts growing longitudinally with the particle remaining at the root. Newly arriving carbon atoms are integrated into the network and the tube grows longer. For experiments involving suspended catalytic nano-particles, the strain of the carbon sheet curving around the nano-particle is higher and conjectured to result in smaller diameter tube formation. A second yarmulke can form underneath the first with approximate spacing between the two equal to the interlayer spacing of graphite crystals (~0.34 nm). As additional yarmulkes grow, one beneath the other, older yarmulkes lift up to form the MWNT. The open ends of these structures remain chemisorbed to the catalytic particle. As the strain resulting from increasing curvature exceeds a certain value, nucleation of new inner walls ceases defining the diameter of the innermost tube. The pre-nucleation step involving saturation of the catalyst particle by dissolved carbon defines the maximum diameter of the catalyst nano-particles for CNT growth.

3. Flame synthesis of carbon nanotubes

3.1 Experimental investigation

The first experimental observation and conjecture of the formation of filamental carbon in flames (Singer & Grumer, 1959) came long before CNTs were discovered. Formation of CNTs by plasma arc discharge method was first reported in 1991 (Iijima, 1991). In the same

year, formation of elongated carbonecous structures on the surface of a probe inserted in methane air diffusion flames (Saito et al., 1991) was reported and presence of C60 and C70 fullerens was detected in premixed flames (Howard et al., 1991). A year later, co-existence of MWNTs with soot like structures was detected in premixed flames (Howard et al., 1992). Prior to these reports, the highly ordered carbon cylindrical structures had been produced only by very energetic processes such plasma and laser vaporization but not in flames. These discoveries prompted scientist to investigate the potential of various types of hydrocarbon flames for synthesis of CNTs.

Flame is a unique synthesis medium that provides both energy and chemical species for the synthesis of CNTs and other carbon nano-forms. Schematics of various flame synthesis processes are shown in figure 4.
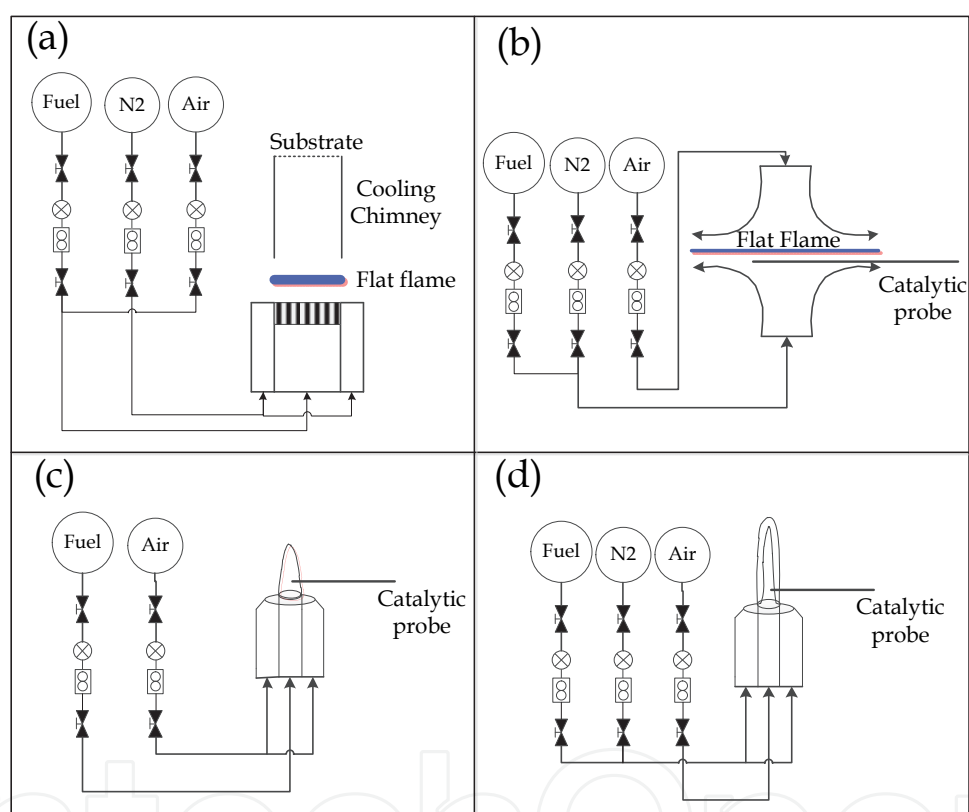

Fig. 4. Schematic for flame synthesis of carbon nanotubes (a) premixed flame (Gopinath & Gore, 2007; Height et al., 2004; Vander Wal et al., 2002) (b) counter-flow diffusion flame (Li et al., 2007; Merchan-Merchan et al., 2003; Saveliev, 2003; Xu et al., 2007)(c) co-flow diffusion flame (Unrau & Axelbaum, 2010; Vander Wal, 2000; Xu, 2007; Yuan et al., 2001; Yuan et al., 2001)(d) inverse diffusion flame(Lee et al., 2004; Unrau et al., 2007; Xu et al., 2006)

In a flame, fuel (generally hydrocarbons such as methane (CH_4), ethylene (C_2H_4), and acetylene (C_2H_2) etc.) reacts with oxidizer (O_2 from air) to produce gaseous mixture that includes carbon dioxide (CO_2), water vapor (H_2O), carbon monoxide (CO), hydrogen (H_2), saturated and unsaturated hydrocarbons(C_2H_2, C_2H_4, C_2H_6 etc.) and radicals. Hydrocarbons and carbon monoxide constitute the gaseous precursor mixture that is the source of solid carbon deposited on catalyst particles to form carbon nanostructures. Metal catalysts, inserted in the flame either in the form of a substrate coating or as aerosol particles, provide

the necessary reaction sites for deposition of solid carbon. Nanotubes are believed to form on the catalyst particle via the same carbon dissolution-diffusion-precipitation mechanism discussed in section 2 above. The structure of the formed carbon nanotube (MWNTs and/or SWNT) depends on the catalyst particle size and carbon deposition rate. Post flame gas phase chemistry, temperature at the surface of the catalyst particle and the structure and type of catalyst particle are the key controlling parameters for growth of nanotubes in the flame synthesis process.

In comparison with the other processes, flame synthesis is an auto-thermal process that is capable of providing temperature optimal for achieving desired synthesis conditions. Flame medium is characterized by a complex homogeneous gas phase kinetics that involves reactions between the fuel and the oxidizer with formation of water, carbon dioxide, and partial oxidation products and fuel pyrolysis with formation of secondary hydrocarbon species such as single and multi-chained hydrocarbons, polycyclic aromatic hydrocarbons, and soot precursors. In comparison with CVD, a flame medium is rich in intermediate radicals that are formed in high concentrations during intense homogeneous gas phase reactions. This homogeneous gas phase kinetics is closely coupled with the heterogeneous kinetics of gas-surface interactions leading to the formation of nano-structured solid carbon.

Post flame gas phase chemistry and temperature are a complex function of fluid dynamics, mass transfer and heat transfer phenomena at play inside a flame. Fuel and oxidizer primarily impact the gas phase composition and the maximum temperature in the flame. Hydrocarbon fuels such as CH_4, C_2H_4 and C_2H_6 when used with oxygen/air as the oxidizer result in unique product gas phase compositions and maximum temperatures (~ 2000 K). The degree of mixing between fuel and the oxidizer that is identified by the parameter of equivalence ratio (ϕ), generally determines the extent to which the chemical oxidation reactions are complete to stable product gases such as CO_2 and H_2O. Intermediate product gases such as CO, C_2H_4, and C_2H_2 and in general C_nH_m provide compositions supportive of solid carbon formation. At steady state equivalence ratio is a spatially varying quantity within the diffusion flame structure. The zone of maximum temperature within the flame is also known as flame front is formed at the location where the local ϕ is equal to 1.

Configuration of the flame plays an important role in establishing the fluid dynamics, the mass and energy transfer and the chemistry in the flames. Flames are classified mainly as premixed, non-premixed (diffusion), and partially premixed. Diffusion flames are further characterized by the orientation of the reactant nozzles into co-flow diffusion, inverse diffusion, and counter flow diffusion. All of these flame configurations have been used for carbon nanotube growth. A premixed flame is defined as a flame where the oxidizer and fuel are completely mixed before burning (e.g. Bunsen flame). A co-flow jet burner establishes a diffusion flame with the fuel issued from an inner tube and the oxidizer is injected from an outer tube. When the fuel and the oxidizer are inverted in a co-flow jet burner, an inverse diffusion flame is formed. A counter-flow flame is established from two converging nozzles arranged in an opposed flow configuration with a fixed distance, where oxidizer issued from one nozzle impinges onto the fuel flow issued from the other. Independent of the flame type used, it must provide a source of carbon to form the graphite layers, utilize the catalytic metal nano-particles to form the solid graphitic layers from gas-phase carbon containing molecules, and provide a heat source for forming and activating the catalytic nano-particles. The flow structure of the flame can be laminar or turbulent

based on the Reynolds number. However, only laminar flames have been used for synthesis of carbon nanotubes due to the uniform structure. In the further discussion only laminar flames have been addressed unless explicitly otherwise stated.

Use of inert diluents also affects the flame chemistry and temperature. Nitrogen (N_2) and Argon (Ar) have been used as the diluents in many carbon nanotube flame synthesis experiments. The ambient conditions of pressure and temperature also impact the flame and hence the synthesis conditions for carbon nanotubes.

Metal catalysts in the form of both substrate and aerosol have been used for growing carbon nanotubes. Typical catalysts include transition metals such as Iron (Fe), Nickel (Ni), and Cobalt (Co). Alloys of transition with other metals like chromium (Cr), copper (Cu) and zinc (Zn) have been used. In the substrate method, a substrate coated with a catalyst layer is positioned at the appropriate location inside the flame. Catalyst nano-particles are formed on the substrate as a result of flame-substrate interactions. These particles further act as the nucleation site for nanotube growth. Stationary substrates have been typically used for synthesis of MWNTs because of the larger size of catalyst nano-particle (~20 nm). Catalyst can be injected inside a flame in the form of a vapor aerosol. Generally, nitrates of transition metals and metallocenes have been used in flame synthesis. Catalyst particles of the size of approximately ~5nm are formed due the condensation of the catalyst vapor, that are suitable for growth of SWNTs. Catalysts have been found to be very active towards a particular gas phase precursor of solid carbon, and hence structure and type of the catalyst play an important role in determining the growth rate as well as the structure of the CNTs.

3.2 Synthesis of MWNTs using flames

MWNTs and larger forms of nanotubes have been successfully synthesized using flames. Substrate type catalysts have been used in most of the experiments because of the inherently closer control over the catalyst formation processes. A variety of flame configurations mentioned above have been used with CH_4, C_2H_4, C_2H_2, C_3H_8 and alcohols as the fuels and air or O_2-N_2 and O_2-Ar mixtures as the oxidizer species.

3.2.1 Premixed flame synthesis

Premixed flames offer distinct advantages for CNT synthesis when compared to non-premixed flames. As the mixing of fuel and air occurs before ignition, equivalence ratios can be easily controlled by varying the mass flow rate of the fuel and/or the oxidizer. Premixed burners with a flat radial profile and variation only in the axial direction (e.g. McKenna burner) have been used for nanotube synthesis. The flame temperature can be reduced to an appropriate value by the use of chimneys. Uniform gas flow composition can be obtained by appropriate arrangements in the burner.

The first evidence for filamentous carbon growth in flames was established using premixed flames (Singer & Grumer, 1959). In the last two decades premixed flat flames have been extensively studied for synthesis of carbon nanotubes (Diener et al., 2000; Gopinath & Gore, 2007; Grieco et al., 2000; Howard et al., 1992; Howard et al., 1991; Vander Wal et al., 2002, 2002). Formation of C60 and C70 fullerenes was first observed in premixed flames by Howard et al. In their studies, sooty discharge from premixed laminar flames of benzene, oxygen and argon at low pressures (1.60 to 13.35 kPa) were analyzed using electron impact mass spectroscopy. The results showed presence of C60 and C70 fullerenes that were confirmed by FTIR (Fourier Transform Infrared Spectroscopy). The yields of C60, and C70

and the C70/C60 ratio were found to depend on temperature, pressure, carbon/oxygen ratio, and residence time in the flame. The amount of fullerenes formed in the flame was very low (0.009% to 0.03 % of the soot mass) as compared to that formed in graphite vaporization (1% to 14%). Nonetheless, this finding motivated combustion scientists to pursue the synthesis of CNTs using flames as the precursors (C60 and C70 fullerenes) were found in flames.

Vander Waal et al. carried out a comprehensive study of the MWNT synthesis in premixed flames. Premixed flat flame McKenna burner was used with SS chimney for cooling. Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8), Ethylene (C_2H_4) and Acetylene (C_2H_2) were used as fuels with air as the oxidizer. At the top of the chimney, a circular molybdenum ring held the mesh (Stainless Steel) supported catalyst (cobalt) within the post-flame gases. The flame equivalence ratio was varied, adjusting the fuel flow rate to the burner while maintaining a constant air flow rate. The post-flame gas temperature was recorded to be (~1100 K). Meshes were retained in the flame gases for 12 minutes, measured from the time of insertion to extraction. Results of chemical equilibrium calculations were correlated with the experimental measurements to determine the optimal gas phase chemistry for the growth of CNTs. CO was identified as the main gas precursor. Both SEM and HRTEM imaging were used to correlate the nanotube morphology and internal structure to the reaction gas composition. The variations observed were understood in light of the gas composition and the interaction of the reactive components with both the deposited Co catalyst particles and supporting metal substrate. Coated and uncoated (with Co catalyst) meshes were subjected to post flame gases. The uncoated SS meshes resulted in a dense random CNT growth because of formation of catalysts through surface break up. However coated meshes showed a uniform and dense growth confirming the dominance of catalyzed CNT formation. With C_2H_2 flames high deposition was found even on uncoated meshes. Most significantly, catalyst particles are observed at many tips using the uncoated SS mesh, characteristic of surface breakup processes.

Gopinath and Gore further investigated the carbon containing gas phase species responsible for deposition of carbon during the synthesis of MWNTs. Premixed flames of ethylene and air were established in a flat flame McKenna burner. Due to the flat flame profile, radial gradients were ignored. This assumption significantly simplified the computational analysis of the flame and post flame chemistry. The yellowish high carbon region just above the flame was found to be best suited for the gas phase chemistry required to encourage CNT growth. In order to enable the required gas phase chemistry and temperature to exist around the catalyst substrate, a chimney was placed just above the flame. The chimney served two functions, (a) it prevented the optimal gas phase chemistry of the near flame zone from dissipating and (b) it provided the necessary wall losses to quench the post flame environment to attain the ideal temperature for rapid CNT growth. A cooling chimney was used to cool the flame products and obtain appropriate post flame temperatures for CNT synthesis. A N_2 co-flow stream was employed to stabilize the flat flame. The air flow rate was held constant at 11.5 lpm and the equivalence ratio (ϕ) was varied by changing the fuel flow rate. A 2 nm thin layer of cobalt catalyst was deposited commercially, using a physical vapor deposition technique, on SS304 200 mesh standard TEM grids. The experimental arrangement is shown in figure 5 (a). The gas phase temperature and substrate temperature were measured using a thermocouple and found to be within 10 K of each other at 1100 K under steady state conditions confirming the observations by Vander Wal.
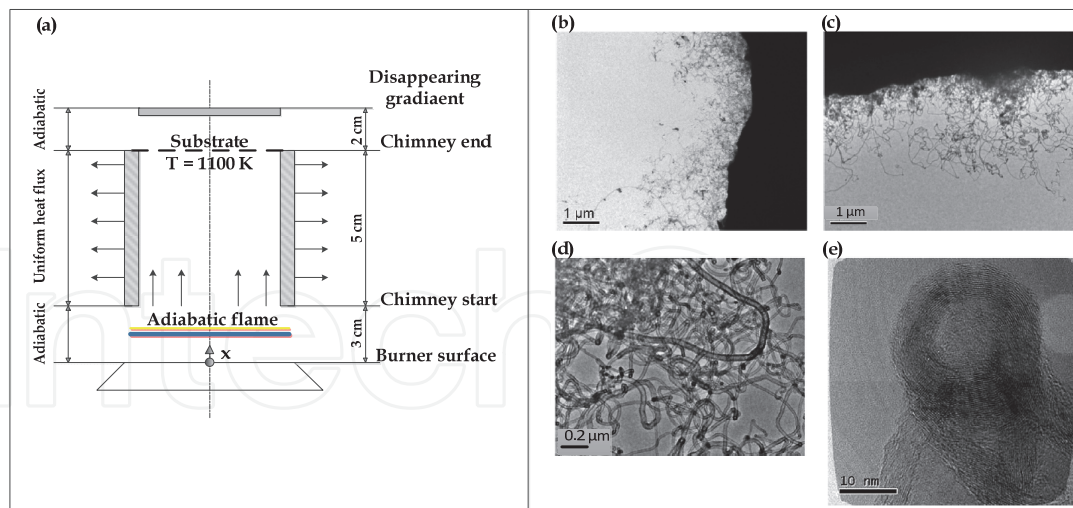
Fig. 5. Experimental synthesis of carbon nanotubes using premixed flames (a) Experimental arrangement, (b) & (c) TEM images of nanotube growth on cobalt catalyst at ϕ = 1.55 (d) HRTEM image of MWNTs at ϕ = 1.55 (e) HRTEM image of closed MWNT (Gopinath & Gore, 2007)

Figure 5 shows the TEM images of the carbon nanotubes synthesized during the experiment at the equivalence ratio of 1.55. Figure 5 (b) and (c) show the low magnification images of the CNTs. Optimum yield of nanotubes was produced at this particular value of equivalence ratio. As shown in figure 5 (d) and (e), the magnified images reveal the multi-walled structure of nanotubes. The well-graphitized structure is evident from this image. These observations were found to be consistent with the experiments performed by Vander Wal.

3.2.2 Diffusion flame synthesis

Formation of fibrous carbon in diffusion flames was first observed by Saito et al. (Saito et al., 1991; Saito et al., 1986) while conducting soot characterization studies on methane air diffusion flames. The growth was observed beyond a certain height above the burner with associated color change from brown to black. Later, Yuan et al. completed detailed characterization studies using methane- air (Yuan et al., 2001), ethylene-air and N_2 diluted ethylene-air flame synthesis (Yuan et al., 2001) of CNTs. The catalytic supports (Ni-Cr) used were in the form of wires and grids undergoing an oxidation process, and grids pre-loaded with Co nano-particles.

In the experiment done with methane by Yuan and co-workers, SEM images suggested that most nanotubes have a particle attached at the base near the substrate. Since the particles were not seeded in the flame and the images indicated their presence it is apparent that the particles are lifted from the surface. The base location of most of the particles supports the base growth model for the CNTs. Nevertheless, some particles were found at the tip of the nanotube indicating catalyst surface breakup. This phenomenon has been reported by Vander Waal et al. in their reports on premixed flame synthesis especially with an uncoated stainless steel mesh. Soot was formed when only Ni-Cr wire was held in the flame without any support mesh. This indicated that the stainless steel mesh may be essential for the formation of CNTs. Soot was found to grow over a broad range of conditions in the flame whereas CNTs grow in a narrower region in the presence of a catalyst. The optimum harvest

conditions were observed within non-dimensional physical locations between h/H = 0.2 to 0.3 and r/R = 0.6 to 0.9. The temperature of nanotube formation was found to be around 1520 K. The CNTs were collected on Ni-Cr wire whereas brown deposits were formed on the stainless steel mesh later identified as iron oxide. CNT formation was observed even at low catalyst concentration indicating that soot formation and CNT growth may be competing phenomenon in the flame. Optimum region for CNT growth was found to be in the region of minimum oxygen concentration. However, the rate of catalyst particle formation was found to be low. Thus, it was suggested that oxygen might play an important role in the formation of metal catalysts. However, high concentrations of oxygen might lead to oxidation of the CNT precursors and incipient CNTs. The zone of temperature was also determined to be a critical parameter for the synthesis of CNTs.

With the ethylene flames Yuan and coworkers tried to study growth mechanism for the carbon nanotubes inside the flame. The effect of N_2 addition to the flame on the growth of nanotubes was assessed. Soot instead of CNT formation occurred when a bare stainless steel mesh was used as the substrate. However, when pre-oxidized substrate was used CNT growth was visible indicating the criticality of formation of metal oxides for CNT growth. When Ni-Cr wire similar to methane experiment was placed in the ethylene flame amorphous carbon growth was visible that signified the difference between formation mechanism of CNTs in methane and ethylene flames. The deposition rate for gray material was found to be more than 3 mg/min. With increase in sampling time the production rate of amorphous carbon increased leading to eventual solidification of the tube due to deposition of carbon on the nanotube walls. The increase in the thickness was attributed to deposition of pyrolytic carbon on to the carbon nanotube walls. Addition of N_2 to the flame resulted in decreased synthesis temperature (from 1820 K to 1517 K) and carbon gas concentration that led to fewer nanotubes. However, more uniform nanotubes resulted in the presence of N_2. Cobalt coated grids resulted in well aligned and uniform CNTs with diameters well correlated to the catalyst particle. Similar observations related to the optimum temperature for nanotube synthesis were made by Lee et al. (Lee et al., 2004) for an ethylene air inverse diffusion flame. It was observed that when the gas temperature was varied from 1400 to 900 K, well-aligned MWNTs with diameters ranging from 20 to 60 nm were formed on the probe's surface. Ni was used as catalyst in the form of $Ni(NO)_3$ particles pre-loaded on the substrate. Reduction up to 60% in melting temperature of the transition metal due to small particle size of the bulk value has been reported (Moisala et al., 2003; Petroski et al., 1998). This fact was used to explain the formation of active catalyst particles in the temperature well below the bulk melting temperature of Ni (~1726 K).

Xu et al. (Xu et al., 2006)examined the effect of different types of catalysts on growth of carbon nanotubes in a methane air inverse diffusion flame. They tried to correlate composition of the catalyst with the observed morphology of the carbon nanotube. A methane air inverse diffusion flame of total height of 15 mm was established. Temperatures and concentrations were determined, at various radial locations at particular heights from the burner, using spontaneous Raman spectroscopy. Optimum range for nanotube growth was found to be at a height of Z = 12 mm and radius r between 2 – 4 mm. Peak concentrations of CO and H_2 were found in the optimum synthesis range. Ideal temperature range for CNT growth was reported to be in between 1200 – 1400 K.

Counter flow diffusion flames are been increasingly used for synthesis of MWNTs due to their 1-D geometry and convenience in positioning the catalyst substrate in the flame (Hou

et al., 2009; Li et al., 2007; Merchan-Merchan et al., 2003; Merchan-Merchan et al., 2004; Merchan-Merchan et al., 2002; Merchan-Merchan et al., 2009; Saveliev, 2003; Xu et al., 2007). Merchan-Merchan et al. (Merchan-Merchan et al., 2002) recorded the formation of CNTs in a methane oxygen counter diffusion flame without any catalysts. They employed an atmospheric, opposed flow burner with N_2 co-flow in which the oxidizer was enhanced to 50% oxygen or greater. High resolution SEM and TEM images revealed soot like structure with presence of carbon nano-particles and nanotubes however, no catalyst particles were found embedded in the soot like structure. The tube diameter and length were approximately 20 and 320 nm, respectively. The distribution of the sizes of nano-particles and nanotubes was found to be bimodal, indicating that both structures originated in similar sized solid carbon precursor seed. Presence of nano-particles and nanotubes inside soot like structure pointed towards a similar mechanism responsible for formation of all three structural forms. Currently, oxy-flames are being pursued for CNT synthesis (Hou et al., 2009; Merchan-Merchan et al., 2009) due to the high temperature and radical concentration obtained at the flame location.

3.3 Flame synthesis of SWNTs

Similar to the synthesis of MWNTs, a combustion system tailored with an ideal source of carbon, heat source, and appropriate catalytic material, can result in the production of single-walled carbon nanotubes. In the flame method, the catalytic precursors are generally introduced into the flame system in the gas-phase and nucleate and condense to solidify into spherical metallic nanoparticles. Flame parameters can be used to obtain an appropriate flame environment that would allow the formation of ideal sizes of catalytic particles for carbon nanotube inception and growth. The available literature on the flame synthesis of SWNTs is scarce, in contrast to flame synthesis of MWNTs, consisting of only a handful of experiments that have been conducted on the synthesis of SWNTs.

To some extent all products obtained in the SWNT synthesis experiment have common morphological trends; even though they are synthesized in flames formed using different burner configurations and conditions. These morphological trends include (Merchan-Merchan et al., 2010): (i) SWNTs always coexist with metallic and/or soot particles, (ii) particles often appear to be poisoned; even when ultra small catalytic particles, ideal for SWNT inception, can be achieved, they can be heavily encapsulated with amorphous carbon becoming inactive as catalysts for nanotubes, (iii) the presence of larger metallic particles with very short SWNTs.

Vander Wal studied the effect of catalysts in aerosol form on the growth of CNTs (Vander Wal, 2002). Primarily SWNTs were grown on aerosol catalyst particles using an acetylene air flame. Same flame configuration was used except the catalyst in form of Fe(III) nitrate $(Fe(NO)_3)$ vapor dissolved in a solvent was introduced through a nebulizer. Absolute ethanol was found to be the optimum solvent for the catalyst. The experiment was directed towards identifying the correct precursor for the SWNT growth by introduction of pyrolysis gas mixtures $(CO/H_2/He$ and $C_2H_2/H_2/He)$ and studying the effect of catalyst particle size on the growth of SWNT. Higher CO concentrations led to metal particles becoming encapsulated within amorphous carbon. There appears to be a minimum limit for presence of CO and H_2 and maximum limit for presence of H_2O for the production of SWNT synthesis. Increase in catalyst vapor concentration led to increased particle size, making them ineffective for fullerenic growth. Therefore, a need for appropriate gas phase precursor and catalyst particle size was identified for SWNT growth. C_2H_2 was found responsible for

poisoning of catalysts and presence of H_2 was deemed essential for etching of the catalyst particle.

Height et al. (Height et al., 2004) studied the transitional conditions between soot formation and CNT formation and the effect of operating conditions on structure of nanotubes. Optimum zone for equivalence ratio was identified that was required for formation of SWNTs. A premixed C_2H_2/O_2 flame with argon dilution of 15 molar percent, cold gas feed velocity of 30 cm/s, and burner pressure of 6.7 kPa formed the basis of the experiments. Iron penta-carbonyl ($Fe(CO)_5$) vapor was used as the catalyst. Carbon nanotubes were formed as the distance above the burner surface is increased. A nanotube formation window for equivalence ratio was anticipated with upper and lower limits determined by sooting and carbon availability factors. Flames with equivalence ratios between 1.4 and 2.0 were examined, with samples extracted at 70 mm HAB (approx. 53 ms). Multistep mechanism for nanotube formation in flames was recognized. Post flame gas chemistry and formation of appropriate size catalyst particles were identified as the most critical steps. An order of magnitude growth-rate for the nanotubes in this interval is between 10 and 100 μm per second. Optimal condition for SWNT growth is around ϕ of 1.6 and appropriate size of catalyst particles.

The growth mechanism for SWNTs has been found to be very similar to the mechanism for other forms of solid carbon like soot. It has been well known that the precursors for soot are Polyaromatic Hydrocarbons (PAH) that are formed through the breakdown of C_2H_2. However, presence of high concentration of C_2H_2 causes the catalyst particle to be coated with amorphous carbon inhibiting the growth of SWNT. An earlier abundance of carbon species might poison the particle and prevent CNT inception earlier on in the flame volume. Therefore, following occurrences can affect the formation of SWNTs in a flame (Diener et al., 2000): (i) soot formation begins at a time where the metal particles have not yet grown large enough to act as a SWNT catalyst; (ii) catalytic particles with suitable size are synthesized but the large amount of acetylenic species poison the catalytic particles preventing their activation and inception of SWNTs.

Even though all the above mentioned experiments were conducted with fixed flame parameters and single catalyst material, the synthesized forms of carbon nano-materials is found to change dramatically. It is observed that change of flame position induces variation in macro-morphology and in the microstructure of the formed carbon nano-materials. The modification of growth conditions is directly related to variation of the flame environment pertinent to the specific flame location. Temperature, radical and hydrocarbon concentrations are strong functions of axial position in the flame. Availability of specific hydrocarbons at given flame location alters the growth mechanism leading to the selective production of various nanoforms. Hence, there is a need for more fundamental study related to the establishment of optimum growth region and the associated structure of carbon nanotubes inside a flame environment.

4. Growth controlling parameters

As mentioned previously, gas phase composition, temperature and the catalyst are the three major factors that determine the optimum region for carbon nanotube growth inside a flame. Careful control of these variables can result in a high yield rate of pure carbon nanotubes when compared to other synthesis methods. In this section, effect of each of these variables on the carbon nanotube growth is outlined.

4.1 Gas phase composition inside a flame

Carbon nanotubes are formed when carbon in gaseous form is deposited in form of the structured solid on to a catalyst particle. The concentration of gaseous precursors and the resulting deposition rate play an important role in determining the structure of the nanotube that is dependent on the concentration of gaseous precursor. These gaseous precursors are formed through the complex phenomena that occur inside a flame.

4.1.1 Fuel type and equivalence ratio

At steady state, the concentration of gaseous precursors in a flame is a function of the type of fuel, configuration of the flame and the local equivalence ratio (ϕ). Fuel rich flames ($\phi > 1$) are utilized for nanotube growth. In a premixed flat flame the equivalence ratio is uniform. Therefore, premixed flames have been studied to understand the effect of equivalence ratio on nanotube growth (Gopinath & Gore, 2007; Height et al., 2004; Vander Wal, 2000; Vander Wal et al., 2002).

Vander Waal et al. characterized the equivalence ratio range that may be ideal for CNT growth for different fuels. They found that methane did not produce any significant CNT growth. Ethane produced various nanostructures for equivalence range of $1.52 < \phi < 1.9$. For ethylene the growth started at $\phi = 1.50$ and best results are obtained at equivalence ratio of 1.62. Acetylene provided high growth of CNTs at all equivalence ratios. However, the growth was non-uniform and MWNTs with large diameter were obtained.

Gopinath and Gore observed that CNTs with maximum yield and best morphology were produced with ethylene flame for the equivalence ratio range of $1.5 < \phi < 1.6$. For a richer equivalence ratio ($1.62 < \phi < 1.75$), the yield of CNTs fell substantially. For a leaner equivalence ratio ($1.47 < \phi < 1.49$), the yield of CNTs was less than the maximum yield range, even for longer residence times. For $\phi < 1.45$, no CNTs were observed to grow and for $\phi > 1.75$, non- CNT structures of low yield were found to be predominant.

In the experiments carried out by Height et al. with $C_2H_2/O_2/Ar$ flames for growth of SWNTs, they examined the flame for equivalence ratio range of $1.4 < \phi < 2.0$. Nanotubes were observed to form between $1.5 < \phi < 1.9$. For low ϕ ($1.4 < \phi < 1.5$) the condensed material (particles and nanotubes) in the flame was dominated by discrete particles. For ϕ of 1.9 and higher, soot-like structures were found to dominate with clustered networks of primary particles ranging in size from 5 to 20 nm.

From these observations it is seen that for ethylene and acetylene there is a general agreement on the range of equivalence ratio ($1.5 < \phi < 1.8$) optimal for CNT growth. However for other fuels like (methane) there is no consensus. This suggests that the growth of CNTs is a function of gas phase concentrations of carbon containing gases which is in turn a combined function of equivalence ratio and type of fuel used.

In case of diffusion flames the mixing and hence the equivalence ratio is determined by the mass transfer due to diffusion between fuel and oxidizer streams. Hence the equivalence ratio is a function of spatial location and is difficult to measure experimentally. Thus the CNT growth region cannot be directly related to the equivalence ratio. However, when similar conditions were used by Yuan et al. (Yuan et al., 2001; Yuan et al., 2001) for CNT growth with ethylene and methane, ethylene deposited amorphous carbon whereas methane deposited CNTs. This observation suggests that, also in case of diffusion flames CNT growth gas composition in the flame.

Vander Wal et al. (Vander Wal et al., 2000) also noted that dilution of fuel with an inert like N_2 or Ar might be critical to the nanotube synthesis. Absence of diluent resulted in soot formation and encapsulation of the catalyst nano-particle with amorphous carbon. Yuan et al. (Yuan et al., 2001)observed that addition of diluent (N_2) reduced the temperature in the synthesis region that further resulted in reduced but more uniform yield of CNTs. Addition of diluents leads to altered flame structure which in turn can affect the gas phase composition.
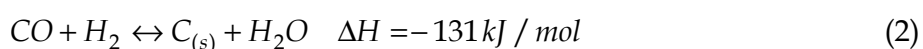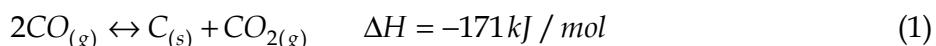
From the discussion above, it is clear that, there remains a need for characterizing different flames for similar gas phase composition that is favorable for CNT growth.

4.2.2 Gas phase precursors: CO and C_2H_2

In a flame environment, various carbon containing gas phase species are formed that are responsible for deposition of solid carbon. The two main contributors are hydrocarbons (C_nH_m) and carbon monoxide (CO).

Hydrocarbons decompose at high temperature to form solid carbon. With increase in number of carbon atoms (CH_4, C_2H_6, C_3H_8) these compounds become unstable. Methane is the most stable hydrocarbon that begins to decompose at 1200 K. Un-saturated hydrocarbons such as C_2H_2 and C_2H_4 are very susceptible to decomposition due to presence of disruptive π bonds. C_2H_2 is found to be unstable even at room temperature. In fact, C_2H_2 is one of the main precursors for soot formation inside flame. It also contributes primarily to the formation of carbon nanotubes if sooting conditions are avoided. Very fast decomposition of acetylene is the main cause of catalyst deactivation due to encapsulation by amorphous carbon.

Carbon monoxide (CO) participates in deposition of solid carbon via the Boudard (CO disproportionation) reaction and the hydrogenation reaction that are shown in equation (1) and (2) respectively.

$$2CO_{(g)} \leftrightarrow C_{(s)} + CO_{2(g)} \qquad \Delta H = -171\,kJ\,/\,mol \qquad (1)$$

$$CO + H_2 \leftrightarrow C_{(s)} + H_2O \quad \Delta H = -131\,kJ\,/\,mol \qquad (2)$$

The decomposition rate of CO disproportionation reaction is found to be low when compared with the acetylene decomposition, making it the ideal precursor for SWNT formation. Based on thermodynamic equilibrium, temperature range of 800 - 1100 K has been found to be ideal for CO disproportionation at normal pressure (Moisala et al., 2003). However, this range may not be ideal for catalyst particle formation, carbon dissolution and carbon precipitation. CNT yield is found to increase with increase in the CO pressure.

C_2H_2 and CO exhibit preferential activity towards certain catalysts. Comparative studies between these two gaseous precursors (Vander Wal, 2002; Vander Wal & Hall, 2001) in pyrolysis flames indicated that CO reacts with Fe based catalyst through carbide formation whereas C_2H_2 is active towards Ni based catalysts. Particle size plays a critical role towards determining the catalytic activity. Fe nano-particles of all sizes are generally inactive (toward nanotube synthesis) within C_2H_2 mixtures.

To assess the effect of carbon precursor on nanotube growth, gas phase chemistry in a premixed flame was studied by Vander Wal et al. (Vander Wal et al., 2002). Concentrations of various gases in the post flame environment were determined using gas phase

equilibrium calculations. Water gas shift reaction was assumed to be at equilibrium. Based on the experimental results and calculations a strong relation emerged between the optimum CNT synthesis conditions and the concentration of CO and H_2. An optimum window for nanotube synthesis based on CO and H_2 concentrations was deduced as shown in figure 6 (a). The concentration of C_2 species was found to be negligible in comparison to CO based on detailed chemistry calculations. Hence, CO was considered to be the main carbon source. However, the study lacked a comparison between the amount of solid carbon deposited and the gas phase carbon present in various species, making the above assumption speculative. The post flame temperatures were found to be constant irrespective of variation in the adiabatic flame temperature. With an identical H_2 concentration, there was a dramatic increase in the CNT yield with increases in CO concentration. At very high CO concentrations (in case of C_2H_2 flames) PAH and soot formation may result in the encapsulation of the catalyst material and reduction in CNT yields. At very high CO concentrations, surface carbon builds up to form an inactive layer on the catalyst surface (coking layer) without a carbon removal mechanism. Once formed, such a layer prevents further contact with carbon gas-phase species and thus stops the carbon atom supply.

Detailed chemistry calculations instead of equilibrium were performed by Gopinath and Gore (Gopinath & Gore, 2007) for a similar premixed flame arrangement. The hypothesis of water gas equilibrium at the CNT synthesis conditions was assessed. The effect of variation in equivalence ratio on the substrate temperature was found to be negligible confirming the observations by Vander Wal. The effect of changing equivalence ratios on CNT yield was interpreted, based on gas phase chemistry, using chemical kinetics computations. A one-dimensional premixed flame code with a post flame heat loss model, including detailed chemistry, was used to estimate the gas phase chemical compositions in the region of interest. The CNTs formed were in a very small amount even at the highest yield location. Hence it was difficult to quantitatively relate the change in the gas phase chemistry to CNT synthesis. Comparison of variation of concentration with equivalence ratio for different gas phase species was done to assess the effect of gas phase chemistry. Significant rise of up to 10 orders of magnitude was found to occur for C_2 hydrocarbons and up to 6 orders of magnitude of CH_4 relative to hydrogen mole fraction near the maximum yield equivalence ratio. On the other hand, the trends for CO and H_2 concentration showed monotonic variation with equivalence ratio. Rapid departures from the partial equilibrium of the water gas shift reaction and rapid changes in mole fraction ratios of C_2 unburned hydrocarbon to H_2 were observed in the range of equivalence ratios suitable for CNT growth. Based on this observation, it was argued that C_2 species might play an important role in carbon deposition as compared to CO. The slow kinetics of the CO disproportionation reaction at the experimental conditions was found to be in favor of the argument. Based on chemical kinetics calculations the optimum window was found to shift slightly to the lower side (as shown in Figure 6 (b) with maximum CO concentration ~10 %). Water gas shift reaction was found to diverge from the equilibrium at the CNT synthesis conditions. Hence the need of detailed chemistry calculations was established to correctly assess the effect of gas phase chemistry on the synthesis of CNTs in flames.

From the discussion it is evident that CO and C_2H_2 both contribute to the nanotube synthesis. However, further experimental and computational studies are required to examine the competing effects of C_2H_2 and CO on solid carbon formation in a flame.
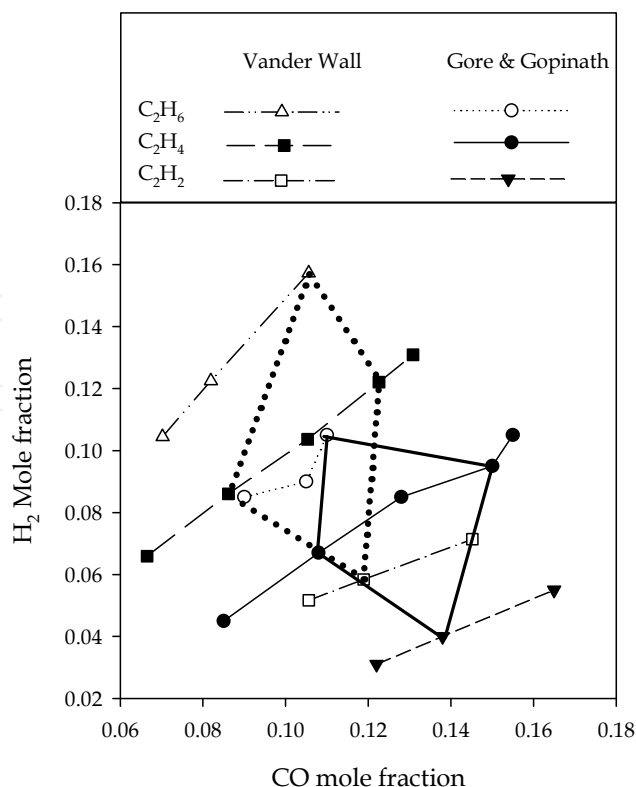
Fig. 6. Optimal CO and H_2 conditions for CNT synthesis based on partial equilibrium calculations **........** (Vander Wal et al., 2002) and detailed chemistry calculations _____ (Gopinath & Gore, 2007)4.2.3 Effect of other gas phase constituents: H_2, CO_2 and H_2O

Other gas phase constituents of the flame chemistry also have significant effect on CNT growth. H_2 acts as the primary etching agent to remove surface-adsorbed carbon. Higher H_2 concentrations greatly facilitate the catalysis of uniform and graphitic CNTs. However, very high concentrations of H_2 could compete for adsorption sites on the catalyst surface, thereby slowing the rate of CO adsorption and subsequent carbon supply to the CNT. H_2O and CO_2 participate indirectly in the CNT synthesis by altering the water-gas shift equilibrium. CO_2 is not known to contribute to the surface reactions nor can to interfere with adsorption of H_2 or CO. H_2O interacts with the adsorbed carbon on the particle surface. Gasification of surface carbon by H_2O at elevated temperatures can also hinder CNT growth. Thus CNT synthesis is hindered at lean conditions due to higher concentrations of H_2O, CO_2.

4.3 Temperature
Temperature is one of the important parameter that governs the growth of carbon nanotubes inside a flame. Evolution of temperature field and gas phase chemistry occurs simultaneously inside a flame, because of the coupled energy and mass transfer phenomena. The gas-solid interactions responsible for deposition of carbon are endothermic and thus are favored by high temperature (~ 1000 K). Flame environment provides an inherent source of heat and thus high temperature which makes it one of the ideal candidates for CNT growth. However, the temperature field inside the flame shows a large variation ranging from ~ 2000 K near the flame front to the cooler regions of ~ 800 K. Thus, appropriate regions of the flame need to be probed for the growth of carbon nanotubes. Li et al. (Li et al., 2009) tried to characterize the effect of temperature on the CNT growth in counter-flow flames. According to their study the ideal range for CNT growth was found to be 1000-1200 K which is also

comparable to the temperature range of CVD synthesis method. At this location in the flame the concentration of various carbon precursors is also found to be high. Similar observations have been reported by Vander Wal et al. (Vander Wal et al., 2002) and Gopinath and Gore (Gopinath & Gore, 2007) in case of premixed flames. Xu et al. also reported similar temperature range around ~1200 K for synthesis of MWNTs in an inverse diffusion flame.

The gas phase composition and temperature range discussed above are typically measured at scales much larger than those corresponding to that of the C60 molecule inception, growth and organization. Therefore, the ranges defined above can be deceptively broad and yet support a narrower range at the micro scale. In situ measurements of carbon growth species such as C_2H_2 and abstraction and addition processes involving H and C atoms are needed to develop nano scale and micro scale models.

4.4 Catalyst

Mainly, transition metals such as Iron (Fe), Nickel (Ni), Cobalt (Co) have been employed for CNT synthesis in a flame. Alloys of these metals with metals like Copper (Cu) and Zinc (Zn) have also been used. Properties of these catalyst materials can be found in literature (Moisala et al., 2003). Fe has the highest melting point (~1800 K) amongst the transition metal catalysts and is found to be reactive towards CO as compared to C_2H_2 (Baker et al., 1972; Baker et al., 1973; Vander Wal, 2002, 2002). It is found to be active even at smaller particle diameters (~1 nm) and hence has been successfully used for synthesis of SWNTs. It supports formation of MWNTs at sufficiently high temperature and CO concentration (Xu et al., 2006). MWNT formation has been extensively reported on stainless steel (Baker et al., 1973; Soneda & Makino, 2000; Vander Wal et al., 2002). Nickel has the lowest melting point amongst the transition metals (~1725 K) and is active towards C_2H_2 as compared to CO. It has a diametrical size threshold of ~5 nm above which it becomes active towards solid carbon deposition. Ni has been used for growth of MWNTs in flames with other carbon forms. Nickel when used as a substrate inside a flame undergoes surface break-up similar to Fe. Usually, with nickel the catalyst particles are found on the tip of the nanotubes indicating tip growth through surface growth. The MWNTs produced by nickel are well aligned as compared to Fe, however when subjected to high concentration of C_2H_2 nickel particles are poisoned due amorphous carbon deposition.

In case of substrate catalyst, the required catalytic nano-particles responsible for CNT growth are formed inside the flame primarily through the probe surface breakup induced by surface carbonization. The surface breakup occurs due lattice stress mismatch which a result of oversaturation of metal surface with solid carbon. This formation mechanism of catalyst nano-particles generally creates a wide variety of sizes and geometries (Baird et al., 1974; Moisala et al., 2003; Soneda et al., 2002; Soneda & Makino, 2000) which are determined by various factors, such as temperature, chemical species, and carbon solubility of the metal. Two other possible mechanisms for the direct formation of nano-particles on a metal probe surface in flames are OH oxidation-hydrogen reduction and evaporation–condensation. The inherent presence of oxygen-bearing species (e.g. OH) near the flame front on the fuel side can lead to local oxidization of the metal probe. However, these two mechanisms contribute little to nano-particle formation due to limited oxygen content and lower temperature. Furthermore, carbon-bearing species are overwhelmingly dominant in the local flame structure such that the surface breakup mechanism dominates for nano-particle formation.

In case of aerosol form, vapor molecule containing catalyst particle (nitrates, carbonyls or metallocenes of transition metals) undergoes rapid decomposition inside the flame to form the atoms of transition metal catalyst. These atoms coagulate further downstream in the flame giving rise to metal catalyst particle distribution that form the active sites for

nanotube growth. The particle sizes generated in this case are of the order of ~ 5nm that are suitable for SWNT growth. In fact, simultaneous growth of SWNT and the catalyst particle has been reported (Vander Wal, 2002). Ferrocene and nickelocene were used as the catalyst precursors for formation of catalyst particles. It was observed that it was difficult to form catalyst particle sizes above 5nm by the aerosol method due to large number of particles needed for coagulation (5 nm particle corresponds to ~10^4 atoms). It has been observed that Nickel becomes active towards nanotube synthesis for particle sizes above 5 nm. Thus it has been difficult to synthesize SWNTs using Ni.

5. Mathematical models for growth of CNTs in flames

Growth of carbon nanotubes in a flame environment is a multistep multi-scale phenomenon. Mathematical modeling of the various processes occurring during the synthesis is essential for gaining predictive capability and minimizing the number of experiments. As shown in figure 7 various processes occur either simultaneously or consecutively at different length scales. The two main spatial scales can be identified as (i) the bulk scale that includes the entire flame ~ 10 cm (as shown in figure 7 (a)) and (ii) the catalyst particle scale where the deposition of solid carbon occurs at small-scale ~ 100 nm (as shown in figure 7 (c)). The growth process can be broken down into following steps, (a) establishment of the flame that acts as the source for gaseous precursors and heat (b) simultaneous formation of catalyst particles and growth of carbon nanotube occurring at nano-scale. Each of the above mentioned process requires mathematical modeling along with a model to couple the models at various length scales.
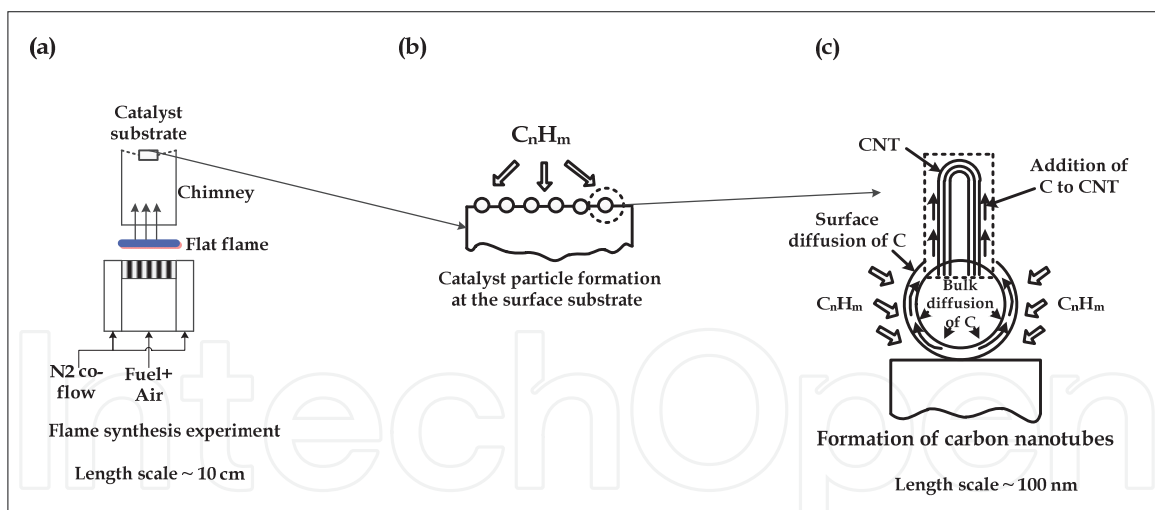

Fig. 7. Formation of carbon nanotubes in a flame environment

Accurate mathematical description of advection, diffusion and chemical processes is necessary in order to predict the gas phase composition and temperature in the flame environment. The fluid dynamics of the flame is captured through the solution of Navier-Stokes (NS) equations. Energy and species equation need to be solved simultaneously with the NS equations to completely capture the mass and energy transfer. Most of the reported experiments have used laminar flames for nanotube growth. Thus, a 2-D axisymmetric CFD calculation may be sufficient for capturing the flow in most of the cases. As described in section 3, in case of premixed flames, or counter flow diffusion flames, flat flame profiles

have been employed in CNT synthesis. For these flames, even a 1-D formulation can provide acceptable solutions, where in which 1-D continuity and momentum equation are solved along with energy and species equations. The equation of state provides the required relation between density, pressure and temperature. CHEMKIN packages based on this philosophy (e.g., premix and oppdiff) and other similar ones have been extensively used to model premixed and counter diffusion flames. The chemistry is modeled via detailed chemical kinetics mechanisms. However, in some of the growth experiments these flame environments have been modified by use of cooling chimneys (Gopinath & Gore, 2007; Vander Wal et al., 2002) in case of premixed flames and by the insertion catalyst substrates in case of counter flow flames (Li et al., 2007; Merchan-Merchan et al., 2003; Xu et al., 2007). In these situations, 2-D simulation that accurately captures the development of boundary layer along the walls needs to be used for better prediction of quantities inside the flame and post flame environment. In case of co-flow and inverse flow diffusion flames 2-D computations coupled with mixture fraction formulation comprise a good solution strategy. As the flow is inherently 2-D in these flames, one dimensional solution does not fare well. Axisymmetric combustion codes like UNICORN have been successfully used to model axisymmetric diffusion flames (Katta et al., 2005; Unrau et al., 2010). Complete mathematical description of the flame environment provides the required information of the gas phase composition and temperature at the bulk reactor scale. This information is further used to calculate various parameters related to the growth of carbon nanotubes.

Growth of carbon nanotubes at the catalyst particle surface through the deposition of solid carbon constitutes the next length scale i.e. the particle scale. The literature related to the flame synthesis of CNTs/CNFs is overwhelmingly experimental and provides observations rather than fundamental explanations and models (Naha et al., 2007). However, there have been few good attempts of describing the growth process of carbon nanotubes inside a flame (Celnik et al., 2008; Naha & Puri, 2008; Naha et al., 2007; Unrau et al., 2010; Wen et al., 2008; Zhang & Smith, 2005).

Development of gas phase chemistry and formation of catalyst particles occur simultaneously in a flame environment as shown in figure 7 (b). Catalyst particle coagulation in the aerosol form needs to be mathematically described along with the gas phase chemistry (Celnik et al., 2008; Kuwana & Saito, 2005; Wen et al., 2008). Kuwana and Saito (Kuwana & Saito, 2005) have described nano-particle growth from ferrocene in which they provided a two-step catalytic reaction model for the formation of Fe nano-particles. Wen et al. (Wen et al., 2008; Wen et al., 2007) employed a sectional method developed on simultaneous particle and molecule modeling (SPAMM) approach developed by Pope and Howard (Pope & Howard, 1997). In this approach, catalyst particle formation is modeled as reactions, that can be incorporated into a gas-phase reaction mechanism and allow for the simultaneous modeling of the gas-phase chemistry and the nano-particle formation processes.

Growth of carbon nanotube at the catalyst particle can be visualized as a collection of following process, (a) diffusion of carbon precursor gas species and their conversion to solid carbon (b) diffusion of the solid carbon over the surface of the catalyst particle and through the bulk, (c) encapsulation of the catalyst particle by the solid carbon and (d) nucleation and growth of the carbon nanotube. A schematic of these processes occurring together is shown in figure 7 (c).Diffusion of gaseous carbon species to the catalyst particle followed by the deposition of carbon is usually assumed to occur at the leading face of the particle. In most of the studies, this combined process has been modeled in terms of impingement rate based

on the kinetic theory (Naha & Puri, 2008; Naha et al., 2007; Wen et al., 2008). It can also be modeled in terms of reaction kinetics for the dissociation reaction of the individual gas species as mentioned in section 4.1. The deposited carbon is also desorbed, which can be described in an Arrhenius type equation. The solid carbon remaining at the leading face of the particle can now diffuse either along the surface of the catalyst nano-particle or through the particle. Surface diffusion leads to coating of the particle by the solid carbon. This process can be captured through a rate equation (Naha et al., 2007; Zhang & Smith, 2005). On the other hand the diffusion of solid carbon through the bulk of the particle establishes a concentration gradient across the particle. The concentration of solid carbon inside the catalyst particle can be obtained by solving the unsteady mass diffusion equation over the volume of the particle. At the trailing face of the catalyst particle, CNT nucleation can be considered to occur due to precipitation of the bulk diffused solid carbon. The nucleation and growth of the CNTs can be modeled based on a critical threshold cluster density number similar to the soot growth mechanism.

In conclusion, the mathematical description of the CNT growth process, involves large temperature and species variation occurring at the scale of flame environment, whereas the processes at the nano-scale are determined by the mass and energy transfer across the boundary layer. Thus, a careful multi-scale modeling approach is necessary to capture the essence of the nanotube growth.

6. Conclusions and future trends

From this review it is evident that flames have emerged as a viable method for bulk synthesis of CNTs and related nanostructures. The synthesis of CNTs and related nanostructures is affected by the flame environment's temperature and chemical species, geometry, burner configuration, and catalyst composition. Flames provide the chemical species and the thermal energy necessary for driving the synthesis process. Flame synthesis processes are scalable and large scale production of SWNTs has been reported (Richter et al., 2008). However, control over the complex processes occurring in a flame is deemed critical for generation of appropriate condition for CNT growth. A large variety of hydrocarbons have been used as fuels for flames. Thus identification of the optimum ingredients, fuel and oxidizer, for the development of industrial processes is essential. Measurements of carbon nanotube growth rates under well defined micro-scale gas phase environment are scarce. Development of boundary layer around the catalyst particle or substrate inside a flame environment needs to be carefully examined. More sophisticated models are required for capturing mass and energy transfer across the boundary layer. Multi-scale modeling approach is essential for these computations. Spectroscopic diagnostic techniques at the micro-scale need to be applied in the boundary layer region to obtain insitu measurement of species concentration and temperature near the catalyst surface. These measurements can provide the missing link of data between the large scale and the nano-scale processes occurring simultaneously during the flame synthesis of CNTs. It has been observed that careful control of the synthesis process is essential to preserve the properties of the CNTs and to avoid any impurities. However, flame environment is characterized by presence of large number of chemical species and varying temperature field. Thus control techniques are necessary for pure and uniform yield of CNTs in the flame environment. Electric biasing of the catalyst substrate has been found helpful in alignment of CNTs in flames. Better control over the flame temperature with use of chimneys has led to uniform growth of

CNTs. Addition of diluents to the flame has resulted in temperature reduction and more uniform growth of CNTs. Injection of pyrolysis gases in a non-hydrocarbon flame (H_2-O_2) flame has also been attempted for improved control.

In summary, future work in flame synthesis of CNTs is needed for the definition of a standard set of reactants based on nano-scale and micro-scale measurements and computations of the optimum growth environment. Macro-scale reactor geometries and bulk material composition that lead to desirable product quality and yield need to be defined. Finally, cost versus quality tradeoffs depending on the specific needs of an application will decide the method for synthesis of carbon nanotubes.

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Carbon nanotubes are one of the most intriguing new materials with extraordinary properties being discovered in the last decade. The unique structure of carbon nanotubes provides nanotubes with extraordinary mechanical and electrical properties. The outstanding properties that these materials possess have opened new interesting researches areas in nanoscience and nanotechnology. Although nanotubes are very promising in a wide variety of fields, application of individual nanotubes for large scale production has been limited. The main roadblocks, which hinder its use, are limited understanding of its synthesis and electrical properties which lead to difficulty in structure control, existence of impurities, and poor processability. This book makes an attempt to provide indepth study and analysis of various synthesis methods, processing techniques and characterization of carbon nanotubes that will lead to the increased applications of carbon nanotubes.

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