

**Review Article**

Recent Advances in the Flame Synthesis of Carbon Nanotubes

Junjie Chen^{*}, Xuhui Gao

Department of Energy and Power Engineering, Henan Polytechnic University, Jiaozuo, China

Email address:

juntpj@163.com (Junjie Chen)

^{*}Corresponding author**To cite this article:**Junjie Chen, Xuhui Gao. Recent Advances in the Flame Synthesis of Carbon Nanotubes. *American Journal of Materials Synthesis and Processing*. Vol. 2, No. 6, 2017, pp. 71-89. doi: 10.11648/j.ajmsp.20170206.12**Received:** September 15, 2017; **Accepted:** October 18, 2017; **Published:** November 15, 2017

Abstract: Significant progress has been made not only in improving the yields of carbon nanotubes, but also in gaining a profound fundamental understanding of the growth processes. Flames are emerging as a powerful tool for the synthesis of carbon nanotubes and carbon nanofibers. The flame volume provides a carbon-rich chemically reactive environment capable of generating nanostructures during short residence times in a continuous single-step process. The present work provides a concise review of the advances made over the past two decades in the areas of flame synthesis of carbon nanotubes and carbon nanofibers. An overview of existing flame methods to synthesize carbon nanotubes is first provided. Various catalytic materials, fuel types, and flame configurations have been employed in an attempt to achieve controlled synthesis of carbon nanotubes and carbon nanofibers. Diffusion and premixed flames in counter-flow and co-flow geometries are also discussed. Various hydrocarbon fuels, oxygen enrichment, and dilution with inert gases are then examined in detail. The ability to synthesize and control carbon nanotubes and carbon nanofibers is essential for the fabrication of nanomechanical and electrical devices. A fundamental understanding of the growth mechanism and development of control methods is critically important to address these issues. The purpose of the present review is to clarify the growth mechanisms and achieve controlled flame synthesis of carbon nanotubes and carbon nanofibers.

Keywords: Carbon Nanotubes, Flame Synthesis, Carbon Nanofibers, Growth Mechanisms, Multi-Walled Carbon Nanotubes, Single-Walled Carbon Nanotubes, Vertically Aligned Carbon Nanotubes, Nanostructures

1. Introduction

Carbon is a fundamental element found in a diverse range of natural structures, and can be obtained through versatile techniques. Carbonaceous structures are employed in a wide range of applications due to their outstanding mechanical, electrical, and thermal properties [1-4]. The development of novel carbonaceous structures, such as active carbon [5, 6], carbon nanotubes or carbon nanofibers [7-10], carbon spheroids [11], carbon onions [12], fullerenes [13], and glassy carbon [14] have attracted increasing interest in recent years. Among these carbon structures, carbon nanotubes are the most relevant because they exhibit remarkable mechanical, electrical, and thermal properties which are associated with their unique structure, high aspect ratio, and quantum size

effects, including semiconducting or metallic electrical behavior, high mechanical strength, and interesting chemical and surface properties [15-17]. All these properties depend on the synthesis method [18]. Indeed, the exceptional physical and mechanical properties of carbon nanotubes also present the opportunity to develop multifunctional carbon nanotube composites with tailored physical and mechanical properties. Potential applications include mechanical actuators, electronics, catalysis, sensors, high-strength composites, and adsorbents [15-18].

The discovery of fullerenes results in the discovery of a novel carbon elongated fullerene species, specifically multi-walled carbon nanotubes and later single-walled carbon nanotubes [19]. A flat graphene sheet can be re-arranged to take the shape of a hollow cylindrical or spherical structure

with remarkable mechanical, electrical, and thermal properties [20-27]. In the past two decades, gas-phase flames have emerged as a powerful tool for the synthesis of carbon nanotubes and carbon nanofibers [28]. The flame volume provides a carbon-rich chemically reactive environment capable of generating nanostructures during short residence times in a continuous single-step process. In recent years, gas-phase flame synthesis has not only proved to be one of the most economical and scalable technologies for producing well-controlled nanostructured materials, but also has been recognized as a robust fabrication method of nanomechanical devices [29, 30].

Iijima [31] first observed multi-walled carbon nanotubes in the process of producing fullerenes using an electric-arc discharge technique. This discovery is of particular importance because it brought carbon nanotubes into the awareness of the scientific community as a whole. Since discovered by Iijima [31], carbon nanotubes have been the focus of considerable attention. Numerous investigators have reported remarkable physical and mechanical properties for this new form of carbon. From unique electronic properties and a thermal conductivity higher than diamond to mechanical properties where the stiffness, strength, and resilience exceeds any current materials, carbon nanotubes bring tremendous opportunities for the development of fundamentally new material systems [16]. In particular, the exceptional mechanical properties of carbon nanotubes, combined with their low density, offer great scope for the development of nanotube-reinforced composite materials. The potential for nanocomposites reinforced with carbon tubes having extraordinary specific stiffness and strength represent tremendous opportunity for application in the twenty first century [16]. There has been increasing interest in the synthesis and physical properties of carbon nanotubes due to their important applications.

On the other hand, the discovery of single-walled carbon nanotubes was independently reported by Iijima and Ichihashi [32] and Bethune *et al.* [33], which was in the process of producing endohedral metallofullerenes using a plasma arc discharge technique. Since the discovery of these novel carbon structures, significant effort has been devoted to their potential applications and at the same time to the development of reliable and efficient methods for the production of these structures in commercial quantities. Primary synthesis methods for single and multi-walled carbon nanotubes and carbon nanofibers include arc-discharge, laser ablation, gas-phase catalytic growth from carbon monoxide, and chemical vapor deposition from hydrocarbons methods [16, 28]. For certain applications, large quantities of carbon nanotubes and carbon nanofibers are required, and the scale-up limitations of the arc discharge and laser ablation techniques would make the cost of nanotube-based composites prohibitive. During the synthesis of carbon nanotubes and carbon nanofibers, impurities in the form of catalyst particles, amorphous carbon, and non-tubular fullerenes are also produced. Thus, subsequent purification steps are required to separate the carbon nanotubes and carbon

nanofibers. The gas-phase synthesis processes tend to produce carbon nanotubes and carbon nanofibers with fewer impurities and are more amenable to large-scale processing. Consequently, gas-phase techniques for the growth of carbon nanotubes offer the greatest potential for the scaling-up of the production of carbon nanotubes and carbon nanofibers [16]. Flames as a novel emerging synthesis method for the production of multi-walled carbon nanotubes are reviewed in detail in Section 2. Flame synthesis as well as challenges encountered in order to obtain the well-controlled nanostructured materials are discussed. Various configurations of premixed, partially premixed, diffusion, and inverse diffusion flames have been used as a hydrocarbon feedstock with a metal catalyst for a wide variety of applications in the synthesis of carbon nanotubes. The advantages of an oxygen enriched opposed-flow flame configuration for the synthesis of carbon nanotubes are presented. The effect of fuel and fuel additives along with the effect of catalyst material are evaluated for optimizing growth of carbon nanotubes. Several factors have been found to contribute to the flame synthesis of carbon nanotubes, including the accessibility and chemical composition of catalyst particles for the inception of carbon nanotubes, the accessibility of the carbon source in the gas-phase, and the availability of a continuous process to convert carbon from the gas-phase to the solid-phase.

The control of the growth and orientation of carbon nanotubes in flames is discussed in Section 3. For certain applications, it is required that carbon nanotubes are of high purity, in addition to highly aligned arrays. Recently developed techniques, coupled with the flame synthesis method for controlling the growth directions of carbon nanotubes, include the use of electric field forces and the use of nanotemplates to obtain vertically aligned carbon nanotubes. The ability to control carbon nanotube orientation, alignment, length, diameter, uniformity, purity, straightness, and internal structure is essential for potential fabrication of nanomechanical and electrical devices. Therefore, in order for products based on carbon nanotubes to become a reality, a robust inexpensive flame synthesis method is required that has the capability to produce carbon nanotubes on desirable surfaces and particularly in a controllable manner. Various methods developed using various flame systems for the synthesis of vertically aligned carbon nanotubes are discussed in detail.

Similar to the synthesis of multi-walled carbon nanotubes, a flame system with an appropriate catalytic material, heat source, and ideal source of carbon can lead to the production of single-walled carbon nanotubes. The critical factors that significantly affect the flame synthesis of single-walled carbon nanotubes are discussed, including the type of reactant gas environment, flame pressure, fuel to oxygen equivalence ratio, and composition and insertion rate of catalyst particle into the flame system. The alteration of the flame parameters and catalyst properties can significantly affect the source of carbon and heat, catalyst particle formation, activation and deactivation of the catalyst particle for the flame synthesis of

single-walled carbon nanotubes. The effect of the variation of these parameters on the flame synthesis of single-walled carbon nanotubes is discussed in detail in Section 4.

The growth mechanisms for carbon nanotubes and carbon nanofibers are presented in detail in Section 5. One of the major challenges for the flame synthesis of carbon nanotubes is the ability to produce carbon nanotubes and carbon nanofibers with controllable morphology and of “beyond the lab scale” in an inexpensive manner. In order to develop robust and controllable synthesis methods, it is necessary to understand the growth mechanism of carbon nanotubes and carbon nanofibers. However, the study is only in its infancy and despite great efforts much work remains to be done in this regard. Finally, conclusions and directions for future work are provided in Section 6. This review is not intended to be comprehensive, as the focus is on exploiting the flames as a viable alternative method for the synthesis of carbon nanotubes and carbon nanofibers toward the development of large-scale production in order to satisfy growing industrial demand.

2. Flame as a Synthesis Medium

Combustion is a complex phenomenon involving self-sustaining chemical reactions accompanied by rapid heat release that typically occurs in the form of a high temperature reaction front. Heat, light, and work such as engines are the primary areas for application of combustion processes. In certain cases, however, the main purpose for these reactions is the formation of condensed combustion products, i.e. the synthesized materials. Compared to other high-temperature techniques for fabrication of nanostructures, combustion does not require any external heating sources, since the process uses heat produced by highly exothermic reactions [34, 35]. Furthermore, the short reaction duration and rapid product cooling can lead to the formation of non-equilibrium products with unique electrochemical, physical, and mechanical properties [34, 35].

Since carbon nanotubes were discovered nearly two decades ago, there have been a variety of techniques developed for producing them [28]. There are essentially three key components required for the synthesis of carbon nanotubes or carbon nanofibers: a source of carbon, a source of heat, and presence of metallic catalyst particles [28]. Arc-discharge, laser-ablation, and chemical vapor deposition have been the three main methods used for the synthesis of carbon nanostructures [28, 34]. Most of these processes take place in a vacuum or with process gases. The arc-discharge technique generally involves the use of two high-purity graphite rods as the anode and cathode. The rods are brought together under a helium atmosphere and a voltage is applied until a stable arc is achieved. The exact process variables depend on the size of the graphite rods. As the anode is consumed, a constant gap between the anode and cathode is maintained by adjusting the position of the anode. The material then deposits on the cathode to form a build-up consisting of an outside shell of fused material and a softer

fibrous core containing carbon nanotubes and other carbon particles. Laser ablation was first used for the initial synthesis of fullerenes. In this technique, a laser is used to vaporize a graphite target held in a controlled atmosphere oven at temperatures near 1500 K. While these techniques are capable of producing carbon nanotubes or carbon nanofibers, they are limited to relatively small-scale production and batch-wise operation. Both the arc-discharge and the laser-ablation techniques are limited in the volume of sample they can produce in relation to the size of the carbon source [16]. These limitations have motivated the development of gas-phase synthesis techniques. The gas-phase synthesis techniques are amenable to continuous processes since the carbon source is continually replaced by flowing gas. Additionally, the final purity of the as-produced carbon nanotubes can be quite high, minimizing subsequent purification steps [16]. Flame synthesis is a continuous-flow, readily scale-able method with the potential for considerably lower cost production of carbon nanotubes or carbon nanofibers than is available from other synthesis methods.

A newly reported synthesis method with greater scalable potential, specifically combustion or flame synthesis, has recently emerged and is gaining significant momentum [35-40]. This synthesis method is a continuous process resulting in lower cost and possesses the potential for high volume production of carbon nanotubes or carbon nanofibers. A fuel-rich flame is a high-temperature, carbon-rich environment that can be suitable for the formation of carbon nanotubes if metals are introduced into the system. Furthermore, a premixed, one-dimensional flame can serve as a convenient platform for systematic characterization of the formation dynamics of carbon nanotubes.

The potential of the flames for synthesis of elongated carbon nanoforms was demonstrated [41] long before carbon nanotubes were discovered by Iijima [31] in the process of vaporization of graphite. The formation of elongated filamentous carbon on the surface of a solid support inserted in a diffusion flame was reported in very early flame studies [28]. The formed filaments were hollow with metal granules at the tips. The reported deposit structures closely resembled structures of carbon filaments formed by methane and carbon monoxide decomposition over transition metal catalysts [41]. In the same year when carbon nanotubes were discovered by Iijima [31], Saito *et al.* [42] reported the formation of elongated carbonaceous structures on the surface of a probe introduced in a sooting hydrocarbon flame. The materials deposited on the wire probes were composed of elongated structures that had diameters and lengths resembling the external morphology of carbon nanotubes or carbon nanofibers and was only found in a certain flame position using ethyne as a fuel. However, it is doubtful that the pioneers in the field were adequately equipped to characterize the nanostructures formed in the deposited material. A few years later, Howard *et al.* [43] used spectroscopy studies on samples of condensable compounds collected from a low-pressure flame to study the ratio of fullerene composition. These studies showed that the ratio of fullerene composition is highly dependent on the flame

residence time, carbon to oxygen ratio, flame temperature, and flame pressure. A year after the discovery of single wall carbon nanotubes, Howard *et al.* [44] discovered the presence of multi-walled carbon nanotubes coexisting with soot-like structures in condensable material collected from a low-pressure premixed flame. Prior to these reports, the highly ordered carbon cylindrical structures had been produced only by very energetic processes such as laser and plasma vaporization but not in flames. The above-mentioned studies of Howard *et al.* [44] showed the potential of the flame technology for the synthesis of carbon nanotubes and carbon nanofibers. These early findings were one of the contributing factors that prompted scientists working in combustion to modify their existing combustion systems and apply them to the flame synthesis of carbon nanotubes and carbon nanofibers. Consequently, various flame configurations have been applied in order to synthesize carbon nanotubes and carbon nanofibers, including premixed, diffusion, partially premixed, and inverse diffusion flames [28, 30].

Perhaps, the earliest observation of intriguing tube-like structures in flames was reported in the 1950s and within the past two decades there have been occasional reports of carbon nanotube structures [28]. In recent years, Saito and co-workers [42], Howard *et al.* [43, 44], Vander Wal *et al.* [45], and Merchan-Merchan *et al.* [28] have independently made more detailed studies of formation of carbon nanotubes in flames. Saito *et al.* [42] immersed metallic substrates in methane-fueled and ethene-fueled, co-flow diffusion flames, as well as observed multi-walled carbon nanotubes that had formed on the substrate. Howard *et al.* [43, 44] observed carbon nanotubes from a low-pressure flame while Vander Wal *et al.* [45] has observed single-wall carbon nanotubes and carbon nanofibers in hydrocarbon-air diffusion flames with nitrogen diluent and metallocene catalyst precursor compound added to the fuel stream, and premixed flames with a supported-catalyst technique. Merchan-Merchan *et al.* [28] observed multi-walled carbon nanotubes in an opposed-flow methane diffusion flame without the addition of metal catalysts.

Various flame configurations have been used as a hydrocarbon feedstock with a metal catalyst for material synthesis applications [45-50]. In the flame synthesis method, the gas-phase growth of carbon nanotubes can take place through the introduction of a catalyst as a particle in the form of a solid support or in the gas-phase. Whatever flame configuration is employed, it must provide an ideal source of carbon to form the graphite layers, utilize the catalytic metal nanoparticles to form the solid graphitic layers from gas-phase carbon containing molecules, and provide a heat source for forming and activating the catalyst nanoparticles. Recent experiments have demonstrated that various flame parameters and catalyst properties can be applied to control the above factors [28]. It is worth noting that in diffusion flames, carbon nanotubes and carbon nanofibers can be synthesized within the sooting regions presented in the flame. Frequently, the sooting region is located within the flame volume and shielded by a thin blue flame. On the other hand, in an inverse diffusion

flame, the flame structure is quite different. In this case, the inner blue flame volume is shielded by a large sooting flame which is located outside the flame front. In contrast to the diffusion flame, in an inverse diffusion flame, the formation of carbon nanotubes and carbon nanofibers can be found in a region outside the sooting region. Flames produced under different sets of conditions and in various configurations have been explored for the synthesis of carbon nanotubes and carbon nanofibers.

The flame synthesis conditions can be optimized by controlling pressure, as well as by varying fuel type and additive, flow velocity, and fuel to oxygen equivalence ratio. Furthermore, evolving technologies on the design and development of more efficient catalytic materials and their delivery methods have greatly enhanced the growth control of carbon nanotubes and carbon nanofibers. The application of solid supports for the flame synthesis of carbon nanotubes and carbon nanofibers involves the initial formation of catalyst nanoparticles on the surface of the probe, followed by the inception and growth of carbon nanotubes. Flames are a unique synthesis medium that provides both chemical species and energy for the synthesis of carbon nanotubes and carbon nanofibers. In comparison with the chemical vapor deposition process, flame synthesis is an autothermal process that is capable of providing temperature optimal for achieving desired synthesis conditions. Flames can also be considered as a source of chemical species that include various hydrocarbon molecules, radicals, hydrogen, carbon monoxide, and other chemical species. In comparison with a typical chemical vapor deposition process, a flame medium is characterized by a complex homogeneous kinetics that involves reactions between fuel and oxidizer with formation of water, carbon dioxide, and partial oxidation products and fuel pyrolysis with formation of secondary hydrocarbon species such as light and heavy hydrocarbons, polycyclic aromatic hydrocarbons, and soot precursors. In comparison with the chemical vapor deposition, a flame medium is rich in intermediate radicals formed in high concentrations during intense homogeneous reactions. This homogeneous kinetics is closely coupled with heterogeneous kinetics of the formation of nanostructured solid carbon.

Yuan *et al.* [51, 52] evaluated the effects of residence time, fuel type, catalytic support type, and its delivery method using a laminar co-flow diffusion flame for the synthesis of multi-walled carbon nanotubes. SEM (scanning electron microscope) and TEM (transmission electron microscopy) images of multi-walled carbon nanotubes from co-flow flames at atmospheric pressures are shown in Figure 1. The synthesis of multi-walled carbon nanotubes was carried out using methane-air, ethene-air, and nitrogen-diluted ethene diffusion flames, respectively, under atmospheric pressure condition. The catalyst supports employed were in the form of grids and wires undergoing an oxidation process, and grids pre-loaded with cobalt nanoparticles. The grid was pre-oxidized using a lean premixed propane-air flame. The pre-oxidation allowed for nanodispersed catalyst particles to form on the surface of the grid before inserting it into the flame for the synthesis of

multi-walled carbon nanotubes. The cobalt pre-loaded grids were prepared by electrodepositing the single cobalt nanoparticles on the surface. A catalyst support with a chemical composition of nickel and chromium was introduced in the methane-air flame system. The methane-air flame produced entangled multi-walled carbon nanotubes with a

diameter range of 20 to 60 nm, as illustrated in Figure 1 (a) and (b). It has been found that multi-walled carbon nanotubes can grow based on the mechanism of “base growth model” as nickel oxide particles where found embedded inside some of the carbon nanotubes, as shown in Figure 1 (b).

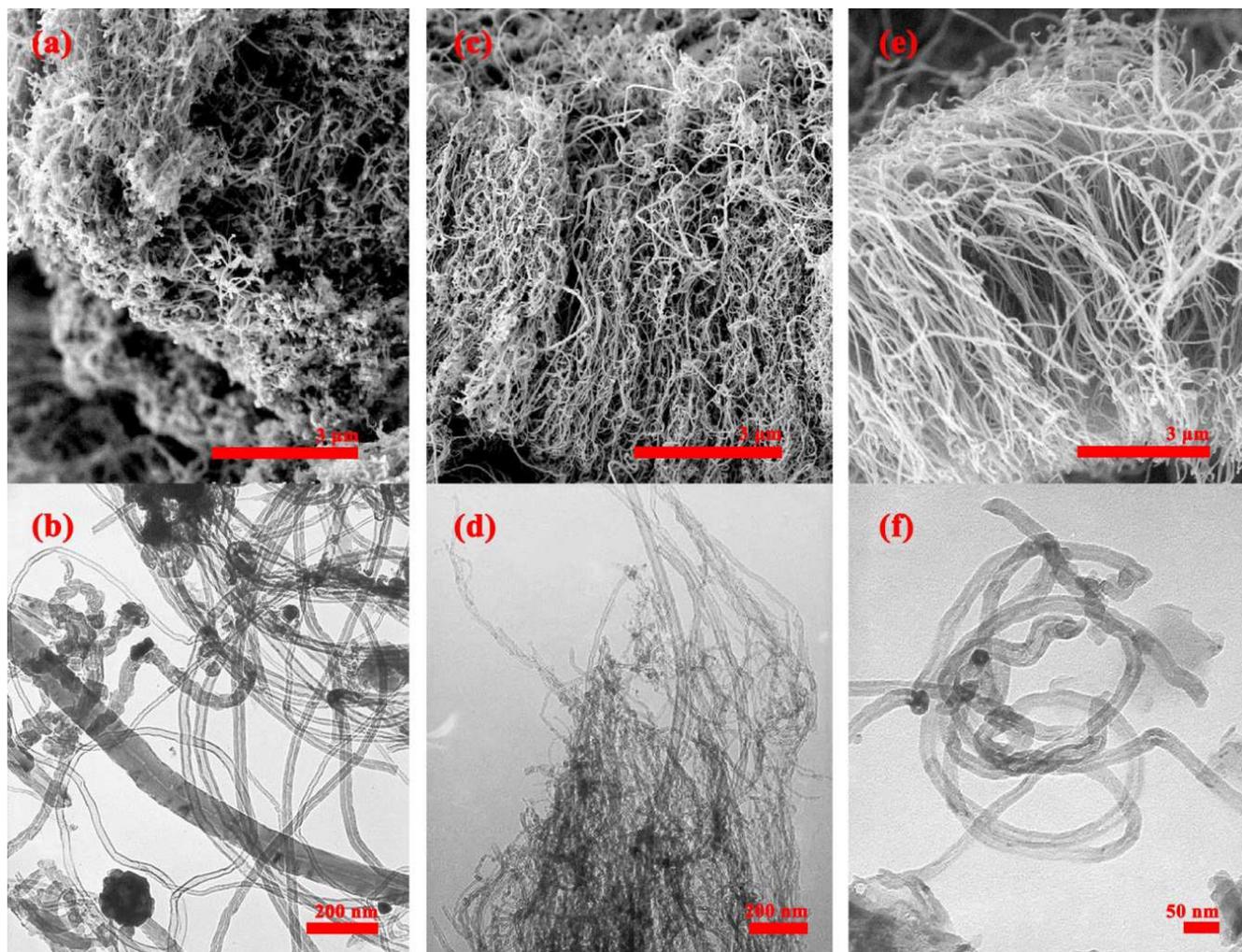


Figure 1. SEM and TEM images of multi-walled carbon nanotubes from co-flow flames under atmospheric pressure condition, from Refs. [51, 52]. Panels (a) and (b) show carbon nanotubes synthesized from a methane-air flame on a nickel-chromium wire; Panels (c) and (d) show carbon nanotubes synthesized from a nitrogen-diluted ethene diffusion-flame using a pre-oxidized stainless steel sampling grid coated with catalyst particles created by a premixed propane flame; Panels (e) and (f) carbon nanotubes synthesized from a nitrogen-diluted ethene diffusion-flame using a cobalt-coated stainless steel grid.

Adapted with permission from *Chemical Physics Letters*, Volume 340, Issues 3-4, Liming Yuan, Kozo Saito, Chunxu Pan, F. A Williams, and A. S Gordon. Nanotubes from methane flames, Pages 237-241; and from *Chemical Physics Letters*, Volume 346, Issues 1-2, Liming Yuan, Kozo Saito, Wenchong Hu, and Zhi Chen. Ethylene flame synthesis of well-aligned multi-walled carbon nanotubes, Pages 23-28. Copyright (2001), with permission from Elsevier.

In contrast to the exposure of the nickel-chromium wire in the methane-air flame, the insertion of the nickel-chromium wire in the ethene-air flame led to the formation of some carbon fibers loaded with amorphous carbon particles, indicating the oxidation process in the ethene flame to be somewhat different from the methane-air flame, as well as that the shape of the catalytic support is essential. The ethene nitrogen-diluted diffusion flame synthesis performed using the pre-oxidized stainless steel grid containing iron, chromium, and nickel oxide deposits on its surface, led to structures similar to those grown in the methane-air flame on the surface

of a nickel-chromium wire. That is, bundles of entangled and curved multi-walled carbon nanotubes with diameters ranging from 10 to 60 nm coexisting with some carbon fibers, as shown in Figure 1 (c) and (d). A flame system formed using a nitrogen-diluted ethene diffusion flame with the catalytic support prepared in the form of a stainless steel grid with cobalt particles electrodeposited on its surface resulted in aligned multi-walled carbon nanotubes with a monodisperse diameter size distribution, as shown in Figure 1 (e) and (f). At a certain flame position, it was found that the introduction of nitrogen can decrease the flame temperature by approximately

300 K. Furthermore, the nitrogen addition into the flame system has been found to be a critical parameter to straighten the entangled carbon nanotubes, which may be attributed to the lowering of the flame temperature leading to aligned

multi-walled carbon nanotubes, as shown in Figure 1 (c). In the methane-air flame synthesis, the pyrolysis products were stable as well as the pyrolytic carbon concentration was much lower than that in ethene-air flames.

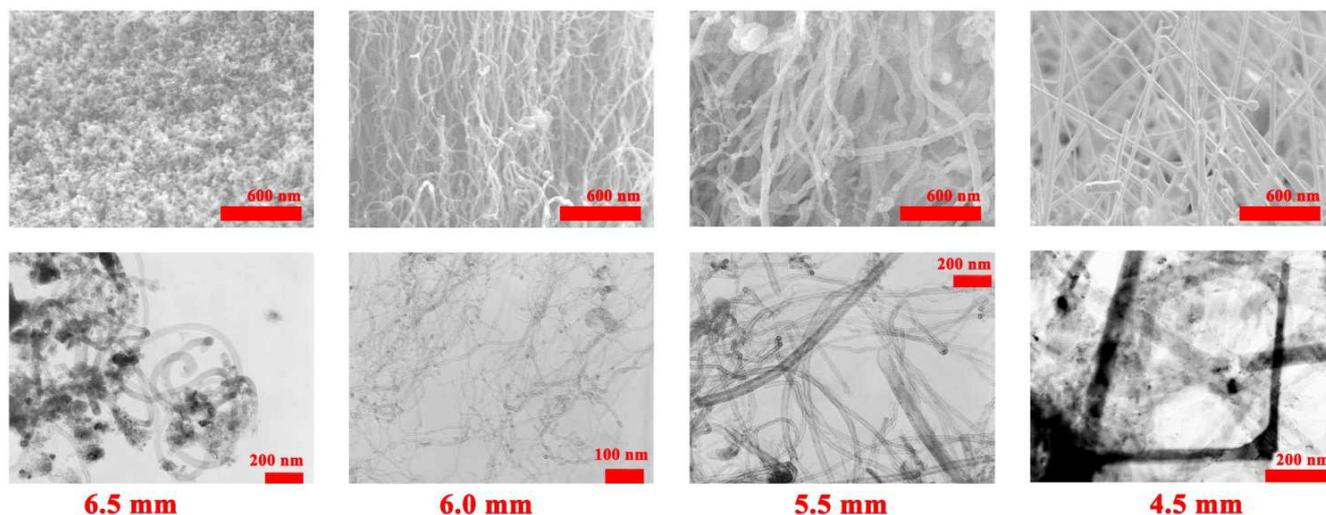


Figure 2. SEM and TEM images of carbon nanotubes formed on the substrate positioned at 6.5, 6.0, 5.5, and 4.5 mm, respectively, in the radial direction from the flame center, from Ref. [53].

Adapted with permission from *Combustion and Flame*, Volume 139, Issues 1-2, Gyo Woo Lee, Jongsoo Jurng, and Jungho Hwang. Formation of Ni-catalyzed multiwalled carbon nanotubes and nanofibers on a substrate using an ethylene inverse diffusion flame, Pages 167-175. Copyright (2004), with permission from Elsevier.

Experiments performed by Lee *et al.* [53] supported the above-mentioned results of Yuan *et al.* [51, 52], and showed that the flame temperature can play an important role in the synthesis and orientation of carbon nanotubes. Scanning electron microscope and transmission electron microscopy images of carbon nanotubes formed on the substrate are shown in Figure 2. To synthesize the nanostructures, an inverse ethene nitrogen-diluted flame was employed [53]. It was found that the well-aligned multi-walled carbon nanotubes with diameters ranging from 20 to 60 nm were formed on the surface of the probe when the flame temperature was varied from 1400 to 900 K. In contrast, only carbon nanofibers were synthesized in the flame volumes where the flame temperature was lower than 900 K, which can be attributed to the activation efficiency and the life of the nickel catalyst particles formed at lower temperatures. The nickel particles for the flame synthesis of the carbon nanotubes originated from the nickel nitrate coated on a stainless steel substrate. The melting point of bulk nickel is approximately 1728 K. The nickel critical temperatures are significantly higher than the flame temperature. The temperature of the probe inserted in the flame is usually lower than the flame temperature due to intense radiative heat losses. Since catalytic nanoparticles were already pre-loaded on the substrate, it significantly reduces the melting and evaporation temperatures while significantly increasing its function for the gas-phase growth of carbon nanotubes.

Xu *et al.* [54] employed as drawn transition-metal alloy probes of various compositions in the form of wires to study the synthesis of carbon nanotubes in a methane inverse

diffusion flame with a co-flow configuration. The effect of catalytic material as a function of local gas temperature and availability of carbon species including carbon monoxide, ethyne, and hydrogen for the flame synthesis of carbon nanotubes was studied. The correlation of flame material synthesis on the surface of probes with the measurements of the gas temperature and chemical species provides information on what promoted the gas-phase growth of carbon nanotubes within this particular flame environment. Probes of various chemical compositions were tested for the flame synthesis of carbon nanotubes. A variety of structures, including carbon nanotubes and carbon fibers with entangled and twisted morphology, can be synthesized in a single flame as a function of the various probe compositions and flame heights. One of the most intriguing results of Xu *et al.* [54] is the application of the binary and ternary alloys as catalysts for the flame synthesis of carbon nanotubes. This effect was tested at various flame positions. From the employed probes it was found that the best alloy composition for the gas-phase growth of carbon nanotubes is the ternary nickel-chromium-iron. Carbon nanotubes synthesized on the ternary probe show better diameter uniformity and at a location closer to the tip short vertically aligned carbon nanotubes with lengths of a few microns are synthesized. The binary and the ternary alloys are exposed to the same flame height and, thus, flame regions with similar temperature and chemical species. However, the morphology of the synthesized carbon structures is very different. From their findings it is clear that the chemical compositions of the probe itself can play an important role in the flame synthesis of

carbon nanotubes as well as morphological control. Furthermore, Xu *et al.* [54] evaluated the effect of voltage bias on the nickel-chromium-iron sampling probe on the gas-phase growth of carbon nanotubes. The ideas behind using electrical assistance are to electrophoretically keep soot particles and their precursors from contaminating the yield of carbon nanotubes, and to optimize hydrocarbon precursor delivery to the catalyst nanoparticles through chemical effects induced by

transposing and re-distributing ionic species by the action of the electric fields. The results showed that voltage bias on the substrate is conducive to aligning carbon nanotubes, as well as enhancing their growth rates as compared to grounded conditions, as depicted in Figure 3. Both negative and positive voltages seem to improve the alignment and gas-phase growth of carbon nanotubes, with negative voltages being a bit better.

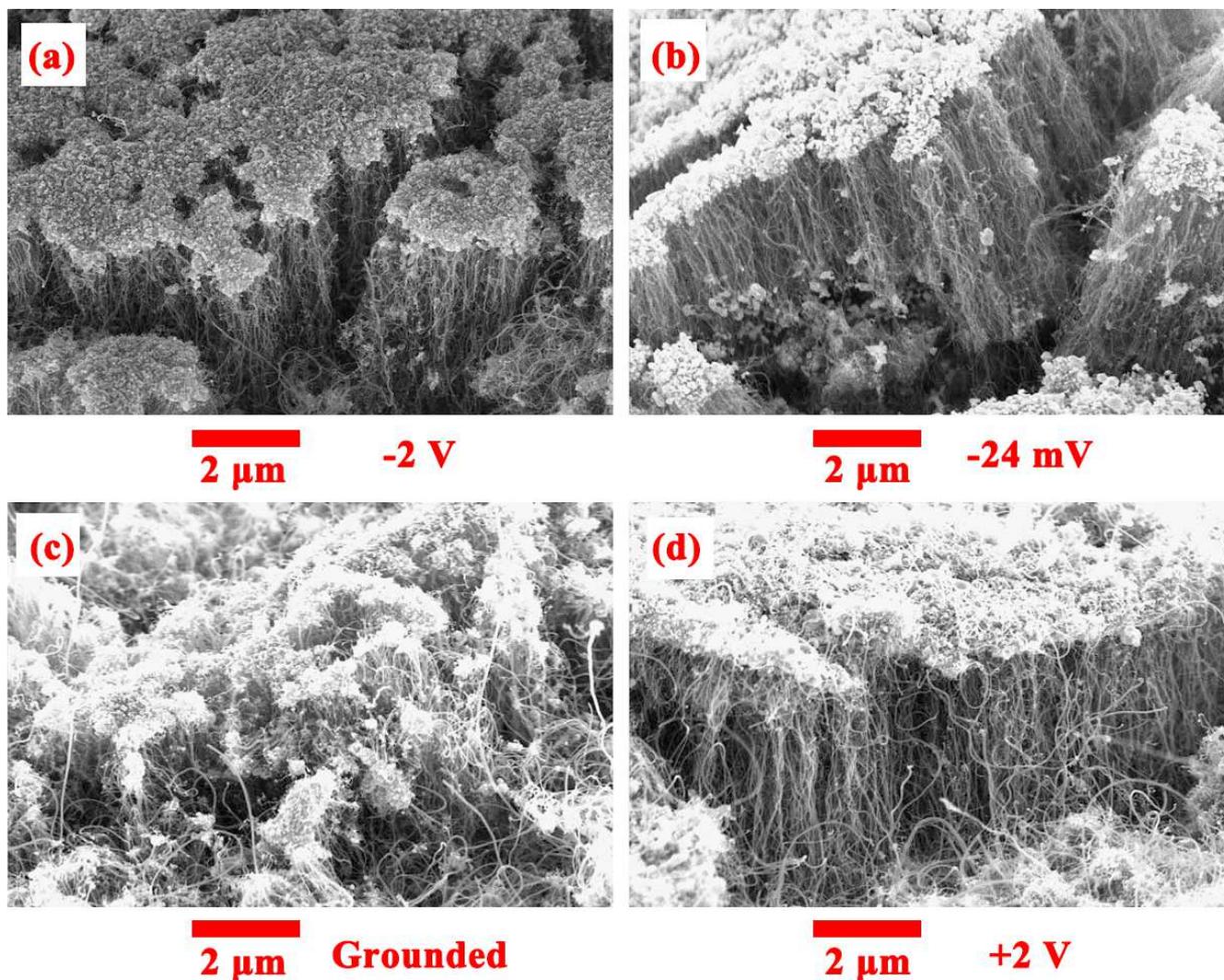


Figure 3. Effect of voltage bias applied to nickel-chromium-iron catalytic probe at the vertical sampling position of 12 mm and the radial sampling position ranging from 1.75 to 3.25 mm in a methane inverse diffusion flame with a co-flow configuration, from Ref. [54].

Adapted with permission from *Carbon*, Volume 44, Issue 3, Fusheng Xu, Xiaofei Liu, and Stephen D. Tse. Synthesis of carbon nanotubes on metal alloy substrates with voltage bias in methane inverse diffusion flames, Pages 570-577. Copyright (2006), with permission from Elsevier.

Co-flow diffusion, laminar, and inverse diffusion flames have been employed for the synthesis of multi-walled carbon nanotubes and carbon nanofibers. Although significant progress has been made in co-flow flames, it is increasingly recognized that the use of an opposed-flow flame configuration can provide better sampling possibilities as well as improve the interpretation of results, especially in the case of oxygen enriched flames [49]. First, an opposed-flow flame has essentially a one-dimensional geometry providing sufficient sampling area of uniform chemical composition and

temperature. At the same time, the influence of catalytic substrate positioning in the flame can be adequately studied by precise axial displacement of the probe. Second, the opposed-flow flame remains stable and well-confined in a wide range of strain rates and with variations of fuel type and oxygen enrichment. Third, due to the simple geometry, the opposed-flow flame can be simulated using a one-dimensional numerical model that allows implementation and valuation of complex multi-step kinetic mechanisms. Furthermore, counter-flow oxy-flames have strong potential for the

gas-phase growth of carbon nanotubes, producing high temperatures and high radical concentrations [49].

Recently, flame synthesis of carbon nanotubes was performed by Chong *et al.* [37] using a laminar premixed flame combustor at open atmospheric condition. The gas-phase growth of carbon nanotubes on the substrate was supported catalytically by a transition metal under high temperature, hydrocarbon-rich environment. A premixed flame combustor was utilized to establish an open, cone-shaped flame at atmospheric condition. The body of the combustor is cylindrical in shape. Propane was employed as fuel source to premix with air to establish a fuel-rich flame, providing the carbon source for the growth of carbon nanotubes. Nano-sized nickel catalysts are coated on a substrate of stainless steel wire mesh placed above the premixed combustor for the growth of carbon nanotubes. Analysis of the carbon nanotubes using high resolution electron microscope revealed the structure of synthesized carbon nanotubes in disarray, clustered and tubular form. The graphitic structure of the carbon nanotubes were rather similar for all fuel-rich equivalence ratios tested, with an average diameter of 11 to 13 nm. High resolution transmission electron microscopy images of carbon nanotubes in disarray form, nickel catalyst encapsulated by graphitic structure at the tip of

carbon nanotubes, and amorphous carbon formed in the sample are shown in Figure 4. The carbon nanotubes were found to be long, cylindrical in shape and hollow in the middle of the carbon tube. The physical appearance of carbon nanotubes was in disarray, often in entangled form with different bends and curvatures due to their long structural length, as shown in Figure 4 (a). High-resolution micrograph of transmission electron microscopy showed that catalyst particles were encapsulated by the graphitic structure and located at the tip of carbon nanotubes, as shown in Figure 4 (b). Based on the vapor-liquid-solid mechanism, the carbon radical species produced during decomposition of propane were absorbed on the surface of the nickel catalysts, followed by bulk diffusion of carbon atom into the metal catalysts. When liquid metastable carbide reached supersaturated stage, solid carbon precipitated to form carbon nanotubes [37]. The measured temperature on the substrate during the flame synthesis of carbon nanotubes was within the range of 1142 to 1287 K, which is favorable for carbon deposition due to gas-solid interactions. Figure 4 (c) shows the micrograph of amorphous carbon in the samples. Amorphous carbon encapsulated the nickel particles, resulting in catalyst deactivation, and subsequently prohibited the formation of carbon nanotubes [37].

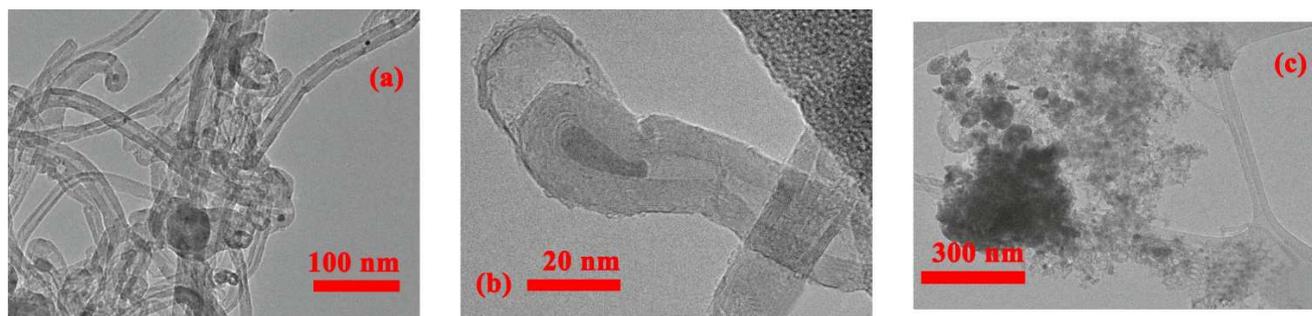


Figure 4. High resolution TEM images of (a) carbon nanotubes in disarray form, (b) nickel catalyst encapsulated by graphitic structure at the tip of carbon nanotubes and (c) amorphous carbon formed in the sample, from Ref. [37].

Adapted with permission from *Materials Chemistry and Physics*, Volume 197, Cheng Tung Chong, Win Hon Tan, Siew Ling Lee, William Woei Fong Chong, Su Shiung Lam, and Agustin Valera-Medina. Morphology and growth of carbon nanotubes catalytically synthesised by premixed hydrocarbon-rich flames, Pages 246-255. Copyright (2017), with permission from Elsevier.

On the other hand, before the discovery of carbon nanotubes, for the better part of the twentieth century carbon nanofibers, then often referred to as carbon filaments or filamentous carbon, were often considered a nuisance [9, 10, 20]. In the industrial arena these fibers-like structures were responsible for the destruction of catalysis and rupture of reactor walls [9, 10, 20]. Ironically, in an effort to control the formation of these harmful fibers studies on their growth mechanism were carried out in order to prevent their existence. After the discovery of carbon nanotubes and numerous studies that found carbon nanotubes to exhibit unique mechanical, thermal, and electrical properties, carbon nanotubes became an attractive field of study for various potential applications. The addition of carbon nanotubes to polymers can improve the strength and stiffness of the composite system. The incorporation of carbon nanotubes to form composites can also add multifunctionality - electrical and thermal

conductivity - to the composite system [9, 10, 20]. The solid fibers, based on the angle of graphene layers with respect to the fiber axis, have distinct structural arrangements of carbon, including staked and herringbone [9, 10, 20]. Similarly to carbon nanotubes, considerable efforts have been made to control the properties of the carbon nanofibers by controlling their length, diameter, straightness, site density, and morphology. Similar to carbon nanotubes, various catalytic materials have been used for dissolving the carbon gas on one side of the metal surface and forming the solid carbon nanotubes on the other. The metals include alloys of iron, cobalt, and nickel, high melting temperature metals such as chromium, molybdenum, and vanadium have also been employed for the flame synthesis of carbon nanotubes. The diameter of the synthesized carbon nanotubes frequently resembles the diameter of the metal catalyst, as is often found in carbon nanotubes.

The gas-phase growth of carbon nanofibers occurs through the extrusion of carbon dissolved in a metallic catalytic particle [9, 10, 20]. The carbon constantly precipitates on one side of the catalyst particle leading to a carbon oversaturation and diffusion through the catalyst particle. As a consequence, graphene sheets are formed on the other side of the catalyst particle forming a tubule with a diameter resembling the catalyst particle size. The gas-phase growth of carbon nanotubes is usually influenced by the catalyst properties, which play an important role in the morphology of the final synthesized products. From the point of view of the flame, temperature and availability of chemical species play an important role for the type of carbon nanotubes. Furthermore, the extrusion rates of diffused carbon from the catalyst particle can influence the shape of the synthesized structures. Alterations in the carbon extrusion rates taking place at the catalyst particle will create abnormalities in the carbon fiber morphologies, i.e. wrapping-bending-coiling of the carbon structure.

The synthesis of carbon nanofibers in flames for the most part has been in the process of utilizing flames for the formation of carbon nanotubes. Many of the studies on the flame synthesis of carbon nanotubes have been empirical, employing various flame parameters and catalyst properties for the optimization of carbon nanotubes. Some of the flame methods resulted in the synthesis of carbon nanotubes, carbon nanofibers, a mixture of them, and in certain cases carbon trees.

3. Multi-Walled Carbon Nanotubes

The remarkable properties of carbon nanotubes and carbon nanofibers allow for the development and identification of emerging and novel potential applications. For certain applications it is required that the carbon nanotubes are vertically aligned and free of metal particles and carbon by-products. The ability to control carbon nanotube orientation, alignment, length, diameter and diameter uniformity, straightness, purity, and internal structure is essential for the potential fabrication of microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) such as field emission devices, capacitors, electrocatalyst supports for use in fuel cells, and anodes in lithium-ion batteries, among others. For example, carbon nanotubes due to their remarkable property as electron emitters have been proposed for use in the fabrication of a new generation of flat panel displays but the carbon nanotubes must first be vertically aligned and grown on large flat surface to electrode areas [55]. Therefore, in order for products based on carbon nanotubes to become a reality, an inexpensive flame synthesis method is required that has the capability to produce carbon nanotubes in a controllable manner as well as on desirable surface areas. Various control methods proposed for the flame synthesis of vertically aligned carbon nanotubes are discussed in detail as follows.

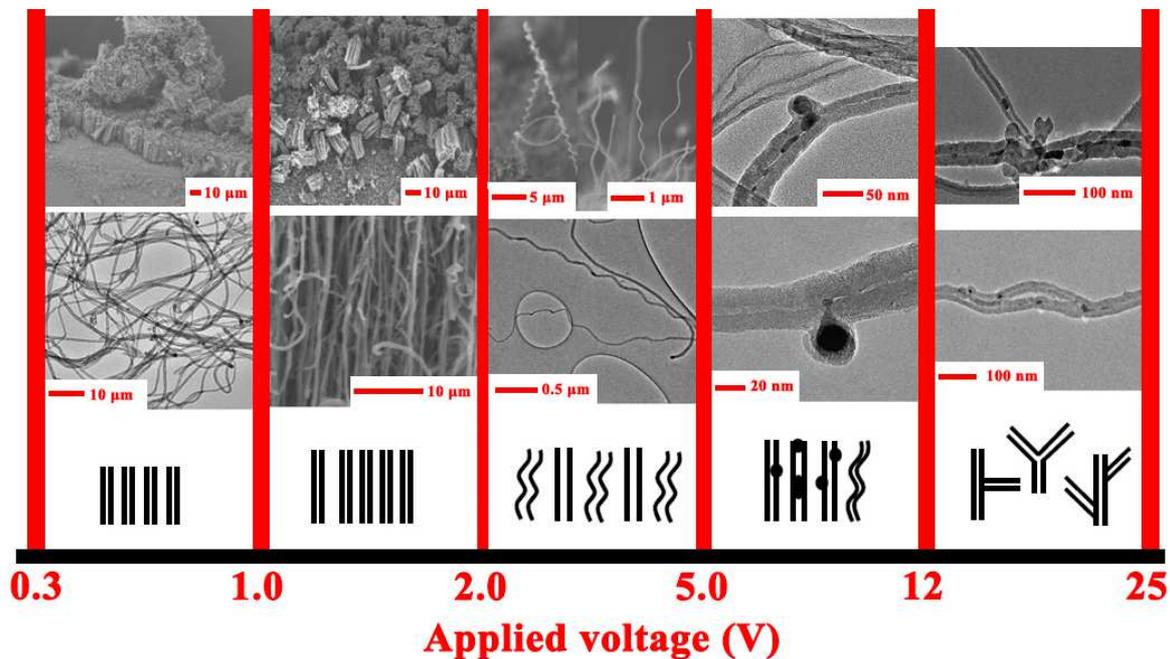


Figure 5. Influence of applied voltage on the structure and properties of generated carbon nanotube arrays: the found carbon nanotube structures were depicted by schematics and representative SEM and TEM images, from Ref. [57].

Adapted with permission from *Carbon*, Volume 44, Issue 15, Wilson Merchan-Merchan, Alexei V. Saveliev, and Lawrence A. Kennedy. Flame nanotube synthesis in moderate electric fields: From alignment and growth rate effects to structural variations and branching phenomena, Pages 3308-3314. Copyright (2006), with permission from Elsevier.

Recently, the electric field control was implemented by electrically isolating the probe from the grounded support and operating it at floating potential mode in a counter-flow flame

medium [56]. The electric field control method was implemented and it has been found to be an effective tool to control the gas-phase growth of carbon nanotubes. The

electric field method can significantly improve the diameter uniformity of the final synthesized carbon nanotubes. Various voltages have been employed in a flame electric field to control the gas-phase growth of carbon nanotubes [54, 57]. Merchan-Merchan *et al.* [57] employed voltages ranging from 0.3 to 25 V in order to evaluate the effect of electric field on the flame synthesis of multi-walled carbon nanotubes. The representative results obtained at a flame position of 9.5 mm are shown in Figure 5, where the effect of applied voltage on the structure and properties of generated carbon nanotube arrays was examined: the found carbon nanotube structures were depicted by schematics and representative scanning electron microscope and transmission electron microscopy images. The carbon nanotubes were grown on a conductive metal-based catalytic probe positioned at the fuel side of the opposed flow oxy-flame. The probe was connected to an external voltage source to generate radial electric fields on its surface. At low applied voltages, the effect of electric field on the alignment and growth rate enhancement indicated the generation of vertically aligned carbon nanotube arrays with uniform distribution of carbon nanotube diameters. The further increase of applied voltage led to structural modification of the carbon nanotubes generated. In particular, helically coiled carbon nanotubes were found at applied voltages of approximately 3 V. At higher voltages, the arrays contained multi-walled carbon nanotubes with fascinating modified morphologies such as Y, T, and multi-junction patterns. Analysis of the samples generated at applied voltage of 5 V showed the presence of particle sprouting and early carbon nanotube junctions in the form of small bumps extruding from the outer surface of the carbon nanotubes. Analysis of material samples synthesized at 12 and 25 V showed the presence of fully branched carbon nanotube structures. Experiment results of Merchan-Merchan *et al.* [57] showed that the introduction of medium and high voltage potentials can modify the external and internal morphology of multi-walled carbon nanotubes.

The application of an electric field was also discussed by Xu *et al.* [54] for stabilizing gas-phase growth of carbon nanotubes and controlling their morphology. An inverse diffusion methane flame with a co-flow configuration was utilized. Vertically well-aligned multi-walled carbon nanotubes with uniform diameters were grown on catalytic probes at high yield rates. Varied typical parameters were examined, including alloy composition, sampling positions within the flame structure, and voltage bias applied to the probe substrate. Spontaneous Raman spectroscopy was utilized to determine the local gas-phase temperature, as well as the concentrations of carbon-based precursor species within the flame structure at specific locations of carbon nanotube growth during flame synthesis. The variation of the above-mentioned typical parameters significantly affects the formation, gas-phase growth rate, diameter, and morphology of carbon nanotubes. Scanning electron microscope analysis showed that the carbon nanotube arrays have a thin layer of material covering the tips of the carbon nanotubes. This thin layer was composed of catalyst particles corroborating that

they were grown under the mechanism of “tip-growth model”. Furthermore, it was found that under the influence of an electric field, the thickness of the carbon nanotube layer does not necessarily increase with increasing applied electric potential. In contrast, the thickness of the carbon nanotube layer grown at the voltage potential of -2.0 V decreased by half from the one grown at -0.24 V. The differences can be rationalized by considering the basic concept of the interaction between the carbon nanotube and electric field forces acting on its tip. The electric force on the carbon nanotube tip can be affected by the amount of catalytic material present at the tip of the carbon nanotubes, therefore, preventing the electric field from effectively increasing the gas-phase growth rates of the carbon nanotubes. The experiment results of Xu *et al.* [54] showed that the introduction of voltage bias on the substrate leads to aligning the carbon nanotubes, enhances the gas-phase growth rates and electrophoretically keeps the soot particles from contaminating the carbon nanotube yield compared to when the probe was in the grounded mode.

Carbon nanotubes synthesized in the flame medium with the assistance of an electric field have similar characteristics to those in other electric-assisted methods [54, 56, 58-63]. The electric field method tends to affect the flame synthesis method of carbon nanotubes by: (a) significantly improving the gas-phase growth rates, (b) stabilizing carbon nanotubes and leading to a more controllable and repeatable process, (c) improving the diameter uniformity, (d) forming carbon nanotube arrays with thickness controlled by utilizing voltages of different strengths, and (e) achieving higher purity of generated carbon nanotubes by repulsing other carbon by-products.

Another technique employed to control the gas-phase growth of carbon nanotubes or carbon nanofibers is the application of anodic aluminum oxide nanotemplates, allowing the gas-phase growth of vertically aligned carbon nanotubes [62-64]. However, compared to the electric field method, the application of anodic aluminum oxide nanotemplates allows for precise control of the diameter of carbon nanotubes. The method is based on the application of anodic aluminum oxide nanotemplates with self-ordered hexagonal nanopores where tube diameters closely correlate with the size of the nanopores. The method of aluminum substrates with porous anodic aluminum oxide nanotemplates for the gas-phase growth of well-aligned carbon nanotubes has been extensively applied in the chemical vapor deposition method. Once the anodic aluminum oxide nanotemplates are fabricated and loaded with catalyst particles, they can be introduced into an active medium such as flames or chemical vapor deposition for the synthesis of carbon nanotubes or carbon nanofibers [62-64].

One of the main advantages of the anodic aluminum oxide nanotemplates is the ability to control the pore diameters, therefore controlling the diameter of carbon nanotubes [62-64]. The pore diameter is adjustable by simply varying the anodization voltage. One of the disadvantages of this method is that the fabrication of porous anodic aluminum oxide templates is a multi-step and time-intensive process [62-64].

The production of porous anodic aluminum oxide nanotemplates requires various anodization steps and the electrodeposition of the catalyst particles inside the pores. Yang *et al.* reported a typical process of 10 hours for fabricating porous anodic aluminum oxide nanotemplates [62]. Others reported up to a 24 hours process for fabricating porous anodic aluminum oxide nanotemplates [63]. Once the porous anodic aluminum oxide nanotemplates are completed and loaded with catalyst particles, they can be introduced into an active medium such as flames or chemical vapor deposition for the synthesis of carbon nanotubes. The synthesis process of carbon nanotubes in chemical vapor deposition can take from one to several hours [62]. The residence time of the anodic aluminum oxide nanotemplates for growing the carbon nanotubes in a certain post-flame region is only minutes compared to one to several hours necessary when using carefully designed chemical vapor deposition methods.

The significant reductions in the time interaction of anodic aluminum oxide nanotemplates with an energetic system such as the flame for the rapid growth of vertically aligned carbon nanotube arrays offer important opportunities for developing a new and simpler technology. The application of one-dimensional and two-dimensional anodic aluminum oxide nanotemplates with different flame geometries, including counter-flow and co-flow flames for the gas-phase growth of carbon nanotubes was studied by the group of Saito [60, 64]. The study focused on the effect of temperature, catalyst, and availability of carbon species regions within a flame volume. The work of Li *et al.* [60, 64], using anodic aluminum oxide nanotemplates in flames, showed that there is a common temperature range for both flame and chemical vapor deposition synthesis within which carbon nanotubes could be synthesized. The gas-phase growth of carbon nanotubes is rapid when the anodic aluminum oxide nanotemplates are exposed to the flame as well as the time is intensive when they are exposed to a chemical vapor deposition process. A numerical model of a counter-flow diffusion flame was developed by Li *et al.* [60, 64] to explore the availability and contribution of the carbon species to the gas-phase growth of carbon nanotubes using the anodic aluminum oxide nanotemplates. A reduced mechanism of methane oxidation, including 18 species and 15 reaction steps, was developed for the simulation. The model demonstrated that possible carbon species which contribute to the gas-phase growth of carbon nanotubes under the current experimental conditions are carbon monoxide, ethyne, ethene, ethane, and methyl radical. The model also showed the presence of hydrogen, water, and carbon dioxide in the synthesis region of the flame. It has been suggested that the presence of these chemical species may activate the catalyst and enhance the catalyst reactions responsible for the fast growth rate of carbon nanotubes.

4. Single-Walled Carbon Nanotubes

Similar to the flame synthesis of multi-walled carbon nanotubes, there are essentially three key components

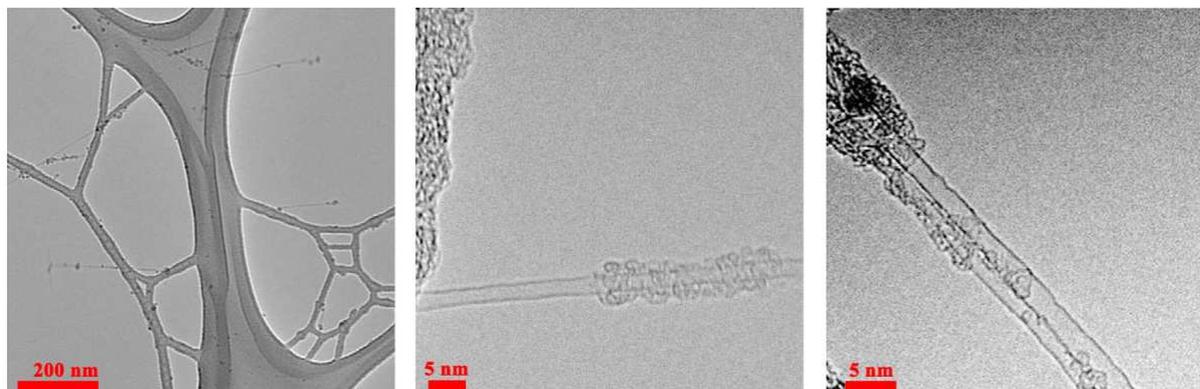
required for the synthesis of single-walled carbon nanotubes: a source of carbon, a source of heat, and presence of metallic catalyst particles. In the flame synthesis method, the catalytic precursors are generally introduced into the flame system in the gas-phase and nucleate and condense to solidify into spherical metallic nanoparticles. Flame parameters can be used to obtain an appropriate flame environment that would allow the formation of ideal sizes of catalyst particles for carbon nanotube inception and growth. The available literature on the flame synthesis of single-walled carbon nanotubes is scarce, in contrast to flame synthesis of multi-walled carbon nanotubes, consisting of only a handful of experiments that have been conducted on the synthesis of single-walled carbon nanotubes. To some extent all products have common morphological trends, even though they are synthesized in flames formed using different operating conditions and combustor configurations. These morphological trends include: (a) single-walled carbon nanotubes always coexist with metallic and soot particles, (b) particles often appear to be poisoned; even when ultra-small catalyst particles, ideal for single-walled carbon nanotube inception, can be achieved, they can be heavily encapsulated with amorphous carbon becoming inactive as catalysts for carbon nanotubes, (c) the presence of larger metallic particles with very short single-walled carbon nanotubes. In an effort to control these morphologies, various catalyst properties and flame parameters can be employed. Recent experiments on the flame synthesis of single-walled carbon nanotubes have demonstrated that there are critical factors that significantly affect the flame synthesis of single-walled carbon nanotubes [65-68], including: (a) type of reactant gas environment; (b) flame pressure; (c) composition and insertion rate of catalyst particle into the flame system; and (d) fuel to oxygen equivalence ratio. The alteration of these catalyst properties and flame parameters can significantly affect the source of heat and carbon, catalyst particle formation, activation and deactivation of the catalyst particle for the flame synthesis of single-walled carbon nanotubes.

The majority of the studies on the flame synthesis of single-walled carbon nanotubes have been carried out in the gas-phase [69, 70]. A continuous nanostructural change occurs through the flame volume, from the formation of the bare catalyst particle at one part of the flame volume to carbon nanotube inception and growth on the same catalyst particle in other parts of the flame volume. Due to the structure of the flame as a non-isothermal medium, the transformation can occur in millisecond residence times. Furthermore, single-walled carbon nanotubes synthesized in flames are usually highly entangled, coexist with catalyst particles and combustion by-products, and grow in a disorderly manner.

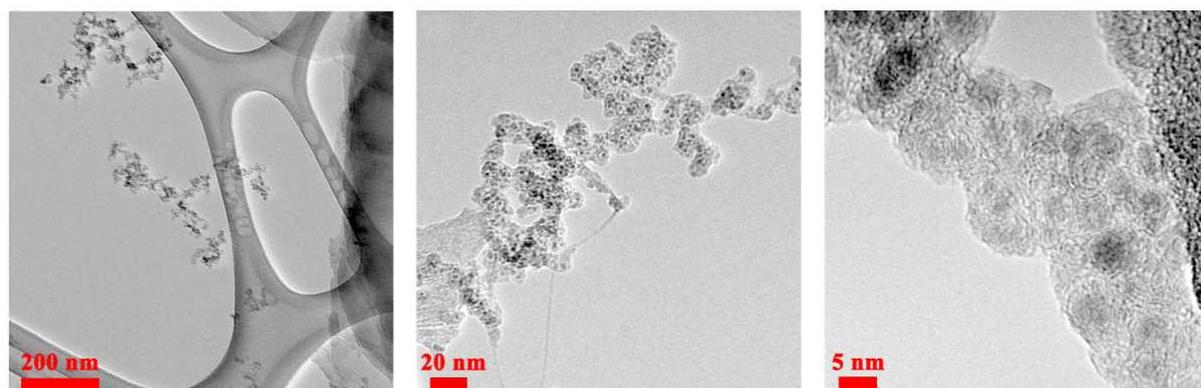
Vander Wal and coworkers [69, 70] have made extensive use of an annular combustor configuration consisting of a 50 mm diameter sintered metal plate with a central tube of 11 mm diameter that is mounted flush with the surface of the combustor plate. For most experiments Vander Wal *et al.* [69, 70] established a fuel-rich premixed flame supported on the outer annular section of a combustor plate while reactant gas

mixtures, including metal catalyst species of interest were fed through a central tube. This configuration is termed a pyrolysis flame as the central gas flow does not undergo combustion due to the lack of oxygen in this flow, but reactions and the formation of carbon nanotubes do proceed in the flow by virtue of the heating influence of the surrounding annular flame. The central gas flow is in effect a reactive streamtube rather than a flame. A stabilizing chimney immersed vertically in the flame gases provides a stabilizing

effect and carbon nanotube samples, including single-wall carbon nanotubes, multi-wall carbon nanotubes, and carbon nanofibers, are collected at the exit of the chimney. There are some important distinctions to note regarding this configuration. First of all, the outer flame is primarily a source of heat and the central gas mixture flow is the primary source of carbon and metallic catalyst. Combustion is not supported in the central gas flow. Consequently, heating and material synthesis processes are substantially separated functions.



(a). Carbon monoxide-hydrogen-helium mixtures.



(b). Ethyne-hydrogen-helium mixtures.

Figure 6. TEM images of (panel a) iron catalyzed single-walled carbon nanotubes using an optimal carbon monoxide-hydrogen-helium mixture and (panel b) encapsulated iron nanoparticles using an ethyne-hydrogen-helium mixture, from Refs. [69, 70].

Adapted with permission from *Combustion and Flame*, Volume 130, Issues 1-2, Randall L Vander Wal and Lee J Hall. Ferrocene as a precursor reagent for metal-catalyzed carbon nanotubes: competing effects, Pages 27-36; and from *Combustion and Flame*, Volume 130, Issues 1-2, Randall L Vander Wal. Fe-catalyzed single-walled carbon nanotube synthesis within a flame environment, Pages 37-47. Copyright (2002), with permission from Elsevier.

Recent experiments of Vander Wal and co-workers [69, 70] evaluated the effects of catalyst properties and flame parameters for controlling the gas-phase growth of single-walled carbon nanotubes, including different reactive gas mixtures, catalyst particle composition, and its introduction rate using a premixed co-flow flame in the gas-phase. The flame synthesis of single-walled carbon nanotubes was explored in a pyrolysis flame configuration seeded with ferrocene as a catalyst precursor reagent [69]. The flame synthesis of single walled carbon nanotubes was demonstrated using iron nanoparticles within a pyrolysis flame configuration [70]. It was found that the concentration of ferrocene is prominent among the factors that determine the

inception and growth of single-walled carbon nanotubes, as well as catalyst particle deactivation. This reflects the role of ferrocene as metal catalyst precursor and as a source of cyclopentadiene species upon its thermal decomposition. Experiment results with different flows and reactant gas mixtures were presented and interpreted in light of a synthesis mechanism of single-walled carbon nanotubes and catalyst deactivation processes. The roles of nebulized solution solvent, surrounding flame gas composition, pyrolysis flame gas composition, and metal nitrate concentration were interpreted as reflecting suitable concentrations of reactants without excessive pyrolysis products or deactivating species. Figure 6 (a) shows the transmission electron microscopy images of iron

catalyzed single-walled carbon nanotubes using an optimal carbon monoxide-hydrogen-helium mixture. Figure 6 (b) shows the transmission electron microscopy images of encased iron nanoparticles using an ethyne-hydrogen-helium mixture. The introduction of pure carbon monoxide for hydrocarbon combustion led to the heavy encapsulation of the iron nanoparticles within the amorphous carbon. The larger iron catalyst particles were found as dark spots - in a matrix of amorphous carbon. The introduction of pure hydrogen in the flame system led to the formation of metallic particles with much cleaner surfaces than those formed with pure carbon monoxide. In both cases, however, carbon and single-walled carbon nanotubes coexist with catalyst particles containing many times their diameter and of variable sizes. The coexistence of both structures of different sizes suggested that during the gas-phase growth of single-walled carbon nanotubes, the catalyst particle grows as well. The growth of catalyst particle surface may be attributed to a continuous absorption of additional metal species in the vapor phase as they travel along the flame axis in the direction of the tip. High carbon monoxide concentrations resulted in an amorphous carbon coating on the particle. The amorphous carbon coating is likely responsible for the termination of gas-phase growth of the single-walled carbon nanotube, by blocking the diffusion of carbon species in the iron nanoparticles. The carbon layer around the particle limits the carbon diffusion through the catalyst particle which can lead to a complete encapsulation of the catalyst particles and deactivates the catalyst [71]. The high hydrogen concentrations tend to have the opposite effect of high carbon monoxide concentration, it removes the surface carbon species from the catalytic surface too rapidly, thus slowing and even inhibiting the gas-phase growth of single-walled carbon nanotubes [70]. Reacting mixtures with fixed amounts of hydrogen and helium and added carbon monoxide and ethyne were also tested for the flame synthesis of single-walled carbon nanotubes. Experiments conducted with mixtures of carbon monoxide, hydrogen, and helium, without the presence of ethyne, proved to be a superior gas mixture for the formation of single-walled carbon nanotubes. An ethyne-hydrogen-helium reacting mixture led to the formation of iron nanoparticles with ideal sizes for single-walled carbon nanotube inception. However, despite the optimal size of the iron nanoparticles, the majority of the metallic particles were deactivated and did not initiate the gas-phase growth of single-walled carbon nanotubes as they became fully encapsulated with carbon showing that the concentration of the gas mixtures plays an important role in the flame synthesis of single-walled carbon nanotubes.

The interaction between flame and probe can be successfully employed to produce multi-walled carbon nanotubes in flames and control their morphology, growth, and purity. The flame synthesis of single-walled carbon nanotubes is difficult as it requires gas-phase introduction of the catalyst to obtain the ultra-small catalyst particles ideal for the inception carbon nanotubes. The gas-phase growth of single-walled carbon nanotubes in the post-flame gases, just above the nozzle of the combustor, can be described by the formation of small discrete

particles with a progression toward the inception and gas-phase growth of carbon nanotubes in the upper region of the flame. This formation pathway is very similar to that encountered in soot formation in flames. At the lower part of the flame, small unsaturated hydrocarbons tend to form the young soot particles. Soot particles can further grow through the coagulation and surface growth processes, and in the upper part of the flame, the appearance of "mature soot" as particles are agglomerated due to collisions as they travel in the upper part of the flame [72-74]. The formation pathway of single-walled carbon nanotubes in flames closely follows that of less organized carbon particles, such as soot. This formation pathway has also been found in the flame synthesis of metal oxide nanoparticles [75]. It is well known that the precursors of crystallized carbon clusters are high-molecular polycyclic aromatic hydrocarbons and aromers [76]. These molecules, which are formed in the main oxidation region of the flame, are direct precursors for fullerenic and soot nanomaterials [77]. The system can yield both or one or the other depending on flame conditions [78]. Vander Wal *et al.* [69, 70] showed that the addition of ethyne in the reacting mixture poisoned the catalyst particle with amorphous carbon preventing the activation of the catalyst particle for the gas-phase growth of single-walled carbon nanotubes. In contrast, the addition of carbon monoxide in the reacting mixture significantly contributes to the flame synthesis of single-walled carbon nanotubes. The process of the flame synthesis for single-walled carbon nanotubes is quite complex as the proper flame parameter must be employed to achieve a suitable size catalyst particle with enough carbon species for particle activation, inception, and their continued growth on their way through the flame. An earlier abundance of carbon species will poison the catalyst particle and prevent the inception of carbon nanotubes earlier in the flame volume.

Diener *et al.* [79] evaluated the role of medium and large hydrocarbon molecule feedstocks for the flame synthesis and gas-phase growth of single-walled carbon nanotubes by using various types of fuels. Figure 7 displays images from the transmission electron microscopy of the single-walled carbon nanotubes in the soot from an 80 Torr ethyne flame with a ferrocene-nickelocene mixture as the catalyst, and from a sooting benzene flame with cobalt introduced as the catalyst. The experiments of Diener *et al.* [79] were carried out using ethyne, ethene, and benzene flames. Ferrocene and nickelocene catalysts were introduced in the flame through the fuel stream by sublimating the powders in an argon stream. It was found that single-walled carbon nanotubes cannot be synthesized from benzene flames under identical ethyne and ethene conditions used to produce single-walled carbon nanotubes. In an effort to synthesize single-walled carbon nanotubes from a benzene flame, different flame parameters and catalyst properties were employed. The catalyst composition, pressure, and fuel to oxygen equivalence ratio were varied in the benzene flame and still no single-walled carbon nanotubes were found. In contrast, products collected from the benzene flame appeared to be composed of large metal particles and a few long and defective multi-walled carbon nanotubes. Although it has been reported that in the

flame and chemical vapor deposition methods using benzene as the carbon source can lead to multi-walled carbon nanotubes, this is not the case for single-walled carbon nanotubes. In the study of Diener *et al.* [79], products collected from a ceramic filter connected to the exhaust nozzle of an ethyne-ethene flame were composed of single-walled carbon nanotube bundles. The ethyne and ethene fuels produced short bundles of single-walled carbon nanotubes accompanied by large numbers of metallic particles. The previously mentioned morphologies were found in these products. During the burning of benzene, most of the benzene rings were rapidly broken into ethyne pieces. The polycyclic aromatic hydrocarbons began from a single aromatic ring and could grow through both the addition of ethyne species and

condensation of aromatics [79]. The ethyne and ethene flame must grow the first ring, while it is already present in the benzene flames. Consequently, the formation of polycyclic aromatic hydrocarbons and subsequent soot began earlier in benzene flames than that in ethyne flames [79]. It can be concluded that the following may affect the catalyst particle for the gas-phase growth of single-walled carbon nanotubes in flames: (a) soot formation begins at a time where the metal particles have not yet grown large enough to act as a single-walled carbon nanotube catalyst; (b) catalyst particles with suitable size are synthesized but the large amount of ethyne pieces poison the catalyst particles preventing their activation and inception of single-walled carbon nanotubes.

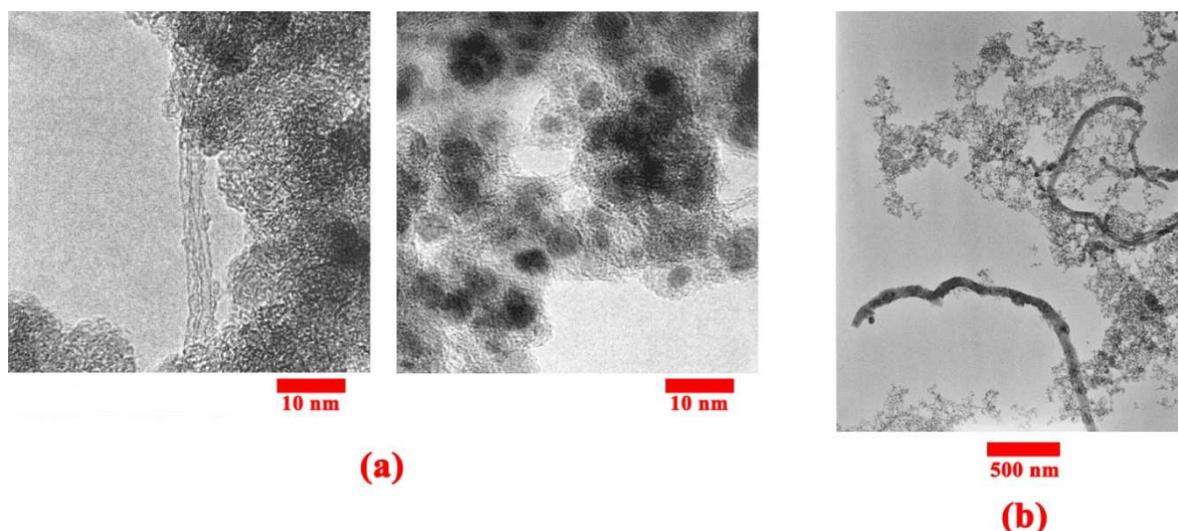


Figure 7. TEM images of (panel a) single-walled carbon nanotube bundles from sooting ethyne flames in the presence of iron-nickel catalyst particles, and (panel b) metal-filled multi-walled carbon nanotubes from a sooting benzene flame with cobalt introduced as the catalyst, from Ref. [79].

Adapted with permission from *The Journal of Physical Chemistry B*, Volume 104, Issue 41, Michael D. Diener, Noah Nicholson, and John M. Alford. Synthesis of single-walled carbon nanotubes in flames, Pages 9615-9620. Copyright (2000), with permission from American Chemical Society.

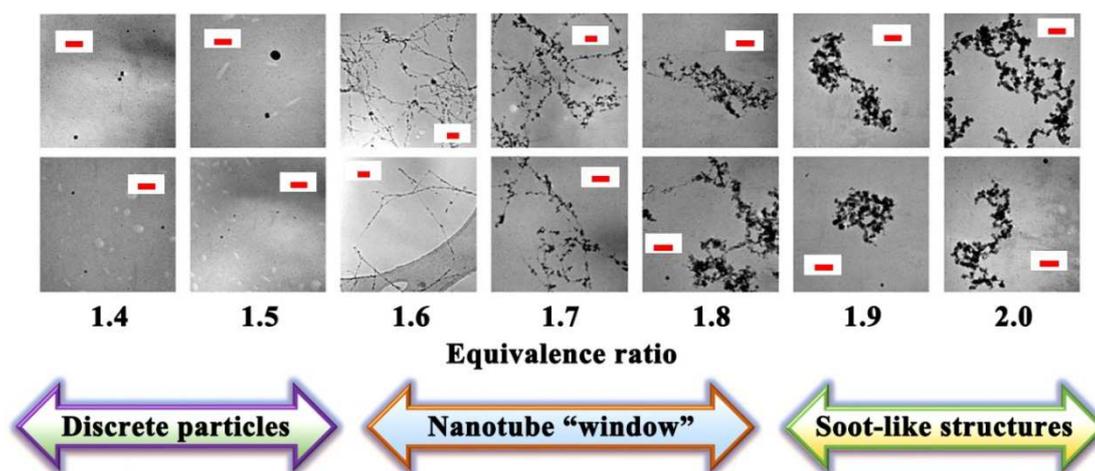


Figure 8. Schematic interpretation of various processes present at various heights above combustor in a flat flame for the synthesis of single-walled carbon nanotubes, from Ref. [65].

Adapted with permission from *Proceedings of the Combustion Institute*, Volume 30, Issue 2, Murray J. Height, Jack B. Howard, and Jefferson W. Tester. Flame synthesis of single-walled carbon nanotubes, Pages 2537-2543. Copyright (2005), with permission from Elsevier.

The introduction of low, moderate, and high densities of ferrocene was used by Vander Wal [69] to study the synthesis of single-walled carbon nanotubes in flames. On the other hand, the introduction of low, moderate, and high density carbon feedstock for the synthesis of single-walled carbon nanotubes in flames was studied by Height and co-workers [65] at various heights above combustor of a flat flame. The motivation for the study was to gain a detailed understanding of carbon nanotube formation in a premixed flame. Furthermore, the study aimed to examine conditions for the formation of carbon nanotubes in premixed flames and to characterize the morphology of solid carbon deposits and their primary formation mechanisms in the combustion environment. For this purpose, the carbon nanotube formation region and growth time scales, transition conditions for the formation of carbon nanotubes, and the carbon nanotube structure were identified. Figure 8 shows the schematic interpretation of various processes present at various heights above the combustor in a flat flame for the synthesis of single-walled carbon nanotubes. The carbon feedstock was controlled by varying the fuel to oxygen equivalence ratio for the formation of single-walled carbon nanotubes in the flame medium. The experiments were carried out in a low pressure, premixed ethyne-oxygen-argon flame doped with 6100 ppm iron-pentacarbonyl vapor as the catalytic precursors. Strategic experiments were carried out to understand the effect of equivalence ratio on the formation of single-walled carbon nanotubes. A nanostructure transformation was found with the change of equivalence ratio. A significant transition in nanostructure was found to take place in a flame region above the combustor nozzle with the application of a wide range of equivalence ratios. Within the range of equivalence ratio from 1.4 to 1.5 the presence of discrete spherical shaped particles was found. The increase of equivalence ratio from 1.6 to 1.8 led to a “formation window” of carbon nanotubes. The continuing increase of the equivalence ratio from 1.9 to 2.0 led to the formation of only combustion by-products such as soot-like structures. From all of the tested equivalence ratios, a “formation window” for the synthesis of carbon nanotubes was achieved between 1.5 and 1.9. Although it was found that the best conditions suitable for the flame synthesis of single-walled carbon nanotubes were achieved in a narrower range of the equivalence ratio at 1.6 and 1.7. A mechanistic interpretation of the formation process of single-walled carbon nanotubes in the premixed flame clearly identified the role of iron oxide particles and suggested ways for significantly improving the yield of carbon nanotubes from the flame. High-resolution transmission electron microscopy and spontaneous Raman spectroscopy revealed carbon nanotube bundles with each carbon nanotube being single-walled with diameters between 0.9 and 1.5 nm [65].

5. Growth Mechanisms

In order to synthesize carbon nanotubes or carbon nanofibers, a catalytic metallic nanoparticle is necessary. The growth of

carbon nanotubes is significantly affected by catalyst properties, which play an important role in the morphology of final synthesized products. Furthermore, a change in the extrusion-precipitation rates of diffused carbon from the catalyst particle can also influence the shape of synthesized structures. Transition metals such as cobalt, iron, molybdenum, nickel, and alloys of different compositions are typically used as catalyst particles in the formation processes of carbon nanotubes or carbon nanofibers. It is necessary to briefly present the main functions and roles of the catalyst particle for the synthesis of carbon nanotubes and carbon nanofibers [80, 81]. As postulated by Baker *et al.* [82], the catalyst particle can be considered as a system containing temperature gradients usually occurring between the upper and lower parts of the particle. Other functions of a catalyst particle involve: (a) absorption of the hydrocarbons that are constantly precipitating on one side of the particle resulting in a carbon oversaturation, and followed by diffusion of the carbon through and around the surface of the catalyst particle to form the graphene solid cylinders on the other side of the particle; (b) the oversaturation of hydrocarbons and diffusion of carbon to form the solid layers on the other part of the particle allows the solid graphene cylinders to grow with the same diameter as that of the catalyst particle; (c) carbon nanotube structures are produced depending on the structure of the formed carbon layers. Graphene layers packed with an angle or perpendicular with respect to the fiber axis are termed “herringbone” and “stacked” structures, respectively. If the precipitated graphene layers are parallel to the fiber axis creating a hollow morphology in its center with a perfect tubular structure of carbon layers, then the catalyst particle has synthesized a carbon nanotube. If the continuous and instantaneous extrusion rates become non-constant at different sites around the carbon tube at the catalytic circumference interface, it will give rise to growth abnormalities providing the wrapping-bending-coiling of the carbon structure. The deactivation of the catalyst particle can occur due to the high deposition of carbon species on the catalyst particles; this material can act as a shield preventing carbon from reaching the catalyst particles, thus hindering the inception and growth of the carbon nanofibers. This process is usually termed as “catalyst poisoning”.

Recent experiments have demonstrated that carbon nanotubes typically contain a metallic particle at one of their ends although in some cases, carbon fibers can also encapsulate metallic particles along the fiber axis [83-86]. The dominant growth mechanism is often defined by the manner in which carbon atoms are transported and absorbed, dissolved, and diffused into the catalyst particle interior and around the catalyst particle surface to give rise to the continuous staking of solid graphitic layers on the catalytic surface. In the solid support synthesis, two different growth mechanisms have been identified and described by Baker *et al.* [82]. Although the mechanism initially proposed by Baker *et al.* [82] was established for understanding and controlling the growth of carbon nanofibers, it is also suitable for carbon nanotubes. The two mechanisms developed by Baker *et al.* [82] are called the

“tip growth model” and the “base growth model”. The initial step in the “tip growth model” is the formation of a catalytic nanoparticle through the interaction of the catalytic surface probe with an active environment. Carbon containing molecules diffuse to the particle sides initiating the graphitization process. A weak particle probe interaction allows the particle to become unattached to the surface and the particle can then be lifted upwards by the continuous growing tubule. A continuous diffusion of carbon molecules to the already formed graphene layers will continue the growth of carbon nanotubes. In contrast, the “base growth model” is based on the nucleation of a carbon nanotube from a spherical shaped particle that remains attached to the catalytic substrate due to the strong particle probe interaction. In the “base growth model”, carbon nanotubes can start forming upwards from the metal particle which remains attached to the substrate. Later in time during the continuous growth of carbon nanotubes, the catalyst particle can become detached and the growth of carbon nanotubes and the graphitization process continues. In both cases, carbon atoms generally move faster along the external surface than the interior of the catalyst particle, thus, forming the hollow core. For both carbon nanotubes and carbon nanofibers, the internal and external morphology of the carbon structure depends on the growth environment and the nature of the metal catalyst. It is speculated that a carbon nanofiber can also grow simultaneously on both sides of the catalyst particle, which is often referred to as the “bidirectional growth mode” [82].

Despite the broad applications of carbon nanotubes and carbon nanofibers in various fields, flame synthesis remains a key field in the science and technology of carbon nanotubes and carbon nanofibers, as well as plays the most important role for their wide applications. The large-scale production of carbon nanotubes and carbon nanofibers with a desired structure under controllable conditions requires a fundamental understanding of the growth mechanism and process. This remains vital even two decades after this area of study started [87, 88].

6. Conclusions

Flame synthesis, in the past two decades, not only has proven to be one of the most scalable and economical technologies for producing nanostructured ceramic materials, but also has been demonstrated to be a robust fabrication method of carbon nanotubes and carbon nanofibers. Recently, significant efforts have been made to produce carbon nanotubes in controlled flame environments. It is evident that flames are emerging as a powerful tool for the synthesis of carbon nanotubes and carbon nanofibers. The present work provides a concise review of recent advances in the flame synthesis of carbon nanotubes and carbon nanofibers. The flame synthesis of carbon nanotubes is significantly affected by the flame temperature and chemical species, flame geometry, combustor configuration, catalyst composition and its delivery into the flame environment for the synthesis and control of carbon nanotubes and carbon nanofibers. The mechanisms of “tip growth model” and “base growth model” are responsible for the catalytically enhanced

growth of carbon nanotubes and carbon nanofibers. The two common types of carbon nanofiber generated in flames include “herringbone” and “stacked” structure. The different methods for controlling the growth of vertically aligned carbon nanotubes, including the use of electric field forces and the use of nanotemplates, are presented. The ability to control carbon nanotube alignment, orientation, diameter, length, straightness, purity, and internal structure is essential for the potential fabrication of nanomechanical and electrical devices. Electric fields and nanotemplates have been successfully applied for the structure control in flame synthesis experiments. Such flame methods have great promise for the large-scale, low-cost synthesis of carbon nanotubes and carbon nanofibers, though they must compete with rapidly developing large scale production using chemical vapor deposition. It is hoped that this review will be beneficial for the specialists working in the combustion synthesis field, and may help them for finding new and non-standard approaches to fabricate carbon nanotubes and carbon nanofibers of various dimensions as well as nanodevices with improved physical, chemical, and mechanical properties.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51506048).

References

- [1] P. S. Karthik, A. L. Himaja, and S. P. Singh. Carbon-allotropes: synthesis methods, applications and future perspectives. *Carbon Letters*, Volume 15, Issue 4, 2014, Pages 219-237.
- [2] G. Mittal, V. Dhand, K. Y. Rhee, H.-J. Kim, and D. H. Jung. Carbon nanotubes synthesis using diffusion and premixed flame methods: a review. *Carbon Letters*, Volume 16, Issue 1, 2015, Pages 1-10.
- [3] K. Watanabe, M. Araidai, and K. Tada. Field emission and electronic structures of carbon allotropes. *Thin Solid Films*, Volumes 464-465, 2004, Pages 354-359.
- [4] A. D. Moghadam, E. Omrani, P. L. Menezes, and P. K. Rohatgi. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbon nanotubes (CNTs) and graphene - A review. *Composites Part B: Engineering*, Volume 77, 2015, Pages 402-420.
- [5] A. Kucinska, A. Cyganiuk, and J. P. Lukaszewicz. A microporous and high surface area active carbon obtained by the heat-treatment of chitosan. *Carbon*, Volume 50, Issue 8, 2012, Pages 3098-3101.
- [6] Y. Cao, Y. Gu, K. Wang, X. Wang, Z. Gu, T. Ambrico, M. A. Castro, J. Lee, W. Gibbons, and J. A. Rice. Adsorption of creatinine on active carbons with nitric acid hydrothermal modification. *Journal of the Taiwan Institute of Chemical Engineers*, Volume 66, 2016, Pages 347-356.
- [7] M. V. Il'ina, O. I. Il'in, Y. F. Blinov, V. A. Smirnov, A. S. Kolomyitsev, A. A. Fedotov, B. G. Konoplev, and O. A. Ageev. Memristive switching mechanism of vertically aligned carbon nanotubes. *Carbon*, Volume 123, 2017, Pages 514-524.

- [8] A. C. Torres-Dias, T. F. T. Cerqueira, W. Cui, M. A. L. Marques, S. Botti, D. Machon, M. A. Hartmann, Y. Sun, D. J. Dunstan, and A. San-Miguel. From mesoscale to nanoscale mechanics in single-wall carbon nanotubes. *Carbon*, Volume 123, 2017, Pages 145-150.
- [9] T. Laurila, S. Sainio, H. Jiang, J. Koskinen, J. Koehne, M. Meyyappan. The role of extra carbon source during the pre-annealing stage in the growth of carbon nanofibers. *Carbon*, Volume 100, 2016, Pages 351-354.
- [10] S. Sainio, H. Jiang, M. A. Caro, J. Koehne, O. Lopez-Acevedo, J. Koskinen, M. Meyyappan, and T. Laurila. Structural morphology of carbon nanofibers grown on different substrates. *Carbon*, Volume 98, 2016, Pages 343-351.
- [11] M. Zheng, Y. Liu, K. Jiang, Y. Xiao, and D. Yuan. Alcohol-assisted hydrothermal carbonization to fabricate spheroidal carbons with a tunable shape and aspect ratio. *Carbon*, Volume 48, Issue 4, 2010, Pages 1224-1233.
- [12] M. Zeiger, N. Jäckel, M. Aslan, D. Weingarth, and V. Presser. Understanding structure and porosity of nanodiamond-derived carbon onions. *Carbon*, Volume 84, 2015, Pages 584-598.
- [13] M. Prato. Fullerene chemistry for materials science applications. *Journal of Materials Chemistry*, Volume 7, Issue 7, 1997, Pages 1097-1109.
- [14] S. D. Dietz, O. Korol, and W. L. Bell. Preparation and characterization of fullerene-doped low-temperature glassy carbon. *Carbon*, Volume 37, Issue 4, 1999, Pages 619-624.
- [15] G. Mittal, V. Dhand, K. Y. Rhee, S.-J. Park, and W. R. Lee. A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. *Journal of Industrial and Engineering Chemistry*, Volume 21, 2015, Pages 11-25.
- [16] E. T. Thostenson, Z. Ren, and T.-W. Chou. Advances in the science and technology of carbon nanotubes and their composites: a review. *Composites Science and Technology*, Volume 61, Issue 13, 2001, Pages 1899-1912.
- [17] S. Berber, Y.-K. Kwon, and D. Tománek. Unusually high thermal conductivity of carbon nanotubes. *Physical Review Letters*, Volume 84, Issue 20, 2000, Pages 4613-4616.
- [18] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, and R. Kizek. Methods for carbon nanotubes synthesis: review. *Journal of Materials Chemistry*, Volume 21, Issue 40, 2011, Pages 15872-15884.
- [19] D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato. Chemistry of carbon nanotubes. *Chemical Reviews*, Volume 106, Issue 3, 2006, Pages 1105-1136.
- [20] K. P. De Jong and J. W. Geus. Carbon nanofibers: Catalytic synthesis and applications. *Catalysis Reviews: Science and Engineering*, Volume 42, Issue 4, 2000, Pages 481-510.
- [21] T. W. Tombler, C. W. Zhou, L. Alexseyev, J. Kong, H. J. Dai, L. Liu, C. S. Jayanthi, M. Tang, and S.-Y. Wu. Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation. *Nature*, Volume 405, Issue 6788, 2000, Pages 769-772.
- [22] E. Frackowiak and F. Béguin. Electrochemical storage of energy in carbon nanotubes and nanostructured carbons. *Carbon*, Volume 40, Issue 10, 2002, Pages 1775-1787.
- [23] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, and F. Béguin. Electrochemical storage of lithium in multiwalled carbon nanotubes. *Carbon*, Volume 37, Issue 1, 1999, Pages 61-69.
- [24] E. Frackowiak, S. Delpeux, K. Jurewicz, K. Szostak, D. Cazorla-Amoros, and F. Béguin. Enhanced capacitance of carbon nanotubes through chemical activation. *Chemical Physics Letters*, Volume 361, Issues 1-2, 2002, Pages 35-41.
- [25] H. Dai. Carbon nanotubes: opportunities and challenges. *Surface Science*, Volume 500, Issues 1-3, 2002, Pages 218-241.
- [26] R. Oriňáková and A. Oriňák. Recent applications of carbon nanotubes in hydrogen production and storage. *Fuel*, Volume 90, Issue 11, 2011, Pages 3123-3140.
- [27] D. Vairavapandian, P. Vichchulada, and M. D. Lay. Preparation and modification of carbon nanotubes: Review of recent advances and applications in catalysis and sensing. *Analytica Chimica Acta*, Volume 626, Issue 2, 2008, Pages 119-129.
- [28] W. Merchan-Merchan, A. V. Saveliev, L. Kennedy, and W. C. Jimenez. Combustion synthesis of carbon nanotubes and related nanostructures. *Progress in Energy and Combustion Science*, Volume 36, Issue 6, 2010, Pages 696-727.
- [29] S. Li, Y. Ren, P. Biswas, S. D. Tse. Flame aerosol synthesis of nanostructured materials and functional devices: Processing, modeling, and diagnostics. *Progress in Energy and Combustion Science*, Volume 55, 2016, Pages 1-59.
- [30] Z. Xu, H. Zhao. Simultaneous measurement of internal and external properties of nanoparticles in flame based on thermophoresis. *Combustion and Flame*, Volume 162, Issue 5, 2015, Pages 2200-2213.
- [31] S. Iijima. Helical microtubules of graphitic carbon. *Nature*, Volume 354, Issue 6348, 1991, Pages 56-58.
- [32] S. Iijima and T. Ichihashi. Single-shell carbon nanotubes of 1-nm diameter. *Nature*, Volume 363, Issue 6430, 1993, Pages 603-605.
- [33] D. S. Bethune, C. H. Klang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature*, Volume 363, Issue 6430, 1993, Pages 605-607.
- [34] H. Dai. Carbon nanotubes: synthesis, integration, and properties. *Accounts of Chemical Research*, Volume 35, Issue 12, 2002, Pages 1035-1044.
- [35] H. H. Nersisyan, J. H. Lee, J.-R. Ding, K.-S. Kim, K. V. Manukyan, and A. S. Mukasyan. Combustion synthesis of zero-, one-, two- and three-dimensional nanostructures: Current trends and future perspectives. *Progress in Energy and Combustion Science*, Volume 63, 2017, Pages 79-118.
- [36] S. Nakazawa, T. Yokomori, and M. Mizomoto. Flame synthesis of carbon nanotubes in a wall stagnation flow. *Chemical Physics Letters*, Volume 403, Issues 1-3, 2005, Pages 158-162.
- [37] C. T. Chong, W. H. Tan, S. L. Lee, W. W. F. Chong, S. S. Lam, and A. Valera-Medina. Morphology and growth of carbon nanotubes catalytically synthesised by premixed hydrocarbon-rich flames. *Materials Chemistry and Physics*, Volume 197, 2017, Pages 246-255.

- [38] H. Oulanti, F. Laurent, T. Le-Huu, B. Durand, J. B. Donnet. Growth of carbon nanotubes on carbon fibers using the combustion flame oxy-acetylene method. *Carbon*, Volume 95, 2015, Pages 261-267.
- [39] N. K. Memon, B. H. Kear, and S. D. Tse. Transition between graphene-film and carbon-nanotube growth on nickel alloys in open-atmosphere flame synthesis. *Chemical Physics Letters*, Volume 570, 2013, Pages 90-94.
- [40] C. P. Arana, I. K. Puri, and S. Sen. Catalyst influence on the flame synthesis of aligned carbon nanotubes and nanofibers. *Proceedings of the Combustion Institute*, Volume 30, Issue 2, 2005, Pages 2553-2560.
- [41] J. M. Singer and J. Grumer. Carbon formation in very rich hydrocarbon-air flames: Studies of chemical content, temperature, ionization and particulate matter. *Symposium (International) on Combustion*, Volume 7, Issue 1, 1958, Pages 559-569.
- [42] K. Saito, A. S. Gordon, F. A. Williams, and W. F. Stickle. A study of the early history of soot formation in various hydrocarbon diffusion flames. *Combustion Science and Technology*, Volume 80, Issues 1-3, 1991, Pages 103-119.
- [43] J. B. Howard, J. T. McKinnon, Y. Makarovskiy, A. L. Lafleur, and M. E. Johnson. Fullerenes C60 and C70 in flames. *Nature*, Volume 352, Issue 6331, 1991, Pages 139-141.
- [44] J. B. Howard, K. D. Chowdhury, and J. B. Vander Sande. Carbon shells in flames. *Nature*, Volume 370, Issue 6491, 1994, Pages 603-604.
- [45] R. L. Vander Wal, L. J. Hall, G. M. Berger. The chemistry of premixed flame synthesis of carbon nanotubes using supported catalysts. *Proceedings of the Combustion Institute*, Volume 29, Issue 1, 2002, Pages 1079-1085.
- [46] S. K. Woo, Y. T. Hong, and O. C. Kwon. Flame synthesis of carbon nanotubes using a double-faced wall stagnation flow burner. *Carbon*, Volume 47, Issue 3, 2009, Pages 912-916.
- [47] P. Gopinath and J. Gore. Chemical kinetic considerations for postflame synthesis of carbon nanotubes in premixed flames using a support catalyst. *Combustion and Flame*, Volume 151, Issue 3, 2007, Pages 542-550.
- [48] N. K. Memon, F. Xu, G. Sun, S. J. B. Dunham, B. H. Kear, and S. D. Tse. Flame synthesis of carbon nanotubes and few-layer graphene on metal-oxide spinel powders. *Carbon*, Volume 63, 2013, Pages 478-486.
- [49] A. V. Saveliev, W. Merchan-Merchan, and L. A. Kennedy. Metal catalyzed synthesis of carbon nanostructures in an opposed flow methane oxygen flame. *Combustion and Flame*, Volume 135, Issue 1, 2003, Pages 27-33.
- [50] R. L. Vander Wal and L. J. Hall. Flame synthesis of Fe catalyzed single-walled carbon nanotubes and Ni catalyzed nanofibers: growth mechanisms and consequences. *Chemical Physics Letters*, Volume 349, Issue 3, 2001, Pages 178-184.
- [51] L. Yuan, K. Saito, C. Pan, F. A. Williams, and A. S. Gordon. Nanotubes from methane flames. *Chemical Physics Letters*, Volume 340, Issues 3-4, 2001, Pages 237-241.
- [52] L. Yuan, K. Saito, W. Hu, and Z. Chen. Ethylene flame synthesis of well-aligned multi-walled carbon nanotubes. *Chemical Physics Letters*, Volume 346, Issues 1-2, 2001, Pages 23-28.
- [53] G. W. Lee, J. Jurng, and J. Hwang. Formation of Ni-catalyzed multiwalled carbon nanotubes and nanofibers on a substrate using an ethylene inverse diffusion flame. *Combustion and Flame*, Volume 139, Issues 1-2, 2004, Pages 167-175.
- [54] F. Xu, X. Liu, and S. D. Tse. Synthesis of carbon nanotubes on metal alloy substrates with voltage bias in methane inverse diffusion flames. *Carbon*, Volume 44, Issue 3, 2006, Pages 570-577.
- [55] W. I. Milne, T. B. K. Teo, G. A. J. Amaratunga, P. Legagneuz, L. Gangloff, J.-P. Schnell, V. Semet, V. T. Binh, and O. Groening. Carbon nanotubes as field emission sources. *Journal of Materials Chemistry*, Volume 14, Issue 6, 2004, Pages 933-943.
- [56] W. Merchan-Merchan, A. V. Saveliev, and L. A. Kennedy. High-rate flame synthesis of vertically aligned carbon nanotubes using electric field control. *Carbon*, Volume 42, Issue 3, 2004, Pages 599-608.
- [57] W. Merchan-Merchan, A. V. Saveliev, and L. A. Kennedy. Flame nanotube synthesis in moderate electric fields: From alignment and growth rate effects to structural variations and branching phenomena. *Carbon*, Volume 44, Issue 15, 2006, Pages 3308-3314.
- [58] R. L. Vander Wal, T. M. Ticich, and V. E. Curtis. Diffusion flame synthesis of single-walled carbon nanotubes. *Chemical Physics Letters*, Volume 323, Issues 3-4, 2000, Pages 217-223.
- [59] M. Silvestrini, W. Merchan-Merchan, H. Richter, A. Saveliev, and L. A. Kennedy. Fullerene formation in atmospheric pressure opposed flow oxy-flames. *Proceedings of the Combustion Institute*, Volume 30, Issue 2, 2005, Pages 2545-2552.
- [60] T. X. Li, H. G. Zhang, F. J. Wang, Z. Chen, and K. Saito. Synthesis of carbon nanotubes on Ni-alloy and Si-substrates using counterflow methane-air diffusion flames. *Proceedings of the Combustion Institute*, Volume 31, Issue 2, 2007, Pages 1849-1856.
- [61] R. Vander Wal, L. J. Hall, and G. M. Berger. Optimization of flame synthesis for carbon nanotubes using supported catalyst. *The Journal of Physical Chemistry B*, Volume 106, Issue 51, 2002, Pages 13122-13132.
- [62] Y. Yang, Z. Hu, Q. Wu, Y. N. Lü, X. Z. Wang, and Y. Chen. Template-confined growth and structural characterization of amorphous carbon nanotubes. *Chemical Physics Letters*, Volume 373, Issues 5-6, 2003, Pages 580-585.
- [63] Z. Yuan, H. Huang, L. Liu, and S. Fan. Controlled growth of carbon nanotubes in diameter and shape using template-synthesis method. *Chemical Physics Letters*, Volume 345, Issues 1-2, 2001, Pages 39-43.
- [64] T. X. Li, K. Kuwana, K. Saito, H. Zhang, and Z. Chen. Temperature and carbon source effects on methane-air flame synthesis of CNTs. *Proceedings of the Combustion Institute*, Volume 32, Issue 2, 2009, Pages 1855-1861.
- [65] M. J. Height, J. B. Howard, J. W. Tester, and J. B. Vander Sande. Flame synthesis of single-walled carbon nanotubes. *Carbon*, Volume 42, Issue 11, 2004, Pages 2295-2307.
- [66] M. J. Height, J. B. Howard, and J. W. Tester. Flame synthesis of single-walled carbon nanotubes. *Proceedings of the Combustion Institute*, Volume 30, Issue 2, 2005, Pages 2537-2543.

- [67] C. J. Unrau, V. R. Katta, and R. L. Axelbaum. Characterization of diffusion flames for synthesis of single-walled carbon nanotubes. *Combustion and Flame*, Volume 157, Issue 9, 2010, Pages 1643-1648.
- [68] C. J. Unrau and R. L. Axelbaum. Gas-phase synthesis of single-walled carbon nanotubes on catalysts producing high yield. *Carbon*, Volume 48, Issue 5, 2010, Pages 1418-1424.
- [69] R. L. Vander Wal and L. J. Hall. Ferrocene as a precursor reagent for metal-catalyzed carbon nanotubes: competing effects. *Combustion and Flame*, Volume 130, Issues 1-2, 2002, Pages 27-36.
- [70] R. L. Vander Wal. Fe-catalyzed single-walled carbon nanotube synthesis within a flame environment. *Combustion and Flame*, Volume 130, Issues 1-2, 2002, Pages 37-47.
- [71] J.-W. Snoeck, G. F. Froment, and M. Fowles. Filamentous carbon formation and gasification: Thermodynamics, driving force, nucleation, and steady-state growth. *Journal of Catalysis*, Volume 169, Issue 1, 1997, Pages 240-249.
- [72] H. Wang and M. Frenklach. A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames. *Combustion and Flame*, Volume 110, Issues 1-2, 1997, Pages 173-221.
- [73] M. Frenklach and H. Wang. Detailed modeling of soot particle nucleation and growth. *Symposium (International) on Combustion*, Volume 23, Issue 1, 1991, Pages 1559-1566.
- [74] K. Saito, A. S. Gordon, and W. F. Stickler. A study of the early history of soot formation in various hydrocarbon diffusion flames. *Combustion Science and Technology*, Volume 80, Issues 1-3, 1991, Pages 103-119.
- [75] M. Farmahini-Farahani, A. V. Saveliev, and W. Merchan-Merchan. Volumetric flame synthesis of mixed tungsten-molybdenum oxide nanostructures. *Proceedings of the Combustion Institute*, Volume 36, Issue 1, 2017, Pages 1055-1063.
- [76] C. Jäger, F. Huisken, H. Mutschke, Th. Henning, W. Poppitz, and I. Voicu. Identification and spectral properties of PAHs in carbonaceous material produced by laser pyrolysis. *Carbon*, Volume 45, Issue 15, 2007, Pages 2981-2994.
- [77] A. Emelianov, A. Eremin, A. Makeich, H. Jander, H. Gg. Wagner, R. Starke, and C. Schulz. Heat release of carbon particle formation from hydrogen-free precursors behind shock waves. *Proceedings of the Combustion Institute*, Volume 31, Issue 1, 2007, Pages 649-656.
- [78] N. Krishnankutty, C. Park, N. M. Rodriguez, and R. T. K. Baker. The effect of copper on the structural characteristics of carbon filaments produced from iron catalyzed decomposition of ethylene. *Catalysis Today*, Volume 37, Issue 3, 1997, Pages 295-307.
- [79] M. D. Diener, N. Nicholson, and J. M. Alford. Synthesis of single-walled carbon nanotubes in flames. *The Journal of Physical Chemistry B*, Volume 104, Issue 41, 2000, Pages 9615-9620.
- [80] S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy. A formation mechanism for catalytically grown helix-shaped graphite nanotubes. *Science*, Volume 265, Issue 5172, 1997, Pages 635-639.
- [81] L. Yuan, T. Li, and K. Saito. Growth mechanism of carbon nanotubes in methane diffusion flames. *Carbon*, Volume 41, Issue 10, 2003, Pages 1889-1896.
- [82] R. T. K. Baker. Catalytic growth of carbon filaments. *Carbon*, Volume 27, Issue 3, 1989, Pages 315-323.
- [83] M. Tarfaoui, K. Lafdi, and A. E. Moumen. Mechanical properties of carbon nanotubes based polymer composites. *Composites Part B: Engineering*, Volume 103, 2016, Pages 113-121.
- [84] D. Hu, Y. Xing, M. Chen, B. Gu, B. Sun, Q. Li. Ultrastrong and excellent dynamic mechanical properties of carbon nanotube composites. *Composites Science and Technology*, Volume 141, 2017, Pages 137-144.
- [85] Q. Guan, L. Yuan, Y. Zhang, A. Gu, and G. Liang. Improving the mechanical, thermal, dielectric and flame retardancy properties of cyanate ester with the encapsulated epoxy resin-penetrated aligned carbon nanotube bundle. *Composites Part B: Engineering*, Volume 123, 2017, Pages 81-91.
- [86] S. Zhao, Z. Zheng, Z. Huang, S. Dong, P. Luo, Z. Zhang, and Y. Wang. Cu matrix composites reinforced with aligned carbon nanotubes: Mechanical, electrical and thermal properties. *Materials Science and Engineering: A*, Volume 675, 2016, Pages 82-91.
- [87] J.-P. Tessonnier and D. S. Su. Recent progress on the growth mechanism of carbon nanotubes: A review. *ChemSusChem*, Volume 4, Issue 7, 2011, Pages 824-847.
- [88] C. F. Cornwell and L. T. Wille. Proposed growth mechanism of single-walled carbon nanotubes. *Chemical Physics Letters*, Volume 278, Issue 4, 1997, Pages 262-266.