Selected Topics on the Synthesis, Properties and Applications of Multiwalled Carbon Nanotubes

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Summary

In summary, MWCNTs have been examined for a variety of electronic applications due to their unique structure and chemistry. Electrodes for field emission, energy and sensor applications hold particular interest. MWCNTs provide a very high surface area, relatively easy methods of surface modification, controllable and high concentration of reactive surface sites, and high specific capacitance. Combining MWCNTs with graphene structures, oxide and metal nanoparticles and certain polymers extends their performance and functionality. Such hybrid structures have been produced in situ during CNT growth and in two-step processes. Excellent progress on understanding the mechanisms of CNT growth has enabled numerous growth methods to all yield MWCNT structures in a variety of morphologies.

Introduction

Carbon nanotubes (CNTs) have an astounding array of properties that make them interesting candidates for numerous applications. The geometric and chemical variations found in CNTs provide a rich area of study for both science and *applications* [1, 2]. These variations are created by the unique bonding configurations of carbon that make it a ubiquitous part of our environment. The one dimensional nature of the basic CNT structure enabling ultra-high surface area, the ability to act as a semiconductor or a metal, the existence of multiple direct bandgaps, the relative ease of attachment for numerous chemical functional groups and ability to decorate CNTs with nanoparticles, all drive an array of scientific and technology issues that have been studied by research groups across the globe in recent years [3, 4]. A variant of the standard nanotube can be found by integrating the CNT structure with another unique and valuable property of carbon; its anisotropy. The well-known difference between the basal plane and z-direction properties of graphite for example translate directly into anisotropy between the longitudinal and transverse properties of carbon nanotubes. This large anisotropy in structure and properties is the basis of research exploiting edge vs. basal plane properties of graphite and graphene and increases the variety of properties and applications for CNT systems [5]. In particular, graphene edges are expected to be more

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reactive, hold a higher charge density and concentrate electric fields as in the case of *nanowalls or nanosheets* [6, 7].

With the recent increased understanding of the formation of graphene and its nanostructural compatibility with CNTs, an opportunity exists to enhance CNT properties by integrating the edge properties of graphene with the CNT one dimensional framework. Graphenated carbon nanotubes (g-CNTs) are one way to achieve this hybrid structure [8, 9]. This enables an optimization of charge and reactivity per unit volume not previously possible at the nanoscale. It is an engineered network with the concentration of high charge density, high reactivity edges arranged in three dimensional nanoscale space. This enables ultra-high surface area coupled with high charge density. To put these structures in context, we have previously introduced a diagram that classifies the nanostructures by their edge density; the EDGE Triangle [10]. Perhaps the most promising nanostructure involves the use of these g-CNTs in an aerogel network which has yet to be explored [11].

Enhanced charge density and reactivity are expected to improve performance for a variety of applications, including; energy storage (e.g., batteries, supercapacitors), energy conversion (e.g., fuel cells), electrochemical sensors, electrodes for neural stimulation, field emission sources and electrodes for industrial processes (e.g., materials synthesis, purification). Similarly, one-dimensional nanostructures, such as oxide or metal nanoparticles, can be integrated with CNTs to provide enhanced functionality for many of these same applications. These decorated CNTs can be fabricated using post deposition processing or during growth [12, 13]. Many fundamental issues of CNT growth translate to the growth of integrated graphene-CNT or nanoparticle-CNT composites. For example, the use of bulk synthesis in the gas phase vs. synthesis on a substrate, the role of the catalyst to enhance growth, the gas phase precursor ratios or presence of additional reactive species in the gas phase and post deposition processing. Polymer-CNT composites formed by post deposition processing also provide enhanced functionality in these applications. This review will cover the broad area of conventional CNTs growth as well as the formation of hybrid nanostructures, such as g-CNTs.

Due to the remarkable variation in carbon nanotube properties, (e.g., from semiconducting to metallic, inert to reactive, etc.), numerous applications are of potential interest. In this article we will focus on properties related to electrode applications addressed by multi-walled carbon nanotubes (MWCNTs). Integrated graphene-CNT materials are expected to be candidates to improve these applications even beyond the already exciting CNT results. Similarly nanoparticle-CNT hybrid structures are also able to combine the best properties of CNTs and functional nanoparticles. We will not address semiconducting, single wall CNT applications. Although of significant interest, these applications are likely farther from commercialization and simply present a breadth of variety which would be difficult to cover in this limited review.

Structure and Properties

Structural considerations

With the growing importance of energy applications in particular, a need has emerged to characterize the various forms of activated and nanostructured carbons in the context of their electrochemical charge-storage capacity. However, the use of gravimetric or area specific capacitance can be uninformative or even misleading due to the critical role of exposed linear edge density on charge-transfer processes; edges exhibit a 20x greater specific capacitance than basal planes [14]. For example, edge plane sites, either at the tips or along the length of CNTs can dominate both the chemical and electronic properties of the system, thus, a more robust normalization is needed for materials that possess this extreme anisotropy. By classifying nanostructures based on linear edge density, a deeper understanding of materials performance can be obtained and a more informed comparison of nanostructures is enabled. Recently, we proposed a classification for carbon nanostructures based on the dimensional organization of their edge structures (Figure 1) called the EDGE (Electron Density of Graphene Edges) Triangle [10]. This classification is organized based on the dimensional structure of sp^2 bonded carbon edges (i.e., edges of 2 dimensional carbon sheets that occur in graphite, graphene and even the tips of CNTs). Morphological benchmarks of the classification are provided, including the unique ability of CNTs to deposit in a vertically aligned forest and a recently reported [8] graphenated CNT (g-CNT) hybrid which increases the linear edge density of nanostructured carbons by an order of magnitude. As more and more applications draw upon the combined superlative properties of CNTs, graphene, and other nanostructured carbons, this dimensional classification provides new insights into both the optimization of existing materials as well the development of new hybrid nanostructures.

Electronic properties

MWCNTs have been shown to exhibit ballistic transport of charge carriers and possess exceptional electrical conductivity (1.85×10^3 S cm^{-1}) [15]. Current densities approaching 10^9 Acm^{-2} have also been reported [16]. Coupled with their robust mechanical properties, this makes them a strong candidate as interconnects for microelectronic devices and electrodes in numerous applications. Although MWCNTs exhibit metallic conductivity, their band structure varies considerable from the model of a free electron in a metal. Interesting and complex effects arise from the concentric walls of the MWCNT as well as from quantization of the electron wave function around the nanotube circumference with varying diameters. The multiple concentric walls of the MWCNT allow modification of the outer walls with adsorbates and functional groups while maintaining mechanical integrity and electrical conductivity. For example, the formation of graphene-CNT and nanoparticle-CNT hybrid structures benefit from these outer walls. This provides an enhanced functionality for applications that require chemical modification of the CNTs coupled with high conductivity such as electrodes for energy storage, sensors and field emission. Double-walled (or so-called "few-walled") CNTs [17] provide this functionality without unnecessarily increasing weight and volume which would be detrimental to properties such as energy density for energy storage applications.

Electrochemical properties

Carbon nanotubes and graphene are emerging electrode materials currently under intense investigation for various electrochemical applications such as electrochemical sensors and energy storage/conversion devices. Nanostructured carbons are attractive as supports or active layers in electrochemical applications due to their unique chemical and physical properties that offer advantages over traditional carbons including ultra-low resistivity ($\sim$ $10e^{-6}$ Ω cm) [18], high specific surface area (2675 m^2/g for single graphene sheet [19]), greater chemical stability, and controllable mesopore size distributions. The fundamental electrochemical properties of carbon nanotubes are heavily influenced by the relative ratio of graphitic basal-plane (i.e. sidewalls) to edge-plane sites (i.e. tips, ends, or defects) and the absence/presence of surface functional groups that exist at the solid-liquid interface. Generally, the electrochemical reactivity, wettability, and electron transfer (ET) rate of CNTs improves with increasing density of edges and edge-planelike defects, or likewise decreases with greater area of sidewalls in contact with the electrolyte. Thus CNT structures with greater disorder or exposed defects; such as bamboo type [20] rather than hollow cylinder MWCNTs, chemical vapor deposition (CVD)-grown rather than arc-grown [21], vertically aligned rather than randomly oriented [22], certain CNT-graphene hybrids [8], or those subjected to acid treatment for purification or subsequent functionalization have significantly improved ET kinetics. For instance, using the redox probe Fe(CN)$_6$$^{3-}$/ Fe(CN)$_6$$^{4-}$, pristine MWCNTs exhibited slow ET kinetics with a peak separation (E_p) greater than 200 mV whereas acid-treated MWCNTs and a MWCNT microbundle electrode exhibited a E_p of $\sim$ 60 mV indicative of reversible ET kinetics [23, 24]. The ability to achieve a very fast ET rate evidenced by ideal E_p for these defective CNT structures compared to basal plane structures (E_p = 700 mV) is advantageous for sensing or electrocatalytic applications. It is believed that the mechanism for greater ET kinetics in nanotube structures is due to the helicity, low dimensionality, and topological defects that cause a higher local-density of states (including surface and defect induced states) compared to graphite [24].

Selected Electrode Applications

Field Emission Applications

CNTs are attractive candidates for field emission devices due to their low turn-on voltage, high stability, high current density, and long lifetime. Typical turn-on fields for CNTs range between 1-5 V/μm with SWNTs exhibiting lower values [25]. Wide ranges of stability and lifetime are observed from several minutes to hundreds of hours, depending on specific samples and operating parameters. Most importantly, enhancements are achieved through the use of either bundles of SWNTs or aligned arrays of MWCNTS whereby neighboring tubes may turn on when others fail [26]. Early applications ranged from luminescent displays to x-ray sources. In contrast to metal field emission sources (e.g. tungsten and molybdenum) MWCNTs are covalently bonded, making them less susceptible to surface migration under high electric fields and current densities. The tips of the CNTs are more likely to keep their shape giving them longer lifetime and stability. Carbon also has a relatively low sputter coefficient in comparison to other cathode materials, minimizing degradation due to ion sputtering in applications that require pressures above the 0.1

milliTorr range. In contrast to Spindt-like cathodes [27], CNT based cathodes are dominated by emission from a small percentage of the tubes. This minority domination means that it is often difficult, or misleading, to try to correlate microstructure with overall cathode performance. Field emission from a mat or film of CNTs might be dominated by a single CNT that is longer, or smaller diameter, and thus significantly different from the average microstructure [28]. Furthermore, packing a larger number of tubes, uniformly into an emission area in attempts to maximize current density and uniformity, has a screening effect, whereby the field enhancement factor of any given tube is minimized by the neighboring tubes [29]. Maximizing current density and lifetime becomes a trade-off between controlling spacing and morphology. Figure 2 (a) and (b) show variations in CNT film morphology, the former showing significant variations in CNT length as compared to (b). Figure 2 (c) shows the film from (b) after a post-growth processing designed to increase emitter spacing by binding bundles of tubes in a thin polymer matrix [30]. Since current density, lifetime, and stability are all functions of device geometry and operational conditions, we have defined a current-density-lifetime product with some of the better performing cathodes reporting 0.5-1.0 A-hrs/cm^2 [26].

Electrochemical sensors

As a result of the unique electrochemical properties of CNTs such as the high activity and kinetics of edge-plane-like graphitic sites on the nanotube ends and sidewall-defects, they are particularly important structures for electrochemical sensing applications. In general, electrochemical sensors (ECS) are proven commercial technology with many benefits over instrumental analysis methods due to their remarkable detection sensitivity, reproducibility, ease of miniaturization, portability, low cost, and ultra-low power consumption. ECS typically consist of an electrode as the transduction element covered by a chemical or biological recognition layer to impart selectivity. This layer interacts with the target analyte, and the chemical changes resulting from the interaction are translated by the electrode into electrical signals enabling detection. The ability to modify or functionalize CNT electrodes using physical absorption (non-covalent) and chemical binding (covalent) offers a versatile and convenient approach for integrating the transduction and recognition layers of the sensor. This is coupled with the very high surface area of most CNT structures which provides orders of magnitude more reaction sites than a flat surface. Thus, CNT-based ECS (CNT-ECS) exhibit lower detection limits, higher sensitivity, and faster response than conventional ECS due to the signal enhancement provided by the high surface area, low overvoltage, and rapid ET kinetics.

Sensor types and target analytes—A large variety of CNT-ECS exist that have each been uniquely designed for detection of specific target analytes. These CNT-ECS may use a variety of electrochemical methods for signal transduction including DC potentiometric and voltammetric techniques as well AC impedance methods. To name just a few categories, CNT-ECS have been used to detect: (a) toxic or combustible gases in a confined space (i.e. gas sensing) [31]; (b) explosive residues such as trinitrotoluene (TNT) and other nitroaromatics in contaminated waterways or soils [32]; (c) metal ions in solution (i.e. ion sensing) [33]; (d) various biomolecules (e.g. neurotransmitters, proteins, DNA, enzymes, peptides, amino acids, microorganisms, and other cells) and pharmaceuticals (e.g. dopamine,

insulin, rutin) in the body or in *ex-vivo* samples of blood, urine, or saliva (i.e. biosensing) [34, 35]; and (e) to detect undesired chemical residues resulting from animal drugs, food additives, pesticides, and other environmental contaminants in raw and processed foods [36].

CNT electrode fabrication for ECS—The vast majority of literature reports on CNT-ECS use electrodes fabricated by randomly dispersed CNTs on a glassy carbon electrode (GCE). This approach in itself is a challenge due to the high hydrophobicity of pristine CNTs and the difficulty of uniformly dispersing them in solvents prior to casting onto a GCE. In addition, the random orientation which exposes primarily sidewalls detracts from the key advantages of CNTs which are their very large aspect ratios and exposed ends that allow them to be used as molecular wires for facilitating rapid ET between biomolecules and electrodes. There are significant benefits from aligning CNTs rather than random immobilization since the electroactive CNT ends are then presented to the biological entity in the correct orientation such that the electron transfer between the usually buried redox active centers is achieved [37]. Graphenated CNT structures (Figure 1) would have an obvious advantage in this case since the anisotropic exposure of graphitic edge sites would obviate the need for controlling orientation.

One way to maximize the sensitivity and minimize the size of CNT-ECS is to utilize a single vertically oriented nanoelectrode or nanoelectrode arrays that can be obtained using nanoparticle catalyst patterning techniques (e.g. UV/E-beam lithography [38, 39], or electrochemical deposition [40]) and direct growth by CVD methods. In order to obtain a nanoelectrode array in which each nanoelectrode (from a submicron sized CNT bundle down to a single nanotube) behaves as an independent entity, a sufficiently low site density of aligned CNTs must be achieved such that destructive interference caused by diffusion field overlap does not diminish the transduction signal. In addition, the CNT sidewalls (with slower ET kinetics and increased background charging noise) are often masked with non-active layer (epoxy, SiO_2) to expose only the tips. In doing so, greater analytical sensitivity and improvement in signal-to-noise ratio is achieved due to the change in mass-transport from planar diffusion, which is observed at macroelectrodes, to that of radial diffusion observed at micro- and nanoelectrodes. Since a single microelectrode may have currents in the nanoampere to picoampere range which cannot compete with electrochemical noise, a microelectrode array can be used where each microelectrode is effectively wired in parallel due to the radial diffusion. The electrochemical signal thus observed at the array is that of a single microelectrode multiplied by the total number of electrodes comprising the array producing a large analytical signal with low background currents [37]. The detection limits of aligned CNTs in nanoelectrode arrays has reached picomolar levels [41]. Once again g-CNTs (Figure 1) are expected to offer an advantage by obviating the masking step and providing high edge density for signal enhancement along the entire sidewalls greatly increasing the number of active sensing sites per nominal area. Further, one might also envision a g-CNT structure with sufficiently low foliate (i.e. graphene edge) density such that each foliate operates as a nanoelectrode with radial diffusion properties. Thus, each individual g-CNT would inherently incorporate its own foliate nanoelectrode array.

Energy storage and conversion devices

Nanostructured carbons, particularly MWCNTs and graphene, are of great interest for a variety of advanced energy storage and conversion applications, including: (a) supercapacitors; (b) lithium batteries (i.e. Li-ion, Li-sulfur, and Li-air batteries); (c) electrocatalysts/supports for fuel cells; (d) organic solar cells (i.e. dye-sensitized) and; (e) gas storage (i.e. methane and hydrogen). We will briefly address the first three given the great interest of the research and development community for implementation into future commercial devices.

Supercapacitors—Carbon nanotube based supercapacitors have been investigated as an alternative to commercial-off-the-shelf (COTS) activated carbon supercapacitors. Activated carbons (ACs) are attractive due to their relatively low production costs at high volumes and their superior specific surface area (3000 m^2/g) compared to mesoporous carbons (i.e. aerogel, CMK-3 at 1730 m^2/g) [42] and pristine MWCNTs (430 m^2/g) . However, unlike ACs, carbon nanotube structures have improved electronic and ionic conductivity, due to their tailorable pore size distribution, ultra-low resistivity, and low contact resistance as a result of no absolute requirement for an insulating binder (e.g. freestanding buckypaper). These properties of pristine CNTs enable superior power density and an increase in electrochemically active surface area such that their specific capacitance is comparable to ACs (15 – 135 F/g and 40 to 140 F/g), respectively [43, 44]. Four routes being explored for improving the energy storage capability of CNTs beyond ACs include:

1. Careful thermal, chemical, or electrochemical treatment to increase accessible surface area and surface functional groups.

2. The use of CNTs as a conductive backbone/support for high redox pseudocapacitance coatings such as conducting polymers or metal oxides that can increase specific capacitance by an order of magnitude (e.g. 1100 F/g for MnO_2 coated CNTs [45]).

3. Growth of dense vertically aligned CNT forest directly on bulk metal current collectors by PECVD.

4. Development of hybrid capacitors (Li-battery cathode or anode, and capacitor auxiliary electrode) to achieve double the energy density of a standard electrochemical capacitor with similar power density.

Routes **(1)** and **(2)** have recognized drawbacks. Treatments that render surface oxygen groups may increase carbon resistance, capacitor instability/deterioration, and have limited to no effect with organic electrolyte. Surface-coatings of pseudocapacitive materials typically limit cycle stability and decrease conductivity of the composite. In contrast, route **(3)** has received strong attention recently due to the ability for direct growth of nanostructures perpendicular to metal current collectors [46, 47], the ability to expose a preponderance of graphitic edge-planes [9] known to have an order of magnitude greater double-layer capacitance (50-70 $\mu F/cm^2$) than the basal plane sites (3 $\mu F/cm^2$) [14], and increases in capacitance by fine-tuning the inter-tube distance [48, 49]. The incorporation of graphitic edge planes has been shown to enable a 7× improvement in specific capacitance at high frequencies [8, 9]. Figure 3 shows the gravimetric and area specific capacitance as a

function of deposition time for g-CNTs with increasing foliate density. Longer deposition times lead to higher graphene foliate density and commensurately higher capacitance. Furthermore, Signorelli et al. [49] demonstrated growth of a 100 μm vertical CNT forest on Al foil, and calculated that if the CNT density is improved to 10^{12} /cm^2 and working voltage increased to 3.5 V using an electrolyte of 2.7 M acetonitrile, energy densities of 35 Wh/kg and 37 Wh/l could be achieved which is seven times higher than the energy density available with COTS AC supercapacitors.

Lithium Batteries—Li-batteries currently offer high energy density (> 100 Wh/kg) but lack high specific power for applications such as power tools, electric vehicles, and renewable energy storage. Nanostructured carbons such as CNTs in Li-battery electrodes offer improved accessible surface area for active sites, highly conductive 3-D network for electron transport, and high Li-ion diffusivity compared to bulk graphite that can improve power densities. Carbon nanotubes have also demonstrated improved anodic charge storage capacity (MWNT anode = 80 – 640 mAh/g) compared to a traditional graphite anode (372 mAh/g) [50]. Recent research has focused on how to form safe, stable, and high capacity Li electrodes by forming nanocomposites made from conductive high area CNTs and other high capacity but insulating nanostructures (e.g. CNT – Si nanowire composite anode, CNT – sulfur composite cathode) [51].

Fuel Cell Electrocatalysts/Supports—Carbon nanotubes have also been demonstrated as a superior electrocatalyst support compared to commercial Vulcan XC-72 for proton-exchange membrane fuel cells (PEMFCs) due to: (a) increased durability under fuel cell conditions; (b) better conductivity; (c) better specific interaction between Pt and CNT support (i.e. interaction of delocalized π-electrons and Pt d-electrons) resulting in higher catalytic activity and; (d) absence of deep-crack structures that minimize catalytic activity from the Pt nanoparticles [52]. Emerging as the most significant problem with PEMFC catalysts supports is corrosion under fuel cell conditions that leads to degradation and poor durability of the electrocatalysts. Since the corrosion rate depends primarily on the degree of graphitization of the carbon, CNTs are inherently better supports than carbon black [52]. The high surface area of CNT supports is also advantageous for emerging development of extended surfaces or continuous thin catalyst films (e.g. Pt-skin and Pt-skeleton structures) which have shown improved catalytic activity and durability compared to nanoparticle catalysts which are prone to agglomeration and activity degradation with cycling. In particular, vertically aligned CNTs appear to be an excellent platform for extended surfaces due to the high surface area of the coating achieved by atomic layer deposition or other chemical methods [53]. Extended surfaces also enable minimization of Pt in the catalyst layer compared to nanoparticle catalysts. Moreover, to minimize cost of electrocatalysts even further, non-precious metal catalysts deposited on CNTs [54] and nitrogen-doped CNT arrays [55] (serving as the catalysts themselves) have shown equal or greater activity/durability compared to traditional Pt/Vulcan carbon electrocatalysts.

Growth Processes and Theories

Primary parameters that control MWCNT growth

MWCNTs are typically defined as concentric cylindrical structures with a hollow central core. MWCNTs can involve either a stacked-cone or bamboo cross section (sometimes referred to as carbon nanotube fibers or simply carbon nanofibers) rather than a hollow cylindrical core. There are two primary approaches for the deposition of CNTs: i) bulk synthesis (e.g. arc discharge or laser ablation), and ii) substrate or template synthesis (e.g. CVD [56-58]). Bulk synthesis enables larger quantities of materials to be produced, refined (e.g. removal of metal particle or amorphous carbon) as a powder or film and then later patterned or incorporated into devices. Substrate growth allows the CNTs to be deposited directly onto the device substrates. The pros and cons of the various techniques depend very much on the specific application and how the CNTs will be integrated with other devices or device components. In most applications, there is need to control both the microstructure of the CNT film or construct along with the nanostructure of the CNTs.

Theories of catalyst mechanisms

The role of the catalyst is to facilitate decomposition of hydrocarbons and provide a dissolution host for the carbon and template for CNT formation. There are exceptions, but in general, the metal should have solubility for carbon and react chemically but should not be a "strong" carbide former. Typical catalysts are Fe, Ni, and Co but most other transition and refractory metals have also been demonstrated to enable CNT growth. Hollow cylinder MWCNTs typically follow a base-growth mode while bamboo structured MWCNTs can exhibit either base (as in Figure 4(a)) or tip-growth modes depending on process conditions and the interaction between catalyst and substrate [59]. Figure 4(a) shows a TEM of a bamboo-structured CNT grown on a silicon AFM tip using iron catalyst. The typical bamboo CNT has a periodic shell (Figure 4(b)) that replicates the catalyst structure throughout the fiber length. Figure 4(c) shows the electron diffraction pattern of the iron catalyst following growth, identifying it as single crystal Fe_3C. The growth follows a common VLS process used in whisker fiber growth (Figure 4(d)), in the case of catalyst nanoparticles on a substrate: i) adsorption and decomposition at the edge of the catalyst particle where it meets the substrate, ii) dissolution of carbon atoms into the catalyst and bulk diffusion through the particle, and iii) precipitation of the carbon on the surface of the particle, forming a graphene layer or incorporating onto the edges at the base of a growing nanotube. Most of the CNT literature has proposed a process limited by bulk diffusion of carbon through the catalyst particle for both surface and tip based growth. However, some researchers have shown evidence of a surface diffusion mechanism, suggesting that more complex structures such as MWCNTs and bamboo-type MWCNTs might involve a combination of both.

Controlling CNT Nanostructure and Spatial Orientation

The dependence of process parameters on the CNT micro- and nanostructures is neither well understood nor controlled at the process level [60]. This represents a significant issue if some of the applications discussed above, and demonstrated only at the laboratory scale, are to be realized commercially. CNTs are typically grown with either CO or hydrocarbon

source gases using thermal and PECVD processes. Additional hydrogen in the gas phase appears to favor the bamboo structure, passivating the dangling bonds from the graphene edges of either the cone or bamboo sub-structures [61]. Shown in Figure 4(d), above, the primary factor that affects the formation of a nanofiber (i.e. bamboo) vs. nanotubular structure is the presence of atomic hydrogen. By passivating the covalently bonded edges of the graphene structure at the base of the growing CNT, hydrogen will terminate the edge growth freeing carbon for dissolution, bulk diffusion and renucleation of the graphene cap that nucleates another section of the bamboo structure which is equivalent to the tip in a hollow cylindrical CNT structure. If the edges are not passivated, then the majority of carbon can be incorporated directly into the outer cylindrical shell creating a hollow, cylindrical structure.

A typical growth process follows that shown in Figure 5(a): There is a parabolic increase in tube length with time (I) followed by a transition (II) and saturation (III). Region I is characterized by dissociation and bulk diffusion, typically limited by the latter. The Transition Region (II) is characterized by a decrease in gas-phase diffusion and growth rate due to interactions between hydrocarbon radicals and existing nanotubes. Termination (III) occurs primarily due to the inability of the diffusing carbon species to reach the catalyst particle. Increased interaction between incoming radicals and CNTs causes carbon deposition on the CNTs and less carbon is supplied to the catalyst. The maximum length and tube diameter are thus a function of the major process variables (temperature and gas composition) and catalyst thickness, as in Figure 5(b-d). The various hybrid structures discussed previously such as graphenated-CNTs and integrated oxide/metal nanoparticle CNTs have not yet been studied sufficiently to provide such a detailed model of growth. However, it seems likely that some of the same mechanisms will be at work for the CNT framework in these structures, modified to various extents depending on the morphology and chemistry of the structures.

Although growth from bulk carbon such as arc-discharge and laser ablation is capable of producing high quality CNTs in large quantities, it is difficult to achieve aligned CNT's with these techniques. In contrast, catalytic chemical vapor deposition (C-CVD) allows greater control over the spatial orientation, diameter, and even length of CNTs. C-CVD can utilize either thermal or plasma gas phase activation. Limited general observations about the impact of catalyst nanoparticle characteristics, vapor phase temperature and carbon concentration can be made for some situations. However, the large variety of growth parameters (e.g., temperature, gas phase concentration, gas phase purity, substrate temperature, pressure, flow rate, catalyst material, catalyst size and distribution) can give rise to complex response surfaces for CNT growth with opposite trends observed for any given parameter-response pair depending on the other growth parameter values. Nonetheless, it is clear that by controlling the spatial distribution of catalyst nanoparticles on the substrate, CNTs can be oriented due to the steric hindrance of neighboring CNTs. Thus, as the interparticle spacing and diameter decrease, vertical alignment can often be enhanced. The nanoparticle catalyst size also impacts the diameter of the CNTs, with a general trend from single-walled to few-walled to multi-walled growth as the size increases. In addition, the extent of supersaturation in the vapor phase (i.e., the concentration of activated carbon) and the temperature of both the substrate and the vapor phase impact CNT morphology and nanostructure. The growth

of single walled is often favored if the catalyst particles are very small (< 10 nm) and the carbon supply is low, with sufficient energy in the system (T > 900 °C). In the case of plasma enhanced CVD (PECVD) the alignment of carbon nanostructures can also be enhanced due to interactions with the electric field [62, 63]. The plasma can also enable decoupling of the vapor phase activation from the substrate temperature. A wide range of parameters allow CNT growth in such systems but typical conditions for oriented MWCNT growth are often: Temperature = 700 – 800 C; Plasma Power = 150 – 1000 watts (depends on frequency, 2.45 GHz is the most common source, falling in the lower end of this range, i.e. 150 – 300 W); Gas composition, $CH_4:NH_3$, $C_2H_2:NH_3$ or $CH_4:H_2$ = 0.5 – 2.0 [60]

Emerging Issues

Growth. Morphology of the CNTs; particularly length, diameter, alignment and even chirality, are fundamental properties which must be controlled more effectively. Although wide ranges of these properties have been reported, the growth is not yet a robust process. Multiple samples grown under nominally the same conditions do not have the same properties. Chamber history and uncontrolled parameters (e.g., humidity and impurities) can have significant impact on the final CNT characteristics. Controlling the spatial distribution of CNTs on the substrates, the quality of alignment with lower density CNTs and the density of defects and edges are all areas of importance. To create controlled and robust processes, it is likely that refined gas phase chemistries as well as modified reactor designs will be required to insure that growth is not on a steep slope of the input vs. response curves and that fundamental parameters such as temperature and flow rate are well controlled.

Commercialization

Efforts to commercialize CNTs are increasing as evidenced by the increasing number of patents citing CNTs [64]. However, efforts are limited by lack of uniformity in CNT morphology and properties. Post deposition processing is also an area in need of improvements before commercial applications become viable. Functionalization, uniform decoration with nanoparticles and device fabrication are all areas that are in relatively primitive stages of development. Thus, while research continues to offer indications of the exceptional promise of CNTs by providing first demonstration of best in class device operation in numerous areas, commercialization will require significant resources to enable uniform, reproducible robust material fabrication. Of course, the cost of this synthesis must also continue to decrease to enable broad applicability. Electronic applications for MWCNTs that have been demonstrated as very promising in the research lab include batteries, supercapacitors, fuel cells, field emission sources and various types of sensors.

Integration

This is still an issue, whether the CNTs are bulk produced and then incorporating into devices or when the CNTs are grown in place. In the former, materials integration and uniformity are issues, while high temperature deposition often limits the latter [60]. To achieve broad application of many of the devices reported above, deposition and device fabrication processed require better materials uniformity, screening, and integration

methodologies for bulk synthesis; and lower temperature growth and better overall device integration strategies for CVD deposition approaches.

Acknowledgments

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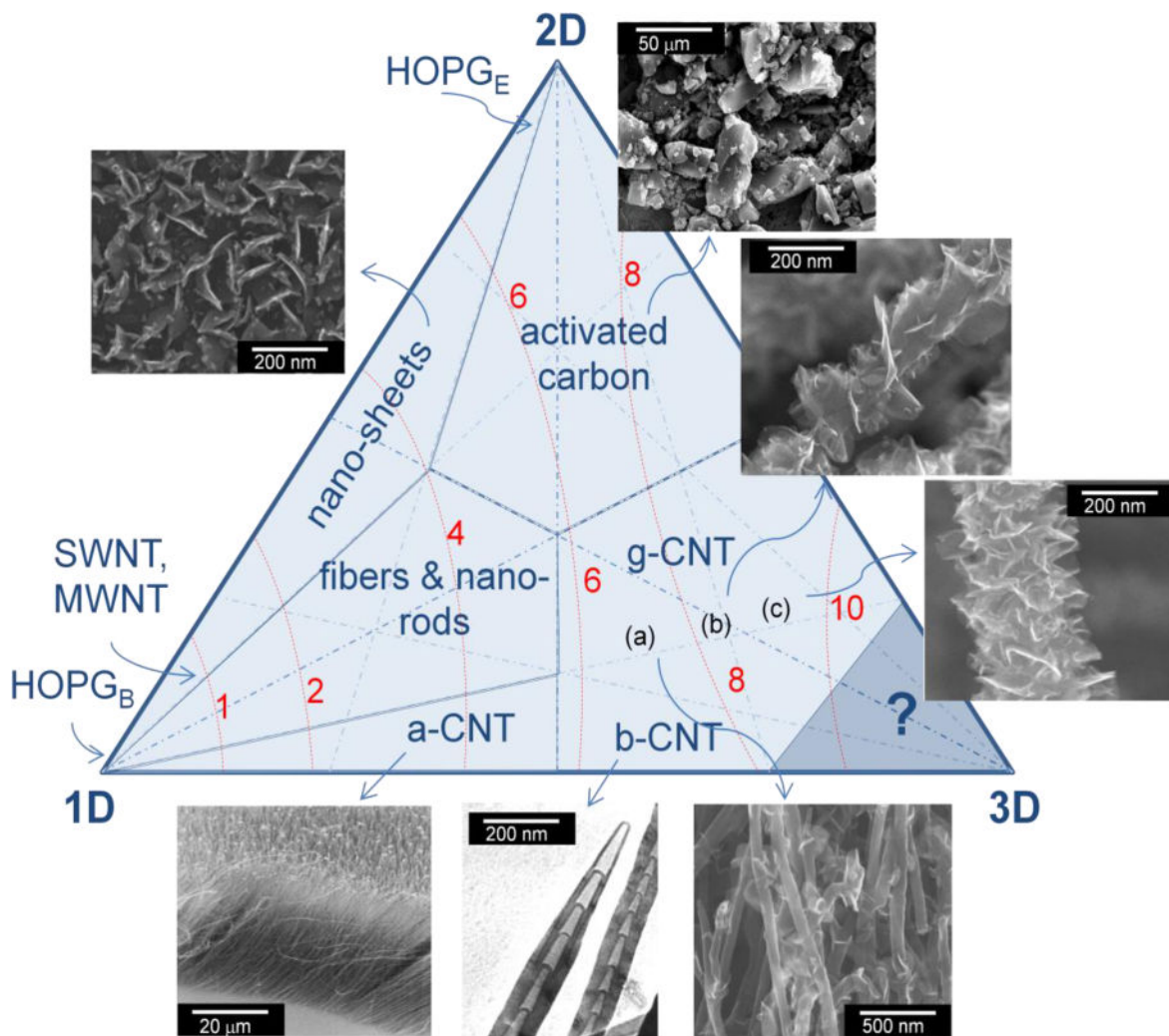
Figure 1.
[1] Classification for Carbon Nanostructures based on dimensional organization of dangling bonds, showing SEMs of select carbon nanostructures: nanosheets (NS); activated carbon (AC); aligned CNTs (a-CNTs); a TEM showing microstructure of the bamboo-structured CNTs (b-CNTs); and a series of graphenated, aligned CNTs (g-CNTs) with increasing graphene foliate density (a)-(c). The red-dotted contours represent the magnitude of the linear density of dangling bonds, $\log(\rho_L)$ in cm^{-1}. The optimum structure in the lower right corner (?) represents a hypothetical, maximum density of 3D-interconnected edge-exposed structures.
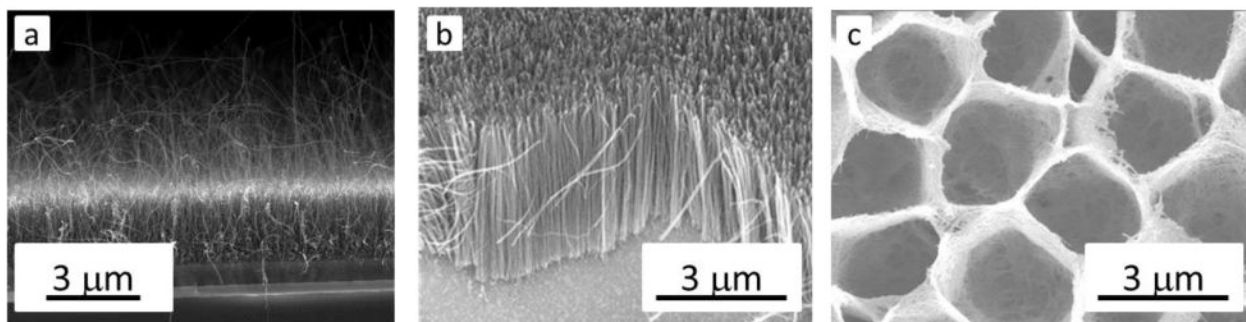
Figure 2.
SEMs showing (a) variations in tube length with a minority of tubes significantly longer than the average as compared to (b) a more uniform distributions of aligned CNTs; and (c) a polymer-CNT composite made from the film in (b) designed to optimize emission site spacing while keeping overall CNT density high.
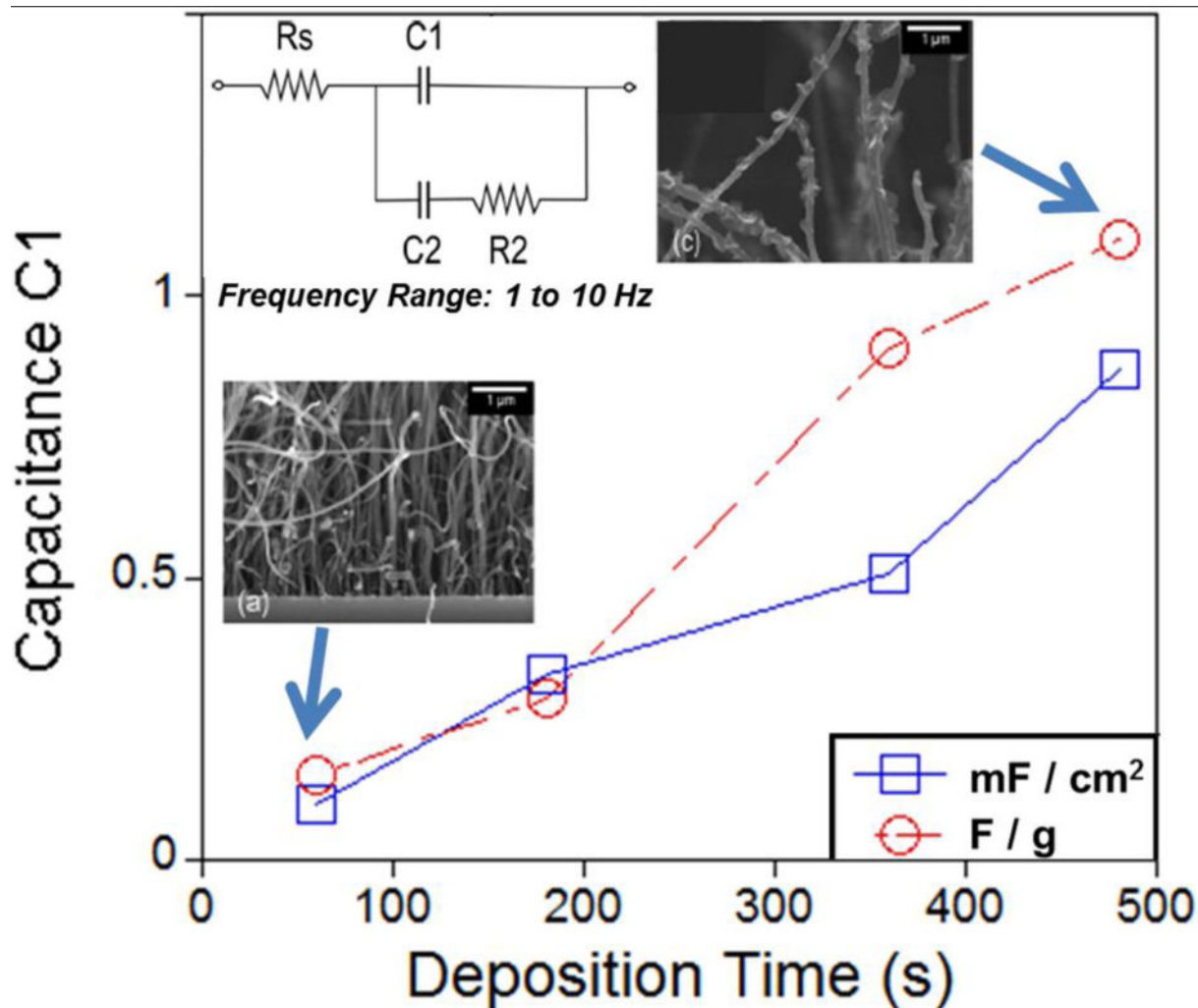
Figure 3.
Capacitance as a function of deposition time for graphenated CNTs with increasing foliate density (measured in a saline based electrolyte). Insets show SEM images of foliate density increasing with deposition time and the impedance spectroscopy circuit model used to determine the capacitance data. Capacitance C1 represents the double layer capacitance that is proportional to the electrochemically accessible surface area at the specified frequency range.
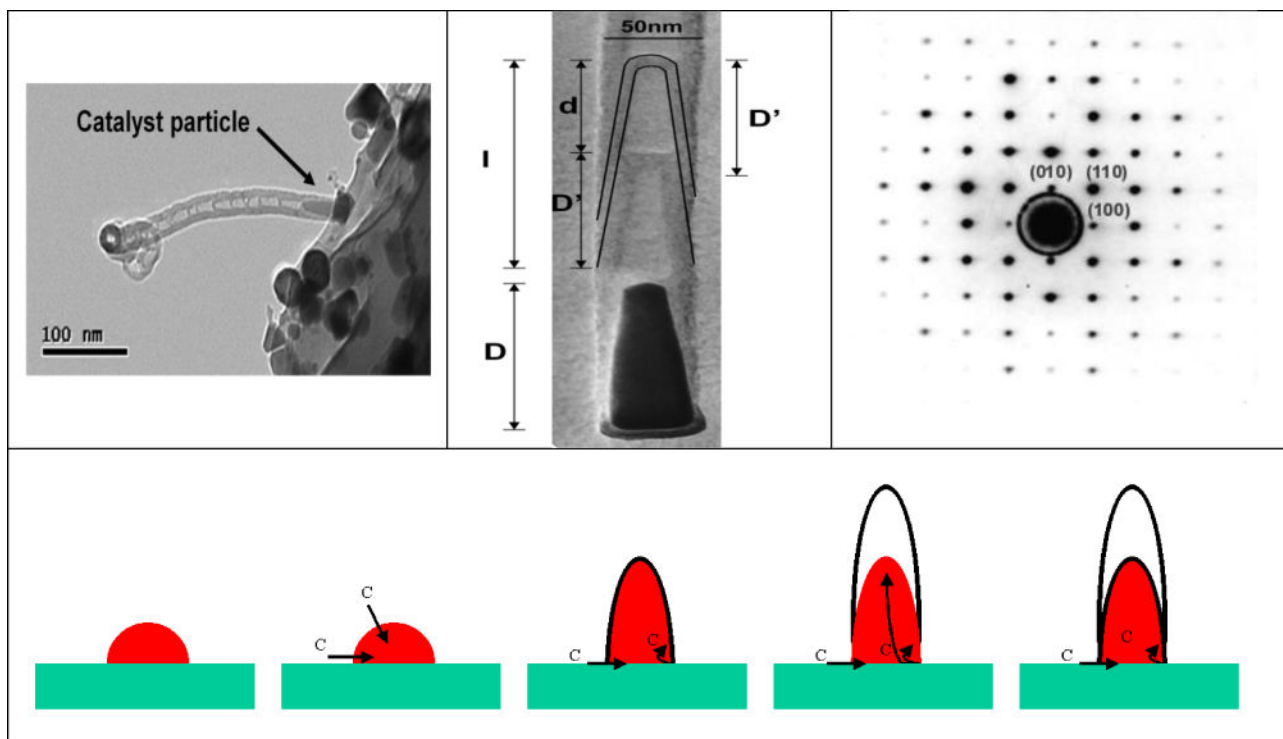
Figure 4.
(a) TEM of bamboo structured CNTs showing catalyst particle at the base, (b) high resolution TEM showing repeating bamboo structure relative to the iron catalyst, and (c) TED pattern of the catalyst it to be single crystal Fe_3C. (d) Schematic flow of the repeating nucleation and growth process for bamboo-structured CNTs.
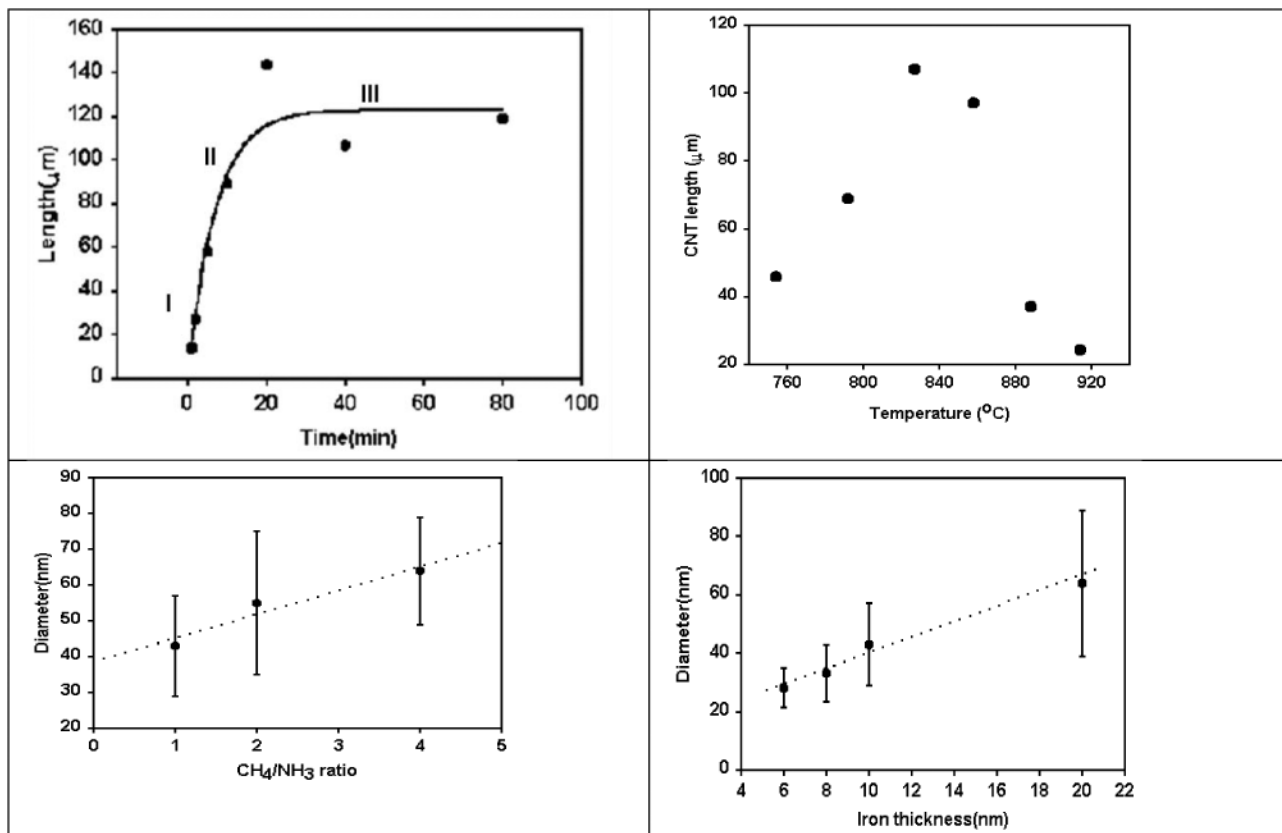
Figure 5.
(a) Typical length vs time curve for MWCNT or CNF deposition showing length saturation, (b) CNT length as a function of substrate temperature, (c) Diameter as a function of gas ratio, and (d) Diameter as a function of catalyst thickness.