Growth of Well-Aligned Carbon Nanotube Structures in Successive Layers

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Layered structures of well-aligned carbon nanotubes were grown using three variations of vapor-phase chemical vapor deposition growth processes. The reactants (typically ferrocene and benzene) were introduced either directly to a heated furnace or carried into the furnace by evaporation or spray pyrolysis in an argon flow. Thick mats of densely packed, well-aligned nanotubes were produced when the reactants were continuously introduced to the reaction; however, when the reactant flow was interrupted, the pauses allowed growth to stop and then restart as a new layer. These pauses were achieved by either completely stopping the reactant flow for a given time or by modifying the dispensing system to introduce the reactants in discrete drops. Time intervals between drops were varied between 20 s and 120 s, with distinct layers observed for pauses of 30 s or greater. The best results were achieved when drops of a catalyst-rich solution were alternated with drops of pure benzene. Layers were grown with thicknesses ranging from several microns to several hundred microns, and structures were grown with well over 100 layers.

Introduction

Carbon nanotubes (CNTs) are a recently discovered form of carbon with a graphitic lattice and a long, tubular structure.[1] They have been the subject of much interest in recent years because of their attractive mechanical properties (~1000 GPa Young's modulus),[2] tunable electronic behavior (conducting or semiconducting depending on tube chirality),[3,4] and unique dimensions (~1 nm to 100 nm diameter, up to several mm length).[5−7] As a result of these properties, nanotubes have potential applications in many fields, including composite reinforcement,[8,9] transistors and logic circuits,[10,11] field emission sources,[12] and hydrogen storage.[13] CNTs can be grown by a variety of means, the most common of which are arc discharge,[14] laser ablation,[15] and chemical vapor deposition (CVD).[16,17] A large number of variations in CVD processes have been reported as successfully growing carbon nanotubes.[18,19] Many of these procedures use substrates with a catalytic layer deposited prior to the growth reaction; however, through a vapor-phase CVD method, CNTs can be grown on untreated substrates by supplying both a catalyst source and a carbon source during the reaction.[7,20]

To fully optimize the production of carbon nanotubes, the growth mechanisms involved in their formation must be completely understood, and many theories have been introduced to describe this growth. A mechanism to describe the formation of carbon nanotubes in the presence of a metal catalyst has been proposed by Sinnott et al.,[21] which is based on the processes involved in carbon fiber formation as described by Baker et al.[22,23] In this model, carbon diffuses into nanometer-scale catalytic particles, and when the solubility limit within the metal is reached, this carbon precipitates out with a graphitic structure. Depending on the size of the catalyst particle, either graphite sheets, carbon fibers, multi-walled carbon nanotubes, or single-walled nanotubes can form. During the formation of carbon

fibers or nanotubes, the original catalyst particles will either remain fixed to the substrate (called root growth) or detach from the surface and remain encapsulated within the opposite end (called tip growth). Metal catalyst can be deposited on the substrate prior to growth or can be introduced to the reaction chamber during growth; the latter process is called vapor-phase growth.

The objective of the present work is to investigate methods of controlling vapor-phase growth procedures, to lead to the formation of carbon nanotubes in a structure with a distinct layered pattern. Each layer in this structure is composed of a well-aligned, densely packed mat of carbon nanotubes, and the interfaces between layers are not bridged by the tubes.

Experimental Section

Carbon nanotubes were grown using three chemical vapor deposition methods: a spray pyrolysis CVD procedure modeled after that described by Kamalakaran et al.[20] and two vapor-phase growth versions of this process. Reactant solutions of between 5 wt % and 10 wt % ferrocene ($(C_5H_5)_2Fe$) dissolved in benzene were used in most procedures, with $CoCl_2$ and Cobaltocene ($(C_5H_5)_2Co$) also used as catalysts in some cases. For spray pyrolysis, this reactant mixture was stored in a syringe and dispensed through a 27 gauge needle into an argon jet ranging between 7×10^4 sccm and 9×10^4 sccm. This gas jet sprayed the reactant solution into a 27-mm inner diameter quartz tube held inside a furnace at 850 °C; the equipment used is shown in Figure 1.

The vapor-phase growth methods were performed using the same equipment and solutions, however, the reactants were introduced to a slower argon flow (200−400 sccm), rather than jetting into the furnace. In the first process, the solution was dispensed either from the syringe or a peristaltic pump; it pooled at the bottom of the tube and evaporated into the gas flow. The second procedure was performed by rotating the entire furnace-growth assembly by 90° to orient the tube axis perpendicular to the ground. Reactants were introduced in the same manner
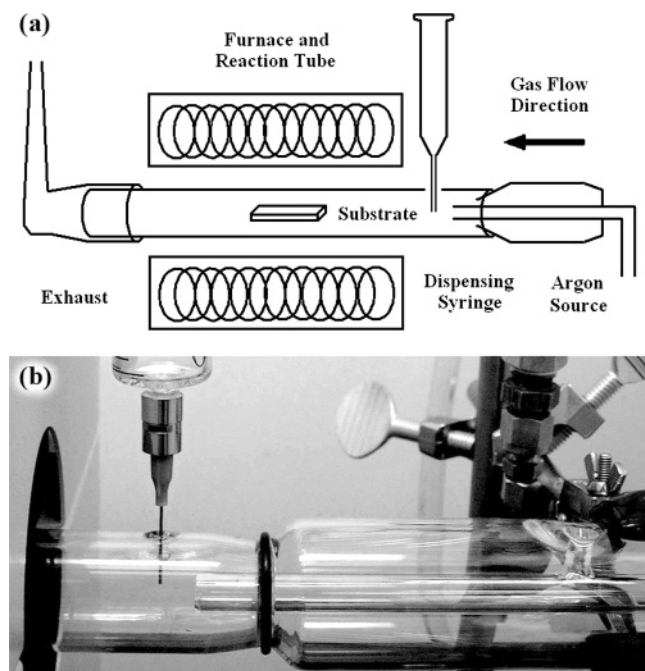
Figure 1. (a) Schematic diagram and (b) photograph of argon jetting apparatus, reaction tube, and syringe dispensing mechanism used for CVD growth of carbon nanotubes.

Figure 2. New carbon nanotube growth (upper portion of image) on the surface of existing carbon nanotubes (lower portion of the image) (run #071204-1).

Figure 3. Layered pattern of higher catalyst concentration regions in ferrocene catalyzed carbon nanotubes (run #042004-1).

as described in the first vapor-phase process; however, because of the new orientation, they fell directly into the reaction zone rather than being slowly evaporated. Growth occurred on quartz substrates, and the resulting materials were examined using a Philips XL-20 scanning electron microscope and a Philips EM420 transmission electron microscope.

With the continuous addition of reactants to the growth chamber, thick mats of long carbon nanotubes were formed using either the spray pyrolysis or vapor-phase growth methods described above. Variations to these procedures were required to create the layered structures described herein.

In the first process variation, using the slow-evaporation vapor-phase CVD method, a well-aligned, densely packed mat of carbon nanotubes was grown using a predetermined amount of reactants. Once the ferrocene−benzene solution had been completely consumed, a set period of time was allowed to pass during which no new reactants were introduced into the chamber. Following this pause, an additional quantity of the reactant solution was introduced and growth continued. During the pause, the sample could either be held at temperature inside the argon environment or it could be cooled, removed, examined, and then reinserted into the growth chamber.

Both the spray pyrolysis method of reactant introduction and the vertically aligned vapor-phase growth process were used to achieve similar results in the production of these layered structures. Instead of providing a continuous supply of catalyst and carbon source to the growth reaction, the reactants were introduced as drops, with fixed time intervals between successive drops. This dropwise method was similar to that used by Cao et al.[24] Different sequences of drops were studied as well as different interval times. Drop sequences included evenly spaced drops of the ferrocene−benzene solution, alternating drops of the ferrocene solution with drops of pure benzene, and alternating between ferrocene−benzene solutions and cobaltocene ($(C_5H_5)_2Co$)−benzene solutions. Time intervals varied between 20 and 120 s.
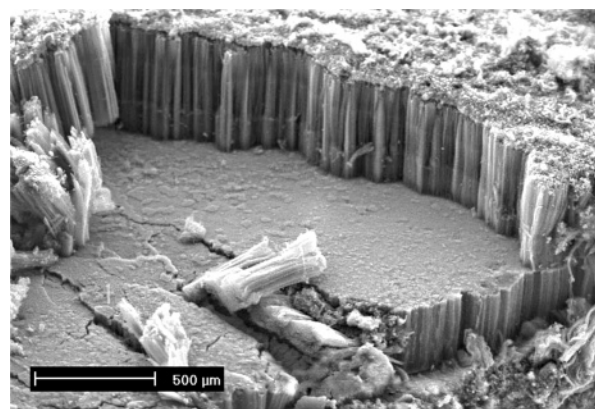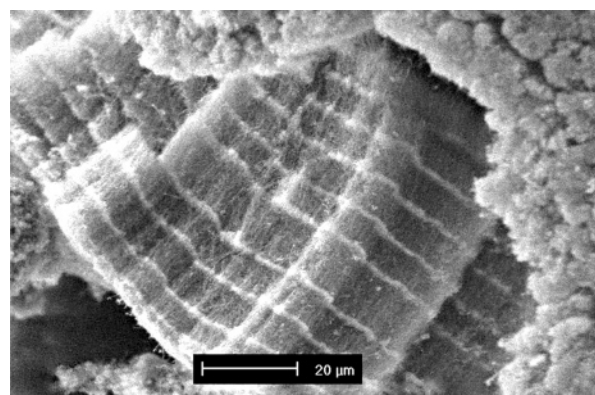
Results and Discussion

Layered carbon nanotube structures were successfully produced using all versions of the interrupted reactant flow described in the procedure. In many samples where densely packed well-aligned nanotube mats were produced, the upper surface of these bundles was observed to be relatively smooth and defect-free, providing a good surface upon which additional vapor-phase nucleation could occur. In the first vapor-phase growth procedure, nanotubes were grown, the nanotube-covered substrate was then partially cleaned, and then it was subjected to the growth reaction again. Nanotubes grew on both the cleaned region of the slide as well as in a new layer on the surface of the existing layer of carbon nanotubes; this result is shown in Figure 2.

When the new growth on the existing nanotubes was compared to the new growth on the cleaned quartz surface, the two sets of tubes had similar size and appearance. Both regions were covered with well-aligned mats of carbon nanotubes, and the densities and dimensions of these mats appeared to be the same.

A dropwise variation of this method was also employed, where the entire process occurred during a single spray pyrolysis growth run. Using the spray pyrolysis procedure, a small drop of ferrocene−benzene solution was dispensed, followed shortly by a small amount of pure benzene. A 1-min pause was allowed, and then this dispensing procedure was repeated. Results from this process are shown in Figure 3.

This experiment was repeated several times, and the layered structure disappeared when the length of pauses between drops were reduced below 30 s. Additionally, the layer thickness varied

Growth of Well-Aligned Carbon Nanotube Structures

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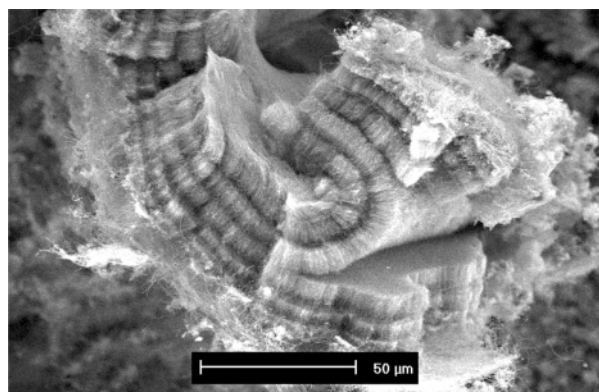
Figure 4. Layer separation of dropwise catalyzed nanotubes, indicating tube growth is not continuous (run #052304-1).

TABLE 1: Results Summary of Spray Pyrolysis Growth Reactions Performed Using Dropwise Reactant Addition

| run #	catalyst	sequence	interval	result
092903-1	Fe	Fe, Fe, Fe, Fe	40 s	no layers
102304-1	Fe	Fe, Fe, Fe, Fe[a]	120 s	no layers
030904-1	Fe & CoCl$_2$	Fe, Co, Fe, Co	120 s	no layers
031104-1	Fe	Fe, Fe, Fe, Fe[a]	120 s	no layers
041604-2	Fe	Fe, Fe, Fe, Fe	120 s	some layers
042004-1	Fe	Fe, B, Fe, B	60 s	distinct layers
042204-1	Fe & CoCl$_2$	Fe, B, Co, B	60 s	some layers
042904-1	Fe	Fe, B, Fe, B, B	60 s	some layers
050604-1	Fe	Fe, B, Fe, B	40 s	distinct layers
052304-1	Fe & Co	Fe, B, Co, B	30 s, 60 s	distinct layers
120504-1	Fe	Fe, B, Fe, B	20 s	no layers

[a] Runs performed with continuous benzene introduction, with only catalyst addition performed at an interval.

with the amount of reactant solution dispensed with each drop, with layers growing longer as more reactants were used. The results of these dropwise spray pyrolysis experiments are summarized in Table 1, wherein the Fe and Co stand for ferrocene and cobaltocene catalysts, respectively, and B represents pure benzene.

It was initially thought, on the basis of SEM observations and the comments by Cao et al. on their similar experiments,[24] that the tubes in these samples remained open and grew through each layer of high catalyst concentration. Tubes were believed to grow continuously because of the presence of benzene, with catalyst particles encapsulated inside each time a ferrocene−benzene drop was introduced.

However, on the basis of observations from our current experiments, it was determined that the tubes are not in fact continuous through each catalyst-rich layer. The pauses between the introductions of each reactant drop were sufficient to allow the closure and termination of growth of the preexisting layer of tubes. At the arrival of new reactants from the next drop, new tubes were nucleated and deposited on the upper surface of the previous tube layer. The discontinuous nature of these tubes was observed when mechanical force was used to separate the layers, as shown in Figure 4. The individual CNT layers can easily be delaminated from each other, clearly indicating that the nanotubes are not continuous through the entire thickness of the mat.

When growth was performed on clean substrates and with carefully controlled drops, it was observed that the number of layers present in the sample closely matched the number of drops introduced. Since the growth achieved by each drop leaves a new densely packed mat of carbon nanotubes on the upper surface of the sample, the stepwise growth process can continue as long as additional reactant is supplied. This was investigated
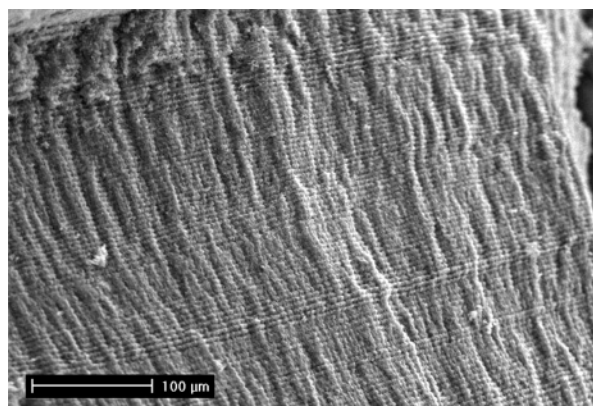
Figure 5. Extended duration, dropwise-grown carbon nanotube mats roughly 2 mm thick.
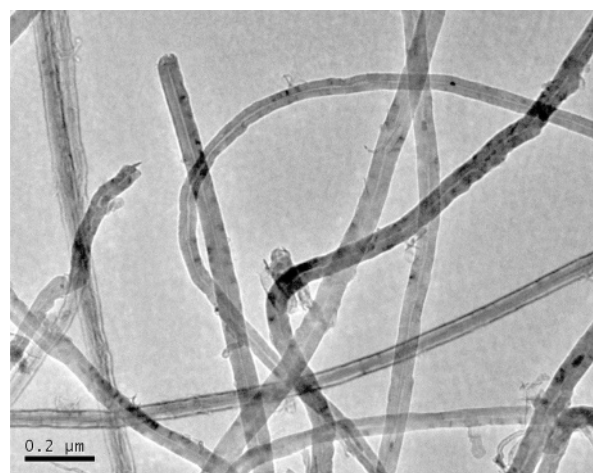

Figure 6. TEM image of typical multiwalled carbon nanotubes grown in these experiments.

by allowing a total of 100 mL of reactant solution to dispense directly into the heated reaction zone using a vapor-phase growth process, where the reaction tube was oriented vertically. The flow rate was controlled by a peristaltic pump and set to provide one drop at approximately 1-min intervals. However, the actual interval between drops varied slightly, as a result of some ferrocene deposits on the needle tip which interfered with drop separation. With an approximate drop size of 0.2 mL, it was estimated that over 500 drops were deposited over the course of roughly 4 h. The resulting nanotube structure was roughly 2-mm thick and was composed of well over 100 layers, as shown in Figure 5. Most of these layers were between 5 μm and 10 μm in length, although several larger sections comprised the remainder of the thickness.

The nanotubes grown using these methods were also characterized using transmission electron microscopy (TEM). The tubes were multiwalled with diameters ranging from 40 nm to 80 nm. Catalyst particles were encapsulated within the tubes and were located predominantly at the ends rather than along the middle of the tube's length. In some instances, multiple particles were found within the length of a single tube. Since the tips of tubes grown by a tip-growth mechanism are sealed with the catalyst, the presence of multiple particles suggests that these tubes are formed via a root-growth process (in which growth can proceed open-ended, allowing additional particles to become encapsulated). A typical TEM micrograph of the nanotubes grown and examined in this work is shown in Figure 6.

Experiments were also performed where layered mats of tubes were grown, and the metal catalyst used in each layer was
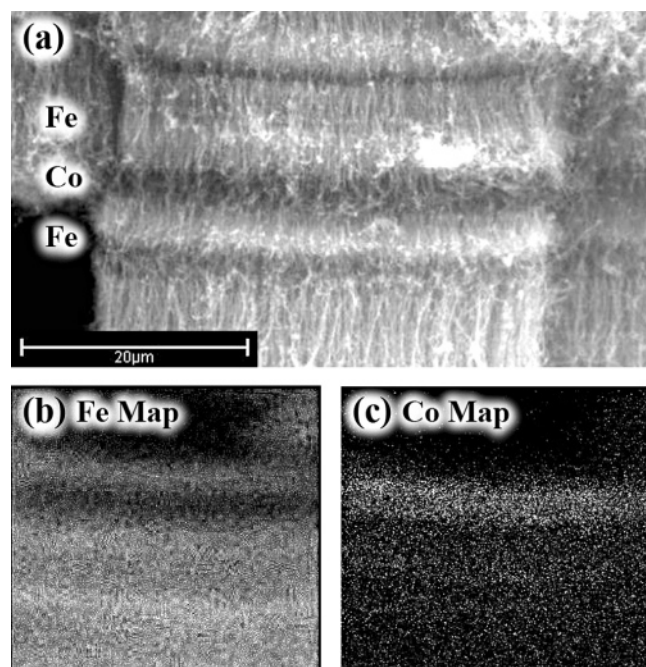
Figure 7. SEM image of carbon nanotubes grown with alternating catalysts, with EDS maps of iron (b) and cobalt (c) regions (run #052304-1).

varied. Figure 7a shows a layered carbon nanotube structure obtained by alternating ferrocene and cobaltocene catalyst solutions for each drop. Energy-dispersive X-ray spectroscopy (EDS) was used to identify the elements present in the different regions of the sample, and the results clearly indicate alternating cobalt-rich and iron-rich layers, shown in Figure 7b and Figure 7c.

The ability to create layered carbon nanotube structures within a single growth reaction not only provides information about CNT formation methods but also could lead to the development of novel layered nanotube composite structures. The complete separation observed when successive layers were split apart by mechanical force clearly indicates that carbon nanotube growth does not continue between layers, and growth of all tubes in a layer ceases before the next layer begins to form. Our TEM results, along with previous work,[25] have indicated that tubes grown using these vapor-phase methods grow open-ended, via root growth, and tube growth can continue while additional catalyst and carbon source are available to deposit on and lengthen the tube end. This suggests that growth could continue on a previous CNT layer as long as the tube ends remained open. The discontinuous transition from one layer to the next indicates this is not the case and that the tube ends may become capped during the pauses between reactant introductions; this process is illustrated in Figure 8.

Molecular dynamics and ab initio studies described by Kwon et al.[26] and others in the literature have suggested that temporary lip–lip bonds can form between carbon atoms at the open ends, eventually leading to a capped tube, which is energetically favorable compared to an open-ended structure.[26–28]

A comparison between the experimental results shows that distinct layers were not achieved with drop intervals of less than 30 s. This suggests that, for this particular equipment, temperature, and method of reactant introduction, the time required for the carbon and catalyst sources to be exhausted and for tube closure to occur is roughly 30 s. Experiments performed with shorter time intervals did not produce distinct layers, suggesting
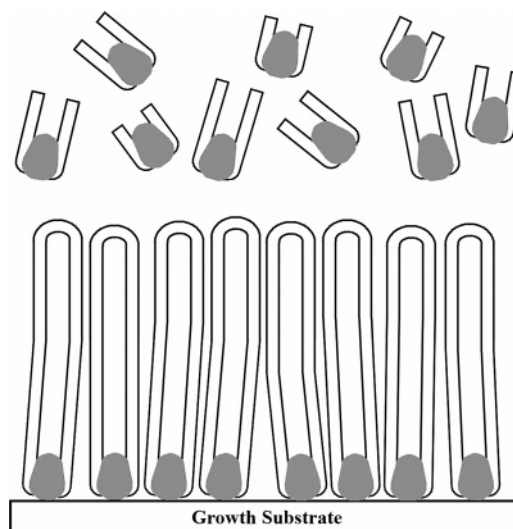
Figure 8. Formation process of a new carbon nanotube layer on the capped surface of the preceding nanotube layer.

tube closure did not occur and growth was not interrupted between drops.

In addition to this minimum interval time, it was also found that the sequence of reactant drop introduction also influenced the results. Attempts to grow layered CNT structures, where all drops had a uniform catalyst concentration (i.e., catalyst and benzene in solution rather than separate catalyst introduction and benzene dosings), were not successful, despite using intervals ranging from 40 s to 120 s. A variation of this process, where drops of constant catalyst concentration were introduced with a continuous flow of carbon source, was also unsuccessful in producing distinct layers. Consistent, distinct layered results were only produced when drops of catalyst-rich and catalyst-deficient (pure benzene) solutions were alternated. This sequence produced growth of a region with high catalyst concentration followed by a region of low catalyst concentration within each layer.

For the first layered structure formation method, where the entire growth reaction was interrupted rather than just the reactant flow, layers were formed using a uniform catalyst concentration during growth. This reactant introduction sequence (constant rather than varied composition) was not successful during dropwise growth; however, the pauses during this growth method were much greater ($>$10 min) than those in the dropwise procedures. The addition of uniformly high-catalyst concentration drops or the continuous introduction of a carbon source allows growth to continue through the pause lengths used in the dropwise methods, preventing the formation of layers. Longer pauses (on the scale of those used in the first growth method) are required to form layered structures with these processes. Therefore, for the rapid growth of a large number of layers, the ideal method of reactant introduction would be alternating catalyst-rich drops and catalyst-free solutions.

Conclusions

Layered carbon nanotube structures were successfully grown using three distinct procedures. The layer heights could be controlled from a few microns (using spray pyrolysis) to several hundred microns (using a slow evaporation vapor-phase growth method) and could be adjusted from layer to layer. The metal used to catalyze the growth of the nanotubes could also be varied from one layer to the next. Since metal-rich particles of the catalyst become encapsulated within the tubes during growth,

and these particles could influence the resulting material properties, this approach could be used to develop nanoscale structures with carefully controlled, layered characteristics. Additionally, a large amount (multiple layers) of nanotubes could be grown to a desired length in a single process and later separated, rather than using multiple, individual processes. Nanotubes were discontinuous between layers, suggesting that the tube ends become capped at the completion of each layer's growth. By varying the interval between solution introductions, it was found that the time required for the reactant supply to be exhausted, and this capping to occur, was roughly 30 s.

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