Low Temperature Carbon Nanotube Synthesis

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ABSTRACT

This report reviews the different methods for carbon nanotube synthesis. Low temperature plasma enhanced chemical vapor deposition is emphasized. Particular carbon sources, catalysts, supports, and atmospheric environments are described as well.

1. Introduction

Carbon nanotubes are a cutting edge material of the future. They were first discovered on the cathode of an arc discharge system designed to produce fullerenes, which are spherical hexagonal and pentagonal structures of carbon. Similar to fullerenes, carbon nanotubes are hexagonal columns of carbon, with each carbon atom covalently bonding three times to other carbon atoms. These nanotubes display an extremely high degree of atomic perfection and own an impressive combination of material properties. They can be nanometers in diameter and up to centimeters in length. This massive length to diameter aspect ratio can exceed a scale of 10^7, yielding remarkably unique characteristics. Carbon nanotubes are two orders stronger than steel in tension at 1/6th the weight. They can withstand temperatures up to 4,000 Kelvin and are excellent conductors of heat. These nanotubes are predicted to surpass isotropically pure diamond in terms of heat conduction. They also display other semiconductor properties due to the extra delocalized valence electron revolving around a carbon atom with only three bonds. Carbon nanotubes appear to be biocompatible as well. In addition, they also emit a unique electromagnetic field at the tip that seems to originate from the incredible aspect ratio of length to diameter. Nanotubes can have a single wall (SWNT) or multiple walls (MWNT). Large scale properties depend highly on the geometry of the nanotubes. Today, carbon nanotubes are seen to be utilized as additives in lithium ion batteries, coatings for stealth jets, and specialized ballistic protection in competition with kevlar when spun. Figure 1 displays a forest of carbon nanotubes being spun into a fiber captured through a scanning electron microscope. [1]

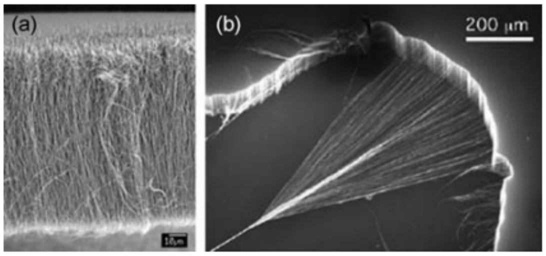

Figure 1. The above capture displays dry spinning of a forest of multiwalled carbon nanotubes. [1]

2. Industrial Synthesis

There are multiple ways to synthesize carbon nanotubes. New methods are also being discovered. However, the majority of these techniques seem to flow in three primary distinct directions. The most readily utilized methods of manufacture for carbon nanotubes are arc discharge, laser ablation, and chemical vapor deposition. [2] Arc discharge relies on extremely high voltages applied in pulses to a carbon source cathode like graphite. The carbon particles are transported via electromagnetism in the form of electrical arcs to an anode catalyst. Arc discharge produces extremely straight nanotubes but

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many other impurities as well like fullerenes and irregular soot. Figure 2 conveys the impure nature of arc discharge. Laser ablation requires a high powered laser to vaporize a solid carbon cathode. This process requires extremely focused light in order to function, not allowing it to scale up. Both arc discharge and laser ablation are relatively high cost and low yield. In addition, both processes operate at temperatures far above 1000° C. [3]

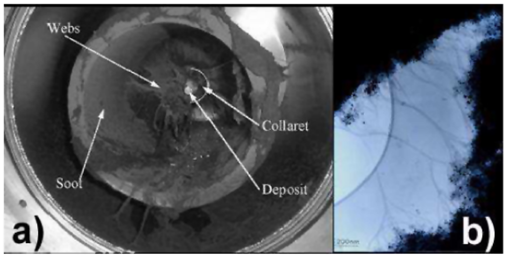

Figure 2. Image a) depicts an arc discharge reactor layered with impurities and byproducts. Image b) magnifies the multiwalled carbon nanotube bundles that formed on the collaret with tunneling electron microscopy. [3]

Chemical vapor deposition is the low cost and high yield alternative. In this process, carbon sources are thermally activated by various methods to a gaseous temperature. This carbon rich gas is then deposited on the surface of a catalyst where the nanotubes will grow. Different techniques are practiced in order to lower the overall reaction temperature like utilizing an already gaseous or liquid carbon source. Various enhancements can be assembled into machinery to influence a more thermally efficient environment. This reduces the amount of energy required to nucleate the nanotubes and allows for larger scale production. Also, the chemical vapor deposition process is constant. This provides the opportunity for extremely long nanotube growth which is useful for mass production and future manufacture. The carbon source, atmospheric chemistry, pressure, temperature, and catalyst all alter the overall geometry of the nanotubes produced. [4]

3. Carbon Sources

The carbon source in the chemical vapor deposition process is known formally as the anode. The purpose of this anode is to donate carbon atoms to the catalyst, which will nucleate and then grow nanotubes through various mechanisms. The specific cause of growth is still ill understood and various mechanisms are proposed. The two most accepted mechanisms in the scientific community are tip growth and base growth. In tip growth, the carbon atoms are stacked on top of each other, constructing a skyscraper-like structure nanometers tall. Base growth is a little more complex. Carbon atoms are first deposited onto the surface of a catalyst. Then the atoms diffuse through the surface of the catalyst to a nucleation site or already growing nanotube. The atoms combine into the base of the structure lifting the nanotube further away from the catalyst. Figure 3 illustrates the differences between these two mechanisms. [5]

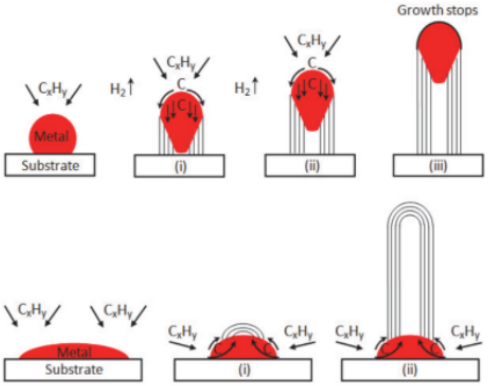

Figure 3. The two mechanisms for nanotube growth are illustrated above. Tip growth resides on top and base growth lies below. [5]

Carbon is one of the most abundant elements in the universe as well as on the surface of the Earth. Therefore, it is not difficult to find an object filled with carbon. However, in order to avoid defects it is ideal to use a pure carbon source. One of the most common solid carbon sources is graphite. Graphite is a relatively low density isotrope of carbon with hexagonal crystallinity. [6] It is commonly used as pencil lead. A new experimental solid carbon source is coal, specifically anthracite. Coal is an extremely cheap alternative to pure graphite and has the potential to scale up almost indefinitely. [7]

However, non-solid carbon sources are even more promising in terms of mass production. Coconut oil in its liquid state has the remarkable conductive capability to be vaporized relatively easily. Carbon tetrachloride was also found to be easily manipulated leaving behind a more pure chlorine residue. Still, gasses are top tier when it comes to bond readability and thermal reactivity. Commonly used gaseous carbon sources are methane, ethylene, acetylene, benzene, xylene, carbon monoxide, carbon dioxide, and various other hydrocarbons. Sometimes, metallocenes are utilized, which are essentially hydrocarbons consisting of two cyclopentadienyl anions bound to a metallic center raised to the second oxidation state. All these different carbon sources result in different overall reactions and alter the geometry of the carbon nanotubes. It is crucial to moderate the feed rate of the carbon source. Underfeeding will result in a poison nucleation site and the mound of carbon that formed will diffuse into the surface of the catalyst. Overfeeding will smother an infantile nucleate in what is called a nanocage and prevent further growth. Figure 4 conveys the result of overfeeding exceptionally well. [8]

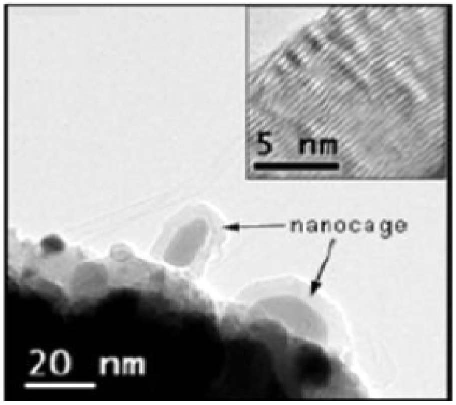

Figure 4. The above image displays two overfed nuclei encapsulated in a carbon nanocage. [8]

4. Catalysts & Characterization

During the chemical vapor deposition process, the acceptor of carbon donations is known as the catalyst. This is the surface where carbon nanotubes will nucleate and grow. The chemistry and surface morphology of the catalyst are extremely important in determining the overall shape of produced carbon nanotubes. The porosity and finish of the catalyst can be the difference between nanometer long or centimeter long nanotubes. Strong adhesion of carbon nanotubes to the catalyst may affect geometry through chirality when being removed, as can be seen in Figure 5. [9]

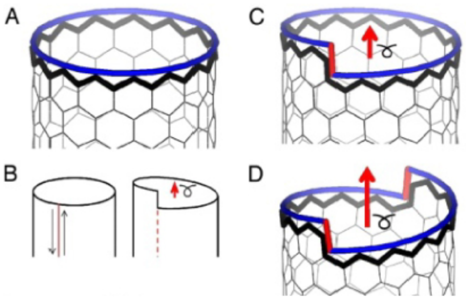

Figure 5. During the removal of carbon nanotubes from the catalyst, dislocations may occur that run through the length of the nanotube. The new stress states display an altered chirality from the original nanotube. [9]

Some common catalyst compositions are iron, nickel, cobalt, silicon, silicon carbide, silica, alumina, alumino-silicate (zeolite), calcium carbonate, magnesium oxide etc. In order to promote precise nanotube growth, supports are installed in intricate patterns on the surface of a catalyst. These support sites inspire nucleation for diffusing carbon atoms and are especially useful when nanotubes are first developing. They serve almost as a guide for lost particles and later influence high density traffic. [10] Figure 6 displays how useful a support system can be during nucleation. Support composition is commonly made from iron, nickel, cobalt, and silicon as well. However, a catalyst and support rarely have the same composition, as this would hinder nucleation and pattern identification and differentiation. The combined structure of the catalyst support system is generated through photolithography, the same process used in microchip fabrication. If an overlay of extra thin film layers or embedded atoms are needed, molecular beam epitaxy may be used. [11]

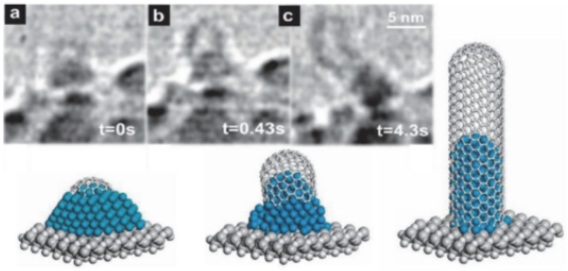

Figure 6. Atomic supports on the catalyst promote stabilized carbon nanotube growth. Images a) b) and c) are in situ captures of carbon nanotube nucleation atop a support site. [11]

There are almost endless ways to identify the kind of carbon nanotube synthesized. Some of the most common methods are scanning electron microscopy, tunneling electron microscopy, atomic force microscopy, micro-raman spectroscopy, x-ray diffraction, etc. Through these methods, it is possible to identify the geometry of the carbon nanotubes produced. More specifically, it is possible to analyze length, diameter, chirality, crystallinity, layering, and tip composition. [12] Occasionally, bits of the support may be carried as the roof of a carbon nanotube structure rather than the carbon simply collapsing in on itself to close the top. This can change the readings for certain x-ray diffraction measurements as seen in Figure 7. [13]

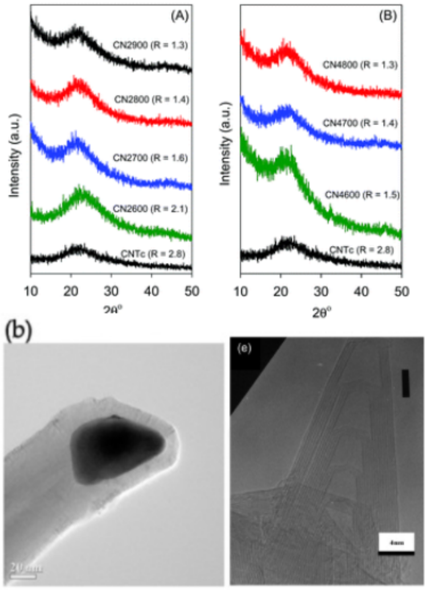

Figure 7. There are multiple mechanisms for tip closure in carbon nanotubes. Two of the most common are carbon collapse and embedded supports. X-ray diffraction can be utilized to sort differently walled nanotubes. [13]

5. Plasma Enhanced Chemical Vapor Deposition

Chemical vapor deposition is the cheapest, highest yield, most scalable, and most alterable method. It can be easily customized and enhanced through different techniques to optimize the energy utilized for each reaction load. Typically, nanotube growth occurs at temperatures above 500° C. This range is high enough to permanently damage most electronics, which hinders nanotube growth on delicate electronic substrates. However, through plasma enhanced chemical vapor deposition, researchers have been able to grow an array of carbon nanotube geometries at temperatures as low as 120° C. Figure 8 displays the kinds of nanotubes grown with this particular process. [14]

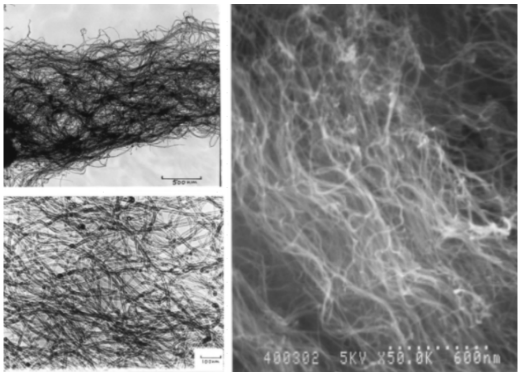

Figure 8. Above are images from scanning and tunneling electron microscopes. The results are multiwalled carbon nanotubes. [14]

The following is a step by step procedure suggested to construct carbon nanotubes through plasma enhanced chemical vapor deposition. The carbon source will be acetylene (C_2H_2) gas. The acetylene gas will be introduced into an ammonia (NH_3) atmosphere. The catalyst can be created starting with a 20 nm thick silicon dioxide layer (SiO_2) grown by thermal oxidation or low temperature electron cyclotron resonance onto a polished n-type Si(100) substrate to prevent silicide formation. Then, a 6 nm thick nickel film can be deposited onto the oxide by magnetron sputtering. The catalyst should then be patterned with cobalt to look like islands and lines by tunneling electron microscope grids as disposable shadow masks for feature sizes of 10 um. Electron beam lithography with polymethyl methacrylate as photoresist can be utilized for 100 nm feature sizes. The catalyst can then be transferred to a growth chamber. The chamber itself should be a stainless steel diffusion pumped vacuum. The chamber should be pumped to base pressure and filled to 1.2 mbar with electronic grade ammonia. The sample should then be heated for 15 minutes to a desired temperature using a resistively heated graphite stage. For plasma deposition, a direct current discharge between the heater stage (cathode) and a gas showerhead (anode, 2 cm above the stage) can be ignited by applying a fixed voltage of 600 V. The carbon source, C_2H_2 (grade 1.5) can be introduced via a separate mass flow controller. The C_2H_2 : NH_3 ratio should be kept constant at 50 : 200 sccm at a total pressure of 1.5 mbar. A stable discharge current of typycally 30 mA should be maintained for a fixed deposition time of 30 minutes. Temperatures can be measured with thermocouples mounted on a silicon substrate of equivalent sample thickness to moderate a 120° C environment. This will allow for nanotube growth on sensitive nanoelectronic devices. The nanotubes can then later be sorted through electric field posts and dielectrophoresis as shown in Figure 9. [15]

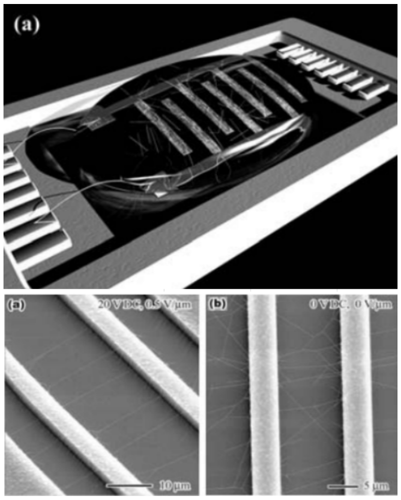

Figure 9. Displayed above are two forms of electromagnetism being utilized to sort carbon nanotubes. The above image illustrates dielectrophoresis and the below display separate electric field posts in parallel. [15]

With this experimental set up, the activation energy for growth rate should be 0.23 eV, which is much less than thermal chemical vapor deposition (1.2 - 1.5 eV). The energy difference is similar to the difference in surface and bulk diffusion of carbon in nickel (0.3 and 1.5 eV). This suggests carbon diffusion along the surface of the nickel catalyst and supports a base growth mechanism. [16] Alternatively, as temperature increases, a bulk diffusion model becomes more evident. Typically low temperature and pressure growth produces unaligned single walled nanotubes. However, through plasma enhancements, the results are different. Not only does the plasma help vertically align the tubes, but it also increases the dissociation of C_2H_2 and etches away any impurities on the surface of the cobalt islands. Unfortunately, the degree of crystallinity does still decrease with growth temperature. A decrease in the C_2H_2 : NH_3 ratio may prevent tapering once the nanotubes have reached a certain length, resulting in longer tubes altogether. [17]

6. Conclusion

Carbon nanotubes are an extraordinarily unique material. There are multiple ways to manufacture single walled and multi walled carbon nanotubes. Chemical vapor deposition is a promising technique for large scale production. Plasma enhancements allow for lower temperature synthesis. This will enable carbon nanotube nucleation and controlled growth on sensitive nanoelectronic devices for the future.

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