Carbon Nanotubes

By Chris Scoville, Robin Cole, Jason Hogg, Omar Farooque, and Archie Russell

Introduction

The Amazing and Versatile Carbon – Chemical basis for life

With an atomic number of 6, Carbon is the 4th most abundant element in the Universe by mass after (Hydrogen Helium and Oxygen). It forms more compounds that any other element, with almost 10 million pure organic compounds. Abundance, together with the unique diversity of organic compounds and their unusual polymer forming ability at the temperatures commonly encountered on Earth makes the element the chemical basis of all known life.

Carbon Nanotubes

Carbon Nanotubes, long, thin cylinders of carbon, were discovered in 1991 by Sumio Iijima. These are large macromolecules that are unique for their size, shape, and remarkable physical properties. They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in recent years and a large amount of research has been dedicated to their understanding. Currently, the physical properties are still being discovered and disputed. Nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). To make things more interesting, besides having a single cylindrical wall (SWNTs), Nanotubes can have multiple walls (MWNTs)--cylinders inside the other cylinders.

Carbon Nanotubes and Moore's Law

At the rate Moore's Law is progressing, by 2019 it will result in transistor just a few atoms in width. This means that the strategy of ever finer photolithography will have run its course; we have already seen a progression from a micron, to sub micron to 45 nm scale. Carbon Nanotubes, whose walls are just 1 atom thick, with diameters of only 1 to 2 nm, seems to be one of the perfect candidates to take us right to the end of Moore's Law curve. We possibly cannot go beyond that. So certainly carbon Nanotubes has a promising future!

Key properties of Carbon Nanotubes

Carbon Nanotubes are an example of true nanotechnology: they are less than 100 nanometers in diameter and can be as thin as 1 or 2 nm. They are molecules that can be manipulated chemically and physically in very useful ways. They open an incredible range of applications in materials science, electronics, chemical processing, energy management, and many other fields. Some properties include

- Extraordinary electrical conductivity, heat conductivity, and mechanical properties.
- They are probably the best electron field-emitter known, largely due to their high length-to-diameter ratios
- As pure carbon polymers, they can be manipulated using the well-known and the tremendously rich chemistry of that element.

Some of the above properties provide opportunity to modify their structure, and to optimize their solubility and dispersion. These extraordinary characteristics give CNTs potential in numerous applications.

Key application areas

- Field Emitters/Emission:
- Conductive or reinforced plastics
- Molecular electronics: CNT based non volatile RAM
- CNT based transistors
- Energy Storage
- CNT based fibers and fabrics
- CNT based ceramics
- Biomedical applications etc ...

Timeline References

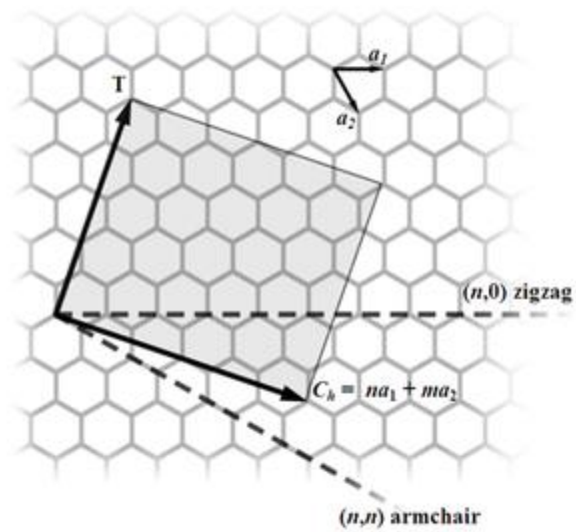
- http://www.answers.com/topic/timeline-of-carbon-nanotubes?cat=technology
- http://www.pa.msu.edu/cmp/csc/nttimeline.html

Properties of Carbon Nanotubes

The structure of a carbon nanotube is formed by a layer of carbon atoms that are bonded together in a hexagonal (honeycomb) mesh. This one-atom thick layer of carbon is called graphene, and it is wrapped in the shape of a cylinder and bonded together to form a carbon nanotube. Nanotubes can have a single outer wall of carbon, or they can be made of multiple walls (cylinders inside other cylinders of carbon). Carbon nanotubes have a range of electric, thermal, and structural properties that can change based on the physical design of the nanotube.

Single-walled carbon nanotube structure

Single-walled carbon nanotubes can be formed in three different designs: Armchair, Chiral, and Zigzag. The design depends on the way the graphene is wrapped into a cylinder. For example, imagine rolling a sheet of paper from its corner, which can be considered one design, and a different design can be formed by rolling the paper from its edge. A single-walled nanotube's structure is represented by a pair of indices (n,m) called the chiral vector. The chiral vector is defined in the image below.



The structural design has a direct effect on the nanotube's electrical properties. When n − m is a multiple of 3, then the nanotube is described as "metallic" (highly conducting), otherwise the nanotube is a semiconductor. The Armchair design is always metallic while other designs can make the nanotube a semiconductor.

Multi-walled carbon nanotube structure

There are two structural models of multi-walled nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube). In the Parchment model, a single graphene sheet is rolled around itself multiple times, resembling a rolled up scroll of paper. Multi-walled carbon nanotubes have similar properties to single-walled nanotubes, yet the outer walls on multi-walled nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials. Multi-walled nanotubes also have a higher tensile strength than single-walled nanotubes [7].

Strength

Carbon nanotubes have a higher tensile strength than steel and Kevlar. Their strength comes from the sp^2 bonds between the individual carbon atoms. This bond is even stronger than the sp^3 bond found in diamond. Under high pressure, individual nanotubes can bond together, trading some sp^2 bonds for sp^3 bonds. This gives the possibility of producing long nanotube wires. Carbon nanotubes are not only strong, they are also elastic. You can press on the tip of a nanotube and cause it to bend without damaging to the nanotube, and the nanotube will return to its original shape when the force is removed. A nanotube's elasticity does have a limit, and under very strong forces, it is possible to permanently deform to shape of a nanotube. A nanotube's strength can be weakened by defects in the structure of the nanotube. Defects occur from atomic vacancies or a rearrangement of the carbon bonds. Defects in the structure can cause a small segment of the nanotube to become weaker, which in turn causes the tensile strength of the entire nanotube to weaken. The tensile strength of a nanotube depends on the strength of the weakest segment in the tube similar to the way the strength of a cahin depends on the weakest link in the chain.

Electrical properties

As mentioned previously, the structure of a carbon nanotube determines how conductive the nanotube is. When the structure of atoms in a carbon nanotube minimizes the collisions between conduction electrons and atoms, a carbon nanotube is highly conductive. The strong bonds between carbon atoms also allow carbon nanotubes to withstand higher electric currents than copper. Electron transport occurs only along the axis of the tube. Single walled nanotubes can route electrical signals at speeds up to 10 GHz when used as interconnects on semi-conducting devices. Nanotubes also have a constant resistively [10].

Thermal Properties

The strength of the atomic bonds in carbon nanotubes allows them to withstand high temperatures. Because of this, carbon nanotubes have been shown to be very good thermal conductors. When compared to copper wires, which are commonly used as thermal conductors, the carbon nanotubes can transmit over 15 times the amount of watts per meter per Kelvin. The thermal conductivity of carbon nanotubes is dependent on the temperature of the tubes and the outside environment [10].

Potential Uses

There are many potential applications for Carbon nanotubes from waterproof and tear resistant cloth fabrics, concrete and steel like applications (a space elevator has even been proposed) based on the property of strength, electrical circuits based on the property of electrical conductivity, sensors based on the property of thermal conductivity, vacuum proof food packaging, and even as a vessel for delivering drugs. For the purpose of this paper we are going to focus on the applications related to nano-eletronics.

Nano-Electronics

One of the most significant potential applications of single-walled nanotubes is believed to be in the domain of nano-electronics. This is as a result of SWNT's being highly-conductive. In fact, according to [2] single-walled nanotube ropes are the most conductive carbon fibers known. Alternative configurations of a carbon nanotube can result in the resultant material being semi-conductive like silicon.

Conductivity in nanotubes is based on the degree of chirality – i.e. the degree of twist and size of the diameter of the actual nanotube - which results in a nanotube that is actually extremely conductive (making it suitable as an interconnect on an integrated circuit) or non-conductive (making it suitable as the basis for semi-conductors).

Interconnect

Chip manufacturers require metallic compounds to serve as the basis for interconnects between transistors on chips. Up until around seven years ago chip manufacturers used aluminum at which point they switched to copper. However copper's resistance to electricity flow increases as the metals dimensions decrease, creating a lower bound for the size of copper based interconnects. By 2012 [11] it is expected that higher performance chips combined with more tightly packed transistors require interconnects less than 40 nanometers wide, at which point copper's resistance will prove to be ineffective as an interconnection technology.

With high conductivity and small dimensions, carbon nanotubes may provide an alternative interconnect option to copper. Toshiba and Stanford University recently published results[3] demonstrating a CNT-based interconnect operating at 1Ghz on a chip containing 11000 transistors on a chip the size of 1/100th of a square inch.

This research demonstrates that carbon nanotubes are not just a viable alternative to copper, but that they can also be used alongside existing IC manufacturing processes. Another advantage to carbon nanotubes is that unlike copper there is no need to embed the interconnects into trenches on the circuit board, which could make for a simpler manufacturing process.

Transistors

Transistors form the basis for modern integrated circuits functioning as digital switches. Alternative configurations of carbon-nanotubes result in defects being present that allow single walled nanotubes to act as transistors. Nanotube based switches the size of an individual electron had been envisioned but had originally required cryogenic like temperatures.

In such a switch a molecule can be positioned inside a carbon nanotube to affect the electronic current flowing across it. The result is a molecular-scare gate in which the position of the molecule controls the flow of the electrical current. In this model, the gate is about one nanometer in size, or three orders of magnitude smaller than a silicon chip. In 2001 researchers [4] demonstrated that nanotube transistors could be realized that would operate at room temperature. IBM has also demonstrated fabrication of nanotube transistors [5].

Energy Production and Storage

Carbon Nanotube technology also holds promise for a wide range of energy-related applications.

Batteries

Most portable electronic devices use rechargeable lithium-ion batteries. These batteries release charge when lithium ions move between two electrodes - one of which is graphite and the other is metal oxide. Researchers at the University of North Carolina [9] have demonstrated that by replacing the graphite with SWCNTs they can double storage capacity.

Electrodes made of carbon nanotubes can be ten times thinner and lighter than amorphous carbon electrodes and their conductivity is more than one thousand times greater. In some cases, such as electric vehicles, the reduction in weight can make a significant reduction in battery power requirements. Carbon nanotubes have been used in supercapacitors producing a power density of 30kw/kg (compared to 4kw/kg for commercially available devices). Such supercapacitors could drastically reduce the time it takes to recharge devices such as laptops and cell phones.

Ultra-thin flexible batteries have been made with CNT infused paper [13]. Ionic liquid is soaked into the paper as the battery's electrolyte. Electrolytes in human blood, sweat, and urine can also help to power the battery which may be useful in implantable medical devices. These batteries can be rolled, folded, or cut without loss of efficiency. They can also be stacked to boost their output power. Although the materials used in the batteries, which are over 90% cellulose, are very inexpensive an inexpensive method of mass-production has not yet been developed.

Solar Cells

Researchers at Georgia Tech Research Institute [14] have created solar cells consisting of 100-micrometer-high towers built of CNTs grown on iron-coated silicon wafers. There are 40,000 of these towers in each square centimeter of the surface; Each tower is an array of millions of vertically aligned CNTs. These cells absorb more light as it reflects off the sides of the towers. Unlike typical solar cells that have peak efficiency when the sun is at 90º, these cells have two peaks at 45° and operate with relatively high efficiency during most of the day. This makes them particularly appropriate for applications in space because it eliminates the requirement of having a mechanical means of orienting the cells to face the sun.

Current hurdles

There are several remaining obstacles, technical and non-technical to CNT success. Covering these in detail is length and probably impossible; flipped on its head, such a passage would be a path to success with nanotubes! But here are a couple of the major impediments.

Electronic Heterogeneity

One problem with nanotube production for electronics is that batches of nanotubes are heterogeneous mixtures of metallic and semiconducting tube types. Electrical devices typically require these types to be separated, but so far it has been difficult to tune production in this regard [6]. There also remain issues with doping, or tuning conductivity, and electrical behavior at contact points. (Rogers, UIUC).

Orientation

A problem with nanotubes where recent progress has been made is controlling their orientation. Nanotubes are commonly grown in a chaotic organization (affectionately known as a "rat's nest"), which are difficult to use in microprocessors. Recently John Rogers and his team at the University of Illinois, Urbana Champagne, discovered that carefully growing nanotubes on quartz wafers can lead to a highly organized configuration.

Size and Density

The size of manufactured nanotubes typically varies widely. For commercial use, nanotube manufacturers will need to make size more consistent [6]. Though nanotubes are very narrow, nanotube matrices typically have quite large (100nm) spacing between tubes.

Export Policy

As with other multi-use technologies, nanotubes may be subject to export controls. Finding information about this was difficult, multiple sources were unaware of restrictions but in at least one case a foreign researcher was denied access to nanotubes. Adelina Santos, a Brazilian nuclear scientist, says a U.S. based supplier refused to ship him nanotubes due to federal regulations. However, restrictions seem difficult to enforce; Santos had a friend smuggle a gram of nanotubes to him Current customs protocols probably do not place a priority on detecting nanotubes.[20]

Export restrictions could slow adoption of nanotube technologies and prevent standardization. Regulation of commerce in nanotube technology will increase costs.

Environmental concerns

The environmental risks of nanotubes are still unclear[6]. Naturally occurring carbon is fairly benign, and is largely unregulated, but nanotubes interact with the environment differently. There have been several studies performed to test the effects of carbon nanotubes on living systems.

- Fruit fly larvae fed a diet containing nanotubes appeared to develop normally.[7]
- One study showed that CNTs delay embryo development in zebrafish, *but* the fish otherwise appeared normal.[8].
- Mice lungs became inflamed when exposed to nanotubes. Though the inflammation subsided within a few months, this has stark parallels to the affect of asbestos on human lungs.[9].
- Some human tumor cells seem to proliferate more rapidly in the presence of nanotubes[10].

In some situations, coatings applied to the nanotubes, rather than the nanotubes themselves, may become environmental culprits. The solar cells described earlier are coated with a cadmium-telluride mix, which would be too toxic for widespread use. Perhaps most sobering to consider is that some forms of nanotubes biodegrade slowly, tubes released into the environment may make their way into our food supply, and from there, throughout our bodies. Some researchers believe that nanotube use in electronics is probably not very risky because of the small volumes involved, but this argument hinges on computing being limited to small numbers of devices.

Some are pushing for more investigation and regulation. One possibility is treating nanotubes as a new chemical, rather than as an isoform of Carbon. Another approach is to adjust regulations on toxic exposures to take into account the *number of particles* in an exposure or their surface area, as opposed to the mass.[12].

However, there is a silver lining. CNTs also hold promise for cleaning up polluted environments. Nanotubes are very effective at absorbing chemicals from their surroundings and have possible applications in water filtration and in air filters, such as smokestacks.[11]

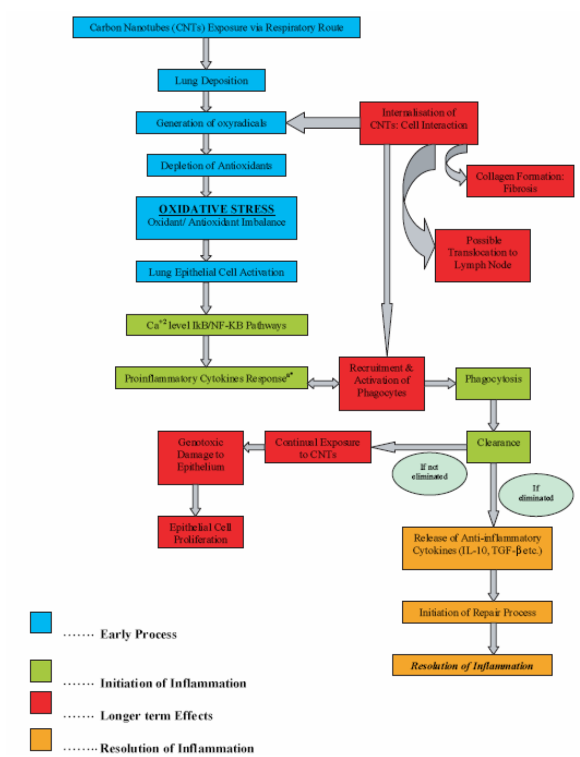


Figure 1: Pathways after CNT inhalation (A Jain, Nanotoxicology)

Entrenched dominance

The single biggest hurdle to nanotube success in integrated circuits is the continued success of silicon-based devices. Nanotubes have some outstanding properties, but exploiting these properties to build robust chips could prove very difficult. One company, Nantero, received funding in 2001 for a nanotube-based RAM (NRAM) product. At the time, NRAM promised to be better than DRAM in several dimensions, but, seven years later they don't have a product or even a vague timeline for when something might be available. By the time a product is released, if ever, NRAMs advantages will undoubtedly have diminished. Competing with silicon apples-to-apples has been the downfall of other promising materials technologies; CNT *nanofabrics*, which use a design paradigm that considers defects in nanomaterials to be the norm rather than the exception, hold considerable promise, but nanotube-based products will probably find their first successes in specialized applications such as interconnect.

Fabrication

The furtherment of fabrication technology will require the ability to target nanotubes with high yield of specified lengths, diameter, number of walls, and chirality. There are several procedures that have been developed for fabricating CNT structures. In this section, we give an overview of a few of them.

Arc Discharge Method

A chamber containing a graphite cathode and anode contains evaportated carbon molecules in a buffer gas such as helium. The chamber also contains some amount of metal catalyst particles (such as cobalt, nickel, and/or iron). DC current is passed through the chamber while the chamber is also pressurized and heated to ~4000K. In the course of this procedure, about half of the evaporated carbon solidifies on the cathode tip into a "cylindrical hard deposit." The remaining carbon condenses into "chamber soot" around the walls of the chamber and "cathode soot" on the cathode.

The cathode soot and chamber soot yield either single-walled or multi-walled carbon nanotubes. The cylindrical hard deposit doesn't yield anything particularly interesting.

The choice of buffer gas, the pressure of the chamber, and the metallic catalyst added to the chamber. Apparently the nanotubes grow from the surfaces of the metallic catalyst particles. These choices determine the shape and whether they are single- or multi-walled.

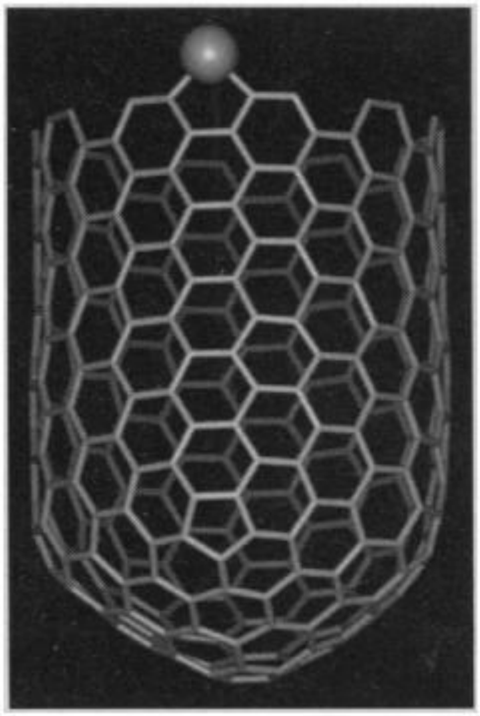
The advantage of this method is that it produces a large quantity of nanotubes. But the main disadvantage is that there is relatively little control over the alignment (i.e. chirality) of the produced nanotubes, which is critical to their characterization and role. Furthermore, due to the metallic catalyst included in the reaction, the products need to be purified afterwards. Methods such as oxidation, centrifugation, filtration, and acid treatment have been used.

Laser Ablation Method

A quartz tube containing a block of graphite is heated in a furnace. A flow of argon gas is maintained throughout the reaction. A laser is used to vaporize the graphite within the quartz. The carbon vaporizes, is carried away by the argon, and condenses downstream on the cooler walls of the quartz.

This condensation is SWNT and metallic particles. Thereafter, purification methods are applied to this mixture.

The key to the proper formation of the condensed nanotubes is that the location where the carbon atoms begin to condense should be set up as a curved sheet of graphene with a catalyst metallic atom nearby. As carbon atoms begin to attach and form rings, the metallic atom, if it has the proper electonegativity properties, will preserve the open edge of the tube and prevent it from drawing to a close. The authors of the paper describe this phenomenon as the "scooter" effect, because the metallic atom "scoots" around the open edge, preventing it from closing.



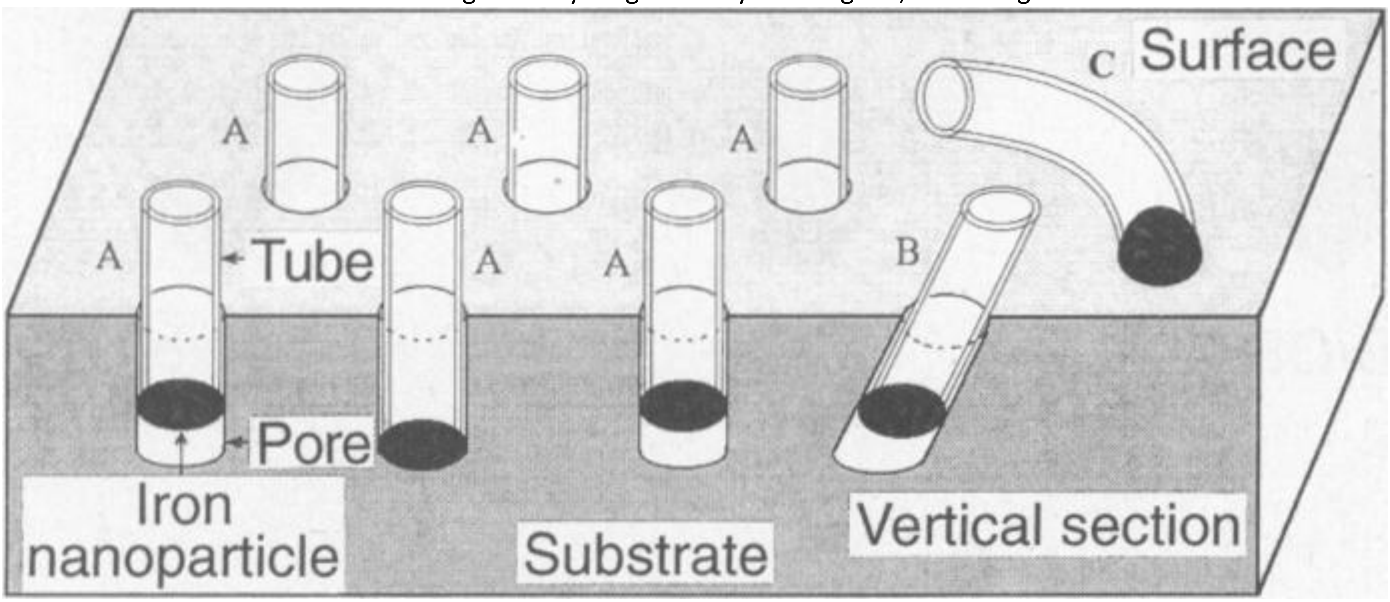
The large atom in this figure is the "scooting" metallic atom

Advantages of this technique include a relatively high yield and relatively low metallic impurities, since the metallic atoms involved tend to evaporate from the end of the tube once it is closed. One disadvantage is that the nanotubes produced from this method are not necessarily uniformly straight, but instead do contain some branching.

Chemical Vapor Deposition

The CVD approach allows CNTs to grow on a variety of materials, which makes it more viable to integrate into already existent processes for synthesizing electronics. This process involves the chemical breakdown of a hydrocarbon on a substrate.

It's already been shown in previous methods, such as the arc discharge method, that a main way to grow carbon nanotubes is by exciting carbon atoms that are in contact with metallic catalyst particles. The CVD method extends this idea by embedding these metallic particles (iron, in the case of the seminal paper) in properly aligned holes in a substrate (silicon, in this case). Essentially, tubes are drilled into silicon and implanted with iron nanoparticles at the bottom. Then, a hydrocarbon such as acetylene is heated and decomposed onto the substrate. The carbon comes into contact with the metal particles embedded in the holes and start to form nanotubes that are "templated" from the shape of the tunnel. It turns out that the carbon nanotubes grow very long and very well aligned, in the angle of the tunnel.



The advantages of this method are that the yield is very high, the alignment of the nanotubes is consistent (which is crucial for creating particular types of nanotubes, e.g. semiconductor or metallic), and the size of the growth area is theoretically arbitrary.

The main disadvantage is that, though the size of the growth area is basically arbitrary, large sized areas (several millimeters) tend to crack, shrink, and otherwise warp. The substrates need to be dried very thoroughly to prevent against this.

n-hexane Pyrolysis

Researchers developed a method to synthesize large, long single walled nanotube bundles in a vertical furnace by pyrolyzing hexane molecules. These n-hexane molecules are mixed with certain other chemicals that have been shown independently to help with growth of nanotubes. These are burned (pyrolyzed) at a very high temperature in a flow of hydrogen and other optional gases. According to the paper, using a different hydrocarbon or using a different gas prevented the formation of long nanotubes.

The primary advantage of this method is that it produces macroscopic nanotube bundles ("microtubes"): their diameters are typically larger than that of human hair, and their length is several centimeters. The disadvantage is that the alignment is not as produced from other methods, making it viable for creating "microcables", but not nanotubes with precise electrical properties. Another disadvantage is that from the researchers' measurements, the elasticity of these nanotube bundles is not as great as hoped (i.e. they are more brittle).

Conclusion

There is much about carbon nanotubes that is still unknown. More research needs to be done regarding the environmental and health impacts of producing large quantities of them. There is also much work to be done towards cheaper mass-production and incorporation with other materials before many of the current applications being researched can be commercialized. There is no doubt however that carbon nanotubes will play a significant role in a wide range of commercial applications in the very near future. Not only will they help create some very cool tech gadgets, they may also help solve the world's energy problems.

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