Past, Present and Future of Fullerene Nanotubes: Buckytubes

Daniel T. Colbert\textsuperscript{a} and Richard E. Smalley\textsuperscript{b}

\textsuperscript{a}Carbon Nanotechnologies, Inc., 16200 Park Row, Houston, TX 77084  
\textsuperscript{b}Rice University, Houston, TX 77005

Carbon fibers having nanoscale dimensions have been known for well over a hundred years. In 1889, a U.S. patent was awarded to Hughes and Chambers for teaching a method for growing carbon filaments from ‘swamp gas’ – primarily methane – using a metallic crucible which, unwittingly, catalyzed the reaction [1]. Until the 1970s, the formation of such carbon nanofibers (also known as, carbon filaments or filamentous carbon) was mostly regarded as an undesirable side reaction in processes such as Fischer–Tropsch or steam-methane reforming reactions. Nanofibers were a nuisance: now we know better.

Excitement over the potential utility of nanoscale carbon fibers has grown over the years as fibers with ever-smaller diameters and correspondingly greater structural perfection possessing superior material properties have been produced. Concurrently, however, the history of their discovery, production, and development has been somewhat neglected. We hope that the present chapter helps to clarify and puts into historical perspective some of the key discoveries and developments along the way toward the eventual widespread use of carbon nanofibers, and the realization that in their finest implementation these nanofibers are fullerenes, composed of perfect, continuous tubes – buckytubes.

1. Roger Bacon Revisited

In 1960 Roger Bacon, working for the National Carbon Company, a division of Union Carbide Corporation, reported, in a remarkably lucid and thorough account, his discovery of sub-micrometer diameter graphite whiskers grown in a d.c. carbon arc under high pressure (93 atm) of an inert gas [2]. These whiskers consisted ‘of one or more concentric tubes, each tube being in the form of a scroll, or rolled-up sheet of graphite layers, extending continuously along the length of the whisker’, and possessed very high Young’s modulus and tensile strength, and low electrical resistivity. With supporting X-ray diffraction data, he concluded that these whiskers had a scroll morphology rather than a concentric tube one by observing the structure resulting from exploding the end of one by suddenly passing a large current through it. These graphite ‘whiskers’ still today hold the world record for strength and electrical conductivity of a macroscopic carbon fiber.

Iijima’s [3] observation of ‘multiwall nanotubes’ in the soot from a carbon arc (essentially the same d.c. carbon arc experiment as Bacon’s, except that now only 1 atm of gas was used), appropriately generated considerable excitement over these thinner and much more clearly imaged examples of carbon nanofibers. Iijima was one of the foremost electron microscopists in the world, and with his powerful TEM he could ‘see’ what his
predecessor of 31 years before could not. The special, additional caché of Iijima’s discovery was that it was done under conditions that had just recently been found to produce buckyballs. In carefully imaging the closed ends, it appeared that the multiwalled tubes made in the arc really were concentric tubular fullerenes, and this fact more than any other aspect elevated these new ‘nanotubes’ to a stature largely blinded to the Bacon forerunner. Iijima’s 1991 discovery had the important – even seminal – effect of ‘fullerenizing’ the frontier of carbon fiber research, the logical limit of which is the emergence of single-wall nanotubes – buckytubes.

However, despite occasional recognition of his discovery, the earlier work of Bacon has been largely ignored. This relative obscurity of Bacon’s work has been sustained, in part, by the presumed difference in structure between Bacon’s ‘scrolls’ and the purported concentric fullerene ‘tubes’ of Iijima and the many researchers who have followed thereafter. Bacon made scrolls; Iijima made tubes – or so we all thought.

However, it has recently come to light that multiwall carbon nanotubes, at least in most instances when they are formed in a carbon arc as originally practiced by Iijima in 1991, really are composed of a mixture of scrolls and tubes – just the same structures observed by Roger Bacon over 40 years ago. This has been shown elegantly in experiments by Mordkovich et al. [4], who intercalated multiwall nanotubes with either K or FeCl₃. Significant swelling of the interlayer spacing was observed for arc-grown nanotubes, but not for Ni- or Fe-catalyzed CVD-grown nanotubes. Intercalation preserved the basic morphology of the arc-grown tubes, which can only occur for a scroll structure, since the strain of concentric layers swollen to the degree observed would be overwhelming, prohibiting intercalation in the first place. Thus the CVD-grown tubes, which underwent no observable swelling, are most likely concentric tubes, whereas the arc-grown tubes appear to be, for the most-part, scrolls.

This brings us back to Bacon, whose well-conceived experiments and careful analysis advanced the concentric tubes-of-scrolls morphology for arc-grown whiskers nearly a half century ago. His work at Union Carbide went on for many years, and was a major factor in the development of high strength carbon fibers used in aerospace today. He must rightfully share, in our opinion, credit for the discovery and elucidation of carbon nanotubes.

But Iijima’s 1991 paper on multiwalled nanotubes was still seminal. Even if the carbon multiwalled nanotubes he discovered were in actuality just thin still-scrolled versions of what Bacon had already made and discussed many years before, it was the idea that counted: perfect, concentric carbon tubes – fullerene nanotubes. It wasn’t so much what they were, but what we thought they were, that emboldened hundreds of researchers and helped to get us to where we are today.

2. Commercial Production of Multiwall Nanotubes

In the years between Bacon’s and Iijima’s pioneering work on multiwall nanotubes produced in carbon arcs, other workers experimented with methods for producing carbon nanofibers that more closely resembled the original gas-phase work of Hughes and Chambers [1]. The most notable of these were Endo [5], and Tibbetts [6], working for
General Motors. These processes, like that of Hughes and Chambers, catalytically converted gas-phase hydrocarbons to nanofibers by flowing catalyst precursor through a growth region with feedstock. The resulting nanofibers are typically relatively wide and overcoated with a thick layer of amorphous carbon. However, advances in recent years have improved the quality and cost-effectiveness of these processes to enable commercialization by companies such as Showa Denko and Applied Sciences.

In the 1980s, an improvement in the quality of multiwall nanotubes grown from hydrocarbons (e.g. ethylene) was achieved by catalysts on supports such as fumed alumina. The nanotubes produced by this process, developed principally by Howard Tennant of Hyperion Catalysis Inc. [7], are freer of amorphous overcoating than other multiwall nanotubes. They, like other multiwall nanotubes, did, and still do, however, contain some small amount of amorphous carbon overcoating, and numerous defects in the inner layers, although they are much improved in this respect over the previous vapor-grown fibers. Arc-grown multiwall nanotubes have somewhat fewer defects, although they are more costly to produce than either the gas-phase or supported catalytic methods, both of which are readily scalable to large commercial production.

3. Buckytubes

In 1993, Iijima and Ichihashi [8] and Bethune et al. [9], working independently, showed in beautiful experiments that carbon nanotubes with only a single wall can be formed in a carbon arc in the presence of transition metal catalysts (in retrospect it is clear that the early method of Morinobu Endo [5] produced small amounts if buckytubes as well—they were always there, but in very tiny amounts). Although the soots they obtained only contained at most a few per cent nanotubes, this development sparked a shift in the field from multiwall to single-wall nanotubes that continues to this day.

One reason for this shift was pragmatic: theorists had been calculating structures and properties for nanotubes since 1991, but multiple layers were inaccessible to all but crude computations; they settled for elucidating the properties of single-wall tubes out of necessity. The predictions were both scientifically and technologically exciting: rich electronic properties, including metallic conductivity, unparalleled strength and stiffness, and tremendous thermal conductivity. This was a notable and rare example of theory being well out in front of experiment (and being correct!).

Even after the discovery of single-wall nanotubes in 1993, theory remained out in front because the arc process (the only process known until 1995) provided such impure SWNT material as to effectively prevent any substantial characterization, aside from imaging in a TEM. Despite the theoretical predictions, the special nature of SWNTs was not yet fully appreciated. Also, the difficulty in making accurate predictions of the properties of MWNTs, which would have had to include defects in order to be realistic, allowed the misconception to propagate that multiwall nanotubes could be as perfect as single-wall tubes, and therefore share in the latter’s tremendous technological promise. In some quarters, this misconception still survives.

As carbon fiber diameters have decreased over the years, their structural perfection, and thus, their material properties, have increased correspondingly. At the largest size,
we have the traditional 5–10 μm diameter carbon fibers. Although these are sometimes
called graphite fibers, this name is a poor descriptor, since they contain very little of
what could be properly described as graphite. In fact, they consist mainly of small,
defect-riddled graphitic domains agglomerated together to form a fiber. Despite the
dominance of defects in their structure, these fibers are amazingly strong, and have been
applied in many important technologies.

Beginning with Bacon, through the work of Endo, Tibbetts, Iijima, and others, carbon
fibers having nanoscale dimensions have been produced and characterized over the past
40 years. In many cases, they can be made with a very high degree of graphitization –
much higher than ‘graphite’ fibers. In the best production of these multiwall nanotubes,
concentric layers of these fibers run parallel to one another for hundreds to thousands of
times their diameters, manifesting far more order than graphite fibers. Nevertheless, all
multiwall nanotubes, no matter how they are made, contain numerous defects along their
sidewalls – as frequently as once every few nanometers on average. MWNTs can sustain
these defects, mainly consisting of missing atoms in one or more of the sidewalls, by
forming ‘scars’ of bridging atoms to satisfy any dangling bonds that the missing atoms
would otherwise leave behind [10,11].

It is only when we reach the minimum number of layers – one – that a much-higher
degree of structural perfection – molecular perfection – is realized in the form of single-
wall nanotubes, or buckytubes. (We prefer the latter name to emphasize that SWNTs are,
in fact, a species of fullerenes, just as C_{60} is the first tubular fullerene – the first, and tini-
est, buckytube.) SWNTs do not have the possibility that MWNTs have to heal defects by
bridging to neighboring walls. Furthermore, the only other atom in the periodic table that
can possibly substitute for a missing carbon atom in the tube sidewall would be boron,
and there is no boron around during growth. Finally, the energetic cost of even a single
atomic vacancy is so high (about 7 eV), that if one were to develop, the tube would
almost certainly seal off at that point as the carbon atoms rearrange to tie up their
dangling bonds. These, then are the ultimate carbon fibers, with the ultimate associated
properties.

For these reasons, we think of SWNTs as molecules – polymers of pure carbon. This
has notable implications. The properties of any material are greatly limited by the occurrence
of structural defects. For example, a wire of high strength steel typically has a ten-
sile strength only 1–2% of its theoretical value, i.e., the strength predicted by imagining
all the bonds across a plane perpendicular to the wire axis breaking simultaneously. Of
course, this never happens in practice because grain boundaries and dislocations – struc-
tural defects – cause a concentration of applied stresses, leading to crack propagation
and catastrophic failure. Defects similarly limit – often severely – other material proper-
ties, such as electrical and thermal, as well.

In real materials, structural perfection is generally limited to molecules. But molecules
are generally nanoscopic in all dimensions. Buckytubes are nanoscopic in two dimen-
sions, but most importantly, thousands of times longer in the third dimension, giving rise
to the possibility that their properties can be manifested on microscopic, and even
macroscopic scales. Furthermore, being made of pure carbon, the intrinsic properties of
buckytubes are superior to almost anything else. The basic structure is the hexagonal
array of graphene, which is the densest possible packing of atoms in two dimensions.
This, together with the extraordinary strength of C–C sp² bonds, results in remarkable mechanical and thermal properties of SWNTs.

Even more remarkable, however, is the special electronic characteristics of this new polymer. Depending on how the graphene sheet is wrapped into a seamless tube, SWNTs can be either small- to medium-gap semiconductors, or truly metallic conductors of electrons [12]. In fact, because the allowed energy bands are so widely separated, it is very difficult for electrons to scatter as they travel down the tube in specific waveguide transmission modes; this results in ballistic transport over long (many micrometer) distances. SWNTs are effectively single-mode light-pipes for electrons, preserving their quantum mechanical phase over long distances.

In addition, being aromatic, the very electrons doing the conduction are very difficult to steal away by oxidation – the same principle that makes benzene and other aromatic molecules resist any chemical reaction that would break up the delocalized electronic structure (you can derivatize the edge of an aromatic structure, but not easily its top or bottom). Thus we have, by virtue of aromaticity, the unique situation of having metallic conductivity that is insensitive to chemical attack. Any metal wire shrunk to nanometer dimensions where most atoms are on the surface would, when exposed to air or moisture, have its conducting electrons oxidized away instantly. Even if it were possible to make a gold wire 1 nm in diameter, when placed in water it would simply dissolve to form the Au²⁺ ion, or bead up into tiny disconnected balls. Conjugated hydrocarbon polymers are much more viable alternatives, and for many years chemists have been developing conducting molecules such as polyphenylacetylene and polythiophene. Some of these are quite impressive, particularly as bulk materials, but compared to the true metallic conductivity of a buckytube, when used as individual ‘molecular wires’ these polymer molecules are better described as ‘molecular resistors’. It appears unlikely that there will ever be a better nanoscale carrier of electrical current than a buckytube.

Aromaticity also makes these the most polarizable molecules known, making their interaction with electromagnetic radiation unique and practical, for example, for light-harvesting, super dielectrics, and all manner of electromechanical and electro-optomechanical devices.

4. The Laser-oven Stopgap

From their first observation in 1993 until late 1995, single-wall nanotubes were essentially unavailable in any form suitable for characterization. To the extent that only a few researchers had any material to work with, it was from an arc process that in its initial form produced soots containing only a few per cent SWNTs by weight. In 1995, researchers at Rice found a vastly more effective method for producing SWNTs: the laser-oven method. In this process, which closely resembles the method used when fullerenes were first discovered, a laser vaporizes a composite graphite/transition metal (e.g., Co, Ni), target inside a heated quartz flow tube. The condensing vapor is swept down the tube, and collected downstream. Optimally, it produces soots comprised of as much as 90% SWNTs.

The soot produced by this process was qualitatively different from that first produced by the arc process (the arc process has now been dramatically improved, but still does
not achieve the quality of the laser-oven process). The nanotubes were formed in high enough abundance to assemble naturally side-by-side to form ropes of hundreds of tubes packed together like pipes in a hardware store. Tubes in these ropes run parallel to one another, adhering by their strong van der Waals affinity. Ropes are much longer than individual tubes – so long that ends are almost never observed in electron micrographs. Most importantly, the raw material produced by the laser-oven process was sufficiently dominated by SWNT that the remaining amorphous carbon could be removed by differential oxidation, providing a material that was a mat of substantially pure SWNT ropes. For the first time, researchers had available pure enough material to enable characterization of the fundamental properties of SWNTs. Hundreds of research papers have resulted from the availability of this material [13]. Happily, this research, to a very large extent, confirmed the earlier predictions of the fundamental properties – this was very special stuff.

While much basic research was done on the laser-oven material, particularly on the electronic and chemical properties, only small amounts of material were available at a cost of several thousand dollars per gram. Some very clever research into the structural aspects (strength, stiffness, and toughness) was done with these small samples, but they were not sufficient to enable other more applied research, such as the structural properties of composites, fibers, etc. These activities, not to mention commercialization of nanotubes for almost all applications, would require vastly more material than could economically be produced by the existing methods.

5. HiPco

Despite the impact of the availability of laser-oven material through Tubes@Rice, indeed partly because of the advances made in studying that material, the group at Rice felt an urgency to find a scalable process for production of buckytubes. The carbon arc method and laser-oven methods are economically prohibitive for mass production, due to the large input of energy required to vaporize graphite, the cost of the feedstock, and the lack of the sort of economies of scale that always characterize large chemical processes. The clear direction for scaling appeared to be looking for an all gas-phase process. The single most difficult problem was quickly found to be pyrolysis: at the temperatures necessary to produced perfect buckytubes all hydrocarbons, even methane, spontaneously pyrolyze to produce amorphous carbon. Luckily, carbon monoxide is perfectly stable under these conditions, as long as there is no surface around that can catalyze its decomposition, the Boudouard reaction, to produce carbon plus CO₂. Having already found that single-wall nanotubes could be produced from carbon monoxide using supported catalysts [14] (all other gas-phase feedstocks to that point had been hydrocarbons for multiwall nanotubes), it was natural to explore this avenue in an all gas-phase process.

At the core of the HiPco process [15] is an almost poetic simplicity. A cool, high-pressure stream of CO feedstock seeded with a stable metal carbonyl catalyst precursor (mostly Fe(CO)₅) is heated to ~1000°C in less than a millisecond by mixing with more CO feedstock that has been preheated to 1200°C. While the gas is cool, the
high-pressure CO helps to kept the Fe atoms in the gas phase. Fe(CO)₅ is the most thermodynamically stable form of iron under these conditions, and CO with the strongest diatomic bond in the universe (11 eV, much stronger even than the bond in N₂) is an exceedingly stable gas. Thermodynamically, the pure CO is actually metastable: it would rather be graphite plus CO₂, but the high CO bond strength and absence of a catalyst prevent this from happening.

But when suddenly heated to 1000 °C, Fe(CO)₅ is no longer stable. As it dissociates it collides with other iron carbonyl fragments and nucleates a tiny nanoparticle of iron. At a very early stage, perhaps even when only two iron atoms are present in the cluster, the CO now finds an efficient catalytic path to produce CO₂ and leave behind a bare carbon atom on the tiny cluster. As more reactions occur on the particle the carbons begin to knit together to form an aromatic carbon sheet, and this sheet begins to curve to minimize its edge energy. The high temperature helps this curvature proceed rapidly — temperature is just as critical here in the HiPco process as it is in the laser-oven process. Sometimes the growing carbon sheet curves so successfully that it actually makes C₆₀ or some larger spheroidal fullerene. But usually the closure of this little proto-fullerene is blocked by the catalyst particle, and a perfect, single-walled tube begins to grow. On a macroscopic iron surface this Boudard reaction would produce graphitic structures, but in the nanoworld of the just-born iron cluster catalyst, the most favored thermodynamic form of carbon is not yet graphite; instead it is a perfect buckytube. When done at very high pressure, and adequately high temperature, the HiPco process tends to make buckytubes with about the same diameter as the C₆₀ buckyball.

Time and nucleation are of the essence. The challenge is to maximize the number of iron cluster nuclei, and to protract the active life of these catalyst particles as long as possible. These goals are intricately linked, since any iron not involved in active catalyst clusters at the earliest time (e.g., bare iron atoms) cause mischief beyond not contributing nanotube progeny of their own: they actually hasten the death of otherwise active catalyst particles by adding to them, and growing them. Larger catalyst particles are at risk of a side reaction resulting in their becoming overcoated by carbon, resulting in their inactivation. The HiPco trick is therefore rapid heating of the catalyst precursor to harbor all the metal safely into active and long-lived catalysts.

After a few years of research we have developed two HiPco research reactors at Rice University that run 24 h a day for weeks at a time, producing 25 g of buckytubes per day. Further developments are scheduled on both these reactors to up the production to over 100 g per day, and extensive research will be conducted over the coming years to fully understand the intricacies of this new process. In the meantime, however, a new company has been formed, Carbon Nanotechnologies, Inc, CNI, which will rapidly be building a pilot plant facility to begin the scale-up of this all gas-phase process by several orders of magnitude and beyond.

Overall, the HiPco process is very similar to two chemical processes that have long been implemented worldwide on a huge scale. One is the Haber–Bosch synthesis of ammonia, which like HiPco is a very high pressure process done over a transition metal catalyst, except in the HiPco case, one of the products is a solid (but, happily, we find we can blow them around and through tubes as though they were a gas). The other similar process is the vast worldwide production of polypropylene, which is also solid produced
in a gas-phase scheme using a particulate catalyst. We expect the history of the HiPco process 10–20 years from now will resemble the last 50 years of development of the Ziegler–Natta process for polypropylene, a process that is now so highly refined, with such an active catalyst, that one seldom has to worry about removing it from the product polymer.

Carbon nanotubes are best when they are perfect single-walled fullerenes – buckytubes. They are best understood as a new wonder polymer, a follow-on to nylon, polypropylene, and Kevlar. In time they will be produced worldwide in amounts of millions of tons per year. They will be cheap, environmentally friendly, and do wonders for the future of humankind.

Acknowledgement

The fullerene nanotube research at Rice University described here has been supported by NASA, the Office of Naval Research, the National Science Foundation, the Texas Advanced Technology Program and the Robert A. Welch Foundation.

References

13. In 1998, Rice University established a non-profit facility on campus, Tubes@Rice, to provide SWNT material from the laser-vaporization process to the research community at cost (actually, Rice heavily subsidized these sales). This operation has now been taken over by Carbon Nanotechnologies, Inc.